IANCAS
Bulletin

Nuclear Forensics

Editorial

The Department of Atomic Energy (DAE) and Government of India have been giving high importance to nuclear security and allied matters in the Indian nuclear programme,and accordingly, a thematic issue of IANCAS Bulletin was recently published covering the Nuclear Security aspects, through a number of articles contributed by experts in the field.The goal of ensuring security of nuclear materials and facilities has however got a strong dependence on building and nurturing 'nuclear forensic skills and facilities', in addition to instituting systems and procedures for implementing and monitoring measures.

Nuclear forensics is an essential component of national nuclear security infrastructure to address the threat of nuclear and other radioactive material,some of which may be outside of regulatory control,and also to assess nuclear security vulnerabilities.The current volume is thus an accompanying one to the Nuclear Security volume and is devoted to the various aspects of Nuclear Forensics.

The articles chosen for the volume (including a contribution from the European Commission -Joint Research Centre, Karlsruhe, Germany) cover the overall status of nuclear forensics, specific techniques applicable in nuclear forensics for identification and quantification of suspect or seized materials, challenge for forensics in the face of threat situations (be it nuclear or radiological), and a final piece outlining global initiative citing governments' commitment to act in unison to prevent any potential acts of terrorism using nuclear materials.

The International Atomic Energy Agency (IAEA), in leading the global cooperation effort, held a Conference on the topic in 2002. Based on the recommendations of this conference, and feedback from Member States, the IAEA had implemented three coordinated research projects (CRPs) during 2003 to 2011dealing with the improvement of technical measures to detect illicit trafficking in nuclear and other radioactive materials, the development of instruments and methods for the detection of nuclear and other radioactive material outside of regulatory control, and the application of nuclear forensics to prevent and respond to nuclear security events. During 2003 to 2012, the IAEA had also prepared a number of guidance documents on nuclear forensics, including a Reference Manual entitled Nuclear Forensics Support (IAEA Nuclear Security Series No. 2) in 2006.

The IAEA General Conference has adopted resolutions on nuclear security emphasising the importance of nuclear forensics as a component of a Member State's nuclear security infrastructure. Nuclear

CONTENTS

Nuclear Forensics: An Overview of Present Status and Future Needs

Suresh K. Aggarwal

Fuel Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India; E-mail: skaggr2002@gmail.com

Introduction

Nuclear forensics is an interdisciplinary science which has assumed a great importance in the last two decades owing to changes in the world scenario and has come a long way in relatively short time. Nuclear forensics can be defined as collection and analysis of nuclear and radiological materials to support investigations into diversion, trafficking and illicit use. The main objective of nuclear forensics 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 devices (RDS) also referred to as "dirty bomb". Nuclear forensics encompasses a number of sub-disciplines including analytical chemistry, nuclear and radiochemistry, reactor physics, nuclear engineering, process engineering, enrichment engineering, geology, material science, quality assurance, statistics etc. This 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 illicit trafficking 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. The availability of 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 by different international laboratories. Demonstrated capability of nuclear forensics in a country would surely serve as a deterrent to would-be smugglers of nuclear materials and would be useful to develop and implement a national response plan. This manuscript gives an overview of present status of nuclear forensics related activities and highlights the future needs.

Different kinds of Materials

The materials which are of interest for nuclear forensics are those containing actinides e.g. uranium (U), plutonium (Pu), thorium (Th) etc. These include all the materials handled at different stages of the nuclear fuel cycle e.g. minerals/rocks/ores from which U and Th are extracted, uranium ore concentrates (UOC), U from [235]U enrichment plants, fuels from fabrication facilities and purified materials (U, Pu etc.) from spent fuel reprocessing plants. Data on the chemical composition of the non-nuclear materials associated can provide some clues about the production site.

Different provenancing signatures which can be used for the attribution of uranium ore concentrates (UOC) are summarised in Table 1.

Various Signatures and Methodologies

Age Determination of Uranium and Plutonium

The age of any radioactive sample can be determined by measuring the daughter/parent ratio as a function of decay time. Since 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 amounts of daughters grown are quite limited. This demands chemical separation followed by mass spectrometric or radiometric measurements. High resolution gamma spectrometry is another alternative non-destructive technique which has been used for uranium materials age dating. Age determination of uranium and plutonium refers to "Model ages" since it is assumed that (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 lead to erroneous results on the age. If possible, it is preferred to determine the age of the material by using two independent chronometers. Good agreement (concordance) in the data obtained by two independent radio-chronometers enhances the confidence in the results. In case of disagreement, the lower age is taken since the initial presence of some of the daughter nuclide would give a longer age in the calculation.

Gamma spectrometry has been used to find out the age of uranium. The age of uranium sample is determined by measuring the activity ratio of ^{214}Bi (609 keV)/^{234}U (120.9 keV) by gamma spectrometry. The different activity ratios measured are those of ^{234}U/^{235}U, ^{235}U/^{238}U and ^{214}Bi/^{238}U using intrinsic efficiency calibration. The age of uranium which refers to time T after purification or enrichment can be calculated from:

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

This method is non-destructive and can be applied to materials in any physical form and geometrical shape.

Multi-collector inductively coupled mass spectrometry (MC-ICPMS) has been used to determine the age of ^{235}U enriched materials employing ^{235}U-^{231}Pa chronometer. Isotope dilution mass spectrometry (IDMS) was employed using ^{233}Pa ($t_{1/2}$= 26.967 days) milked from ^{237}Np as a spike for ^{231}Pa ($t_{1/2}$= 32,760 yr) and ^{233}U 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 (U100 containing 10% of ^{235}U). Good agreement in the ages obtained by the two chronometers enhanced the confidence in the data about the

most recent chemical purification/processing date. For uranium samples containing ^{233}U and ^{232}U originating from thorium based fuels, the useful chronometers ^{233}U-^{229}Th and ^{232}U-^{228}Th, respectively, can be employed for age determination.

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

Signatures	Technique used
Morphology	Scanning electron microscopy (SEM)
U 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 (ICPMS)
^{143}Nd/^{144}Nd isotope ratio	Mass spectrometry (TIMS/MC-HR-ICPMS)
^{87}Sr/^{86}Sr isotope ratio	Mass spectrometry (TIMS/ICPMS)
^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, ^{208}Pb/^{204}Pb isotope ratios	Mass spectrometry (TIMS, ICPMS)
Sulphur isotopes ratio	Mass spectrometry (MC-HR-ICPMS)
Oxygen isotopes ratio	Mass spectrometry (SIMS, TIMS)

Age determination of Pu sample is an important parameter to find out the origin of Pu sample since it can help in excluding certain production or reprocessing plants. The age can be determined by using different chronometers. Table 2 gives a list of different radio-chronometers which can be employed for any Pu sample. 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 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 consistency in the ages obtained by two chronometers is useful to exclude the possibility of residual U or Am from reprocessing plant, originally present in the Pu sample since the last chemical separation.

Isotopic Composition of Elements other than Actinides

Isotope ratio measurements on Sr, Nd and Pb present in uranium ore concentrate or any uranium sample can be used to trace the origin of uranium. This is due to the fact that there would be small differences in the contents of ^{87}Sr (daughter of ^{87}Rb), ^{143}Nd (decay product of ^{147}Sm, $T_{1/2}$=1.06 x 10^{11} yr)) and radiogenic lead isotopes (viz. ^{206}Pb, ^{207}Pb and ^{208}Pb) 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 highly precise determination of isotopic composition by either thermal ionisation mass spectrometry (TIMS) or multi-collector high resolution inductively coupled plasma source mass spectrometry (MC-HR-ICPMS).

^{143}Nd/^{144}Nd isotope ratio has been shown to be a useful signature to assess the origin of uranium ore concentrates. This ratio provides a robust signature since it is less prone to weathering. Significant differences in ^{143}Nd/^{144}Nd isotope ratio have been observed between different uranium mines. This ratio depends upon the age of the minerals present 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. ^{143}Nd/^{144}Nd isotope 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 high precision using TIMS or magnetic sector multi-collector ICPMS.

The determination of ^{18}O/^{16}O isotope ratio in the actinides compounds can also be a useful indicator for tracing their origin. Small changes in ^{18}O/^{16}O isotope ratio have been observed in uranium oxide samples of different origins using secondary ion mass spectrometry (SIMS) and thermal ionisation mass spectrometry (TIMS). The small differences (less than 3%) originate due to variations in the oxygen isotopic content of air and ground water at various geographical places as well as chemicals and water used to process the uranium ore into uranium ore concentrate. The use of magnetic sector SIMS was demonstrated for determination of ^{18}O/^{16}O isotope ratio in uranium dioxide micro particles using carbon planchets and gold substrates and carrying out the measurements on O$^-$ ions using Cs$^+$ as the primary ion beam. TIMS was used to monitor UO$^+$ ions from solution deposited on the filament for determining ^{18}O/^{16}O isotope ratios.

^{34}S/^{32}S ratios in the uranium ore concentrates were recently determined using MC-ICPMS. 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 has been applied to 18 different uranium ore concentrates from different parts of the world i.e. Africa, Australia, Canada, USA and significant differences were found in the $^{34}S/^{32}S$ isotope ratios. The potential to correlate $ä^{34}S$ value of the ore to the origin of the UOC exists in future.

Cationic and Anionic Impurities

Rare-earth elements (La to Lu) concentrations pattern provides useful information in attributing uranium ore and ore concentrates. The rare-earth elements are determined by ICPMS and their concentrations are normalised with respect to chondrite rare earth elements concentrations. Since the chemical properties of the rare-earth elements are quite similar, except for Ce(IV) and Eu(II), their relative abundance pattern can be useful to authenticate the source of the rock. 38 uranium ore concentrates 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 . Determination of other non-radioactive impurities elements can be sued to identify nuclear forensic signatures of 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 uranium ore concentrate.

Ratio of sulphate to chloride in the aqueous leachate of uranium ore concentrate (UOC) samples gives information 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 uranium ore concentrate sample seized during 2009 in a criminal investigation in Australia. Information about other anions e.g. F^-, Br^-, NO_3^-, PO_4^{3-} can also be useful for nuclear forensic applications.

Organic Impurities

Residual organic impurities present in the uranium ore concentrate can provide information about 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

The 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. X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) and transmission electron microscopy (TEM) are used to obtain phase composition and morphological information.

Isotope Correlations

Plutonium isotope correlations are useful to find out the type of reactor since it is an important parameter for any seized plutonium sample. Since the evolution of isotopic composition 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 Pu-242/Pu-240 ratio versus Pu-238 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 Pu-238 is governed by initial ^{235}U enrichment and the isotope ratio Pu-242/Pu-240 increases with softer neutron spectrum. Correlations involving different isotopes of uranium and plutonium have been demonstrated to differentiate various fuel-reactor combinations.

Round Robin Exercises

Round robin exercises are highly useful to the individual participating laboratories to compare/evaluate 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 time frames (24 hr, 1 week and 2 months after receipt of sample).

Statistical Treatment of Data

Chemometric analysis is an important tool to compare the analytical data obtained on the confiscated material with that existing on 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 uranium ore concentrate (UOC) with that available in data base.

Principal Component Analysis (PCA) is an unsupervised technique and does not depend upon prior knowledge of sample classification. The use of PCA helps to reduce dimensionality and visualise underlying patterns. Another statistical approach known as Canonical Analysis of Principal Coordinates (CAP) is a supervised routine. This takes into account the 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 compared to PCA,

TABLE 2. Different chronometers for age determination of plutonium samples

Parent nuclide (Half-life)	Daughter nuclide	Spike isotope needed for isotope dilution mass spectrometry	Remarks
Pu-238 (87.7 yr)	U-234	Pu-239, U-235	Low abundance of Pu-238, Isobaric interference from U-238
Pu-239 (24110 yr)	U-235	Pu-244, U-233	Pu-244 spike availability restricted/limited
Pu-240 (6553 yr)	U-236	Pu-244, U-233	Pu-244 spike availability restricted/limited
Pu-241 (14.4 yr)	Am-241, Np-237	Pu-244, Am-243	Spikes not available, Am-241 and Np-237 by ICPMS, γ spectrometry for ^{241}Am
Pu-242 (3.76×10^5 yr)	U-238	————–	Long half-life of parent , not of interest

particularly in cases where patterns of overall dispersion obtained by PCA can mask real patterns of differences.

Cluster analysis of rare-earth elements 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 give useful information for nuclear forensics.

A Few Cases of Nuclear Forensics Applications

1994 Munich Plutonium

Intercepted at Munich Airport in August 1994 on a Lufthansa flight from Moscow. The material was found to contain 363 g of Pu (87% Pu-239), 122 g of U and 210 g of enriched Li metal (89.4% Li-6). Most likely, the plutonium was a mixture of different spent fuels (e.g. a low-burn-up or weapons-grade plutonium and a high-burn-up fuel) and had no direct connection with the uranium present.

1999 Bulgarian HEU

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

Environmental Sampling Techniques

Images of micron-sized particles were made with a Secondary Ion Mass Spectrometer. The various findings were : Undeclared Pu separation in North Korea (from samples taken in 1992), HEU particles on Iranian centrifuges (discovered in June 2003), HEU particles on Al tubings found in North Korea (revealed in July 2008).

Muon Radiography

Muon radiography based on cosmic ray muons is a promising technique for detecting nuclear materials being smuggled into any country. About 1000 muons per square meter strike the earth's surface and their trajectory changes as they pass through the objects. High Z nuclear materials including heavy shielding materials like 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 (i) no radioactive source replacement is needed as for gamma ray source (ii) three dimensional views can be obtained and (iii) muons have greater penetration depth. It has recently been proposed in 2014 to employ two muon detectors to determine the location and condition of the nuclear fuel inside Fukushima Daiichi reactors.

Antineutrinos for Nuclear Monitoring:

Antineutrinos are promising for nuclear monitoring and offer a non-intrusive method to reveal the plutonium content in a reactor. About 2×10^{20} antineutrinos per second are emitted by $1GW_{th}$ nuclear power plant. Futher, 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 tons outside the reactor building) and employing the principal of inverse beta decay for antineutrino detection, it is feasible to find out the amount of Pu in a reactor. 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 get thermalized in the plastic scintillator and are captured by ^{155}Gd and ^{157}Gd embedded in between plastic scintillator. They give rise to 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 antinneutrinos measurements.

Proposal are underway to test the feasibility of the approach for IR-40 reactor in Arak, Iran as a test case, where the researchers will aim to detect the removal of 2 Kg of Pu within a period of 90 days as required by International Atomic Energy Agency (IAEA).

Future Needs

There is a strong need to develop and exploit ^{235}U-^{231}Pa chronometer for high enriched uranium (HEU: ^{235}U> 20 atom%) and low enriched U (LEU: ^{235}U < 20 atom%) samples by different international laboratories, in addition to the commonly used ^{234}U-^{230}Th chronometer. This also demands the availability of ^{233}Pa isotope to be used as a spike in isotope dilution and understanding on the separation chemistry of Pa, by adding fluoride, to avoid its hydrolysis when dealing with trace amounts. As a matter of fact, the commercial availability of different spike isotopes (^{229}Th, ^{236}Np, ^{243}Am etc.) is necessary to employ various parent-daughter chronometers. There is also an urgent requirement of preparing and certifying various reference materials e.g. for uranium age dating, to validate the methodologies and put them on robust footings for legally defending the data produced on interdicted/smuggled nuclear materials. It is heartening to know that one such uranium based reference material IRMM-1000 will be available, in future, to international nuclear forensic community. Muon radiography based on cosmic-ray muons tried at Los Alamos National Laboratory in 2003 holds a great promise to detect nuclear materials being smuggled into any country. Reactor antineutrino monitoring outside the reactor building appears promising as a non-intrusive method of Pu monitoring in a reactor. Last but not the least, it is extremely important to develop the 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.

Suggested Readings

[1]   C.T.Nguyen and J.Zsigrai, Gamma spectrometric uranium age dating using intrinsic efficiency calibration, Nucl. Instr. Methods B 243 (2006) 187-192.

[2]   G.R.Eppich, R.W.Williams, A.M.Gaffney, K.C.Schorzman, ^{235}U-^{231}Pa age dating of uranium materials for nuclear forensic investigations, J. Anal. At. Spectrom. 28 (2013) 666-674.

[3]   R.W.Williams and A.M.Gaffney, ^{230}Th-^{234}U model ages of some uranium standard reference materials, Radiochim. Acta 1 (2011) 31-35.

[4]   IAEA-TECDOC-1730, Application of nuclear forensics in combating illicit trafficking of nuclear and other radioactive material, 74p. (January 2014).

[5]   International Conference on Advances in Nuclear Forensics: Countering the evolving threat of nuclear and other radioactive material out of regulatory control, IAEA-CN-218, July 7-10, 2014, Book of extended synopses, 242p. (2014).

[6]   Kenton J. Moody, Ian D. Hutcheon and Patrick M. Grant, Nuclear Forensic Analysis, Taylor & Francis (2005).

[7]   Klaus Mayer, Maria Wallenius and Zsolt Varga, Nuclear Forensic Science : Correlating measurable material parameters to the history of nuclear material, Chem. Rev. 113 (2013) 884-900.

[8]   E.Keegan, M.J.Kristo, M.Colella, M.Robel, R. Williams, R. Lindvall, G. Eppich, S.Roberts, L.Borg, A.Gaffney, J.Plaue, H.Wong, J.Davis, E.Loi, M. Reinhard and I. Hutcheon, Nuclear forensic analysis of an unknown uranium ore concentrate sample seized in a criminal investigation in Australia, Forensic Science International 240 (2014) 111-121.

[9]   H.E. Frimmel, S.Schedel, H. Bratz, Uraninite chemistry as forensic tool for provenance analysis, Applied Geochemistry 48 (2014) 104-121.

[10]   E.Keegan, M.Wallenius, K. Mayer, Z. Varga and G. Rasmussen, Attribution of uranium ore concentrates using elemental and anionic data, Applied Geochemistry 27 (2012) 1600-1609.

[11]   Floyd E. Stanley, A.M.Stalcup, H.B.Spitz, A brief introduction to analytical methods in nuclear forensics, J. radioanal. Nucl. Chem. 295 (2013) 1385-1393.

[12]   Xiandeng Hou, Wen Chen, Yihua He and Bradley T. Jones, Analytical atomic spectrometry for nuclear forensics, Applied Spectroscopy Reviews 40 (2013) 245-267.

[13]   Klaus Mayer, Maria Wallenius and Ian Ray, Nuclear forensics - a methodology providing clues on the origin of illicitly trafficked nuclear materials, Analyst 130 (2005) 433-441.

[14]   L.Pajo, G.Tamborini, G.Rasmussen, K.Mayer and L.Koch, A novel isotope analysis of oxygen in uranium oxides: comparison of secondary ion mass spectrometry, glow discharge mass spectrometry and thermal ionisation mass spectrometry, Spectrochimica Acta B56 (2001) 541-549.

[15]   G.Tamborini, D.Phinney, O.Bildstein and M.Betti, Oxygen isotopic measurements by secondary ion mass spectrometry in uranium oxide microparticles: a nuclear forensic diagnostics, Anal. Chem. 74 (2002) 6098-6101.

[16]   K.Mayer, M.Wallenius and T. Fanghanel, Nuclear forensic science - From cradle to maturity, Journal of Alloys and Compounds, 444-445 (2007) 50-56.

[17]   Zsolt Varga, Adrian Nicholl, Maria Wallenius, Klaus Mayer, Development and validation of a methodology for uranium radiochronometry reference material preparation, Anal. Chim. Acta 718 (2012) 25-31.

[18]   Sun-Ho Han, Zsolt Varga, Judit Krajko, Maria Wallenius, Kyuseok Song and Klaus Mayer, Measurement of the sulphur isotope ratio ($^{34}S/^{32}S$) in uranium ore concentrates (yellow cakes) for origin assessment, J. Anal. At. Spectrom. 28 (2013) 1919-1925.

[19]   S.K.Aggarwal and D.Alamelu, A novel approach for the determination of ^{238}Pu by thermal ionization mass spectrometry (TIMS) using interfering element correction methodology, Int. J. Mass Spectrometry 241 (2005) 83-88.

[20] S.K.Aggarwal and D.Alamelu, Isotope correlations for determining the isotopic composition of plutonium produced in research and power reactors using the experimental data obtained by alpha and mass spectrometry, Int. J. Nucl. Energy Science and Technology 1 (2005) 215-219.

[21] Z.Varga, M.Wallenius and K. Mayer, Origin assessment of uranium ore concentrates based on their rare-earth elemental impurity pattern, Radiochim. Acta 98 (2010) 771-778.

[22] Judit Krajko, Zsolt Varga, Ezgi Yalcintas, Maria Wallenius and Klaus Mayer, Application of neodymium isotope ratio measurements for the origin assessment of uranium ore concentrates, Talanta 129 (2014) 499-504.

[23] Maria Wallenius, Klaus Lutzenkirchen, Klaus Mayer, Ian Ray, Laura Aldave de las Heras, Maria Betti, Omer Cromboom, Marc Hild, Brian Lynch, Adrian Nicholl, Herbert Ottmar, Gert Rasmussen, Arndt Schubert, Gabriele Tamborini, Hartmut Thiele, Werner Wagner, Clive Walker and Evelyn Zuleger, Nuclear forensic investigations with a focus on plutonium, Journal of Alloys and Compounds 444-445 (2007) 57-62.

[24] S.K.Aggarwal, Recent trends in mass spectrometry for nuclear forensics, DAE-BRNS Fifth Symposium on Nuclear Analytical Chemistry (NAC-V), January 20-24, 2014, BARC, Mumbai, India, Invited Talk, IT-16, pp. 42-43.

[25] G.B.Dudder, Proceedings of the IAEA Conference on Security of Material, Stockholm, Sweden, May 7-11, 2011.

[26] Brian Fishbine, Muon radiography: Detecting nuclear contraband, Los Alamos Research Quarterly, 13-16, Spring 2003.

[27] G.Nikolaou, Determination of the origin of unknown nuclear material through an isotopic fingerprinting method, IAEA TECDOC 1730, 48-56 (2014).

[28] Eric Christensen, Patrick Huber, Patrick Jaffke and Thomas E. Shea, Antineutrino monitoring for heavy water reactors, Phys. Rev. Lett. 113 (2014) 042503.

[29] S.Oguri, Y.Kuroda, Y.Kato, R.Nakata, Y.Inoue, C. Ito and M.Minowa, Reactor antineutrino monitoring with a plastic scintillator array as a new safeguards method, Nucl. Instr. Methods Phys. Res. A 757 (2014) 33-39.

[30 A. Bernstein, G. Baldwin, B. Boyer, M. Goodman, J. Learned, J. Lund, D. Reyna and R. Svoboda, Nuclear security applications of antineutrino detectors: current capabilities and future prospects, Science and Global Security 18 (2010) 127–192.

Dr. Suresh K. Aggarwal, is presently Associate Director, Radiochemistry & Isotope Group and Head of Fuel Chemistry Division at Bhabha Atomic Research Centre (BARC) in Mumbai, India. He joined BARC in 1973 after graduating from 16th batch of BARC Training School (1972-73) with Bhabha Medal Award and has been continuing at BARC in various capacities since 1973. At present, he holds the grade of Distinguished Scientist. He obtained his Ph.D. degree in 1980 from Mumbai University and had Post-doctoral Training at University of Virginia at Charlottesville, USA during 1987-89. He also served for four months at International Atomic Energy Agency (IAEA) laboratories at Seibersdorf,. He is a Ph.D. guide of Mumbai University and Senior Professor of Chemistry at Homi Bhabha National Institute (HBNI) at Mumbai. He has more than 700 publications to his credit, including more than 200 papers in peer reviewed International Journals. He is the Founder President of Indian Society for ElectroAnalytical Chemistry (ISEAC) since 2003 and is presently the elected president of Indian Society for Mass Spectrometry (ISMAS). He received several Awards including the "Eminent Mass Spectrometrist" award by ISMAS. He is a well known expert in the fields of electrochemistry, mass spectrometry and nuclear sciences.

Application of Inorganic Mass Spectrometry in Nuclear Forensics

K. Mayer, M. Wallenius, Z. Varga, M. Hedberg

European Commission – Joint Research Centre, Institute for Transuranium Elements, 76125 Karlsruhe, Germany; E-mail:

Abstract

Mass spectrometric techniques are widely applied analytical tools in different fields of science. They enable identifying unknown compounds, quantifying known materials and elucidating the structural and chemical properties of molecules. In inorganic mass spectrometry emphasis is given to elemental and isotopic composition of materials, while in organic mass spectrometry structural aspects are in the focus of the analysis. In forensic investigations of nuclear material, mass spectrometric techniques play an important role. The versatility and the sensitivity of mass spectrometric methods provide access to a wealth of information inherent to the nuclear material. Different variants of mass spectrometry are applied in order to provide the best possible answers required for supporting nuclear forensic investigations. They provide hints on the history and on the intended use of the material, based on elemental and isotopic data. This includes major constituents of the material, as well as trace impurities. The physical and chemical appearance of the material and the information required determine the choice of the analytical method to be applied. The principles of the most prominent mass spectrometric techniques, thermal ionization mass spectrometry, inductively coupled plasma mass spectrometry and secondary ion mass spectrometry are described and their application in nuclear forensics are presented. More sophisticated techniques, like accelerator mass spectrometry and resonance ionisation mass spectrometry are briefly introduced and their use in nuclear forensic investigations is illustrated using appropriate examples.

