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RADIUM DETERMINATION IN SOIL SAMPLES USING A GAMMA-RAY COINCIDENCE SPECTROMETER

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A technique for the assay of radium by detection of coincident γ-radiation is evaluated. The sensitivity of various counting modalities is compared. The influence of finite sample size and density is discussed. Interference from other natural radioactivities is investigated and it is shown that a two channel arrangement is sufficient to take this into account.

Introduction

The ability to assay soil samples for the presence of ^{226}Ra using a procedure combining specificity and sensitivity with minimal sample preparation is desirable, if large numbers of analyses are required such as in environmental surveys. This work describes a study of an analysis method in which this aspect is stressed. The scope of the work includes both computer simulation and experimental investigation of the analysis system.

Due to the high penetrability of gamma-rays, spectroscopy involving detection of this radiation has the decided advantage that it may be used directly on relatively large unprocessed samples. This is in direct contrast to the alternative of α-ray spectroscopy, in which the very short range of the radiation necessitates chemical isolation of the radioactive species to be determined. Unfortunately, the use of gamma-ray spectroscopy in this instance is characterized by inherent limitations imposed by both background levels and possible interfering radiation from the sample. These limitations are to a large extent overcome in the technique to be described here. This technique is based on the coincidence spectrometric determination of the nuclide ^{214}Bi which is a member of the ^{226}Ra decay chain. Detection of natural levels is easily achieved and the method may be made both precise and accurate.

Description of the method

The nucleus of ^{214}Bi beta decays to ^{214}Po, the first excited state of which is located at 0.609 MeV.[1] The corresponding deexcitation γ-ray occurs with an intensity of 47%. In over 90% of those decays leading to the emission of the 0.609 MeV γ-ray, a preceding coincident γ-ray is also emitted. The high probability for the occurrence of such time correlated events is a characteristic which can be deleterious in single counter arrangements, but may be used to advantage in other configurations.

In attempting to detect low levels of activity, it is normal practice to use a source-detector geometry with as large a solid angle as possible and a detector with high intrinsic efficiency. In such cases the probability that both members of a coincident pair of gamma-rays will interact with the detector, becomes significant. When this occurs, the resultant signal is distorted and appears to arise from a single gamma-ray with energy corresponding to the sum of the energies of the coincident pair. Such an event may then not be detected in a spectrometric determination, and this results in an apparent loss of efficiency. Confining the analysis to include only correlations between no more than two members, the following expression for the efficiency may be derived,

$$\epsilon = p_l \ \epsilon_l \ \frac{\Omega}{4\pi} \left[1 - \sum_r f_{lr} \ \overline{W}_{lr}(0) \ \epsilon_r \ \frac{\Omega}{4\pi} \right]. \qquad (1)$$

where ϵ – efficiency of observing a full energy event due to γ_l, the gamma-ray of interest;
p_l – photofraction;
ϵ_l – intrinsic efficiency;
Ω – solid angle subtended by the detector.

The bracketed term represents the correction factor due to coincidence summing. In this term f_{lr} is the coincident intensity of γ_r and $W_{lr}(0)$ is the angular correlation function averaged over the detector solid angle. Physically, the second term represents the conditional probability of not detecting γ_r, when γ_l has been detected. In the limiting case of 2π geometry and unit intrinsic efficiency, this corresponds to emission of γ_r in the opposite hemisphere to that of γ_l.

