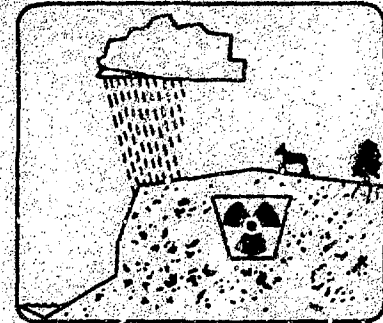


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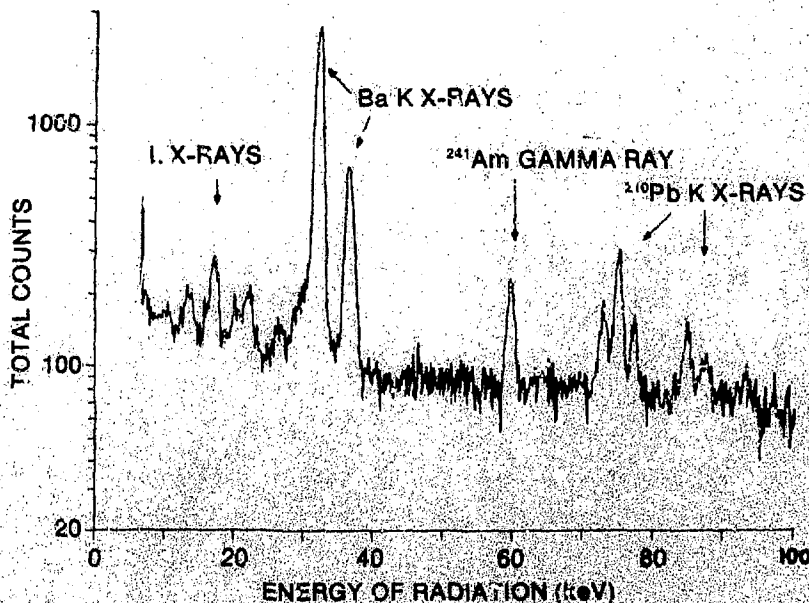
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RADIOACTIVE WASTE MANAGEMENT PROGRAM

EVALUATION OF AN AUTOMATED ASSAY SYSTEM TO MEASURE SOIL RADIONUCLIDES BY L X-RAY AND GAMMA-RAY SPECTROMETRY



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EVALUATION OF AN AUTOMATED ASSAY SYSTEM TO MEASURE SOIL RADIONUCLIDES BY L X-RAY AND GAMMA-RAY SPECTROMETRY

by

J. W. Nyhan, B. J. Drennon, and J. M. Crowell

ABSTRACT

An automated radionuclide assay system for conducting soil radioassays using L x-ray and gamma-ray spectrometry was evaluated. Wet chemistry assay procedures were shown to be considerably more time consuming than similar analyses of soil on this radionuclide assay system. The detection limits of ^{241}Am and plutonium were determined, as well as the reproducibility of radionuclide assay results. The L x-ray spectrometric measurements were compared with radiochemical analyses on several tuff samples. The assay system's intrinsic germanium detector was found to respond linearly to varying low concentrations of ^{241}Am and plutonium, both of which were easily detected in the presence of elevated concentrations of ^{137}Cs .

I. INTRODUCTION

Measurements of low-level radioactivity in samples of soil, sediment, and biota are usually performed using a radiochemical procedure whereby the radionuclides are first chemically separated from the soil, then purified, and finally analyzed using spectrometric techniques. The accuracy of this method has an inherent limitation in that it depends on the completeness of the chemical extraction. Thorough separation and purification is time consuming and laborious, and therefore costly. Direct photon spectrometry of a soil sample circumvents the above limitations because it requires no chemical separation and, therefore, offers an attractive alternative with the potential of being faster as well as more cost effective.

In spite of the advantages of direct photon spectrometry, very few analytical systems have been developed for assays of environmental samples. The ^{241}Am and plutonium content of a soil sample were measured

by photon spectrometry using a coaxial lithium-drifted germanium (GeLi) detector for the assay of the 59.54 keV gamma ray from ^{241}Am , and a lithium-drifted silicon detector (SiLi) detector for the assay of the Pu/ ^{241}Am L x-ray ratio (Brauer et al. 1977). A feasibility study on a unique SiLi-NaI(Tl) x-ray spectrometer with an expected measurement sensitivity of 1 pCi Pu/g soil, representing a concentration of about 10^{-6} ppm by weight, was also conducted (Strauss et al. 1978). The first experimental results obtained with another SiLi-NaI(Tl) prototype spectrometer indicated that this spectrometer had four times the sensitivity of a conventional SiLi spectrometer and could measure activity as low as 1 pCi/g of the natural uranium and thorium in soil (Sherman et al. 1980).

