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Age determination of Pu-bearing samples using gamma spectrometry for safeguards and nuclear forensics applications

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Abstract: *Age dating of plutonium (Pu), i.e. determination of the elapsed time since the last chemical purification of the material, is one of characteristics or signatures important to deduce the history of Pu-material in nuclear safeguards and forensics applications. This work describes a method to determine the age of some Pu-bearing samples using non–destructive gamma spectrometry. The presented method is relatively fast in comparison with destructive methods, does not require any reference materials, and could be applied to measure Pu-material in any physical and chemical forms. The Pu age is estimated from the $^{241}Am/^{241}Pu$ activity ratio. The ^{241}Am and ^{241}Pu activities are measured using the In Situ Object Counting System (ISOCS). The determined ages are compared to those obtained using the "Multi-Group Analysis (MGA)" Code. A maximum deviation of about 11% between the two methods is found for the investigated samples. The estimated Pu purification age of the samples is of an average value of51.914±0.02% years.*

Keywords: Age dating, Plutonium, Nuclear safeguards, Nuclear forensics.

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I. Introduction

Nuclear material (NM) characterization is an essential activity for both nuclear safeguards and forensics purposes. In addition to national obligations, a State nuclear regulatory authority may have additional international responsibilities that necessitate it to implement an inspection regime. Nuclear Material (NM) verification and, sometimes, characterization is an essential activity in this regime. In some cases the age determination of NM sample could provide some explanation about its declaration, for example most orphan samples might be declared after local laws and/or international agreements came into force just because they were prepared long time ago before the existence of any legally binding instruments. On other hand, nuclear forensics entails the analysis of intercepted illicit nuclear or radioactive material and any associated material to provide evidence for nuclear attribution. It employs measurement and analysis methods to reveal as much information as possible about a NM of unknown origin (e.g. seized material) in order to aid the authorities in criminal investigation as well as in determining the history and the origin of the material. Correlation of the measured signatures with the origin of NMs, their history and age of production could help to understand the intended use of such material [1-2].Several characteristic parameters or signatures of the material can be used for nuclear forensics, such as isotopic composition, elemental impurities, trace-level radionuclide content, crystal structure, anionic residues and age.

Several measurement techniques are used to verify/characterize quantitatively the amount of NMs declared/detected.They depend on the type of emitted radiation, its mass, activity and a number of other parameters [3-6].

Pu is an important element for nuclear forensics and safeguards as it is one of the primary materials targeted for non-proliferation issues. Pu is typically produced in a nuclear reactor through neutron capture of uranium (U) and subsequent beta decays. Therefore, the isotopic composition of seized Pu-material can be used to determine the irradiation history of the material, such as reactor type, irradiation condition, and enrichment of the starting material. In addition, the age of the Pu-material is important in nuclear forensics as it can establish the production date or last separation date of the sample and consequently age dating is one of the requirements for understanding the source of Pu in nuclear forensics [7-9].

ZsoltVarga et al., stated that the age is the first parameter to be determined when deducing the history of the nuclear material. In contrast to most other characteristic parameters used in nuclear safeguards or forensics, the production or purification date of the material is a predictive signature; thus, it does not require comparison data for nuclear forensic interpretation (i.e., it is a self-explaining parameter). This feature makes the production date one of the most prominent signatures in nuclear forensics [10].

M. Wallenius et al., also stated that the age is a very important parameter for the origin determination because it may serve to exclude certain production or reprocessing plants, which were not operating at the given time or were not processing the type of material in question[11].

To avoid the loss of information while using destructive methods, and for easier and relatively faster measurements, in this work, a non-destructive method was utilized to determine the age of the samples.

II. Age estimation of Pu samples

The age of a Pu-bearing sample can be calculated from the measured atomic ratio between a parent nuclide and its derived progenyusing the radioactive decay equation [12].The age determination technique is based on the assumption that initially the sample is free of progeny nuclides and a continuous increase of progeny nuclides occurs after the last chemical separation of parent nuclide. This unique possibility is based on the presence of radionuclides and their radioactive decay (progeny) while during the production or purification, the radioactive material is chemically purified from the impurities, including also its radioactive decay products. After chemical separation of a radionuclide, its radioactive progenies start to grow-in into the material. [13-14]

In this work, the in-growth of ^{241}Am due to the decay of ^{241}Pu was used for age dating as it provides an excellent chronometer of the material. The theoretical amount of daughter nuclide formed by the decay can be calculated using the radioactive decay equations (Bateman equations).The ratio of the daughter nuclide amount relative to the amount of its parent nuclide in a sample can be calculated as follows:

$$\frac{N_d}{N_p} = \frac{\lambda_p}{\lambda_d - \lambda_p}\left(e^{-\lambda_p t} - e^{-\lambda_d t}\right) + \frac{N_d^0}{N_p} e^{-\lambda_d t} \qquad (1)$$

where:

N_d , N_p are the number of daughter and parent atoms in the sample, respectively;

λ_d, λ_p are the decay constants of daughter and parent nuclides, respectively;

$N_d^0$is the residual daughternuclide after the chemical separation; and

t is the elapsed time since the separation of the radionuclides.

