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^{239}Pu, ^{240}Pu, and ^{241}Am Determination in Hot Particles by Low Level Gamma-Spectrometry

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A nondestructive method based on low-energy, high-resolution photon spectrometry is presented which allows accurate determination of ^{239}Pu, ^{240}Pu, and ^{241}Am (as a daughter of ^{241}Pu) activities in radioactive particles containing relatively high levels of plutonium isotopes. The proposed method requires only one measurement for the establishment of an absolute efficiency curve. Since the density and composition of the radioactive particles of interest may vary, a self-absorption correction is required for the accurate determination of isotopic activities and ratios. This correction is carried out for each individual particle using the convenient gamma-ray emissions of ^{241}Am.

Introduction

Transuranium nuclides have been released into the environment since the beginning of the nuclear age in 1945. Among these, plutonium has been of particular interest due to its radiotoxicity and complex environmental behavior. To the present day, the largest amount of plutonium released to the global environment remains fallout from atmospheric nuclear weapons tests carried out mainly in the 1950s and the 1960s (*1*). It has been estimated that ∼12 PBq of ^{239,240}Pu were globally dispersed as a result of these tests, with a further 4 PBq deposited as close-in fallout. Additional amounts of this element have been released at a local scale as a consequence of civil nuclear reactor accidents (e.g., Chernobyl accident), releases from nuclear reprocessing facilities (e.g., Sellafield, UK; La Hague, France; Mayak PA, Russia) and nuclear weapons accidents (e.g., Palomares, Spain; Thule, Greenland). In many of the areas so contaminated, a significant fraction of the plutonium appears under the form of radioactive particles (also called "hot" particles). These hot particles can be defined as localized aggregates of material containing radioactive atoms, having diameters larger than 0.45 μm, that give rise to an inhomogeneous distribution of radionuclides significantly different from that of the bulk matrix (*2*). Characterization of these particles by different instrumental methods is an essential requirement in understanding the transport and behavior of these radionuclides in the environment, as well as in assessing its long-term radioecological impact (*3*−*6*). In the first instance, this characterization should, if possible, be performed with nondestructive instrumental techniques in order to maintain the integrity of the particles prior to further analysis.

Among the four environmentally significant plutonium isotopes (^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{241}Pu), three of them (^{238}Pu, ^{239}Pu, and ^{240}Pu) are alpha-emitters, and are most commonly determined in environmental samples by low-background, high-resolution alpha spectrometry. However, owing to their very similar alpha-energy emissions, ^{240}Pu and ^{239}Pu cannot be easily quantified independently by this technique and are normally reported together as $^{239+240}$Pu.

Examination of plutonium isotopic ratios can provide unambiguous information about the origin of the plutonium. The ^{240}Pu/^{239}Pu atom ratio is of particular value, ranging as it does from 0.03−0.06 for weapons-grade plutonium to in excess of 0.4 for reactor-grade plutonium (after certain burn-up time in the reactor) (*7*). Because of the difficulty in separately quantifying ^{239}Pu and ^{240}Pu by alpha spectrometry, this ratio is normally measured by mass spectrometric (MS) techniques such as thermal ionization mass spectrometry (TIMS) (*8*), resonant ionization mass spectrometry (RIMS) (*9*), inductively coupled plasma mass spectrometry (ICP-MS) (*10*), or accelerator mass spectrometry (AMS) (*11*). All of these MS techniques offer very low-detection limits, typically in the fg (μBq) range for both ^{239}Pu and ^{240}Pu, depending on the application and on the interference level, but share a common drawback: radiochemical sample destruction and purification are an essential prerequisite.

Since the environmental behavior of plutonium in a particulate form is particularly sensitive to the properties of the material (e.g., chemical composition, crystal structure, particle size, and oxidation state of the plutonium), characterization of the particles using a range of different nondestructive analytical techniques is required in order to gain information about possible particle mobilization, weathering and subsequent ecosystem transfer of associated plutonium radionuclides (*12, 2*). In this context, the development of nondestructive techniques for the accurate determination of ^{239}Pu, ^{240}Pu, and ^{241}Am levels and their associated activity (atom) ratios in Pu-bearing particles is highly desirable.

