REVIEW ARTICLE

Nuclear forensics: what, why and how?

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Nuclear forensics is a relatively young branch of science in nuclear science and technology. It is a multidisciplinary field with an aim to answer questions regarding any interjected or smuggled material. The main objectives of these studies are to find out the origin/source of the material, date and place of production, age of the material, i.e. the date when it was last chemically processed or purified and if possible, the intended use of the material. Different analytical techniques, both non-destructive and destructive, e.g. gamma spectrometry, mass spectrometry, Raman spectroscopy, Fourier-transform infra red spectroscopy, scanning electron microscopy, transmission electron microscopy and laser-induced breakdown spectroscopy are employed to obtain the maximum possible information about the radioactive nuclear material. Information about structure and morphology of signatures, isotopic composition of the element, total amount, associated cations and anions, and isotope data on other elements, e.g. sulphur, Sr, Nd and Pb as to arrive at definite conclusions for material attribution.

Keywords: Age determination, mass spectrometry, nuclear forensics, plutonium, radioactive elements, uranium.

NUCLEAR forensics is a relatively young discipline in nuclear science and technology. It is truly an interdisciplinary science which has evolved in the last two decades and has assumed great importance owing to changes in the world scenario. Nuclear forensics can be defined as the collection and analysis of nuclear and radioactive materials to support investigations into diversion, trafficking and illicit use. Radioactive materials (e.g. actinides) are generally kept under strict physical control with continuous surveillance, yet the malicious intention of the wrong-doers cannot be ruled out. Since these materials emit radiations and are harmful to human health, if they enter the human body even at extremely low levels (i.e. microgram amounts), it is necessary to monitor their presence in various biological and environmental samples. The main objective of nuclear forensics studies and investigations is to find out the origin of interdicted, stolen, or lost material to eliminate its accessibility to illicit traffickers and to prevent any damage due to radiological dispersive device (RDD) also referred to as 'dirty bomb'. Nuclear forensics encompasses a number of sub-disciplines including radio-analytical chemistry, nuclear and radiochemistry, reactor physics, nuclear engineering, process engineering, enrichment engineering, geology, material science, quality assurance, statistics, etc. It involves measurements using a variety of analytical techniques to find out the origin/source of the material, process/production history, model age of the material and possibly, the intended use of the material. The unequivocal determination of the source of the material requires data on a number of quantities including the trace, minor and major elements (chemical composition); isotopic composition of different elements (O, S, Sr, Nd, Pb, U, Pu, etc.); morphology of the material and different phases present; anionic impurities and residual organic solvents, present, if any. A textbook[1], one conference proceedings[2], a few introductory and review papers[3–14] and some dissertations[15–20] are available in open literature, presenting details on various aspects of nuclear forensics.

A national nuclear forensics library for data on various nuclear materials being used in a country (state) will be very useful to find out the source of the confiscated material. Further, an unrestricted easy access to all the international laboratories for different certified reference materials will go a long way in validating the different procedures and analytical methodologies being used at various laboratories. Demonstrated capability of nuclear forensics in a country would surely serve as a deterrent to would-be smugglers of nuclear materials and is very useful to develop and implement a national response plan for nuclear-counter terrorism and counter-proliferation. Internationally, during 1993–2013, there have been 2477 registered cases by 125 member states, with 424 involving unauthorized possession and related criminal activities and 16 of these dealing with high enriched uranium (HEU) and plutonium (Pu), as reported by International Atomic Energy Agency (IAEA), Vienna in its incident and trafficking data base (ITDB)[21]. Though these undesirable activities are on decline, nuclear terrorism is considered to be the biggest threat in view of the health hazards and this requires strengthening the capabilities in fighting this menace.

This article introduces the discipline of nuclear forensics to novices, highlights its present status and provides an overview of the future challenges to the practitioners of nuclear forensics. The questions to be answered are

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'What is the material and what was its purpose?'; 'How was it produced?' and 'Who was the last legal owner?'.

Different materials

The materials which are of interest to nuclear forensics are those containing actinide elements, e.g. thorium (Th), uranium (U), neptunium (Np), plutonium (Pu), americium (Am), etc. and other radioactive nuclides (^{60}Co, ^{90}Sr, ^{137}Cs) that can be used in RDDs. These are the materials handled at different stages of the nuclear fuel cycle starting from mining, milling, extraction and purification, enrichment, fuel fabrication, nuclear reactor (power or research), irradiated fuel reprocessing, nuclear waste management, storage as well as used for medical and industrial applications. The materials of interest are minerals/rocks/ores from which U and Th are extracted, uranium ore concentrates (UOCs), U from ^{235}U enrichment plants, U, Pu and Th based fuels from fabrication facilities and purified materials (U, Pu, etc.) from spent fuel reprocessing plants. An interesting case reported recently[22] is of Seaborg's plutonium (2.44 μg ^{239}Pu) which was the first sample produced in 1942, large enough to be weighed at that time. This sample which was on display for a number of years at the Lawrence Hall of Science in Berkeley, CA was to be removed by UC Berkeley's Environment, Health and Safety Department. Passive X-ray and gamma ray analysis confirmed the authenticity of the sample amount of Pu and its isotope as only ^{239}Pu, before it could be considered for display at the Smithsonian.