Introduction

Nuclear smuggling and illicit trafficking of radioactive and nuclear materials pose a serious threat to the international community. Concerns arise in particular with regard to nuclear proliferation and to the threat of nuclear terrorism. In consequence, measures for further enhancing the nuclear safeguards system and for improving nuclear security need to be implemented. The Nuclear Security Summit held in Washington in April 2010 clearly underlined the need for additional measures to prevent the malicious use of nuclear material. Nuclear material is subject to strict international controls to prevent nuclear proliferation. The international safeguards system of the International Atomic Energy Agency (IAEA) aims at the timely detection of diversion of such materials. Comprehensive safeguards agreements are designed to verify the correctness and completeness of States' declarations. By this means, it provides credible assurance of the absence of undeclared nuclear activities. According to the definition of the IAEA, fissionable materials (^{233}U, ^{235}U and ^{239}Pu) and source materials (e.g. natural uranium and thorium or depleted uranium in metal, alloy or compound form) belong to the category of nuclear materials.

Nuclear Forensics is a fairly new branch in science which aims at providing hints on the history of nuclear material. This may include information on the place of production, on the production process, on the age of the material, on the intended use and on the geographic origin of the source material. To this end, nuclear forensics makes use of characteristic parameters that are inherent to the material. Such parameters may include chemical composition, isotopic composition of the nuclear material, chemical impurities, macroscopic appearance, microstructural features or the isotopic composition of minor constituents. A variety of analytical techniques are applied for determining the various parameters in samples of nuclear material [1]. Such samples may appear in a wide spectrum of chemical and physical forms, ranging from micrometer sized particles to grams or even kilograms of material. Illicit nuclear material was detected as single uranium particles on swipe samples, as surface contamination adherent to scrap metal, as uranium oxide powder (low enriched and highly enriched), as depleted uranium metal, as low enriched uranium oxide pellets and as powder mixture of uranium and plutonium oxide.

Mass spectrometry is a highly versatile technique and offers high sensitivity, high selectivity and high precision in combination with the potential for high accuracy. In consequence, mass spectrometric techniques play a key role in measuring parameters relevant to nuclear forensics, as can be seen from Table 1. Different variants of mass spectrometry are applied and provide valuable information to nuclear scientists analyzing the material and enable drawing conclusions which support the source attribution of illicit nuclear material. Hereafter we will provide some details on different mass spectrometric techniques, recall their general principles and limitations and illustrate their application in nuclear forensic investigations. This comprises the most prominent mass spectrometric techniques: thermal ionization mass spectrometry, inductively couples plasma mass spectrometry, secondary ion mass spectrometry and a shorter chapter will illuminate special techniques such as accelerator mass spectrometry and resonance ionization mass spectrometry, applied only in special cases.

Thermal Ionization Mass Spectrometry

Thermal Ionization Mass Spectrometry (TIMS) is widely applied for high precision isotope ratio measurements for elements with reasonably low ionization potential. Nuclear materials such as uranium and plutonium satisfy this requirement and the methodologies for U and Pu isotope ratio measurement by TIMS have been established already in the early days of nuclear technology. With improvements in instrumentation and with progress in data

TABLE 1. Relevant parameters to be measured in a nuclear forensic investigation, examples of applicable measurement methods and generic concept for data interpretation. The list of measurement techniques in non-exhaustive and gives priority to mass spectrometric techniques. (GC-MS: gas chromatography coupled to mass spectrometry, GD-MS: Glow-discharge mass spectrometry, ICP-OES: Inductively coupled plasma optical emission spectrometry; other acronyms are explained in the text).

Parameter	Measurement Method	Evaluation by comparison against
U isotope ratios	TIMS, ICP-MS, SIMS, AMS,RIMS	Data base
Pu isotope ratios	TIMS, ICP-MS, SIMS, RIMS, gamma spectrometry	Model calculations
		Data base
Metallic impurities (concentrations, patterns)	ICP-MS, ICP-OES, GD-MS	Process knowledge
		Data base, known samples
Stable isotope ratios	ICP-MS, GC-MS	Data base, known samples
Macroscopic appearance	Optical microscopy	Process knowledge
		Database, known samples
Microscopic appearance	Scanning electron microscopy, transmission electron microscopy	Process knowledge
		Database, known samples
Radioisotopes	Gamma spectrometry, Liquid scintillation counting, ICP-MS	Model calculations
Non-metallic impurities	Gas chromatography	Process knowledge
		Data base, known samples

processing techniques, the quality of results has largely improved and today we are exploiting the potential of TIMS as a very powerful analytical technique. TIMS offers high selectivity, high sensitivity, specificity and has proven to be highly precise and to have the potential for being very accurate. In particular for U and Pu measurements, accurate information on the isotopic composition is useful, as it helps distinguishing between materials of different batches, different origins and intended for different applications.

A variant of TIMS is the isotope dilution thermal ionization mass spectrometry (ID-TIMS), which enables the exact quantification of an element of interest in a sample. With ID-TIMS (or more generally with ID-MS) the quantity of an element present in a material is determined from the change produced in the isotopic composition of the element when a known amount of "spike" (i.e. an enriched isotope of the same chemical element) is added. More detailed descriptions of the technique can be found in references [2-4]. ID-TIMS is suited for the highest possible accuracy but is essentially a single element technique. Therefore it is

well applicable for the quantification of uranium and plutonium. In nuclear forensics, however, the isotopic composition proves often to be the more useful "fingerprint" and we will limit our discussion further on to the application of TIMS for determining the isotopic composition.

Principle and General Description

Thermal ionization mass spectrometry is a well established technique and described in a number of textbooks [5-7]. It is particularly suitable for chemical elements with a low first ionisation potential. A sample preparation step prior to the actual measurement is required: this consists of the chemical separation of the element of interest from other elements (e.g. matrix materials or impurities). The purified sample is then deposited onto a metal ribbon, called filament. Typically, amounts ranging from few micrograms down to picograms of material are deposited on a filament. The filament consists of a refractory, high work-function metal such as Re, Ta, Pt or W. The filament is then heated by passing an electrical current through it. This leads to a vaporization of the sample, to

atomization and finally to the ionization of the atoms at a hot surface (which is actually the filament). This process of removing an electron from the outer shell by thermal energy coined the name "thermal ionization". For uranium samples, the species U^+ will be formed and the ions are accelerated by applying a high voltage and subsequent mass separation (e.g. $^{234}U^+$, $^{235}U^+$, $^{236}U^+$, $^{238}U^+$) by means of a mass analyzer, i.e. a magnetic field, an electrostatic field or a quadrupole. In uranium and plutonium measurements thermal ionization ion sources are typically combined with magnetic sector fields for mass separation and with faraday cups or secondary electron multipliers for ion detection.

Application of TIMS in Nuclear Forensics

Thermal ionisation mass spectrometry is a key measurement technique in nuclear forensic investigations. Such investigations typically start with non-destructive determination (i.e. high resolution gamma spectrometry) of the radionuclides present in the sample. Gamma spectrometry also allows drawing first conclusions on the isotopic composition of uranium and plutonium. Some nuclides (such as ^{236}U or ^{242}Pu), however, do not emit useful gamma lines and can therefore not be detected. In order to establish the full isotopic composition, mass spectrometry has to be applied. This will also result in significantly lower uncertainties on the isotope ratios, compared to gamma spectrometry. After a visual inspection and optical microscopy of the material, samples are taken for electron microscopy and for destructive analysis. The first step in sample preparation for most of the mass spectrometric techniques is dissolution. Subsamples for thermal ionization mass spectrometry are then subjected to dilution and to chemical separation. A small aliquot of the purified fraction is then loaded onto a Rhenium filament.

The uranium isotopic composition provides information on the intended use of the material. Depleted uranium (i.e. $^{235}U/U < 0.7\%$) is often encountered in metallic form in shielding material of strong radioactive sources. Natural uranium (i.e. $^{235}U/U = 0.7\%$) is mined in large quantities and serves a feed material of the nuclear fuel cycle. Some reactor types operate with fuel of natural isotopic composition. Most of power reactors around the world are so-called light water reactors and operate with low enriched uranium, more precisely with ^{235}U enrichments up to 4.5 %. Research reactors typically require higher enrichments, up to 90%. Also the minor abundant isotopes provide useful forensic information. The $^{234}U/^{238}U$ ratio in natural uranium shows small, but measureable variations which correlate with the geographic origin of the uranium [8]. ^{236}U is not present in natural uranium, it is produced in a reactor by neutron capture of ^{235}U. Thus, the presence of this isotope in a uranium sample points at the irradiation history of uranium.

We will illustrate the application of TIMS measurements using the example of a uranium ore concentrate which was seized in 2003 at the harbour of Rotterdam (Netherlands). Several kilograms of material

Fig. 1   Sample of uranium ore concentrate after arrival at the nuclear forensics laboratory

were detected amongst a shipload of scrap metal arriving from Jordan. Some external indicators pointed at Iraq as the potential origin of the material. Nuclear forensic analysis was requested in order to acquire more information on the history of the material and prove (or disprove) this hypothesis. A sample (Fig. 1) was taken to the Institute for Transuranium Elements (ITU) for further analysis.

The measured $^{235}U/^{238}U$ and $^{234}U/^{238}U$ isotope abundance ratios were $(7.253 \pm 0.013) \times 10^{-3}$ and $(5.522 \pm 0.072) \times 10^{-5}$, respectively, identical with those of the natural uranium isotopic composition. The anthropogenic isotope ^{236}U was initially not detectable by TIMS usng a Finnigan MAT 261 instrument ($^{236}U/^{238}U$ ratio is below 3×10^{-7}). A more recent measurement in a Triton instrument (Thermo Scientific, Bremen, Germany) equipped with decelerating device and ion counting capability revealed a $^{236}U/^{238}U$ ratio of $(1.545 \pm 0.002) \times 10^{-7}$. This result changes the picture significantly: the traces of ^{236}U indicate the contamination of the material with previously irradiated (and recycled) uranium. Thus, this parameter is clearly pointing at a nuclear activity. The $^{234}U/^{235}U$ ratio, which shows small variations in nature, was 0.00761 ± 0.00011. This value agrees well with the published $^{234}U/^{235}U$ ratio in undeclared UO_4 material produced in Al Qaim using phosphorite from Akashat (0.00765 ± 0.00002), and it is different from that of the ratio found in natural uranium materials confiscated in Iraq ($^{234}U/^{235}U$ ratio: 0.00742-0.00757) deriving from a declared source, i.e. imported from Italy [9]. The observed $^{234}U/^{238}U$ ratio suggests the ore from which the uranium was mined to be a low temperature redox deposit [10], which is consistent with the phosphorite deposit in northern Iraq.

Inductively Coupled Plasma Mass Spectrometry

Inductively coupled plasma mass spectrometry (ICP-MS) is at present the most frequently used inorganic mass spectrometric technique for both concentration and isotope ratio measurements down to fg g^{-1} level. This powerful analytical technique is also increasingly used for the measurement of long-lived radionuclides, providing a

complementary tool to the traditional radioanalytical techniques. As ICP-MS is capable to measure not only the elemental concentration, but provides isotopic information on the material, this technique is highly versatile in nuclear forensics. This is also supported by the high sensitivity (which involves low sample consumption), good precision and accuracy as well as the high diversity of sample types and introduction methods [11,12].

Principle and General Description

ICP-MS uses inductively coupled plasma as an ion source. The sample solution can be introduced into the plasma by various sample introduction systems (e.g. pneumatic nebulizer, ultrasonic nebulizer, electrothermal vaporization or laser ablation), where the sample decomposes into its atomic constituents in the (most frequently) argon plasma at a temperature of approximately 6000–8000 K and ionized at a high degree of ionization (ionization efficiency is higher than 90% for most chemical elements) with a low fraction of multiply charged ions. The positively charged ions are extracted from the plasma operating at atmospheric pressure into the high vacuum region of the mass spectrometer via an interface. Several types of analyzers can be used for the separation of the ions, such as quadrupole analyzers, time-of-flight or combinations of electrostatic and magnetic sector field analyzers (so-called double focusing instruments). Though ICP-MS instruments with quadrupole analyzers (ICP-QMS) are cheaper, more robust and easier to operate, for ultratrace-level measurements (typically below ng g^{-1}) mainly instruments with double focusing sector-field analyzer (ICP-SFMS) are used due to the better detection limits (approximately with 1-3 orders of magnitude). Moreover, such mass analyzers can achieve higher mass resolution (denoted as R, sometimes also m/Äm notation is used). Most commercially available ICP-SFMS instruments can operate with a mass resolution up to 10000. Use of the higher mass resolution is very useful for the separation of the analyte peak from the spectral interferences, for instance, at m/z = 56 the $^{56}Fe^+$ analyte peak from the interfering $^{40}Ar^{16}O^+$ peak. However, it also results in lower ion transmission, thus lower sensitivity. After the separation of the analyte ions according to their mass-to-charge ratios, the ions are detected and counted. Use of multiple detectors (so-called multi-collector ICP-SFMS instruments, MC-ICP-SFMS) improves the precision of the measurement (usually expressed in relative standard deviation, RSD), as it detects the isotopes of interest simultaneously and eliminates the fluctuations of the sample introduction and ion source [12].

The major problem in trace-level analysis by ICP-MS is the appearance of isobaric interferences in the investigated mass region. These isobaric interferences derive from polyatomic ions, which are generated in the plasma by the combination of the matrix elements in the sample (e.g. Bi, Pb, Pt, Hg, U), the elements of the solvent (e.g. H, O or N in case of nitric acid) and the elements of the plasma (e.g. Ar, C, O). These elements form polyatomic ions that appear in the mass spectrum causing elevated background and – in consequence - false results. In nuclear forensics the hydride (e.g. $^{238}U^1H^+$, $^{238}U^1H_2^+$) and oxide (e.g. $^{206}Pb^{16}O_2^+$) interferences are of high concern for trace-level plutonium and minor ^{236}U analysis. In order to eliminate most hydride and oxide interferences, special sample introduction devices have been developed for the removal of solvents and for the generation of dry aerosol. The principal of these instruments is the same: the wet aerosol produced by the conventional pneumatic or ultrasonic nebulizer is driven through a heated chamber, where the solvent evaporates. In the forthcoming step, the solvent vapour is removed either by condensation or by membrane desolvation. These instruments do not only decrease the oxide and hydride background, but also have better transfer efficiency of the analyte, thus better sensitivity compared to the conventional nebulizers [13]. However, the complete removal of these interferences, especially if they are present in a large quantity, should better be accomplished by chemical sample preparation.

In those cases, when dissolution of the sample should be avoided (e.g. analysis of highly radioactive materials, confiscated samples, which are evidences in the course of forensic investigations), sample introduction by laser ablation (LA) can be a possible option [14,15]. In this case, a small portion of the investigated material is evaporated by a high-energy laser beam from a confined surface. The laser beam diameter is in the micrometer range. The ablated material is transferred into the plasma of the ICP-MS instrument as an aerosol using a carrier gas. Laser ablation offers an easy possibility for the direct isotope ratio measurements of solid materials, as the ablation and ionization properties of the isotopes of the same element are identical [16,17]. For the concentration measurements, however, one has to take into account the different ablation and ionization efficiencies, which depends on the analyte, the matrix and the laser ablation characteristics [18,19]. Laser ablation coupled to an ICP-SFMS fulfils several requirements, which would be desirable for nuclear forensics: besides its excellent detection capabilities down to the ng g^{-1} range, it is not only a quasi non-destructive technique (less than microgram amount of sample is consumed for the analysis), but also it is not necessary to carry out lengthy and hazardous chemical manipulations with the nuclear materials, which require special laboratory conditions and expertise. This also implies the minimization of the generated nuclear (radioactive) waste. The disadvantages of laser ablation ICP-MS methods are the cumbersome calibration for concentration measurement and usually the limitation of the maximum volume of the ablation chamber, which encompasses the sample. The fact that LA-ICP-MS is a surface analytical technique can be exploited to obtain isotopic and elemental information from the sample at micrometer scale. However, it can result in significantly different results from the bulk analysis due to the sampling.

Determination of Elemental Composition and Impurities

The elemental composition of the investigated nuclear forensic evidence is one of the major characteristics of the material, providing hints on the possible origin and intended use of the material. The ICP-MS technique is capable to detect most of the elements, except a few, such as H, O, N or Ar. This feature is especially important in nuclear forensics for establishing the history of the illicit material. The composition of the sample can be given after the measurement of the major constituents (e.g. identification of the uranium or plutonium compound, types of uranium ore concentrate, determination of alloys or various glasses), which already point at the possible source and use of the material [20,21,]. Generally, the minor constituents (i.e. trace elements) give more detailed bases for the origin assessment. These impurities derive either as a residual of the feed material due to the incomplete purification (so-called source-material inherited signatures) or from the metallurgical production (e.g. by the added chemicals or contamination; so-called process inherited signatures). These subtle variations can be used to compare samples with similar composition to verify the possibly same origin or process [20]. During the last years impurity analysis is increasingly used to compare various uranium ores or ore concentrates to identify the source of an unknown material [22-25]. Such measurements, supported by multivariate statistical techniques, could give a foundational input either for the verification of the declared origin or for origin assessment. For instance, elevated levels of phosphorous was found to be an indicator in uranium ore concentrates produced as a by-product from fertilizer industry or higher level of thorium and its decay product, [208]Pb was indicative for yellow cakes milled from Th-rich ores (e.g. quartz-pebble conglomerate) [26,27]. In case of the yellow cake material seized at Rotterdam harbour (example quoted already above) the elevated level of P indicated the possible use of phosphate rock as feed material. Also the rare-earth element pattern, which was measured by ICP- SF MS pointed in the same direction: a flat, shale-like pattern without Ce or Eu anomaly similar to those previously found in UOCs produced from certain sandstone-type deposits and in reworked sedimentary phosphorites was obtained.

To perform the measurement several approaches have been used, as the types of the materials vary extensively. Most frequently matrix-matched calibration is used due to the high uranium or plutonium content. In case of interferences or if the analyte is present in very low concentration, prior chemical separation and pre-concentration can be used to enhance the measurement capabilities. This is typically the case for rare-earth elements [22,28], trace-level activation or fission products (e.g. indication the use of a reprocessed materials) [19] or for the decay products of the host nuclear material [19,29,30]. This latter measurement allows the determination of the "age" of the material, which actually describes the time elapsed since the last chemical separation. The method is based on the
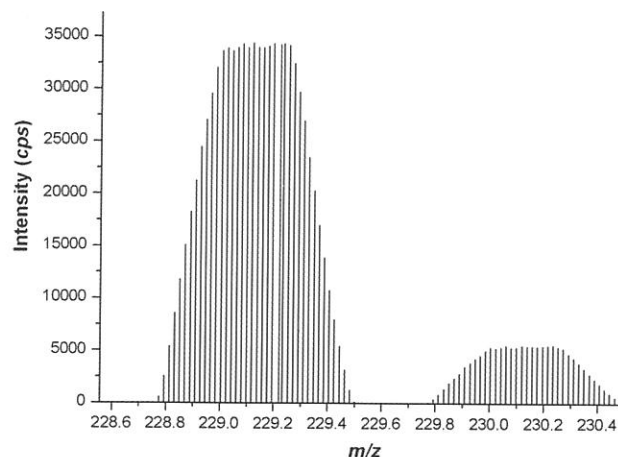

Fig. 2   A typical mass spectrum of the thorium fraction for age measurement as obtained for a confiscated material. The [230]Th analyte (daughter product, approximately 5 pg g^{-1} in the measure aliquot) was quantified using [229]Th tracer.

assumption that the base nuclear material (i.e. the parent nuclide) is completely separated from its daughter radionuclides during the production. These daughter nuclides afterwards start to grow-in in the material due to the radioactive decay of uranium or plutonium. By measuring the parent to daughter ratio (e.g. [234]U/[230]Th or [239]Pu/[235]U), and using the equations of the radioactive decay, the time elapsed since the last chemical separation can be calculated. Compared to the other applicable techniques, such as alpha spectrometry or TIMS, ICP-MS has the advantage of the better detection limit (the parent to daughter ratios of uranium materials are typically in the 10^{-12}-10^{-9} range). As an example, the mass spectrum of the measured thorium isotopes of a real sample is shown in Fig. 2. The [230]Th concentration in the measured sample was approximately 5 pg g^{-1}, and it was quantified using a [229]Th isotope tracer (usually not present in typical uranium fuel materials). Based on the [234]U/[230]Th ratio the calculated age of the material was calculated to be 47.6 ± 0.6 years (with a reference date of 22 December, 2009), which means that the calculated production of the material took place in May 1962 (± 7 months).

As the decay products are at trace-level, chemical separation is necessary in most cases. However, due to the excellent detection limits of sector-field ICP-MS instruments, direct measurement methods have also been proposed either by laser ablation ICP-MS (without any sample preparation) [29] or using post-measurement spectral deconvolution of the mass spectrum (after the measurement only the dissolved material without chemical separation) [29].

The capabilities of the ICP-MS instruments for the isotope ratio measurements are primarily determined by the sample introduction, the analyzer and the detection system, since the ion source is the same. The typical figures of merit

TABLE 2. The typical figures of merit of different ICP-MS instruments for fissile nuclides [31-34]

Instrument	Typical detection limit	Precision (RSD%)
ICP-MS with a quadrupole analyzer	0.01 – 0.6 pg	0.1 – 0.5%
ICP-MS with a quadrupole analyzer and collision cell	0.003 – 0.01 pg	0.07 – 0.1%
ICP-MS with a time-of-flight analyzer	0.1 – 1 pg	0.1 –1%
ICP-MS with a double-focusing sector field analyzer	0.02 – 1 fg	0.02 – 0.3%
MC-ICP-MS with a double-focusing sector field analyzer	0.6 – 0.2 fg	0.002 – 0.05%

of different ICP-MS instruments for uranium and plutonium analysis are summarized in Table 2.

Isotope Ratio Measurements by MC-ICP-MS

Multi-Collector Inductively Couple Plasma Mass Spectrometry (MC-ICP-MS) aims a providing high precision isotope ratio measurements. To this end, MC-ICP-MS instruments combine the most suitable combination of ion source (a plasma), mass analyzer (a double focusing set-up of electrostatic analyzer and magnetic sector field) and a detection system enabling the simultaneous detection of ion beams for different mass to charge ratios. The double focusing mass analyser is well established in SF-ICP-MS and the multi-collector array has a proven record in isotope ratio measurements by thermal ionization mass spectrometry. Usually, the detector array consists of two different types of detectors, namely Faraday cups and ion counters (using either discrete dynode Secondary Electron Multipliers, Daly detector or micro-channeltrons), in order to cover large range of ion current intensities.

The benefits of MC-ICP-MS are best exploited in isotope ratio measurements, although these instruments can in principle also be used for measuring elemental concentrations. As pointed out above, the plasma source allows measuring almost all chemical elements for their isotopic composition by MC-ICP-MS while TIMS is applicable only to elements having a low first ionisation potential. Therefore, MC-ICP-MS is the preferred measurement technique e.g. in geology and archaeology, where often elements with high ionisation potentials and present only at low concentrations have to be analyzed. Also the often time consuming chemical separations can be avoided when using MC-ICP-MS combined with laser ablation.

In this chapter the isotopic analyses of uranium, lead and strontium are discussed in more details, because these elements are also of interest for nuclear forensics. The $^{234}U/^{238}U$ ratio varies in nature mainly due to the combined effects of alpha-recoil from mineral grains during ^{238}U decay

and subsequent damage to the crystal lattice. As a result, loosely bound ^{234}U is more susceptible to preferential extraction (leaching) from minerals than lattice-bound ^{238}U. In geology the $^{234}U/^{238}U$ ratio is measured e.g. to monitor weathering rates and river- and ground-water flow patterns. In addition, the $^{234}U/^{238}U$ ratio is a necessary component in the age equation of U-series age dating [35]. Lead isotopics are commonly used also in age dating, but besides that they can serve as tracers for the geochemical provenance and as evidence for transport, redeposition and preferential leaching processes as well as in geochemical studies [36-38]. Very common application, but from different discipline, is the lead isotopic analysis in forensic studies when bullets are analysed in shooting incident investigations [39,40].

The $^{87}Sr/^{86}Sr$ isotope ratio, which is widely used in geology for the age determination, can be used also for the origin assessment, e.g. in archaeology to examine human migration or in food authenticity to distinguish products from various geographic origins [41,42]. The variation of the $^{87}Sr/^{86}Sr$ is due to the decay of long-lived ^{87}Rb (half-life, 4.8 × 10^{10} year) to ^{87}Sr and the highly variable Rb/Sr ratio in nature.