The daughter-to-parent ratio (N_d/N_p) is often referred to as a chronometer, while the elapsed time (t) is called the age of the material.

The age dating model assumes that the sample behaves as a closed system, meaning that there is no loss or increase either for the parent nuclide or for the decay products after production. If the initial concentration ofthe daughter nuclide is zero after the last chemical separation(i.e. the separation was complete, N_d^0= zero), and the amount ratio of the parent and daughter nuclide is measured, the elapsed time (t) can be calculated as follows:

$$t = \frac{1}{\lambda_p - \lambda_d} \ln\left(1 - \frac{N_d}{N_p} \cdot \frac{\lambda_d - \lambda_p}{\lambda_p}\right) \qquad (2)$$

Using the decay equation ($A = \lambda N$) the age of the nuclear material can be calculated according to the following equation:

$$t = \frac{1}{\lambda_p - \lambda_d} \ln\left(1 - \frac{A_d}{A_p} \cdot \frac{\lambda_d - \lambda_p}{\lambda_d}\right) \qquad (3)$$

where A_d/A_p is the daughter to parent activity ratio. So, the age (t) of the sample can be determined using the measured activity ratio of daughter to parent. It can be shown easily that the standard error in age is calculated using the following equation:

$$\sigma_t = \frac{a}{\left(\frac{x}{yb} - 1\right)} \cdot \sqrt{\frac{\sigma_x^2}{x^2} + \frac{\sigma_y^2}{y^2}} \qquad (4)$$

where:

a is a constant given by $a = \frac{1}{(\lambda_p - \lambda_d)}$;

b is a constant given by $b = 1 - \frac{\lambda_p}{\lambda_d}$;

x, y are the activity concentrations of the parent and daughter nuclides, respectively;

σ_x, $\sigma_y$are the standard errors in activities of parent and daughter nuclides, respectively;

III. Technique and experimental setup

Measurements of NMs using gamma-spectroscopy become possible if the detector absolute efficiency is established for the gamma-lines of interest. Normally, the absolute efficiency is measured using standard sources. However, typical standards representing the samples under investigation are not always available. In such cases, semi-absolute or absolute methods have to be considered. The In Situ Object Counting Software (ISOCS)-based measurement system brings the possibility to establish absolute efficiency curve for the detector at the desired gamma energy range. This is done based on pre-calibrated detectors by the manufacturer using

numerical simulation. The user has to provide the system with someparameters for the measured sample such as geometries, dimensions, material compositions of sample and container. In this work, one of these systems was used to measure the assayed samples. Falcon 5000 unit was used with model S573 ISOCS calibration software. The unit incorporates a HPGe detector with 60x30 mm dimensions for spectrometry with energy range between 20keV to 3.0MeV.

Another system which does not require calibration standards and used in this work is the MGA software-based system. The used gamma ray spectrometer is a portable γ - ray spectrometer (Canberra-U-Pu inspector 2000) based on a Digital Multi channel Analyzer (MCA) with a planar HPGe detector (Canberra GL0515R). As provided by the manufactured, the detector has a Ge crystal with 25.2 mm active diameter and 15 mm thickness and an Aluminum window of 0.5mm thickness. The detector has a measured resolution of 650 eV at the 122 keV (^{57}Co) gamma energy. The output signal of the detector is processed through a Canberra preamplifier (model 2002CP).The data acquisition was carried out via gamma spectroscopy software based on Canberra Genie 2000. The only requirement for such system is the adjustment of specific gamma rays with certain energy at a specific channel of the used multichannel analyzer using the amplifier course/fine gain.

In this work, 49 samples of thin layer of plutonium precipitated on discs with diameter of 3.4 cm were measured. Since the measured material is a very thin layer, self-attenuation due to material thickness and matrix material was neglected. For that reason, the material was defined in ISOCS as pure Pu with very low density.