The recent availability of a new intrinsic germanium (IG) detector, which could more efficiently detect low-energy radiation, led to the development of a radionuclide assay system at Los Alamos. An initial feasibility study of this system was performed, and the system

components presented in detail, including the IG and GeLi detectors, the multichannel analyzer, a PDP-11/04 computer, and an automatic sample changer (Trujillo et al. 1980). In this report we present a detailed evaluation of this assay system's characteristics and performance.

II. MATERIALS AND METHODS

A. Instrumentation

The germanium detectors of the radionuclide assay system consist of a GeLi detector with a total active volume of 125 cm³ (Model 81, purchased from Ortec, Inc., Oak Ridge, Tennessee) and an IG detector with a total active volume of 14.7 cm³ (Model PGT HT, purchased from Princeton Gamma Tech, Princeton, New Jersey). The IG detector is calibrated from 0-200 keV, with 0.1387 ± 0.00006 keV/channel, and the GeLi detector is calibrated in the 200-2000 keV range, with 1.08601 ± 0.00000 keV/channel. Both detectors are interfaced to a Canberra Model 8100 multichannel analyzer (purchased from Canberra Industries, Inc., Meriden, Connecticut) and a PDP-11/04 minicomputer with an accompanying Dec Writer Model II LA-36 terminal console.

Dried soil samples are placed in 2.1 by 0.74 cm thick petri dish-like containers made of acrylonitrile butadiene styrene. These sample containers were designed so that the lid of the container, which is less than 1 mm thick, faces the IG detector, where the sample is assayed for low-energy (<200 keV) gamma-ray emitters. The bottom of the sample container has about twice the thickness of the lid and is positioned toward the GeLi detector, where assays for high-energy (>200 keV) gamma emissions take place. Twenty sample containers, each holding approximately 25 g of soil, are positioned vertically in the lead-lined wheel (0.91 m diam, 2.5 cm thick) of the sample changer.

Samples are counted for the minimum time required to get <3% counting error, with a maximum counting period of 16 000 sec (about 4.4 h). After subtraction of the room background contribution to each energy band, the number of counts above the background continuum in each energy band is determined and the concentration of the corresponding radionuclide is calculated, along with the probable error in measurement. The ²⁴¹Am, ²³⁵U, and any other contributions to the L x-ray region of interest are determined and subtracted from the gross count rates in those energy ranges, that is, for the α , β , and γ L x-rays of plutonium with major emission peaks

at 13.57, 16.88, and 20.24 keV (see Sherman et al. 1980 for amplification). The remaining count in the L x-ray region is assumed to be plutonium, and the weighted sum of the three principal L x-rays is used to determine the plutonium concentration.

B. Preparation of Standard Samples

Several samples of dried, crushed tuff were amended with known amounts of radionuclides to calibrate the radionuclide assay system and to test for linearity of detector response to varying concentrations of radionuclides. Approximately 23 g of tuff were added to each sample container and 8.30 ml of a radionuclide standard solution added to bring this sample to complete saturation. Several dilutions of primary standard solutions of weapon grade plutonium nitrate, ²⁴¹Am nitrate, and ¹³⁷Cs chloride were added to each sample individually and in a few combinations. The amended samples were then dried at 60°C for 48 h, quantitatively removed from their sample container and homogenized by mixing on a sheet of paper, and then returned to a sample container. These entire samples were then assayed for radionuclide content using our radionuclide assay system, and then using wet chemistry assays* for plutonium and americium involving alpha spectrometric determinations as described previously (Nyhan et al. 1976a, Nyhan et al. 1976b).

C. Environmental Samples

In an effort to evaluate the detection limits and performance of the assay system for analyzing environmental waste management samples for low levels of radionuclides, a set of about 400 samples collected beneath two liquid waste absorption beds at a waste disposal site (Area T) at Los Alamos were assayed with the radionuclide assay system.

III. RESULTS AND DISCUSSION

After conducting more than 1000 radionuclide analyses with our assay system, we were able to complete a cost comparison between the standard wet chemistry techniques* procedure and our radionuclide assay methodology (Table I). The wet chemistry assays for transuranics shown in Table I are actually quite abbreviated,

*Analytical technique known as the LASL-HASL transuranic assay procedure.

TABLE I
COST COMPARISON OF TWO RADIONUCLIDE ASSAY TECHNIQUES

<u>Wet Chemistry Assay</u>		<u>Total Cost*</u> <u>Man-Days</u>
Plutonium	Sample Preparation Acid Digestion Ion Exchange Electroplating Alpha Spectrometry	
Americium	Evaporation of Column Effluent Solvent Extraction Ion Exchange Precipitation Alpha Spectrometry	75
<u>Automated Radionuclide Assay System</u>		
Plutonium and Americium	Sample Preparation and Counting by Gamma Spectrometry	22

*The assumption is made in these estimates that only one technician is used to perform the assays.

but show the major steps, that is, there is an additional ion exchange column procedure that is used after the plutonium assay, which separates the uranium from the americium. In spite of this fact, the wet chemistry procedure requires more than three times the number of man-days to complete 100 samples than the radionuclide assay method.