Similar to the above-mentioned applications, precise isotopic composition analysis of U, Pb and Sr are needed in nuclear forensics to obtain information on the origin of uranium. These elements were chosen as their isotopic compositions are presumed to reflect that of the ore and give information on the type and age of the ore body, hence on the source material.

An example of the variations in the minor isotope ratios of uranium, i.e. $^{234}U/^{238}U$ and $^{236}U/^{238}U$, as measured by MC-ICP-MS in natural uranium samples from various locations is provided in the study by Buchholz et.al. [10].

Three out of the four stable lead isotopes, ^{206}Pb, ^{207}Pb and ^{208}Pb, are the final decay products of the ^{238}U, ^{235}U and ^{232}Th decay series, respectively. Depending on the history of the uranium deposit (e.g. fractionation of the U and Pb due to the weathering), its age and initial U/Th ratio in the ore, differences in the radiogenic lead composition have been observed [24,27]. Besides detecting differences between the
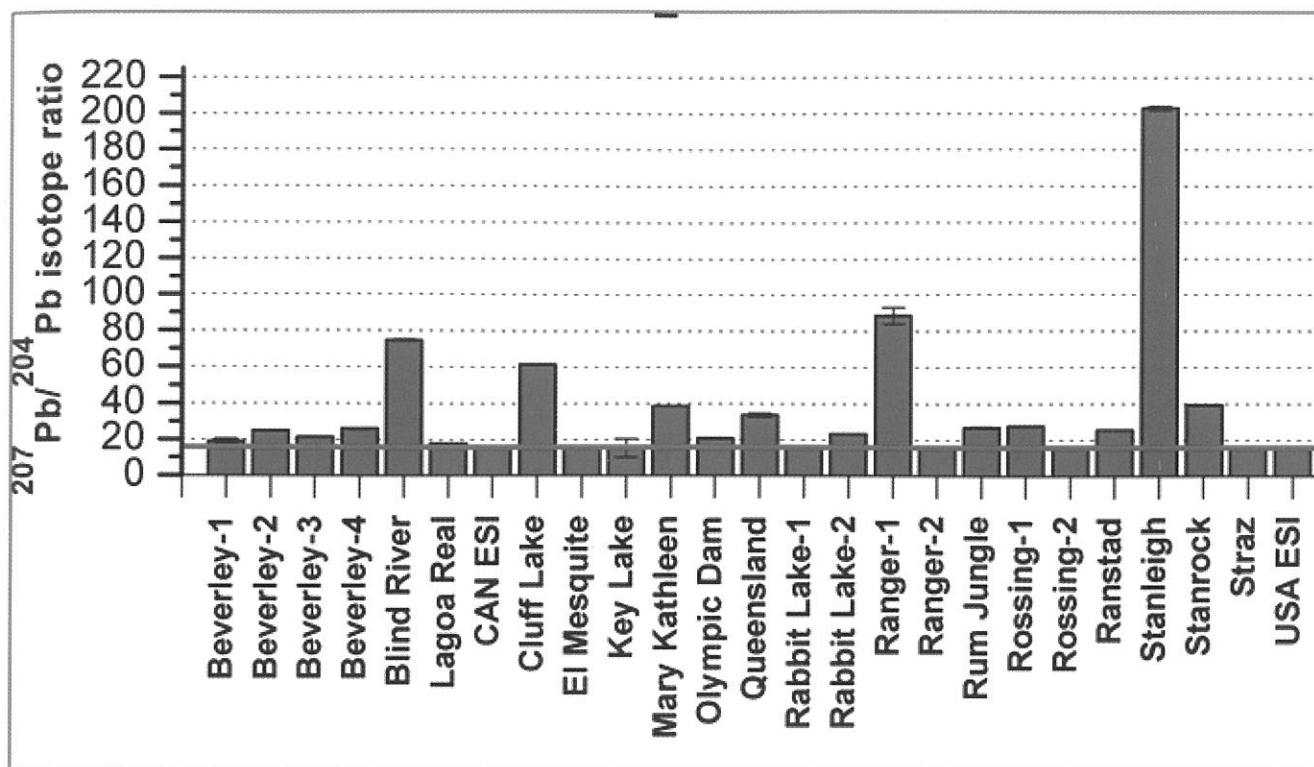
Fig. 3   Measured $^{207}Pb/^{204}Pb$ ratio in selected uranium ore concentrate samples [27]. The present-day natural $^{207}Pb/^{204}Pb$ ratio of 15.8 ± 1.1 is marked with the solid line

uranium deposits (Fig. 3), lead isotopics can be used in nuclear forensics to estimate the age of the deposit similar to geology and therefore limit the types of deposit that can come in question, when looking for the origin of natural uranium. However, as lead is a very common element, careful blank control has to be implemented during the analysis in order to ensure unbiased results.

The $^{87}Sr/^{86}Sr$ isotope ratio can also be utilised in nuclear forensics, because it is a characteristic of the geological background of uranium deposits. The analysis of several natural uranium samples have shown that the within mine site variations, which is the drawback in lead and uranium isotope analysis, are much less (Fig. 4).

Example

As an example of the use of above described methods in nuclear forensics, the results obtained on yellow cake seized at Rotterdam harbour (i.e. the example quoted above) will be discussed.

The uranium isotopic composition was measured with Nu Plasma MC-ICP-MS (Nu Instruments, Wrexham, UK) using ion counting for the minor isotopes ^{234}U and ^{236}U and Faraday cups for the major isotopes ^{235}U and ^{238}U. Also mass 239 ($^{238}U + {}^1H$) was measured by ion counting in order to correct the hydrogen contribution at mass position 236. The following isotope ratios were found: $^{234}U/^{238}U = 5.502 \pm 0.066 \times 10^{-5}$, $^{235}U/^{238}U = 7.253 \pm 0.013 \times 10^{-3}$ and $^{236}U/^{238}U = 1.4 \pm 0.2 \times 10^{-7}$. The isotopic composition shows that the

material is of natural origin, however a small abundance of ^{236}U suggests a minute contamination with previously irradiates and reprocessed uranium.

The isotope composition of lead was measured to be: (the ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb were 1.357 ± 0.005, 25.91 ± 0.21, 21.03 ± 0.11 and 51.70 ± 0.13, respectively), and it is indistinguishable from the natural composition of lead. This indicates that the uranium originates most probably from a young uranium deposits containing low grade ore, i.e. leading to a minimum ingrowth of radiogenic lead.

The $^{87}Sr/^{86}Sr$ ratio was measured to be 0.708 [26]. This value is relatively low (compare with Fig. 4), which indicates that there is Rb incompatibility, as observed e.g. for phosphorite-based materials.

All these signatures support the initial hypothesis that the material is originating from the Middle East, most likely from Iraq.

Secondary Ion Mass Spectrometry (SIMS)

SIMS is a powerful analytical technique for investigating the surfaces of solid materials. The technique provides information on spatial as well as depth dependent concentration of constituents of interest. It has been of inestimable value to cosmochemistry (i.e. for particles of cosmic dust) and for characterization of interfaces and surface layers. SIMS offers the possibility to measure elemental composition, isotope ratios and allows ion imaging (i.e. visualizing the spatial distribution of selected
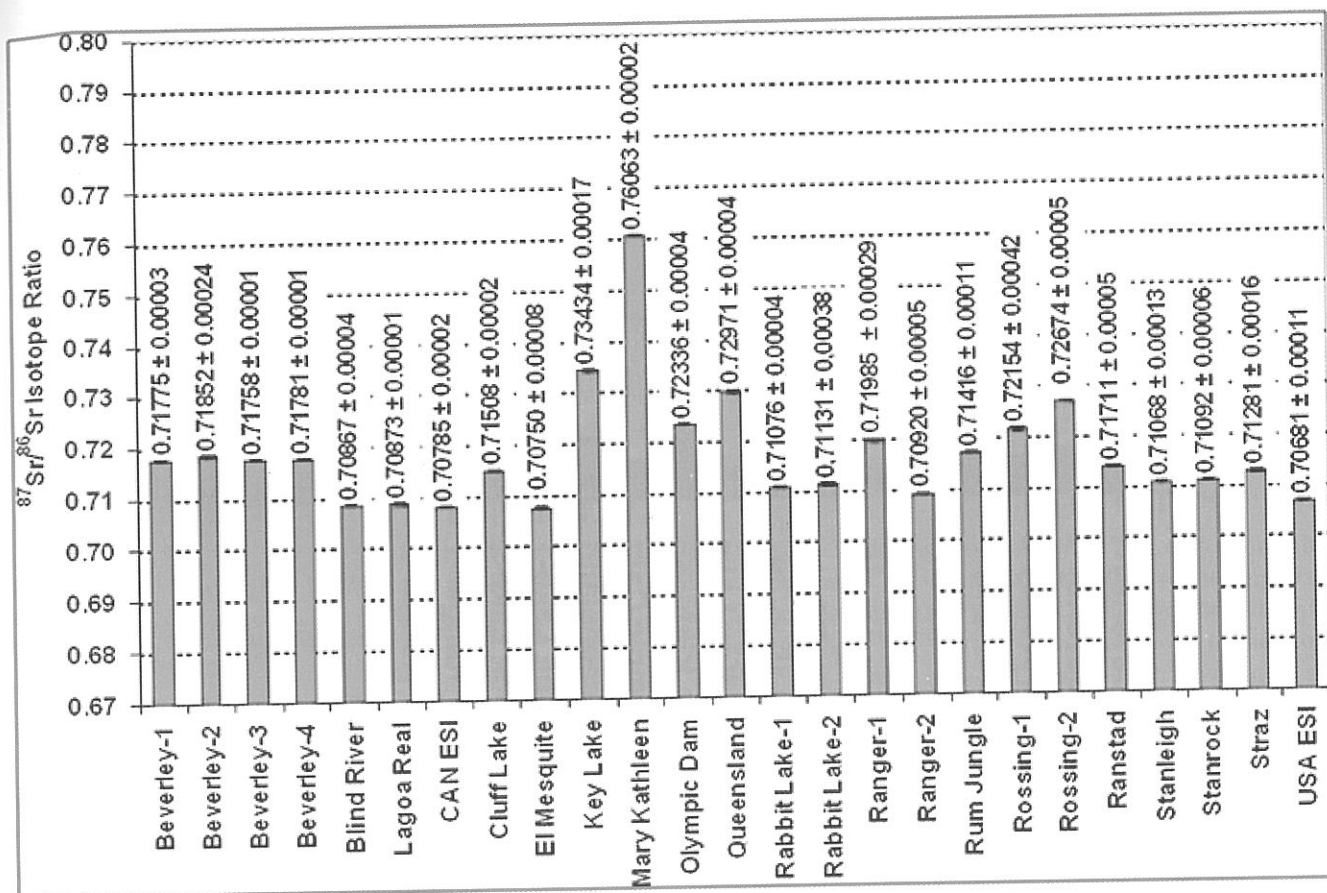
Fig. 4 $^{87}Sr/^{86}Sr$ *ratio in selected uranium ore concentrate samples [27].*

isotopes on the surface. For almost two decades, SIMS has also been used in nuclear safeguards for analysing uranium microparticles.

Principle and General Description

In secondary ion mass spectrometry, the surface of the sample under investigation is bombarded with a focused beam of primary ions. High energy ions (ranging from 0.5 to 20 keV) such as O^-, O_2^- or Cs^+ may be used. Under this bombardment, atoms from the surface are sputtered of. A fraction of the sputtered species is emitted as electrically charged particles (secondary ions). These secondary ions are passed to a mass analyser and then to a detections system. Magnetic sector field, time-of-flight or quadrupole mass analysers may be used. Double focusing instruments combining electrostatic analyser with a magnetic sector field offer high resolution (300 up to 30000) and allow high precision analysis of thin films or particles. An example of such an instrument is given in Fig. 5.

Classical Safeguards Application of U Particle Analysis by SIMS

SIMS has been a mainstay technique for more than a decade in safeguards applications to detect undeclared nuclear activities [43]. The main application has been in the search for particles that were released by nuclear material handling, see Fig. 6. The basics of these particle analyses for Safeguards purposes are that:
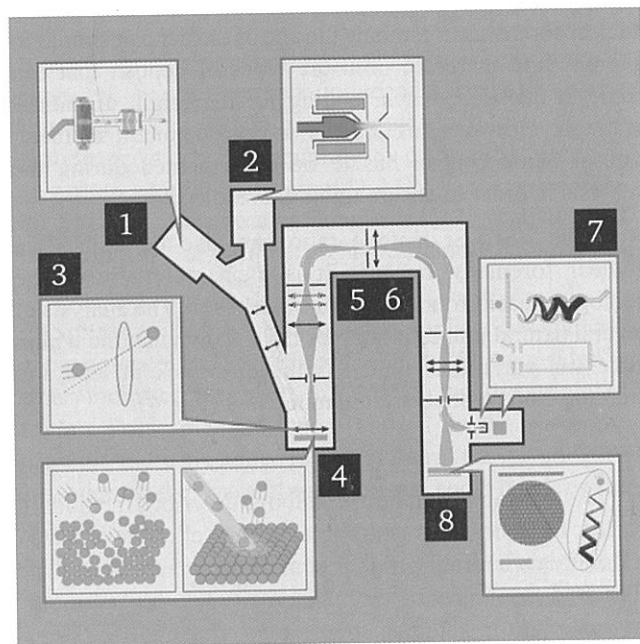

Fig. 5 *Schematic description of the SIMS technique and instrument (1.Cesium ion source; 2 Duoplasmatron; 3 Electrostatic lens; 4 Sample; 5 Electrostatic sector - ion energy analyzer; 6 Electromagnet - mass analyzer; 7 Electron multiplier / Faraday cup; 8 Channel-plate / Fluorescent screen - ion image detector)*

- Fine particulate material or aerosols are often released in the handling of nuclear material. The normal nuclear safety monitoring (using radiometric techniques) can not detect this material as the activity is below background.
- The particles are representative of the original material and their composition provides specific information about the source.
- The released particles are highly mobile and can be found in many locations within a nuclear facility.
- It is difficult to clean up and remove the released particles.
- Samples taken (e.g. by a Safeguards inspector) at a facility that has been operated over a long period can provide an insight into the entire history of the operation.

The analytical SIMS work can be separated into three main tasks that must be performed with the best balance of speed, sensitivity, and the highest levels of accuracy and quality control:

1. The first is to remove particles from a cotton swipe and to place them on a planchet with a homogeneous dispersion. This removal of the particles is made with the use of a vacuum impactor technique, which pulls particles from the sample swipe with a vacuum suction and sprays them directly on a sample planchet [44]. This work has to be made in a clean laboratory following a strict procedure to avoid contamination of the traces of uranium in the sample (see Fig. 6b).

2. The second task is to search through the particles deposited on the planchet to find the particles of interest. One of the fundamental strengths of SIMS is its ability to very quickly perform particle searches of deposits containing millions of particles in order to find the ones of interest in a short time with a high detection capability. This is done by fast screening measurements using the unique ion imaging capabilities of the instrument. An important improvement that has recently been made is the development of a new Automated Particle Measurement (APM) software that can make the screening measurements in a fully automated sequence, see Fig. 3. These measurements provide both the exact location of the uranium particles and a first estimate of their enrichment [45].

3. The final task is to perform accurate and precise measurements, determining the isotopic composition of the particles selected. This requires the highest possible ion yield in the uranium measurements. SIMS has a higher ion yield for uranium compare to commercial TIMS instruments, thus it can perform analyses of smaller particles with a lower uncertainty. A new development is the use of Large Geometry – SIMS instruments for the Safeguards application, sees Fig. 7. The basic property of the LG-SIMS that provides the improved performance in uranium particle analysis is its high sensitivity at high mass resolution.
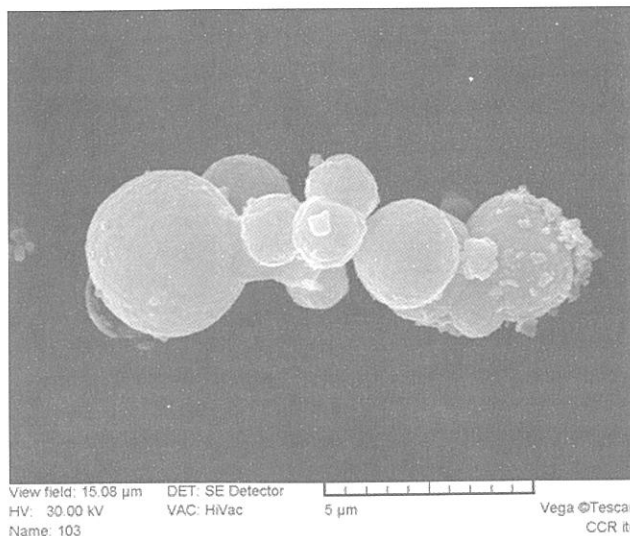

View field: 15.08 μm   DET: SE Detector
HV: 30.00 kV   VAC: HiVac   5 μm
Name: 103   Vega ©Tescan   CCR itu

Fig. 6a SEM picture of a conglomerate of uranium particles (H. Thiele, JRC/ITU)
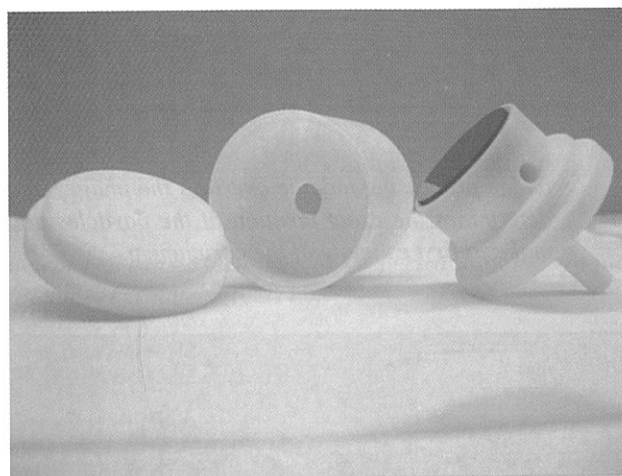

Fig. 6b Vacuum impactor. The particles are sucked through a small hole and sprayed onto a graphite planchet. The disassembled impactor has the graphite planchet in the holder to the right.

Common molecular interferences that can hamper the measurement in normal SIMS analysis are removed effortless, thus improving the minor isotope measurements

Examples of Forensic Application of SIMS Analysis

There have been a number of forensic cases were there is a need for uranium particle analysis complementing the more traditional bulk measurements. One recent example of this is a case where a European steel producing company found that a number of pieces of imported scrap metal showed an enhanced level of radiation. The material turned out to be contaminated by uranium. Measurements from one piece of the contaminant material were made by TIMS to establish the isotopic composition of the material. It was found to have an ^{235}U enrichment of 9.0333 ±0.0052 wt%. Also other analysis were made including impurity
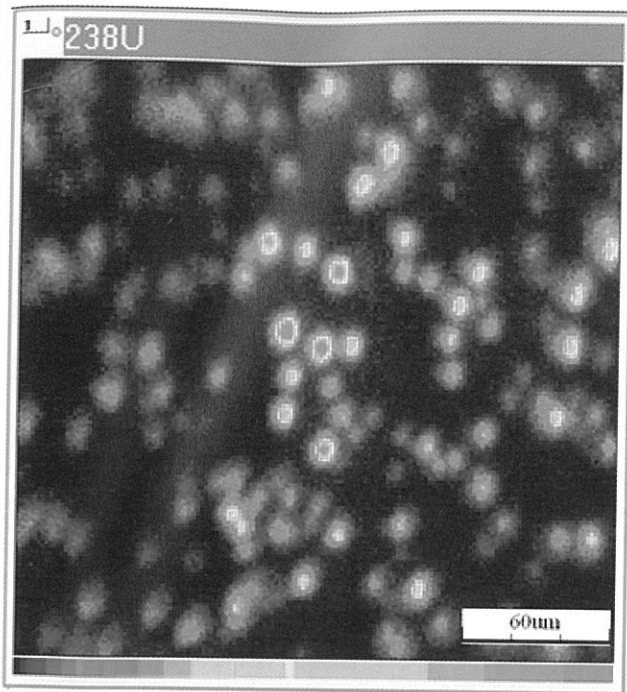
Fig. 7a A 250um x 250um image of ^{238}U. The new APM software allows for ^{234}U, ^{235}U, ^{236}U and ^{238}U images to be taken simultaneously on the LG-SIMS. An image processing module overlays the images and determines the exact position of the particles and makes a first estimate of the enrichment.
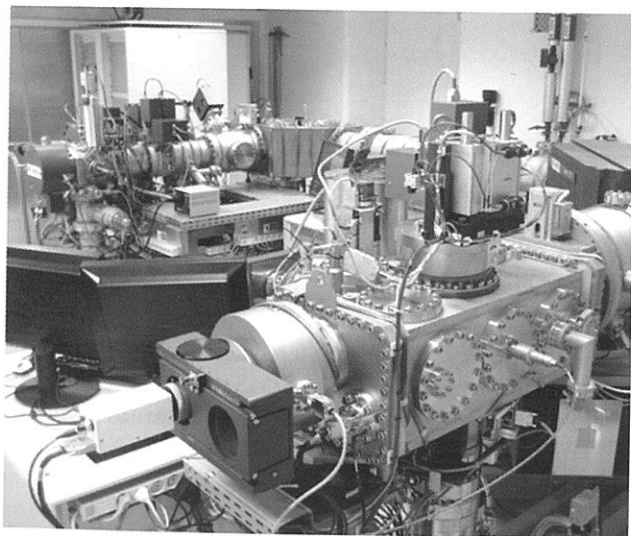

Fig. 7b A LG-SIMS, Cameca IMS 1280, at the NORSIM facility in Stockholm. This instrument is physically 5 times larger than the conventional SIMS used today. Main advantages compared to a normal SIMS, apart from the high mass resolution at high transmission, is the multi-collector Electron Multiplier detector system. This detector system can be seen in the front of the picture. (Picture M. Whithouse, NORDSIM)
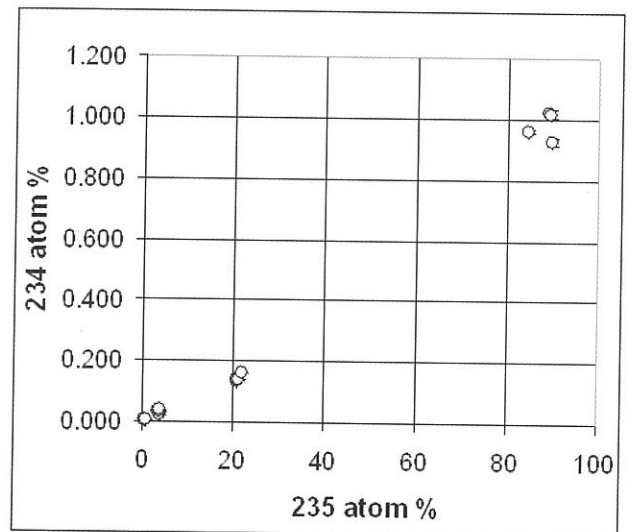

Fig. 8a Plot of individual particle analysis showing ^{234}U versus ^{235}U. Four groups of enrichment can be seen
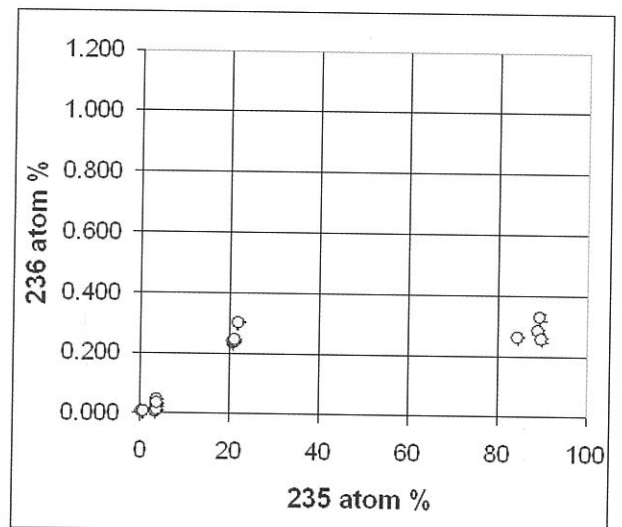

Fig. 8b Plot of individual particle analysis showing ^{236}U versus ^{235}U. The 90% enriched material has a distinctly different $^{236}U/^{235}U$ ratio compared to the other materials.

