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## **IN SITU GAMMA-RAY SPECTROMETRIC MEASUREMENT OF URANIUM IN PHOSPHATE SOILS**

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### Abstract

Radioactivity concentration of  $^{238}\text{U}$  in a phosphate ores quarry was measured *in situ*. Independently, soil samples collected in the site were measured in the laboratory. It was disclosed that radon emanation from the soil lowers *in situ* results that are derived from radon daughters. Uranium concentration was found to be  $121.6 \pm 1.9 \text{ mg kg}^{-1}$ .

### Introduction

*In situ* (Latin, in site) gamma-ray spectrometry using high resolution Ge detectors is a nondestructive passive method for the detection, identification and quantitative determination of radioactivity in the environment, especially in the ground. Literature papers on the applications of this reliable and rapid method include, *inter alia*, the measurement of nuclear weapons fallout, accidental and waste releases of radionuclides, monitoring the progress of site cleanup and remediation operations, measurement of naturally-occurring background radioactivities for mineral prospecting, indoor radiation studies and analysis of reactor plumes. For a review see (Finck, 1992) and (ICRU 53, 1994). Recent studies describe *in situ* measurements of surface soils in the vicinity of a plant formerly used in the fabrication of uranium metal for defence projects (Miller et al., 1994), measurements of cleanup operation of plutonium in surface soil in a safety shot area at a nuclear test site (Fong and Alvarez, 1997) and analyses of natural radionuclides in desert soil (Benke and Kearfott, 1997).

The present investigation was a preliminary study of application of a portable gamma-ray spectrometry system for *in situ* analysis of soil radioactivity. An independent analytical method was applied to substantiate the *in situ* measurements by collecting soil samples from the site and measuring them in the laboratory. Soil sampling was performed to obtain information on radioactivity depth distribution and on the uniformity of surficial concentration of top-soil radioactivity.

### Theory

The theoretical principles of *in situ* gamma-ray spectrometry were developed in the early 1970s (Beck et al., 1972). The three-factor assay formula is given by

$$\frac{N_f}{A} = \frac{N_f}{N_0} \cdot \frac{N_0}{\phi} \cdot \frac{\phi}{A} \quad (1)$$

where  $N_f$  is the full-energy peak count rate of the measured radionuclide (in counts per second),  $A$  is the source radioactivity concentration (in  $\text{Bq m}^{-2}$ ,  $\text{Bq kg}^{-1}$  or  $\text{Bq m}^{-3}$ ),  $N_0$  is the full-energy count rate of that radionuclide for a parallel beam of gamma-rays that is incident on the detector parallel to its symmetry axis, and  $\phi$  is the gamma-ray unscattered flux on the detector (in  $\text{cm}^{-2} \text{ s}^{-1}$ ). The factor  $N_f/N_0$  is a correction for the detector angular response and is dependent on both the detector characteristics and source geometry. This factor can be determined experimentally in the laboratory by point sources of different energies measured at different azimuthal angles ( $\theta$ ) of incidence with respect to the detector symmetry axis at a constant distance of 1 m.

The factor  $N_0/\phi$  depends solely on the detector and can be determined experimentally in the laboratory by point source gamma-ray standards of different energies measured at a distance of 1 m normal to the detector face.

The factor  $\phi/A$  is independent of the detector, but dependent on the source distribution in the soil. Differential flux values, i.e. fluxes  $\phi_i$  at  $\theta_i$  per unit angle, can be calculated using eqs. (4) and (6) in (Beck et al., 1972).

A general expression for source radioactivity distribution in soil is given by the equation

$$S=S_0 \cdot \exp[-(\alpha/\rho) \cdot \rho \cdot z] \quad (2)$$

where  $S$  is the concentration (in e.g. Bq kg<sup>-1</sup>) at depth  $z$  (in cm) beneath the surface,  $S_0$  is the concentration at the surface (in Bq kg<sup>-1</sup>),  $\alpha/\rho$  is the attenuation coefficient of the radioactivity concentration in the soil (in cm<sup>2</sup>/g), and  $\rho$  is the soil density (in g cm<sup>-3</sup>). The inverse of  $\alpha$  is called the relaxation length (in cm). Natural radionuclides are distributed almost uniformly and in this case  $\alpha=0$ . Fresh anthropogenic emitters (e.g. weapon debris deposition, reactor effluent fallout) have a planar distribution with  $\alpha=\infty$ . An aged emitter can be described by eq. (2) with a typical relaxation length representing its exponential depth distribution.

