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ABSTRACT

The Radiological Survey Activities (RASA) Group of the Health and Safety Research Division at Oak Ridge National Laboratory (ORNL) is an Inclusion Survey Contractor (ISC) for the Uranium Mill Tailings Remedial Action Program (UMTRAP). The purpose of the ISC is to survey designated sites potentially contaminated with radioactive material originating from the 24 inactive uranium mill sites and make recommendations as to whether the site should be included in or excluded from further consideration by UMTRAP. An important aspect of the program is a prompt and inexpensive estimation of Radium-226 (^{226}Ra) concentration in soil samples. A large sodium iodide (NaI) well crystal coupled to a multichannel analyzer is used to count soil samples. Count data are currently analyzed with an algorithm that utilizes three regions of interest (ROI). A lack of agreement was observed when samples were also analyzed with lithium-drifted germanium (GeLi) spectrometers. The average estimate of ^{226}Ra obtained using the current algorithm was 19% greater than the GeLi determination. Some possible reasons for these differences were examined. In 8.5% of the samples, the relative concentration of Cesium-137 (^{137}Cs) was highly correlated to the extent of error. Using alternative analysis techniques, the error for ^{226}Ra estimations may be reduced by a factor of 2 for randomly selected samples and by a factor of 4 for samples containing high concentrations of ^{137}Cs relative to the concentrations of ^{226}Ra.

INTRODUCTION

Public Law 95-604, the Uranium Mill Tailings Radiation Control Act of 1978, requires the Federal government to perform remedial action on 24 inactive uranium mill tailings sites and their associated vicinity properties. In accordance with standards recommended by the Environmental Protection Agency (EPA), a property contaminated by mill tailings may be included in UMTRAP if the concentration of ^{226}Ra in land averaged over any area 100 m^2 exceeds 5 pCi/g above background averaged over the first 15 cm of soil below the surface or 15 pCi/g above background averaged over 15 cm thick layers of soil more than 15 cm below the surface (1).

Soil samples taken during inclusion surveys performed by the RASA Group of the Grand Junction Office of ORNL are analyzed for ^{226}Ra using a NaI counting system. In a group of 1500 randomly selected soil sample analyses reviewed, 8.5% were denoted as "Cs-flagged." Such a flagged sample was indicative of analytical interferences due to the presence of additional radionuclides in the soil, thus resulting in false overestimations of ^{226}Ra content. The radionuclides considered were ^{137}Cs due to global fallout as well as naturally-occurring Potassium-40 (^{40}K) and Thorium-232 (^{232}TH).

This paper addresses the limitations of the currently used algorithm that utilizes three ROI, and three alternative methods that reduced the error inherent in that algorithm.

SAMPLING AND PREPARATION PROCEDURES

During a radiological survey, soil sampling is required if a property is not included based on sufficiently elevated indoor or outdoor gamma exposure rates. Soil sampling and preparation procedures are described in detail in the RASA/UMTRA Procedures Manual (2). Generally, a surface soil sample, 0-15 cm in depth, is taken at a background location. If necessary, surface and subsurface samples are taken at the highest outdoor gamma location. Additional samples may be taken to further characterize the extent of on-site contamination. Soil is removed with a post-hole digger, mixed for homogeneity, and a sample of approximately 500 g is deposited into an aluminum pan.

Soil samples are oven dried at 43° C for a minimum of twelve hours. Dried samples are subsequently crushed to a maximum particle size of 0.6 cm^3 and placed in 0.5 L plastic jars to a specified fill level (approximately 400 cm^3). Net weights of the samples are recorded; then the jars are sealed with tape to prevent the escape of radon. Samples are stored for at least twelve days prior to analysis to allow for ingrowth of radon progeny.

COUNTING SYSTEM

Three sodium iodide-thallium activated crystals 15 cm by 23 cm in size with 8.3 cm by 8.9 cm wells are surrounded by copper and cadmium liners and housed in 8 cm thick "pickle barrel" lead shields. The crystals are coupled to an ND-66 multichannel analyzer via an ORTEC #113 pre-amplifier, ORTEC #490B linear amplifier, and ND-575 analog to digital converter. High voltage is supplied by an ORTEC #456 power supply. The ND-66 is interfaced with an IBM microcomputer and line printer.

