NON-DESTRUCTIVE ANALYSIS FOR CHARACTERISATION OF MATERIALS FOUND OUTSIDE THE REGULATORY CONTROL

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Abstract

The aim of this research is to apply High Resolution Gamma Spectrometry (HRGS), X-Ray Fluorescence (XRF) and Ion Beam Analysis (IBA) to determine the isotopic and elemental composition of radioactive samples for nuclear forensics purposes. Four types of industrial gamma radiography devices made of depleted uranium were analysed using a HPGe detector. Moreover, all the four types of samples were analysed using a portable XRF device and its analysis software. In order to increase confidence in nuclear forensics findings, all four samples were also analysed using Particle Induced X-ray Emission (PIXE) and Particle Induce Gamma-ray Emission (PIGE) methods. The samples of interest were irradiated by 3 MeV protons at the 3 MV Tandetron™ of the "Horia Hulubei" National Institute for Physics and Nuclear Engineering. All the measurements were done using an external beam set-up, using a HPGe detector for measuring gamma rays and a silicon drift detector (SDD) for measuring characteristic X-rays.

Keywords: *Nuclear forensics, Criminal investigation, Gamma spectrometry, Ion Beam Analysis*

Introduction

When it comes to dealing with radioactive materials found outside of regulatory control (MORC), one of the most encountered types of exhibits are materials used in industry. According to IAEA's Incident and Trafficking Database, between 1993 and 2022, approximately 59% of the reported incidents involved radioactive materials, most of them being radioactive sources used in industry, material analysis or medical applications [1]. Amongst the primary causes of materials becoming MORC is loss or theft due to the poor implementation of physical protection principles [2].

One of the most encountered types of radioactive material outside of regulatory control is depleted uranium (DU), commonly used in industrial devices. That is due to its high density (19.1 g/cm^3), which makes it very suitable for shielding radiation coming from various highly radioactive sources used for non-destructive analysis of materials. For instance, gamma radiography devices which usually containing ^{192}Ir sources, with activities up to a few TBq, are commonly found outside of regulatory control due to the improper dismantling process of the industrial facility that owned them or them being stolen for financial gains.

The present paper describes the scientific approach of the Nuclear Forensics Laboratory NFL-RO within "Horia Hulubei" National Institute for R&D in Physics and Nuclear Engineering (IFIN-HH), Magurele, Romania, in the investigative process initiated as a response to a large quantity of depleted uranium being found on the site of an abandoned industrial facility in Bucharest.

The findings of the non-destructive analysis techniques which were used during the investigation were provided to the competent investigative authorities.

Case and exhibits presentation

In 2021, the National Commission for Nuclear Activities of Romanian notified the National Nuclear Forensics Laboratory (NFL-RO) of IFIN-HH about the discovery of a large quantity of depleted uranium on the ruins of an industrial facility in Bucharest.

After the first assessment of the situation, it was discovered that this material consisted in four types of gamma radiography devices, adding up to a total of 35 such devices. These included Gammamat T1-F (P1), Gamavolt SU 100N (P2), GDP U5 (P3) and Gamarid (P4) type devices, which are presented in Fig.1.

Following the Criminal Procedural Code of Romania [3], an investigation was started and the prosecutor in charge of the case asked for specialized expertise for assessing the situation.

** This author led part of the work in the study and contributed to its writing before accepting current position at the International Atomic Energy Agency*

Following recommendations published by the IAEA regarding the investigation of a criminal case involving radioactive material [4] NFL-RO submitted an analytical plan to the prosecutor, in which it was clearly stated what types of analyses were going to be performed and what are the outcomes of the conducted activities.

The analytical plan had to be approved by the prosecutor. One important aspect which required special attention was the type of analysis techniques that was used, i.e. destructive or non-destructive, because like in any other criminal investigation, the analysed samples can serve as evidence in court.

