Emergency Preparedness

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Nuclear Forensics Approach to Address Nuclear Emergencies & Radiological Preparedness

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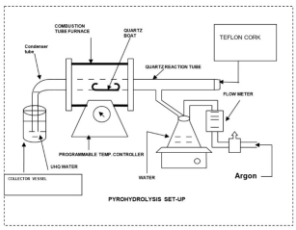

Pyro-hydrolysis setup

ABSTRACT

HSEG, BARC has taken the initiative to develop reference library of forensic signatures in front end nuclear materials. Analytical methods have been developed for elemental, isotopic, anionic, radiological and chronological characterization of uranium rich materials. Uranium mine and mill samples have been collected from different locations in India and analyzed for different Nuclear Forensic (NF) signatures to generate India- specific NF library. Artificial intelligence and machine learning based NF analysis tool has been developed in-house for signature pattern tracking and possible origin assessment.

KEYWORDS: *Nuclear and Radiological Threats, Nuclear forensics, Nuclear material*

Introduction

Nuclear Forensic Analysis (NFA) is an interdisciplinary science requiring collection of information from various stages of nuclear fuel cycle, production of radioactive sources, expertise in various domains of physico-chemical analysis and interpretation. NFA involves comprehensive characterization of the Nuclear Material (NM) or radioactive material found out of regulatory control and comparison with reference information. It provides clues for tracing the history, origin and intended use of the material, which ultimately supports the investigating agency in the prosecution of those responsible. Provenance determination of an interdicted material is a vital step in Nuclear Forensic investigation. Therefore, it is required to have a National Nuclear Forensic Library (NNFL) of the NF signatures (elemental, anionic, isotopic composition, morphology etc.) of the nuclear material encountered in nuclear fuel cycle starting from uranium ore.

Important NF signatures, techniques used for their measurement, derived information and the references used for interpretation are given in the illustration in the following page. For generation of NNFL and to identify the characteristic signatures in front end nuclear fuel cycle materials, representative U-mine and mill samples from operational plants have been collected including U-ore and Uranium Ore Concentrate (UOC) samples. UOC commonly known as yellow cake, comprises sodium di uranate (SDU), magnesium di uranate (MDU), ammonium di uranate (ADU), uranyl oxides, uranyl peroxides etc. and are the starting material for nuclear fuel production. These materials are of high interest from forensic point of view and are the most intercepted material [1]. These compounds are produced by mining and milling of uranium ore or from secondary sources like phosphorites and other sources.

A large number of samples from these sources were collected and characterized for different NF signatures.

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Radio-analytical Techniques in NF Analysis

In direct Radiometric techniques, alpha or gamma spectrometry are used directly to measure the characteristic radiation in the samples, whereas in indirect methods nuclei of the element of interest is either excited or activated to emit radiation which is then used to quantify the elemental concentration in the sample. Particle Induced Gamma Emission (PIGE) and Neutron Activation Analysis (NAA) are two such techniques used for quantifying elemental composition in the bulk matrix.

Gamma Spectrometry

P-type High Purity Germanium (HPGe) detector with carbon window having a relative efficiency of 60% and 50% HPGe with Al window are used. Digital spectrometric device with Multi-Channel Analyser (MCA) and spectral analysis InterWinner 8.0 and Gamma Vison software are used for the characterisation.

In secular equilibrium matrix (^{238}U–^{234m}Pa), the gamma energies 63.3 keV (3.7%) of ^{234}Th, 766 keV (0.317%) and 1001 keV (0.842%) of daughter ^{234m}Pa, are considered for analytical purposes [2]. The prominent gamma energies emitted by ^{235}U are 143.7 keV (10.96%), 163.3 keV (5.08%), 185.7 keV (57.2%) and 205.3 keV (5.01%). The 185 keV gamma-line of ^{235}U and 1001 keV gamma-line ^{234m}Pa are used for the estimation of ^{235}U and ^{238}U concentration, respectively. Fig. 1 shows the gamma spectrum of U metal samples.

Presence of fission products or activation products, ^{236}U and ^{232}U in the investigated samples gives the clue to the production history and initial feed of the sample [3].