Gross count data are acquired in 512 channels calibrated at approximately 6 keV/channel. Data for background, standards and soil samples are acquired for five minutes in the ND-66 spectral display groups. A computer program written in BASIC transfers data from the ND-66 to floppy disks from which ^{226}Ra concentration estimations are determined. Uncertainty is based solely on counting statistics.

ANALYTICAL METHODS

Concentrations of ^{226}Ra, ^{137}Cs, ^{40}K, and ^{232}Th in randomly selected soil samples were determined by the ORNL RASA Group using GeLi spectrometers that had been calibrated with an NBS standard. A group of samples was also analyzed by Bendix Field Engineering Corporation in Grand Junction, Colorado using GeLi spectrometers for the purpose of quality assurance. The comparison between these two GeLi analyses was satisfactory although the ^{226}Ra concentrations averaged about 10% higher than ORNL GeLi determinations.

The algorithm currently used to obtain estimations of ^{226}Ra from NaI spectra is based on the addition of net counts in three ROI (3ROI method). ROI1, ROI2, and ROI3 correspond to Bismuth-214 (^{214}Bi) gamma energies of 609 keV, 1120 keV, and 1764 keV, respectively. These three ROI are demarcated on the NaI spectrum of a ^{226}Ra reference in Figure 1. Table 1 contains a summary of NaI spectral groups which indicates the lower and upper limit energy levels (at approximately 6 keV/channel) for each ROI utilized by the 3ROI method and the three alternative methods referred to as THS, RAK, and WESTON.

For the 3ROI method, a value of (cpm/g) is determined using the following formula:

$$\text{cpm/g} = \frac{(\text{ROI1} + \text{ROI2} + \text{ROI3})}{\text{weight(g)} \times \text{time(min)}} \tag{1}$$

This value (cpm/g) is inserted into an equation which ultimately yields an estimation of ^{226}Ra concentration in pCi/g. The method was developed by ORNL based on GeLi and NaI data (3). The average ratio value for ROI2/ROI1 was established to be 0.41. Since some of the counts in ROI1 can be contributed by the Barium-137m gamma from ^{137}Cs at 662 keV, the sample analysis is flagged for possible ^{137}Cs contamination if the ratio value is less than 0.41. These samples will be referred to henceforth as "Cs-flagged".

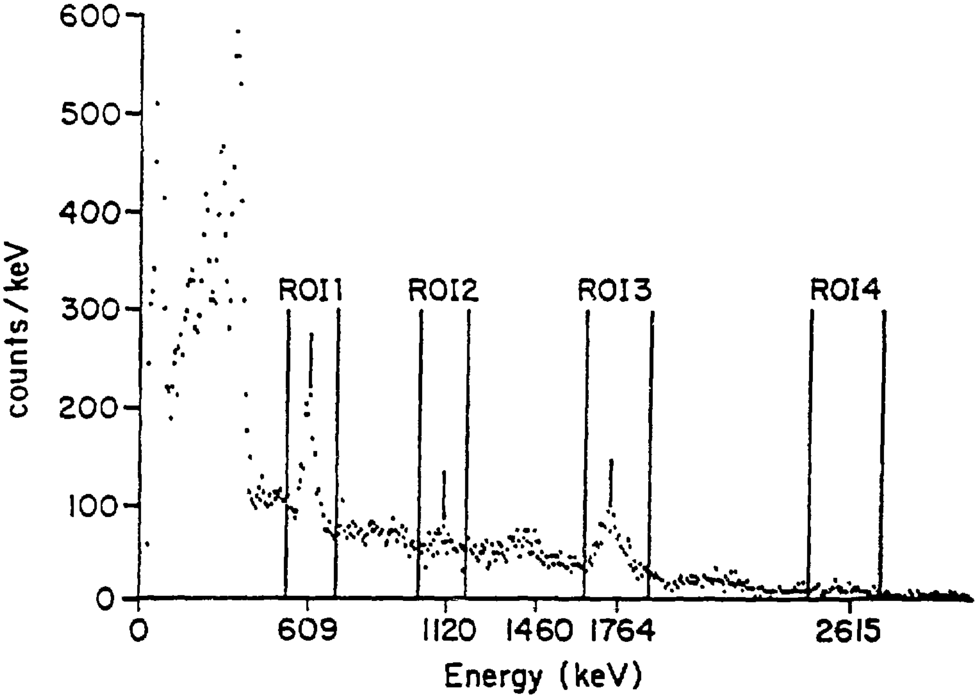

Fig. 1. NaI differential spectrum of ^{226}Ra reference (5.1 pCi/g).

