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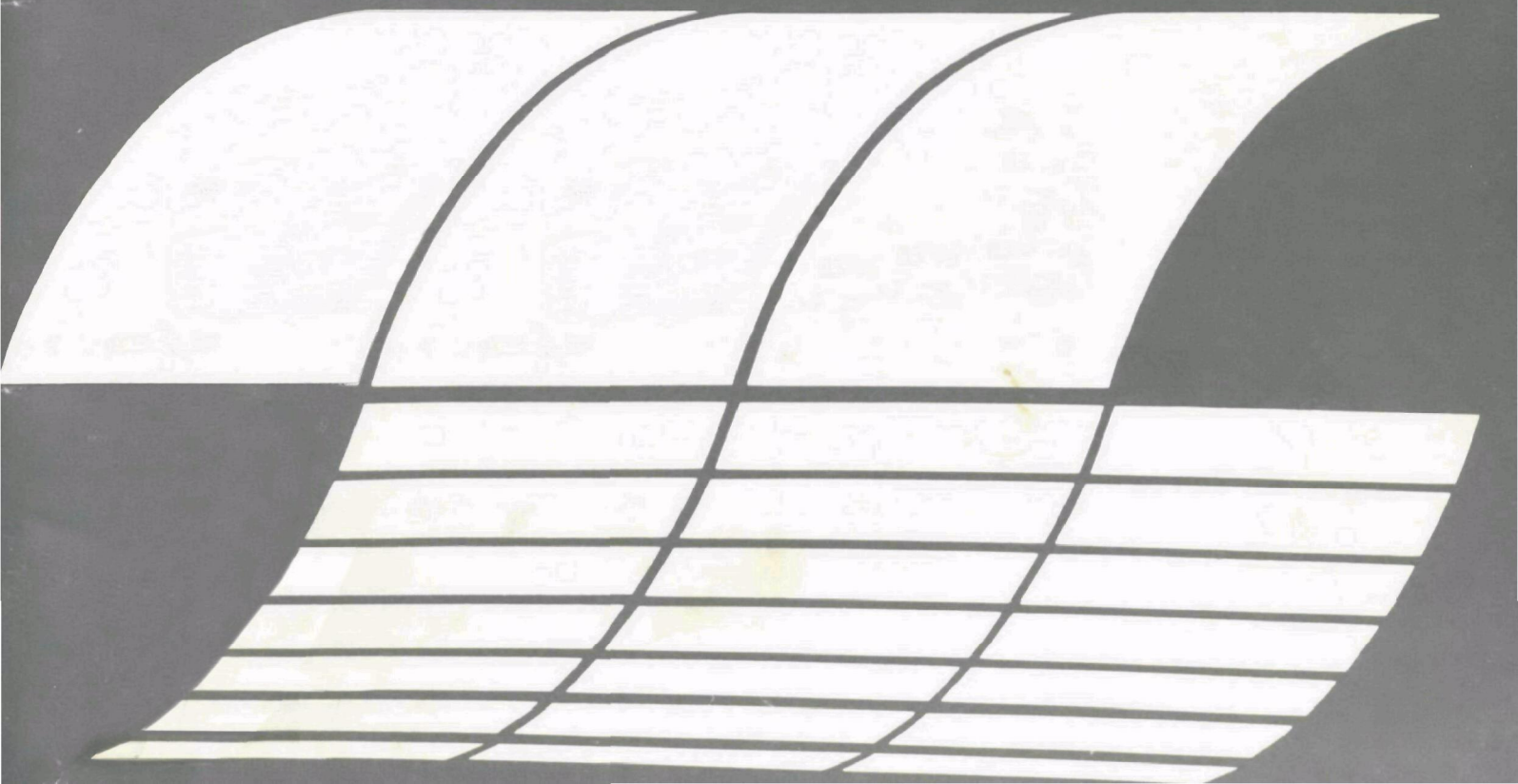
FUSION METHOD FOR THE MEASUREMENT OF PLUTONIUM IN SOIL: Single-Laboratory Evaluation of Interlaboratory Collaborative Test

Interagency Energy-Environment Research and Development Program Report



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FUSION METHOD FOR THE MEASUREMENT OF PLUTONIUM IN SOIL: Single-Laboratory Evaluation and Interlaboratory Collaborative Test

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FOREWORD

Protection of the environment requires effective regulatory actions which are based on sound technical and scientific information. This information must include the quantitative description and linking of pollutant sources, transport mechanisms, interactions, and resulting effects on man and his environment. Because of the complexities involved, assessment of specific pollutants in the environment requires a total systems approach which transcends the media of air, water, and land. The Environmental Monitoring and Support Laboratory-Las Vegas contributes to the formation and enhancement of a sound integrated monitoring data base through multidisciplinary, multimedia programs designed to:

- develop and optimize systems and strategies for monitoring pollutants and their impact on the environment
- demonstrate new monitoring systems and technologies by applying them to fulfill special monitoring needs of the Agency's operating programs.

This report presents the results of a single-laboratory evaluation and an interlaboratory collaborative test of a method for measuring plutonium in soil. The Environmental Protection Agency is presently preparing a Federal Guidance Document for plutonium-in-soil and the results of this study should provide valuable input for the Guidance. Such studies are extremely useful as they demonstrate the state of the art of the analytical methodology which will ultimately provide the information for decisions associated with environmental standards and guidelines. Collaborative tests also allow each participating laboratory to critically evaluate its capabilities in comparison to other laboratories and often document the need for taking corrective action to improve techniques. For further information, contact the Methods Development and Analytical Support Branch, Monitoring Systems Research and Development Division, Environmental Monitoring and Support Laboratory, Las Vegas, Nevada.

George B. Morgan
Director
Environmental Monitoring and Support Laboratory
Las Vegas

ABSTRACT

This report presents the results of a single-laboratory evaluation and an interlaboratory collaborative test of a method for measuring plutonium in soil. The method employs potassium fluoride and potassium pyrosulfate fusions to decompose a 10-gram sample, barium sulfate precipitations, solvent extraction and electrodeposition to isolate the plutonium, and alpha spectrometry to measure the plutonium. The method is appended to the report.

The single-laboratory evaluation demonstrated that the overall within-laboratory precision of the method can approach the precision of nuclear counting statistics alone. The interlaboratory collaborative test showed the coefficient variation representing differences between laboratories to be approximately 10% for concentration levels exceeding 1 disintegration per minute per gram.

Also discussed are several problem areas associated with environmental actinide analyses. These include the difficulties which may be anticipated in requiring monitoring laboratories to adopt a specific complex method of this type. Suggestions are presented for improving agreement between laboratories by establishing criteria for analytical results rather than requiring specific methodology.

This report covers a period from January 1, 1974, to September 30, 1976, and work was completed as of December 31, 1976.

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Special thanks are given to Mr. Claude W. Sill of the U.S. Energy Research and Development Administration's Health Services Laboratory, Idaho Falls, Idaho, for his continuing support during this study and for preparing the reference samples used in the single-laboratory evaluation and the interlaboratory collaborative test.

INTRODUCTION

In early 1974 the U.S. Environmental Protection Agency (EPA) considered promulgating a standard or guideline to protect against detrimental human health effects resulting from land surfaces contaminated with plutonium.

Most types of standards or guidelines which could then be envisaged would require the use of appropriate methodology for measuring plutonium in soil. At that time a collaboratively tested method for the measurement of plutonium in soil did not exist. A decision was therefore made to develop a method which could be used as an EPA Reference Method should the Agency promulgate a "standard or guideline" requiring one.

EPA policy is to select a single reference method for a single environmental pollutant. A method so designated must have acceptable accuracy and precision performance characteristics which have been scientifically and statistically validated by multiple-laboratory collaborative tests under a variety of anticipated user conditions. The method must be one that can be readily implemented by prospective user laboratories. This precludes designation of very expensive, sophisticated methods as reference methods even though they may be the most accurate methods available.

This study was designed to evaluate one of the best available methods for measuring plutonium in soil for consideration as an EPA Reference Method.

SUMMARY

This report presents the results of both a single-laboratory evaluation and an interlaboratory collaborative test of a candidate method for the measurement of plutonium in soil. The method was developed by the U.S. Atomic Energy Commission's (AEC) Health Services Laboratory at Idaho Falls, Idaho, and it involves sequential potassium fluoride and potassium pyrosulfate fusions to decompose the soil matrix (Sill 1974b). The method was chosen for evaluation after both a critical review of the literature was performed on currently available methods and after a plutonium-in-soils workshop was held in Las Vegas, Nevada, in April 1974. The candidate method is included with this report as an appendix.

The single-laboratory evaluation of the method was conducted at the U.S. Environmental Protection Agency's Environmental Monitoring and Support Laboratory-Las Vegas by performing replicate analyses on soil samples containing known levels of plutonium ranging from 0.1 to 10 disintegrations per minute per gram (dpm/g). The standard soils were prepared at the AEC Health Services

Laboratory at Idaho Falls, Idaho. The soils were fired at a high temperature and are considered to contain plutonium in a highly refractory form. The same soils were used for the interlaboratory collaborative test.

A preliminary interlaboratory study involving four laboratories was conducted before the full-scale collaborative test in order to obtain information regarding potential problem areas in the proposed collaborative test and to obtain comments on the conciseness and clarity of the document describing the procedural steps of the method. For this preliminary study the laboratories were provided with a soil sample of known plutonium concentration and requested to perform the analysis as described in the document.

Six laboratories out of approximately 30 contacted participated in the interlaboratory collaborative test. They were requested to perform triplicate analyses of four soil samples containing known levels of plutonium. Each of the participating laboratories completed a questionnaire regarding the degree to which they had deviated from the documented method, the problems they had encountered with the method, and their opinion of the method. After the results were received, one of the laboratories was found to disagree significantly with the other five. Miscalibration of the plutonium tracer used in the analysis was the suspected cause of this disagreement. It was therefore decided to perform an interlaboratory calibration of the tracers used by the six laboratories. A calibrated plutonium-239 solution was forwarded to the laboratories with specific instructions on how to standardize their tracer. The results of the collaborative test were corrected on the basis of the recalibration and are presented and evaluated along with the original results.

The statistical evaluation of the interlaboratory collaborative test followed the general approach suggested by Youden (1975). A separate statistical analysis was made for each sample because the assumption of equal variance for different activity levels could not be accepted. No attempt was made to transform the data in order to group samples at different activity levels for an analysis of variance. Individual results have been provided so that additional statistical analyses, considered beyond the scope of this report, may be performed.

CONCLUSIONS AND RECOMMENDATIONS

The single-laboratory evaluation demonstrated the capability of the candidate method to achieve a single-laboratory accuracy and precision approaching that of counting statistics alone when samples containing 1 to 10 dpm/g of plutonium-239 are analyzed. The results from replicate analyses of 10-g soil samples at the 6 and 9 dpm ^{239}Pu/g levels indicated a total analysis coefficient of variation on the order of 2% to 3%. Systematic error or bias above the 2% to 3% level could not be detected, demonstrating essentially complete exchange between the refractory plutonium in the soil samples and the plutonium tracer during the fusion operations.

Complete decomposition of the soil matrix was achieved in the fusions for

every standard sample analyzed. This was also found to be true for several other types of soils investigated. Plutonium recoveries were excellent, averaging 88% ± 7% for the single-laboratory evaluation. The resolution obtained in the final alpha spectra for all analyses was sufficient to resolve and quantify plutonium-238 in the presence of plutonium-239 and the plutonium-236 tracer. The method was also found to be applicable to soils containing extremely large quantities of calcium (up to 80% $CaCO_3$) with only minor modifications.

The single-laboratory evaluation demonstrated a small potential bias for the method. Protactinium-231, which occurs naturally in soils, quantitatively follows plutonium through the analysis and it may be difficult to resolve from or even be mistaken for the plutonium-239 and plutonium-240 peak in the alpha spectrum. The analysis of blank soils from Idaho and Alabama showed this bias to be on the order of 0.1 dpm/g.

The interlaboratory collaborative test showed the candidate method, when used by a typical group of laboratories, to have an overall, between laboratory single determination coefficient of variation on the order of 10% at concentration levels in excess of 1 dpm/g. This overall variability increased to approximately 30% at the 0.1 dpm/g level. The coefficients of variation representing the precision for replicate analyses performed within a given laboratory ranged between 5% and 10% at the 1 and 10 dpm/g concentration levels. The coefficients of variation representing variability between the laboratories also ranged between 5% and 10% at the 1 and 10 dpm/g concentration levels.