Two additional points should be made in this cost comparison. Once the technician begins a wet chemistry assay, he is essentially tied to the bench working on the samples. However, with the radionuclide assay system, once the samples are placed in the automatic sample changer, the technician is free to perform other tasks. In addition, if questionable results are obtained with a wet chemistry assay, the entire procedure listed in Table I must be repeated, whereas with our assay system, the technician merely fills another sample container and counts another sample aliquot.

Radionuclide assays were conducted on a set of over 400 tuff samples collected beneath a nuclear waste disposal site at Los Alamos (Nyhan 1979, Nyhan and Trujillo 1980) in an attempt to characterize the detection limits of our radionuclide assay system for plutonium (Fig. 1) and ²⁴¹Am (Fig. 2). These figures express radionuclide concentrations, determined using the IG detector, as a function of per cent counting error (expressed at the three sigma level of probability).

For plutonium, we set the detection limit at 30 pCi/g for our routine assays, assuming a 16 000 sec maximum count time. The reasoning behind this decision was that samples with plutonium concentrations from 30 to 13 000 pCi/g exhibited counting errors of only 5-15%, whereas samples with plutonium concentrations ≤ 30 pCi/g exhibited much higher counting errors (Fig. 1).

A similar analysis of the ²⁴¹Am data for these samples exhibited marked differences over the detection limits for

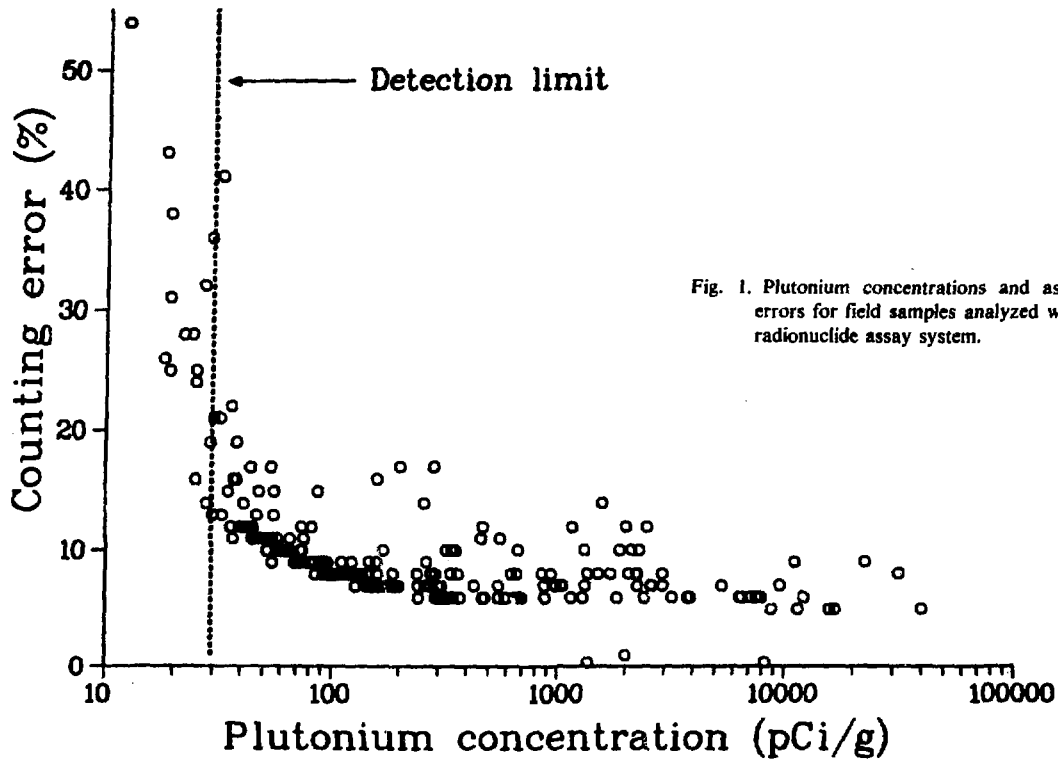


Fig. 1. Plutonium concentrations and associated counting errors for field samples analyzed with the automated radionuclide assay system.