Table 1. Lower and upper channel numbers which correspond to energy levels (approximately 6 keV/channel) of each ROI used for the four NaI analytical methods. The ROI utilized by each method are indicated

Method	ROI1 90-120 (channel)	ROI2 170-200 (channel)	ROI3 274-314 (channel)	ROI3′ 274-413 (channel)	ROI4 410-455 (channel)	ROI4′ 426-455 (channel)	ROI4′′ 427-512 (channel)
3RO1	X	X	X				
THS			X		X		
RAK			X			X	
WESTON				X			X

The study undertaken during the summer of 1985 involved re-analysis of randomly selected soil samples in an effort to reduce the disagreement in ^{226}Ra estimations using the three ROI method compared with GeLi results. The three alternative analytical methods did not utilize ROI1 and ROI2 because of the probable interference of ^{137}Cs and ^{40}K in environmental soil sample analyses. An attempt was also made to eliminate the effect of ^{232}Th on ^{226}Ra estimations.

One alternative analysis was a simple ^{232}Th-stripping algorithm that utilized ^{226}Ra and ^{232}Th reference materials supplied by the Technical Measurements Center of the U.S. Department of Energy (4,5). This method, THS, used net counts in ROI3 and ROI4: ROI3 corresponds to the 1764 keV ^{214}Bi gamma from ^{226}Ra, and ROI4 to the 2615 keV Thallium-208 (^{208}Tl) gamma from ^{232}Th (6). In Figure 2, ROI3 and ROI4 are demarcated on the NaI spectrum of the ^{232}Th reference. The counts in ROI3 due to the presence of ^{232}Th were presumed to be eliminated by subtraction of the counts that appeared in ROI3. The fraction determined was unique to this counting system at this location. The following formula was implemented:

$$^{226}\text{Ra(pCi/g)} = \frac{\text{N(sample)}}{\text{N(}^{226}\text{Ra ref)}} \times \frac{\text{Wt(}^{226}\text{Ra ref)}}{\text{Wt(sample)}} \times \text{pCi/g(}^{226}\text{Ra ref)} \qquad (2)$$

$$\text{where:} \quad N = \left[\text{ROI3} - (0.818 \times \text{ROI4})\right]$$

Further investigation warranted a revision of the THS method. Essentially, the RAK method was the same as THS except that ROI4 was reduced in size to eliminate counts from two low-yield photons with energies of 2204 keV and 2447 keV from ^{214}Bi. RO14′ is demarcated on Figure 3. This modification dramatically improved the estimate of the contribution from ^{232}Th into ROI3. The following formula was used for the RAK method:

$$^{226}\text{Ra(pCi/g)} = \frac{\text{N(sample)}}{\text{N(}^{226}\text{Ra ref)}} \times \frac{\text{Wt(}^{226}\text{Ra ref)}}{\text{Wt(sample)}} \times \text{pCi/g(}^{226}\text{Ra ref)} \qquad (3)$$

$$\text{where:} \quad N = \left[\text{ROI3} - (1.1 \times \text{ROI4}')\right]$$

The WESTON analysis uses a complex routine to strip ^{232}Th. ROI4 was enlarged to include not only the 2615 keV ^{208}Tl peak, but also counts contributed by Compton scattering from ^{208}Tl sum peaks. ROI3′ was an enlargement of ROI3 that encompassed the low-yield ^{214}Bi peaks. Additional computations were performed. The ^{226}Ra contribution to ROI4′′ was determined, and the fraction of those that appeared in ROI3′ were subtracted from ROI3′ (7).