It was discovered through the questionnaire that the participating laboratories generally had not calibrated the plutonium tracer used in the study as specified by the candidate method. Because the tracer calibration is considered to be one of the prime factors in achieving interlaboratory agreement in a method of this type, it was decided to have each laboratory standardize the tracer used in the collaborative test against a common, known plutonium-239 solution and to correct and re-evaluate all of their analytical results. The interlaboratory calibration did not significantly improve the agreement between the laboratories; however, it allowed the inclusion of one collaborator's data in the evaluation who had originally deviated from the concensus by more than 40%. The original calibrations of the remaining five collaborators were found to agree with a coefficient of variation of 4.3%.

The method itself showed no bias. The Student's t-test demonstrated the grand average for each sample to be statistically equal to the known value at the 95% confidence level. This was true for the original results of five laboratories and the corrected results for all six laboratories.

In addition to the tracer calibration, the electrodeposition was another portion of the method where the collaborators deviated significantly from the instructions. Three of the laboratories used the prescribed electrodeposition technique while the other three either used their own technique or modified the prescribed technique. Both the final plutonium recovery and the quality of resolution in the final alpha spectrum are greatly dependent on the electrodeposition. Average recoveries for the collaborators ranged from 35% to 70% and good resolution was obtained by three laboratories while the other three

reported marginal resolution. There was no correlation between the electrodeposition technique used and the recoveries and quality of resolution obtained.

The authors cannot at this time make any firm recommendations regarding the applicability of this method as a reference method. The primary reason is that no criteria have yet been established for such a reference method. Only the performance characteristics of this method have been described in this report. The authors hope these performance characteristics will prove valuable in establishing the criteria for a reference method.

The method provided excellent results in the single-laboratory evaluation and in another study documented in the literature (Sill 1974a). Its fusion techniques make it, in theory, the most applicable of all available methods for the analysis of the widest variety of soil samples. Any reference method chosen should be proven equivalent to this method if this method is ultimately not chosen.

The authors feel that it would be difficult for a typical user laboratory to adopt this method for routine analysis of large numbers of samples. This opinion results from our own personal experience with the method, comments from half the collaborators and from the fact that only 6 of more than 30 laboratories contacted actually participated in the collaborative test.

On the basis of this study, four recommendations can be made regarding any reference actinide method:

1. A common tracer, extensively cross-calibrated by several laboratories, should be used by all laboratories performing actinide analyses.

2. Each laboratory should be allowed to use its own proven electrodeposition technique for cost effectiveness.

3. Performance criteria should be established and each laboratory should be required to periodically demonstrate that it can meet these criteria by analyzing reference samples such as those used in this study.

4. Criteria should be set for individual analyses in terms of minimum acceptable recovery, quality of resolution of the alpha spectrum, maximum counting error allowed, maximum activity allowed in a reagent blank run simultaneously, and a rigidly defined quality assurance program.

With these recommendations a reference method would not be required if indeed one ever existed. The question of how far one deviated from the method need never be asked.

CHOICE OF METHOD

Since an environmental plutonium standard for soil had not yet been promulgated, exact criteria for sensitivity, accuracy and precision for a

plutonium-in-soil reference method were unavailable. Also, there was widespread and well-documented uncertainty in the scientific community as to whether any of the available methods could meet certain of the anticipated Agency and user criteria.

The candidate method would have to be reliable, exhibiting reasonable accuracy and precision, and applicable to the wide variety of soil types found in the United States. It would have to be capable of accurate analysis of all chemical and physical forms of plutonium known to exist in the environment whether at background or highly elevated levels. Also, if the method should not be applicable to a given sample type, this would have to become unequivocally apparent either during the course of the analysis or from the results obtained.

The first task was to perform a critical review of currently available methods. Two approaches were employed. The first approach was to conduct an internal laboratory screening of potentially applicable methodology by reviewing the literature and conducting laboratory evaluations. The second approach was to sponsor a workshop to obtain input from attendees on existing methodology.

Agreement on a reference method by recognized scientists in the subject area was viewed as indispensable to the successful accomplishment of the task, because an agreement would be invaluable in ultimately obtaining acceptance of the method by the rest of the scientific community. Such a workshop was sponsored by the National Environmental Research Center-Las Vegas* and was held April 2-3, 1974, in Las Vegas, Nevada. Workshop attendees included principal scientists from three U.S. Atomic Energy Commission (AEC)† laboratories, two EPA laboratories, and three private laboratories. These laboratories perform at least 80 percent of all plutonium-in-soil analyses conducted in the United States. Scientists from other organizations having expertise in plutonium analysis also attended, as did selected personnel representing elements of agencies administratively responsible for plutonium analysis of soil. Included were two senior scientists from EPA's Office of Radiation Programs, EPA quality assurance officials, and officials from certain AEC Operations Offices. The attendees were nearly unanimous in agreeing on certain criteria. Those criteria were as follows:

1. A 10-gram sample size would be adequate for the sensitivity required.

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*Effective June 29, 1975, the National Environmental Research Center-Las Vegas (NERC-LV) was designated the Environmental Monitoring and Support Laboratory-Las Vegas (EMSL-LV). This Laboratory is one of the three Environmental Monitoring and Support Laboratories of the Office of Monitoring and Technical Support in the U.S. Environmental Protection Agency's Office of Research and Development.

†Effective January 19, 1975, the AEC was replaced by the U.S. Energy Research and Development Administration (ERDA) and the U.S. Nuclear Regulatory Commission (NRC).

2. Extremely important considerations in the analysis of soil for plutonium are the decomposition of the sample, the equilibration of the plutonium tracer with the plutonium in the sample and the extraction of plutonium from the soil matrix for subsequent purification and counting. Certain forms of plutonium, especially those which have been fired at high temperatures, are known to be highly refractory and consequently are difficult to extract from a soil matrix. The method would have to be applicable to such forms of plutonium.

3. Available methodology for the analysis of plutonium in soils can be classified into three major groups according to sample decomposition techniques: acid leaching, total dissolution with nitric and hydrofluoric acids, and total decomposition by sequential potassium fluoride and potassium pyrosulfate fusions. Acid-leaching techniques were considered unacceptable because of the large quantities of residue which generally remain after such treatment. Total dissolution of soils with nitric and hydrofluoric acids is often not truly total and small quantities of residue or turbidity remain after 10 grams of soil have been treated. The fusion technique, however, is known to dissolve the most refractory and intractable plutonium compounds while at the same time completely dissolving the soil matrix. This allows for the complete exchange between the plutonium in the sample and the plutonium-236 tracer used to trace the plutonium recovery through the analysis.

4. Both fusion and total dissolution techniques have certain advantages and a representative method from each type should be evaluated.

Based on these criteria, it was decided that a fusion method had the widest applicability and would be evaluated first. A second method, involving a total dissolution technique is presently being evaluated and the results will be reported at a later date.

The candidate method (see Appendix) evaluated in this report is based on a method developed by the U.S. Atomic Energy Commission's Health Services Laboratory at Idaho Falls, Idaho (Sill 1974b). In this method a known quantity of plutonium-236 tracer is added to 10 grams of soil which is decomposed completely by sequential potassium fluoride and potassium pyrosulfate fusions. The fused sample is dissolved in dilute hydrochloric acid and the plutonium is isolated and separated from uranium by co-precipitation with barium sulfate. The barium sulfate is dissolved in perchloric acid, the solution is adjusted to approximately 2M in aluminum nitrate and the plutonium is reduced to the tetravalent state with sodium nitrite and extracted into Aliquat-336 (methyltricaprylyl ammonium chloride). The trivalent actinides are separated by scrubbing the organic extract with nitric acid, and thorium is separated by scrubbing with hydrochloric acid. Plutonium is then stripped with a perchloric-oxalic acid solution and electrodeposited onto stainless steel disks. Plutonium-236, plutonium-238, and plutonium-239 plus plutonium-240 are determined by alpha spectrometry.

The candidate method employs these sample decomposition and plutonium separation techniques coupled with an electrodeposition technique from an ammonium sulfate solution (Talvitie 1972).

PREPARATION OF REFERENCE MATERIAL

Several soil samples containing known levels of plutonium were prepared as described in the Quality Assurance Section (Section 8.0) of the candidate method. Known amounts of plutonium-239 and plutonium-238 (calibrated as described in the candidate method) were thoroughly mixed with approximately 200 grams of wet -200 mesh soil and dried under a heat lamp. After drying, the soil was muffled at approximately 700° C for several hours to convert the plutonium to a refractory oxide. Plutonium in this form is considered to be the most difficult to analyze and would therefore be the best test of a candidate method.

The spiked soil was pulverized to -200 mesh, sieved and added to approximately 3 kilograms of unspiked soil. The composite was weighed to determine the final plutonium concentration and blended for 2 days to ensure homogeneity. Losses were compensated for by collecting all of the residues from the drying, pulverizing, and sieving operations and analyzing for plutonium and subtracting this value from the original amount of plutonium added. The stock soil was further blended with unspiked soil to prepare the five samples of known plutonium concentrations listed in Table 1. All blending operations were for at least 24 hours.

TABLE 1. PREPARATION OF KNOWN SOIL SAMPLES

Samples	^{239}Pu Added (dpm)	Final Weight (g)	^{239}Pu Concentration (dpm/g)[c]	^{238}Pu Concentration (dpm/g)[c,d]
Stock	$(6.12^{a} - 0.06^{b}) \times 10^{4}$	3012	20.13 ± 0.07	0.309 ± 0.003
D	(1464 g)(20.13 dpm/g)	3277	8.99 ± 0.03	0.138 ± 0.001
P	(983 g)(20.13 dpm/g)	3428	5.77 ± 0.02	0.089 ± 0.001
C[e]	(302.0 g)(8.99 dpm/g)	2632	1.03 ± 0.01	-
B	(390.0 g)(8.99 dpm/g)	3893	0.901 ± 0.003	-
A	(44.0 g)(8.99 dpm/g)	3498	0.113 ± 0.001	-

[a] Activity of ^{239}Pu added to original soil.

[b] Activity of ^{239}Pu found in composite residues.

[c] Uncertainty propagated from 2σ counting uncertainties in calibration of tracer, uncertainty in volume of tracer added, and uncertainties in weighing.

[d] Calculated from ^{238}Pu contaminant in ^{239}Pu tracer used as spike (^{238}Pu/^{239}Pu = 0.0152).

[e] Higher level calcium soil (2-3% $CaCO_3$).

SINGLE-LABORATORY EVALUATION

The candidate method was tested by analyzing soil samples (Table 1) containing the various known levels of plutonium. Table 2 presents the results of the plutonium-239 analyses performed at our laboratory. Presented in this table are the individual results plus the 1σ counting error, the length of the count, the plutonium recovery and the approximate quantity of plutonium-236 tracer used in the analysis. For the two samples (D and P) analyzed several times, the average ($\bar{X}$), the standard deviation of the individual analyses (S_x), the coefficient of variation (C.V. = 100 $S_x/\bar{X}$) and the ratio of the average to the known are calculated.

The results obtained demonstrate the capability of the candidate method to achieve a single-laboratory accuracy and precision approaching that of counting statistics alone when samples containing 1 to 10 disintegrations per minute per gram (dpm/g) of plutonium-239 are analyzed.

Systematic error or bias above the 2 to 3 percent level could not be detected from the analytical results for the 5.77 and 8.99 dpm/g level soils. Plutonium recoveries averaged 88% ± 7%, providing nearly optimum sensitivity and precision. Complete decomposition of the soil matrix was achieved during the fusions for every sample analyzed. This was also the case for several other types of soil which were decomposed by the fusion techniques. Similar analytical results have been documented in the literature from the analysis of soils at the 30- and 0.5-dpm/g levels using a method similar in all respects except for the electrodeposition (Sill 1974a).

Plutonium-238 results were not reported in this single-laboratory evaluation because of plutonium-238 contamination of the working area caused by previous experiments with high concentrations of that isotope. Considerable effort was dedicated to decontamination; however, the lowest blank level achieved was about 0.5 dpm, which was a significant fraction of the plutonium-238 in the soils being analyzed. Although numerical results could not be reported, the resolution obtained in the final alpha spectra was sufficient to resolve and quantify plutonium-238 in the presence of plutonium-239 and the plutonium-236 tracer.