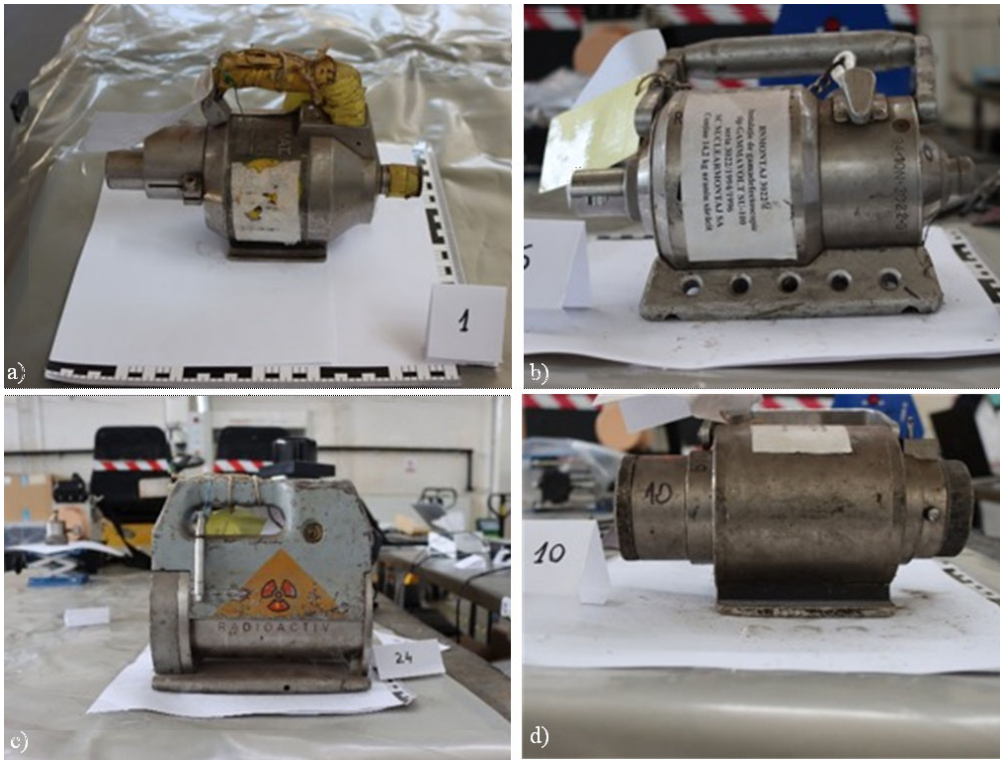


Fig. 1. Photos of the four types of gamma radiography devices that were analyzed:
a) GAMMAMAT TI-F (P1); b) GAMAVOLT SU 100N (P2);
c) GDP-U5 (P3); d) GAMARID (P4)

Analytical methods

In order to determine the full spectrum of signatures that are of interest for a nuclear forensics investigation, i.e. physical characterisation and isotopic composition alongside the elemental composition of the casing material, each sample of interest was analysed using high resolution gamma spectrometry, X-ray fluorescence spectroscopy and proton induced x-ray emission. Moreover, in order to comply with the radiological safety procedure, each exhibit was first the subject of dosimetry measurements and all the analyses were performed in radiologically controlled areas.

- ***Dosimetry measurements***

The dose rate due to the natural radiological background in the area where the samples were analyzed was of about 0.11 µSv/h. Based on this, the dose rates measured at different distances from the exhibits are presented below, in Table 1. All the measurements were performed using the device RadEYE B20-ER.

In order to assess the presence or absence of surface contamination, swipe samples were collected from each sample. Dosimetry measurements of these swipes revealed that there is no surface contamination.

Table 1. Dose rates measured at different distances from each type of sample

Sample ID	Gama radiography installation type	Dose(µSv/h)					
		contact	Uncert. (abs)	10 cm	Uncert. (abs)	100 cm	Uncert. (abs)
P 1	GAMMAMAT TI-F	26.27	1.80	5.31	0.50	0.20	0.020
P 2	GAMAVOLT SU 100N	10.34	0.67	1.42	0.12	0.17	0.023
P 3	GDP-U5	26.12	1.41	1.96	0.30	0.14	0.012
P 4	GAMARID	26.61	0.25	2.23	0.25	0.25	0.020

- ***High-resolution gamma spectrometry***

In order to determine the isotopic composition of the depleted uranium (DU) inside the exhibits, high-resolution gamma spectrometry was used. The characteristics of the detector that was used are presented in Table 2 below.