Alpha Spectrometry

Alpha spectrometry (AS) is used for quantifying both short lived ^{210}Po, ^{232}U, ^{228}Th and ^{238}Pu and long-lived ^{238}U and ^{230}Th radionuclides, for uranium isotopic composition analysis and radiochronometry.

Parameter	Measurement Method	Information	Interpretation by comparison
Uranium isotopes and ratio	AS, TIMS, MC-ICP-MS, SIMS, AMS, RIMS	Intended use, origin	NFL
Plutonium isotopes and ratio	AS, HRGS, TIMS, MC-ICP-MS, SIMS, RIMS	Type of reactor	Model Calculations, NFL
Radionuclide impurities	HRGS	Process history, Irradiation status	NFL
Metallic impurities (Concentration, patterns)	ICP-MS, ICP-OES, GD-MS, GF-AAS, NAA, EDXRF, PIGE	Process history, Origin	Process Knowledge, NFL, known samples
Anionic Impurities	Ion Chromatograph	Process history, Origin	Process Knowledge, NFL, known samples
Stable isotope ratios (Nd, Sr, Pb, O, S)	TIMS, MC-ICPMS, HR-ICP-MS, IRMS	Origin, Process history	NFL, known samples
Macroscopic appearance	Optical Microscopy	Process history	Process knowledge
Microscopic appearance	SEM, TEM	Process history	Process Knowledge, NFL, known samples
Radio isotopes	HRGS, LSC, AS, ICP-MS	Intended use, Age	Model Calculations
Non-metallic impurities	GC-MS	Process history	Process Knowledge, NFL, known samples
Particle analysis	SIMS, FT-TIMS	Origin, Process history	Process Knowledge, NFL, known samples

NFL: Nuclear Forensic Library, AS: Alpha Spectrometer, TIMS: Thermal Ionisation Mass Spectrometer, MC-ICP-MS: Multi Collector-Inductively Coupled Plasma Mass Spectrometer, SIMS: Secondary Ionisation Mass Spectrometer, AMS: Accelerator Mass Spectrometer, RIMS: Resonance Ionisation Mass Spectrometer, HRGS: High Resolution Gamma Spectrometer, ICP-OES: Inductively Coupled Plasma Optical Emission Spectrometry, GD-MS: Glow Discharge Mass Spectrometer, NAA: Neutron Activation Analysis, EDXRF: Energy Dispersive X Ray Fluorescence, PIGE: Particle Induced Gamma Emission, HR-ICP-MS: High Resolution- Inductively Coupled Plasma Mass Spectrometer, IRMS: Isotope Resolution Mass Spectrometer, SEM: Scanning Electron Microscope, TEM: Transmission Electron Microscope, LSC: Liquid Scintillation Counter, GC-MS: Gas Chromatograph-Mass Spectrometer, FT-TIMS: Fourier Transform-Thermal Ionisation Mass Spectrometer.