### Experimental materials and technique

#### •*In situ* gamma-ray spectrometer

Gamma-ray spectra were measured by a tripod-mounted, downward-facing HPGe detector (Canberra) of 20.4% relative efficiency and 1.70 keV FWHM (both at 1332.5 keV) energy resolution, located 1 m above ground. Spectra of 8192 channels were analyzed by the NOMAD Plus System (EG&G Ortec). The spectrometer was operated by a Versa V-50 notebook PC (NEC).

#### •Gamma-ray calibrands

Measurement of  $N_0/\phi$  was performed at a 1 m distance by a mixed radionuclide gamma-ray standard reference solution (Amersham) containing the following radionuclides (energies  $E$  in keV, emission probabilities  $P_\gamma$  in %): <sup>133</sup>Ba (276.398, 7.164; 302.853, 18.33; 356.017, 62.05; 383.851, 8.94), <sup>137</sup>Cs (661.660, 85.1), <sup>60</sup>Co (1173.237, 99.90; 1332.501, 99.982). Gamma-ray emission rates of the standards were calculated from the standards certificates, using the lapse of time from the reference date. The flux is given by gamma-ray emission rate divided by  $4\pi$  and by 100<sup>2</sup> cm<sup>2</sup>. A second order polynomial least-squares fit determined the  $\log(N_0/\phi)$  versus  $\log(\text{gamma-ray energy})$  dependence.

#### •Measurement of $N_\theta/N_0$

The angular response of the detector was measured by placing a mixed radionuclide point source on a vertical quadrant of 1 m radius with 10-degree angular divisions, where the 0-degree azimuth is at the nadir point and the 90-degree represents a source at an infinite distance.  $N_\theta/N_0$  values are obtained from the relative (to 0-degree) angular responses multiplied by the partial-differential gamma fluxes.

#### •The site

The *in situ* measurement was performed in a large 300 m x 300 m flat, unobstructed, open-pit phosphate ores quarry in the Rothem plain-Negev (southern of Israel). The thickness of the phosphate ores layer was approximately 2 m, i.e. infinite in this application. Acquisition live-time was approximately 3344 s.

#### •Soil samples

Top-soil samples were collected to a depth of 5 cm at distances 0 m, 1 m, 2 m, 5 m, 10 m, and 20 m from the detector, along 3 radii in these directions: north, southeast, and southwest. In the north-4 m point, a 15 cm deep profile sampling was made with four fractions of 2.5 cm each and the inner of 5 cm. Samples were crushed, milled and dried at 105<sup>0</sup> C for 24 hours. Moisture of top-soil samples was uniform at approximately 12.4%, while the soil profile showed a linear moisture gradient of +0.62% per cm. The mean density and its standard deviation of 13 top-soil samples was 1.067±0.005 g cm<sup>-3</sup>, while at the ground-zero, north-1 and north-20, the density was 1.151,

1.135 and 1.124 g cm<sup>-3</sup>, respectively. Constant sample volumes of 200 cm<sup>3</sup> in sealed cylindrical polyethylene containers of 6.9 cm dia. and 5.35 cm height were measured after 30 days to achieve secular equilibrium of the <sup>238</sup>U progeny.

- Uranium calibrands

Uranium calibrands were prepared by blending accurately weighed amounts of certified uranium reference ores (CANMET; Energy, Mines and Resources Canada) with sodium carbonate. These reference materials were certified for <sup>226</sup>Ra and the recommended values are within 2% of the predicted, assuming secular equilibrium in the <sup>238</sup>U decay series. The blended calibrands had geometries identical to those of the soil samples and very similar densities.

- Laboratory HPGe detector

Soil samples and uranium calibrands were measured on top of the laboratory HPGe detector (Canberra) of 25.6% relative efficiency and 1.76 keV energy resolution. The gamma-ray detection efficiency of this detector was calibrated by a mixed radionuclide gamma-ray standard reference solution (see above) and by a solution of potassium carbonate (for the 1460.832 keV, 10.67% emission probability gamma-rays of <sup>40</sup>K). All calibrands had geometries identical to those of the samples and very similar densities.