The acquisition time was approximately 1 hour for each type of installation, and the samples were placed at 10 cm from the detector's window, in order to limit the dead time. The obtained spectra for each type of gamma radiography installation are presented in the following figures (see Figs 2 to 5).

Table 2. Detective EX100T Coaxial Detector characteristics

Detective EX100T Coaxial detector	
Crystal diameter	67 mm
Crystal length	52.4 mm
End cap to crystal distance	8 mm
Relative efficiency	40%
Energy resolution at the ^{57}Co energy of 122 keV	1.6 keV
Energy resolution at the ^{60}Co energy of 1.33 MeV	2.3 keV

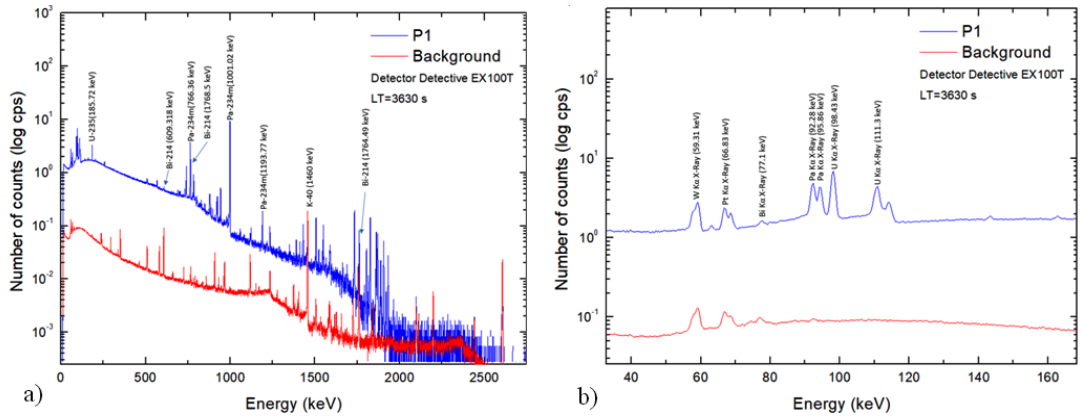


Fig. 2. a) Gamma spectrum of Gammamat TIF type installation (P1)
b) Low energy region of the gamma spectrum of Gammamat TIF type installation (P1)

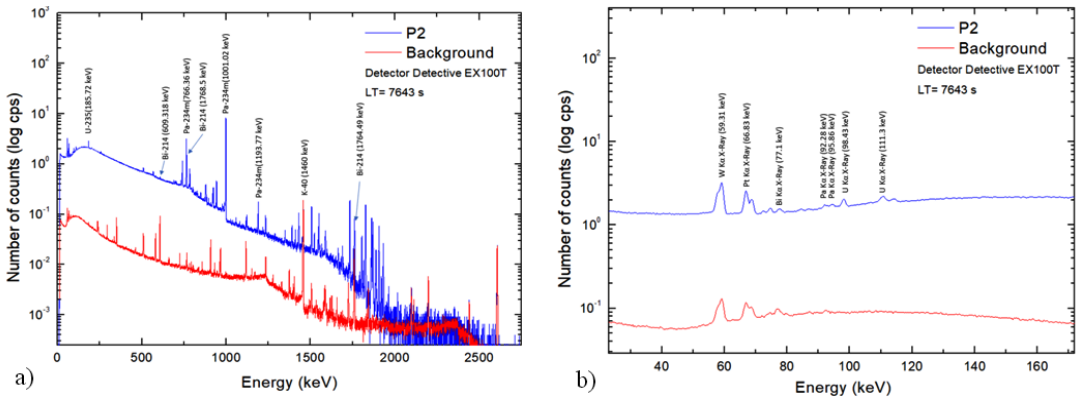


Fig. 3. a) Gamma spectrum of Gammavolt type installation (P2)
b) Low energy region of the gamma spectrum of Gammavolt type installation (P2)