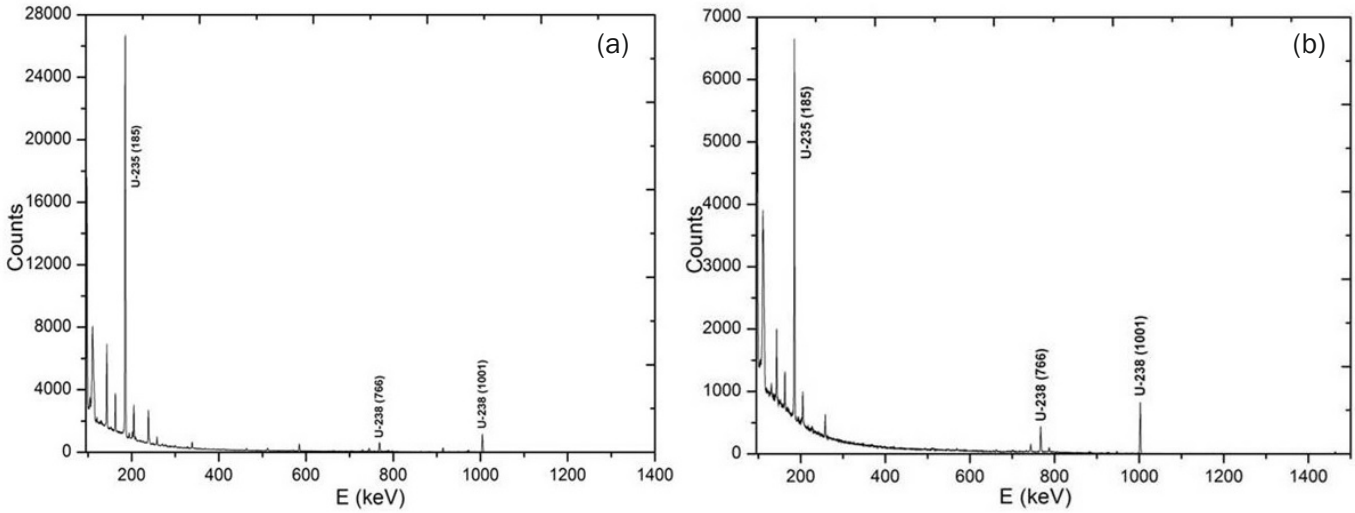

Fig.1: Gamma spectrum of investigated Natural Uranium (left) and Depleted Uranium (right) samples.