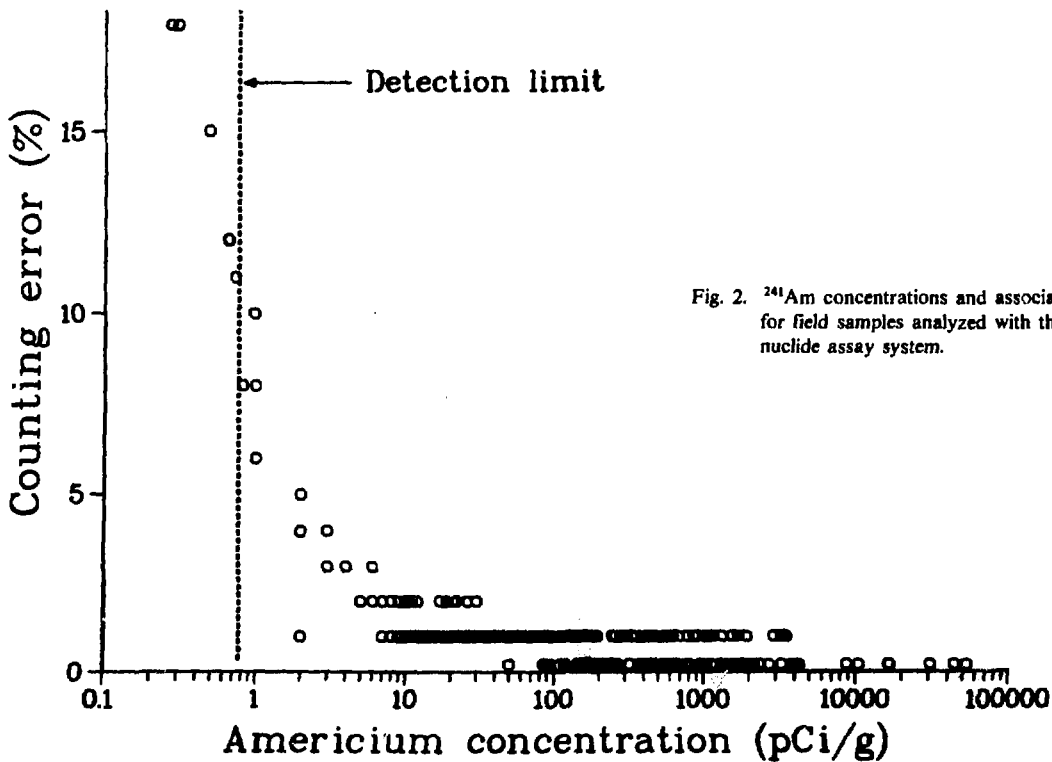


Fig. 2. ^{241}Am concentrations and associated counting errors for field samples analyzed with the automated radionuclide assay system.

plutonium. For ^{241}Am , the majority of the samples had counting errors of $<2\%$ (Fig. 2), in contrast to the plutonium data, and we set the detection limit at 0.8 pCi/g for ^{241}Am . Part of the reason for the observed differences between these two radionuclides is their radiological characteristics: the gamma-ray energy and intensity levels are higher for ^{241}Am than for the plutonium L x-rays. Practically speaking, we detect ^{241}Am throughout the entire soil sample in the sample container, whereas we estimate that we detect plutonium only in the top few millimeters of sample in our assay systems, with the low energy of the plutonium L x-rays.

Radionuclide assays were conducted on several of the tuff samples described in Figs. 1 and 2 to determine the

reproducibility of the radionuclide assay system. Each sample was first counted three times and then the average ^{241}Am and plutonium concentration was calculated, as well as the coefficient of variation [(standard deviation of the average concentration divided by the radionuclide concentration) multiplied by 100] for each sample (Fig. 3). Coefficients of variation (CVs) for ^{241}Am assays ranged from 1.0 to 5.5% (Fig. 3). In contrast, the CVs for plutonium analyses ranged from 0.3 to 29%, although most of the CVs were less than 20% (Fig. 3). In addition, although we were not able to plot the data in Fig. 3, 50 of these tuff samples were assayed three times and consistently showed nondetectable (zero) concentrations of plutonium.