Some outside laboratories questioned whether the method would be applicable to soils containing large quantities of calcium. We experienced no problem in this regard. A simple modification of the original method allowed for the analysis of 10 grams of soil containing 80% $CaCO_3$ with plutonium recoveries on the order of 60%.

There is one potential weakness in this method: protactinium-231 quantitatively follows plutonium through the analysis and it can, at times, be difficult to resolve the protactinium-231 peak from the plutonium-239 and plutonium-240 peaks by alpha spectroscopy. The effect is most acute when analyzing for lower levels of plutonium (<0.2 dpm/g) and apparently negligible at the higher levels (>1 dpm/g). The analysis of blank soils from Idaho and Alabama indicated protactinium-231 levels on the order of 0.1 dpm/g and a positive

TABLE 2. RESULTS OF SINGLE-LABORATORY EVALUATION

Known ^{239}Pu Level (dpm/g)	Result (dpm/g)[a]	Length of Count (Min)	^{236}Pu Tracer Used (Approx. dpm)	Plutonium Recovery (%)
8.99	8.79 ± 0.20	312	50	88
	8.76 ± 0.10	1246		92
	8.72 ± 0.18	363		92
	8.61 ± 0.11	1013		91
	9.32 ± 0.26	271		68
	8.78 ± 0.31	128		88
	8.60 ± 0.10	1298		91
$\bar{X}$ = 8.797	S_x = 0.243	C.V. = 2.8%	$\bar{X}$/Known = 0.979 ± 0.025[b]	
5.77	5.77 ± 0.05	2502	50	88
	5.82 ± 0.08	1408		61[c]
	5.88 ± 0.07	1330		83
	5.78 ± 0.07	1463		88
	5.83 ± 0.09	935		81
	5.65 ± 0.08	965		87
	5.66 ± 0.15	300		79
	5.47 ± 0.15	239		93
$\bar{X}$ = 5.733	S_x = 0.133	C.V. = 2.3%	$\bar{X}$/Known = 0.994 ± 0.019[b]	
0.901	0.858 ± 0.025	1162	10	93
	0.844 ± 0.025	1190		89
1.03[d]	1.014 ± 0.025	1513	10	92
	1.003 ± 0.016	3864		95
6.36[e]	6.79 ± 0.25	100	500	57
	5.94 ± 0.22	100		64
			Average Recovery[f] =	88 ± 7

[a] Including 1σ counting uncertainty.

[b] Error in $\bar{X}$/Known calculated at the 95% confidence level from $(ts_x/\sqrt{n})$/Known Value using the Student t-distribution.

[c] Partial spill of sample.

[d] Soil contained 2% to 3% $CaCO_3$.

[e] Soil contained 80% $CaCO_3$.

[f] Excluding c and e.

bias of this order of magnitude may be expected for results obtained using the candidate method. The significance of such a bias cannot be ascertained until specific EPA guidelines concerning plutonium-239 in soil are established. The protactinium-231 interferes only with the measurement of plutonium-239 and would have no effect on a plutonium-238 measurement. The protactinium-231 interference can be completely eliminated by extracting it into diisobutylcarbonol (DIBC) just prior to the plutonium extraction (Sill 1976).

PREPARATION OF THE MANUSCRIPT DESCRIBING THE CANDIDATE METHOD

The manuscript describing the method was prepared from the appropriate publications in the literature with extensive consultation with the primary authors and others familiar with the various techniques. The descriptions of individual steps were continuously revised during the single-laboratory evaluation performed at this laboratory, again consulting with the primary authors.

Several outside laboratories which expressed interest in the collaborative testing of the method agreed to analyze a practice sample by the candidate method and provide results and comments on both the method and the manuscript describing the method. Table 3 presents the results from four outside laboratories attempting the analysis for the first time on sample P containing 5.77 ± 0.02 dpm/g of plutonium-239 and 0.089 ± 0.001 dpm/g of plutonium-238.

The preliminary results from the practice analyses performed by the outside laboratories were encouraging. Although low and inconsistant plutonium recoveries were obtained by two of the laboratories, this was understandable as a certain amount of experience by the analyst is necessary before optimum results can be expected. A similar situation existed at our laboratory when we first attempted the method. The internal precision exhibited by each of the laboratories was excellent, especially in view of the fact they were provided with only enough sample to perform triplicate analyses. Differences between three of the outside laboratories and this laboratory (see previous section) appeared minor, being on the order of 5%.

Each of these four laboratories plus another which did not perform the analyses provided excellent comments for revising the wording of several critical steps in the procedure. These comments were incorporated in the current revision of the method (see Appendix) which was distributed for the interlaboratory collaborative test.

INTERLABORATORY COLLABORATIVE TEST

The candidate method was distributed to approximately 30 laboratories which perform plutonium analyses, requesting their participation in a collaborative test which would involve triplicate analysis of four soil samples for

TABLE 3. RESULTS OF PRELIMINARY INTERLABORATORY EVALUATION

Laboratory	^{239}Pu Concentration (dpm/g)	^{238}Pu Concentration (dpm/g)	Plutonium Recovery (%)
W	5.81	0.072	54
	5.65	0.082	52
X	5.45[a]	0.090	2
	5.50[a]	0.070	33
	5.34[a]	0.074	53
Y	5.44	0.6	22
	5.51	0.4	52
	5.53	0.4	37
Z	4.92[b]	0.08	69
	5.02[b,c]	0.08	65
Expected Concentrations	5.77 ± 0.02	0.089 ± 0.001	

[a]Used own electrodeposition technique in sulfate media.

[b]Used plutonium-242 tracer and own electrodeposition technique in chloride media.

[c]Used own adaptation of the fusion method.

plutonium-239 and plutonium-238 by the candidate method. Thirteen laboratories responded and were forwarded 35 grams of soils A, B, C, and D. The laboratories which did not participate in the preliminary study were also provided with 35 grams of the practice sample (P) and its known value and instructed to try the method before analyzing the test samples.

Six of the thirteen laboratories completed the study and the individual results are tabulated according to sample in Tables 4-8. Also presented in each of these tables for each laboratory are averages of the replicate results, $\bar{x}_i$; the experimental (within-laboratory) standard deviations, S_i; the ratios of the average value to the known value; and the plutonium recovery for each of the analyses. S_i is a measure of the random error (precision) for each individual laboratory for the given sample and is calculated from Equation 1.

$$S_i = \left(\frac{\sum_{j=1}^{n_i} (x_{ij} - \bar{x}_i)^2}{n_i - 1} \right)^{\frac{1}{2}} \qquad (1)$$

TABLE 4. RESULTS FOR SAMPLE A
(Known Value: 0.113 ± 0.001 dpm $^{239}Pu/g$)

Lab	Result (dpm/g)	S_i (dpm/g)	$\bar{x}_i$ (dpm/g)	Ratio of Ave. to Known Conc.[a]	Pu Recovery (%)
1	0.18				9
	0.09	0.059	0.113	1.00 ± 1.30	46
	0.07				34
2	0.12				52
	0.09	0.015	0.103	0.91 ± 0.33	53
	0.10				47
3	0.22				92
	0.16	0.035	0.180	1.59 ± 0.77	73
	0.16				44
4	0.136				68
	0.140	0.003	0.138	1.24 ± 0.24	64
5	0.13				48
	0.13	0.012	0.123	1.09 ± 0.26	17
	0.11				42
6	0.12				68
	0.09	0.015	0.103	0.91 ± 0.33	66
	0.10				67

[a]Error in the Ratio of Average to Known Concentration calculated at the 95% confidence level from $(tS_i/\sqrt{n_i})$/Known Value, using the Student t-distribution.

TABLE 5. RESULTS FOR SAMPLE B
(Known Value: 0.901 ± 0.003 dpm ^{239}Pu/g)

Lab	Result (dpm/g)	S_i (dpm/g)	$\bar{x}_i$ (dpm/g)	Ratio of Ave. to Known Conc.[a]	Pu Recovery (%)
1	0.84				28
	1.04	0.101	0.930	1.032 ± 0.278	45
	0.91				35
2	0.75				56
	0.88	0.065	0.813	0.902 ± 0.179	63
	0.81				83
3	0.89				75
	0.86	0.021	0.883	0.980 ± 0.058	74
	0.90				58
4	0.94				87
	0.98	0.031	0.947	1.051 ± 0.085	64
	0.92				61
5	0.82				38
	0.83	0.026	0.840	0.932 ± 0.072	32
	0.87				19
6	0.40				66
	0.58	0.127	0.490	0.544 ± 1.266	69

[a]Error in the Ratio of Average to Known Concentration calculated at the 95% confidence level from $(tS_i/\sqrt{n_i})$/Known Value, using the Student t-distribution.

TABLE 6. RESULTS OF SAMPLE C
(Known Value: 1.03 ± 0.01 dpm ^{239}Pu/g)

Lab	Result (dpm/g)	S_i (dpm/g)	$\bar{x}_i$ (dpm/g)	Ratio of Ave. to Known Conc.[a]	Pu Recovery (%)
1	1.11				50
	1.09	0.020	1.110	1.078 ± 0.048	54
	1.13				30
2	0.89				24
	0.91	0.042	0.923	0.896 ± 0.101	32
	0.97				69
3	1.00				56
	1.04	0.020	1.020	0.990 ± 0.048	82
	1.02				75
4	1.10				78
	1.05	0.050	1.050	1.019 ± 0.121	80
	1.00				72
5	0.90				69
	0.94	0.028	0.920	0.893 ± 0.244	66
6	0.78				39
	0.71	0.060	0.717	0.696 ± 0.145	68
	0.66				66

[a]Error in the Ratio of Average to Known Concentration calculated at the 95% confidence level from $(tS_i/\sqrt{n_i})$/Known Value, using the Student t-distribution.

TABLE 7. RESULTS FOR SAMPLE D9
(Known Value: 8.99 ± 0.03 dpm ^{239}Pu/g)

Lab	Result (dpm/g)	S_i (dpm/g)	$\bar{x}_i$ (dpm/g)	Ratio of Ave. to Known Conc.[a]	Pu Recovery (%)
1	11.30				34
	9.32	1.14	9.98	1.110 ± 0.315	35
	9.32				23
2	8.4				60
	8.4	0.29	8.23	0.916 ± 0.080	76
	7.9				63
3	8.21				55
	8.22	0.06	8.18	0.910 ± 0.017	79
	8.12				78
4	9.71				61
	9.17	0.28	9.39	1.044 ± 0.077	76
	9.29				62
5	7.79				70
	8.26	0.33	8.03	0.893 ± 0.330	83
6	7.03				67
	6.65	0.37	6.66	0.741 ± 0.102	69
	6.30				64

[a]Error in the Ratio of Average to Known Concentration calculated at the 95% confidence level from $(tS_i/\sqrt{n_i})$/Known Value, using the Student t-distribution.

TABLE 8. RESULTS FOR SAMPLE D8
(Known Value: 0.138 ± 0.001 dpm $^{238}Pu/g$)

Lab	Result (dpm/g)	S_i (dpm/g)	$\bar{x}_i$ (dpm/g)	Ratio of Ave. to Known Conc.[a]	Pu Recovery (%)
1	0.24				34
	0.13	0.055	0.183	1.33 ± 0.99	35
	0.18				23
2	0.12				60
	0.12	0.012	0.113	0.82 ± 0.22	76
	0.10				63
3	ND				55
	0.49				79
	ND				78
4	0.17				61
	0.18	0.006	0.173	1.26 ± 0.11	76
	0.17				62
5	0.15				70
	0.13	0.014	0.140	1.01 ± 0.91	83
6	0.16				67
	0.13	0.030	0.130	0.94 ± 0.54	69
	0.10				64

[a]Error in the Ratio of Average to Known Concentration calculated at the 95% confidence level from $(tS_i/\sqrt{n_i})$/Known Value, using the Student t-distribution.

where x_{ij} = the individual results (1 through n_i) obtained by laboratory i

$\bar{x}_i$ = the average of the individual results for laboratory i

n_i = the number of replicates performed by laboratory i

Table 9 summarizes the data for each sample analysis. It presents the average result ($\bar{x}_i$) according to laboratory. It shows the grand average of all the laboratories, $\bar{\bar{X}} = \Sigma \bar{x}_i/m$; where m is the number of collaborators and it gives three additional statistics (S_d, S_r, and S_b) explained and defined later. The results of Laboratory 6 were excluded in the calculation of the $\bar{\bar{X}}$; S_d; S_r; and S_b statistics.