The count rates due to the most intense gamma energy lines for both ^{241}Pu (148.567keV) and ^{241}Am (59.54keV) isotopes are used for activity calculation using ISOCS.

For both systems, and due to the very low activities, the assayed samples were placed in direct contact with the detector cap such that the axes of symmetry of both sample and detector are coincidence. For the Falcon system, an average measuring life times of 22 hours were preset, while for the second system with smaller crystal size an average counting life time of 26 hours was preset to obtain acceptable statistics. In all cases the dead time was always less the 1% for both systems.

IV. Results and discussion

The activity concentrations of ^{241}Pu and ^{241}Am as estimated using ISOCS are given in Table (1). The calculated ages of the samples with their percentage associated uncertainties as calculate by equations (3) and (4)are also given.The Activities of ^{241}Pu ranges between 913.794 and 46627.100Bq, while the activities of and ^{241}Am ranges between 455.971and 11271.500Bq. The lower uncertainty in calculated activities of ^{241}Am isotope is due to the high count rate of its 59.54 keV gamma line energy (branching ratio of 35.9%). Theestimated uncertainty for the^{241}Am isotopehas a maximum value of 0.002% while it ranges between 0.02 to 37% for the ^{241}Pu isotope.

Tabe1.Samples activities of ^{241}Pu and ^{241}Am as estimated using ISOCSwith corresponding calculatedages.

Sample code	^{241}Pu Activity (Bq) $A_{Pu} \pm \sigma_{A_{Pu}}$	^{241}Amactivity (Bq) $A_{Am} \pm \sigma_{A_{Am}}$	Age (y) $t \pm \sigma_t$ %
N6140	2312.700±47.154	498.311±0.009	42.509±0.014%
N6141	1212.170±95.627	462.523±0.009	53.429±0.054%
N6142	1799.019±172.783	487.581±0.009	46.811±0.065%
N6144	913.794±339.760	455.971±0.009	58.756±0.253%
N6146	3166.290±96.5773	699.808±0.009	42.979±0.021%
N6147	1388.307±248.029	721.063±0.009	59.560±0.121%
N6148	1641.641±64.761	663.191±0.009	54.554±0.027%
N6149	1710.803±124.352	761.991±0.009	56.488±0.049%
N6150	2861.305±114.308	653.273±0.009	43.583±0.027%
N6151	1186.721±126.202	622.142±0.009	59.748±0.072%
N6152	1461.998±181.363	715.557±0.009	58.369±0.084%
N6153	4141.182±104.072	1479.785±0.009	52.143±0.017%
N6154	2555.212±109.513	1296.603±0.009	59.093±0.029%
N6155	3404.874±63.532	1266.266±0.009	52.925±0.013%
N6156	5922.461±58.579	1312.565±0.009	43.030±0.007%
N6157	6542.877±35.528	1374.474±0.009	42.041±0.004%
N6158	3409.433±58.863	1284.867±0.009	53.185±0.012%
N6160	4931.258±69.035	1721.251±0.010	51.685±0.009%
N6161	2614.482±102.294	1613.639±0.009	63.045±0.027%
N6162	5185.173±34.312	1773.370±0.008	51.288±0.004%
N6163	4203.322±31.119	1835.599±0.009	56.096±0.005%
N6164	3687.600±49.507	1577.278±0.009	55.684±0.009%
N6165	3745.300±109.589	1706.566±0.009	56.941±0.019%
N6166	4723.437±76.950	1700.919±0.009	52.294±0.011%