Qualitatively, this limiting condition leads to the following interesting conclusion. At very high efficiency and solid angle conditions, detection of undistorted signals due to a single member of a coincident pair requires that the other member of the pair be emitted in the back direction. This member may then be also detected in coincidence in a second detector, which, again in the limit of unit intrinsic efficiency and 2π solid angle, would result in no reduction in counting rate, assuming a 100% coincidence branching. The expression for the coincidence efficiency using two identical detectors in a symmetrical arrangement along a common axis is given by

$$\epsilon_{\text{coin.}} = p\ \epsilon_l\ [\sum_r f_{lr}\ \overline{W}_{lr}(\pi)\ \epsilon_r]\ \Omega^2/16\pi^2. \tag{2}$$

In Eq. (2), $W_{lr}(\pi)$ represents the average angular correlation function for emission in opposite directions, which, due to symmetry satisfies $\overline{W}_{lr}(\pi) = \overline{W}_{lr}(0)$. This factor is always near unity, and will be neglected in what follows. If one defines an average efficiency as

$$\epsilon_{\text{ave.}} = (\sum_r f_{lr}\ \epsilon_r)/\sum_r f_{lr} \tag{3}$$

then the ratio of coincidence to single detector efficiencies may be written

$$\frac{\epsilon_{\text{coin.}}}{\epsilon} = \frac{\epsilon_{\text{ave.}}\ \dfrac{\Omega}{4\pi}\ \sum_r f_{lr}}{1 - \epsilon_{\text{ave.}}\ \dfrac{\Omega}{4\pi}\ \sum_r f_{lr}} \tag{4}$$

As mentioned previously, in cases such as ^{214}Bi, for which $\sum_r f_{lr}$ approaches unity, the ratio in Eq. (4) is also near unity for the high efficiency limit of $\epsilon_{\text{ave.}}\ \Omega/4\pi = 1/2$. While this extreme case is not reached in practice, the fact remains that because of the summing effect, the efficiency for coincidence detection relative to that for detection of the single gamma-ray may be higher than would appear at first sight.

There are two main advantages to using coincidence spectrometry analysis. Firstly, the coincidence condition tends to discriminate preferentially against the room background. Note that as evident from Eq. (2), the coincidence efficiency depends upon the detector solid angle subtended at the source to the second order. Thus cascade radiation emitted from remote points in the room is detected with very small probability. A fact not evident from Eq. (2) is that cascade radiation originating outside the detector shielding will be attenuated by a factor, which is the product of the attenuation factors for each member of the cascade pair. This effect also mitigates against detection of background radiation.

The second advantage to the use of coincidence spectrometry in the present application is the relative insensitivity of the method to ^{40}K, the dominant soil activity. The decay of this radioisotope is characterized by the emission of a single γ-ray at 1.46 MeV and hence there is no coincident pair present. It might be argued that the single gamma-ray system is sufficient in this respect because the energy (0.609 MeV) of the ^{214}Bi is so different from that of ^{40}K. It should be remembered, however, that Compton scattering in the sample and the response function of the NaI spectrometer both lead to an enhancement of low energy events.

On the basis of these considerations it was decided to study a method for analysis of ^{214}Bi using a high efficiency coincidence spectrometer consisting of two large NaI(Tl) detectors. Since it is necessary to use samples with dimensions comparable to the size of the detector, a numerical analysis of the effects of finite sample size was also performed.

Experimental

The spectrometer consisted of two 12.5 cm high × 12.5 cm diameter NaI(Tl) detectors arranged along a common axis. The detectors were shielded by an annulus of lead 5 cm thick which extended the length of the two detectors, and enclosed the photomultiplier bases. An additional 2.5 cm thick annulus of lead surrounded each crystal section of the detector. Finally, a split annulues of lead 1 cm thick with an inner diameter of 9 cm was positioned between the detector faces. Specially selected low background lead was not obtained for this arrangement.

The anode pulse from each detector was integrated with a charge sensitive preamplifier and further processed in a double delay line linear amplifier. The time of occurrence was marked by the zero crossing point of the amplifier output pulse. These timing markers were coupled to a coincidence circuit having a 0.3 μsec resolving time. Pulse height range restrictions were imposed with timing single channel analyzers. The coincident pulse height spectrum in one detector was recorded in a gated multichannel analyzer.

Samples were packed into cylindrical plexiglass containers 9 cm in diameter and 1.5 cm thick, corresponding to a sample volume of 95 cm^3. These were then sealed with a parafilm cover and left for counting. In practice, if radon is emanating from the sample in significant amounts, it would be necessary to store the sealed samples for approximately one month to restore equilibrium.