It is to be noted that natural U contains three different isotopes of U, viz. ^{234}U (0.005 atom% or 50 ppm), ^{235}U (about 0.72 atom%) and ^{238}U (about 99.275 atom%). Uranium with ^{235}U greater than 20 atom% is labelled as HEU; uranium containing ^{235}U less than 20 atom% is known as low enriched uranium (LEU) and with ^{235}U about 5 atom% is called enriched commercial grade uranium (ECGU)[23]. The limits for ^{232}U and ^{236}U with respect to ^{235}U in ECGU are $<2 \times 10^{-9}$ g/g and $<5 \times 10^{-3}$ g/g respectively. The presence of ^{236}U indicates that the U sample has either originated from a reactor or has been mixed with irradiated U. Also, since ^{232}U does not occur in natural U and is formed during reactor irradiation of thorium or uranium, its presence in any U sample indicates that the sample contains reprocessed U or has been mixed with such U. Depleted uranium after reactor irradiation will contain ultra-trace amounts of ^{232}U (ppt levels) and thus the recycling of such U can lead to the presence of ^{232}U in fresh fuel samples. In addition, calculations made on enrichment cascades showed that ^{232}U increases due to cascade enrichment by a factor of 200–1000 and that depleted U contains 1600–8000 times less ^{232}U than HEU[23].

At the front end of the nuclear fuel cycle, UOC, also known as yellow cake, is an important product. This could comprise uranium oxide, ammonium diuranate [ADU: $2UO_3 \cdot NH_3 \cdot 3H_2O$], ammonium uranyl carbonate [AUC: $(NH_4)_4UO_2(CO_3)_3$], hydrated uranium peroxide [$UO_4 \cdot 2H_2O$], etc. depending upon the raw material and the procedure used for extraction and concentration. For example, in addition to extracting uranium from its ores, U can also be obtained as a by-product of phosphoric acid (e.g. Earth Sciences Extraction Company, Calgary, Canada) or copper (Olympic Dam Mine, Australia) production. Therefore, the metallurgical form of UOC, its properties, e.g., microstructure and impurity content will vary and data on all these can provide useful signatures for source attribution of these materials. Many studies have been reported on these materials in view of their relatively easy accessibility at the front end of the fuel cycle compared to plutonium at the back end of the fuel cycle.

IAEA has listed five categories of nuclear materials: un-irradiated direct use material, irradiated direct use material, alternative material, indirect use material and commercial radioactive sources. The materials of greatest concern are highly enriched uranium with >20 atom% ^{235}U and plutonium with <7 atom% ^{240}Pu, since these can be used to construct nuclear weapons.

Signatures and methodologies

Different provenance signatures which have been studied for the attribution of UOCs are given in Table 1. Data on the isotopic composition and chemical composition of the associated non-nuclear materials serve as a silent witness[24] and can provide clues about the production site and processing methodology adopted. The importance of experimental data on the isotopic composition of weapons grade Pu generated in natural uranium fuelled, heavy water moderated reactors, for nuclear forensics applications was emphasised since theoretical neutronics calculations[25] could not conclusively discriminate the Pu generated from such reactors in different countries. Hence, this multi-faceted young field of nuclear forensics demands the development of highly sensitive and preferably, non-destructive analytical techniques, to provide as many fingerprint signatures as possible, both efficiently and accurately.

Isotopic composition of uranium and plutonium

Data on the isotope amount ratios of U and Pu are obtained by multi-collector thermal ionization mass spectrometry (MC–TIMS) or by multi-collector inductively coupled plasma mass spectrometry (MC–ICPMS). These data provide useful signatures for fingerprinting the material. For example, $n(^{234}\text{U})/n(^{238}\text{U})$ isotope amount ratios in uranium from three different mines (Beverly, Ranger and Olympic Dam) in Australia were reported to be

Table 1. Typical examples of various signatures in uranium ore concentrates (UOCs)/yellow cake