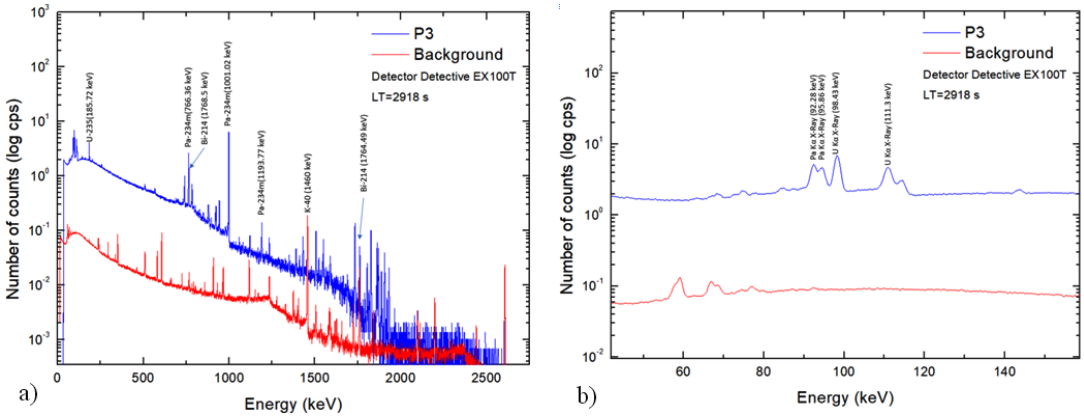


Fig. 4. a) Gamma spectrum of GDP-U5 type installation (P3)
b) Low energy region of the gamma spectrum of GDP-U5 type installation (P3)

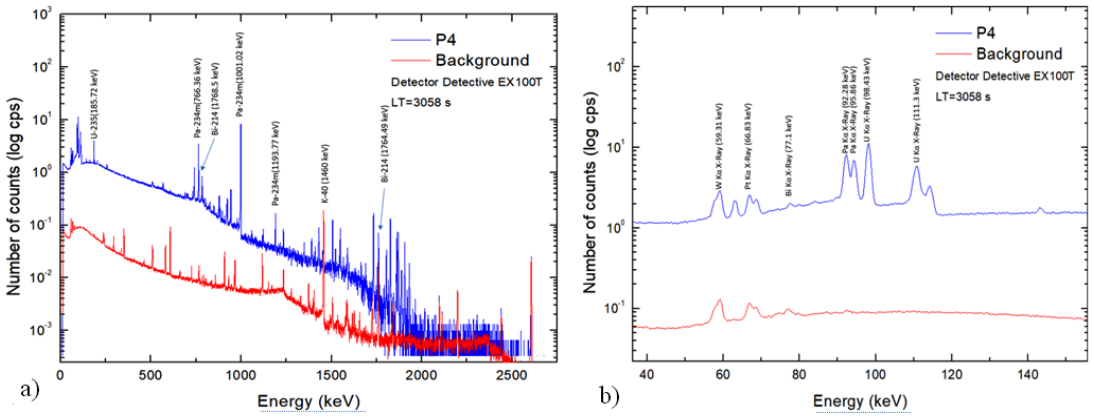


Fig. 5. a) Gamma spectrum of Gammarid type installation (P4)
b) Low energy region of the gamma spectrum of Gammarid type installation (P4)

After analyzing the gamma spectral of all four types of samples, gamma lines coming from the decay chain of ^{238}U were identified, more precisely: gamma-rays corresponding to the disintegration of ^{234m}Pa (766.36 keV, 1001.02 keV, 1193.77 keV), and its following radionuclides in the decay chain, like ^{214}Bi (1764.49 keV). Moreover, the 185.72 keV line of ^{235}U was also identified. In 40-140 keV region of spectra, the characteristic X-rays of uranium were identified (94.43 keV, 111.3 keV), alongside the characteristic X-rays of protactinium (92.28 keV, 95.86 keV). The 59.11 keV line that is visible in some spectra is the result of characteristic X photons emitted by wolfram, which is found in the protective cover of the detector's window. Moreover, it was concluded that there are no ^{192}Ir sources inside the devices.

As part of the isotopic composition analysis, focusing on the concentration of ^{235}U isotope, PC\FRAM v5.1 software was used. Due to the high concentration of ^{238}U, a special parameter file was created to analyse the samples of interest. The obtained results for the isotopic composition are presented in Table 3 below.