measurements, morphology studies by SEM and age determinations. As such an enrichment is not very common, the sample was grind into a powder and SIMS analysis on individual particles of the material was also made to check the isotopic homogeneity. The result of the SIMS analysis can be seen in Fig. 8. The SIMS analysis revealed that the material is in fact a mixture of different materials with different history and possible different origin. Several groups of material were identified with different enrichments (0.5%, 3.6%, 21% and 90% ^{235}U enrichment). Without the SIMS analysis it would not be possible to detect that the material is in fact a mixture of several materials. Another example are when SEM analysis find a specific morphology on a particle like a fuel material, see Fig. 9. With the SIMS one can relocate the same particle after the SEM
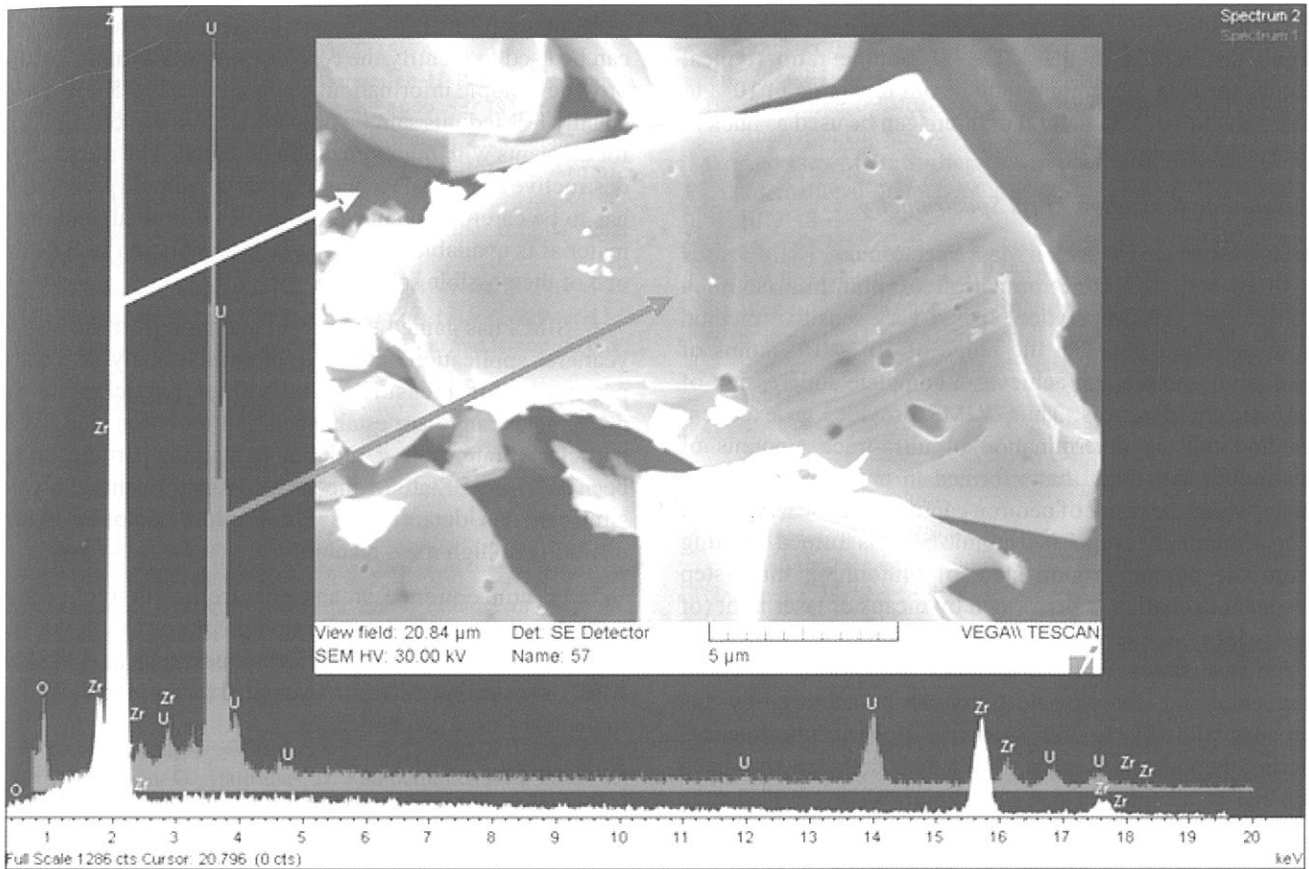
Fig. 9   The typical structure form a particle originating from a nuclear fuel can be seen. Two EDX spectra show the uranium in the fuel and the zirconium from a cladding material. (Picture H. Thiele, JRC/ITU).

analysis and determine the isotopic of a specific material, thus morphology, elemental composition and isotopic composition can be derived from an individual particle.

Other Mass Spectrometric Techniques

Specific problems may require more sophisticated analytical techniques. Within the present paper, we will focus the discussion on two techniques suitable for addressing the challenges arising from extremely low isotope abundances and from ultra-trace quantities of a chemical element. In either case the measurement challenge arises from the huge excess of matrix material, be it the same chemical element (yet other isotopes) or be it another chemical element. The first category is more pertinent to uranium isotopes, in particular to ^{236}U and ^{233}U, where a measurement technique needs to be applied that can discriminate between a variety of molecular and atomic species as well as tails of neighbouring masses that interfere at nearly the same mass position as the isotopes of interest. Accelerator mass spectrometry offers sufficiently high abundance sensitivity for measuring extremely small isotope ratios. The second category refers to minute traces of plutonium present in a huge excess of uranium. Here, resonance ionization mass spectrometry proved to be highly selective and to offer sufficient sensitivity.

Accelerator Mass Spectrometry

The fundamental difference between Accelerator Mass Spectrometry (AMS) and conventional mass spectrometric techniques is one of energy. Ions are accelerated to attain energies in the MeV range. AMS comprises an ion source, an ion accelerator, multiple selection stages for energy, momentum, velocity and atomic charge plus final identifcation of nuclear mass and charge with an ion detector. The use of charge, energy and mass signatures are the basis for this type of ultrasensitive mass spectrometry. Using the example of measuring the abundance of the isotope ^{236}U in a uranium sample the principle of AMS shall be illustrated: the uranium is sputtered with a Cs^+ beam, and in a first analysis $^{236}UO^-$ (mass ~ 252 amu) is selected; this ion is accompanied by molecular isobars, most abundant $^{235}U^{16}OH^-$. While conventional mass spectrometry (ICP-MS, TIMS) cannot suppress this background sufficiently, AMS destroys the molecules by acceleration to high energies (up to several MeV) and stripping to a high positive charge state in a dilute gas cell. After another stage of acceleration, $^{236}U^{5+}$ is selected in a second mass analysis. The ions are detected in a time-of-flight spectrometer and a final ionization chamber. Other ions can reach the detectors only on irregular trajectories, e.g. due to charge exchange on residual gas or scattering on surface in the spectrometer. This allows reaching detection limits for the $^{236}U/^{238}U$ isotope

ratio of below 10^{-11}. Recent investigations have shown that small differences in the $^{236}U/^{238}U$ isotope ratio (typical values for natural uranium range from few parts in 10^{-10} to few parts in 10^{-11}) in natural uranium can be used as nuclear forensic signature [46].

Resonance Ionization Mass Spectrometry

Resonance Ionization Mass Spectrometry (RIMS) uses a three step resonant ionization of plutonium with a subsequent mass separation. It is a very sensitive method with detection limits in the range of $10^6 - 10^7$ atoms of plutonium/sample and achieves a complete suppression of isobaric interferences. Thus, RIMS provides an excellent method for the determination of ultra-trace amounts of plutonium that might have formed in uranium containing materials as the result of neutron capture reactions. As a first step, a thermally evaporated atomic beam is formed. Starting from the atomic ground state of plutonium, multi-step resonant excitation is performed by means of laser light (of well defined energy) in order to populate high-lying electronic states with subsequent ionization. Excellent elemental and isotopic selectivity can be achieved by this process, allowing to fully suppress isobaric interferences during the ionization process [47]. This technique has been applied to samples of natural uranium dating back to the German nuclear program on the 1940's [48] identifying $^{239}Pu/^{238}U$ ratios as low as few parts in 10^{-14}. Thus, this parameter is clearly indicating that the material had not been exposed to significant neutron fluences, which in turn confirms that the attempts for building a nuclear reactor in Germany during World War II did not succeed in a self-sustaining chain reaction.

Conclusion

The emerging field of nuclear forensics makes to a large extent use of well established techniques based on mass spectrometry. Different variants of mass spectrometry are applied and allow drawing useful conclusions for supporting non-proliferation and law enforcement investigations. Credible nuclear forensics conclusions, however, need to be based on validated procedures and on measurement techniques that are well understood. Thermal ionization mass spectrometry, inductively coupled plasma mass spectrometry and secondary ion mass spectrometry allow to determine key parameters such as isotopic composition of major and minor constituents and the concentration of chemical impurities in the nuclear material. TIMS is a mature technique with a proven record of high accuracy measurement capability for uranium and plutonium isotopic composition. The technique requires sample sizes between few micrograms and few picograms for an individual measurement. It is, however, limited to chemical elements with a reasonably low first ionization potential.

The most important advantage of ICP-MS is the versatility: it can be used for concentration measurement as well as for isotope ratio determination of various elements. It is a very sensitive measurement tool down to $10^{-12} - 10^{-15}$ g/g concentration level for almost all elements. The technique can be used to identify the type of the material and can also provide isotopic information. Compared to TIMS it requires usually less tedious sample preparation and can be used also for elements with high ionization potential. The method is a destructive analytical technique, thus the sample preparation has to be carefully planned, especially if limited amount of material is available. In this case, laser ablation ICP-MS is one of the possible solutions.

SIMS has gained significant attention over the last 15 years for application in the area of particle analysis. Today, protocols for measuring individual particles in the micrometer range are established and tools for identifying particles of interest (e.g. uranium containing particles) have been developed. State-of-the-art SIMS instruments allow the simultaneous detection of all uranium isotopes, while operating at high mass resolution.

In consequence, mass spectrometric techniques provide an essential contribution to the area of nuclear forensics. More sophisticated techniques, such as AMS and RIMS, are currently being investigated for their applicability to nuclear forensics challenges.

References

[1]   Mayer, K.; Wallenius, M.; Ray, I. Analyst 2005, 130, 433-441.

[2]   Fassett, J. D.; Paulsen, P. J. Analytical Chemistry 1989, 61, 643A-649A.

[3]   De Bievre, P. Fresenius' Journal of Analytical Chemistry 1990, 337, 766-771.

[4]   Gopalan, K. Introduction to Mass Spectrometry, In: Indian Society for Mass Spectrometry, Eds.: Aggarwal, S.K., Chain, H.C. 1997.

[5]   De Laeter, J. R. Applications of Inorganic Mass Spectrometry, Wiley & Sons, ISBN 0-471-34539-3 2001.

[6]   Platzner, I. T. Modern Isotope Ratio Mass Spectrometry, Wiley & Sons, ISBN 0-471-97416-1 1997.

[7]   Aggarwal, S. K.; Chain, H. C. Introduction to Mass Spectrometry, In: Indian Society for Mass Spectrometry, Eds.: Aggarwal, S.K., Chain, H.C. 1997.

[8]   Richter, S.; Alonso, A.; De Bolle, W.; Wellum, R.; Taylor, P. D. P. International Journal of Mass Spectrometry 1999, 193, 9-14.

[9]   International Atomic Energy Agency: Fourth semi-annual report on the implementation by the IAEA on the plan for the destruction, removal or rendering harmless of items, IAEA report to the United Nations Security Council, S/25983, 1993.

[10] Buchholz, B. A.; Brown, T. A.; Hamilton, T. F.; Hutcheon, I. D.; Marchetti, A. A.; Martinelli, R. E.; Ramon, E. C.; Tumey, S. J.; Williams, R. W. Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms 2007, 259, 733-738.

[11] Becker, J. S.; Dietze, H.-J. Spectrochimica Acta Part B: Atomic Spectroscopy 1998, 53, 1475-1506.

[12] Montaser, A.; Golightly, D. W. Inductively coupled plasmas in Analytical Atomic Spectrometry, 2nd ed.; VCH Publishers Inc.: New York, New York, USA, 1993.

[13] Zoriy, M. V.; Halicz, L.; Ketterer, M. E.; Pickhardt, C.; Ostapczuk, P.; Becker, J. S. Journal of Analytical Atomic Spectrometry 2004, 19, 362-367.

[14] Günther, D.; Horn, I.; Hattendorf, B. Fresenius' Journal of Analytical Chemistry 2000, 368, 45-51.

[15] Günther, D.; Jackson, S. E.; Longerich, H. P. Spectrochimica acta, Part B: Atomic spectroscopy 1999, 54, 381-409.

[16] Guillong, M.; Heimgartner, P.; Kopajtic, Z.; Günther, D.; Günther-Leopold, I. Journal of Analytical Atomic Spectrometry 2007, 22, 399-402.

[17] Stefanka, Z.; Katona, R.; Varga, Z. Journal of Analytical Atomic Spectrometry 2008, 23, 1030-1033.

[18] Leloup, C.; Marty, P.; Dall'Ava, D.; Perdereau, M. Journal of Analytical Atomic Spectrometry 1997, 12, 945-950.

[19] Varga, Z.; Surányi, G. Applied Radiation and Isotopes 2009, 67, 516-522.

[20] Wallenius, M.; Mayer, K.; Ray, I. Forensic Sci. Int. 2006, 156, 55-62.

[21] Mayer, K.; Rasmussen, G.; Hild, M.; Zuleger, E.; Ottmar, H.; Abousahl, S.; Hrnecek, E. In Advances in Destructive and Non-destructive Analysis for Environmental Monitoring and Nuclear Forensics; International Atomic Energy Agency, Vienna, 2002, pp 63-70.

[22] Varga, Z.; Wallenius, M.; Mayer, K. Radiochim. Acta 98, 1–8 (2010) / DOI 10.1524/ract.2010.1777 2010.

[23] Keegan, E.; Richter, S.; Kelly, I.; Wong, H.; Gadd, P.; Kuehn, H.; Alonso-Munoz, A. Applied Geochemistry 2008, 23, 765-777.

[24] Svedkauskaite-LeGore, J.; Mayer, K.; Millet, S.; Nicholl, A.; Rasmussen, G.; Baltrunas, D. Radiochimica Acta 2007, 95, 601-605.

[25] Svedkauskaite-LeGore, J.; Rasmussen, G.; Abousahl, S.; Van Belle, P. Journal of Radioanalytical and Nuclear Chemistry 2008, 278, 201-209.

[26] Varga, Z.; Wallenius, M.; Mayer, K.; Meppen, M. accepted in Radiochimica Acta 2010.

[27] Varga, Z.; Wallenius, M.; Mayer, K.; Keegan, E.; Millet, S. Analytical Chemistry 2009, 81, 8327-8334.

[28] Varga, Z.; Katona, R.; Stefanka, Z.; Wallenius, M.; Mayer, K.; Nicholl, A. Talanta 2009, 80, 1744-1749.

[29] Varga, Z.; Wallenius, M.; Mayer, K. Journal of Analytical Atomic Spectrometry 2010, DOI: 10.1039/c1030ja00048e.

[30] Wallenius, M.; Mayer, K. Fresenius Journal of Analytical Chemistry 2000, 366, 234-238.

[31] Becker, J. S. Spectrochimica Acta Part B 2003, 58, 1757-1784.

[32] Becker, J. S. International Journal of Mass Spectrometry 2005, 242, 183-195.

[33] Agarande, M.; Benzoubir, S.; Neiva-Marques, A. M.; Bouisset, P. Journal of Environmental Radioactivity 2004, 72, 169-176.

[34] Vanhaecke, F.; Moens, L.; Dams, R.; Papadakis, I.; Taylor, P. Analytical Chemistry 1997, 69, 268-273.

[35] Andersen, M. B.; Stirling, C. H.; Potter, E. K.; Halliday, A. N. International Journal of Mass Spectrometry 2004, 237, 107-118.

[36] Ehrlich, S.; Harlavan, Y.; Bar-Matthews, M.; Halicz, L. Applied Geochemistry 2004, 19, 1927-1936.

[37] Weiss, D. J.; Kober, B.; Dolgopolova, A.; Gallagher, K.; Spiro, B.; Le Roux, G.; Mason, T. F. D.; Kylander, M.; Coles, B. J. International Journal of Mass Spectrometry 2004, 232, 205-215.

[38] Cocherie, A.; Robert, M. Chemical Geology 2007, 243, 90-104.

[39] Zeichner, A.; Ehrlich, S.; Shoshani, E.; Halicz, L. Forensic Sci. Int. 2006, 158, 52-64.

[40] Buttigieg, G. A.; Baker, M. E.; Ruiz, J.; Bonner Denton, M. Analytical Chemistry 2003, 75, 5022-5029.

[41] Buzon, M. R.; Simonetti, A.; Creaser, R. A. Journal of Archaeological Science 2007, 34, 1391-1401.

[42] Garcia-Ruiz, S.; Moldovan, M.; Fortunato, G.; Wunderli, S.; Garcia Alonso, J. I. Analytica Chimica Acta 2007, 590, 55-66.

[43] Ranebo, Y.; Hedberg, P. M. L.; Whitehouse, M. J.; Ingeneri, K.; Littmann, S. Journal of Analytical Atomic Spectrometry 2009, 24, 277-287.

[44] Esaka, F.; Esaka, K. T.; Lee, C. G.; Magara, M.; Sakurai, S.; Usuda, S.; Watanabe, K. Talanta 2007, 71, 1011-1015.

[45] Hedberg, P. M. L.; Peres, P.; Cliff, J. B.; Rabemananjara, F.; Littmann, S.; Thiele, H.; Vincent, S.; Albert, N. Journal of Analytical Atomic Spectrometry 2010.

[46] Srncik, M.; Mayer, K.; Hrnecek, E.; Wallenius, M.; Varga, Z.; Steier, P.; Wallner, G. submitted to Radiochimica Acta 2010.

[47] Gruning, C.; Huber, G.; Klopp, P.; Kratz, J. V.; Kunz, P.; Passler, G.; Trautmann, N.; Waldek, A.; Wendt, K. International Journal of Mass Spectrometry 2004, 235, 171-178.

[48] Mayer, K. et al. 2010 International Nuclear Physics Conference, 4-9 July 2010, Vancouver, Canada 2010.

Dr. Klaus Mayer, *obtained his Ph.D. work in 1987 in the field of radiochemistry and analytical chemistry from the University of Karlsruhe. He then worked for two years at the Institute for Transuranium Elements as post-doctoral researcher. From 1990-1996, he was working for the European Commission at IRMM Geel (Belgium) on actinide isotopic reference materials, high accuracy mass spectrometric measurements of U, Pu and Th, the organization of an external quality control programme for nuclear material measurements and the coordination of support activities to Euratom safeguards office and to IAEA. In 1996, he started working at ITU Karlsruhe on the development and application of destructive analytical methods for nuclear safeguards purposes. From 1997 to 2010 he chaired the ESARDA Working Group on Destructive Analysis. Today, he is in charge of ITU's activities on combating illicit trafficking and nuclear forensics. Since 2004 he is co-chairman of the Nuclear Forensics International Technical Working Group (ITWG). He is the author of more than 150 scientific publications in the field of nuclear material analysis for safeguards and nuclear security applications, including peer-reviewed articles, book chapters, conference papers and keynote presentations. In 2011 he has been recognized by the "Focus" magazine as one of the top 100 most influential German people. He is lecturing radiochemistry at the University of Heidelberg.*

Non-Destructive Analysis for Nuclear Forensics

B.S. Tomar

Radioanalytical Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085; E-mail: bstomar@barc.gov.in

Introduction

Advancements in nuclear science and technology have benefited the mankind through (i) electricity from nuclear power, (ii) nuclear medicine in the form of radiopharmaceuticals and (iii) other peaceful applications in the field of industry, agriculture, food technology, etc. On the other hand, it has also led the race for acquiring nuclear weapons among the countries in the world. Unfortunately, the public opinion about the nuclear energy is still masked by the destructive power of nuclear weapons, rather than the peaceful applications. This is further aggravated by growing threat of nuclear terrorism, wherein the fissile materials may get into the hands of the terrorists thereby creating a fear of nuclear disaster in the public. Radiological accidents, such as, Chernobyl, Fukushima, etc., have added to the problems of nuclear scientists in its negative impact. It is with this perception that nuclear scientists need to pay utmost attention towards safety and security of the nuclear materials. Towards this end, the International Atomic Energy Agency (IAEA) has been actively engaging its member states in achieving the nuclear safeguards and security [1,2].

As the nuclear materials emit ionizing radiations, their presence can be detected by suitable radiation detection systems. Destructive methods, such as, inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS) etc., have the advantage of high precision and accuracy and, in some cases even lower detection limits (e.g., modern variants of ICP-MS), but their applicability is limited particularly in the case of detecting nuclear materials in sealed containers, unconventional samples (e.g. biological materials, environmental materials) which need faster detection, on line monitoring, etc. Non destructive analysis (NDA) techniques offer advantage of rapid analysis, on-line monitoring and assay of unconventional samples mentioned above and hence are more popular among the forensic analysts. The present article will give an overview of the different NDA techniques, which are being used for nuclear forensic applications.

Nondestructive Analysis (NDA) Methods

The methods are based on the measurement of radiations emitted by the nuclear material, either spontaneously or induced by interrogation with a projectile, such as, neutron, charged particle, or photon. These methods have the greatest advantage that the sample is intact even after the investigation and hence can be preserved for any future investigation. NDA methods are of two types. (i) Passive methods, wherein the spontaneously emitted radiations, namely neutrons and gamma rays from the radioisotopes are detected using suitable detectors, (ii) Active methods, which are employed in cases where passive methods are not sensitive enough, viz., in case of uranium samples. In active methods, the sample is subjected to activation by neutrons or any other projectile and the induced activity is measured to infer about the material.

Passive NDA Methods

We have heard about the Mayapuri incident, wherein the people ignorant about the radioactive cobalt (^{60}Co) in their possession got exposed to the high level of radiation. This could have been avoided had the owner of the source taken proper care in disposing it. Radiation survey meters are the first line of tools at the hands of the radiation workers to detect the presence of radioactive substance in any environment. These are based on Geiger Muller (GM) counter or ionization chambers and can detect the presence of beta or gamma radioactivity. For identification of the radioisotopes, gamma ray spectrometers based on scintillation detectors (viz., NaI(Tl), LaBr$_3$(Ce)) or semiconductor detectors (HPGe, CdZnTe) can be used. Semiconductor detectors offer better energy resolution than the scintillators, owing to the higher number of charge carriers produced per unit energy deposited in the detector, but are more sophisticated and costly. Needless to say, any quantitative measurement would require the standards, preferably matching the samples in terms of the composition, so that the detection efficiency can be determined accurately. The detection limits achievable with these detectors are in the range of Bq/kg of sample. The commonly used radioisotopes for application in industry, food irradiation, radiotherapy, etc, are ^{60}Co, ^{137}Cs, ^{131}I, ^{192}Ir, etc., out of which the first two are long lived and hence need be taken care even after their use. Table 1 gives the nuclear data of the useful radioisotopes commonly used.

Custom made interceptors are now available for passive measurements of gamma emitting radioisotopes in nuclear forensic applications. In the case of fissile materials, such as, ^{235}U, ^{239}Pu, passive gamma ray spectrometry with NaI(Tl) may give only qualitative idea of the presence of these radioisotopes. Gamma ray spectrometry with HPGe can be used to obtain the isotopic composition ^{235}U/^{238}U, ^{239}Pu/^{240}Pu, etc., and hence the fissile content of the consignment with respect to the total mass [3]. Quantitative information about the Pu content in the sample requires passive counting of neutrons emitted during the spontaneous fission of even mass number isotopes of Plutonium ($^{238, 240, 242}$Pu) using a neutron well coincidence counter (NWCC). Alternatively decay heat measurement in a calorimeter can also be used to accurately determine the plutonium content in the sample. Both these techniques require prior knowledge of the isotopic composition of plutonium, that is, the relative amounts of $^{238,239, 240, 241}$Pu, which is determined by high

TABLE 1. Nuclear data of commonly used radioisotopes

| Radioisotope	Half-life	Decay mode	Gamma energy (keV)	Intensity (%)	Application
^{60}Co	5.27 y	β^-	1173.2 1332.5	99.9 99.9	Teletherapy, Food irradiation
^{137}Cs	30.04y	β^-	661.6	85.1	Brachytherapy, Blood irradiators
^{131}I	8.02 d	β^-	364.5	81.7	Thyroid radiotherapy
^{125}I	59.4 d	EC	35.5	6.7	Radioimmunoassay
^{241}Am	432.6 y	α	59.5	35.9	Neutron source, XRF source
^{109}Cd	461.4 d	EC	88.03	3.7	XRF source
^{192}Ir	73.8 d	β^-	316.5 468.07 308.4 295.95	82.86 47.84 29.70 28.71	Non destructive testing, Brachytherapy
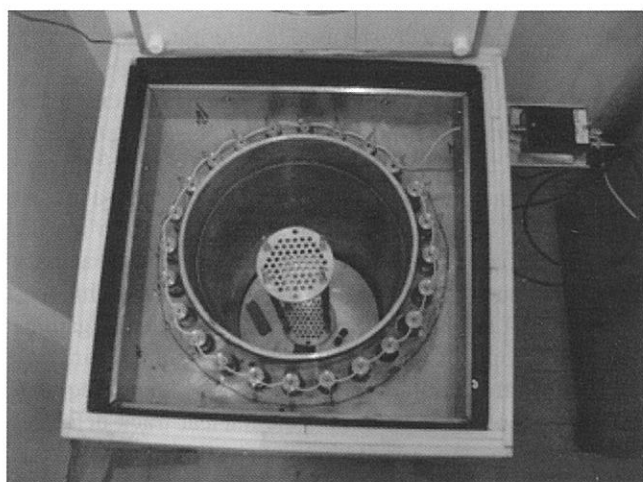
Fig. 1   NWCC used for NDA of FBTR fuel pins [4]

resolution gamma spectrometry employing planar low volume HPGe detectors having energy resolution better than 500 eV at 129 keV of ^{239}Pu [4]. The fuel pins for fast breeder test reactor (FBTR) have been assayed by the indigenously build NWCC [4].