Also presented in Table 9 is the ranking test for the laboratories (Youden 1975) to help decide whether a given laboratory has a pronounced systematic error or bias and if its results should be rejected from the statistical evaluation of the collaborative study.

Preliminary consideration of the average results immediately places suspicion on the performance of Laboratory 6. Its results appeared significantly low for samples B, C and D9, the three higher level samples where a bias not associated with contamination would be most apparent. The ranking test confirms this suspicion, giving Laboratory 6 a score of 28.5. For six laboratories and five samples there is less than 5% chance that such a table made up by a random process will contain a score as large or larger than 28 or as small or smaller than 7.

Miscalibration of the plutonium-236 tracer was considered the most likely cause of this bias. Therefore, an intercalibration was performed between the participating laboratories both to confirm the suspected reason for the Laboratory 6 bias and to assess the validity of an alternate, perhaps more foolproof, calibration technique.

The intercalibration involved:

(1) supplying each participant with a calibrated plutonium-239 solution (Amersham/Searle),

(2) requesting each laboratory to combine measured volumes of the plutonium-239 solution and the plutonium tracer they used in the collaborative study (~100 dpm of each), to electroplate the combined tracers and to count the plate for 1000 minutes by alpha spectrometry, and

(3) having each laboratory provide the referee information on the volumes of each tracer used, the net counts in the plutonium-236 and plutonium-239 regions of the alpha spectrum and the original value at which their tracer was calibrated.

The referee calculated the tracer activity for each laboratory based on the known plutonium-239 activity. Table 10 presents the ratio of the value of the recalibrated tracer to the original value the laboratories had used.

TABLE 9. SUMMARY OF COLLABORATIVE TEST RESULTS

	Average Values ($\bar{x}_i$) for Samples Analyzed (dpm/g)					Ranked Results for Samples Analyzed					
Lab	A	B	C	D9	D8	A	B	C	D9	D8	Score
1	0.113	0.930	1.110	9.98	0.183	4	2	1	1	1	9
2	0.103	0.813	0.923	8.23	0.113	5.5	5	4	3	6	23.5
3	0.180	0.883	1.020	8.18	-	1	3	3	4	3.5	14.5
4	0.140	0.947	1.050	9.39	0.173	2	1	2	2	2	9
5	0.123	0.840	0.920	8.03	0.140	3	4	5	5	3.5	20.5
6[b]	0.103	0.490	0.717	6.66	0.130	5.5	6	6	6	5	28.5[a]
Known	0.113	0.901	1.03	8.99	0.138						
$\bar{X}$	0.132	0.883	1.005	8.762	0.152						
S_d	0.0302	0.0571	0.0825	0.871	0.0320						
S_r	0.0333	0.0577	0.0348	0.583	0.0307						
S_b	0.0233	0.0464	0.0800	0.803	0.0266						

[a]Unusually high score representing consistently low results.

[b]Data from Laboratory 6 not used in statistical analysis.

TABLE 10. INTERLABORATORY CALIBRATION OF THE PLUTONIUM TRACER

Laboratory	Ratio of Recalibrated Value to Original Value[a]
1	1.011 ± 0.015
2	1.036 ± 0.030
3[b]	1.055 ± 0.023
4	0.943 ± 0.014
5	1.029 ± 0.024
6	1.448 ± 0.090

[a]Error based on 2σ counting uncertainty associated with calibration.

[b]Recalibration performed on new dilution of the same original batch of tracer which had been used to prepare the tracer used in the collaborative test.

The results of the interlaboratory calibration showed that Laboratory 6 had been significantly out of calibration in comparison to the other laboratories and the uncorrected collaborative test data from this laboratory should not be used in the statistical evaluation of the method. The Dixon test was used for rejecting this laboratory (Steiner 1975):

$$r_{10} = \frac{x_n - x_{(n-1)}}{x_n - x_1} = 0.778 \qquad (2)$$

where x_n = the highest (suspect) value

$x_{(n-1)}$ = the next highest value and

x_1 = the lowest value

The critical value for this statistic for a sample size of six and an α risk level of 5% is 0.560.

The statistics S_r; S_d; and S_b presented in Table 9 are required to perform the evaluation of the candidate method in terms of the limits of error which can be expected when the method is used by a typical group of analysts.

In addition to the individual within-laboratory standard deviations (S_i) presented in Tables 4-8, a pooled or combined within-laboratory standard deviation which is based on the results of all the collaborators for a given sample is of interest. This statistic, S_r, is calculated from Equation 3.

$$(\Sigma n_i - m)\, S_r^2 = \sum_{i=1}^{m} \sum_{j=1}^{n_i} (x_{ij} - \bar{x}_i)^2 \qquad (3)$$

where n_i = the number of replicate determinations performed by laboratory i

m = the number of collaborators

x_{ij} = the individual results (1 through n_i) obtained by laboratory i

$\bar{x}_i$ = the average of the individual results for laboratory i

This statistic is calculated for each sample and is listed in Table 9. Also presented is the standard deviation of the actual data, S_d, which is calculated from the laboratory averages according to Equation 4.

$$S_d = \left(\frac{\Sigma (\bar{x}_i - \bar{X})^2}{m - 1} \right)^{\frac{1}{2}} \quad (4)$$

Of great interest in the evaluation of a method is a statistic which provides a measure of the differences or precision of the method between laboratories. This statistic, S_b, the standard deviation of the systematic errors, is calculated from S_d and S_r using Equation 5 (Youden 1975). S_b is listed along with S_r and S_d for each sample in Table 9.

$$S_b^2 = S_d^2 - S_r^2/k \quad (5)$$

where k = the number of replicate determinations performed by the laboratories on a given sample

The collaborative test was designed to evaluate the precision and accuracy of the candidate method over two orders of magnitude concentration range (0.1 to 10 dpm plutonium/gram). Triplicate analyses were performed twice at both the 0.1 and 1 dpm/g levels and once at the 10 dpm/g level. The statistics S_d, S_r, and S_b were calculated for each series of analyses to evaluate the precision of the method over the 0.1 to 10 dpm/g concentration range. As mentioned earlier, S_d is the standard deviation of the actual data based on the individual laboratory averages of triplicate analyses of a given sample. The S_r statistic is the pooled estimate of the within-laboratory standard deviation, and S_b is an estimate of the standard deviation of the systematic errors or differences between laboratories.

Under normal conditions, only a single analysis would be routinely performed on a sample and the evaluation of the precision for this situation is therefore warranted. For a single analysis the previous estimates of S_r and S_b would be applicable but S_d, the estimate of the total error or precision between the laboratories, would have to be recalculated from S_r and S_b using Equation 5 with k = 1. Table 11 summarizes the precision data by listing the coefficients of variation (100 $S/\bar{X}$) for within-laboratory error, systematic error between laboratories, and the total error between laboratories based on a single analysis.

The precision data indicate the method has an overall single determination precision on the order of 10% at levels greater than 1 dpm/g increasing to approximately 30% at a level of 0.1 dpm/g.

TABLE 11. SUMMARY OF PRECISION DATA

Sample	Known (dpm/g)	$\bar{X}$ (dpm/g)	Coefficients of Variation (%) Within Lab	Between Labs	Total (Single Analysis)
A	0.113	0.132	25.2	17.7	30.8
D8	0.138	0.152	20.2	17.5	26.7
B	0.901	0.883	6.5	5.3	8.4
C	1.03	1.005	3.5	8.0	8.7
D9	8.99	8.762	6.7	9.2	11.4

It must be emphasized however, that such precision values are only estimates based on a limited number of observations. The within-laboratory error was based on 14 or 15 observations (9 or 10 degrees of freedom) and the between-laboratory and total error were based on 5 observations (4 degrees of freedom). The chi-squared distribution may be used to place a 95% confidence interval on each of the calculated standard deviations or coefficient of variations (Ostle 1963). For 9 or 10 degrees of freedom, the lower and upper limits are obtained by multiplying the calculated standard deviation or coefficient of variation by factors of 0.7 and 1.8 respectively. For 4 degrees of freedom the respective factors are 0.6 and 2.9.

There appears to be no overall bias to the method when comparing the average result for each sample to the known value. The t-test was conducted at the $\alpha = 5\%$ risk level for each analysis and in no case does the calculated value (Equation 6) exceed the critical value for rejection of the hypothesis that $\bar{X}$ equals the known value.

$$t = \frac{|\bar{X} - R| \sqrt{m}}{S_d} \quad ; \quad m-1 \text{ degrees of freedom} \qquad (6)$$

where R = the known or reference value
m = the number of collaborators
S_d = the standard deviation of the data (Equation 4)

Table 12 presents the results of the t-test for each of the analyses.

TABLE 12. t-TEST TO DETECT METHOD BIAS

Analysis	m	t-calc.	t-crit.
A	5	1.40	2.78
D8	4	0.88	3.18
B	5	0.71	2.78
C	5	0.68	2.78
D9	5	0.59	2.78

ADDITIONAL CONSIDERATIONS

A questionnaire was forwarded to each of the participants to ascertain the degree to which they had deviated from the documented method and the problems they had encountered with the method.

The area of major concern was the standardization of the plutonium tracer as this is considered to be the primary factor in the bias between laboratories. Other areas of interest included the quantity of tracer used, modifications in the electrodeposition technique, the degree of resolution between the alpha peaks in the alpha spectra and the collaborators' opinions of routinely adapting the procedure. The following paragraphs summarize the major comments provided by the individual participants.

Laboratory 1 used 22 dpm of plutonium-236 tracer purified by anion exchange rather than the recommended procedure. The tracer was standardized as recommended except the 2π counter was calibrated using an NBS plutonium-238 standard. A 100-ml platinum dish was used for the fusions. Electrodeposition was performed using the suggested electrolyte, but at 250 milliamps for 3 hours. The final planchet was flamed before counting and adequate resolution was achieved to resolve plutonium-236, -238, and -239. The solvent extraction steps were considered tedious and the laboratory is not willing to run the procedure routinely.

Laboratory 2 used 12 dpm of plutonium-242 tracer which was not further purified. Standardization was done as recommended but an NBS gadolinium-148 standard was used to calibrate the 2π counter. No other modifications of the procedure were made. Adequate resolution of the plutonium isotopes was achieved and the laboratory is willing to run the procedure routinely.

Laboratory 3 used 55 dpm of plutonium-236 tracer which was standardized against a known plutonium-239 standard which had been cross calibrated with other laboratories. Electrodeposition was performed as recommended but the plates were generally "very dirty in appearance" compared with plates produced by their standard technique. Adequate spectral resolution was obtained for samples A and B, but the plates for samples C and D had to be washed in 6M HCl to obtain adequate resolution. Although this laboratory stated that a higher level of effort was required for this method over its standard method, it is willing to run it on a routine basis.

Laboratory 4 used 22 dpm of plutonium-236 tracer which was not further purified. Calibration was performed as recommended but using a thin-window alpha counter and an Eberline Instrument Corp. plutonium-239 source to determine counter efficiency. Electrodeposition was performed for 2 hours at 450 milliamps after the sample was evaporated to 1 ml of sulfuric acid, diluted, and neutralized with ammonium hydroxide to the methyl red end point. The plates were ignited in a flame before counting. The laboratory reported that no residue was present on the final plates so spectral resolution was assumed adequate. This laboratory is not willing to run the method on a routine basis because they found it to be too time consuming.

Laboratory 5 used 11 dpm of plutonium-236 tracer which was purified by anion exchange rather than the recommended procedure. Standardization of the tracer was performed as recommended, however an NBS plutonium-238 source was used to calibrate the 2π counter. Electrodeposition was performed as recommended. Spectral resolution was considered to be "generally adequate" except that in some cases (especially Sample C) residue was found on the plates making it difficult to obtain an accurate determination of plutonium-238 and -239 in the presence of the plutonium-236 tracer. This laboratory said that the fusion procedure takes twice as much time as the leaching procedure it normally employs and would not recommend it on a routine basis, unless resources were available to support it.

Laboratory 6 used 14 dpm of plutonium-236 tracer purified and calibrated as recommended except they did not calibrate the 2π counter with the NBS americium-241 source concurrent with counting the evaporated tracer. Instead, they used an efficiency factor that had been determined earlier. During the interlaboratory calibration it became apparent that the value for this laboratory's tracer was approximately 50% low, suggesting that its 2π counter was malfunctioning when the tracer was calibrated. Electrodeposition was performed from a 4% ammonium oxalate - 4M hydrochloric acid solution at 210 milliamps for 2.5 hours. Planchets were flamed before counting and spectral resolution was considered adequate for plutonium-239 but marginal for plutonium-238. This laboratory is willing to run the procedure routinely.