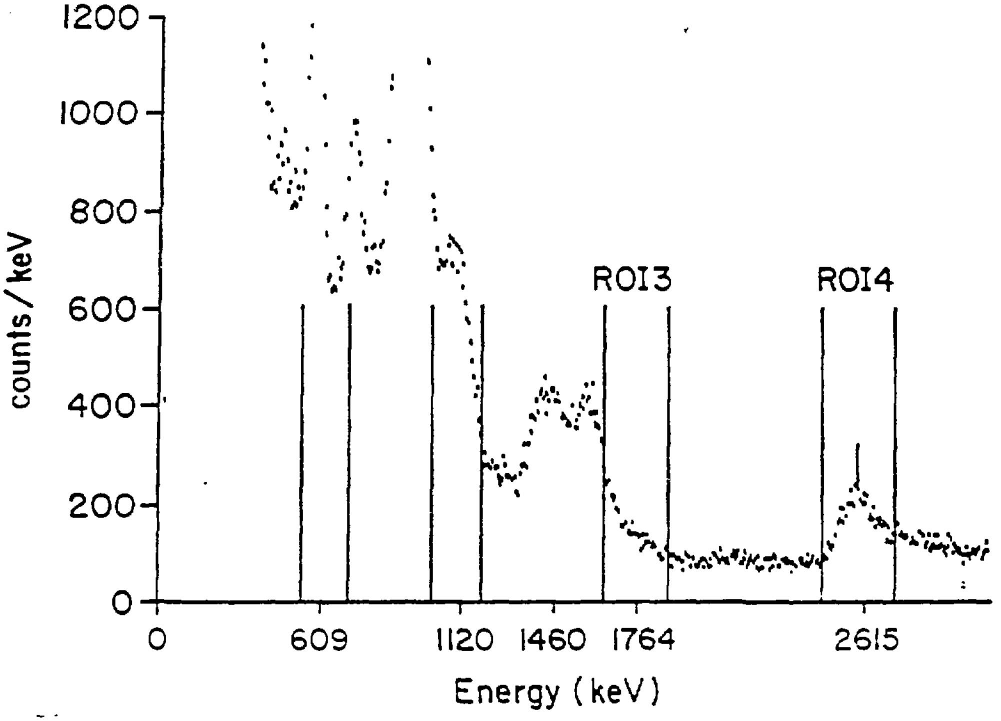

Fig. 2. NaI differential spectrum of ^{232}Th reference(70.2 pCi/g).

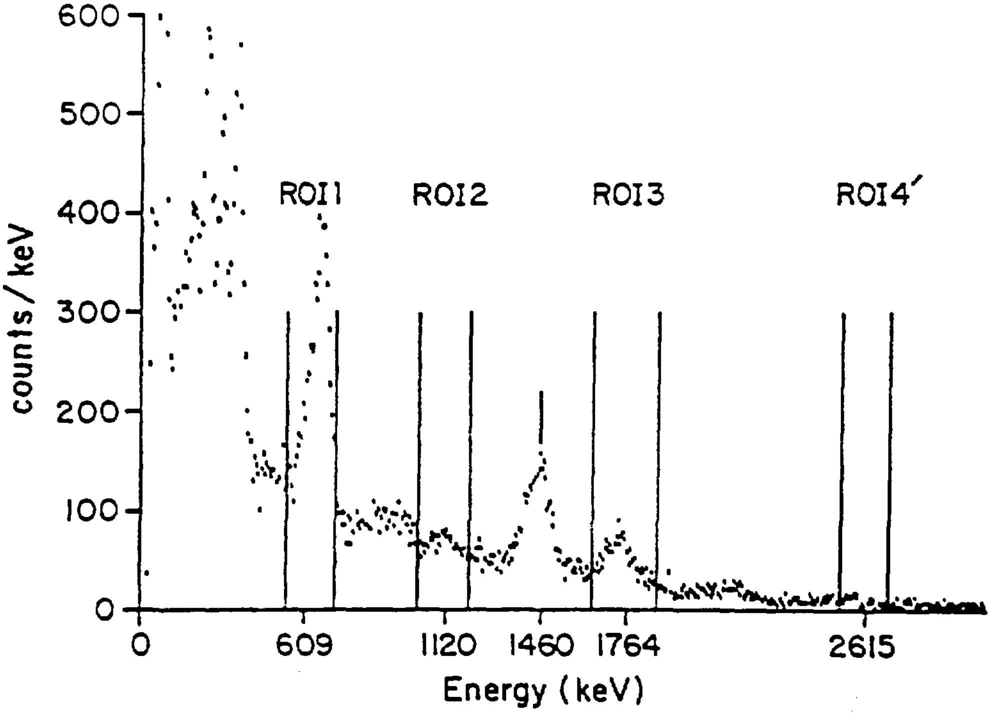

Fig. 3. NaI differential spectrum of "Cs-flagged" soil sample containing: ^{226}Ra(4.1 pCi/g), ^{137}Cs(2.6 pCi/g), ^{40}K(23 pCi/g), and ^{232}Th(0.81 pCi/g).