The information obtained about Pu content from NWCC is compounded as the counter measures only the singles and double coincidences, and hence gives information of ^{240}Pu (effective) and (α,n) neutrons, but does not take into consideration self multiplication in the sample. Neutron multiplicity counter offers more reliable data on Pu amount, as it measures single, doubles and triplets and hence, provides information about the ^{240}Pu(effective), (α,n) neutrons and self multiplication in the sample. Of course,

multiplicity counter requires more number of ^{3}He detectors owing to low detection efficiency for triplets [3].

Portal monitors are placed at the entry /exit of the ports to detect the presence of radioactive substances in the containers. Typically there are two monitors separated by a few tens of meters. The first monitor is made of plastic scintillator and merely gives a signal of a gamma ray emitting substance in the container. The second monitor consists of a NaI(Tl) detector and ^{3}He detector bank which detect the presence of gamma and neutron emitting substances, respectively such as plutonium or any other substance. Once the presence of the radioisotopes has been confirmed, the type of plutonium, e.g., research reactor or power reactor grade is ascertained by gamma ray spectrometry with HPGe. This also forms a part of the second line of defense against illicit trafficking of fissile material, from a nuclear establishment.

Active NDA Methods

In the case of ^{235}U, passive neutron counting is not possible owing to its very long spontaneous fission half-life. Instead, active interrogation of the fissile isotope with a neutron source is used to induce fission in ^{235}U and the prompt or delayed neutrons emitted in the fission of ^{235}U are used to determine the ^{235}U content in the sample. Active well coincidence counter (AWCC) is based on the irradiation of the uranium sample with neutrons from a (Am,Li) or ^{252}Cf source followed by measurement of fission neutrons by an array of ^{3}He neutron detectors. However, the background counts due to neutrons from the source mask the results. In some counters, such as shufflers, the neutron source is moved away from the sample after irradiation for a short time
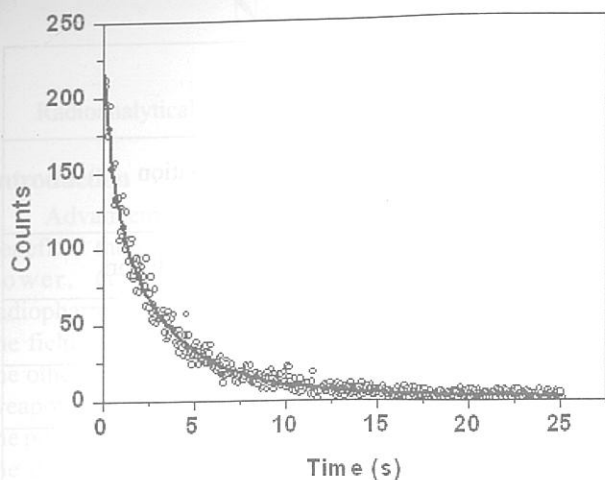
Fig. 2 *Temporal profile of delayed neutrons from ^{235}U fission induced by neutrons from a plasma focus device [5].*

and the delayed neutrons are measured to provide information about the U, Pu content in the sample [3]. Delayed neutron counting after neutron interrogation can also be used to distinguish if the fissile isotope is that of U or Pu as the delayed neutron fractions of different half-lives are different in the fission of ^{235}U and ^{239}Pu. In this respect, plasma focus device with one pulse at a time is ideal for delayed neutron counting after the interrogation. Recently the plasma focus device has been used as a neutron source for active interrogation and delayed neutron counting (AIDNEC) of low enriched uranium samples [5], with extremely low background. The detection limit of the method was found to be 18 mg of ^{235}U.

Active methods are also used to determine the elemental composition of a confiscated consignment suspected to contain any illegal item or explosive. For this purpose, neutron activation analysis (NAA) technique is used. In NAA, a small portion of the sample is irradiated with neutrons in a reactor or with any other neutron source, e.g., (Am,Li), (D-T), or plasma focus device. The beta delayed gamma rays emitted from the radioisotopes produced as a result of (n,γ) reaction on the stable isotope in the sample are then measured on a HPGe detector to infer about the elements present in the sample. The technique is mostly applicable to elements with atomic number (Z) higher than 10, with the detection limits being in the range of ppm to ppb. For determination of lighter elements, proton induced gamma emission (PIGE) wherein the sample is bombarded with low energy protons and the prompt gamma rays emitted in the reactions of the type (p,pγ), (p,αγ), etc., with the target nuclei are measured using a HPGe detector placed at 90° with respect to the beam direction to minimize any peak shift/broadening due to Doppler effects. The target is kept in vacuum to minimize the energy loss of the projectile, while the detector is placed in air through one of the ports of the

scattering chamber. Light elements, such as, Li, B, C, N, O, F, Al, etc., are determined by the technique with detection limits typically in hundreds of ppm [6].

Other NDA methods for forensic applications, based on active interrogation include X-ray fluorescence (XRF) and proton induced X-ray emission (PIXE), which differ merely with regard to the excitation source. In the case of XRF, the excitation source can be a radioisotopic source, such as, ^{241}Am, ^{109}Cd, etc or an X-ray tube, while in the case of PIXE, the target atoms are excited using low energy (~2 MeV) proton beam from an accelerator. The detection system is same in both the methods, that is, measurement of characteristic X-rays of the target elements using Si(Li) detector, which has excellent energy resolution for X-rays, typically 150 eV at 5.9 keV of ^{55}Fe. The detection limits achieved in XRF are in the region of a few ppm, while in PIXE ppb levels of concentrations can be determined particularly for the heavier elements.

Fission Signatures

Surveillance of the geosphere (air, water, soil) of a territory for the traces of radioactivity can be used to detect any undeclared activity in and around a facility. For instance, the measurement of ^{137}Cs, ^{90}Sr, ^{239}Pu etc., in soil samples is a signature of the spent fuel reprocessing in a facility. The fission signatures can also be used to determine the yield of a nuclear test [7]. Traces of ^{235}U with $^{235}U/^{238}U$ higher than that in natural uranium are a signature of enrichment facility. The effluents discharged from a facility can be screened for the fission products activity. Traces of iodine (^{131}I) in the thyroid of goats for slaughter are a signature of fallout from a reactor to the nearby fields. High levels of plutonium in marine organisms (fish, crab, etc.) indicate reprocessing activity nearby. For such measurements, highly sensitive techniques are needed. Low background and high efficiency gamma detectors for ^{137}Cs and ^{131}I, pre-concentration and radiochemical separation methods for ^{90}Sr, Pu are required for reliable conclusions. Solid state nuclear track detectors (SSNTDs) are very sensitive for detecting low levels of alpha and spontaneous fission activity.

One of the important aspects of nuclear forensic investigation is to determine the source of the consignment. For this purpose, detailed investigations of the isotopic composition provide valuable information. For instance presence of ^{236}Pu and ^{232}U is a uranium sample is evidence of the reprocessed uranium as these isotopes are produced during reactor operation by reactions such as,

$$^{238}U(n,2n)\ ^{237}U\ (\beta\text{-}) \rightarrow ^{237}Np\ (n,2n)^{236}Np(\beta\text{-})$$
$$\rightarrow\ ^{236}Pu(\alpha)\rightarrow^{232}U$$
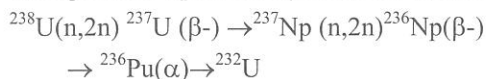
As only a select few countries have the reprocessing facilities for spent fuel, the consignment can be traced to one of them. Depleted uranium devoid of ^{235}U is a signature of enrichment facility as source. Further, the analysis of environmental samples for daughter products of ^{235}U can provide valuable inputs to the detection of undeclared operation in a nuclear establishment. Destructive analysis, of

late, has been found to achieve much lower detection limits than NDA techniques and hence are becoming common among the nuclear forensic analysts.

Conclusion

Nondestructive analysis is an important part of the nuclear forensic investigations. To obtain unambiguous and concrete evidence of the source and the type of activity, highly sensitive and efficient methodologies are essential. By enforcing stringent controls on the movement of radioisotopes and reliable monitoring systems, it is possible to reduce the risk of the nuclear materials landing in the possession of terrorists, and thereby save the public from radiation exposure. The public needs be educated on the safety issues related to the radioactivity and the occupational workers need be trained on safe handling and security of nuclear materials. Only then, the nuclear energy can be called as a safe option.

References

[1] Nuclear safeguards, Security and Nonproliferation, Editor James E. Doyle, Elsevier Publication (2008).

[2] Nuclear safeguards and Non-Proliferation, Editor, G. Janssens-Maenhout JRC European Commission (2008).

[3] Passive Nondestructive assay of nuclear materials, Eds., Doug Reilly, Norbert Ensslin, and Hastings Smith Jr., LA-UR-90-732 (1991).

[4] Nondestructive assay of the fissile content in FBTR fuel pins, S.Muralidhar, R.Tripathi, B.S.Tomar, G.K.Gubbi, S.P.Dange, S.Majumdar and S.B.Manohar, Nucl. Inst. Meth. A 511, 437 (2003).

[5] Non destructive assay of fissile materials through active neutron interrogation technique using pulsed neutron (plasma focus) device, B.S. Tomar, T.C. Kaushik, Sanjay Andola, Ramniranjan, R.K. Rout, Ashwani Kumar, D.B.Paranjape, Pradeep Kumar, K.L. Ramakumar, Satish C. Gupta, and R. K. Sinha, Nucl. Instr. Meth. A 703, 11-15 (2013).

[6] Ion Beam Analysis, B.S.Tomar, in Advanced Trace Analysis, Editor Susanta Lahiri, Narosa Publishing House, New Delhi (2010), p107.

[7] Post Shot Radioactivity Measurements in Samples Extracted from Thermonuclear Test Site, S.B.Manohar, B.S.Tomar, S.S.Rattan, V.K.Shukla, V.V.Kulkarni and Anil Kakodkar, BARC News Letter, No. 186, July 1999, p1

Dr. B.S. Tomar *is currently Head, Radioanalytical Chemistry Division, BARC and Dean Academic (BARC), Chemical Sciences, Homi Bhabha National Institute, DAE. His areas of expertise include, Nuclear Chemistry, Ion beam analysis, perturbed angular correlation and actinide speciation. His current areas of research include speciation, radio-analytical chemistry of actinides and non destructive assay of special nuclear materials. He is a Ph.D guide of Mumbai University and Homi Bhabha National Institute in Chemistry and so far 10 students have completed their PhD under his supervision. He has 150 publications in international journals.*

Photon Activation Analysis in Nuclear Forensics

Priyamvada M. Dighe

Electronics Division, Bhabha Atomic Research Centre, Mumbai 400 085, INDIA; E-mail: pmdighe@barc.gov.in

Nuclear Forensics

Nuclear forensics is the analysis of nuclear or radioactive sample to extract information to provide evidence for determining the history of the sample material. Nuclear forensic analysis includes characterization (determination of a sample's characteristics), interpretation of data and reconstruction of the event (attribution). The primary objective of nuclear forensic analysis is to determine the attributes of questioned radioactive specimens. Reduced to simple terms, the salient forensic questions for a nuclear sample are: What is it? What was its origin? How did it get there? Who was involved? Because law-enforcement organizations usually drive such investigations, their evidentiary requirements for subsequent prosecution in court are imperative.

Methods used in Nuclear Forensics

Nuclear forensics, the analysis of nuclear materials recovered from either the capture of unused materials, or from the radioactive debris following a nuclear explosion, can contribute significantly to the identification of the sources of the materials and the industrial processes used to obtain them. Therefore, nuclear forensic analysis includes the characterization of the material and correlation with its production history. The nuclear materials are analyzed for following parameters:

- Isotopic composition
- Elemental composition
- Impurities
- Macroscopic appearance
- Microstructure
- Decay products

The measurement techniques applied in nuclear forensics comprise of methods that have been traditionally used in nuclear safeguards, in isotope geology or in material sciences. Following methods are commonly used in analysis:

- Chemical analysis (chemical titration and controlled potential coulometry)
- Radiochemistry (chemical separation and purification)
- Radioactive counting technique (passive alpha, beta gamma radiation measurement)
- Mass spectrometry
- X-ray fluorescence analysis
- X-ray diffraction analysis
- Imaging tools (Optical microscopy, Scanning electron microscopy, Transmission electron microscopy)
- Microanalysis tools (X-ray microanalysis, Secondary ion mass spectrometry)

- Active Non-destructive Techniques (Neutron Activation Analysis, Photon activation analysis, Charged particle activation analysis)

This article describes the photon activation analysis methods.

Active Non-destructive Technique

Activation analysis is a nuclear method of qualitative and quantitative elemental analysis, applicable to the analysis of all kinds of liquid or solid samples. The samples are made radioactive by bombarding them with beam of neutrons/high energy photons/charged particles for a suitable length of time following a suitable radioactive decay period. The induced radioactivity of the sample is measured with the help of high resolution gamma spectrometers. Activation analysis method has an important feature of excellent detection sensitivities for a large number of elements; each of which can be firmly identified via the energies of the gamma-ray photons of its induced radiation isotope, a high degree of accuracy and excellent measurement precision. In the purely instrumental form, the activation analysis is non-destructive. That means, analytical results are obtained without destroying the evidence sample. This is important in forensic work, as the sample is thus preserved for possible later presentation in court.

Photon Activation Analysis (PAA)

Photon activation analysis can be regarded as a complementary technique to "classical" neutron activation analysis (NAA), which makes use of thermal neutrons from reactors. Even though NAA gives much greater detection sensitivity in many cases, there are number of elements and materials such as beryllium, carbon, nitrogen, oxygen, iron and lead which are not highly activated with thermal neutrons. In addition, severe difficulties due to sample self-shielding are encountered when a mixture to be analyzed contains substantial amount of elements with large thermal neutron capture cross-sections. PAA is useful in many of these situations.

Method

In PAA, the sample under study is exposed to photons rays whose energy must exceed the threshold energy of the desired photonuclear reaction. Initially, PAA was performed using gamma sources such as ^{124}Sb as activating photon source. For this purpose, suitable gamma sources are required to analyze variety of samples with varying photonuclear threshold energies. For PAA, high energy bremsstrahlung produced by high energy electron accelerators is the most suitable source. Use of bremsstrahlung as a source gives flexibility to use different
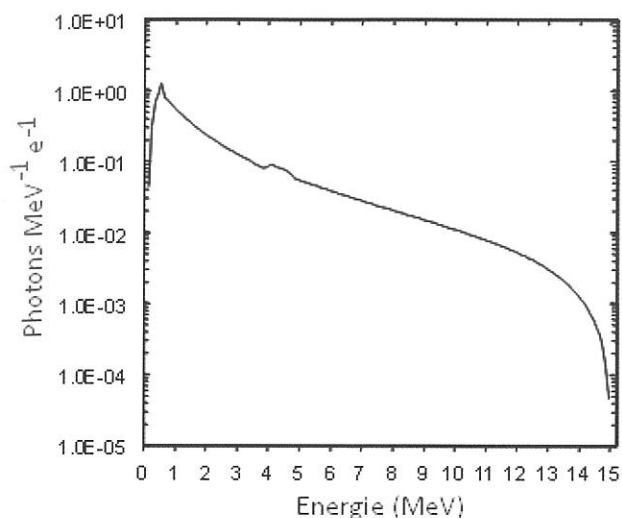
Fig. 1 *Bremsstrahlung energy spectrum produced by 15 MeV energy electrons*

Fig. 2 *Bremsstrahlung produced from a thick target*

threshold energy photonuclear reactions using suitable filters.

Bremsstrahlung Production

When high energy electrons interact with matter, part of their energy is converted to electromagnetic radiation. This radiation is called as bremsstrahlung, which means breaking of radiation. High atomic number (Z) targets convert a larger fraction of electron's energy into bremsstrahlung. However, most of the energy is spent in collision interactions resulting in target heating. Tungsten is a common choice for target due to high Z and high melting point. The production efficiency of bremsstrahlung depends on energy of incident electron. The monoenergetic electrons that completely stop in the target, the resultant bremsstrahlung energy spectrum produced is continuum. Fig. 1 shows the energy spectrum produced by 15 MeV energy electron beam bombarded on Tungsten target. The end point energy of the bremsstrahlung spectrum is the energy of the incident monoenergetic electrons. The bremsstrahlung is also forward peaked at high energies as shown in Fig. 2. The shape of the bremsstrahlung energy spectrum can be altered using suitable filters. This feature makes it useful in nuclear forensic analysis for selective threshold energies in activation analysis.

Examples of PAA

PAA can be applied for analysis of variety of materials. A few examples of applications of PAA are listed below:

Analysis of Actinides

Major and minor actinides are produced in the nuclear fuel cycle and are required to be quantified for safety, security, safeguards and ultimately for forensics purpose. A number of actinides are produced in the process of nuclear reactions. The samples seized for forensic analysis need be characterized for the isotopic composition and relative mass
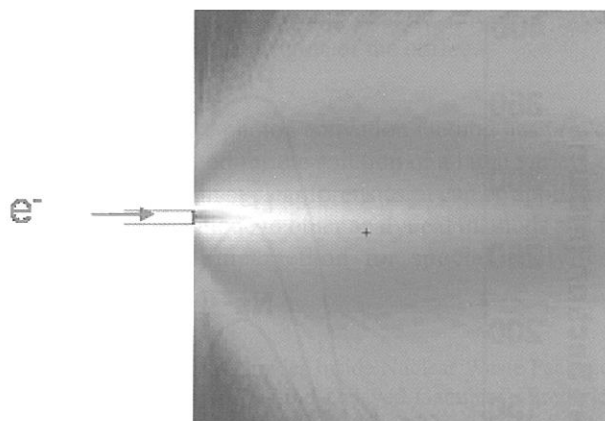
proportions. The analysis can give very important information on the origin of the sample. Generally, the forensic analysis of most of the actinides is carried out by measuring alpha, gamma and neutron radiations emitted by the sample itself. A problem in assaying actinides arises when the material is well shielded [1]. Conventional passive gamma-ray techniques use low-energy (less than 500 keV) gamma rays to identify ^{235}U and ^{239}Pu and are not applicable. The attenuation of gamma rays of these energies by lead, for example, is such that about 1% penetrates 2.54 cm of lead shielding. Therefore, higher energy gamma rays are needed for assaying shielded material. High energy gamma rays are produced by the fission products. To generate fission products, it is required to induce fission in the actinide sample. The fission can be induced by photon activation. The fission products thus produced give rise to gamma photons of energies above 1000 keV. About 22% of 1500-keV gamma rays would penetrate 2.54 cm of lead.

Photons of energies above 6 MeV can induce fission in actinides and the process is called as photofission. The photofission cross-section depends upon the photon energy and peaks at around 15 MeV as shown in Fig. 3. The high energy photons excite the actinide nucleus and when the excitation energy exceeds the fission threshold energy, the nucleus deforms and in the process, the disruptive coulomb repulsive forces overcomes attractive surface energy forces and the nucleus undergoes division into two fragments. The fragments formed are radioactive in nature and undergo beta decay by emitting neutron and gamma radiation. The fission fragments formed are in the range of atomic mass (A)= 70-160 and atomic number (Z)=30-65. The mass distribution has double hump shape as shown in Fig. 4 and peaks at two positions viz. for lighter mass A=90-100 and higher mass A=134-144. For all the nuclei of different isotopes undergoing fission, the centroid for the high mass distribution is nearly constant, while that for the low mass distribution changes almost linearly with the mass of the target. This suggests that unique gamma-ray intensity distributions exist for each fissionable isotope. Fig. 5 shows the gamma energy spectrum of fission fragments of four isotopes after photofission illustrated from reference [2]. The
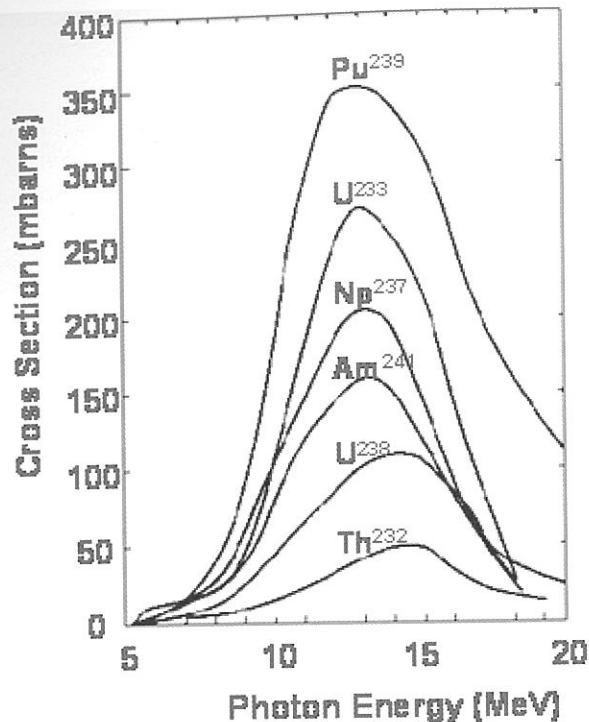
Fig. 3   Photofission cross-section of actinides with respect to photon energy
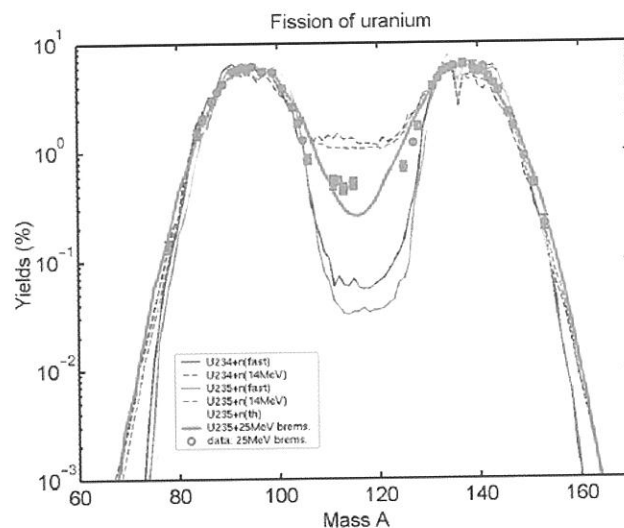

Fig. 4   Fission fragment mass distributions of Uranium in different conditions of fission [3].
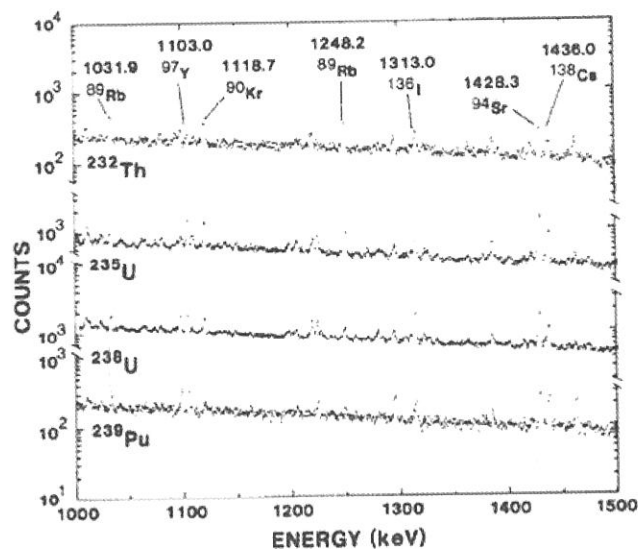
Fig. 5   Energy spectrum of fission product of isotopes after photon induced fission

intensity ratios for the 1436-keV gamma ray from ^{137}Cs fragments and 1428 keV (^{94}Sr) can be used for identification and quantification of a particular actinide isotope. The isotopic composition of an unknown sample of material can be obtained by performing a linear fit of a mixture of the individual response functions to the gamma-ray response function of the unknown material.