In this work, a nondestructive method for the accurate determination of ^{239}Pu, ^{240}Pu, and ^{241}Am activities in individual plutonium-bearing particles by high-resolution gamma-ray spectrometry is presented and discussed. The method is based on the measurement of the low intensity gamma emissions of ^{240}Pu (45.2 keV) and ^{239}Pu (51.6 keV), as well as the main gamma emission of ^{241}Am (59.2 keV), using a low-energy, high sensitivity planar gamma ray spectrometer. The efficiency of the detector is determined using a semiempirical approach, whereas self-absorption corrections are carried out for each particle using the different gamma-emissions of ^{241}Am (26.34V, 33.19, 59.54, and 102.98 keV).

The method has been applied to the characterization of particles isolated from contaminated soil samples collected at Palomares (Spain) and at the Semipalatinsk Test Site (Kazakhstan). The results obtained using this method proved to be in good agreement with those determined using destructive techniques in samples from the same sites.

Experimental Section

Sampling and Isolation of Particles. Two hot particles (identification codes: A1-5 and HP3) were isolated from surface soil samples collected in 2001 from a plutonium-

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contaminated area located to the west of the village of Palomares (Spain), site of a nuclear accident involving the release of four nuclear weapons following the midair collision of two U.S. military aircraft in January 1966. While two of the weapons were subsequently recovered intact, the chemical explosives in the other two were triggered on impact on land, causing the dispersion of a large amount of fissile material (plutonium and uranium) over an area of approximately 230 ha. Although various cleanup operations were carried out after the accident to reduce/dilute contamination levels, some of the fissile material dispersed during the accident can still be found in soils from the affected area (*13*). A considerable fraction of this residual contamination is present as hot particles. These hot particles vary in size (10−100 μm), are generally coated by soil material, and contain relatively significant activities of plutonium and enriched uranium (*14, 15*).

In addition, three hot particles (identification codes: HK30C, Tk13a, and Tk14) were isolated from soil samples collected in 2001 from the Semipalatinsk Nuclear Test Site in northeast Kazakhstan. This area was one of the main proving grounds for the testing of nuclear weapons by the former Soviet Union in the period 1949−1989. The soils analyzed were collected from the ring of spoil surrounding the crater produced by the Tel'kem 2 excavation experiment of 1968 (*16*). The experiment, carried out in order to evaluate the potential of using nuclear explosives for civil engineering purposes, involved the simultaneous detonation of three low-yield (240 t TNT equivalent), plutonium-fuelled fission devices, and resulted in an elliptical crater, ∼142 m long × 64 m wide (*17*). Previous studies have shown that a considerable fraction of the activity surrounding the crater is in the form of inhomogeneous, discrete particles of up to 1 mm size, with a vitrified, glass-like structure typical of fused material (*18*).

In all cases, soil samples were dried at room temperature prior to the isolation of individual particles. Hot particles were separated using the ^{241}Am signal at 59.54 keV which, daughter isotope of ^{241}Pu, can be taken as an indicator of the presence of plutonium. Hot particles were isolated using a binary separation technique based on the successive subdivision of the sample. For the Palomares soils, this subdivision process continued until only a small amount of sample (in the order of μg), containing the radioactive particle, was left. For the Tel'kem 2 samples, commencing with sample aliquots of 1−2 g, it proved possible to isolate individual grains containing elevated levels of ^{241}Am (and, consequently, Pu) after 10−20 separation steps.

Instruments and Methods. All of the isolated particles were analyzed for ^{239}Pu, ^{240}Pu, and ^{241}Am content by high-resolution gamma spectrometry using an n-type planar Low Energy Germanium detector (LEGe) equipped with a 0.5 mm beryllium entrance window (CANBERRA model GL1015R). A list of the isotopes of interest, together with the gamma-ray energies and intensities of relevance to this work, are given in Table 1.