RESULTS AND DISCUSSION

A group of 64 samples that had previously been analyzed using the ORNL GeLi spectrometers was also analyzed for ^{226}Ra using the 3ROI method and the three alternative analysis methods: THS, RAK, and WESTON. In order to assess the error for ^{226}Ra concentration estimations using the various NaI methods, the results were compared with ^{226}Ra concentrations determined by GeLi analysis. The % difference for each ^{226}Ra estimation from the GeLi concentration was calculated in the following manner:

$$\% \text{ Difference} = \left(\frac{\text{NaI estimation} - \text{GeLi determination}}{\text{GeLi determination}}\right) \times 100 \qquad (4)$$

Figure 4 contains box plots depicting the distribution of the % differences between NaI ^{226}Ra estimations and GeLi determinations for both groups of 64 randomly selected and 64 "Cs-flagged" soil samples. In a box plot, the spread of the bulk of the data (the central 50%) is seen as the length of the box. The median is portrayed by a horizontal line segment within the rectangle. Vertical lines extend from the ends of the box to adjacent values. The upper adjacent value is defined as the observed value that is less than or equal to the upper value of the box plus 1.5 times the range of values defined by the box. The lower adjacent value is defined similarly for values falling below the box. Outside values, which fall beyond the adjacent values, are plotted as individual points (8).