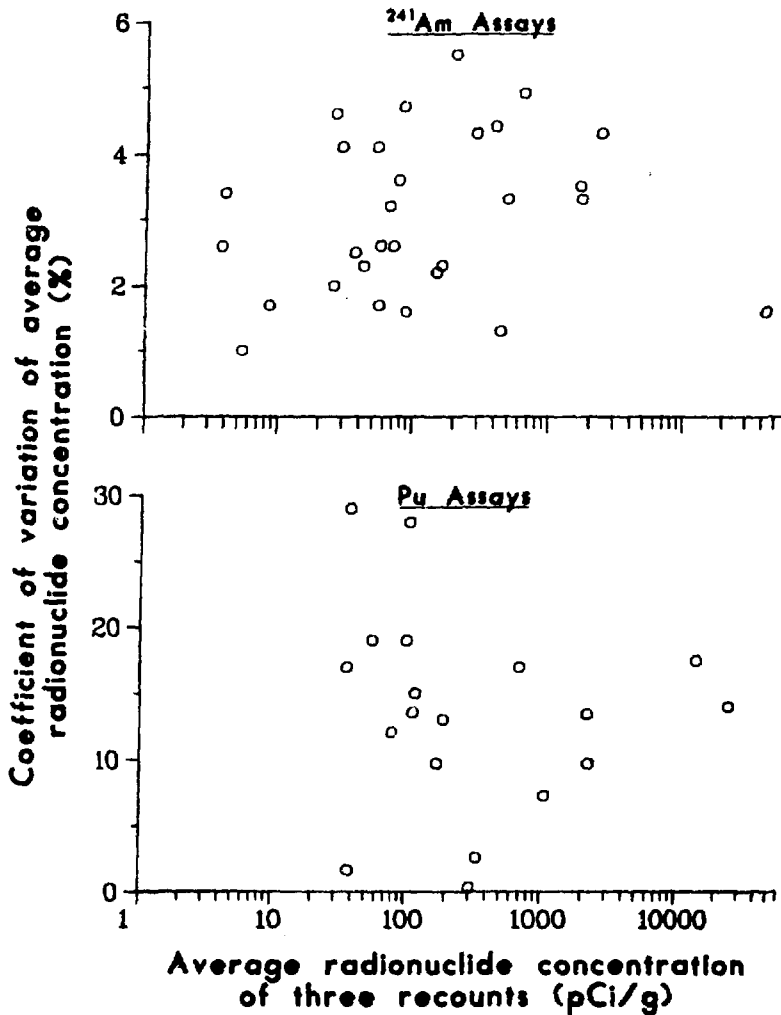


Fig. 3. Reproducibility of ^{241}Am and plutonium assays on the automated radionuclide assay system.

To further evaluate reproducibility of radionuclide assays, additional quality control studies were performed with standard tuff samples spiked with plutonium and americium. One plutonium tuff standard, containing 985 pCi Pu/g, was counted 79 times over a period of one year and demonstrated a CV of only 6.3%. Another tuff sample contained 1240 pCi ^{241}Am /g, and exhibited a CV of only 4.2% after being recounted 40 times in one year. The CVs for both of these standard samples are smaller than the CVs for radionuclide assays on the field samples (Fig. 3), largely because the field samples were recounted only three times.

Both the reproducibility studies of the field samples and the standards indicated a larger amount of variation for plutonium assays than for ^{241}Am assays. Part of the explanation for this observation is that plutonium assays have a larger analytical (counting) error than ^{241}Am assays (compare Figs. 1 and 2). However, there is also an unexplained component of assay variation for both radionuclides found when assay results are compared over a period of a year. We can only speculate that

electronic "noise" contributions are occasionally made to assay spectra at discrete energy levels, which are not accounted for in our sample and counting room background subtraction factors.

Another important performance characteristic of our automated radionuclide assay system was the linearity of response of the IG detector to varying low-radionuclide concentrations. Primary tuff standards were first prepared by amending noncontaminated tuff with varying concentrations of plutonium and ^{241}Am , and were then counted on our assay system. The results of these two studies (Figs. 4 and 5) demonstrated that the IG detector does respond linearly with increasing concentrations of plutonium, as evidenced by a slope of 1.05 for the linear regression equation (Snedecor and Cochran 1967) relating the observed plutonium concentration to the known plutonium concentration in the tuff standards ($R^2 = 0.95$). This relationship also held for ^{241}Am , where the regression equation slope was found to be equal to 1.00 with a coefficient of determination equal to 0.99 (Fig. 5).

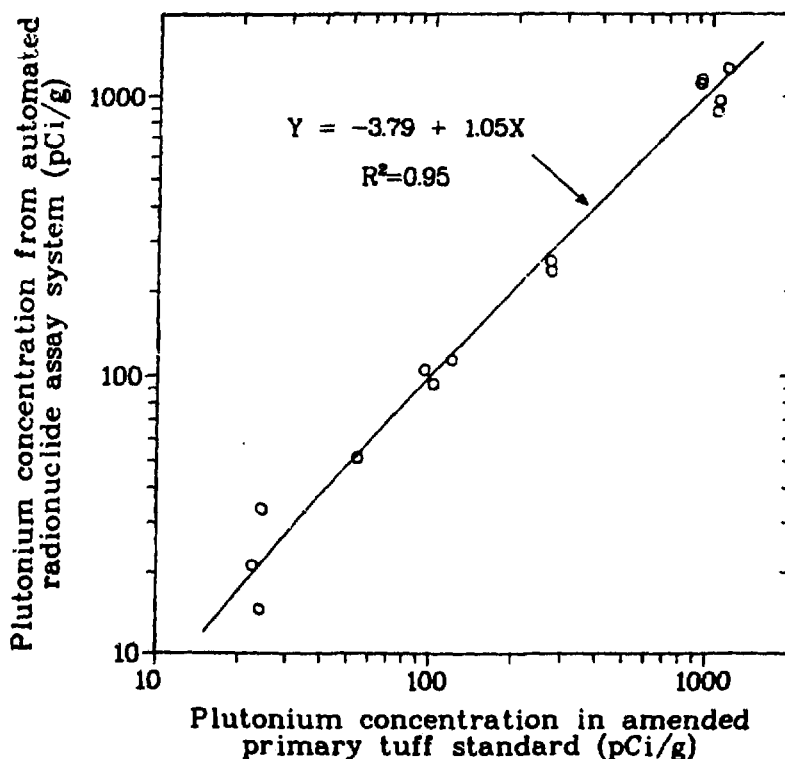


Fig. 4. Concentrations of plutonium as determined using the automated radionuclide assay system as a function of the plutonium concentration in the corresponding primary tuff standard.