Signature	Technique used
Morphology	Scanning electron microscopy (SEM)
Speciation	X-ray diffraction (XRD), Raman spectroscopy
Anionic impurities (Cl', SO_4'', NO_3') in the aqueous leachate	Ion chromatography (IC)
Organic impurities	Gas chromatography mass spectrometry (GCMS)
Rare-earth elements pattern	Mass spectrometry (HR-ICPMS)
Different elemental impurities	Laser induced breakdown spectroscopy (LIBS)
^{143}Nd/^{144}Nd isotope amount ratio	Mass spectrometry (MC-TIMS/MC-ICPMS)
^{87}Sr/^{86}Sr isotope amount ratio	Mass spectrometry (MC-TIMS/MC-ICPMS)
^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, ^{208}Pb/^{204}Pb isotope amount ratios	Mass spectrometry (MC-TIMS/MC-ICPMS)
^{34}S/^{32}S isotopes amount ratio	Mass spectrometry (MC-ICPMS)
^{18}O/^{16}O isotopes amount ratio	Mass spectrometry (SIMS, TIMS)
Isotopic composition	Passive gamma spectrometry, alpha spectrometry, mass spectrometry

HR-ICPMS, High resolution inductively coupled plasma source mass spectrometry; SIMS, Secondary ion mass spectrometry.

distinctly different[26]. The isotope amount ratios in Pu are also distinguishable from different kinds of reactors, as demonstrated by various isotope correlations[27,28]. Any plutonium sample from nuclear reactor will have five isotopes of Pu, i.e. ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu and ^{242}Pu. The amount of each isotope depends upon a number of parameters including the type of reactor (research reactor or power reactor), burn-up of the fuel, neutron spectrum, etc. Generally, plutonium with ^{239}Pu more than 90 atom% is obtained from research reactors and is known as weapon grade plutonium. Plutonium containing ^{239}Pu less than 70 atom% is produced in power reactors and is known as reactor grade plutonium.

Age determination of uranium and plutonium

The age of any radioactive sample can be determined by measuring the progeny (daughter) to parent amount ratio and calculating with Bateman equation, well-known in radioactive decay[29–35]. Because the age of nuclear materials will not exceed a few decades compared to the long half-lives of radioactive isotopes of U and Pu, the formation of daughter products is quite limited. This demands chemical separation followed by mass spectrometric or radiometric measurements, without introducing any blank contamination from reagents and laboratory. For this purpose, a specialized facility with ultra-clean laboratories is essential to handle extremely small amounts of actinides. In view of the longer half-lives of uranium isotopes than those of Pu isotopes, the age determination of U-based materials is more difficult.

Age determination of uranium and plutonium refers to ‘Model ages’. It involves two assumptions: (i) complete separation of the daughters was achieved at the time of initial preparation/purification of the material, and (ii) the system has remained closed after that. Any deviation from these two assumptions would yield erroneous results on the age. Good agreement (concordance) in the ages obtained by two independent radio-chronometers enhances the confidence. Therefore, wherever possible, the age of the material should be determined by using two independent chronometers. In case of disagreement, the lower age is taken since the daughter nuclide, present initially, would yield a longer age.

Multi-collector ICPMS was used to determine the age of ^{235}U-enriched materials employing ^{235}U–^{231}Pa chronometer[35–37]. Isotope dilution mass spectrometry was employed for determining both U and Pa. ^{233}Pa ($t_{1/2} = 26.97$ days) milked from ^{237}Np was used as a spike for ^{231}Pa ($t_{1/2} = 32{,}760$ yr) and ^{233}U was used as a spike for ^{235}U. The ^{233}Pa spike can also be prepared by neutron irradiation of ^{232}Th. ^{234}U–^{230}Th chronometer was also employed for determining the age of this material which was NIST-CRM-U100 containing 10% of ^{235}U. Good agreement on the ages obtained by the two chronometers enhanced the confidence on the data about the most recent chemical purification/processing date. Model ages of many other isotopic reference materials of U available commercially have been determined by various investigators using isotope dilution alpha spectrometry, TIMS and ICPMS. For uranium samples containing ^{233}U and ^{232}U originating from thorium-based fuels, the chronometers ^{233}U–^{229}Th and ^{232}U–^{228}Th can be employed for age determination. Table 2 lists different chronometers which can be used to determine the age of uranium samples.

For U samples, ^{234}U–^{230}Th is one of the best radio-chronometers in view of the long half-life of ^{230}Th. This is because once ^{230}Th is removed using a chemical process, it takes about 5×10^5 years to reach secular equilibrium.