The responses to the questionnaire pose some basic questions about the significance of the collaborative test. Does it represent the collaborators rigidly following the prescribed method? Or does it represent the collaborators following a general analytical approach? The former is certainly not true, but the latter does not appear to be strictly true either. The collaborators rigidly followed portions of the procedure, i.e., the decomposition and chemical separation steps, but they generally used their own electrodeposition and calibration techniques.

An important consideration is the fact that in the time frame allotted for the study, the collaborators were unable to procure a new batch of the tracer and the necessary NBS americium-241 source to purify and calibrate the tracer as specified. As a consequence, the collaborators used the tracer they had on hand which had been calibrated earlier by techniques which were generally similar to the prescribed technique, but by no means standardized between the laboratories. The degree of uncertainty contributed to the method from the tracer calibration can be estimated from the results of the interlaboratory calibration (Table 10). The five laboratories whose collaborative test results were evaluated had an average correction factor (recalibrated value/original value) of 1.015 with a standard deviation of 0.043. This corresponds to a coefficient of variation of 4.3%. The coefficient of variations representing the bias between laboratories for the entire method at the 1- and 10-dpm/g levels ranged between 5% and 9% (Table 11).

To determine whether the interlaboratory calibration significantly improved the results, the same statistical evaluations were performed after correcting each result by multiplying it by the appropriate correction factor (Table 10). The results of the collaborative test based on the recalibration

are summarized in Tables 13 to 15. The corrected results of Laboratory 6 were included in this evaluation.

The recalibration did not appear to significantly improve the agreement between laboratories as might have been expected. The between-laboratory coefficient of variation remained basically the same for the 1 and 10 dpm/g concentration levels (6% to 8% after recalibration versus 5% to 9% originally). We must therefore conclude, when both techniques are done properly, the proposed alternate calibration technique is no better than the combination of techniques used by the laboratories to originally calibrate their tracer. The recalibration, however, can serve an important function by providing a check on suspect results from a given laboratory. As for the original results, there was no bias detected for the method when the alternate calibration of the tracer was employed (Table 15).

DISCUSSION OF RESULTS

One conclusion which could be drawn concerning this collaborative study is perhaps best said in the words of Youden (1969): "If every laboratory departs capriciously from the procedure as specified, then the whole business of interlaboratory testing might as well be forgotten because no single version of the procedure can be tried out." It would, however, have been indeed unfortunate had this collaborative test not been conducted due to the valuable information and insights obtained concerning the state of the art of environmental plutonium analysis and perhaps environmental actinide analysis in general.

The collaborative test, in one sense, could be considered a ruggedness test for the method (Youden 1975) even though it was not statistically designed as such and conclusions regarding potential problem areas could not be drawn on a statistical basis. The test however involved the actual variables affecting agreement between laboratories, many of which would have been overlooked in a properly designed single-laboratory ruggedness test. Many of these variables are not numerical and statistics are of no help in evaluating them.

A greater effort should be placed on standardization of the tracer and consistency between different batches standardized independently. It was discovered through this collaborative test that one laboratory was routinely using two tracers with a calibration bias between the two on the order of 40%. Another laboratory had an apparent calibration bias of about 20% when it first submitted the results for the interlaboratory calibration. This was the laboratory which performed the calibration on a new dilution of the originally calibrated stock solution. However, when the new dilution was prepared an error was made in calculating the decay factor (1 year was overlooked).

A disconcerting finding emerged when the recalibration of the tracer was requested. One laboratory had just enough tracer left from the given batch to perform the recalibration. The laboratory which recalibrated using a different dilution, did so without even realizing it until certain discrepancies were pointed out by the referee. This laboratory had none of the original dilution

TABLE 13. SUMMARY OF COLLABORATIVE TEST RESULTS
(after recalibration)

Lab	Average Values for Samples Analyzed (dpm/g) A	B	C	D9	D8	Ranked Results for Samples Analyzed A	B	C	D9	D8	Score[a]
1	0.114	0.940	1.122	10.09	0.185	5	1	1	1	2	10
2	0.107	0.842	0.956	8.53	0.117	6	5	5	5	6	27
3	0.193	0.930	1.073	8.63	-	1	2	2	4	3.5	12.5
4	0.132	0.893	0.990	8.85	0.163	3	3	4	3	3.5	16.5
5	0.127	0.864	0.947	8.26	0.144	4	4	6	6	5	25
6	0.149	0.710	1.038	9.64	0.188	2	6	3	2	1	14
Known	0.113	0.901	1.03	8.99	0.138						
$\bar{X}$	0.137	0.863	1.021	9.000	0.159						
S_d	0.0311	0.0838	0.0691	0.711	0.0297						
S_r	0.0327	0.0785	0.0478	0.572	0.0345						
S_b	0.0247	0.0705	0.0633	0.630	0.0220						

[a]For 6 laboratories and 5 samples, the 5% two-tailed limits for ranking scores are 7 and 28.

TABLE 14. SUMMARY OF PRECISION DATA
(after recalibration)

Sample	Known (dpm/g)	$\bar{X}$ (dpm/g)	Coefficients of Variation (%) Within Lab	Between Labs	Total (Single Analysis)
A	0.113	0.137	23.9	18.0	29.9
D8	0.138	0.159	21.7	13.8	25.7
B	0.901	0.863	9.1	8.2	12.2
C	1.03	1.021	4.7	6.2	7.8
D9	8.99	9.000	6.4	7.0	9.5

TABLE 15. t-TEST TO DETECT BIAS
(after recalibration)

Analysis	m	t-calc.	t-crit.
A	6	1.89	2.57
D8	5	1.58	2.78
B	6	1.11	2.57
C	6	0.32	2.57
D9	6	0.03	2.57

left. If 6 months more had elapsed would any of the laboratories have been able to recalibrate? Is any laboratory routinely and periodically sealing portions of its actinide tracers in glass vials to enable it to answer future questions regarding calibration?

It has been demonstrated that tracer calibration procedures do indeed vary between laboratories. One laboratory, having the facilities to segregate high- and low-level operations may perform a calibration using high activities and short counting times. A laboratory without such facilities must wisely use much lower levels and longer counting times to avoid potential contamination. Long counts are more susceptable to error due to long-term instrument variations. Such an error introduced during the initial calibration of the tracer would subsequently bias all analytical results based on that tracer.

During the interlaboratory calibration, three of the laboratories calibrated the pipets or weighed solutions; the other three did not, even though they were specifically instructed to do so. One laboratory did not perform duplicate calibrations as requested and then counted the single sample only long enough to achieve a 2σ counting error of 6%. We must therefore conclude

that many laboratories, at times, appear reluctant to take even simple precautions to reduce the chance and degree of bias. Perhaps the answer here is to have all of the laboratories involved in environmental actinide analyses obtain the various tracers from a single batch, prepared and calibrated by the National Bureau of Standards or another qualified supplier. The laboratories would then independently recalibrate the supplied tracer only to reconfirm the certified value and would use only the certified value in their calculations. Such an approach would certainly improve the agreement between laboratories for a method of this type.

There are several comments to be made on how the individual laboratories handled the analytical portion of the method, the significance of the modifications they employed and the problem areas they encountered.

The collaborating laboratories reported that they did not significantly modify the sample decomposition or the chemical separation portions of the procedure. It can thus be assumed that uniform results were obtained in terms of equilibrating the tracer with the plutonium in the sample and decontaminating the plutonium from interfering actinides. Tracer equilibration and decontamination factors are discussed by the original developers of the method (Sill 1974b, Sill 1975). The laboratories unfamiliar with the method had problems mastering certain operations at first, but they felt there would be no problem once they obtained sufficient experience. This was also true for the single-laboratory evaluation performed at our laboratory. This inexperience could be partially responsible for the differences between our laboratory and the collaborating laboratories in the recoveries and the within-laboratory coefficient variations at the 1 to 10 dpm/g level (80% to 90% versus 30% to 80% and 2% to 3% versus 5% to 10%).

One of the most critical variables affecting both the plutonium recovery and the ability to resolve isotopes of plutonium by alpha spectrometry is the electrodeposition. Microgram quantities of elements carried through the procedure from the soil and the reagents, can result in lowered yields and degraded spectra (Sill 1974b). Lower yields can be compensated for by longer counting times, but degraded spectra can seriously affect the accuracy and precision of the analysis. The effect is more critical for plutonium-238 than it is for plutonium-239 when plutonium-236 is used as a tracer. Degradation is also directly proportional to the quantity of tracer used. The laboratories participating in this study employed a variety of electrodeposition techniques yielding a variety of results (Table 16).

There appears to be little correlation between the electrodeposition technique and the quality of results obtained. Marginal to good recoveries were obtained by the laboratories using the prescribed or their own electrodeposition technique while the laboratory attempting to compromise had significantly lower recoveries. No correlation could be made between the quality of resolution and the electrodeposition technique. Two of the four laboratories using the prescribed technique obtained good resolution while the other two obtained marginal resolution. Of the two laboratories using their own techniques, one obtained good resolution while the other did not.

Flaming the planchet before counting can either degrade or improve spectral resolution depending on the condition of the original plate (Sill 1976).

TABLE 16. ELECTRODEPOSITION RESULTS

Technique	Laboratory	Planchet Flamed	Average Recovery (%)[a]	Spectral Resolution
As prescribed	2	no	56 ± 17	Good
	3	no	70 ± 14	Marginal
	5	no	48 ± 23	Marginal
	This Lab	no	88 ± 7	Good
As prescribed but low amperage	1	yes	35 ± 12	Good
Own Technique	4	yes	70 ± 9	Good
	6	yes	64 ± 9	Marginal

[a]Including one standard deviation.

Flaming is not recommended for plates having a shiny appearance as it will generally degrade resolution. Two of the laboratories, however, reported good resolution in spite of flaming the planchet.

There could be fundamental problems in recommending a specific plutonium or actinide procedure which has performed well in a given laboratory to the rest of the scientific community and expecting comparable results. Actinide procedures are extremely sensitive to analyst technique and an analyst must thoroughly master the procedural operations before optimum results can be expected. There can also be subtle and unquantified variables that may critically affect the outcome of an analysis. These can be attributed to both technique and/or sample composition. If such variables are undefined they may be allowed to vary or not be compensated for in the prescribed written procedure and adversely affect results.

An additional important consideration is that a well-qualified laboratory may be unwilling to cope with certain specifically defined operations. Such operations may be those difficult or expensive to tool up for or even incompatible with existing facilities and ongoing activities. Several aspects of the single-laboratory evaluation and the collaborative test bear this out. The prescribed electrodeposition was not the one recommended by the laboratory which had originally developed the method (Puphal 1972). It was a compromise between our technique and theirs because we could not tool up to test the method using their electrodeposition as specified. Our equipment and facilities did not allow us to electroplate at as high an amperage as their procedure required nor could we electroplate in a fume hood to exhaust the chlorine evolved. The modifications were designed to make the method more available to other laboratories and they worked well at our laboratory. Even so, three of

the six collaborating laboratories found it necessary to electroplate at an even lower amperage.

Willingness to follow prescribed operations was not limited to the electrodeposition. The variations in the tracer calibration have been described earlier. Two of the laboratories were strongly against running the procedure routinely because of the tedium of the solvent extraction separations as well as other operations not associated with calibration or electrodeposition.

A few comments must be made regarding the choice between using plutonium-236 or plutonium-242 to trace the plutonium analysis. Laboratories have their own preference for very good reason and should be allowed the option of their choice. If a laboratory may unknowingly encounter levels of plutonium-239 high enough to subsequently mask the plutonium-242 tracer peak, then a plutonium-236 tracer would be the obvious choice. For laboratories routinely analyzing for low or near-background levels of plutonium-238, then a plutonium-242 tracer would result in a lower risk of method failure. If plutonium-240 to plutonium-239 ratios are to be determined by mass spectrometry to obtain information regarding the source of plutonium, then plutonium-242 would have to be used to trace the plutonium analysis.

Consideration must also be given to the fact that only 6 of approximately 30 laboratories performing plutonium analyses participated in the collaborative test and even these 6 did not follow the candidate method as specified. At present the situation can be ascribed neither to the procedure nor to the laboratories. In some instances, the procedure could not be implemented by the prospective user laboratories. In other instances, the laboratories themselves were hesitant to use techniques other than their own which they spent years developing and making cost effective. Perhaps a second collaborative test, already in progress, will aid in answering the question. This test will evaluate an acid dissolution technique for the measurement of plutonium in soil.