Analysis of Art Materials

The art material such as medieval coins containing combination of Au, Ag and Cu metals pose difficulty in analysis using neutron activation. The neutron beam gets attenuated at variable thicknesses of metals and this poses self shielding effects in characterizing a given sample. PAA is suitable for nondestructive analysis of the above mentioned metal samples [4] because of the following advantages: the nuclear parameters (cross-sections, threshold energies) for the (γ,n)-reactions of the three elements as well as the attenuation coefficients of the activating bremsstrahlung and the emitted gamma radiation are quite similar. The severe self-shielding effects of thermal neutron activation analysis do not exist in PAA. The attenuation coefficient for high energy photons is almost constant and, therefore, the shielding effects can be easily and accurately accounted for. Similarly other types of art material such as medieval sword, helmets containing Zinc, Arsenic, Antimony, Gold, Lead Copper are reported to be analyzed using PAA [5,6].

Analysis of Dust Particles

Instrumental analytical methods are preferable in studying sub-milligram quantities of airborne particulates collected in dust filters. The multi-step analytical procedure used in treating samples through chemical separation can be quite complicated. Further, due to the minute masses of the airborne particulates collected on filters, such chemical treatment can easily lead to significant levels of contamination. Radio-analytical techniques, and in particular, activation analysis methods offer a far cleaner alternative. Activation methods require minimal sample preparation and provide sufficient sensitivity for detecting the vast majority of the elements throughout the periodic table. By activating dust particles with 10 to 30 MeV bremsstrahlung photons [7], the elemental composition can be ascertained. The samples are embedded in dust-collection filters and are irradiated "as is" by the bremsstrahlung

Fig. 6 Gamma spectrum of electronic waste after photon activation
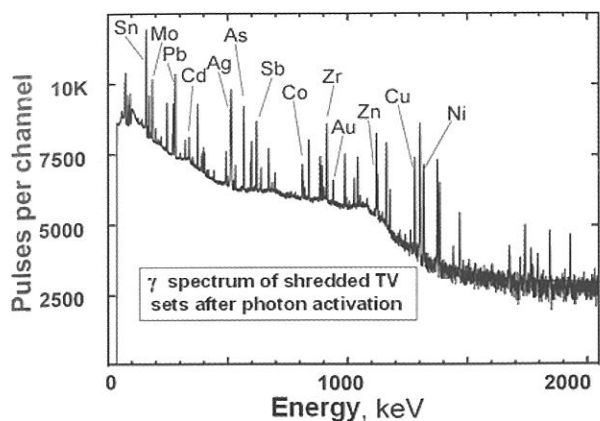
photons. The radioactivity of the photonuclear reaction products is measured with appropriate spectrometers and the respective elements are quantified using multi-component calibration materials.

Analysis of Electronic Waste

Segedade et al [8] analyzed kilogram samples of electronic waste using 30 MeV bremsstrahlung. The material being extremely inhomogeneous, was shredded and was packed in plastic container and then irradiated under high energy photon beam. After irradiation, the sample was transferred in small beakers to minimize uncertainties due to matrix absorption of low energy gamma rays emitted from the irradiated waste samples. High resolution gamma spectrum as given in Fig. 6 was acquired from the irradiated waste and the quantification of various elements present in the waste was done with good accuracy.

Analysis of Coffee Samples

PAA analysis on coffee samples [9] is done from several locations around the world as an initial step in assessing the relationship between trace elements in illicit drugs and the soils in which they were grown. The preliminary results show coffees from different locations have different concentrations of trace elements. Thus, it is conceivable that the elemental content could serve as "fingerprint" to trace the origins of the coffee.

Conclusions

Non-destructive photon activation method has proved to be a suitable method for the solution of a large variety of analytical problems in nuclear forensics. It can be applied as complimentary technique to other analytical methods and in some cases as unique method for special analytical applications.

References

[1] "Identification of Actinides Inside Nuclear Waste Packages by Measurement of Fission Delayed Gammas", Frederick Carrel et al, 2006 IEEE Nuclear Science Symposium Conference Record N28-1

[2] "Analysis of fissionable material using delayed gamma rays from photofission", C.L. Hollas et al, Nuclear Instruments and Methods in Physics Research B24/25 (1987) 503-505

[3] "Création d'une bibliothPque d'activation photo-nucléaire et mesures de spectres d'émission de neutrons retardés", Giacri-Mauborgne M. L., Ph. D thesis l'université de Caen de Basse-Normandie : Physique, 198 p., 2005

[4] "Photon activation analysis of coins and objects of art", Reimers, P. et al, Journal of Radioanalytical Chemistry, Volume 39, Issue 1-2, March 1977, Pages 93-97.

[5] "The non-destructive investigation on medieval iron-based weapons", C. Segebade, Nuclear Instruments and Methods in Physics Research A 353 (1994) 654-657.

[6] "Edward's sword?-A non-destructive study of a medieval king's sword", C. Segebade, AIP Conference Proceedings, 1525, 2013, Pages 417-421.

[7] "Photon activation analysis of dust particles for environmental research and applications using the 44-MeV electron LINAC at the Idaho Accelerator Center", Mamtimin, M. et al, 10th International Topical Meeting on Nuclear Applications of Accelerators 2011, AccApp 2011 2011, Pages 64-72.

[8] "The problem of large samples: An activation analysis study of electronic waste material", C. Segebade, et al, J. Radioanal. Nucl. Chem. 271, 261-268 (2007).

[9] "A provenance study of coffee by photon activation analysis", Sun Z.J. et al, J. Radioanal. Nucl. Chem., 296, Issue 1, April 2013, Pages 293-299.

Dr. (Mrs.) Priyamvada M. Dighe *joined B.A.R.C. in 1988 after completing Post Graduation in Physics from Devi Ahilya University Indore, India. She obtained Ph.D. in Physics from Mumbai University in 2006. She has developed advanced innovative design of gas-filled neutron and gamma detectors for light water reactors, PFBR reactor and INDUS-1 and 2 accelerator facilities for control and safety instrumentation. She has more than 50 research papers to her credit. Currently she is carrying out studies on active interrogation techniques.*

Challenges on Prevention and Response to Nuclear / Radiological Threats and Nuclear Forensics

S. Murali[1], Anilkumar S.[1], Pradeepkumar K.S.[1] and D.N. Sharma[2]

1. *Radiation Safety Systems Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085 ,*

2. *Health Safety & Environment Group, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085;*
    E-mail: dnsharma@barc.gov.in

Introduction

The three main steps in combating illicit trafficking, nuclear terrorism and proliferation are prevention, detection and response. Prevention is certainly the most effective and efficient way of keeping nuclear material under control. Regaining control over material that has been diverted or stolen requires significantly higher efforts. Nuclear Forensic (NF) provides clues on the history and on the origin of nuclear material. It is the systematic and comprehensive analytical approach for analyzing the seized material. The measurement techniques comprise of methods used in nuclear safeguards, in isotope geology or in material sciences or fuel cycle operations. Investigative radiochemistry remains the backbone of any analysis. It is the scientific technique for characterization of the intercepted intact or retrieved from material debris and associated materials in terms of elemental / isotopic composition and other physical parameters using fingerprinting and help in identifying its origin, route taken till seizure, its legal owner and its intended use by comparing its features with a versatile data base of reference material. It is the investigation of nuclear materials to find evidence on the radiation source, its characterization of the material trafficking and the enrichment of the nuclear material, interpretation and categorization of the threat.

Fingerprint of a nuclear material or a radioactive material is the goal of nuclear forensics. This includes besides physical material characteristics the origin of the unknown material, its intended use, the smuggling-route and its last legal owner. It helps in assessing 'cause of diversion / theft' and helps in identifying and implementing measures to prevent such events. The material for investigation can be recovered from various sources including dust from the vicinity of a nuclear facility or from the radioactive debris following a nuclear explosion [1,2]. Results of the analysis are used by different organizations to make interpretations and attributions. It works best in conjunction with law enforcement (policing and traditional forensics) and intelligence agencies to provide the basis for attributing the materials and/or nuclear device to its originators. It does not consist of routine procedures that can be universally applied to all evidence. The information is typically combined with other sources of information such as law enforcement and intelligence information [2,3]. It is an iterative scientific approach – analytical results guide subsequent analysis. The first seizures of nuclear materials from trafficking in the early 1990s allowed the nuclear forensic methodology to be adopted by a wider scientific community. When scientific laboratories outside the weapons and intelligence community took an interest in this methodology was when the term 'Nuclear Forensics' was coined.

Unlike traditional forensics, nuclear forensics focuses mainly on the nuclear or radioactive material and aims to provide knowledge of the intended use of the materials. It may be helpful in tracking Nuclear Terrorism which involves (a) Smuggling/illicit trafficking of nuclear material intended for the fabrication of nuclear device, (b) Theft of nuclear weapon and (c) usage of Improvised Nuclear Device (IND). Though the probability of these events are very low, the consequences being very high and far reaching, NF has to use all available information for investigation. Radiological threats/radiological terrorism involve malicious usage of radioactive material either as Radiological Dispersal Device (RDD, also known as Dirty Bomb) or as Radiological Exposure Device (RED). Attack on any radiological facility or on the transport of radioactive material also can have severe radiological consequences. In these cases, the consequences are confined to smaller locality and are less lethal than usage of IND. International Atomic Energy Agency (IAEA) has brought out guidelines for radiation emergency preparedness [4] towards these nuclear events and categorized them under some of the classes of threats [5]. The origin of the radiological terrorism can be due to the loss of control of radioactive material or by theft, thereby resulting into Orphan Sources. Such case of reported orphan sources is large as per the international data base and may lead to illicit trafficking through entry / exit ports or borders. For the last few years, international efforts are being made by IAEA and other agencies to prevent, detect and respond to illicit trafficking of radioactive materials as well as malicious acts involving radioactive material.

Threat Categorization and Preparedness Plan

An emergency is defined by IAEA [4] as 'a non-routine situation or event that necessitates prompt action, primarily to mitigate a hazard or adverse consequences for human health, quality of life, property or the environment. This includes Radiation Emergencies (nuclear and radiological emergencies) [6] and conventional emergencies such as fire, release of hazardous chemicals, storms or earthquakes for which prompt action is warranted to mitigate the effects of a perceived hazard'.

Several Nuclear / Radiological emergencies [6] have occurred, Windscale (1957), the Three Mile Island accident (1979), the Chernobyl accident (1986), Tokaimura accident (1999) and Fukushima accident being the major nuclear emergencies. Several Radiation emergencies have occurred throughout the world and IAEA has undertaken

comprehensive reviews of the events, the purpose of which is to compile information about the causes of the accidents, the subsequent emergency response including medical management, dose reconstruction, public communication, nuclear material security etc., so that any lessons can be shared with national authorities and regulatory organizations, emergency planners and a broad range of analytical specialists, including physicists, technicians, medical specialists and persons responsible for radiation protection.

Since 1968 to 2008, large number of radiological events are reported [6] worldwide, wherein the Orphan source and the consequent radiological emergency has resulted in large number of cases of high exposures, mainly attributed to lack of training, loss of administrative control on radiation sources (orphan sources) and inadequate knowledge on radiation effects/safety have led to inadvertent radiation exposures led to loss of a few lives. Thus, early detection of orphan sources, identification and recovery of radioactive material, administrative control, enforcement of nuclear security and safety etc would go a long way in reducing the consequences including psychological impact. Radiological surveys help in –

(a) Identify nuclides and its amount present causing hotspots using gamma spectrometry

(b) to improve radiological safety by helping dictate PPE and respiratory protection,

(c) Immediate distinction between fissile and non-fissile material,

(d) To use data to determine time duration, safer work areas and establish radiation boundaries and

(e) Law enforcement has keen interest in amount of material recovered/distributed.

IAEA Safety Requirements publication [6], Preparedness and Response for a Nuclear or Radiological Emergency, GS-R-2 [1] emphasize on Nuclear Forensics and Nuclear Security. IAEA in its categorization of Nuclear and Radiation Related Threats (consequences on radiological criterion) has demarcated them into 5 different categories, on the threat category IV wherein lays emphasis on nuclear forensics to investigate non-authorized activities such as activities relating to dangerous sources obtained illicitly. It also includes transport and authorized activities involving dangerous mobile sources such as industrial radiography sources, nuclear powered satellites or radio-thermal generators. Category IV is indicated to represent the minimum level of threat (consequences on radiological criterion) assumed to apply for all States and jurisdictions. The Category IV events can result in a nuclear or radiological emergency that could warrant urgent protective actions in an unforeseeable location. IAEA in GS-R- 2 [1] emphasizes on emergency plans for facilities having potential for radiological implications.

Analytical tools for identification, quantification and possible linking of suspected material to its source of origin –

Nuclear Forensics play a vital role in the Radiation Emergency Preparedness – Plan and Procedures. The threat of possible terrorist attacks using Chemical, Biological, Biological and Radiological (CBRN) agents has reinforced the need for an all hazards integrated approach on Nuclear Security. Whatever the emergency affecting the public, the police will have to take the lead role with advice drawn from experts of Nuclear Safety & Security. The identification of nuclear material is prime importance to guide the Emergency Response Mechanism.

The evidence collection mission has to collect 'traditional evidence' such as latent fingerprints, DNA, hairs and fibers that is contaminated with radioactive material and collect evidence on a) Trace levels of contamination through high dose sources and b) fissile and non-fissile isotopes. Such evidence is sent to specialized laboratories for further analysis.

Elemental, micro-structural and isotopic signatures left behind from processing or reprocessing chemistries (e.g. fission product sources - ^{137}Cs, ^{90}Sr) distinguishes one source from the other, Precursor material; Chemical form (salt / metal); Trace impurities (separation chemistry); Trace contaminants (signatures) and age determination by quantifying the buildup of daughter products from isotopes present in the nuclear material. Thus isotopic signatures such as nuclide and its activity serve as finger printing for establishing identity and origin of the nuclear material.

Clearance Levels

Radioactive wastes during the peaceful use of nuclear energy programme are produced during the generation of nuclear power and the use of radioactive materials in industry, research and medicine. The importance of the safe management and security of radioactive material / waste for the protection of human health and the environment has long been recognized. If there is any loss in administrative control on such material (orphan sources) based on levels of radio-nuclides in solid materials below which regulatory control may be relinquished on the grounds that the associated radiation hazards are trivial. The radiological basis for the clearance levels is the international consensus on principles for the exemption of radiation sources and practices from regulatory control reached and published in IAEA Safety Series No. 89. The levels [7] are intended as international reference values.

Sources in the first category are those which do not come under regulatory category, are excluded from regulatory control by a process called exemption. Exempted sources typically include small sources of radiation such as tracers used in research, calibration sources and some consumer products containing small sources or low levels of activity per unit mass. The corresponding levels of activity or activity concentration are called exemption levels. Sources in the second category are those which are released from regulatory control, by a process called clearance. Cleared sources include waste materials and materials for recycling from within the nuclear fuel cycle and wastes from other

regulated facilities such as hospitals, research laboratories and industry. The amounts of material involved in clearances can be substantial and are generally greater than those involved in exemptions of man-made sources. The corresponding levels of activity or activity concentration are called clearance levels. Conditional clearance values could serve as a basis for international trade, may be established by agreement between national authorities or by the appropriate international organizations.

Clearance levels for radio nuclides in solid materials [7] are devised to constrain doses from potential events to 10 ìSv/a – 100 ìSv/a and are indicated in quantities such as mass activity concentration (Bq/g), surface contamination (Bq/cm^2), total activity per unit time (Bq/a) and total mass per unit time (t/a). It is applicable for land fill, incineration, recycling but other than reuse purposes where the value is in an order higher. For Naturally Occurring Radioactive Material (NORM) ^{40}K, ^{226}Ra, ^{238}U and ^{232}Th the average activity concentrations in few common samples are 0.37 Bq/g, 0.04 Bq/g, 0.025 Bq/g and 0.025 Bq/g respectively.

Values of activity concentrations in excess of the indicated clearance values could lead to radiation exposures > 100 ìSv/y and to situations wherein identification of material, quantification and suitable intervention measures come into play in sequential manner. Though clearance values for radio-nuclides in solid samples are smaller in magnitude, they act as precursors to indicate the presence of nuclear material in bulk samples handled in public domain. The analytical tools are used to detect and quantify such materials, even in low concentration in the suspected materials using Nuclear Forensic techniques.

Clearance level for the following radio-nuclides [7] (based on nature of radiation emitted, specific activity and radio-toxicity)

1. Activity Concentration in solid materials is between 0.1 to 1.0 Bq / gm for ^{22}Na, ^{24}Na, ^{54}Mn, ^{60}Co, ^{65}Zn, ^{94}Nb, ^{110m}Ag, ^{124}Sb, ^{134}Cs, ^{234}U, ^{137}Cs, ^{235}U, ^{152}Eu, ^{238}U, ^{210}Pb, ^{237}Np, ^{226}Ra, ^{239}Pu, ^{228}Ra, ^{240}Pu, ^{228}Th, ^{241}Am, ^{230}Th, ^{244}Cm, ^{232}Th

2. Activity Concentration in solid materials is between 1.0 to 10 Bq / gm for ^{58}Co, ^{59}Fe, ^{90}Sr, ^{106}Ru, ^{111}In, ^{131}I, ^{192}Ir, ^{198}Au, ^{210}Po

3. Activity Concentration in solid materials is between 10 to 100 Bq / gm for ^{51}Cr, ^{57}Co, ^{99m}Tc, ^{123}I, ^{125}I, ^{129}I, ^{144}Ce, ^{201}Tl, ^{241}Pu

4. Activity Concentration in solid materials is between 100 to 1000 Bq / gm for ^{14}C, ^{32}P, ^{36}Cl, ^{55}Fe, ^{89}Sr, ^{90}Y, ^{99}Tc, ^{109}Cd

5. Activity Concentration in solid materials is between 1000 – 10,000Bq / gm for ^{3}H, ^{35}S, ^{45}Ca, ^{63}Ni, ^{147}Pm (^{220}Rn and ^{222}Rn have not been considered in the list since they are gaseous emanates.)

For the sake of simplicity in cases where a single value clearance level is required, use of three times the lower limit of the category range is suggested.

IAEA Nuclear Security Documents

Nuclear Security issues related to the prevention, detection and response to any acts of theft, sabotage, unauthorized access and illegal transfer of nuclear materials and other radioactive substances, their related facilities are addressed in IAEA Nuclear Security Series of publications, that could serve as guideline and reference manual [4]. IAEA Nuclear Security series of publications are in the categories – (1) Nuclear Security Fundamentals, (2) Recommendations, (3) Implementing guides and (4) Technical Guidance. IAEA has developed radionuclide specific activity levels for the purpose of emergency planning and response. IAEA ranks the hazard of the radioactive source in 5 different categories based on the A/D ratio where its activity is A, 'D' is the value for it to be considered as dangerous source. Nuclear Forensics and its interpretation are important tools in securing the nuclear and radioactive material and to provide for the decision makers / policy makers / technical experts with guidance for responding to incidents involving interdiction of nuclear and radioactive material.
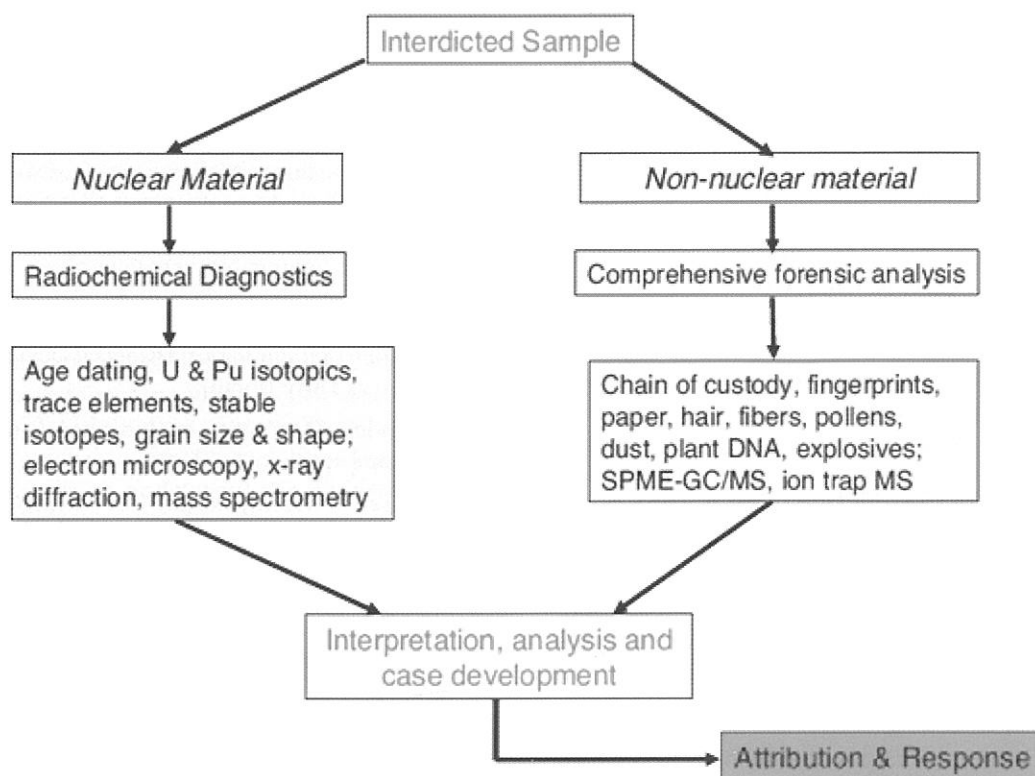
Case Study

In an event reported to have occurred in May, 1999, Seizer of a Pb canister hidden in a car suspected to have HEU at the border of Bulgaria and Romania. The Initial examinations revealed that:

(a) Sample was contained in a glass ampoule that was embedded in a yellow wax which was filled in a cylindrical Pb canister and the papers wrapped around ampoule and Pb container indicated that these belong to Eastern Europe

(b) Gamma spectrometric investigation indicated it to be HEU in uniform fine-grained U_3O_8

(c) Isotopic composition: ^{235}U — 72.7%, ^{236}U – 12.1%, ^{239}Pu – 82% and ratio of ^{240}Pu / ^{239}Pu isotopes = 0.12 and detected contamination of fission products.

Nuclear Forensics study of the isotopic fingerprints of U and Pu indicated through a code computation that it might be originally 90% enriched U fuel used in a research thermal reactor and reprocessed after around 300,000 MWdays burn up to achieve this detected isotopic composition. Mean age determined from Pu / Am ratio and above investigations indicate the sample was of reprocessed enriched U used in LWR and it was reprocessed in Oct. 1993. This matched with all investigations including code based computations.

Emerging Problems

Though it is difficult to foresee the use of unauthorized acts involving nuclear / radioactive material, such activities are increasingly viewed as significant threats, as world over there are reported events of loss of radioactive sources. Orphan sources, material with loss of regulatory control, lack of accountability and poor knowledge on safety and

Interdicted Sample

→ **Nuclear Material**

→ Radiochemical Diagnostics

→ Age dating, U & Pu isotopics, trace elements, stable isotopes, grain size & shape; electron microscopy, x-ray diffraction, mass spectrometry

→ **Non-nuclear material**

→ Comprehensive forensic analysis

→ Chain of custody, fingerprints, paper, hair, fibers, pollens, dust, plant DNA, explosives; SPME-GC/MS, ion trap MS

→ Interpretation, analysis and case development

→ Attribution & Response

Techniques/Methods	Short time (24 hrs)	Intermediate time (One week)	Longer time (One month)
Radiological	Estimated total activity Dose Rate (α, γ, n) Surface Contamination	----	
Physical Characterization	Visual Inspection Radiography Photography Weight Dimension Optical Microscopy Density	SEM (EDS) XRD Organics	TEM (EDS)
Traditional Forensic Analysis		Fingerprints Fibers	
Isotope Analysis	Alpha-spectroscopy Gamma-spectroscopy	Mass spectrometry (SIMS, TIMS, ICP-MS) ICP-MS XRF, ICP-OES	Radiochemical Separations Mass spec. For trace impurities: Pb Stable isotopes

security of the nuclear / radioactive materials pose the problems. Both irradiated reactor fuel and high activity radioactive sources used for applications pose difficulties as the material that could be potentially used in the fabrication of Radiological Dispersal Device (RDD) – generally known as Dirty Bomb. Sources of moderate to low activity could be more attractive as an RDD component, as the main aim of the adversaries will be to create fear psychosis in the public along with mass disruption. Prevention of these potential threats is to heighten the safety, security on control of nuclear and radioactive material, tracing the route of material from diversion to interdiction and determining the source of the material, method of production, its characterization and categorization of the radiological events.

Action plan for the nuclear forensic investigation teams have been formulated in IAEA –TECDOC-1313 [2] with details for On-site analysis, collection of evidence –

radiological and forensic, transportation of evidence, nuclear forensic interpretation and intimation to IAEA [8]. Model Action Plan (MAP) enables us to investigate radioactive and traditional, non-nuclear forensic evidence. It is designed to attribute the nuclear material, including its origin, method of production, the likelihood that more material exists in transit route and the point at which legitimate control was lost. The following part explains analytical techniques those can be used to find the nuclear forensic signatures to fingerprint unknown nuclear material. The composition of different elements, isotopes and the micro- and macroscopic parameters can give hint on origin of the investigated material. Time duration specific detailing by the tools is enlisted [8].