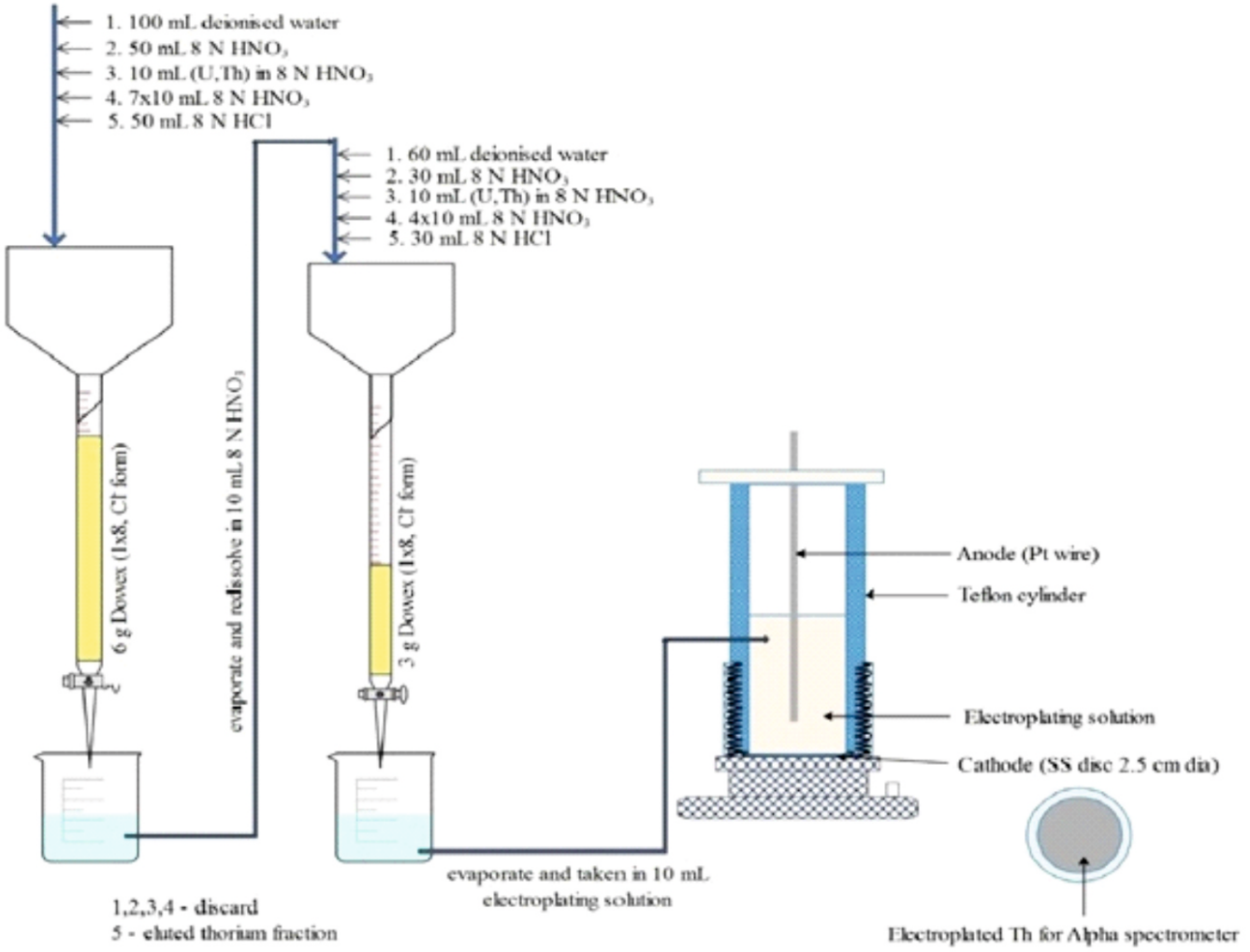

Fig.2: Schematics of anion exchange purification method for thorium and electrodeposition.

A radiochemical method with double column separation was developed using Isotope Dilution-AS for age determination of natural U metal samples using ^{234}U and ^{230}Th parent daughter ratio, with age history from 11 to 50 years. Schematics of thorium purification from bulk uranium metal is depicted in Fig.2. The age of U-metal confiscated from public domain was thus estimated to be 39 ± 4 years [4]. The typical alpha spectrum for nat U and Depleted U samples are shown in Fig.3. Flow-chart of the method to quantify ^{210}Po in various biological samples like hair, blood and teeth for preparedness for polonium poisoning incidents is shown in Fig.4 [5].

Particle Induced Gamma Emission (PIGE)

The external (in air) PIGE setup installed at FOlded Tandem Ion Accelerator (FOTIA), BARC was used for the determination of low Z elements like Al, Si, Na and F in Uranium ore powder samples for NFL.

Cellulose based hydraulic pelletization was replaced by Mylar packed samples for current normalization of low energy proton beam was done using 25 μm tantalum window of the FOTIA setup shown in Fig.5 [6].

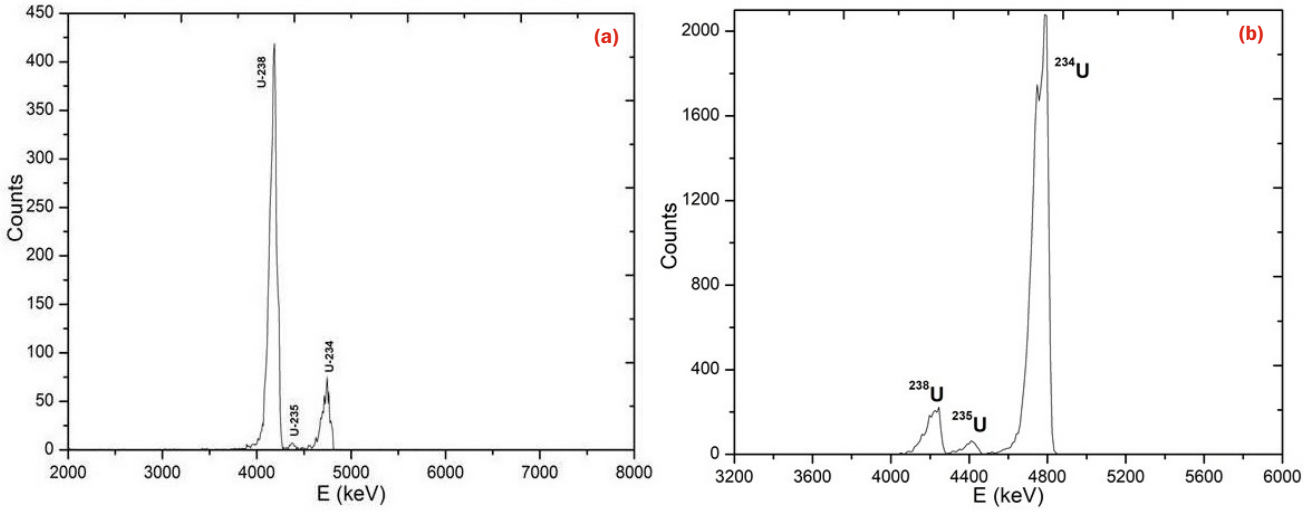

Fig.3: Alpha spectrum of (a) Depleted Uranium; (b) Enriched Uranium.