High resolution gamma spectrometry is a useful non-destructive technique which is used for age dating of uranium materials[38]. The age of uranium sample is determined by knowing the activity ratio of ^{214}Bi (609 keV)/^{234}U (120.9 keV) which is calculated from the ^{234}U/^{235}U, ^{235}U/^{238}U and ^{214}Bi/^{238}U activity ratios measured using intrinsic efficiency calibration. The age of uranium which

Table 2. Different chronometers for age determination of uranium samples

Parent nuclide (half-life)	Daughter nuclide (half-life)	Spike isotope needed for IDMS	Remarks
^{233}U (1.59 × 10^5 yr)	^{229}Th (7350 yr)	^{238}U, ^{230}Th	^{233}U is from ^{232}Th irradiated sample, ^{230}Th not easily available
^{234}U (2.456 × 10^5 yr)	^{230}Th (75584 yr)	^{233}U, ^{232}Th	Most useful radio-chronometer for natural U and enriched U samples
^{235}U (7.04 × 10^8 yr)	^{231}Pa (32760 yr)	^{233}U, ^{233}Pa (26.9 d half-life)	^{233}Pa to be milked from ^{237}Np, not available commercially
^{232}U (69 yr)	^{228}Th (1.9 yr)	IDMS not used, radiometry preferred	Alpha spectrometry/gamma spectrometry to be used
^{236}U (2.34 × 10^7 yr)	^{232}Th (1.4 × 10^{10} yr)	^{233}U and ^{230}Th spikes	Useful for irradiated and reprocessed materials

refers to time T after purification or enrichment can be calculated from

$$A_{(\text{Bi-214})}/A_{(\text{U-234})} = A_{(\text{Ra-226})}/A_{(\text{U-234})} = 0.5\,\lambda_{(\text{Th-230})} \cdot \lambda_{(\text{Ra-226})}\,T^2.$$

This method can be applied to materials in any physical form and geometrical shape.

In view of the worldwide efforts to convert HEU to LEU, by mixing HEU with depleted and/or natural U, the radiochronometer method will not be applicable since the two materials taken for mixing may or may have not been purified on the same date. In such a case, microstructural damage occurring, mainly due to ^{234}U decay chain, within the lattice of the metal over a given period, measured using high resolution transmission electron microscopy (TEM), may provide useful information about the age of the metal. Preliminary simulation showed promising results[39] for HEU and mixture of HEU + LEU. This approach, however, will not be applicable to commercial LEU (^{235}U < 5 atom%) due to limited number of alpha-induced damaged sites in view of the lower percentage of ^{234}U in these samples.

Age determination of Pu sample can help in excluding certain production or reprocessing plants[40–42]. Table 3 provides a list of different radiochronometers which can be employed for Pu samples. The two chronometers most commonly used are ^{239}Pu–^{235}U and ^{241}Pu–^{241}Am. One of the limitations in using ^{238}Pu–^{234}U chronometer is the ubiquitous isobaric interference of ^{238}U at ^{238}Pu in spite of chemical purification. Recently, a method was reported to overcome this limitation of isobaric interference[43] and this methodology would be highly useful for Pu samples with extended burn-up in view of their higher ^{238}Pu content and relatively shorter decay half-life of ^{238}Pu. The radiochronometer ^{242}Pu–^{238}U is generally not used due to the long alpha decay half-life of ^{242}Pu (3.76 × 10^5 yr) as well as the low abundance of ^{242}Pu (0.01 atom% to 1 atom%) in majority of Pu samples. Laboratories working on nuclear forensics are validating the methodologies by determining the age of the certified NIST Pu isotopic reference material (e.g. SRM-947) since its date of production is documented. Both MC–TIMS and MC–ICPMS have been employed for determining parent and daughter nuclides using isotope dilution mass spectrometry. The consistency in the ages obtained by two chronometers is useful to exclude the possibility of residual U or Am from the reprocessing plant, originally present in the Pu sample since the last chemical separation.

Recently, the age-dating of ^{90}Sr source (half-life 28.79 yr) used in blood irradiator was performed[44] by determining ^{90}Zr. Isotope dilution mass spectrometry using ^{86}Sr and ^{92}Zr as spikes, with a TIMS instrument having a single Faraday cup and a Q-ICPMS instrument in the pulse counting mode, was employed. Good agreement was noted in the ages (about 45.2 yr) calculated from TIMS and ICPMS data and this was also supported by the data available from the date of installation of the source at Oak Ridge National Laboratory (ORNL). Other radioactive materials of interest are ^{60}Co, ^{137}Cs, ^{238}Pu and ^{241}Am used for different applications. ^{232}Th, though having a very long half-life (1.4 × 10^{10} yr), is of interest due to its use in preparing the banned drug methamphetamine. Thorium oxide catalyses the production of precursor, viz. phenylacetone (P2P) from phenylacetic and acetic acids and is, therefore, required by illegal drug manufacturers. In such cases, the origin and age of thorium[10] is of interest to law enforcement agencies.

