

NUCLEAR FORENSICS INTERNATIONAL TECHNICAL WORKING GROUP

ITWG GUIDELINE ON ALPHA SPECTROMETRY



EXECUTIVE SUMMARY

Alpha Spectrometry is used for isotopic composition measurement of radioactive elements that decay by the emission of an alpha particle. These include many of the actinide elements (thorium, uranium, neptunium, plutonium, americium and curium) and some of the heavy elements (e.g. polonium and radium). The concentration of an isotope can be determined by using an isotope dilution technique (i.e. spiking the sample with a known quantity of a known isotopic composition). Separation and purification of the element of interest is required prior to analysis. The chemical processes are well developed and the equipment components for analysis are fairly inexpensive.

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ITWG Guidelines are intended as consensus-driven best-practices documents. These documents are general rather than prescriptive, and they are not intended to replace any specific laboratory operating procedures.

1. INTRODUCTION

Prior to analysis by alpha spectrometry, the element of interest is chemically separated from the sample matrix (pure uranium or plutonium samples may not require any additional purification prior to mounting) and then deposited on a metal plate (typically Pt or stainless steel) by stippling or electro-deposition [1], or co-precipitated as a fluoride and mounted on a flat disk [2]. The mounted sample is placed in a chamber under vacuum with a detector at a fixed distance from the sample source. As the sample undergoes alpha decay a portion of the alpha particles strike the detector and the events are recorded. The energy range of measurement is set by upper and lower level discriminators. The lower discriminator is often set at 3 MeV, since there are no alpha decays of interest below that energy. The upper discriminator is often set at 8 or 10 MeV, so as to capture high-energy decays of interest. The efficiency of detection does not depend on the energy of the particle thus the total counts under a peak are related to the isotope ratio in the sample and the branching ratio of the isotope of interest. Peak resolution is on the order of 50 keV or better as determined by the full peak width at half the maximum peak height (FWHM). Alpha spectra of purified uranium spiked with a ²³²U tracer is shown in the Figure 1A below (on the left) and of plutonium (no tracer added) on the right below (1B).

The instrumentation used to determine and quantify the alpha-emitting nuclide in question is usually a surfacebarrier type detector (for low-level nuclear forensic applications) where the energy of the charged particle is deposited in the active volume of the detector. The

energy deposited is proportional to the kinetic energy of the alpha particle emitted, which is well known for each isotope, allowing identification and quantification of the isotopes present. Because some alpha decay energies overlap (see Table 1 from [3]), elements are usually chemically separated prior to measurement. A notable exception is that Am and Cm isotopes are often measured in the same sample aliquot as they are not easily separated by chemical processing and have sufficient differences in their peak energies to be resolved in the spectra. Other impurities should be removed to obtain acceptable resolution of the alpha peaks. Other detector types include a Frisch grid detection system [4] or a liquid scintillation counter [5,6] optimized for alpha measurements; these other systems may be used as screening tools but typically do not provide the lower detection limits and resolution required for nuclear forensics.

2. USE FOR NUCLEAR FORENSICS

Alpha spectrometry can be considered complementary to mass spectrometry, but the instrumentation required is much less expensive than a mass spectrometer [7]. Isotopic ratios of uranium can be determined which provide important signatures as to the intended use of the material [8]. Quantification of ²³⁸Pu is better accomplished by alpha spectrometry than mass spectrometry due to its short half-life and potential mass interference from ²³⁸U; ²³⁸Pu may also provide information as to the history and possible use of a material [8]. Alpha spectrometry is not able to separate the peaks due to 239Pu from 240Pu (see Table 1); this is best accomplished by mass spectrometry analysis.



Alpha spectrometry may be used to quantify ²⁴¹Am (daughter of ²⁴¹Pu), which can then be used to calculate the date of the last plutonium purification performed on a sample (assuming complete purification). Thorium-230 (daughter of ²³⁴U) can similarly be used to determine a last purification date for uranium materials. The presence of ²³⁷Np and higher actinides may be determined by alpha spectrometry and are useful to understand the reactor in which the material was produced.

Polonium-210 is naturally occurring; it may also be made in a nuclear reactor for military or commercial purposes. Recently, it was the "poison" used to kill Alexander Litvinenko in the UK in 2006 [9]. Polonium-210 is an alpha emitter; hundreds of alpha spectrometry measurements were made in the investigation following Litvinenko's death.

isotope

half_lifo

3. SAMPLE REQUIREMENTS

In order to quantify the desired radioisotopes in a sample, the element of interest should be chemically separated from other elements so that no spectral interferences occur (e.g. ²³⁴U can overlap ²³⁷Np and ²⁴¹Am can overlap ²³⁸Pu) and so that the deleterious effect on peak width and resolution due to remaining matrix elements is minimised. Chemical separation and purification methods are often the same as used to prepare samples for thermal ionization mass spectrometry. Following purification, the sample may be electro-deposited on the disk in a diluted salt matrix, usually ammonium sulfate. [1] In this case, following alpha spectrometry the sample may be stripped from the disk and, with further purification, analyzed by mass spectrometry. Alternatively, the purified sample can be precipitated as a rare earth fluoride and collected

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onoray (koV) intensity (%)