Because of the large dimensions it was necessary to prepare a transfer standard to calibrate the system. Powdered (Beaver Lodge, Saskatchewan) uranium ore was packed into a standard container. In a separate experiment, a small sample of this ore was counted in a standard geometry using a 7.5 cm X 7.5 cm diameter NaI(Tl) spectrometer. This spectrometer was in turn calibrated using a 0.1 μCi radium standard obtained from the National Bureau of Standards, Washington, D.C.

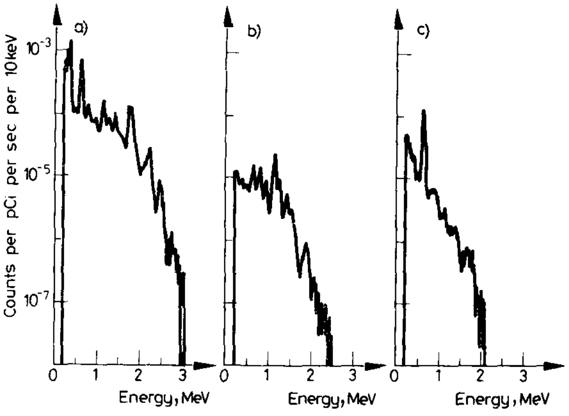

Fig. 1. Here A shows single counter spectrum for ^{226}Ra sample, B the coincidence spectrum with second counter selecting 609 keV gamma-ray, and C the coincidence spectrum with second counter selecting all photoms above 609 keV

In Fig. 1 is shown spectra recorded for a ^{226}Ra sample under a range of electronically imposed conditions. For convenience, the intensity is given as counts per pCi of ^{226}Ra per second of counting for a 10 keV energy window. Section A shows the spectrum obtained with a single counter. The components visible in the energy range from 200 to 400 keV arise from the decay of ^{214}Pb while virtually all the intensity above 500 keV is attributable to decay of ^{214}Bi. The inclusion of a second detector set to respond to events corresponding to the 609 keV gamma-ray as well as the imposition of a coincidence condition gave rise to the spectrum shown in B. The final spectrum, C, was acquired under a coincidence arrangement in which the second detector responded to all events of energy greater than 609 keV. The strong coincidence feed to the first state in ^{214}Po is clearly evidenced by the intense component at 609 keV.

Results and calculations

The first aspect to be investigated was that of optimum sample thickness. For a uniform sample, the total activity increases linearly with sample thickness. This gain is offset by two factors. The increased sample thickness requires a corresponding increase in inter-crystal spacing which is accompanied by a decrease in efficiency. In addition, the detection sensitivity decreases with sample thickness because of the resultant increase in self absorption of the radiation. The latter is dependant upon the sample density and interaction cross-section. For the geometry illustrated in Fig. 2, and a sample of volume V, and activity concentration p, the coincidence rate is given by

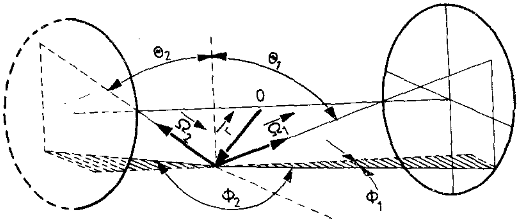

Fig. 2. Geometry arrangement used to compute spectrometer efficiency

$$R_{\text{coin.}} = \frac{p\,\epsilon_l\,p}{16\pi^2} \sum_r f_{lr}\,\epsilon_{lr} \int_V \int_{\Omega_1(\vec{r})} \int_{\Omega_2(\vec{r})} e^{-F_r(\vec{\Omega}_1,\vec{\Omega}_2,\vec{r})}\,d\Omega\,d\Omega_2\,d^3\vec{r}. \quad (5)$$