### Results and discussion

Table 1 shows the radioactivity concentration values of the <sup>238</sup>U progeny, analyzed for the most abundant gamma-rays in the *in situ* spectrum. In the <sup>238</sup>U progeny, the short half-lives of <sup>234</sup>Th (24.10 d) and <sup>234m</sup>Pa (1.17 m) ensure radioactive equilibrium. Hence, the 1001.0 keV gamma-ray of <sup>234m</sup>Pa is a correct monitor for the amount of <sup>238</sup>U, although its emission probability is low. A ±10% statistical precision was associated with the count rate of this peak in the *in situ* measurement. In the 186.2 keV peak of <sup>226</sup>Ra, the unresolved 185.7 keV gamma-ray contribution of <sup>235</sup>U was subtracted. This correction was calculated by assuming a natural uranium isotopic composition and using published half-lives of <sup>235</sup>U and <sup>238</sup>U and emission probabilities of the two gamma-rays in the composite peak (Firestone, 1996). The apparent inconsistency of these results shown in Table 1 is discussed below.

Table 2 shows the radioactivity concentration values of <sup>238</sup>U in the soil samples, on a wet weight basis, as measured with the uranium calibrands. Wet weight is pertinent to *in situ* measurements, and therefore, the results of the two methods are presented on the same basis for comparison. Concentration values in Table 2 were calculated by the three most prominent gamma-ray peaks, namely 295.224, 351.932, and 609.312 keV. The unweighted mean and standard deviation of the 16 top-soil samples is 1502±95 Bq kg<sup>-1</sup>. These values are narrowly dispersed, demonstrating a uniform uranium concentration in the top-soil. Only the sample at N-20 deviates by 2.2 standard deviations from the mean. The unweighted mean of the radioactivity concentration of the soil profile is 1544±67 Bq kg<sup>-1</sup>, i.e. within one standard deviation of the top-soil samples. The decrease observed in the single concentration profile, does not permit a general conclusion.

The mean radioactivity concentration of soil samples agrees very well with the two values of the *in situ* measurement which were derived from <sup>234m</sup>Pa and <sup>226</sup>Ra which are in equilibrium and are predecessors of <sup>222</sup>Rn. The radon daughters <sup>214</sup>Pb and <sup>214</sup>Bi gave values around 1320 Bq kg<sup>-1</sup>, lower by 12% relative to the soil samples. This deficit is explained by radon emanation from the soil to the atmosphere. The radon fraction that escapes depends on the soil matrix and meteorological conditions. An error of up to 50% could be caused when processing an *in situ* measurement of <sup>214</sup>Pb and <sup>214</sup>Bi to determine <sup>238</sup>U concentration in soil. Because the emanation factor is unknown, it is recommended to analyze uranium by gamma-rays of <sup>234</sup>Th, <sup>234m</sup>Pa and <sup>235</sup>U.

An excellent (0.4%) agreement was found when radioactivity values obtained from the uranium calibrands at 609.312 keV were compared with values based on the gamma-ray detection efficiency of the laboratory detector.

The concentration of uranium in the tested phosphate ores layer can be converted from radioactivity to mass, using the factor 12347.5±6.7 Bq of <sup>238</sup>U per g of natural uranium. According to the soil samples, the concentration is 121.6±1.9 mg kg<sup>-1</sup> (st. dev. of the mean).

Table 1: Radioactivity concentration of  $^{238}\text{U}$  progeny measured *in situ*

Nuclide	E keV	$P_\gamma$ %	$N_p/A$ cps/(Bq kg <sup>-1</sup> )	A Bq kg <sup>-1</sup>
$^{226}\text{Ra}$	186.211	3.59	2.444	1587±58
$^{214}\text{Pb}$	295.224	19.3	6.356	1309±39
$^{214}\text{Pb}$	351.932	37.6	11.298	1313±39
$^{214}\text{Bi}$	609.312	46.1	10.775	1311±39
$^{234\text{m}}\text{Pa}$	1001.03	0.837	0.159	1480±160
$^{214}\text{Bi}$	1120.287	15.1	2.697	1346±42
$^{214}\text{Bi}$	1764.494	15.4	2.304	1335±42

Table 2: Radioactivity concentration of  $^{238}\text{U}$  progeny measured in soil samples

Gr. zero	N-1	N-2	N-5	N-10	N-20
1403±8	1456±9	1524±20	1412±7	1445±25	1295±36

SE-1	SE-2	SE-5	SE-10	SE-20
1618±38	1605±18	1597±21	1410±3	1505±17

SW-1	SW-2	SW-5	SW-10	SW-20
1621±10	1610±11	1494±17	1489±15	1542±20

Profile

0-2.5	2.5-5.0	5.0-7.5	7.5-10.0	10.0-15.0
1624±39	1608±18	1516±18	1495±14	1479±9

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