The germanium crystal employed was 15 mm thick, with an active area of 1000 mm^2. The detector preamplifier output was connected directly to a digital signal processing module (CANBERRA model InSpector 2000 DSP). Resolutions (fwhm) of 398 eV at 5.9 keV (^{55}Fe) and 535 eV at 122 keV (^{57}Co) were achieved using optimized values for the rise and flat times (8.8 and 0.8 μs, respectively) of the trapezoidal filtering utilized in the DSP module. The LEGe detector was surrounded by 10 cm of low-activity lead shielding (∼60 Bq kg^{-1} of ^{210}Pb; (*19*)).

Good energy resolution is a key parameter when seeking to discriminate close-lying gamma-ray emissions. Here, the 51.62 keV emission of ^{239}Pu must be separated from Ge escape peaks at 48.6 and 49.7 keV, as well as from the Am backscatter peak at 48.3 keV, while the 45.24 keV emission of ^{240}Pu must be discriminated from the "background" peak of ^{210}Pb at 46.5 keV, and from the 43.4 and 43.5 keV emissions of ^{241}Am and ^{238}Pu, respectively. LEGe detectors generally offer better resolution and sensitivity than coaxial germanium detectors at these low energies, and are capable of discriminating between the Pu gamma-ray emissions of interest (see Figure 1).

TABLE 1. List of Isotopes with Their Gamma-Ray Energies and Intensities (Uncertainties Given in Parentheses), from Firestone et al., 2004 (*31*)

isotope	E (keV)	I (%)
	13.761[a]	1.07 (11)
	13.946	9.6 (10)
	26.3448 (2)	2.40 (2)
Am-241	33.1964 (3)	0.126 (3)
	43.423 (10)	0.073 (8)
	59.5412 (2)	35.9 (4)
	102.98 (2)	0.0195 (4)
Pu-239	51.624 (1)	0.0271 (5)
Pu-240	45.242 (3)	0.0450 (8)
Eu-152	121.7817 (3)	28.58 (6)

[a] WWW Table of Radioactive Isotopes (*32*).

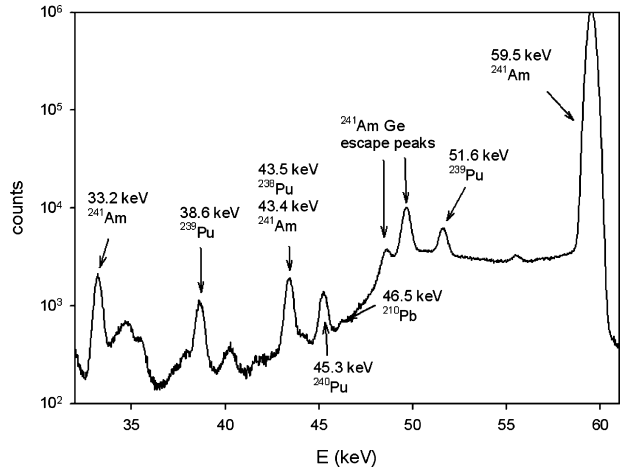

FIGURE 1. Experimental spectrum of a Palomares hot particle showing the gamma-ray emissions of ^{239}Pu, ^{240}Pu and ^{241}Am, as well as interference and background peaks. (measuring time of 1000 s).

In order to quantify the levels of ^{239}Pu, ^{240}Pu, and ^{241}Am in the isolated hot particles, the LEGe detector was calibrated for energy, peak-shape, and efficiency. The energy and peak-shape (including fwhm) calibration was conventionally performed using a certified 0.98 ± 0.01 kBq point source of ^{241}Am, supplied by the Physikalisch-Technische Bundesanstalt (Germany). The efficiency calibration curve for the energy range of interest was based on the following expression (*20*):

$$\varepsilon_E = \varepsilon^{\circ}\exp(-\mu_{E,Be}\delta(Be))\exp(-\mu_{E,Ge}\delta(Ge)) \quad (1)$$

Here, ε_E is the observed efficiency in the energy region, ε^{o} is the ideal (zero absorption) efficiency, $\mu_{E,Be}$, and $\mu_{E,Ge}$ are the mass absorption coefficients (cm^2/g) for beryllium and germanium, and δ(Be), δ(Ge) are the thicknesses of the beryllium entrance window and germanium dead layer, respectively.