In Eq. (5) $\Omega_1(\vec{r})$ and $\Omega_2(\vec{r})$ represent the solid angles subtended by each detector at source point $\vec{r}$, $\vec{\Omega}_i = (\Theta_i, \Phi_i)$, the polar angles with respect to the system axis and

$$F_r(\vec{\Omega}_1, \vec{\Omega}_2, \vec{r}) = \mu_l l_1(\vec{\Omega}_1, \vec{r}) + \mu_r l_2(\vec{\Omega}_r, \vec{r}). \quad (6)$$

In the above expression μ_l, μ_r are the linear attenuation coefficients for gamma-ray pairs γ_l and γ_r, respectively, and $l_1(\vec{\Omega}_1, \vec{r})$, $l_2(\vec{\Omega}_2, \vec{r})$ are the path lengths to the detector face from source point $\vec{r}$ along directions $\vec{\Omega}_1$, $\vec{\Omega}_2$, respectively. Eq. (5) was integrated numerically for various sample densities and thicknesses, taking the coincident pair to have energies of 0.6 and 1.6 MeV. The latter is the average energy of the ^{214}Bi spectrum in coincidence with the 0.609 MeV γ-ray. The photon cross-sections for representative soil and for the energies of concern here are dominated by the Compton process.

The results of the calculation are shown in Fig. 3. Section A shows how count rate varies with sample thickness for a range of densities when the activity per unit volume in constant. In Eq. (5) the approximation is made that the intrinsic efficiency is independent of source position. This is related to the Laplace transform of the chord distribution through the detector and should be fairly insensitive to position for sample diameters, which are not too large with respect to the detector diameter. The ratio of sample to detector diameter of 0.7 used here should permit this approximation to be used. Also shown in the figure is the relationship between optimum thickness and density. Loci of thicknesses which are 90% of the modal value are also shown. To provide near optimum efficiency for densities between 0.8 and 2.5 the thickness should be about 2.5 cm. The relationship between thickness and efficiency was verified through use of a uranium bearing sand having $\rho = 2.5$ g/cm^3 packaged in containers of varying thickness.

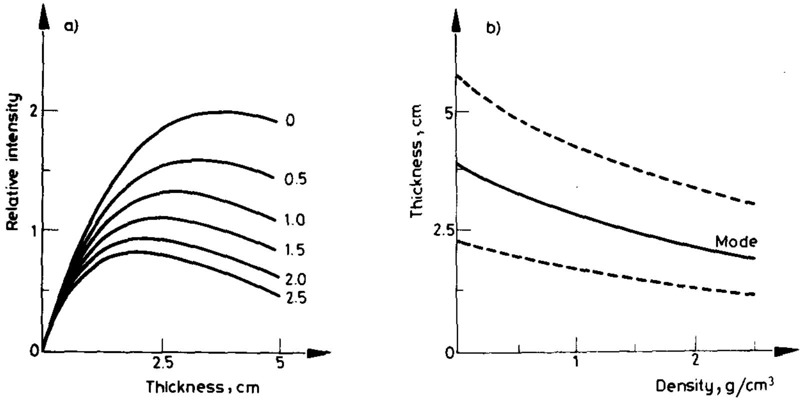

Fig. 3. In A is shown the relative intensity observed as a function of inter-detector spacing. Curves are given for a range of densities. Part B indicates the modal value dependance on density. Here the dashed lines are 90% of the mode

The degree with which sample inhomogeneity affects the precision of a measurement is dependent upon the dispersion of efficiency within the sample volume. When counting several samples obtained from a common material, one can show that in general the sampling itself produces variations which mask this effect. However, this variation in efficiency with position does become important when one