Table 3. Isotopic composition of the samples

Sample ID	Gama radiography installation type	Uranium-234	Uranium-235	Uranium-238
		Concentration (%) +/- σ (abs)	Concentration (%) +/- σ (abs)	Concentration (%) +/- σ (abs)
P 1	GAMMAMAT TI-F	<LD	0.2255 +/- 0.0211	99.7618 +/- 0.0270
P 2	GAMAVOLT SU 100N	<LD	0.1843 +/- 0.0295	99.8155 +/- 0.0507
P 3	GDP-U5	<LD	0.3427 +/- 0.0468	99.6504 +/- 0.0472
P 4	GAMARID	<LD	0.2191 +/- 0.0563	99.7788 +/- 0.0566

*LD = limit of detection

- ***Ion beam analysis and X-Ray Fluorescence***

To obtain the elemental composition of the casing material, all samples of interest were analyzed using both the PIXE and XRF techniques. For the PIXE analysis, the 3MV Tandetron^{TM} accelerator of IFIN-HH was used, and for the XRF procedure a portable XRF Tracer S1 Titan spectrometer was used.

In IBA analysis, due to the physical characteristics of the samples, placing them inside the vacuum chamber of the accelerator was not possible. Taking this into account, all measurements were performed using an external beam setup. The collimated proton beam energy was 3 MeV, and the exhibits were placed perpendicular with respect to the beam direction, whilst the X-ray detector (X-123 SDD FAST Complete X-Ray spectrometer) was placed at approximately 33° with respect to the beam direction. Due to the use of the external beam set-up, direct measurements of the beam current and the electric charge were not possible. In order to monitor the fluctuations of the incident proton beam, a thin carbon foil was placed inside the IBA reaction chamber and Rutherford backscattering spectrometry was used as an alternative to monitor the beam's characteristics. This was realized by collecting a RBS spectrum at about every 5 minutes. The energy loss by the protons passing through this carbon foil was considered negligible. The gamma radiography installations (P1, P2, P3 and P4) were measured for 20 minutes each and two points from the casing of each sample were investigated. The materials used as reference for the PIXE analysis were IRMM (Institute for Reference Materials and Measurements) metallic foils of certified mass fractions alongside a 99% purity molybdenum pellet. The reference materials spectra were acquired using the same experimental configuration as the one used when measuring the samples of interest. The spectra for both reference materials and samples of interest were processed using GUPIX software [5]. The Iterative Matrix Solution was applied. The calibration factors (H-factors) were set as energy dependent and were determined using the reference materials mentioned above. After the spectra associated to the samples of interest were analyzed, up to twelve elements were identified in the casing materials of each gamma radiography installation. The obtained results can be seen in Table 4.

Table 4. PIXE results regarding the elemental composition of the casing material of the samples

Element	P1(GAMMAMAT installation)		P2(GAMAVOLT installation)		P3(GDP-U5 installation)		P4(GAMARID installation)	
	PIXE results (wt%)	XRF results (wt%)	PIXE results (wt%)	XRF results (wt%)	PIXE results (wt%)	XRF results (wt%)	PIXE results (wt%)	XRF results (wt%)
Al	nd	nd	nd	nd	70.23755 +/- 3.51257	73.651 +/- 1.596	0.39554 +/- 0.05213	1.319 +/- 1.042
Si	0.1357 +/- 0.01337	0.484 +/- 0.472	nd	nd	14.5855 +/- 0.73063	15.402 +/- 0.502	0.86891 +/- 0.08829	0.857 +/- 0.268
P	0.00255 +/- 0.00162	0.017 +/- 0.006	nd	nd	1.29163 +/- 0.06513	nd	nd	nd
S	0.03783 +/- 0.00412	nd	nd	nd	0.34889 +/- 0.01753	nd	0.03539 +/- 0.00543	nd
Ti	nd	nd	0.35494 +/- 0.03561	0.5277 +/- 0.284	0.13446 +/- 0.00679	1.329 +/- 0.032	98.56075 +/- 1.75824	97.52 +/- 1.22
Cr	16.13433 +/- 1.61349	17.648 +/- 0.61	15.80666 +/- 1.58072	16.726 +/- 0.762	1.99707 +/- 0.09991	0.317 +/- 0.075	0.01912 +/- 0.00486	0.023 +/- 0.062
Fe	70.48405 +/- 7.04852	69.847 +/- 1.642	66.91995 +/- 6.6921	66.011 +/- 1.914	0.0596 +/- 0.00317	2.083 +/- 0.132	0.03539 +/- 0.01206	0.107 +/- 0.043
Ni	10.77616 +/- 1.07801	9.622 +/- 0.68	13.32003 +/- 1.33234	11.73 +/- 0.88	4.18166 +/- 0.20928	0.085 +/- 0.019	nd	nd
Cu	0.25332 +/- 0.03003	nd	nd	nd	7.08702 +/- 0.35542	3.188 +/- 0.093	nd	nd
Zn	nd	nd	nd	nd	0.09048 +/- 0.00961	1.32 +/- 0.055	nd	nd
Mo	0.17354 +/- 0.02531	0.177 +/- 0.048	3.59647 +/- 0.36766	2.548 +/- 0.188	nd	nd	nd	nd
Mn	2.00955 +/- 0.21342	1.715 +/- 0.37	2.10288 +/- 0.22065	2.059 +/- 0.448	nd	nd	nd	nd