The results of the completed collaborative study lend credence to an alternate approach to that of proposing reference methods for achieving uniformity of results between laboratories in plutonium and other actinide analyses. This alternate approach would be to set criteria on the final results rather than on the method itself and to allow each individual laboratory to use its own method. It would specify single-laboratory precision and bias levels which a laboratory must demonstrate before its analytical results would be acceptable. Each laboratory would then be required to qualify its method on the basis of an effort similar to the collaborative test just described. Additional criteria would also be set for a given analysis. These would include minimum yield, maximum counting error and quality of spectral resolution. By allowing each laboratory to use its own method, all laboratories seriously interested in performing actinide analysis, instead of a small percentage, would become involved in similar collaborative studies. This would give a realistic view of the true state of the art of such analyses among the laboratories and would provide information regarding both potential problem areas and exceptional approaches which could be shared by the scientific community.

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APPENDIX

TENTATIVE METHOD FOR THE ANALYSIS OF PLUTONIUM-239 AND PLUTONIUM-238 IN SOIL (Fusion Technique)

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The method described in this Appendix was distributed to the participating laboratories for the interlaboratory collaborative test.

PREFACE

The analytical method described in this document is the proposed EPA reference method for the measurement of plutonium in soil.

The method was selected on the basis of theoretical considerations by a group of experts in the field of plutonium analysis. The method was then subjected to intensive single-laboratory testing to determine precision, accuracy, specificity, reliability, and interferences.

The method is proposed for collaborative testing to determine its suitability as a reference method. Data from the collaborative tests will be used to determine, on a statistical basis, the limits of error which can be expected when the method is used by a typical group of analysts.

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1. SCOPE AND APPLICATION

1.1 This method covers the analysis of soils for plutonium at levels greater than 0.01 disintegrations per minute per gram (dpm/g) in all chemical and physical forms known to exist in soils encountered in the United States. Such universal applicability, however, can be guaranteed only in the event of complete sample dissolution during the potassium fluoride and potassium pyrosulfate fusions.

1.2 The minimum detection level (MDL) of the method will depend on both the background counting rate of the alpha spectrometer and the amount of plutonium-238 and plutonium-239 contamination in the plutonium-236 tracer. Plutonium-236 having only a few hundredths percent of plutonium-238 and plutonium-239 contamination is now commercially available and is recommended for this procedure. For an analysis of 10 g of soil, employing 10 dpm of plutonium-236 tracer, a 1000-minute counting time on a spectrometer having a 17% counting efficiency and a background of 0.010 counts per minute (cpm) over each energy region of interest, and realizing an 80% plutonium recovery, the MDL is estimated to be 0.008 dpm/g.

1.3 The single-laboratory precision of the method at the 30- and 0.5-dpm/g levels of plutonium has been demonstrated to approach that of counting statistics alone. The accuracy of the method is expected to be within limits propagated from counting statistics and the ±2% error associated with the preparation of a standard soil sample used to evaluate the method.[8]

1.4 This method is recommended for use by experienced technicians under the supervision of a radiochemist or other qualified person who fully understands the concepts involved in the analysis and instrument calibrations. Furthermore, the method should be utilized only after satisfactory results are obtained by the analyst in Section 8, "Quality Assurance Program" in which

triplicate standard soil samples are analyzed.

2. SUMMARY

2.1 The principle of the analytical procedure follows. A known quantity of plutonium-236 tracer is added to the sample which is decomposed completely by a combination of potassium fluoride and pyrosulfate fusions with simultaneous volatilization of hydrogen fluoride and silicon tetrafluoride. The fused cake is dissolved in dilute hydrochloric acid and plutonium is precipitated with barium sulfate. The barium sulfate is dissolved in acidic aluminum nitrate and plutonium is extracted into a organic solvent. After scrubbing the organic extract with nitric and hydrochloric acids, plutonium is stripped with perchloric-oxalic acid solution, electrodeposited and determined by alpha spectrometry. Sequential potassium fluoride and pyrosulfate fusions are known to dissolve the most refractory and intractable plutonium compounds, allowing the complete exchange between the tracer and the plutonium in the sample. The chemical yield, counting efficiency, counting time, etc., are the same for all plutonium isotopes which simplifies calculations. In addition to the activity of plutonium-236 added and the weight of the sample, only the total number of counts of plutonium-236, plutonium-239, and/or plutonium-238 recovered is necessary to calculate the concentration of plutonium-239 and/or plutonium-238 in the sample.

3. INTERFERENCES

3.1 Reagents, glassware, and other sample processing hardware may cause contamination. All of these materials must be demonstrated free from contamination under the conditions of the analysis. Specific selection of reagents and sample processing hardware is detailed in the procedure.

3.2 Possible procedural interferences are noted when apt to be encountered.

4. APPARATUS (as described, or functionally equivalent)

4.1 INSTRUMENTATION AND ACCESSORIES

4.1.1 A windowless 2π gas flow proportional counter.

4.1.2 An alpha spectrometer capable of 40- to 50-kiloelectronvolt (keV) resolution of actual samples electrodeposited on flat, mirror-finished stainless steel planchets with a counting efficiency greater than 17% and a background less than 0.010 cpm over each designated energy region. Resolution is defined as the full width half maximum (FWHM) in keV, the distance between those points on either side of the alpha peak where the count is equal to one-half the maximum count. [1]

4.1.3 Disposable electrodeposition cells are constructed from 20-ml, linear-polyethylene, liquid-scintillation vials. (See Figure 1.) A 1.59-centimeter (cm) (5/8-inch) hole is cut in the bottom for introduction of the anode. The foil-lined caps are replaced by 22-millimeter (mm) Polyseal® caps having a GCMI 400 thread design. The tubular portion of the polyethylene liner is removed and the conical portion retained as a cover for the assembled cell. A 0.36-cm (9/64-inch) hole having a beveled inside edge is bored through the center of the cap. A 1.91-cm (3/4-inch) diameter washer with a 0.32-cm (1/8 inch) hole is cut from 0.08-cm (1/32-inch) neoprene and placed in the cap. The shank of a hollow brass rivet (Dot Speedy Rivets, #BS4830, Carr Fastener Co., Cambridge, Mass.) is passed through the washer and cap to serve as an electrical contact for the planchet cathode. [12]

4.1.3.1 The cathodes are 1.91-cm (3/4-inch) diameter, 0.38-mm (15 mil) thick, type 304 stainless-steel planchets pre-polished to a mirror finish. The exposed cathode area is 2.3 square centimeters (cm^2). Prior to use, the planchets are degreased with detergent and/or acetone, immersed in hot concentrated nitric acid for 10 minutes, rinsed, and stored under distilled water until needed.

4.1.3.2 The anode is a 1.27-cm (1/2-inch) diameter, 0.08-cm (1/32-inch platinum or platinum-iridium disk having six 0.32-cm (1/8-inch)

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perforations and attached at the center to a 10-cm (4-inch) length of 0.16-cm (1/16-inch) platinum or platinum-iridium rod.

4.1.3.3 To assemble the cell, the planchet is centered on the threaded end of the cell and held in place by vacuum applied through one of the holes of a two-hole rubber stopper butted against the other end. The cap assembly is screwed on and leakage checked by adding water to the cell and observing the rise of air bubbles when the vacuum is reapplied. Flexing the cell by alternately applying and releasing the vacuum improves the seal of leaky cells. The combined resilience of planchet and washer maintains the liquid seal and electrical contact during electrolysis.

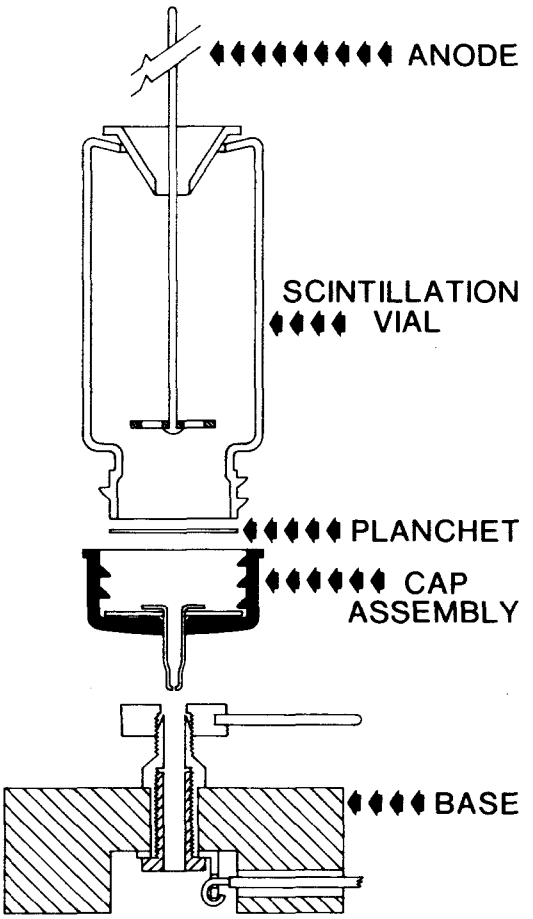

Figure 1. Disposable electrodeposition cell and support

4.1.3.4 Electrolysis is conducted without stirring, using an electroplating unit such as a 10-volt, 5-ampere Sargent-Slomin Electrolytic

Analyzer. The cell support and cathode socket consist of a non-insulating banana jack attached to a Lucite® base.

4.2 LABORATORY EQUIPMENT

4.2.1 Comminution equipment.

4.2.1.1 Mortar and pestle — porcelain, with 275-ml capacity.

4.2.1.2 Pulverizer — Arthur H. Thomas 3367-D05 pulverizer, pulverizes 1-pound quartz ore 0.64 cm in diameter to 0.15 mm (100 mesh) in 1 minute, requires 1-horsepower motor (optional).

4.2.2 Blender — Patterson-Kelly twin-shell blender, 4-liter capacity (optional).

4.2.3 Balance — Mettler top-loading balance, capacity 1200 g, precision ±0.05 g.

4.2.4 Drying equipment.

4.2.4.1 Drying oven — maximum temperature >110° C, including trays to fit.

4.2.4.2 Muffle furnace — maximum temperature >700° C.

4.2.4.3 Infrared drying lamp.

4.2.5 Temperature regulators.

4.2.5.1 Hot plate — capable of providing a temperature range of 10° C above ambient to 370° C.

4.2.5.2 Hot plate covered with asbestos cloth.

4.2.5.3 Fisher blast burner with a 4-cm grid — uses compressed air with gas, capable of producing a temperature of approximately 1000° C.

4.2.5.4 Cold water bath — open variety with provision to cool a platinum dish.

4.2.6 Shaker — mechanical, wrist action (optional).

4.2.7 Set of U.S. Standard Sieves — 10 mesh (2.0-mm opening), 200 mesh (74-μm opening) and 325 mesh (43-μm opening) (200 and 300 mesh sieves optional).

4.2.8 Centrifuge — capable of 2000 revolutions per minute (rpm) complete with 40-ml heavy-walled centrifuge tubes.

4.2.9 pH meter with electrodes.

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4.3 LABWARE

4.3.1 Pipets.

4.3.1.1 Automatic pipets with disposable tips — optional sizes.

4.3.1.2 Measuring pipets, Mohr type — 10, 5, and 1 ml.

4.3.1.3 Pipets treated with silicone water repellent to eliminate drainage and calibrated "to contain" by blowing residual liquid from the tip — 1 ml.

4.3.2 Dropping bottles.

4.3.3 Beakers — 2000, 1000, 800, 150, and 100 ml.

4.3.4 Watch glasses — for 800-, 150-, and 100-ml beakers.

4.3.5 Graduated cylinders — 1000, 500, 100, 50, 25, and 10 ml.

4.3.6 Erlenmeyer flasks — 250 ml graduated.

4.3.7 Separatory funnels — 2000 and 250 ml.

4.3.8 Volumetric flask — 50 ml.

4.3.9 Millipore® filter holder — Pyrex® 47-mm filter holder apparatus.

4.3.10 Buchner filtering apparatus — 11-cm diameter.

4.3.11 Membrane filters — 47-mm diameter, 0.45-μm-pore size, GA-6 cellulose Metricel filters and DM-450 membrane filters.