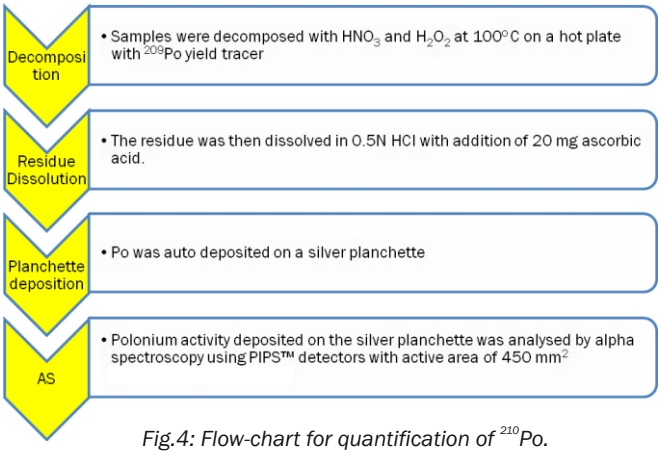

Fig.4: Flow-chart for quantification of ^{210}Po.

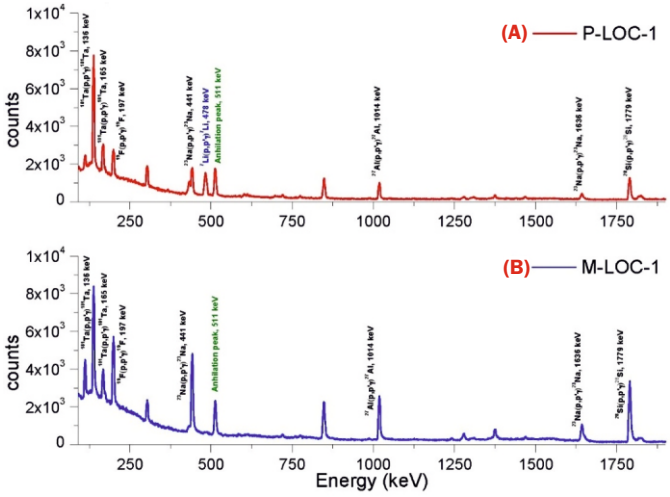

Fig.5: PIGE spectrum of ore sample (A) in-situ pelletised sample; (B) Mylar packed sample.

PIGE technique using high energy proton can be used to identify the type of uranium fuel (like uranium carbide, uranium oxide, uranium nitride or uranium silicide) without destroying the sample.

Neutron Activation Analysis

NAA is used for analysis of trace element and many REEs in Uranium ore samples. By varying the irradiation and cooling time, a range of elements like Na, Sc, Cr, Mn, Zn, Fe, Co, Sb, Cs, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta and Th can be analyzed using instrumental NAA whereas Pr and Er requires RNAA [7]. Irradiation facilities at Dhruva and APSARA-U research reactors are being used for analysis of mine samples using NAA in HS&EG, BARC.

Mass Spectrometry in NF Analysis

Considering the complexity and specificity of NF samples, various analytical procedures have been developed for various signatures using MS. Trace elemental impurities, rare earth element (REE) pattern and uranium isotopic ratio has been identified as important NF signatures in front end materials. Dissolution techniques for U-ore samples have been developed using both Microwave digestion (ETHOS UP, Milestone) and electrically alkali fusion fluxer (K1 Prime Fluxer, Katanax). For analysis of trace metals, GF-AAS (ContrAA 800: Analyticjena) and ICP-AES (Ultima 2: Horiba JobinYvon) from our laboratory and TQ-ICPMS(iCAPTQ, Thermo Scientific) at IIT-B Monash Research Academy, Mumbai are used. The mine and mill samples are analysed for different trace elements like (Sc, V, Cr, Mn, Co, Ni, Cu, As, Se, Rb, Sr, Y, Mo, Ag, Cd,Sb, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Tl, Pb, Th, U) and these data can serve as reference database for NF investigation. Chondrite-normalized REE pattern (CN-REE) for U-ore samples from different mines has been generated and shown in Fig.6. Uranium separation methodology has been developed for these samples using ion exchange and extraction chromatography. CN-REE pattern has been generated for UOC samples and is found to be unaltered when compared with the parent ore sample from which it is produced [8].