Since the thickness of the beryllium window is known from the manufacturer's specifications, only two parameters (δ(Ge) and ε^{o}) must be calculated to obtain the final

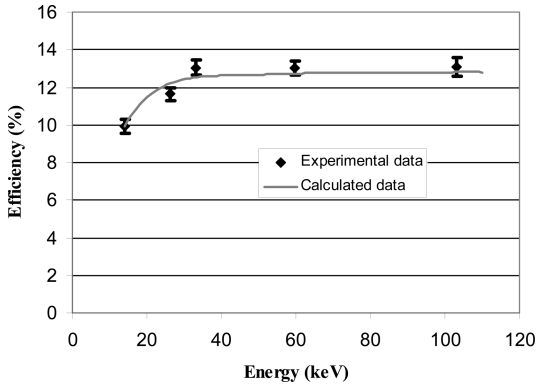

FIGURE 2. Experimental efficiency of the LeGe detector obtained with the certified ^{241}Am point source. The solid curve corresponds to the calculated efficiency using eq 1.

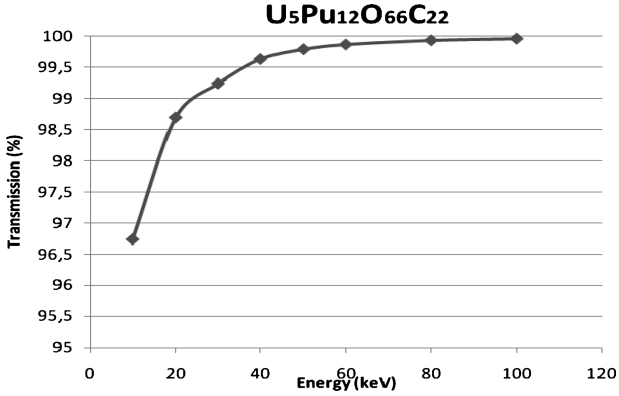

FIGURE 3. Transmission vs energy through a 100 μm hot particle with composition $U_5Pu_{12}O_{66}C_{22}$ and density 2.3 g/cm^3.

expression for efficiency. The experimental efficiencies for the (13.76 + 13.95) keV X-rays and 26.34 keV gamma-ray, determined with the ^{241}Am point source, were used to calculate these two remaining parameters. The resulting efficiency calibration curve is shown in Figure 2, together with experimental efficiency data obtained using the ^{241}Am point source.

Given the dimensions of the hot particles analyzed (essentially equivalent to point-like geometry), it was possible to use the above efficiency calibration curve to quantify the ^{239}Pu, ^{240}Pu, and ^{241}Am activities in these particles. The relative uncertainties of the calculated efficiencies for ^{239}Pu and ^{240}Pu were assumed to be the same as those determined from the ^{241}Am peaks.

No coincidence-summing effects were considered due to the low probability of the gamma-rays emitted even at close detector distance. The coincidence summing corrections were expected to be less than 2% for similar measurement geometry (*21*).