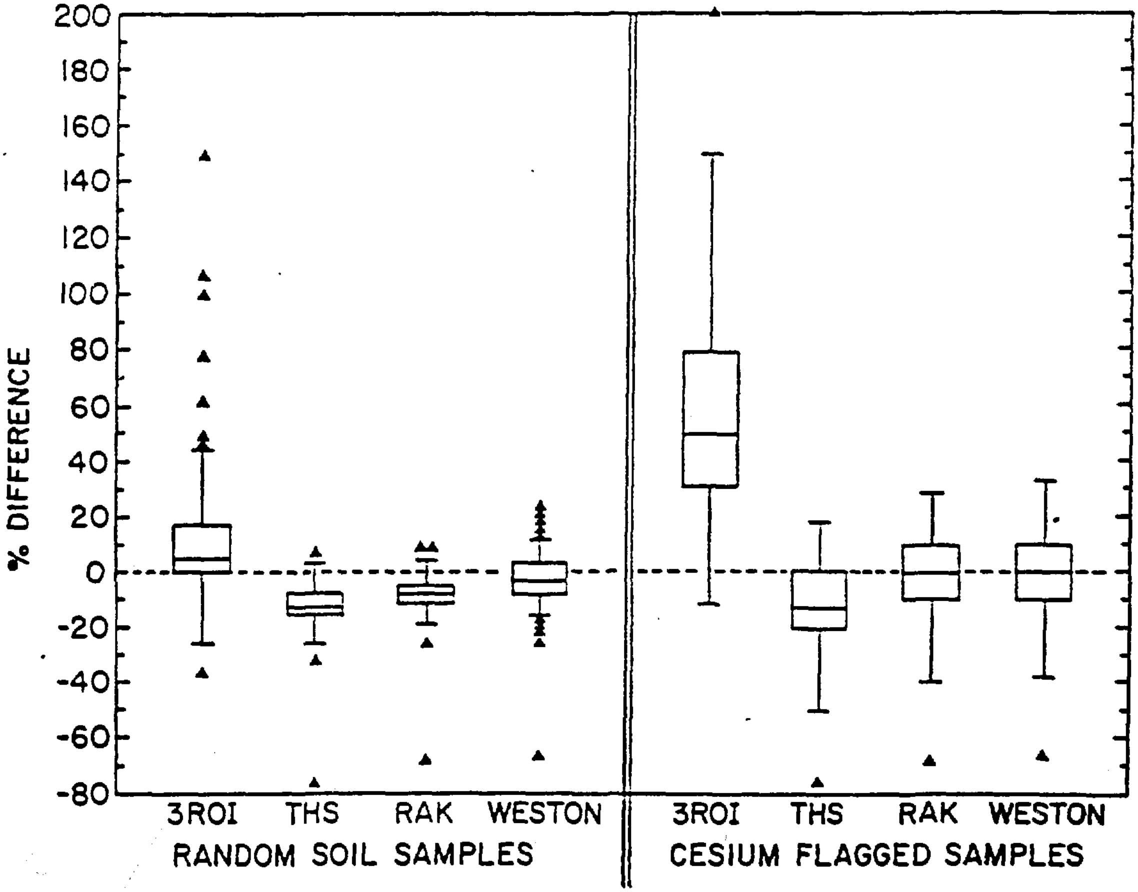

Fig. 4. Box plots showing the distribution of the % difference between estimates of ^{226}Ra in soil using NaI analysis techniques and Geli determinations.

All four NaI methods resulted in estimations of ^{226}Ra which were in fairly good agreement with GeLi determinations for random samples. Excluding outside values, the range of errors for the 3ROI method was 70% compared with about 26% for the three alternative methods. The median value for the 3ROI method corresponds to an overestimate of 5%, while the other algorithms yielded a value corresponding to an underestimate of ^{226}Ra. It should be noted that 6 of 25 outside values indicated on the box plots for random soil samples were for "Cs-flagged" samples in that group.

The ranges of % differences for "Cs-flagged" samples were more than twice as large as those for randomly selected samples. Nearly all of the estimates of ^{226}Ra concentration using the 3ROI method were substantially higher than the GeLi determinations. The THS method yielded underestimations that averaged 12% lower than corresponding GeLi results. Analyses using the RAK and WESTON methods resulted in estimations of ^{226}Ra which were in excellent agreement with GeLi determinations; 50% of the estimations were within 10% of the ^{226}Ra concentrations determined by GeLi analysis.

In order to determine if the errors in ^{226}Ra concentrations using the four NaI analytical methods were directly related to the concentrations of additional radionuclides present in the soil samples, correlation coefficients were computed for the % difference and the concentration ratios of (^{226}Ra/^{137}Cs), (^{226}Ra/^{40}K), and (^{226}Ra/^{232}Th). The use of a correlation coefficient implies that there is an association between two variables, however, it is not a cause and effect relationship. When dealing with multiple variables, the correlation coefficient between any two might be low, nevertheless, the correlation could be both appreciable and significant. Table 2 contains a summary of correlation coefficients for a group of 15 random samples and 15 samples that were "Cs-flagged". Confidence in the correlation coefficients can be determined using r_{test} values. If the correlation coefficient is greater than the r_{test} value, one can be certain (to the degree selected) that the calculated correlation coefficient was not due to chance alone (9). Table 3 contains applicable r_{test} values.

Table 2. Correlation coefficients (r values) calculated for % differences of NaI ^{226}Ra concentration estimations from GeLi ^{226}Ra concentration determinations and soil sample concentration ratios of (^{226}Ra/^{137}Cs), (^{226}Ra/^{40}K), and (^{226}Ra/^{232}Th)

Sample Group	Concentration Ratio	3ROI (r)	THS (r)	RAK (r)	**WESTON (r)**
Random	(^{226}Ra/^{137}Cs)	-0.199	-0.0170	-0.0580	**-0.134**
Random	(^{226}Ra/^{40}K)	-0.453	-0.195	-0.431	**-0.359**
Random	(^{226}Ra/^{232}Th)	-0.480	-0.0910	-0.359	**-0.309**
"Cs-flagged"	(^{226}Ra/^{137}Cs)	-0.957	-0.342	-0.517	**-0.428**
"Cs-flagged"	(^{226}Ra/^{40}K)	-0.275	0.143	-0.179	**-0.0886**
"Cs-flagged"	(^{226}Ra/^{232}Th)	-0.126	0.288	0.00469	**0.171**