For achieving a time resolution of 50 days for the age of the material, over a period of say 1–50 years, the half-life uncertainties for the parent and the progeny (daughter) nuclides should be lower than 0.25%, which has not yet been achieved for some of the important radio-nuclides[45–48]. For example, a detailed statistical analysis of data and simulation used to calculate uncertainty on the beta decay half-life of ^{241}Pu suggested a need to conduct a measurement exchange programme for plutonium which should be analysed at different laboratories worldwide by a variety of mass spectrometers to resolve whether mass fractionation effect exists on the half-life or not[47]. A similar effort to re-determine the α-decay half-life of ^{233}U by specific activity method, with measurements performed at four different laboratories (IRMM, Belgium; PTB, Germany; CIEMAT, Spain; CEA, France) yielded a value of (1.5867 ± 0.0014) × 10^5 yr, which is lower than the currently recommended value and led to a new best estimate[48] of (1.5903 ± 0013) × 10^5 yr.

Table 3. Different chronometers for age determination of plutonium samples

Parent nuclide (half-life)	Daughter nuclide (half-life)	Spike isotope needed for isotope dilution mass spectrometry	Remarks
^{238}Pu (87.7 yr)	^{234}U (2.456×10^5 yr)	^{239}Pu, ^{235}U or ^{233}U	Low abundance of ^{238}Pu, isobaric interference from ^{238}U in mass spectrometry
^{239}Pu (24110 yr)	^{235}U (7.04×10^8 yr)	^{244}Pu or ^{242}Pu, ^{233}U	^{244}Pu and ^{242}Pu spike availability restricted/limited
^{240}Pu (6563 yr)	^{236}U (2.34×10^7 yr)	^{244}Pu or ^{242}Pu, ^{233}U	^{244}Pu and ^{242}Pu spike availability restricted/limited
^{241}Pu (14.4 yr)	^{241}Am (432.6 yr)	^{244}Pu or ^{242}Pu, ^{243}Am	Spikes not easily available, ^{241}Am by ICPMS and γ spectrometry
^{242}Pu (3.76×10^5 yr)	^{238}U (4.5×10^9 yr)	^{238}Pu, ^{235}U, ^{233}U	Low abundance and long half-life of parent, amount of daughter produced is very low, limited applicability and interest

Attribution tags were proposed[49] in 2001 with an idea of identifying any theft of HEU and Pu. One ppb of ^{232}U (present in 20–100 ppm of ^{233}U) and 200 ppb of ^{244}Pu were proposed as intrinsic tags. It was also seen that these tags do not add to the radiation hazard or disrupt possible future fuel use, but enhance the weapon usable material security. These tags could be identified from 2.6 MeV gamma ray of ^{208}Tl which is a daughter product in the decay chain of ^{232}U and mass spectrometry for ^{244}Pu since the latter is not produced in research or power reactors.

Isotopic composition of elements other than actinides

Isotope ratio measurements on Sr, Nd and Pb present in UOC or any uranium sample can be used to trace the origin of uranium[50,51]. This is because there would be small differences in the contents of ^{87}Sr (daughter of ^{87}Rb, $T_{1/2} = 4.88 \times 10^{10}$ yr), ^{143}Nd (decay product of ^{147}Sm, $T_{1/2} = 1.06 \times 10^{11}$ yr)) and radiogenic lead isotopes (viz. ^{206}Pb, ^{207}Pb and ^{208}Pb, which are the end-products of decay chains of ^{238}U, ^{235}U and ^{232}Th respectively) arising due to the geological history of the mine. The measurements require chemical separation of these elements in the purest form using suitable ion exchange procedures and very high precision determination of isotopic composition by either multi-collector thermal ionization mass spectrometry (MC–TIMS) or multi-collector inductively coupled plasma source mass spectrometry (MC-ICPMS).

^{143}Nd/^{144}Nd isotope amount ratio has been shown to be a useful signature to assess the origin of UOCs[50]. This ratio provides a robust signature since it is less prone to weathering. Significant differences in ^{143}Nd/^{144}Nd isotope ratios have been observed among different uranium mines. This ratio depends upon the age of the minerals and the initial Sm/Nd amount ratio of uranium ore. For determining ^{143}Nd/^{144}Nd ratio, the purification of Nd from Ce and Sm needs be done to avoid isobaric interferences at Nd mass numbers during mass spectrometric analysis. ^{143}Nd/^{144}Nd isotope amount ratio has been shown to vary from 0.511 to 0.516 (1% only) with Sm/Nd amount ratios ranging from 0.05 to 0.8 in various uranium ores and ore concentrate samples. Hence, it is necessary to perform the isotope ratio measurements with very high precision (close to 10 to 20 ppm).