Small variation in $^{234}U/^{238}U$ and $^{235}U/^{238}U$ isotopic ratio can distinguish geographic origin of NU material. For precise Uranium isotopic ratio measurement, separation methodology in uranium ore and UOC samples has been developed using ion exchange and extraction chromatography. The extraction scheme for U separation in U ore samples using UTEVA spec resin (Fig.7) and a typical alpha spectrum of U isotopes in a uranium separated ore sample (Fig.8) are given. The isotope ratio in ore samples was analyzed using TIMS [9].

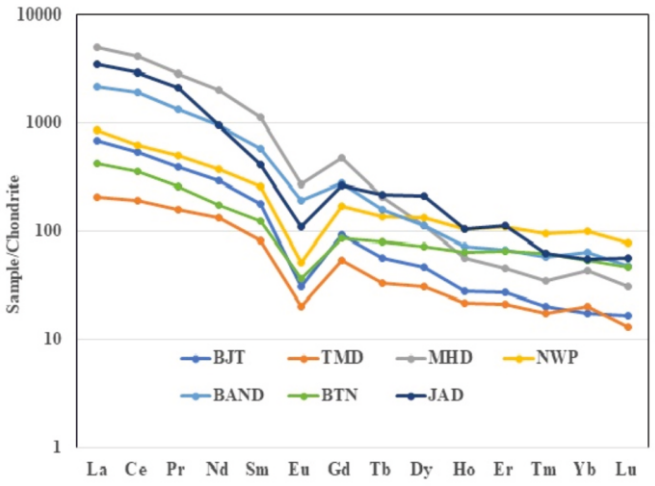

Fig.6: Typical Chondrite Normalised REE pattern for U-ore samples from different mines at Shinghbhum Shear Zone, Jharkhand.

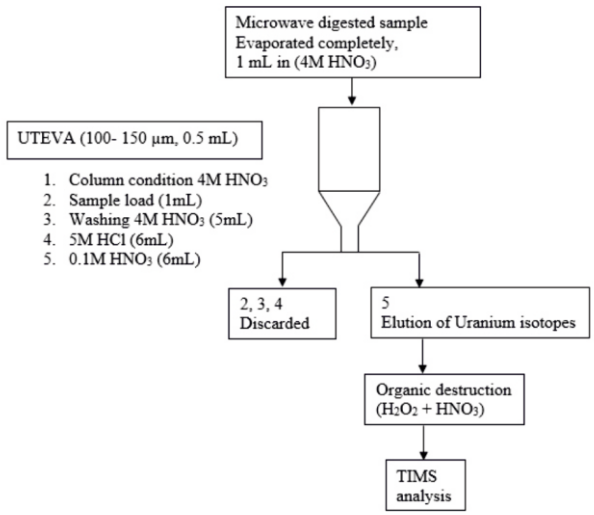

Fig.7: Extraction scheme for uranium separation in uranium ore by extraction chromatography.

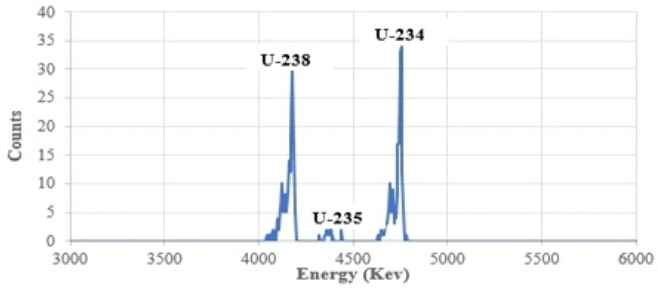

Fig.8: Typical alpha spectrum of U isotopes in separated ore sample.

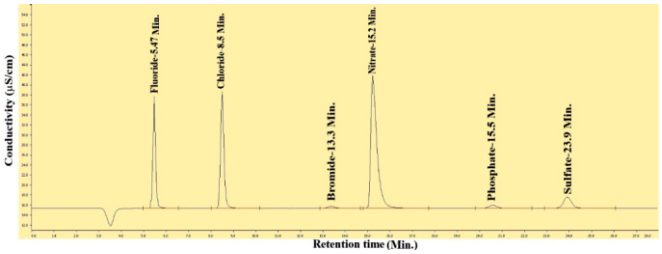

Fig.9: Typical Ion chromatograph for water extracted uranium ore sample.