An attenuation correction was required to account for the density and composition (high Z elements) of each individual plutonium-bearing particle. This correction is both particle and energy dependent, and was determined for each particle using the different gamma-ray emissions of ^{241}Am. In a first approach, if the emission of ^{241}Am at 102.98 keV is presented in the spectrum, then this peak is selected as the reference emission (assumed to be unaffected by self-absorption), and the additional 26.34, 33.19, and 59.54 keV emissions of ^{241}Am are used to calculate the values of the attenuation correction factors at these energies via the following equation:

$$f(\mathrm{E}) = (N_\mathrm{E}/\varepsilon_\mathrm{E} I_\mathrm{E})(N_\mathrm{ref}/\varepsilon_\mathrm{ref} I_\mathrm{ref}) \qquad (2)$$

TABLE 2. List of Attenuation Correction Factors (f) at the Emissions of ^{240}Pu and ^{239}Pu for All Samples

	f(%)	
sample	^{240}Pu (45.2 keV)	^{239}Pu (51,6 keV)
A1−5	90,9 ± 0,9	94,8 ± 0,9
HP3	90,1 ± 0,9	94,4 ± 0,9
HK30c	93,1 ± 0,9	96,2 ± 1,0
Tk13a	92,9 ± 0,9	96,1 ± 1,0
Tk14	93,1 ± 0,9	96,2 ± 1,0

where N_E and N_ref correspond to the peak net count for the ^{241}Am emissions and the reference emission, respectively, I_E and I_ref their emission intensities, and ε_E and ε_ref their calculated efficiencies using eq 1. The values of f obtained for the 59.54 keV emission from the particles analyzed were close to unity, and support the assumption that the 102.98 keV emission is not affected by self-absorption in particles (see Figure 3) of this size (100 μm) and composition ($U_5Pu_{12}O_{66}C_{22}$) (*15*). If not 102.98 keV is presented in the spectrum then the 59.54 keV emission is selected as the reference emission (*12*) following the previous procedure.

For each individual hot particle, the calculated attenuation correction factors for the three emissions of ^{241}Am (26.34, 33.19, and 59.54 keV) were finally fitted using a linear relationship. The fitting energy range covers the gamma-ray

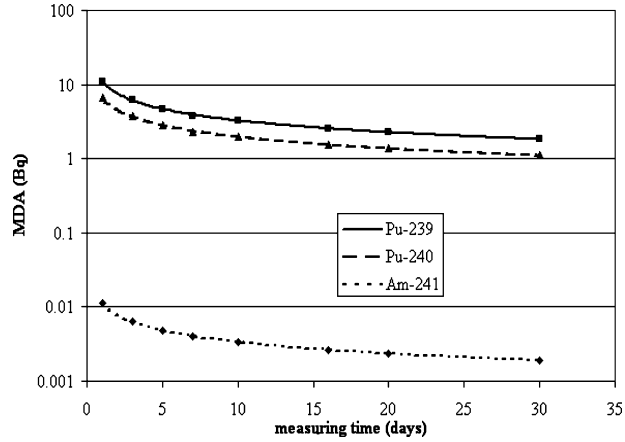

FIGURE 4. Minimum detectable activity (MDA) for ^{241}Am (59.5 keV), ^{239}Pu and ^{240}Pu calculated using background spectra recorded for different counting times.

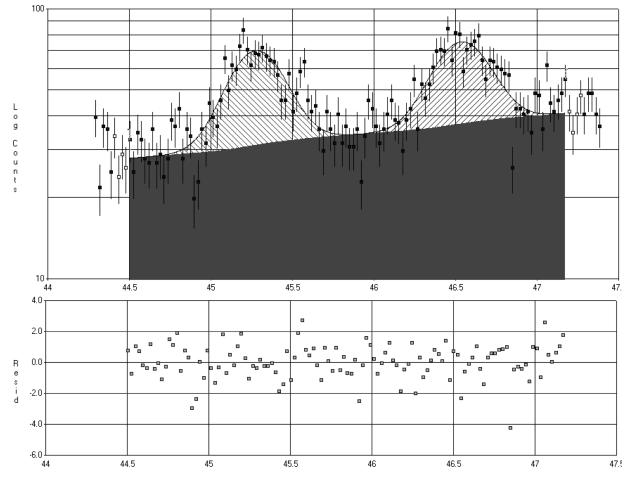

FIGURE 5. Fitted spectrum and residuals obtained with GENIE 2000 software for ^{240}Pu (45.2 keV) and ^{210}Pb (46.5 keV) peaks of Tk14 sample. Measuring time = 280576 s.