N6167	8386.999±45.683	2508.895±0.009	48.697±0.004%
N6168	6469.620±41.924	2589.722±0.009	54.372±0.004%
N6169	5186.004±35.709	2806.457±0.009	60.387±0.005%
N6170	8652.405±34.491	2504.216±0.009	48.064±0.003%
N6172	11869.320±18.643	2323.740±0.009	40.749±0.001%
N6173	8071.847±37.392	2726.670±0.009	51.047±0.003%
N6174	11934.110±20.255	4784.583±0.009	54.403±0.001%
N6176	17127.000±14.889	4430.204±0.009	45.926±0.001%
N6177	9012.224±23.023	4462.471±0.009	58.602±0.002%
N6178	11346.780±44.763	4179.062±0.009	52.735±0.003%
N6179	12726.220±26.275	3710.098±0.009	48.203±0.001%
N6180	8610.204±43.768	4436.961±0.009	59.402±0.003%
N6181	21838.800±14.192	7221.409±0.009	50.633±0.001%
N6182	13201.700±20.032	7225.543±0.009	60.615±0.001%
N6183	21048.850±13.764	7027.817±0.009	50.820±0.001%
N6184	23803.730±10.329	7090.098±0.009	48.615±0.001%
N6185	24128.800±26.836	7014.614±0.009	48.149±0.001%
N6187	30679.670±14.398	6643.647±0.009	42.601±0.001%
N6188	23704.010±9.170	7905.715±0.009	50.799±0.001%
N6189	19327.300±20.249	10765.740±0.009	60.969±0.001%
N6191	24975.400±12.158	10685.810±0.009	55.689±0.001%
N6192	46627.100±14.995	9842.537±0.009	42.130±0.001%
N6193	28099.530±16.545	11174.110±0.009	54.242±0.001%
N6194	37817.000±15.479	11271.500±0.009	48.627±0.001%
N6195	42228.360±7.683	10161.650±0.009	44.565±0.001%
Range	**913.794±339.760-46627.100±14.995**	**455.971±0.009-11271.500±0.009**	**40.749±0.001%-63.045±0.027%**
Average	**11257.03±63.193**	**3717.916±0.009**	**51.985±0.020%**

The relatively small values of activity concentrations in the samples indicate that they were prepared for calibration of α-spectrometersand/or research purposes.

The correlation between ^{241}Pu and ^{241}Am activities is shown in Figure (1). It seems that there is a good correlation between both activities (R^2 = 0.8377), which indicates that the samples were prepared within a specific period of time (within about 21 years). However, it is clear from the results that they were prepared with different activity concentrations. It could be shown from the obtained results also that as the ratio between activities (Pu/Am) increase, the age of sample decreases. For example, samples N6161 and N6157 with ^{241}Pu/^{241}Am ratios of 1.62 and 4.76 have ages of 63.045 and 42.041 years, respectively. This is in consistence with the fact that there is no equilibrium between the two isotopes since the half-life of the parent (^{241}Pu) is 14.35 y and of the daughter (^{241}Am) is 432.2 y.

As it is also clear from the Table, Thehigher the errors associated with measuring these isotopes,the high the resulting errors in the ^{241}Am/^{241}Pu model age.

The identical shape and dimensions of all samples indicates that they are from the same origin and manufactured for the same purpose. Also the founded isotopes indicate that they were receipted from a foreign country.

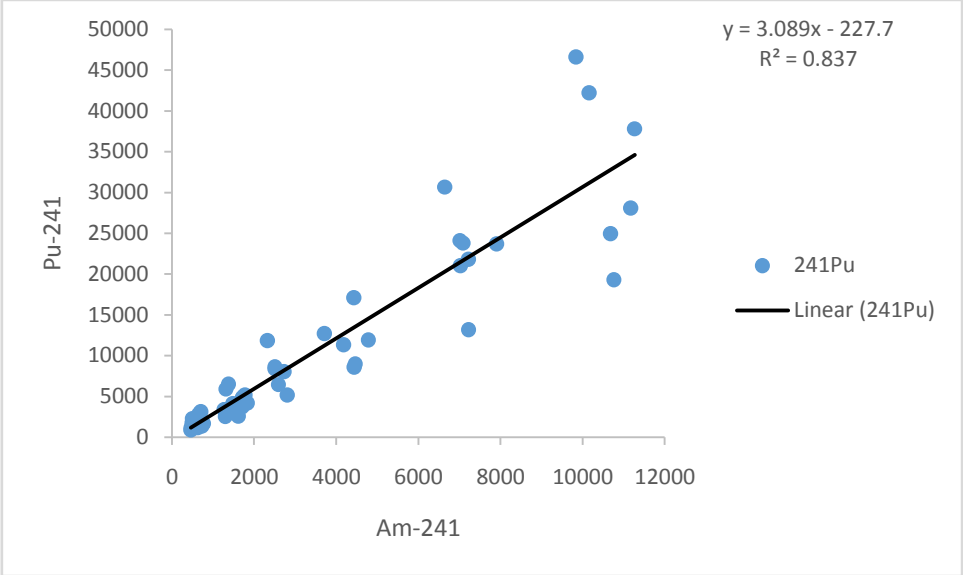

Fig. 1.Correlation between activities of^{241}Pu and ^{241}Am isotopes.