4.3.12 Filter paper, glass fiber, Whatman — grade GFC.

4.3.13 Platinum dish — semi-flat reinforced bottom, 250 ml.

4.3.14 Polyethylene containers — screw cap, capacity for 300 g powder.

4.3.15 Polyethylene wash bottles — optional sizes.

4.3.16 Teflon® FEP bottles — optional sizes.

4.3.17 Safety glasses.

4.3.18 Ring-stand assembly — with nichrome triangle to accommodate 250-ml semi-flat-bottomed platinum dish.

4.3.19 Tongs — platinum-tipped crucible type and test tube type.

4.3.20 Asbestos cloth — to cover hot plate and serve as pads, 0.16-cm thick.

4.3.21 Boiling chips — silicon carbide, 8 mesh.

4.3.22 Timer — minute intervals.

4.3.23 Scissors.

4.3.24 Spatulas — optional sizes.

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4.3.25 Glazed paper sheets.

4.3.26 Disposable aluminum pans for use in muffle furnace.

4.3.27 Rubber policemen.

4.3.28 Glass stirring rods.

4.3.29 Glass bottle — screw cap, capacity for 2.5 liters.

4.3.30 Stainless-steel disks — to set under platinum dishes, 5-cm (2-inch) diameter.

5. STANDARDS, ACIDS, REAGENTS

5.1 STANDARDS

5.1.1 National Bureau of Standards (NBS) americium-241 point source — approximately 3×10^5 dpm, deposited on platinum and certified to ±1% of its stated activity.

5.1.2 Plutonium-239 certified standard solution — approximately 5×10^4 dpm per ml of plutonium-239 in 2M nitric acid (available from Oak Ridge National Laboratory) (optional).

5.1.3 Plutonium-236 solution — 2.5×10^4 dpm of plutonium-236 in 2M nitric acid in minimal solution (available from Oak Ridge National Laboratory).

5.1.4 Americium-241 solution — 1×10^5 dpm of americium-241 in 2M nitric acid in minimal solution.

5.2 ACIDS

All solutions are made with distilled water. All acids are reagent grade and meet American Chemical Society (ACS) specifications.

5.2.1 Hydrochloric acid — concentrated (12M), 10M, and 6M adjusted to 0.3M in sulfuric acid.

5.2.2 Hydrofluoric acid — concentrated (48% solution).

5.2.3 Nitric acid — concentrated (16M), 8M, 4M, and 2M.

5.2.4 Oxalic acid — powder.

5.2.5 Perchloric acid — concentrated (72% solution).

5.2.6 Sulfuric acid — concentrated (18M), 1.8M, 0.9M, 0.18M, and 0.09M.

5.3 REAGENTS

All solutions are made with distilled water. All reagents listed are

reagent grade and meet ACS specifications, unless otherwise defined.

5.3.1 Aliquat-336 (NO_3) – 30% (by volume) in xylene.

Dissolve 300 ml of Aliquat-336, methyltricaprylyl ammonium chloride (General Mills, Inc., Kankakee, Ill.), in 700 ml of xylene in a 2-liter separatory funnel. Shake vigorously for 4 minutes with each of two successive 200-ml portions of 4M nitric acid, draining and discarding the aqueous phase each time. (This will convert the amine to the nitrate form.) Shake vigorously for 4 minutes with each of three successive 300-ml portions of distilled water, draining and discarding the aqueous phase each time. Allow final moisture to settle out overnight. Draw the organic phase into a suitable screw-capped, glass bottle for storage.[10]

5.3.2 Aluminum nitrate, acidic – 2.2M.

Weigh 825 g of dry $Al(NO_3)_3 \cdot 9H_2O$ into a 2-liter beaker, add 450 ml of distilled water and warm until the salt dissolves. Add 85 ml of concentrated nitric acid and cool to room temperature. Filter the solution through a well-washed DM-450 membrane filter in a Buchner funnel. (This will remove insoluble materials, particularly iron.) The density of this solution should be 1.370 grams per ml at 25° C. (Pipet and weigh 1.00 ml of solution.) If the density is not 1.370, add additional $Al(NO_3)_3 \cdot 9H_2O$ to produce this density. (The number of grams of additional aluminum nitrate nonahydrate required per liter of solution can be calculated by multiplying the difference between the measured density and 1.370 by 4400.) Do not boil the solution or loss of nitric acid will eventually result in hydrolysis of plutonium and a decrease in both extraction efficiency and ability to dissolve barium sulfate.[10]

5.3.3 Ammonium hydroxide – concentrated (15M), 1.5M, and 0.15M, free of solid material.

5.3.4 Ammonium nitrate, anhydrous.

5.3.5 Ammonium sulfate, crystalline.

5.3.6 Barium chloride dihydrate – 0.45% solution.

5.3.7 Ceric sulfate.

5.3.8 Detergent.

5.3.9 Diethylenetriamine pentaacetic acid (DTPA).

5.3.10 Electrodeposition solution – 1.0M $(NH_4)_2SO_4$, 0.013M $NH_2OH \cdot HCl$, 0.0033M DTPA, 0.01M $H_2C_2O_4$, pH 3.5.

Add 132 g of ammonium sulfate, 1.26 g of oxalic acid dihydrate and 0.90 g hydroxylamine hydrochloride to 900 ml of distilled water in a 2-liter beaker and heat to dissolve. Dissolve 1.31 g of diethylenetriamine pentaacetic acid (DTPA) in a minimum of 1:1 ammonium hydroxide with heating and add to the main solution using a water rinse. (3.33 millimoles of the pentasodium salt of DTPA in aqueous solution may be substituted.) Cool the solution to room temperature and adjust the pH to 3.5 using concentrated sulfuric acid and a pH meter to monitor the pH. Dilute the solution to 1 liter with distilled water.

5.3.11 Ethyl alcohol, alkaline.

Add a few drops of concentrated ammonium hydroxide to approximately 100 ml of ethyl alcohol.

5.3.12 Ferrous ammonium sulfate, hydrous.

5.3.13 Hydrogen peroxide — 30% solution.

5.3.14 Hydroxylamine hydrochloride.

5.3.15 Potassium fluoride, anhydrous.

5.3.16 Potassium hydrogen sulfate, crystalline.

5.3.17 Potassium nitrate, anhydrous.

5.3.18 Potassium metabisulfite — 25% solution.

5.3.19 Potassium sulfate, anhydrous.

5.3.20 Reprecipitating solution.

Dissolve 135 g of anydrous potassium sulfate in 915 ml of distilled water and 50 ml of concentrated hydrochloric acid with warming.[10]

5.3.21 Silicone water-repellent solution.

5.3.22 Sodium hydrogen sulfate, monohydrate.

5.3.23 Sodium sulfate, anhydrous.

5.3.24 Sodium nitrite — 25% solution.

5.3.25 Thymol blue, sodium salt — 0.02% solution.

5.3.26 Xylene.

6. CALIBRATION AND STANDARDIZATION

6.1 CALIBRATION OF THE 2π ALPHA COUNTER AND THE ALPHA SPECTROMETER.[10]

6.1.1 The windowless, 2π alpha counter is standardized by counting the NBS americium-241 source to approximately 5×10^5 total counts.

6.1.2 The efficiency of the 2π alpha counter is calculated by dividing the observed counts per minute (cpm) by the certified disintegrations per minute (dpm) of the NBS americium-241 source.

6.1.3 Correct the counting efficiency for the difference in backscatter between platinum and stainless steel by dividing the calculated efficiency (from 6.1.2) by 1.023.[2,5]

6.1.4 Because a point-source standard electrodeposited on platinum (the NBS americium-241 source) cannot be used to calibrate an alpha spectrometer with an external detector for use with diffuse sources electrodeposited on stainless steel, a secondary standard must be employed. Prepare a secondary standard containing about 1×10^4 dpm of americium-241 electrodeposited on stainless steel under the exact conditions subsequently described for electrodeposition of samples.

6.1.5 Standardize the secondary standard by counting in the 2π counter until at least 2×10^5 counts have been collected.

6.1.6 Use the secondary standard to calibrate the alpha spectrometer and to periodically check the initial calibration of both the spectrometer and the 2π counter.

6.2 PURIFICATION OF THE PLUTONIUM-236 TRACER[6,11]

In order to accurately calibrate the plutonium-236 tracer by 2π counting and alpha spectrometry, it will be necessary to ensure the absence of plutonium-236 daughters (uranium-232, thorium-228, radium-224, etc.) in the tracer. The following purification must be performed just prior to the initial calbiration and annually thereafter if additional calibrations are desired.

6.2.1 Mix 2.5×10^4 dpm of plutonium-236 with 3 g of anhydrous potassium sulfate and 3 ml of concentrated sulfuric acid in a graduated 250-ml Erlenmeyer flask.

6.2.2 Heat the flask on an uncovered hot plate at maximum temperature until the sulfuric acid fumes and the potassium sulfate dissolves.

6.2.3 Heat the solution over a high-temperature blast burner while swirling the flask continuously until a pyrosulfate fusion is obtained. Continue heating until the heavy fuming subsides and most of the excess acid has been volatilized.

6.2.4 Cool the melt to room temperature and add 0.5 ml of concentrated

sulfuric acid and 35 ml of distilled water.

6.2.5 Add 1 drop of 30% hydrogen peroxide and boil for 5 minutes on an uncovered hot plate to oxidize uranium and to ensure complete reduction of plutonium.

6.2.6 Add 1 ml of a 0.45% barium chloride solution to the boiling solution at a rate of 1 drop every 2 seconds while swirling the flask continuously.

6.2.7 Boil the solution for an additional 1 minute and repeat the addition of another 1 ml of barium chloride solution by the same technique.

6.2.8 Boil the solution again for 1 minute and cool for 10 minutes in a bath of cold running water.

6.2.9 Transfer the cold solution and precipitate to a 40-ml heavy-walled centrifuge tube with small portions of distilled water to give a total volume of 30 to 40 ml.

6.2.10 Centrifuge at approximately 2000 rpm for 5 minutes. Decant and discard the supernate. Wash the barium sulfate precipitate with 5 ml of 0.09M sulfuric acid; centrifuge and discard the supernate.

6.2.11 Add 1 ml of 72% perchloric acid to the centrifuge tube and heat carefully over a blast burner with continuous swirling to dissolve the barium sulfate without letting the solution bump.

6.2.12 Cool the solution for 1 minute and immediately add 25 ml of 8M nitric acid and 1 ml of 25% sodium nitrite.

6.2.13 Transfer the solution to a 250-ml separatory funnel with another 25 ml of 8M nitric acid and extract for 2 minutes with 50 ml of 30% Aliquat-336 (NO_3) in xylene.

6.2.14 Scrub the organic extract for 1 minute with 50-ml of 10M hydrochloric acid, and discard the scrub. Repeat this step.

6.2.15 Strip the plutonium from the organic extract first with 50 ml of solution containing 5 ml of 72% perchloric acid and 2 g of oxalic acid and then with 25 ml of water. Transfer the strips to a 250-ml Erlenmeyer flask (preferably one made of Vycor® or quartz to avoid any leaching of non-volatile materials).

6.2.16 Add 5 ml of concentrated nitric acid and evaporate the solution to near dryness. Add nitric acid as necessary throughout the evaporation of

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perchloric acid (especially if the solution darkens) to ensure the smooth and complete oxidation of any organic material. CAUTION: Wet ashing with perchloric acid can be extremely hazardous. It is mandatory that the analyst be thoroughly familiar with these hazards as well as accepted safety practices.

6.2.17 Near the end of the evaporation, swirl the flask continuously over a small flame from a blast burner until virtually all of the perchloric acid has volatilized. Heat the walls of the flask gently to prevent any condensation of the perchloric acid fumes. Do not bake the residue. Remove the flask from the burner just prior to complete dryness and allow the last of the acid to evaporate from the heat in the glass itself.

6.2.18 Add 5 ml each of concentrated hydrochloric and nitric acids to the flask and re-evaporate to about 2 ml on a hot plate.

6.2.19 Add 15 ml of concentrated nitric acid and boil down to about 5 ml to ensure complete dissolution of the plutonium and complete oxidation of chlorides as indicated by the absence of color or fumes of chlorine and/or nitrogen oxides.

6.2.20 Cool, add 25 ml of water, and filter the solution through a DM-450 membrane filter. Wash the flask and filter with enough distilled water to give a final volume of 50 ml.