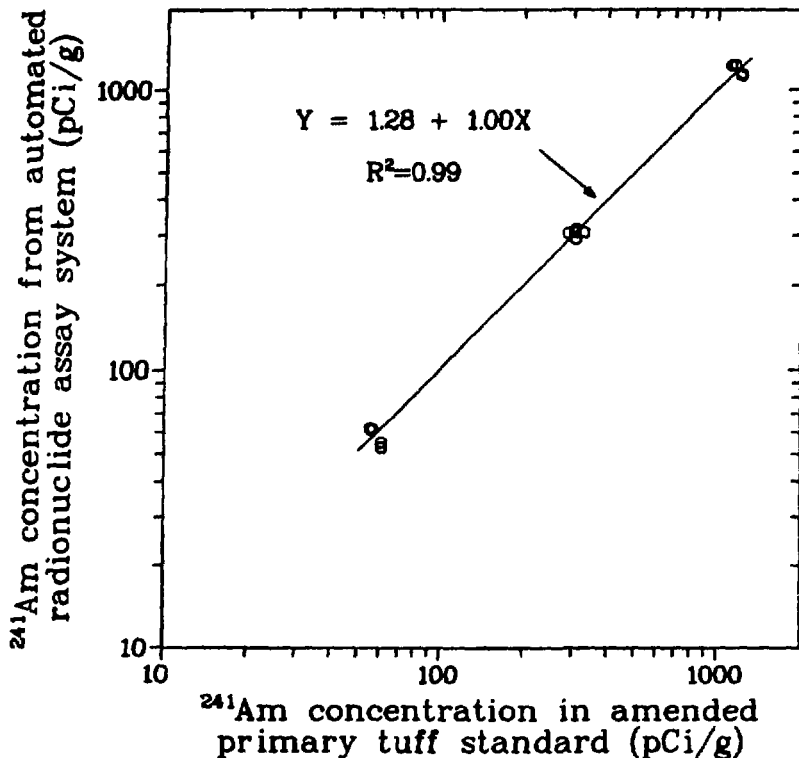


Fig. 5. Concentrations of ^{241}Am as determined using the automated radionuclide assay system as a function of the ^{241}Am concentration in the corresponding primary tuff standard.

Several of the americium and plutonium tuff standards were submitted to radiochemical analysis after having been counted on our automated assay system. The measurements of these samples by x-ray spectrometry are generally in good agreement with the wet chemistry analyses (Fig. 6). The linear regression model used to compare ^{241}Am assays on six samples with both techniques resulted in a coefficient of determination of 0.999 and a standard error of estimate of 12 pCi/g. The plutonium assays on 12 samples were also compared with a linear regression model (Fig. 6). This analysis showed a coefficient of determination of 0.98 and a standard error estimate of 70 pCi/g for plutonium, indicating less agreement between the two assay techniques for plutonium than for ^{241}Am . This is not surprising in view of the larger counting error associated with the plutonium assays than the ^{241}Am determinations, and considering the small amount of the total sample assayed for plutonium in our assay system compared with the radiochemical assay of the entire sample.

In addition to transuranics, soil contaminated by radioactive waste may contain gamma-emitting fission

products. When these gamma rays interact in the IG detector, they Compton scatter, thereby depositing part of their energy in the crystal. This increases the continuum level in the x-ray spectrum, and, in turn, increases the minimum detectable activity of the nuclides of interest, as shown by studies using Si(Li) detectors (Sherman et al. 1980). To study this phenomenon on our assay system, we prepared samples containing plutonium with varying amounts of ^{137}Cs and counted them for 16 000 sec. Furthermore, the concentrations of ^{137}Cs in two of these samples were chosen to represent approximate worldwide fallout levels of ^{137}Cs in local soils (Nyhan et al. 1976b), and a 30-fold higher ^{137}Cs concentration.