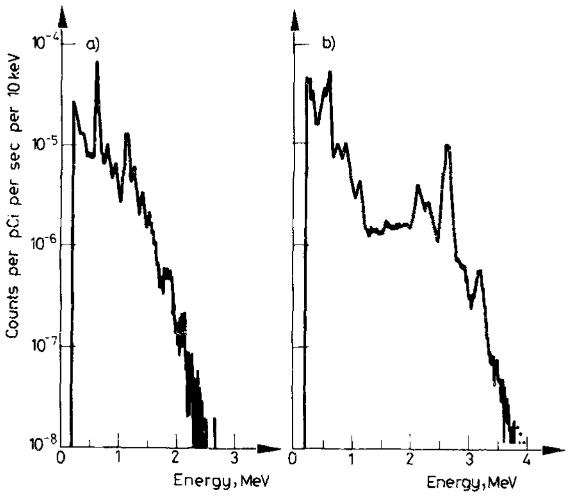

Fig. 4. Coincidence spectra with second counter selecting photons above 540 keV where A is the spectrum for ^{226}Ra, and B that for ^{232}Th

repacks and recounts a given sample. For a volume containing N sources of equal radiation strength the relative error is given by

$$\frac{\sigma_M}{M} = \sqrt{\frac{1}{M} + \frac{\sigma_\epsilon^2}{\epsilon^2}\,\frac{1}{N}} \qquad (7)$$

where M is the recorded number of counts. For the geometry used the value $(\sigma_{\epsilon/\epsilon})^2$ is $6.5 \cdot 10^{-2}$ for a single counter and $3.9 \cdot 10^{-3}$ for a coincidence arrangement. This translates to a much higher tolerance to inhomogeneity for the latter type of spectrometer.

The sensitivity and precision attainable with the spectrometer were investigated for a variety of modes of operation. These included (1) as a single counter, (2) as a coincidence spectrometer with one channel selecting an energy interval about 600 keV and the other, all events above 540 keV, and (3) as a coincidence spectrometer with both channels selecting all events greater than 540 keV. Typical spectra for radium and thorium obtained with the latter configuration are shown in Fig. 4.

The sensitivity or detection limit associated with counting experiments has been examined by CURRIE[2] and DONN and WOLKE.[3] These authors restricted themselves to the case of a single class of experiment and one in which the background was not sample dependent. Here we wish to explore various operating modes, to consider the effect of background and to quantify the degree of interference produced by ^{40}K.

Applying standard hypothesis testing criteria to the case of a counting experiment for which a background component is present, one can evaluate the effectiveness of various counting strategies. If a change in experimental conditions is made and if the counting rate for a standard sample is decreased by the efficiency factor η, it can be shown that sensitivity is retained provided that the background rate is reduced by $\eta^2 f$ where $f \leqslant 1$. Table 1 summarizes the values found for η and the background suppression factor f using different experimental arrangements for samples of radium, thorium and potassium. Since standards were used the figures given are for a 95 cm^3 volume, a density of 2.1, and for radium and thorium, concentrations of 1 pCi/g. The data for potassium has been normalized to 1% by weight.

The results presented in Table 1 clearly indicate that for ^{226}Ra sensitivity is retained by use of a coincidence configuration as alluded to in the introduction. The f value found for a thorium sample reveals that the decay scheme for daughters of ^{232}Th are not as ideal as for the daughters of ^{226}Ra. As might be expected the efficiency for detection of ^{40}K is markedly decreased when coincidence conditions are imposed.

Precision associated with different strategies can be formulated in a way not dissimilar from that for sensitivity. Performing such an analysis reveals that precision can be retained if

$$f \leqslant 1 - (1 - \eta) \frac{S}{\eta B},$$

where S/B is the signal to background rate ratio. Thus f must be less than unity if there is to be no loss in precision for a given counting time. In Table 1 the ratio of the relative error for a given experimental arrangement to that for the single counter, is presented for the cases examined. The relative precisions are for concentrations of 1 pCi/g. For the ^{226}Ra the double window condition $540 < E_\gamma < 2500$ keV very nearly retains the sensitivity and precision of the single counter at this level of concentration.