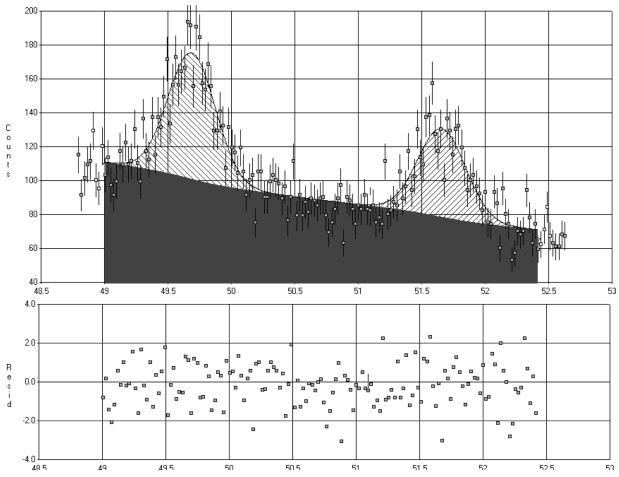

FIGURE 6. Fitted spectrum and residuals obtained with GENIE 2000 software for ^{239}Pu (51.62 keV) and Ge escape peaks of Tk14 sample. Measuring time = 280576 s.

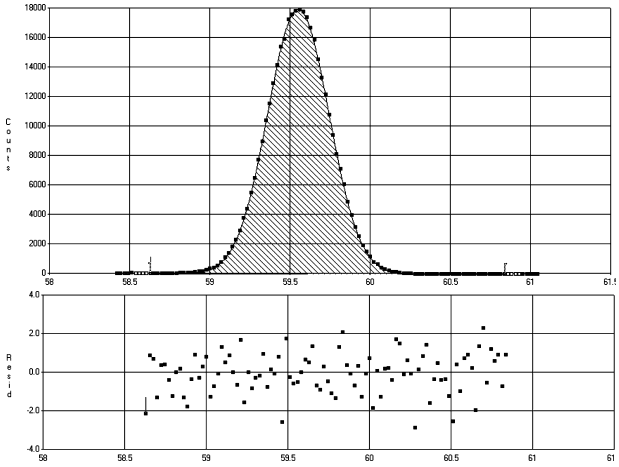

FIGURE 7. Fitted spectrum and residuals obtained with GENIE 2000 software for ^{241}Am peak (59.54 keV) of Tk14 sample. Measuring time = 280576 s.

emissions of ^{239}Pu and ^{240}Pu. The choice of a linear fit is based on the findings of Debertin (2001) (*22*), who observed that the attenuation correction for a thin source ($\mu\delta \ll 1$) is proportional to the absorption coefficient. From this plot, the attenuation correction factors and their uncertainties for the ^{239}Pu and ^{240}Pu gamma-ray emissions were calculated and used to determine the final activities of each hot particle. The ^{239}Pu and ^{240}Pu attenuation correction factors obtained for each particle are shown in Table 2.

In the case of the Tel'kem 2 (Semipalatinsk) particles, a further correction was required to account for the presence of small amounts of ^{152}Sm (daughter of the fission product ^{152}Eu), whose K_β emission interferes with the ^{240}Pu γ-emission at 45.24 keV. The number of counts due to ^{152}Sm was estimated from the ^{152}Eu γ-emission at 121.78 keV, taking the relative intensities and counting efficiencies into account. This was subtracted from the total area of the 45.24 keV peak to obtain the net ^{240}Pu counts. The correction was not required for the Palomares hot particles, as no fission products are present in them.