The ^{18}O/^{16}O isotope amount ratio in the actinides oxides can be used to trace their geo-location[51–55]. This can be done by using SIMS, TIMS, GDMS or gas source mass spectrometry (GSMS). The GSMS requires 25–50 mg of the sample and a high vacuum fluorination system for reaction with ClF_3 or BrF_5 to liberate oxygen which is converted to carbon dioxide. A dual inlet isotope ratio GSMS is used to determine ^{18}O/^{16}O isotope amount ratios. Small changes in ^{18}O/^{16}O isotope amount ratios (less than 3%) were observed in uranium oxide samples of different origins using secondary ion mass spectrometry (SIMS) and TIMS[53]. The use of magnetic sector SIMS was demonstrated for the determination of ^{18}O/^{16}O isotope amount ratio in uranium dioxide micro particles using carbon planchets and gold substrates and performing the measurements on O^- ions using Cs^+ as the primary ion beam. TIMS, by generating UO^+ ions from solution deposited on the filament, was used to determine ^{18}O/^{16}O isotope ratios. Latest studies, however, were not very conclusive and further investigations are necessary to explore the utility of this signature for nuclear forensics.

^{34}S/^{32}S amount ratios in the UOCs were recently determined using MC–ICPMS[56]. The leachable sulphate in the yellow cake was separated and pre-concentrated by anion exchange procedure. The isotope ratio of sulphur isotopes can be indicative of the process used (chemicals used) and the type of uranium ore. It was found necessary to add Ag^+ externally to the sample to avoid the loss of sulphur in the desolvation system used in ICPMS. The method was applied to 18 different UOCs from different parts of the world, i.e., Africa, Australia, Canada and USA and significant differences were found in the ^{34}S/^{32}S isotope ratios. The potential to correlate δ^{34}S value of the ore to the origin of the UOC exists in future.

Cationic and anionic impurities

Rare-earth elements (REE; La to Lu) concentration pattern provides useful information in attributing uranium ore and ore concentrates[57–61]. The REE are determined by HR-ICPMS and their concentrations are normalized with respect to chondrite REE concentrations, to eliminate the nuclear stability effect. Since the chemical properties of the REEs are quite similar to their oxidation state as +3, except for Ce(IV) and Eu(II), they behave identically in geological and industrial chemical processes. Therefore, their relative abundance pattern is useful to authenticate the source of the rock. A total of 38 UOCs from 31 different mines from different countries (Australia, Brazil, Canada, Czech Republic, Namibia, Sweden and USA) were analysed for rare-earth patterns after their chemical separation using TRU resin in 3M HNO_3. Recently, laser ablation (LA)-ICPMS was used to determine REE adsorbed on a strong cation exchange resin bead and the REE profile data demonstrated less isobaric interferences from oxides and hydroxides of lower REE at heavy REE elements observed usually with pneumatic nebulization (PN) using solutions. Determination of other non-radioactive impurities elements can be used to identify nuclear forensic signatures of the process of material production or inherited from the ore body.

X-ray fluorescence (XRF) (energy dispersive or wavelength dispersive) has been used to determine major elemental content (> 0.05 wt.%) in UOC.

Ratio of sulphate to chloride in the aqueous leachate of UOC samples reveals whether H_2SO_4 or HCl was used for processing. The SO_4^{2-}/Cl^- ratios are reported to vary from 0 to 6500 approximately in the aqueous leachate of a number of UOC samples. This information obtained by ion chromatography was found to be useful for an unknown UOC sample seized during 2009 in a criminal investigation in Australia[62]. Information about other anions, e.g. F^-. Br^-, NO_3^-, PO_4^{3-} can also be useful in nuclear forensic applications.

Organic impurities

Residual organic impurities present in UOC can provide information about the solvents/process used for uranium production. For example, tri-*n*-octylamine, tri-*n*-octylphosphine oxide and tri-*n*-butyl phosphate (TBP), which are the most important extractants used for solvent extraction in uranium production, were analysed by GC–MS.

Structure and morphology

Phase composition and microstructure can provide information about the processing histories, e.g. temperature and duration of the heating/drying. It has been well-documented that different processing conditions give rise to different particulate morphologies. XRD, SEM with EDS and TEM are used to obtain phase composition and morphological information. Raman spectroscopy which is based on inelastic scattering of the monochromatic laser light has been used in nuclear forensics[63]. A comparison of the performance of different Raman spectrometers made to evaluate their capabilities showed promising applications for UOCs.