The question of accuracy becomes important for samples of low activity. Here reasonable counting times do not allow the acquisition of high precision spectra which would be amenable to detailed fitting techniques. The potassium content for soils ranges from 0.1 to 3%. Table 1 shows the contribution from potassium at a typical 1% level. Using a single counter the events from the decay of ^{40}K

Table 1
Summary of counting rate results under various experimental conditions

Experimental conditions, keV	Sample rate, cps	Background rate, cps	Efficiency*, η	Suppression**, f	Relative precision***
Sample: ^{226}Ra, 200 g at concentration of 1 pCi/g					
$540 < E < 2500$	1.53	7.42	1		1
$(590 < E < 630) \cdot (540 < E < 2500)$	0.086	0.020	0.056	0.86	1.76
$(540 < E < 2500) \cdot (540 < E < 2500)$	0.187	0.129	0.122	1.17	1.23
$(590 < E < 630) \cdot (1100 < E < 1200)$	0.027	0.0019	0.0175	0.85	2.79
Sample: ^{232}Th, 200 g at concentration of 1 pCi/g					
$540 < E < 3500$	2.71	7.76	1		1
$(560 < E < 620) \cdot (540 < E < 3400)$	0.052	0.021	0.019	7.48	3.71
$(540 < E < 3400) \cdot (540 < E < 3400)$	0.231	0.140	0.086	2.47	1.78
$(540 < E < 1620) \cdot (2500 < E < 2800)$	0.030	$3.7 \cdot 10^{-3}$	0.011	3.92	4.85
Sample: Potassium, 200 g with 1% potassium					
$540 < E < 2500$	0.95	7.42	1		
$(590 < E < 630) \cdot (5400 < E < 2500)$	$1.3 \cdot 10^{-4}$	0.020	$1.4 \cdot 10^{-4}$	$1.5 \cdot 10^{5}$	28.8
$(540 < E < 2500) \cdot (540 < E < 2500)$	$2.9 \cdot 10^{-4}$	0.129	$3.0 \cdot 10^{-4}$	$1.9 \cdot 10^{5}$	20.7

*Counting efficiency for sample compared with rate for single counter.

**Sensitivity is retained if $f \leqslant 1$.

***Precision compared to single counter at concentration of 1 pCi/g.

can easily exceed the ^{226}Ra contribution at the 1 pCi/g level. However under coincidence conditions, the presence of potassium can be ignored.

The suppression of any significant contribution to a measurement from potassium in the sample when the coincidence mode is used, permits one confidence in assays for which the accumulated counts do not allow spectral analysis. However, one must still account for the presence of thorium and its daughters. At base level one must face the fact that the abundance of thorium is usually four times that of uranium. This would lead to equal activities and from Table 1 one sees that the number of coincidence events from each chain would be very nearly equal. For low level measurements detailed spectral analysis is rather ineffective. Instead one may divide the spectral record into two regions and by so doing, infer the intensity of each component. The effectiveness with which this may be done is dependent upon the degree of difference which exists between the two spectral components. The choice of the division point can be ascertained by using least squares and error analysis in conjunction with the spectra obtained for ^{226}Ra and thorium standards such as shown in Fig. 4. Resolution, detector efficiency and sample size all feature in the outcome of such measurements. For our case, for a binary division the associated error was a minimum if the spectrum was separated at 1750 keV. For equal activities of each component the statistical error is increased by a factor of 1.4.

Conclusions

This study indicates that a coincidence spectrometric determination of ^{214}Bi provides an excellent method to assay soil samples for ^{226}Ra, and that levels in the range normally expected may be detected routinely. The advantages of the method are the minimal sample handling, the circumvention of uncertainty in radon removal characteristic of alpha detection systems,[4] and the potential for automation.

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References

1. C. M. LEDERER et al., Table of Isotopes, J. WILEY, New York, 1968.
2. L. A. CURRIE, Anal. Chem., 40 (1968) 586.
3. J. J. DONN, R. L. WOLKE, Health Phys., 32 (1977) 1.
4. W.'R. SUTTON, N. M. SOONAWALA, Can. Min. Met. Bull., 68 (1975) 1.