The minimum detectable activity (MDA) of the proposed technique was calculated according to Currie's criterion (*23*). Figure 4 shows the experimental MDA values for ^{241}Am, ^{239}Pu, and ^{240}Pu, obtained using a background spectrum recorded for different periods. It is clear from this figure that, in practice, the proposed technique can only be employed to accurately determine the ^{239}Pu and ^{240}Pu activity levels in hot particles if these exceed a few becquerels. Nevertheless, for the proper application of this method, it is essential to use a low-level, high-sensitivity gamma spectrometric system with the best possible resolution, in order to minimize background in the region of interest and to obtain clean ^{239}Pu and ^{240}Pu gamma-peaks with little or no interferences.

All spectra were analyzed using GENIE 2000 software (Canberra Industries Inc., U.S.) with an interactive nonlinear fitting algorithm. The use of this interactive facility was required to accurately determine peak areas in these complex spectra, which comprised overlapping Compton continua and backscatter peaks, background peaks, and in some cases, interferences from other radionuclides present in the particles (see Figures 5−7).

Results and Discussion

The ^{239}Pu, ^{240}Pu, and ^{241}Am activities in hot particles isolated from surface soil samples collected at Palomares (Spain), together with the corresponding ^{240}Pu/^{239}Pu and $^{239+240}$Pu/^{241}Am activity/atom ratios, are given in Table 3. The ^{241}Am activities in the two particles analyzed were 5.2 and 10.9 Bq, respectively, whereas the average ^{240}Pu/^{239}Pu atom ratio was 0.055 ± 0.006. The latter is in excellent agreement with the mean value of 0.056 ± 0.003 reported by Mitchell et al. (1997) (*24*) for Palomares soil and sediment samples containing hot particles, determined by the deconvolution of measured alpha spectra following radiochemical separation, and with the ^{240}Pu/^{239}Pu atom ratio of 0.063 ± 0.003 reported for an isolated hot particle from the same area, and analyzed by ICP-MS following total digestion with a mixture of HNO_3 (65%) and HF (50%) in a microwave oven (*25*). It is also consistent with the reported mean ^{240}Pu/^{239}Pu atom ratio of 0.0657 ± 0.0006 determined by accelerator mass spectrometry in soils collected from the same contaminated area, but characterized by lower activity concentrations (*26*).

The ^{240}Pu/^{239}Pu atom ratios determined from the gamma spectrometric measurements in the two Palomares particles analyzed are very different from those expected from global stratospheric fallout, characterized by a typical ^{240}Pu/^{239}Pu atom ratio of 0.18 ± 0.01 (*27*), and are clearly indicative of weapons-grade plutonium (*28*). This is as expected, given the origin of the plutonium in the affected area. The weapons involved in the Palomares accident were subjected to a conventional chemical explosion upon impact on land, dispersing their fissile material over local terrestrial soils.

TABLE 3. ^{239}Pu, ^{240}Pu, ^{241}Am and ^{152}Eu Activities, And Corresponding Isotopic Ratios, in Two Hot-Particles from Palomares (Spain) and Three Hot-Particles from the Tel'kem 2 Site at Semipalatinsk (Kazakhstan), as Determined by Gamma Spectrometry. Uncertainties 2 σ

sample	^{239}Pu (Bq)	^{240}Pu (Bq)	^{241}Am (Bq)	^{152}Eu (mBq)	^{240}Pu/^{239}Pu activity ratio	$^{239+240}$Pu/^{241}Am activity ratio	^{240}Pu/^{239}Pu atom ratio
A1-5	38 ± 4	6.9 ± 0.6	10.9 ± 0.3		0.18 ± 0.03	4.1 ± 0.8	0.050 ± 0.009
HP3	27 ± 3	5.7 ± 0.9	5.2 ± 0.2		0.22 ± 0.05	6.3 ± 1.5	0.059 ± 0.013
HK30C	45 ± 5	6.6 ± 0.7	6.1 ± 0.2	34 ± 3	0.15 ± 0.03	8.5 ± 1.6	0.040 ± 0.007
Tk14	156 ± 11	24 ± 2	22.0 ± 0.7	30 ± 5	0.15 ± 0.03	8.2 ± 1.2	0.041 ± 0.006
Tk13a	97 ± 9	18 ± 2	13.9 ± 0.5	42 ± 5	0.18 ± 0.03	8.3 ± 1.5	0.050 ± 0.009