'Orphan Sources'- an International Issue

Adequate security through approval of secured installations and storage of sources, regulatory, engineered safety features and additional administrative controls ensure 'cradle-to-grave' control of them. A source becomes 'orphan' i.e., goes out of regulatory control due to:

(a) Lack of or breach of the provisions

(b) Import of sources without licence deliberately or out of ignorance

(c) Loss or misplacement

(d) Theft

(e) Unauthorized disposal

(f) Mishandling of source consignments at entry and exit ports of the country

(g) Lack of awareness in the public and the officials

Such sources may also enter into public domain through illegal trafficking. These orphaned sources may be malevolently used by unlawful elements in the society leading to radiological emergency in public domain. Though accidents during transportation of radioactive sources may result into a radiological emergency situation, the probability of such an event is small [10].

Radiological Emergency situations due to orphan sources are reported from many counties. The sources responsible were mainly ^{60}Co, ^{137}Cs and ^{192}Ir. The situations resulted in fatalities or severe injuries to few people who got exposed. In India, there were few cases of lost brachy-therapy sources, industrial radiography sources and nucleonic gauges though there was no fatality reported in such incidents. DAE has developed and field tested state of the art radiation monitoring systems like Aerial Gamma Spectrometry System (AGSS), Quad-rotor based remote Aerial Radiation Monitoring System (QARMS) etc for Search of Orphan Sources and assessment of Ground Contamination in case they are dispersed through the use as a RDD.

Nuclear/Radioactive Material involved in illicit acts and the Challenges

The potential acts on illicit use of radioactive/nuclear material in devices to spread / contaminate radioactivity in public domain, cause radiation exposures to public could lead to radiological consequences and psychological aspects. The challenges involved in countering such acts are–

1. Early Detection of 'potential threats'/sources

2. Handling of Radiological Dispersal Device (RDD, also known as Dirty Bomb)

3. Radiation Dosimetry including reconstruction of exposure scenario

4. Medical Management of Exposure cases (decontamination, de-corporation)

5. Decontamination of affected area and public

Radiological Dispersal Device (RDD) and Response to Radiological Emergencies

Radiological Dispersal Device (RDD) is defined as 'any device, including any weapon or equipment (other than a nuclear explosive device), designed to disperse radioactive material by disseminating it to cause destruction and damage and additional injury due to the radiation emitted by the material'. It is feared that many radioactive materials, including fission products, spent fuel from nuclear reactors, medical and industrial waste also may be integrated with conventional explosives to make a RDD.

Blast and thermal effects of fire due to chemical explosives following a RDD explosion will be the only cause for immediate deaths, since lethal levels of radiation exposure from the dispersed materials requires extremely large quantity of radioactive material assembled in the RDD. Such an eventuality can easily be detected by radiation detector(if it is gamma emitters), suspicion on heavy mass / shield during its transport, persons associated with fabrication of the RDD may receive acute exposures leading to radiation injuries thereby giving clues for security / safety personnel to locate the RDD prior to its explosion. Panic caused by fear of radiation can result into large disruption and the required cleanup of the radioactive material / contamination and any consequent avoidance of the location (if not cleared of contamination even after many attempts of cleanup) may cause huge economic losses for the nation.

Initial Investigation

The first seizures of nuclear or other radioactive material were reported in Switzerland and Italy in 1991and later reports of incidents associated with nuclear material occurred in Germany, the Czech Republic, Hungary and other central European countries [10]. Nuclear forensics relies on measurable parameters – chemical impurities, isotopic composition, microscopic appearance and microstructure, but not limited to these only. By measuring these attributes, conclusions can be drawn as to the origin of the material.

Identification of these aspects is an ongoing area of research, data interpretation, the availability of reference information and on knowledge of the fuel material operations.

The first investigative radiochemical measurements began in the early days of nuclear fission. In 1944, the US Air-force made the first attempts to detect fission generated nuclide ^{133}Xe in the atmosphere in order to indicate the production of Pu through the irradiation of U and chemical reprocessing in an effort to gather intelligence on the status of the German nuclear program. In the subsequent years it became increasingly valuable to gather information on the Soviet nuclear weapons program, which resulted in the development of technologies that could gather airborne particles in a weather reconnaissance plane. These particles were used to determine the detonation time of the first Soviet atomic test, 'Joe 1' [11,12]. Further analysis revealed that this bomb was a replicate of the "Fat Man", which was the bomb dropped on Nagasakig2057 . This investigative methodology combined radio-chemistry and other techniques to gather intelligence on nuclear activities. In 1994, 560 grams of (Pu, U) oxide were intercepted at Munich airport in an airplane coming from Moscow [14].The precise composition was 363 grams Pu (87% of which was ^{239}Pu) and 122 grams of U [14].

Tools for Nuclear Forensic Analysis

This section though not exhaustive, tries to describe some of the most commonly used analytical tools in Nuclear Forensic Analysis. It could be elemental / isotopic analysis as micro or bulk analysis and for imaging purposes.

Chronometry

Chronometry is the science of the measurement of time or timekeeping. Determining a nuclear material's age is critical to nuclear forensic investigations. Dating techniques can be utilized to identify a material's source as well as procedures performed on the material. This can aid in determining the information about the potential participant in the 'age' of the material of interest. Nuclides, related through radioactive decay processes will have relative sample concentrations that can be predicted using parent-daughter in-growth equations and half-lives of respective radio-nuclides. Because radio-nuclides decay at a rate (characteristic property) of the isotope in the sample and the half-life of the parent nuclide, the relative amount of the decay products compared to the parent can be used to determine 'age'. The decay network begins with ^{238}Pu and proceeds through the in-growth of long-lived ^{234}U, ^{230}Th and ^{226}Ra. Any member of the 4n+2 decay series on purification immediately begins to produce descendant species. The time since a sample was last purified can be calculated from the ratio of any two concentrations among the decaying nuclides.

Essentially, if nuclear material has been put through a refinement process to remove the daughter species, the time elapsed since purification can be "back-calculated" using radio-chemical separation techniques in conjunction with
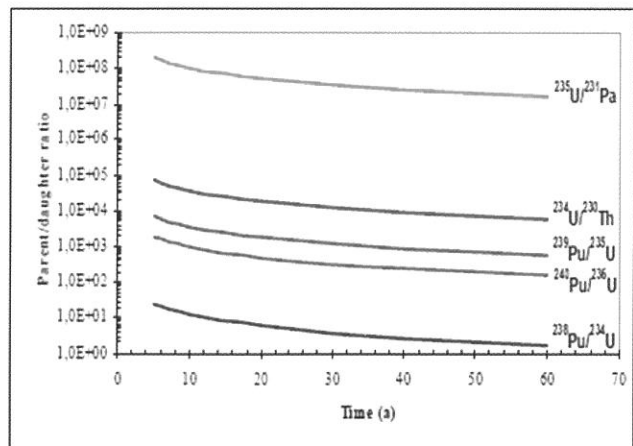

Fig. 1 The actinide parent daughter pairs used for interpreting the sample age

analytical measurement of the existing parent-daughter ratios. For example, the α decay of ^{239}Pu to ^{235}U can be used as an example with the assumption of a perfect purification time T_0 then there will be a linear relationship between the in-growth of ^{235}U and time elapsed since purification. This strategy may not apply when the parent-daughter pair achieve secular equilibrium very rapidly or when the half-life of the daughter nuclide is significantly shorter than the time that has elapsed since purification of the nuclear material, e.g. ^{237}Np/^{233}Pa. Another possible complication is if in environmental samples, non-equivalent metal/ion transport for parents and daughter species may complicate or invalidate the use of chronometric measurements. Special age-dating relationships exist, including the commonly employed ^{234}U/^{230}Th and ^{241}Pu/^{241}Am time scales (chronometers). In few circumstances, parent-grand daughter relationships can also be used to elucidate the age of nuclear materials when the material is intentionally made to look older through the addition of daughter nuclides into the sample. Figure 1 shows the actinide parent daughter pairs used for interpreting the sample age.

Chronometry is based on the concept that the elemental composition of the nuclear material changes as samples are prepared and analyzed. This barrier can be substantial for species that decay quickly or whose daughter products put forth spectral interferences. The decay of ^{233}U, for example, has an approximate half life of 1.6×10^5 yrs which is rapid in comparison to many species and yield ^{229}Th, which emits an α particle having the same energy, as the parent. To avoid this, freshly prepared samples as well as complementary analysis methods are used for nuclear materials characterization. The decay of nuclear samples makes rapid analysis methods highly desirable [13].

Separation Process

A separation process, is any mass transfer process that converts a mixture of substances into two or more distinct product mixtures, at least one of which is enriched in one or more among the mixture's constituents. In some cases, a

separation may fully divide the mixture into its pure sub-constituents. Separations are carried out based on differences in chemical properties or physical properties such as size, shape, mass, density or chemical affinity, between the constituents of a mixture, according to the particular differences they use to achieve separation. In the case that no single difference can be used to accomplish a desired separation, multiple processes will often be performed in combination to achieve the desired end.

The purpose of such a separation may be analytical, i.e. to help analyze components in the original mixture without any attempt to save the fractions, or may be preparative, i.e. to "prepare" fractions or samples of the components. The separation can be done on a small scale – effectively a laboratory scale for analytical purposes, or on a large scale – effectively an industrial scale for preparative purposes or on some intermediate scale. Chemical separation techniques are frequently utilized in nuclear forensics as a method of reducing the interferences and to facilitate the measurement of low level radio-nuclides. Purification that occurs rapidly as progeny in-growth begins immediately following purification is ideal.

Ion-exchange chromatography (or ion chromatography) is a process that allows the separation of ions and polar molecules based on their affinity to the ion exchanger. It can be used for almost any kind of charged molecule. Ion-exchange chromatography retains analyte molecules on the column based on coulombic (ionic) interactions. The stationary phase surface displays ionic functional groups (R-X) that interact with analyte ions of opposite charge. This type of chromatography is further subdivided into cat-ion exchange chromatography and anion exchange chromatography. The ionic compound consisting of the cationic species M+ and the anionic species B⁻ can be retained by the stationary phase. Anion exchange chromatography retains anions using positively charged functional group.

Anion Exchange

Anion exchange separation methods are widely used in the purification of actinides and actinide bearing materials through the use of resin columns. The anionic actinide complexes are retained by anion exchange sites that are on the resin and neutral species pass through the column without getting retained. Then the retained species can be eluted from the column by conversion to a neutral complex, typically by changing the mobile phase passed through the resin bed. Anion exchange-based separations of actinides, while valued for their simplicity and widely used, tend to be time consuming and are infrequently automated. Most are still dependent on gravity. Speeding up the flow of the mobile phase tends to introduce problems such as impurities and jeopardize future investigations. Hence, there is still a need for development of this technique to satisfy the nuclear forensic research priorities.

Co-Precipitation

Co-precipitation (CPT) or co-precipitation is the process carrying down by a precipitate of substances normally soluble under the conditions employed. There are three main mechanisms of co-precipitation: inclusion, occlusion and adsorption. On the other hand, in the analysis of trace elements, as is often the case in radiochemistry, co-precipitation is often the only way of separating an element. Since the trace element is too dilute (sometimes less than a part per trillion) to precipitate by conventional means, it is typically co-precipitated with a carrier, a substance that has a similar crystalline structure that can incorporate the desired element. An example is the separation of francium from other radioactive elements by co-precipitating it with caesium salts such as caesium perchlorate. Besides its applications in chemical analysis and in radio-chemistry, it is also potentially important to many environmental issues related to water resources, radionuclide migration in waste repositories, metal contaminant transport at industrial sites, metal concentrations in aquatic systems and waste water treatment technology.

Co-precipitation is an important issue in chemical analysis, where it is often undesirable, but in some cases it can be exploited. In gravimetric analysis, which consists on precipitating the analyte and measuring its mass to determine its concentration or purity, co-precipitation is a problem because undesired impurities often co-precipitate with the analyte, resulting in excess mass. This problem can often be mitigated by "digestion" (waiting for the precipitate to equilibrate and form larger, purer particles) or by re-dissolving the sample and precipitating it again. Actinide isolation by co-precipitation is frequently used for samples of relatively large volumes to concentrate analytes and remove interferences. Actinide carriers include iron hydroxides, lanthanide fluorides / hydroxides, MnO_2 and a few other species.

Radioactivity Counting Techniques

Counting techniques of α, β, γ or neutron activity can be used as approaches for the analysis of nuclear forensic materials that emit decay species. The most common of these are alpha and gamma spectroscopy. β counting is used infrequently because most short lived β-emitters also give off characteristic γ-rays suitable for spectrometric measurements. Neutron counting are found more rarely in analytical labs due in part to shielding concerns should such neutron emitters be introduced into a counting facility. A wide range of instrumental techniques are employed in nuclear forensics. Radiometric counting techniques are useful when determining decay products of species with short half-lives. Radiometric counting determines the amount of ^{14}C present in a sample by measuring its radioactivity. This is done by converting the carbon in the material being dated to a gas such as CO_2, methane or benzene and placing it in a suitable radiation detector.

- Gas counting: the sample is converted to methane or CO_2 to fill a proportional counter. The decay of a ^{14}C atom triggers an electrical discharge in the gas which is electronically detected. The photo shows the interior of a typical gas counting system, using thick steel plates to shield the counters inside from external radiation.
- Liquid scintillation counting: the sample carbon is converted to benzene, mixed with special organic compounds and placed in a transparent container. The solution emits a pulse of light whenever a ^{14}C atom decays, and the light pulse is detected by sensitive photomultiplier tubes placed close to the container.

The radiometric method can detect the presence of ^{14}C atoms as it undergoes radio decay. By determining the number of ^{14}C decays in a certain time, we can calculate the number of ^{14}C in the detector, and with knowledge of the total amount of carbon atoms to determine the concentration of ^{14}C, in turn enables to estimate the age of a material. As the half life of ^{14}C is 5730 years, we must ensure that there are enough ^{14}C atoms in the detector to undergo enough decay in a reasonable time, amounts to several grams of carbon. Since in most cases the carbon is only one component of the material, radiocarbon dating using decay counting may require many grams of the sample. However, for longer half-lives of radio-nuclides, inorganic mass spectrometry is a used to carry out elemental analysis and determining isotopic relationships. Microscopy approaches can also be useful in characterization of a nuclear material.

Alpha-Particle Spectroscopy

Alpha spectroscopy is a method of measuring the radio-nuclides based on emission of a partciles. They can be measured by a variety of detectors, including liquid scintillation counters, gas ionization detectors, and ion-implanted silicon semiconductor detectors. Typical alpha-particle spectrometers have low backgrounds and measure particles ranging from 3 to 10 MeV. Radio-nuclides that decay through a emission tend to eject them with discrete, characteristic (finger print) energies between 4 to 6 MeV. These energies become attenuated as they pass through the layers of sample. Increasing the distance between the source and the detector can lead to improved resolution, but decreased particle detection. The alpha spectrometry technique is extensively used for studying the isotopic composition of actinides particularly uranium isotopes. Fig. 2 and Fig. 3 show the alpha spectrum of natural and depleted uranium sources.

The advantages of alpha-particle spectroscopy include relatively inexpensive equipment costs, low backgrounds, high selectivity and good throughput capabilities with the use of multi-chamber systems. There are also few disadvantages of alpha-particle spectroscopy. One disadvantage is that there must be significant sample preparation to obtain useful spectroscopy sources. Also, spectral interferences or artifacts from extensive preparation prior to counting, to minimize this high purity acids are needed. Besides, measurements require a large quantity of material leading to poor resolution. Also, undesired spectral overlap and long time duration for the analysis are other disadvantages.

Gamma Spectroscopy

Gamma spectroscopy yields results that are conceptually equivalent to alpha-particle spectroscopy. The
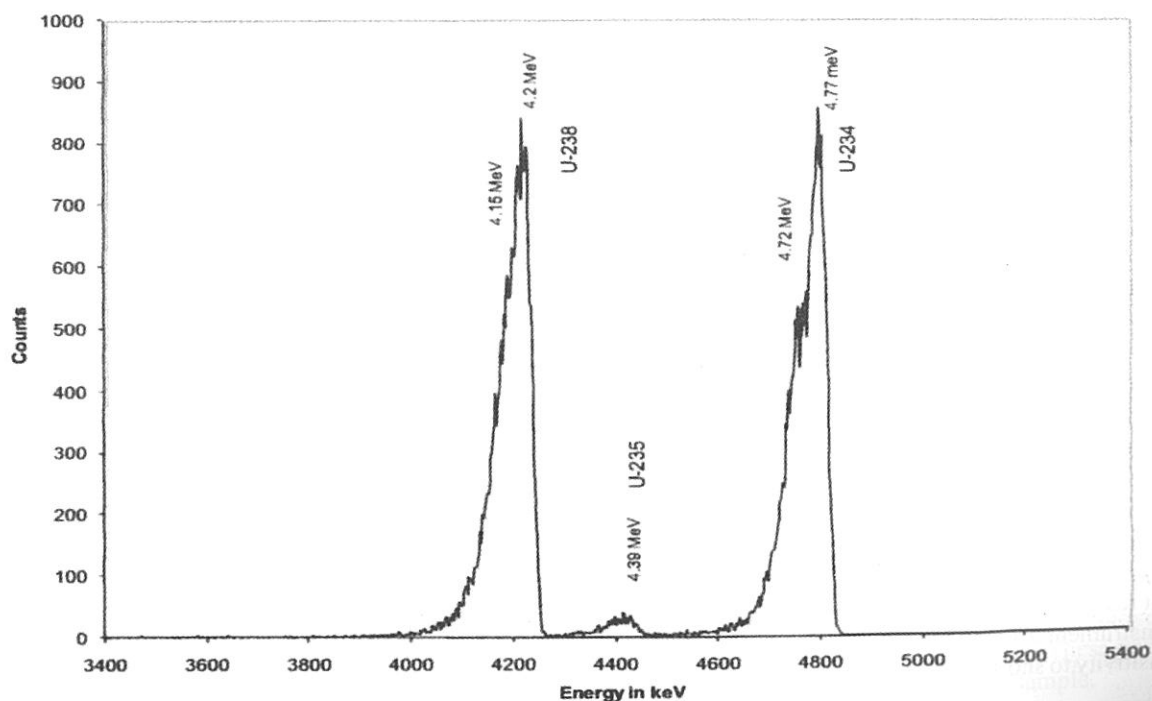

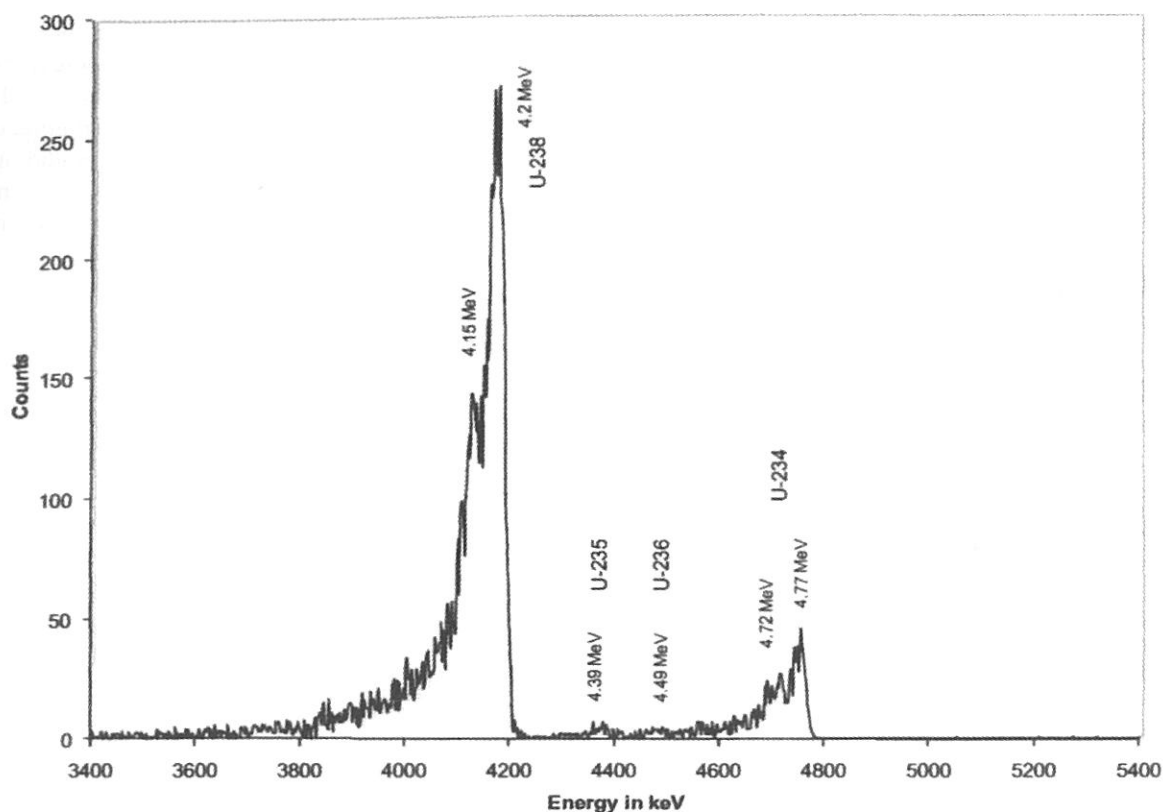Fig. 2   Alpha Spectrum of natural uranium

Fig. 3 Alpha Spectrum of depleted uranium

main advantage of gamma ray spectrometry analysis is that it is non destructive and does not require stringent sample processing. Some radio-nuclides emit characteristic gamma rays in the energy range of few keV to many MeVs which can be very well used for the identification of radionuclide present in the sample. High resolution gamma ray spectrometer using High Purity Germanium (HPGe) is widely used for the analysis of gamma active radionuclide. However this technique is less sensitive for the analysis of actinides as the abundance of gamma emissions are very low. But with a well shielded low background detector system and long time spectra acquisition, it is possible to analyze even uranium isotopes also. The gamma ray spectra of natural and depleted uranium samples obtained from the HPGe detector system is shown in Figs. 4 and 5.

Mass Spectrometry

Mass spectrometric techniques are essential in nuclear forensics analysis. Mass spec can provide elemental and isotopic information. It also requires less sample mass relative to counting techniques. For nuclear forensic purposes it is essential that the mass spectrometry offers excellent resolution in order to distinguish between similar analytes, e.g. ^{235}U and ^{236}U. Ideally, mess spec should offer excellent resolution/mass abundance, low backgrounds, and proper instrumental function. The main disadvantage is its poor sensitivity to short lived actinides like ^{241}Pu, ^{236}Pu, ^{232}U etc.

Thermal Ionization MS

In thermal ionization mass spectrometry, small quantities of highly purified analyte are deposited onto a clean metal filament, rhenium or tungsten are typically used. The sample is heated in a vacuum of the ion source by applying a current to the filaments. A portion of the analyte will be ionized by the filament and then are directed down the flight tube and separated based on mass to charge rations. Major disadvantages include time consuming sample preparation and inefficient analyte ionization.

Multi-Collector Inductively Coupled Plasma-Mass Spectrometry

This is a frequently used technique in nuclear forensics. In this technique a purified sample is nebulized in a spray chamber and then aspirated into plasma. The high temperature of the plasma leads to sample dissociation and high efficiency of ionization of the analyte. The ions then enter the mass spectrometer where they are discriminated based on mass based on a double focusing system. Ions of various masses are detected simultaneously by a bank of detectors similar to those used in the thermal ionization mass spec. MC-ICP-MS has a more rapid analysis.