Isotope correlations

Plutonium isotope correlations are useful to determine the type of reactor since it is an important parameter for any seized plutonium sample[27,28]. The evolution of isotope amounts of Pu depends upon various parameters, e.g. initial enrichment of ^{235}U, burn-up, hardness/softness of the neutron spectrum, etc. Linear correlations between $^{242}Pu/^{240}Pu$ amount ratio and ^{238}Pu content have been published for various kinds of reactors, e.g. heavy water reactors, gas cooled reactors, graphite moderated reactors, light water reactors, fast breeder reactors and material testing reactors. This correlation is found to distinguish the main reactor type since the formation of ^{238}Pu is governed by initial ^{235}U enrichment and the $^{242}Pu/^{240}Pu$ isotope amount ratio increases with softer neutron spectrum. Correlations involving different isotopes of uranium and plutonium have been demonstrated to differentiate various fuel–reactor combinations. Recently, the utility of correlations between $^{241}Pu/^{239}Pu$ versus $^{240}Pu/^{239}Pu$ ratios and $^{241}Am/^{239}Pu$ versus $^{240}Pu/^{239}Pu$ ratios to determine the age and history of Pu from pressurized heavy water reactor (PHWR) was published[41].

Round robin exercises

Round robin exercises are highly useful to the individual participating laboratories in comparing/evaluating their preparedness with respect to other international laboratories. In 1998, a Pu round robin exercise was launched by International Technical Working Group (ITWG) and six laboratories participated in this exercise. The laboratories were requested to report their results within three timeframes (24 h, 1 week and 2 months after receipt of sample). One U-based radio-chronometer standard was distributed recently to various international laboratories who participated in the Institute of Reference Materials and Measurements (IRMM, Belgium) Regular European Interlaboratory Measurement Evaluation Program (REIMEP-22)[30,64,65].

Statistical treatment of data

Chemometric analysis, also known as multivariate statistical analysis, is an important tool to compare analytical data obtained on the confiscated material with that of the same kind of materials in the national forensic library of a particular country or internationally. For example, Lawrence Livermore National Laboratory (LLNL), USA has developed a Discriminant Analysis Verification Engine (DAVE) algorithm employing iterative application of partial least squares discriminant analysis (PLS-DA) for matching the analytical data of an unknown UOC with that available in the database.

Principal component analysis (PCA) is an unsupervized technique and does not depend upon prior knowledge of sample classification. The use of PCA helps to reduce dimensionality and visualize underlying patterns. Another statistical approach known as canonical analysis of principal coordinates (CAP) is a supervized routine. This takes into account situations where proposed groups in the samples exist and the aim is to determine how distinct the groups are. Sometimes, CAP can provide more meaningful interpretation of analytical data than PCA, particularly in cases where patterns of overall dispersion obtained by PCA can mask real patterns of differences.

Cluster analysis of REE abundance pattern has been done. This method divides a group of objects into classes so that similar objects are in the same class. The nearest neighbour method was used and the sum of squared differences between the observations was employed to calculate the distance between the clusters. The dendrogram obtained by cluster analysis of rare elements pattern was found to provide useful information for nuclear forensics.

Applications of nuclear forensics – a few cases

The first cases of interdiction were reported from Switzerland and Italy in 1991, after the fall of the former Soviet Union. More cases were reported, subsequently, from other parts of Europe. A few examples are given here[1,21,62,66].

1994 Munich plutonium. A material was intercepted at Munich Airport in August 1994 on a Lufthansa flight from Moscow. The material consisted of 560 g of mixed uranium + plutonium oxide and was found to contain 363 g of Pu (87% ^{239}Pu), 122 g of U (1.6% of ^{235}U) and 210 g of enriched Li metal (89.4% ^{6}Li). Most likely, the plutonium was a mixture of different spent fuels (i.e. a low-burn-up or weapons-grade plutonium and a high-burn-up fuel) and had no direct connection with the uranium present. This revealed the intention to build a nuclear device.

1999 Bulgarian HEU. The material intercepted at the Turkish–Bulgarian border in May 1999, consisted of 10 g of HEU (72% ^{235}U) with high ^{236}U content (13%). The findings of 9-month forensic analysis showed that it was reprocessed uranium from high burn-up fuel and original ^{235}U content was about 90%.

1992, 2003 and 2008 Environmental samples. Images of micron-sized particles from environmental samples were prepared with a secondary ion mass spectrometer. The various findings were as follows: Undeclared Pu separation in North Korea (from samples taken in 1992), HEU particles on Iranian centrifuges (discovered in June 2003) and HEU particles on Al tubings found in North Korea (revealed in July 2008).

UOC samples. One of the earliest cases was in USA (1978), where five barrels of yellow cake were stolen from the Standard Oil Company of Ohio’s (Sohio) uranium mill facility in New Mexico[28]. Another incident occurred in December 2003, when 3 kg of radioactive material was found in a shipment of scrap metal (from Jordan) in Rotterdam Harbour, the Netherlands. The nuclear forensic investigations showed that UOC originated from a facility in Iraq. Recently, the Australian Nuclear Science and Technology Organisation (ANSTO) published another case of unknown UOC (NSR-F-130509).