A spectrum from tuff containing 273 pCi/g ^{137}Cs , in addition to 53.5 pCi/g plutonium, is compared with that of a tuff sample containing only 9.77 pCi/g ^{137}Cs and 53.5 pCi/g plutonium (Fig. 7). The continuum level caused by elevated levels of ^{137}Cs (upper spectrum) is from 3-4 times higher than that caused by lower levels of ^{137}Cs in a sample, that is, concentrations approximately equal worldwide fallout levels of ^{137}Cs in local soils

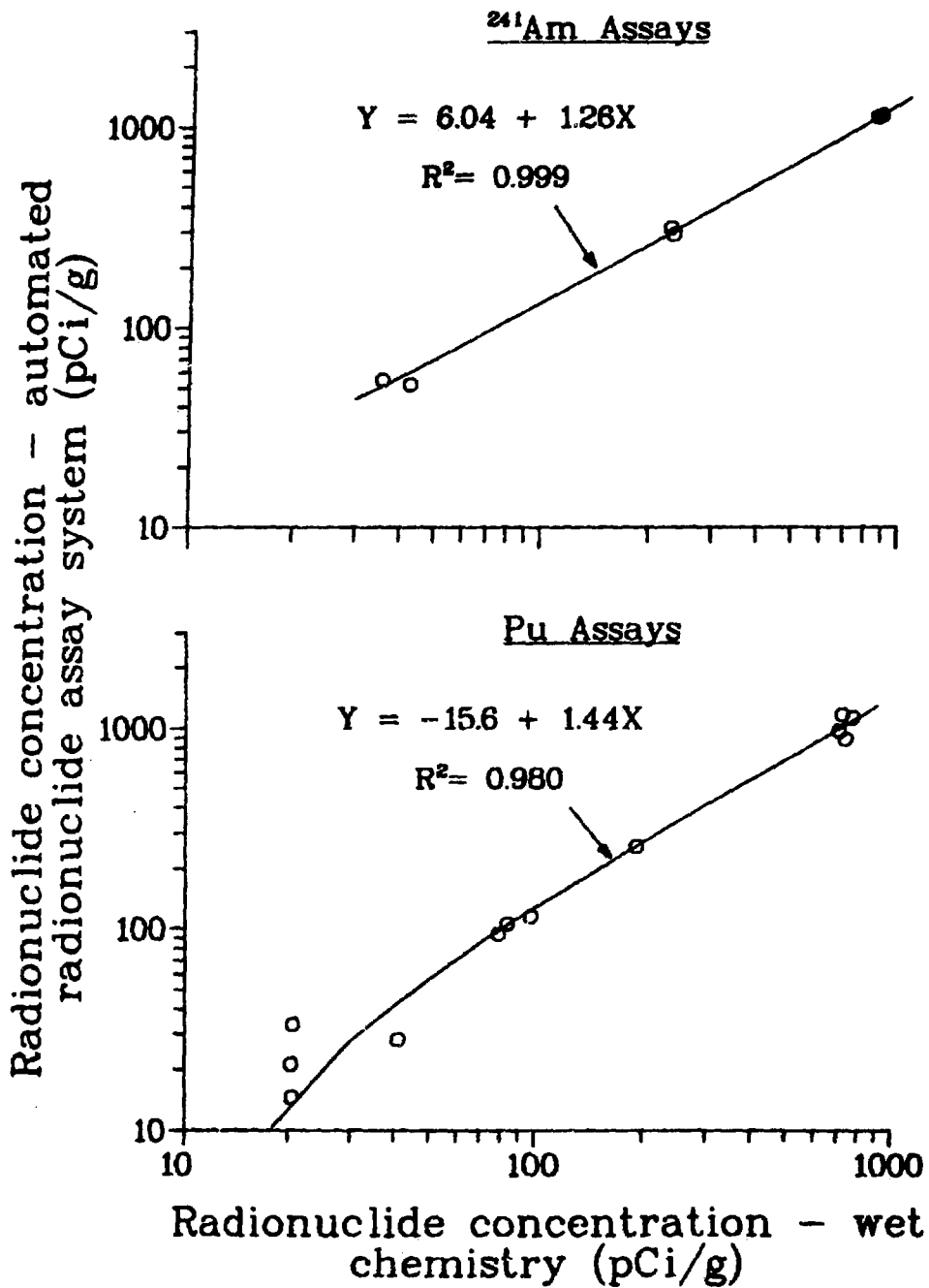


Fig. 6. Comparisons of radionuclide assays on tuff standards using results from wet chemistry assays and automated radionuclide assay system results.