Secondary-Ion MS

It is a micro-analytical technique valuable for three-dimensional analysis of a materials elemental composition and isotopic ratios. This method can be utilized in characterization of bulk materials with a detection limit in
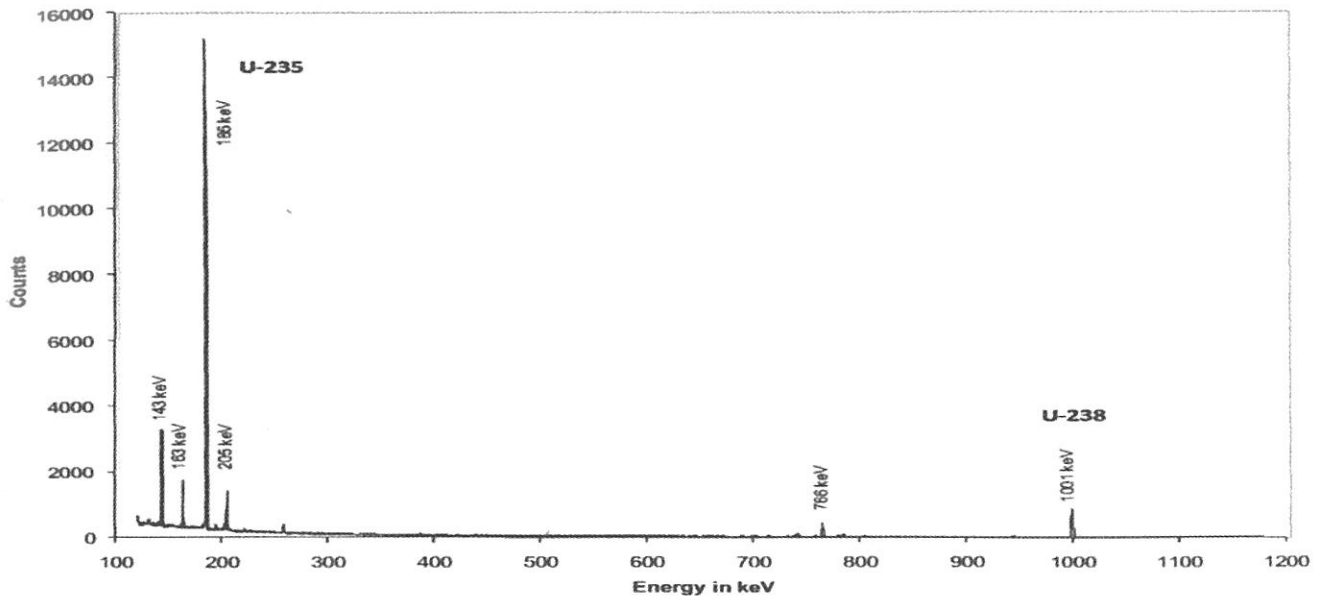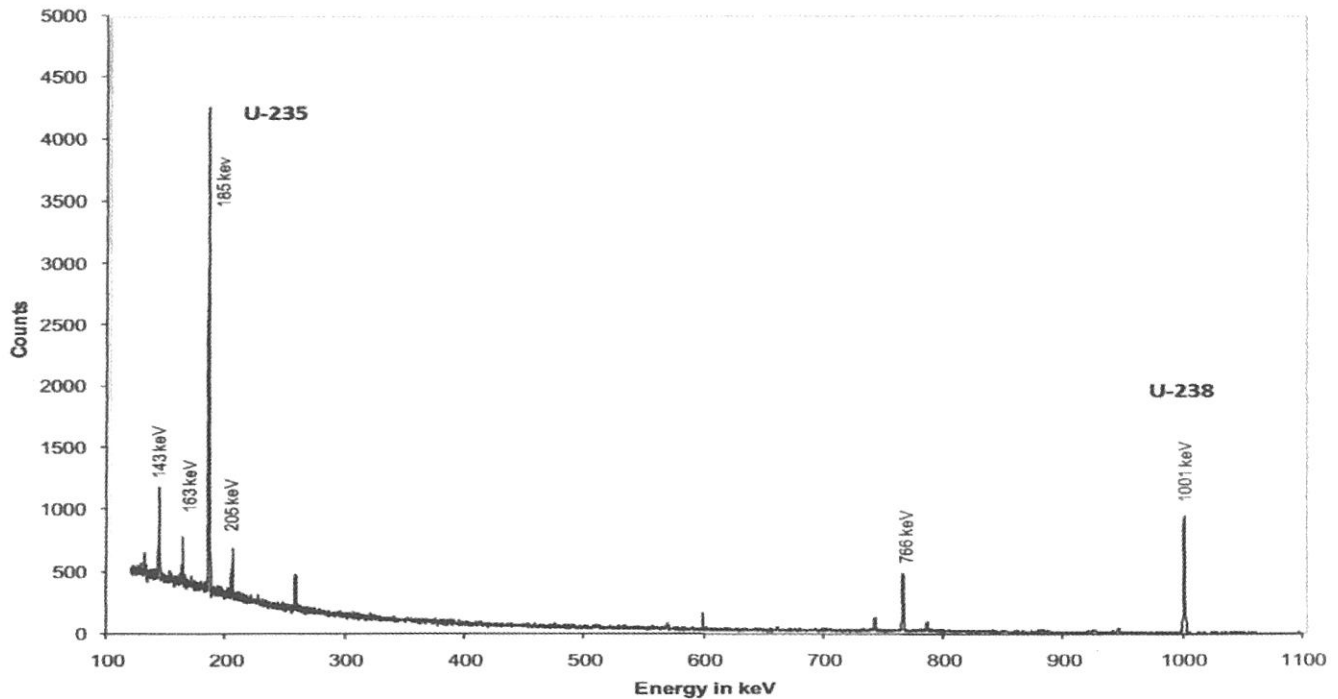
Fig. 4   *Gamma ray spectrum of natural uranium*

Fig. 5   *Gamma ray spectrum of depleted uranium*

the low parts per billion (10^{19} or ng/g) range. Particles as small as a few 100 nanometer can be detected [8]. Ion production in this technique is dependent on the bombardment of solid samples with a focused beam of primary ions. The sputtered, secondary ions are directed onto the mass spectrometry system to be measured. The secondary ions are a result of kinetic energy transfer from the primary ions. These primary ions penetrate into the solid sample to some depth. It can be used to detect any element, is especially useful, because it can be fully automated to find uranium particles in a sample of many million particles. Particles of interest can be imaged and analyzed with high isotopic precision [8].

Additional Nuclear Forensic Methods

Numerous additional approaches are employed in the interrogation of seized nuclear material. These approaches typically, require greater quantities of sample.

Scanning Electron Microscope

The scanning electron microscope can provide images of an object's surface at high magnification with a resolution on the order of nanometers. A focused beam of energetic electrons is scanned over the sample and electrons that a backscattered or emitted from the sample surface are detected. Images are constructed via measuring the fluctuations of electrons from the sample beam scanning position. This data is useful in determining what process may have been employed in the materials production and to distinguish between materials of differing origins. Measurements of backscattered electrons elucidate the average atomic number of the area being scanned. The emitted, or secondary electrons provide topological information. This is a relatively straight forward technique, however samples must be amenable to being under a vacuum and may require pre-treatment.

X-ray Fluorescence

X-ray Fluorescence offers rapid and non-destructive determination of the elemental composition of a nuclear material based on the detection of characteristic X-rays. Direct sample irradiation allows for minimal sample preparation and portable instrumentation for field deployment. The detection limit is 10 ppm. This is well above mass spectrometry limits. This technique tends to be hindered by matrix affects, which must be corrected for.

Neutron Activation Analysis

Neutron activation analysisis a powerful non-destructive method of analyzing elements of mid to high atomic number. This method combines excitation by nuclear reaction and the radiation counting techniques to detect various materials. The measurement of characteristic radiation, following the bombardment completion, is indicative of the elements of interest. The advantages of this technique include multi-element analysis, excellent sensitivity, and high selectivity, and no time-consuming separation procedures. One disadvantage is the requirement of a nuclear reactor for sample preparation.

Conclusions

Nuclear forensics is a relatively new scientific field with its beginning in the early 1990s. Several analytical techniques of other scientific fields can be applied to nuclear forensics to investigate the physical characteristics of nuclear material and material that is related to it. Thus the various tools of spectrometric counting devices, X ray fluorescence methods, Scanning Electron Microscopes (SEM), Secondary Ion mass spectrometry (SIMS), Multi Collector Inductively Coupled Plasma-Mass Spectrometry (MC ICP MS), neutron activation analytical methods compliment in their approach to identify, characterize and estimate the isotopic composition of nuclear material when present even at ppm or ppb levels. These approaches of these analytical tools are complimentary in their techniques and are useful for cross confirmation prior to arriving at forensic evidence of nuclear materials involved in the safety & security of the radioactive materials and for the investigation purposes.

With knowledge on potential radiological situations / hazards, detection, prevention and response for the perceived threats need to be prepared with use of the analytical tools to tracking the material and investigating for nuclear forensics and its evidence. The identification of the origin of a nuclear material is practiced by the exclusion principle via an analysis in a step-by-step approach.

References

[1] May, Michael (ed), "Nuclear Forensics: Role, State of Art, and Program Needs", ISBN 978-0-87168-720-3.

[2] Erdmann, Nicole; Magnus Hedberg, "Particle Analysis - Finding the Needle in the Haystack", November 2013. Cite uses deprecated parameters (help)

[3] "National Technical Nuclear Forensics Center - Definition and Role of Nuclear Forensics", US Department of Homeland Security. May 2013.

[4] INTERNATIONAL ATOMIC ENERGY AGENCY, IAEA Safety Glossary: Terminology Used in Nuclear, Radiation, June 2007.

[5] UNITED NATIONS SCIENTIFIC COMMITTEE ON THE EFFECTS OF ATOMIC RADIATION, Sources and Effects of Ionizing Radiation, UNSCEAR 2008 Report to the General Assembly, with Scientific Annexes, II Effects, Annex C, Radiation Exposures in Accidents, United Nations, New York (2011) 1–43.

[6] Lessons Learned From the Response to Radiation Emergencies 1945 – 2010 – Emergency Preparedness and Response – IAEA August 2012.

[6] Clearance Levels for Radio-nuclides in Solid Materials – IAEA TECDOC 855, 1996

[7] IAEA Nuclear Security Series No. 2, Nuclear Forensic Support, Reference Manual IAEA, Vienna, 2006

[8] Fingerprinting of nuclear material for nuclear forensics by Yvonne Hinrichsen, 2010.

[9] Gonzalez, Lost and found dangers - Orphan Radiation Sources Raise Global Concerns, 1999, Timely action, Strengthening Radiation Safety And Security,2-17,IAEA Bulletin, Vol 41, No.3.

[10] Glaser, Alexander; Tom Bielefeld,"Nuclear Forensics - Revision 5 Capabilities, Limits, and the "CSI Effect"", November 2013. Cite uses deprecated parameters (help)

[11] Wellerstein, Alex. "Semipalatinsk Then and Now". November 2013.

[12] Klaus Mayer; Maria Wallenius (2009). "Atomic Detectives-An Introduction to Nuclear Forensics.". Strahlenschutzpraxis 1: 27–36. Cite uses deprecated parameters ()

[13] Stanley, Floyd E.; Stalcup A.M., Spitz, H.B (2013). "A Brief Introduction to Analytical Methods in Nuclear Forensics". J Radio anal Nucl Chem 295: 1385–1393.

[14] Hedberg, P. M. L.; Peres, P.; Cliff, J. B.; Rabemananjara, F.; Littmann, S.; Thiele, H.; Vincent, C.; Albert, N. (1 January 2011). "Improved particle location and isotopic screening measurements of sub-micron sized particles by Secondary Ion Mass Spectrometry". Journal of Analytical Atomic Spectrometry 26 (2): 406.Cite uses deprecated parameters ()

Dr. S. Murali, is presently the Officer in Charge, Emergency Preparedness and Response Centre (EPARC), Radiation Safety Systems Division (RSSD) BARC. He took his M.Sc (Physics) and PhD degree from Mumbai University. Dr. Murali is responsible for ensuring radiation emergency preparedness and response at all nuclear facilities at BARC, Trombay. He is involved in imparting training to various response agencies for prevention, preparedness for response to nuclear or radiological emergencies including radiological threats and in the preparation of national / departmental documents related to radiological safety and radiation emergency preparedness. For his contributions on 'Radiological Safety' for operational nuclear facilities, he was awarded 'Meritorious Operational Health Physicist' in 2012 by IARP.

Dr. S. Anilkumar joined Radiation Safety Systems Division of Bhabha Atomic Research Centre in 1988. He took his Masters in Physics from University of Kerala and PhD from University of Mumbai. His field of interest is Alpha and Gamma ray spectrometry and their applications as nuclear analytical technique in fuel cycle operations and in nuclear forensic investigations. His major activities involve the qualitative and quantitative evaluation of radioactive materials confiscated during the radiation survey of Emergency Response Centre. He is currently working on application of various radio-analytical techniques for rapid assessment of radioactivity in emergency response programmes.

Dr Pradeepkumar K.S., is presently the Head of Radiation Safety Systems Division (RSSD) BARC. He is responsible for ensuring radiological safety in all nuclear facilities at BARC, Trombay. In addition, he is also entrusted with the development of national level capability for prevention and preparedness for response to nuclear or radiological emergencies including radiological threats. He has developed various state of the art radiation detection systems, monitoring methodologies and software for ensuring radiological safety in DAE facilities and in the environment. Dr Pradeepkumar was also associated with development of international and national documents related to radiological safety and radiation emergency preparedness. As a consultant, he has contributed to IAEA and UNSCEAR on issues related to radiological safety, emergency preparedness and Impact of Chernobyl and Fukushima accident on public and environment. For his contributions to 'Radiological safety' and 'National level emergency preparedness', he was conferred with 'Dr Ganguly Memorial Award' in 2008 and 'DAE Homi Bhabha Science and Technology Award' in the year 2010.

Dr. D.N. Sharma joined BARC in 1971. Since then he has carried out R&D in the area of Radiation Physics, Radiation Protection, Development of radiation safety systems and Emergency Preparedness & Response. The Aerial Gamma Spectrometer developed by him had international recognition when it was used for around 2 years by IAEA team at Georgia (Russia) to search for orphan sources. During his career spanning over 43 years he held important positions in BARC. Currently, he is Director of Health Safety & Environment Group, National Emergency Response Director and member of the Crisis Management Committee (CMG) of DAE. He is member of a number of national committees constituted by Ministry of Home Affairs and NDMA (National Disaster Management Authority). He has steered the initiative of deployment of radiation monitoring systems at all entry and exit ports of the country.

Nuclear Forensics – Global initiatives

Suresh Gangotra and K.L. Ramakumar

Nuclear Controls and Planning Wing, Department of Atomic Energy, Mumbai 400 001; E-mail:

Introduction

Nuclear forensics is the science of uncovering the origin and history of nuclear and other radioactive materials, especially those found at a crime scene. Nuclear forensics is the measurement of the isotopic signatures, chemical properties, and physical features of nuclear or other radioactive material to uncover information about the material's origin and history. Confidence in the resulting analysis is important because the results from a nuclear forensics examination are vital for law enforcement investigations, and help States to make informed decisions that will improve their nuclear security practices.

Ever since the first seizure of nuclear and radioactive material being smuggled from erstwhile Soviet Union into other European Countries in 1991, the international community was forced to take cognisance of this menace and the important role nuclear forensics could play to address this issue.

The objective of nuclear forensics is twofold: (i) to identify the sources of stolen or illicitly trafficked nuclear materials thereby preventing or making more difficult terrorist acts that would use material from these same sources, and (ii) to provide incentives to Countries to better guard their materials and facilities. To this one may add another potential application of this discipline namely prognosis of certain injuries and burns due to exposure to ionising radiation sources not necessarily while performing illegal activities. The last one would help in resorting to immediate remedial measures.

With a view to establishing this discipline on a firmer footing, efforts are being put in to garner as much expertise as possible through international forums. The aim of this short article is to highlight initiatives being taken by the international community in the field of nuclear forensics and list some of the supporting literature available in this field.

International Atomic Energy Agency (IAEA)

The IAEA addresses the issue of nuclear forensics under nuclear security and supports the implementation of (i) International instruments through cooperation and assistance between States in relation to a nuclear security event with trans-boundary implications, and (ii) National framework by supporting a State's legal and regulatory actions related to a nuclear security event, including criminal prosecution. The Agency's Nuclear Security Plan for 2014-2017 reflects the importance of nuclear forensics for the effectiveness and sustainability of national nuclear security measures.

The IAEA assists States with the application of nuclear forensic through:

- Guidance documents
- Coordinated Research Projects (one was organized in 2008)
- Training and workshops
- International cooperation and collaboration

Some of the documents published by IAEA include:

1. Revision of No. 2 "Nuclear Forensics Support"
2. "Development of National Nuclear Forensic Libraries"
3. "Radiological Crime Scene Management"
4. "Core capabilities for nuclear forensics"

Another important document published by IAEA is "Application of Nuclear Forensic in Combating Illicit Trafficking of Nuclear and Other Radioactive Material" (IAEA TECDOC-1730). This TECDOC includes improved procedures and techniques, optimization of nuclear forensic analysis, preservation of evidence, and provision of support to Member States. It addresses technical needs and confidence in the application of analytical methods and understanding of the nuclear fuel cycle applied to nuclear forensics. The topics included are instrumentation and field work for evidence collection, novel laboratory methods, and modelling for interpretation of nuclear forensic results.

Recently in July 2014 the IAEA organised another International Conference on Advances in Nuclear Forensics: Countering the Evolving Threat of Nuclear and Other Radioactive Material out of Regulatory Control. This conference in Vienna had a number of objectives, including reviewing the role of nuclear forensics as an element of a national nuclear security infrastructure, presenting new scientific work, reviewing current practices and introducing new analytical tools, discussing ways of strengthening nuclear forensic capabilities, and proposing mechanisms for advancing international cooperation in nuclear forensics.

Global Initiative to Combat Nuclear Terrorism (GICNT)

The Global Initiative to Combat Nuclear Terrorism (GICNT) is a voluntary partnership of 85 nations along with four international organisations. The aim of the GICNT is to strengthen the global capacity to prevent, detect and respond to the shared threat of nuclear terrorism. The activities of the GICNT are coordinated through the Implementation and Assessment Group, which has three working groups under it. These are the Nuclear Forensics Working Group (NFWG), Nuclear Detection Working Group (NDWG) and the Response and Mitigation Working Group (RMWG).

Nuclear Forensics Working Group (NFWG)

The goal of the working group is to develop documents that raise awareness of nuclear forensics among policymakers, assist the development of core capabilities, foster intergovernmental relationships, conduct joint exercises, and share best practices. While conducting its work, the NFWG looks to collaborate with nuclear forensics efforts that are already underway by the International Atomic Energy Agency (IAEA), the European Union, and the Nuclear Forensics International Technical Working Group (ITWG) in order to synchronise efforts and prevent duplication. This ensures endorsing nations are receiving new, vital information in developing and enhancing their nuclear forensics capabilities.

NFGW develops tools that assist the GICNT partner nations to build capability in nuclear forensics to more effectively combat nuclear terrorism. These tools are designed to;

1. raise awareness of nuclear forensics
2. assist the development of core capabilities
3. foster intergovernmental relationships
4. conduct joint exercises
5. promote best practices

During the year 2011, NFWG conducted seminars and table-top exercises. These helped in raising awareness of nuclear forensics about what it is, what it can do and what it cannot do. In 2012, NFWG prepared a document "Nuclear Forensics Fundamentals for Policy Makers and Decision Makers". The document is aimed at policymakers of nuclear forensics utility as a tool to enhance nuclear material security and help them identify capabilities for development. Currently the NFWG is working on the document on Sharing of Nuclear Forensics Information. The NFWG has also initiated work on the National Nuclear Forensics Library (NNFL). While many partner nations have capabilities to set up individual national libraries of nuclear and radiological material, there is a strong opposition to sharing of these libraries. The NNFL is in its nascent state and members of the NFWG have been requested to contribute to its structure.

Challenges in addressing nuclear forensics issues by NFWG include

Nuclear Forensics Capabilities

(a) Improved definition of NF (the lexicon issue)

(b) Need to balance awareness of NF capabilities with scope and limitations of such capabilities

(c) Development of self assessment tools

Sustainment of Nuclear Forensics Capabilities

(a) Need to address "greying' of nuclear forensics capabilities – Capturing the knowledge

(b) Attractive careers in nuclear forensics

(c) Development of skills in interpretation of nuclear forensics data

(d) Need to comply with national judicial requirements regarding use and presentation of evidence

Implementing Nuclear Forensics in Existing National Response Plans

(a) Timeliness of establishing Nuclear Forensics role and responsibilities

(b) Increased awareness of national and international instruments

(c) Increased understanding and cooperation between law enforcement agencies and scientific organisations

The following activities have been identified by the NFWG to address these challenges:

1. Development of assessment tools to identify gaps in training and other agreed frameworks.

2. Development of compendium of available nuclear forensics training

3. Cross disciplinary exercises. These could be with different agencies involved in the field of nuclear forensics like scientific establishments, law enforcement agencies etc.

4. Combined exercises with other working groups. The NDWG and the RMWG, the other two working groups of GICNT conduct table top and field exercises. There are proposals to hold joint exercises of the three working groups.

5. Involvement of experts during training of NF exercises

6. Development of modules to be available on the portal of GICNT.

National Nuclear Forensics Library (NNFL)

A National Nuclear Forensics Library is an organized collection of information about nuclear another radioactive material produces, used or stored within a State. It contains information on material characteristics in reference databases that help distinguish one nuclear or other radioactive material from another. The NNFL is under the control of the State at all times and the complexity of NNFL is tailored to a State's unique experience.

International Technical Working Group (ITWG)

The ITWG was founded in 1996 upon the initiative of 8 governments (G8). It is open to all states interested in nuclear forensics. The objective of the working group is to encourage technical peer-review of the nuclear forensic discipline. These goals are met through annual meetings, exercises, and informal and formal publications.

The ITWG is supported by and is affiliated with nearly 40 countries and international partner organization The ITWG consists of volunteers from the field of science and legal experts. It is a technical forum and engages in information exchange and analytical exercises. The key

products of the ITWG are Comparative Laboratory Analysis Exercises and development of terms of reference for National Nuclear Forensics Libraries. It disseminates recent progress in nuclear forensic analysis and interpretation with the broader community of technical and security professionals. The priorities of the ITWG include identifying requirements for nuclear forensic applications, evaluating present nuclear forensic capabilities, and recommending cooperative measures that ensure all states can respond to acts involving illicit trafficking and unauthorised possession of nuclear or radiological material.

Other Initiatives on Nuclear Forensics

A number of countries have established nuclear forensics institutions. Nuclear security summits organised biennially since 2010 have given utmost priority to nuclear forensics through effective political momentum. The Nuclear Security Summit (NSS) comprises 52 heads of states and the NSS 2014 communique has the following reference to nuclear forensics.

"Nuclear forensics is developing into an effective tool for determining the origin of nuclear and other radioactive materials and providing evidence for the prosecution of acts of illicit trafficking and other malicious acts. We welcome the progress and recent development of several instruments that improve the use of traditional forensic methods, and emphasise the need to further develop innovative forensic methods and tools for investigating incidents involving nuclear and other radioactive materials. We encourage further international cooperation, within the IAEA and other relevant international organisations, aimed at connecting and enhancing traditional and nuclear forensics capabilities, where feasible, and establishing national nuclear forensics databases to enable better determination of the origin of material."

Nuclear Forensics in India

In India, the nuclear forensics discipline is addressed in Global Centre for Nuclear Energy Partnership (GCNEP). One of the schools of the GCNEP, viz., School of Nuclear Material Characterisation Studies (SNMCS) has the mandate to set up facilities for nuclear forensics. This will include laboratory facilities as well as domestic and international courses for training of personnel in the field of nuclear forensics. India joined the GICNT in 2008 and is also member of all the three Working Groups. The participation in GICNT is by way of contribution to the documents and compendiums.

Concluding Remarks

Nuclear forensics is an emerging science, driven primarily by national security objectives, including those of both law enforcement and national intelligence. It is an important tool to detect and deter activities of nuclear and radiological terrorism. There is a need to create awareness of the capabilities of nuclear forensics among nations. There is a focus on NF in international forums and agencies. The partnership of IAEA, ITWG and GICNT provides international access, technical best practice and political impetus necessary to meet growing expectations for nuclear forensics. The purpose and desired outcomes of the recent IAEA conference on nuclear forensics is to have effective coordination among international partners to improve the science and confidence in nuclear forensics analysis. The IAEA visualises that nuclear forensics will also be elevated to a level on par with material control and accountancy, training, peer review, and other existing activities within the nuclear security regime, so that states rely on nuclear forensics routinely and use it as a tool to fulfill their nuclear security obligations.

Shri Suresh Gangotra is a metallurgist from M.S.U. Baroda, and recipient of gold medal for topping B.E. in 1983. After completing 1-year training at BARC Training School during 1983-84, he worked in the field of nuclear fuel fabrication and design of facilities for plutonium and thorium based fuel cycles. Later, he joined the Strategic Planning Group (SPG) of the Department of Atomic Energy (DAE), which has since been expanded by DAE to Nuclear Control and Planning Wing (NCPW). He has been responsible for the implementation of the International Atomic Energy Agency safeguards in the designated facilities in India. He is a Member of the negotiating team for bilateral civil nuclear cooperation with Canada, Republic of Korea, Japan, Sri Lanka and Australia. He represents India in the Global Initiative to Combat Nuclear Terrorism (GICNT), the 85-country organisation. Currently, he is the Head of the Safeguards, Safety and Security Division of NCPW at DAE.

Dr. K.L. Ramakumar is Director, Radiochemistry & isotope Group, BARC and is concurrently holding the post of Head, Nuclear Controls & Planning wing in the Department of Atomic Energy. Dr. Ramakumar is a graduate of 18th batch of BARC Training School (1974-75). His fields of expertise include nuclear and radiochemistry, analytical chemistry, nuclear safeguards and nuclear material accounting and control. He is the President of IANCAS.