* nd = not detected; ** wt% = weight percentage

In the case of GammaMat TI-F type radiography device, the XRF results did not indicate the presence of any copper or sulphur, while the results obtained using the PIXE method included these two elements. Regarding the concentrations of the other elements (P, Cr, Mn, Fe, Ni and Mo), the results obtained with both XRF and PIXE methods are consistent with each other within two sigma uncertainties. In the case of Si concentration, both PIXE and XRF results might indicate a higher concentration due to the presence of Si in the X-rays detector used for data acquisition.

In the case of GamaVolt type radiography device, both the XRF and PIXE results show the presence of the same elements (Ti, Cr, Fe, Ni, Mo and Mn). Regarding the concentrations of these elements in the casing material of the device, the values obtained with XRF and PIXE are consistent with each other within two sigma uncertainties.

Regarding the results obtained in the case of GDP-U5 type device, there are some discrepancies between the results obtained using the two techniques. The explanation is based on the fact that the casing material was analyzed only after a layer of paint was removed. This process was performed using an abrasive stick alongside sandpaper, which might have led to the spreading of contamination from the paint on the entire surface of the analyzed region. In addition to that, the irregular shape of the analyzed surface made it difficult to point the accelerated beam on the exact same spot which was analyzed using XRF technique.

In the case of Gamarid type radiography device, the PIXE results indicated the same elemental composition as the ones of XRF, with sulphur addition. Besides this, the concentration of the elements present in the casing material of the samples, obtained using both methods, are consistent with each other within two sigma uncertainties.

Conclusions

The research carried out in the paper was aimed to show the application of non-destructive analysis techniques which are carried out by the NFL-RO laboratory of IFIN-HH as part of a nuclear forensics investigation.

The high-resolution gamma spectrometry analysis of the four types of gamma radiography devices revealed that there were no ^{192}Ir sources located inside the exhibits.

Moreover, the isotopic composition analysis confirmed that all four types of devices contain mainly depleted uranium (DU). In addition to that, the results obtained through X-Ray Fluorescence spectroscopy were compared with the results obtained through ion beam analysis techniques to assess the versatility of the portable X-Ray Fluorescence technique in determining the elemental composition of the casing material of this type of devices.

The obtained results using both methods provide results consistent with each other within the uncertainties regarding the concentrations of major elements (Fe, Cu, Ti, Cr, Ni) present in the casing material.

In the case of trace elements (Zn, S, P), IBA techniques (PIXE) indicated the presence of elements which were not observed using XRF technique. Another aspect which should also be considered, when analysing this type of samples using IBA techniques, is to look after the summing peaks and escape peaks that might appear because of the high purity of the materials, and the induced X-ray fluorescence in the crystal of the used detector, respectively. Based on this, to assign a component as being part of one installation, one can use either one of these methods to determine the elemental composition. Nevertheless, it is necessary to combine both the isotopic composition results with the ones regarding the elemental composition in order to provide trustworthy results.

The results obtained during this investigative process were provided to the judiciary authorities and are part of their investigation.

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