TABLE 4. ^{239}Pu and ^{240}Pu Activities, and ^{240}Pu/^{239}Pu Atom Ratios, In the Same Three Hot-Particles from the Tel'kem 2 Site at Semipalatinsk (Kazakhstan), as Determined by AMS. (2σ)

	AMS			GAMMA
sample	^{239}Pu (Bq)	^{240}Pu (Bq)	^{240}Pu/^{239}Pu atom ratio	^{240}Pu/^{239}Pu atom ratio
HK30C	45.2 ± 1.1	7.8 ± 0.3	0.047 ± 0.002	0.040 ± 0.007
Tk14	146 ± 3	26.4 ± 0.5	0.049 ± 0.001	0.041 ± 0.006
Tk13a	83 ± 2	16.1 ± 0.5	0.052 ± 0.002	0.050 ± 0.009

From the recorded spectra, $^{239+240}$Pu/^{241}Am activity ratios of 4.1 ± 0.8 and 6.3 ± 1.5 were also calculated for the Palomares particles A1−5 and HP3, respectively. These ratios are in good agreement with the corresponding ratio reported by Irlweck and Hrnecek (1999), 4.0 ± 1.1 (*29*), for a Palomares soil sample, once account is taken of the difference in measurement dates and the in-growth of ^{241}Am arising from ^{241}Pu decay, which can be estimated using the ^{241}Pu/^{239}Pu ratio reported for Palomares particles by Mitchell et al. (1997) (*24*). It is also in good agreement with the mean $^{239+240}$Pu/^{241}Am activity ratios of 4.2 ± 0.4 (range: 3.6−5.3) reported by Aragón et al. (2008) (*30*) for a set of five isolated hot particles, as determined by alpha spectrometry following total dissolution.

The good agreement between the results obtained in this study and those reported by other researchers for particles collected in the same area by using destructive analytical techniques gives us confidence as to the suitability of the method proposed for the simultaneous determination of ^{239}Pu, ^{240}Pu, and ^{241}Am in plutonium-bearing particles.

The ^{239}Pu, ^{240}Pu, and ^{241}Am levels in three radioactive particles isolated from surface soils from the Semipalatinsk Nuclear Test Site, together with the corresponding ^{240}Pu/^{239}Pu and $^{239+240}$Pu/^{241}Am activity/atom ratios are given in Table 3. The ^{241}Am activities in the hot particles analyzed ranged from 6.1 to 22.0 Bq, while the measured ^{240}Pu/^{239}Pu atom ratios, with a mean value of 0.044 ± 0.006, were again consistent with the presence of weapons-grade plutonium. As these hot particles were collected in areas affected by local fallout originating from a very low-yield cratering explosion, the presence of weapons-grade plutonium was not unexpected. Indeed, a ^{240}Pu/^{239}Pu atom ratio of 0.054 ± 0.003 was previously reported by Jiménez-Nápoles et al. (2004) (*16*) for a soil sample collected from the vicinity of the Tel'kem 2 cratering site, determined by spectral deconvolution of the measured alpha spectrum.

To confirm the validity of the ^{240}Pu/^{239}Pu atom ratios measured by γ-spectrometry, the same particles were analyzed by accelerator mass spectrometry (AMS) following destructive analysis and radiochemical separation. As the data in Table 4 show, both sets of data are in excellent agreement. Although the uncertainties are lower by AMS, gamma methodology in radioactive particles presents an important advantage, which is that gamma spectrometry is a non destructive technique. The average $^{239+240}$Pu/^{241}Am activity ratio in the Tel'kem 2 particles, at 8.3 ± 0.1, is consistent with that reported by Conway et al. (2009) (*18*) for isolated particles collected from the same location using alpha spectrometry (mean value 8.6 ± 0.2), and lends further weight to the efficacy of the nondestructive method proposed in this work.

Acknowledgments

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