Characterization of Anionic Impurities in Ore and UOC Samples as NF Signature

In the case of UOC, the anionic composition will provide the evidence for the type of processing (acid or alkali leaching). Ion chromatography (Eco IC: Metrohm) was used for anion analysis using EPA Method 300. A typical ion chromatogram for ore sample is shown in Fig.9. For the extraction of anions from the U ore samples both water leaching and pyrohydrolysis (Fig.10) methods were used.

Morphological Characterization of UOC Samples for NF Investigation

The image texture analysis (a new method) can be applied for NF investigation, wherein different colours or surface topography can also be obtained. Angle measure technique (AMT) incorporated with multivariate data analysis, may be applied for interpretation of image texture [10]. UOC samples of different process history are being analysed for generation of scanning electron microscopic images.

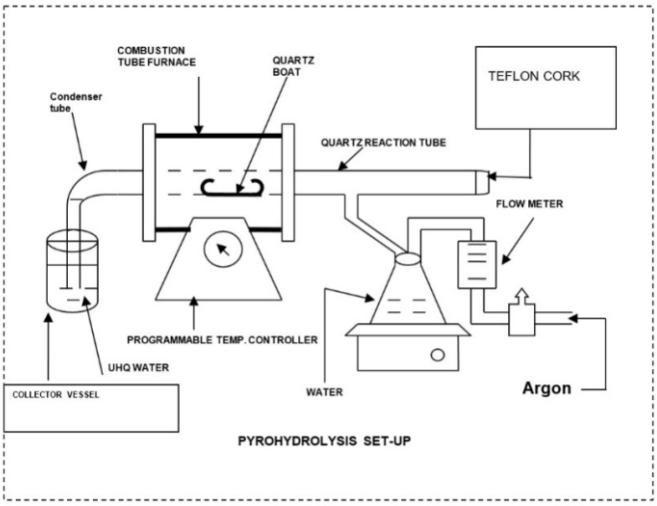

Fig.10: Pyro-hydrolysis set-up facility at EMAD laboratory.

Development of a Nuclear Forensic Analysis Tool

A server based web application in MEGH BARC cloud portal, has been developed for the management of nuclear forensic data and analysis. The developed nuclear forensic analysis tool is named as NFAT, which consists of two parts, PostgreSQL based database module to store and manage the forensic signature data of known samples and an analysis module to provide a forensic assessment of the questioned sample. Machine learning based algorithms have been used for developing the forensic analysis tool. Classification algorithms are appropriate for the multivariate analysis in the nuclear forensics to identify the origin of the intercepted material on the basis of training data in the nuclear forensic library (reference data). The output of the algorithms provides the prediction probability associated with each label for a given input data. The final qualitative prediction result is obtained by finding the label with highest probability. Various classification algorithms were attempted with different sets of nuclear forensic data available in the open literature. Four classification algorithms such as Artificial Neural Network (ANN), Decision tree classification (DT), Random Forest Classification (RF), and Gaussian Naïve Bayes Classifier (GNB) were found to give decent prediction accuracy. The

classification algorithms were built, trained and tested in Python using an open source library called 'Sklearn'. ANN was built with ReLU activation function, Stochastic Gradient Descent Optimiser, and four hidden layers. DT and RF were built with Gini impurity criterion. The algorithms were trained with 70% of the training data and remaining 30% of the data was used for validating it. Developed tool has been tested successfully for the three sets of reference data i.e. Indian Ore Major Elements, Indian Ore Trace Elements and Indian Ore Radioactive Isotopes.

Conclusion

Nuclear Forensics is an efficient tool in support of the prevention, preparedness and response to nuclear or radiological threat, and can also act as a deterrent towards the nuclear smuggling/terrorism with convincing attribution capability. However, many challenges like material type and related handling problems, instrumentation, availability of standard reference material for quality assurance, availability of national and international database, complexity in the data interpretation and the required expertise etc. associated with nuclear forensics practices limits its application only to a few laboratories. Initiatives have been taken for the establishment of nuclear forensic capability at HSEG, BARC and successfully developing the analytical procedures for characterization of nuclear materials and nuclear forensic signature library for front end materials and machine learning based analytical tool for NF interpretation.

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