According to the calculations, the age of the samples ranges between 40.749±0.001% and63.045±0.027% yearswith average age of 51.985±0.020%years old as shown in figure 2

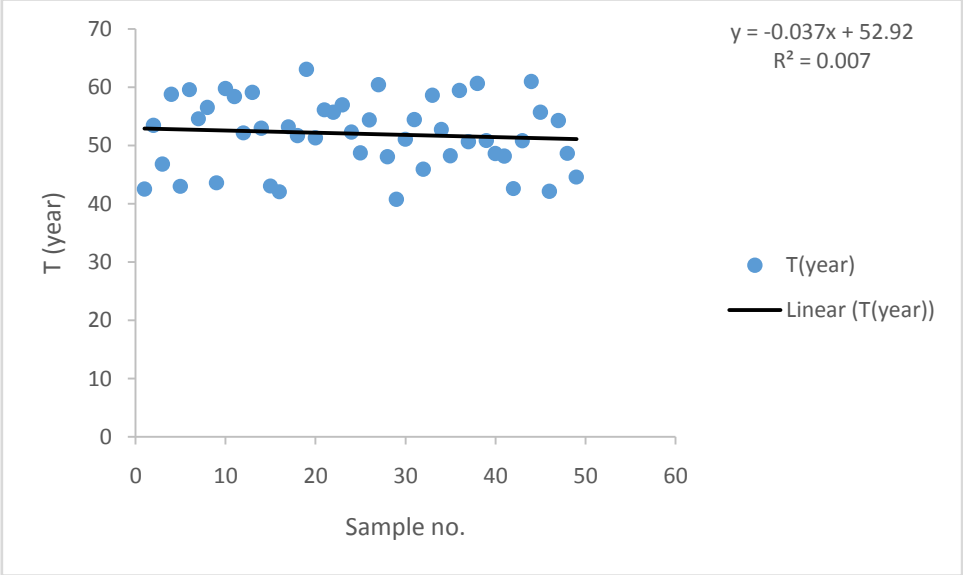

Fig.2. Age of samplesas calculated using ISOCS data.

The age of some of these samples was also determined using the MGA software and compared with the measured results as illustrated in figure (4). The comparison of age calculation results obtained by ISOCS and MGA showed a deviation ranged from -33.209% to +15.458%with an average difference for all samples of about 10.946%. The use of two independent measurements demonstrates the coherence of the results and consequently leads to the conclusion that the proposed method could be used with relatively high precision and 11% accuracy.

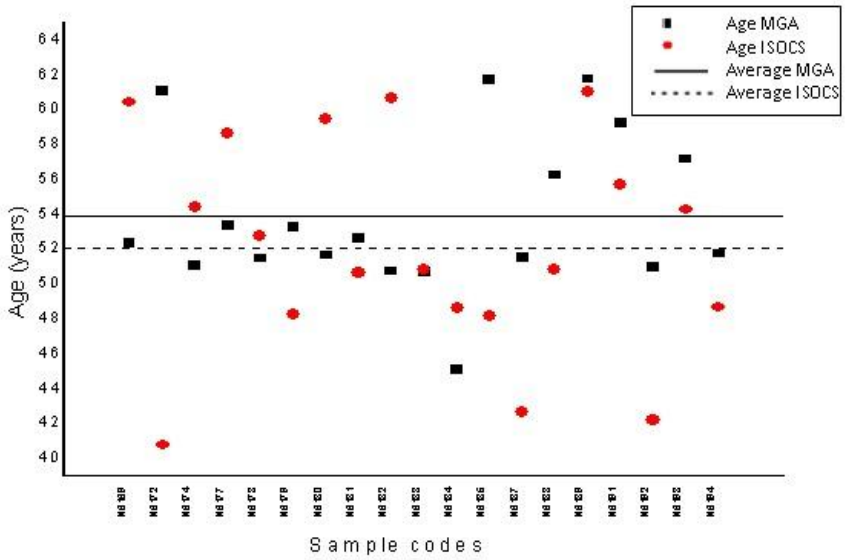

Fig.3. Comparison between samples ages estimated using ISOCS and MGA based methods.

The MGA software has some limitations regarding the low activities of the ^{241}Pu isotope. Consequently, not all samples could be measured on the second system that employs MGA for age isotopic ratios and age calculations.

V. Conclusion:

In this work a gamma-spectrometric method was used for age determination of some Pu samples. The results obtained using the described ISOCS method were confirmed by MGA method which uses the intrinsic efficiency calibration of the detector and the obtained results showed good correlation. The results indicate that the investigated samples were nearly prepared during a specific period ranged between 41 and 63 years, most probably for α-spectrometry and/or research purposes. This measuring method could be applied for aging the nuclear material as a very important parameter used for nuclear safeguards and nuclear forensics purposes.

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