Non-invasive/non-intrusive methods

Muon radiography

Muon radiography based on cosmic ray muons is a promising technique for detecting nuclear materials being smuggled into any country[67]. About 1000 muons per square metre strike the earth's surface and their trajectory changes as they pass through the objects. High Z nuclear materials including heavy shielding materials such as W or Pb used for gamma ray shielding deflect muons. Changes in the direction of the muons can be used to correlate with material density. Muon scans are quite promising compared to gamma-ray scanners since no radioactive source replacement is needed as for gamma ray source; three-dimensional views can be obtained, and muons have greater penetration depth. Recently, in 2014, it was proposed to employ two muon detectors to determine the location and condition of the nuclear fuel inside Fukushima Daiichi reactors.

Anti-neutrinos for nuclear monitoring

Anti-neutrinos can be used to reveal the plutonium content in a reactor[68–70]. About 2×10^{20} antineutrinos per second are emitted by a 1 GW_{th} nuclear power plant. Further, the energy spectra of antineutrinos emitted by fissile nuclides ^{235}U, ^{239}Pu are different; the latter yielding a softer energy spectrum. By using a large volume of plastic scintillator (e.g. 20 tonnes outside the reactor building) and employing the principal of inverse beta decay for antineutrino detection, the amount of Pu in a reactor can be known. Antineutrinos interact with protons in the scintillator (energy threshold 1.8 MeV) and produce positrons and neutrons. Positrons annihilate with electrons and produce two gamma rays referred to as prompt event. Neutrons are thermalized in the plastic scintillator and captured by ^{155}Gd and ^{157}Gd embedded in between plastic scintillators. They produce a gamma ray cascade with an average energy of about 8 MeV, referred to as delayed event. The prompt and the delayed events are detected in delayed conicidence. Gd-loaded water Cerenkov detectors are also being investigated for antineutrinos measurements. Proposals are underway to test the feasibility of this approach for the IR-40 reactor in Arak, Iran as a test case, where researchers will aim to detect the removal of 2 kg of Pu within a period of 90 days as required by IAEA.

Future outlook

Mass spectrometry, alpha spectrometry and high resolution gamma spectrometry are important analytical tools in nuclear forensics. A variety of mass spectrometric techniques, viz. TIMS, ICPMS (both for solutions and solids) and SIMS are being employed. SEM, TEM and Raman spectroscopy are valuable for morphology and structural determination. There is a strong need to develop, validate and exploit ^{235}U–^{231}Pa chronometer for HEU (^{235}U > 20 atom%) and LEU (^{235}U < 20 atom%) samples by different international laboratories, in addition to the commonly used ^{234}U–^{230}Th chronometer. The commercial availability of different spike isotopes (^{229}Th, ^{233}Pa, ^{236}Np, ^{243}Am, etc.) is necessary to employ various parent–daughter chronometers. There is also an urgent requirement for preparing and certifying various reference materials, e.g. in uranium age dating, to validate the methodologies and provide a robust footing for legally defending the data produced on interdicted/smuggled nuclear material. Studies are required for mixed U and Pu based materials[71]. The precision and accuracy of the half-life data needs be improved to minimize the uncertainty on the model age of the radioactive nuclear materials and utilize the full potential of the capabilities of analytical scientists as well as present day MC–ICPMS and MC–TIMS instruments. Muon radiography based on cosmic-ray muons tried at Los Alamos National Laboratory in 2003 holds great promise to detect nuclear materials being smuggled into any country. Reactor anti-neutrino monitoring holds promise as a non-intrusive method to monitor Pu in a reactor. New techniques such as laser-induced breakdown spectroscopy (LIBS) for isotope ratio measurements[72,73], angle measure technique for analysing texture images and the nuclear car wash[74] concept based on interrogating cargos with pulsed high energy neutrons (3–7 MeV) followed by measurement of fission product beta delayed gamma rays above 3 MeV, need be explored and developed further. Last but not the least, it is extremely important to develop a national nuclear forensic library on the materials available/produced in each country. This would be a valuable asset to trace the origin of interdicted/smuggled/stolen nuclear materials. Since research related to nuclear forensics cannot be performed in any conventional forensic laboratory in view of the specialized requirements of the radiological facilities, it is high time that such dedicated laboratories are established in various countries. This is all the more important for countries such as India which are poised to increase their nuclear energy production capacity by many folds. Nevertheless, the expertise to perform these nuclear forensics related research exists in the country.

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