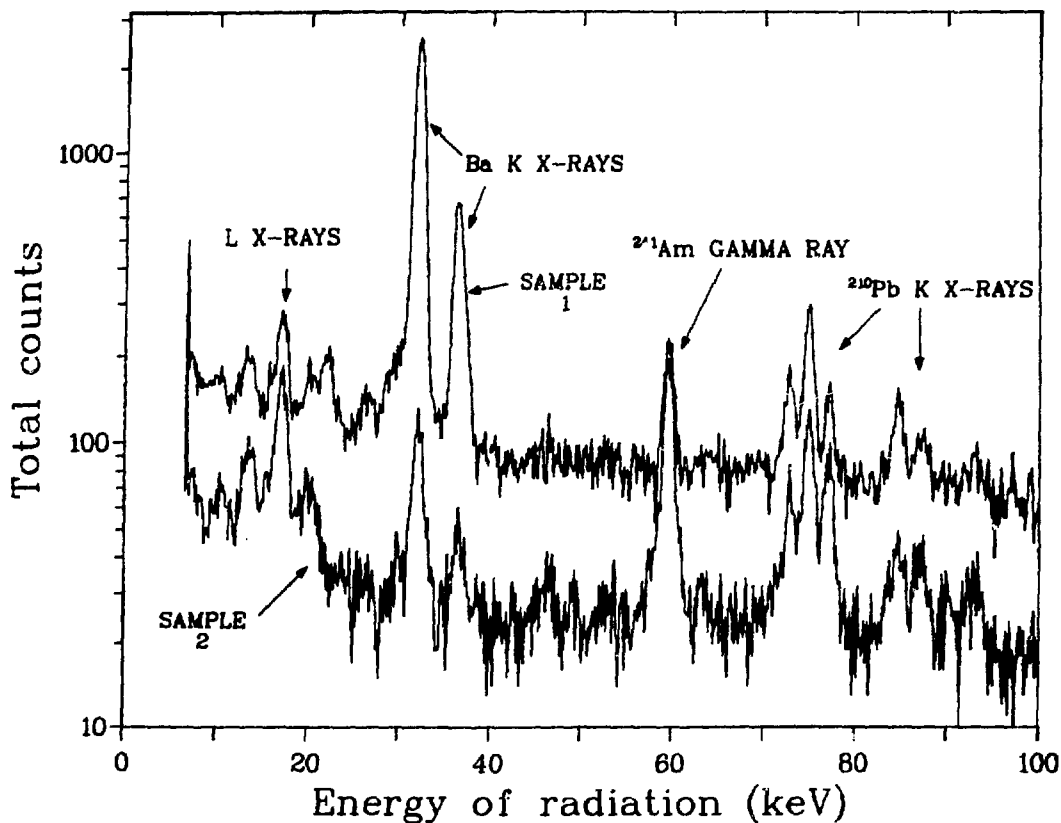


Fig. 7. Spectra for two tuff samples amended with plutonium and varying amounts of ^{137}Cs (16 000 sec counting time).

(lower spectrum). In spite of this substantial increase in the background levels in the ^{241}Am and L x-ray regions of interest (13-21 keV), no significant differences in the concentrations of either ^{241}Am or plutonium were observed between the two samples. For example, the ^{241}Am concentration in the sample with 273 pCi $^{137}\text{Cs}/\text{g}$, was found to be $1.15 \pm 16\%$, whereas the sample amended with only 9.77 pCi $^{137}\text{Cs}/\text{g}$ contained $1.23 \pm 8\%$ pCi $^{241}\text{Am}/\text{g}$. The increased ^{137}Cs content did have an effect on the counting variation of the transuranic assays; however, the high ^{137}Cs sample demonstrated a counting error of $\pm 16\%$ associated with the plutonium assay, whereas the low ^{137}Cs sample had a corresponding error of only 11%.

IV. CONCLUSIONS

Our automated radionuclide assay system, an instrumental technique not requiring radiochemical analysis, has been shown to be effective in assaying low

concentrations of radionuclides in tuff by L x-ray and gamma ray spectrometry. Wet chemistry assay procedures were shown to require more than three times the amount of time needed to complete a radionuclide assay on our automated assay system.

Our spectrometer system consists of an IG detector and a GeLi detector, between which sample containers are positioned vertically in the lead-lined wheel of the sample changer. More than 400 samples of tuff were collected from a waste disposal site at Los Alamos and assayed using this system to determine the detection limits of 30 pCi/g for plutonium and 0.8 pCi/g for ^{241}Am . Assays on environmental samples and tuff samples to which known amounts of ^{241}Am and plutonium were added showed a high degree of reproducibility. The L x-ray spectrometry measurements were also found to be in good agreement with radionuclide assays on several tuff samples containing actinides.

The IG detector was found to respond linearly to varying low concentrations of plutonium and ^{241}Am . These assays were performed very satisfactorily, even in

the presence of concentrations of ^{137}Cs 30 times greater than worldwide fallout levels of ^{137}Cs in local soils.

Our automated radionuclide assay system promises to be a simple, fast, and cost-effective technique for routine soil analyses. It is well suited for environmental monitoring, where it is desired to screen a large number of samples quickly to determine if the radioactivity therein exceeds a given minimal level. Our assay system could also be used in radioecological and waste management research, where concentrations of soil radionuclides usually demonstrate a high degree of variability, and large numbers of samples must be assayed before meaningful research conclusions can be drawn.

In addition to radionuclide assays, and with only a small modification of the existing hardware, this analytical system could be used for stable element assays. A shielded activation source could be added to the sample changer framework, and soil samples could then be assayed using neutron activation analytical techniques.

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