Table 1. Alpha particle energies that may be useful in nuclear forensics

| | lootope | nun nio | | | 1001000 | <u>nun nic</u> | | interiory (70) |
|---|--------------------|----------|------|--------------|---------|----------------|------|----------------|
| | Po-209 | 102 v | 4883 | 80 | Pu-242 | 3.7e5 v | 4856 | 22.4 |
| | | | 4885 | 20 | | | 4900 | 77.5 |
| | Po-208 | 290 y | 5115 | 100 | Pu-239 | 2.4e4 y | 5105 | 11.6 |
| | Po-210 | 138 d | 5304 | 100 | | 2 | 5144 | 15.2 |
| | | | | | | | 5157 | 73.4 |
| | Th-232 | 1.4e10 y | 3947 | 21.7 | Pu-240 | 6563 y | 5124 | 27.1 |
| | | | 4012 | 78.2 | | | 5168 | 72.8 |
| | Th-230 | 7.5e4 y | 4621 | 23.4 | Pu-238 | 87.7 y | 5456 | 29.0 |
| | | | 4687 | 76.3 | | | 5499 | 70.9 |
| | Th-228 | 1.91 y | 5340 | 27.2 | Pu-236 | 2.86 y | 5721 | 30.6 |
| | | | 5423 | 72.2 | | | 5768 | 69.3 |
| | U-238 | 4.5e9 v | 4156 | 20.9 | Am-242m | 141 v | 5142 | 5.8 |
| | | , | 4198 | 79.0 | | , | 5207 | 89.8 |
| | U-235 | 7.0e8 v | 4215 | 5.8 | Am-243 | 7370 y | 5233 | 11.0 |
| | | , | 4366 | 17.2 | | , | 5274 | 87.4 |
| | | | 4398 | 55.3 | Am-241 | 432 y | 5443 | 13.1 |
| | | | 4596 | 5.1 | | | 5486 | 84.5 |
| | U-236 | 2.3e7 y | 4446 | 25.9 | | | | |
| | | | 4494 | 73.8 | Cm-243 | 29.1 y | 5742 | 11.6 |
| | U-234 | 2.5e5 y | 4722 | 28.4 | | | 5785 | 72.9 |
| | | | 4775 | 71.4 | | | 5992 | 5.7 |
| | U-233 | 1.6e5 y | 4784 | 13.2 | | | 6058 | 4.7 |
| | | | 4824 | 84.4 | Cm-244 | 18.1 y | 5762 | 23.6 |
| | U-232 | 68.9 y | 5263 | 31.6 | | | 5805 | 76.4 |
| | | | 5320 | 68.2 | Cm-242 | 163 d | 6069 | 25.1 |
| | NI 00 7 | 0.4.0 | 4000 | | | | 6113 | 74.1 |
| | Np-237 | 2.1e6 y | 4639 | 6.2 | | | | |
| | | | 4/66 | 8.3 | | | | |
| | | | 4//1 | 25.0 | | | | |
| | No 225 | 206 4 | 4/00 | 47.9 | | | | |
| | 1vp-235 | 390 U | 4920 | 11.0 | | | | |
| I | | | 4997 | ~0 | | | | |
| I | | | 5007 | 24.0 53.8 | | | | |
| L | | | 5025 | 00.0 | | | | |

energy (keV) intensity (%) isotope

on a filter for counting. [2] A maximum sample loading of ~1 microgram of total uranium should be followed to obtain a thin deposit and ensure spectral resolution is not deteriorated by the thickness of the sample deposit. If detectors are kept free of contamination and counting times of several days are used, detection limits on the order of fCi (10 e-15 Ci; μ Bq) are attainable. More typical counting times of 1000 minutes result in detection limits of 0.1 pCi (3.7 mBq) or lower.

4. PRO'S AND CON'S OF THE TECHNIQUE

Alpha spectrometry is the preferred technique for the alpha emitting radioisotopes with half-lives less than a few 100 years, e.g., ²¹⁰Po, ²³²U, ²³⁸Pu, Am, and Cm isotopes. It can be used to determine the very long-lived actinides if a mass spectrometer is not available. It is complimentary to TIMS measurement for isotope ratio determinations. Precision of less than a few percent is obtainable using clean detectors (detectors free from all contamination; detector contamination is often due to recoil from previously counted high activity samples or quality control checks) and counting times of a day (1000 minutes).

- Sample preparation is rather time consuming; similar to mass spectrometry.
- + Inexpensive instrumentation.
- Small footprint for detectors and associated electronics (can be physically stacked and multiple detectors controlled by a single computer).
- Long counting times (1 to several days).
- + Good detection limits (sub-pCi, mBq) for shorter-lived alpha emitting isotopes (<500 years).
- + Can be used for any alpha emitting radionuclide.
- Spectral overlap does not typically allow separation of ²³⁹Pu and ²⁴⁰Pu, nor ²³⁵U from ²³⁶U (high activity samples counted using a sample to detector distance of >3 cm may allow some spectral deconvolution).

5. FAQ

- Cost of instrument: approximately \$25,000 USD for an octet (8) detector system.
- Single element technique, unless starting with a pure sample, the sample must be chemically purified from the matrix and other elements.
- Relatively simple to operate; rugged chemical separation methods exist, computer software available to perform peak area determinations and activity calculations.
- Complementary to thermal ionization mass spectrometry for U and Pu (²³²U and ²³⁸Pu best by alpha; ^{239/240}Pu and ^{235/236}U best by TIMS).

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DOCUMENT REVISION HISTORY

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