Table 3. Correlation coefficient test values (r_{test}) that may be compared with r values to establish the degree of certainty with which positive or negative correlation coefficients may be due to chance alone

certainty (80%)	certainty (90%)	certainty (95%)	certainty (99%)	certainty (99.5%)
0.351	0.441	0.514	0.641	0.760

There was no significant correlation between % error and relative concentration of ^{137}Cs for randomly selected soil samples using any analytical method. With 90% certainty, a negative correlation existed between 3ROI error and the relative concentrations of ^{40}K and ^{232}Th. With a lesser degree of certainty (80%), the % differences correlated with ratios of (^{226}Ra/^{40}K) and (^{226}Ra/^{232}Th) for the RAK method. Similarly, there was a negative correlation between WESTON error and the ratio of (^{226}Ra/^{40}K), but not with (^{226}Ra/^{232}Th). With exception to the THS method, approximately 16% of the % differences for the estimations of ^{226}Ra could be described by correlations with the relative concentrations of ^{40}K or ^{232}Th present.

The % differences and relative concentrations of ^{137}Cs were negatively correlated with nearly 100% certainty for "Cs-flagged" samples analyzed using the 3ROI method, and to lesser degrees using alternative methods. About 90% of the ^{226}Ra estimations determined by the 3ROI method in "Cs-flagged" samples were directly influenced by relative concentrations of ^{137}Cs. Less than 20% of the estimations using the alternative methods were influenced by the presence of ^{137}Cs.

There were no significant correlations between % differences and relative concentrations of ^{40}K and ^{232}Th in "Cs-flagged" samples, although approximately 8% of soil samples analyzed using the 3ROI and THS methods have errors which may be described by the concentration ratios of (^{226}Ra/^{40}K) and (^{222}Ra/^{232}Th), respectively.

Figures 1-3 provide illustration of the possible effects of ^{137}Cs, ^{40}K, and ^{232}Th on ^{226}Ra concentration determinations. When comparing Figure 3 (spectrum of "Cs-flagged" soil sample containing 4.1 pCi/g of ^{226}Ra) to Figure 1 (spectrum of reference containing 5.1 pCi/g of ^{226}Ra), it may be observed that not only is the peak in ROI1 about twice as tall, but also it is skewed to the right. Those phenomena are mostly due to the presence of ^{137}Cs in the soil sample. However, the baseline shift evident on Figure 3 as compared with Figure 1 is mainly due to the presence of ^{40}K in the sample. Figure 2 (^{232}Th reference spectrum) shows that ^{232}Th does indeed contribute counts to lower energy ROI. Utilization of the 3ROI method may therefore erroneously attribute count contributions to ^{226}Ra which are actually due to ^{40}K, ^{232}Th, and especially ^{137}Cs.

SUMMARY

Soil samples collected during radiological surveys performed for the RASA/UMTRA Project were analyzed for ^{226}Ra using NaI spectrometers. Of 1500 randomly selected analyses determined by the currently used 3ROI algorithm, 8.5% were flagged for possible ^{137}Cs contamination ("Cs-flagged").

Results using the 3ROI algorithm were compared with results using three alternative analytical methods by calculating the % difference between the ^{226}Ra estimated by each NaI analysis and ^{226}Ra GeLi determinations. For random samples, estimations of ^{226}Ra were fairly accurate using all four methods although the range of error for the 3ROI method was twice as large as those for the other methods. For "Cs-flagged" samples, the 3ROI method generally overestimated the concentration of ^{226}Ra by about 50%. The three alternative methods yielded more accurate results. The RAK and WESTON methods yielded estimations that were within 10% of the GeLi determinations in 50% of the "Cs-flagged" samples.

A statistical analysis using correlation coefficients indicated that for random soil samples, about 13% of the error for all four NaI methods could be related to the concentration ratios of (^{226}Ra/^{40}K) and (^{226}Ra/^{232}Th).

The % differences from ^{222}Ra Geli results when using the 3ROI method were strongly correlated to the ratio of (^{226}Ra/^{127}Cs) for "Cs-flagged" samples.

The RAK and WESTON methods yielded an improvement in the accuracy of estimated ^{226}Ra concentrations when compared with the 3ROI method. Using these alternative methods, 97% of the analyses for ^{226}Ra in soil samples were within 20% of the GeLi determinations.

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