6.2.21 Dilute aliquots of the ∿500 dpm/ml stock solution with 2M nitric acid to give concentrations desired for use. Store all tracers in tightly capped Teflon® FEP bottles.

6.3 STANDARDIZATION OF THE PLUTONIUM-236 TRACER [10]

6.3.1 Transfer a 1-ml aliquot of the purified plutonium-236 stock tracer (∿500 dpm/ml) in 2M nitric acid onto a stainless-steel planchet with a calibrated silicone-treated pipet and slowly evaporate to near dryness under an infrared lamp to minimize any loss. Keep the activity in the center of the planchet in an area limited to approximately 2 cm (3/4-inch) in diameter by alternately adding the tracer a few drops at a time and evaporating. The partially filled silicone-treated pipet can be placed on its side between additions with no loss of solution. To ensure quantitative transfer of the tracer, carefully blow out the last few drops with a rubber bulb.

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6.3.2 When the last of the tracer has been transferred to the planchet and evaporated nearly to dryness, add 2 or 3 drops of concentrated nitric acid to help keep the activity spread as uniformly as possible and evaporate to complete dryness.

6.3.3 Heat the dry planchet over a blast burner just to the first dull red glow. Then quickly lower the temperature by placing the planchet on a cold steel surface to minimize oxidation of the plate.

6.3.4 Count in the 2π alpha counter immediately after cooling to avoid any possibility of absorbing water vapor from the air. Collect at least 5×10^4 counts for the standard to ensure adequate statistical precision.

6.3.5 Prepare and count a duplicate source by repeating steps 6.3.1 through 6.3.4.

6.3.6 The 2π counting rate of the plutonium-236 sources must be corrected by determining the fraction of the total alpha activity due to plutonium-236.

6.3.6.1 Transfer 2 ml of the purified plutonium-236 tracer ($\sim$500 dpm/ml) to a 250-ml Erlenmeyer flask and add 4 ml of a 5% solution of sodium hydrogen sulfate monohydrate in 1:1 sulfuric acid.

6.3.6.2 Evaporate carefully on a hot plate to near dryness.

6.3.6.3 Treat and electrodeposit as described in steps 7.7.3 through 7.7.14.

6.3.6.4 Count the electroplated source on an alpha spectrometer to 250 minutes over an energy range of 3 to 8 MeV. Determine the fraction of the total number of counts in the alpha spectrum that is due to plutonium-236 in the source. This fraction is the correction factor to be applied to the counting rate of the plutonium-236 evaporated source in the 2π proportional counter. NOTE: Prolonged and repeated counting of high-level plutonium-236 sources on the alpha spectrometer should be avoided to minimize daughter recoil contamination of the alpha detector. Alternately, such contamination can be virtually eliminated by leaving a small amount of air in the counting chamber and applying a small negative potential to the source plate.[9]

6.3.7 Calculate the activity concentration of the plutonium-236 tracer (dpm plutonium-236 per ml) by multiplying the observed 2π counting rates of the evaporated sources by the correction factor and dividing by the 2π counter efficiency and the volume of tracer used to prepare the evaporated sources.

7. STEP-BY-STEP PROCEDURE FOR ANALYSIS

7.1 PREPARATION OF SOIL FOR ANALYSIS[10]

7.1.1 Break up soil aggregates, and pull apart any topsoil plugs. Cut up any large pieces of vegetation and combine with the major soil sample.

7.1.2 Oven dry the sample at 110° C for 24 hours and allow it to cool for 2 hours.

7.1.3 Weigh the entire sample to ±0.5%. Denote this weight as K.

7.1.4 If root mat is present, heat the entire sample in a disposable aluminum foil pan in a muffle furnace at 400° C for 3 hours to char the organic material.

7.1.5 Grind the sample lightly using a mortar and pestle, using just enough pressure to break up the clods of soil but not enough to grind the small pieces of rock and sand that are inevitably present.

7.1.6 Pass the soil through a 10-mesh (2.0-mm opening) sieve to remove any large rocks.

7.1.7 Weigh the sample which passed through the 10-mesh sieve. Denote this weight at L.

7.1.8 Transfer the sieved soil to a plastic bag or plastic bottle and shake for a few minutes to ensure adequate mixing.

7.2 SAMPLE DECOMPOSITION[10]

7.2.1 Weigh a representative 10.0 ± 0.1 g of the prepared soil sample and transfer into a dry 250-ml semi-flat-bottomed platinum dish.

7.2.2 Add concentrated nitric acid a few drops at a time to one edge of the powder as fast as the frothing and vigor of the reaction will permit until the entire sample is covered with acid and a free-flowing suspension is obtained. Do not swirl or allow the solution to froth higher than about 2 cm from the top of the dish.

7.2.3 Heat the solution gently on a covered hot plate until all vigorous reaction and frothing has subsided.

7.2.3.1 If significant reaction persists, evaporate the slurry to dryness, cool, and then add concentrated nitric acid to give a thin slurry.

7.2.4 If the activity is expected to be less than 1 dpm/g, or is

unknown, add 10 dpm of the plutonium-236 working tracer. For higher levels, add as much plutonium-236 tracer as the estimated activity of plutonium-239 or plutonium-238 in the sample. The total volume of tracer added should not exceed 5 ml.

7.2.5 Add 48% hydrofluoric acid carefully a few drops at a time with intermittent heating until the vigorous reaction has subsided. CAUTION: Hydrofluoric acid is an extremely hazardous liquid. Use gloves to avoid contact with skin and work in a fume hood to avoid breathing vapors.

7.2.6 Carefully add an additional 10 ml of 48% hydrofluoric acid and evaporate until all liquid disappears and the cake is just moist with acid. (If allowed to bake, the residue sticks tightly to the bottom of the dish, retarding subsequent dissolution and increasing corrosion of the dish in the presence of phosphates. If the sample is particularly high in iron, rapid and complete dissolution in the subsequent fluoride fusion is facilitated if somewhat more hydrofluoric acid is allowed to remain.)

7.2.7 Add 30 g of anhydrous potassium fluoride (flux) and mix the sample and flux with a glass stirring rod for a few seconds to give a coarse mixture.

7.2.8 Place the platinum dish on a nichrome triangle on a ring stand and carefully apply as much heat as possible, with a high-temperature blast burner, until the contents have dissolved completely and a clear melt is obtained. As necessary, swirl gently to dissolve the sample present on the sides of the dish. (The supporting ring must be sufficiently large to ensure even heating of the dish. Approximately 6 to 10 minutes will be required to dissolve the contents completely. Moderate quantities of organic matter will oxidize smoothly without special attention. Oxidation of larger quantities will be facilitated by addition of 1 g of solid potassium nitrate, although high-iron samples will then precipitate earlier in the melt.)

7.2.9 When the sample completely dissolves, heat the sides of the dish so that any solidified flux melts and runs down into the bottom of the dish.

7.2.10 Remove the dish from the flame. As the melt begins to solidify, swirl the dish gently to deposit the cake uniformly thin on the bottom and sides of the dish up to about 2 cm from the top. (This facilitates its transposition and lessens deformation of the dish.)

7.2.11 Cool to room temperature. Slowly add 35 ml concentrated sulfuric acid around the sides of the dish in small increments allowing the frothing to

subside between each addition.

7.2.12 Place the dish on the covered hot plate, and heat gently until the solution begins to froth. If necessary, remove from heat until the frothing subsides. Be prepared to set the dish in a cold water bath to quench the reaction rapidly if the frothing threatens to go over the top of the dish. (Frothing is caused by the evolution of hydrogen fluoride and silicon tetrafluoride.)

7.2.13 Repeat step 7.2.12 as necessary.

7.2.14 When danger of frothing over is past, gently heat the dish — first on the covered hot plate, then on a small stainless steel disk on an uncovered hot plate. Keep the subsequent frothing to a minimum until the potassium fluoride cake has been transposed to a slurry. A layer of solid salts builds up on the sides of the dish, and most of the water and excess sulfuric acid are driven off, leaving a slightly moist cake.

7.2.15 Gently heat the dish over the blast burner until the solids on the sides melt and the last few small chunks of the main cake dissolve. (If the transposition is carried out too rapidly and there are quite large chunks of original potassium fluoride cake still present when the temperature is raised over the blast burner to make the pyrosulfate fusion, hydrofluoric acid will be driven out of the solution faster than the chunks of cake will dissolve and the fluoride remaining will be insufficient to volatilize the last of the silica completely. Consequently, the cake will not transpose completely to give a clear pyrosulfate fusion in the following step.)

7.2.16 Add 20 g of anhydrous sodium sulfate. Heat carefully with a low flame from the blast burner until the thick almost solid suspension changes to a thin one that is easily boiled. As fast as boiling will permit, increase the temperature until the entire sample has dissolved and a clear pyrosulfate fusion is obtained. (Occasionally, if the transposition is performed a little too fast, a slight scum of silica might be present on the surface of the melt but will do no harm. Do not heat the pyrosulfate fusion any hotter or longer than necessary to give a clear melt to minimize dissolution of platinum from the dish.)

7.2.17 Remove the dish from the flame. When the melt starts to solidify, swirl the dish gently to deposit the cake in a thick layer around the sides of the dish. Allow the sample to cool to room temperature.

7.2.18 Add 350 ml distilled water and 25 ml concentrated hydrochloric acid to an 800-ml beaker and heat to boiling on an uncovered hot plate.

7.2.19 As soon as the solution begins to boil, flex the sides of the platinum dish gently to break the cake loose and carefully empty the contents into the hot solution.

7.2.20 Continue to heat the solution and cake as rapidly as possible on the uncovered hot plate with continuous stirring. (This will prevent severe bumping and ensure the immediate dissolution of the calcium sulfate cake as it disintegrates. Calcium sulfate becomes distinctly less soluble in dilute acid the longer it is allowed to stand in the crystalline state.)

7.2.20.1 If the calcium sulfate dissolves completely, or only a slight turbidity remains, add 50 ml of water.

7.2.20.2 If the calcium sulfate does not dissolve completely, add minimal amounts of concentrated hydrochloric acid until the turbidity decreases. A maximum of 50 ml more may be added in this step. Further boiling should yield an essentially transparent solution in a few minutes. Add distilled water until the total volume of additional added concentrated hydrochloric acid and distilled water is 50 ml.

7.2.20.3 In the unusual event that the solution does not clear up sufficiently with the additional 50 ml of concentrated hydrochloric acid, transfer the solution to a 2-liter beaker with 375 ml of distilled water and heat to dissolve the remaining calcium sulfate, adding up to an additional 75 ml of concentrated hydrochloric acid and/or distilled water as necessary. If calcium sulfate still remains undissolved, add another 375 ml of distilled water and up to another 75-ml portion of concentrated hydrochloric acid and continue heating. (This should dissolve a sample containing as much as 3.2 g of calcium in 10 grams of soil.) Add 70 g of solid potassium hydrogen sulfate to the hot solution for each additional 375-ml portion of water used in this step to dissolve the sample (i.e., 70 g for one addition, 140 g for two).

7.2.21 Add 5 ml of 25% potassium metabisulfite and a couple of 8-mesh silicon carbide boiling chips to the solution from step 7.2.20.1, 7.2.20.2, or 7.2.20.3.

7.2.22 Cover the beaker with a watch glass and boil the solution for 10 to 15 minutes to hydrolyze condensed phosphates and to ensure complete reduction of plutonium to the quadrivalent state. Proceed with precipitation of barium sulfate.

7.3 BARIUM SULFATE PRECIPITATION[7,10,11]

7.3.1 Remove the watch glass momentarily and add 5 ml of a 0.45% solution of barium chloride dihydrate to the boiling solution from a 5-ml Mohr pipet in about 0.5-ml increments every 3 seconds while stirring the solution vigorously and continuously with a stirring rod.

7.3.2 Replace the watch glass and continue boiling the solution for 1 minute.

7.3.3 Repeat the addition of 5-ml portions of the barium chloride solution followed by a 1-minute boiling period five more times until a total of 30 ml of the 0.45% barium solution has been added.

7.3.4 Filter the hot solution through a 47-mm GA-6 Metricel filter in the filtering chimney.

7.3.5 Rinse the beaker and the precipitate with 0.09M sulfuric acid delivered from a polyethylene wash bottle. Do not transfer the boiling chips.

7.3.6 Discard the filtrate and wash solution.

7.4 REPRECIPITATION OF BARIUM SULFATE[7,10,11]

7.4.1 Place the GA-6 Metricel filter containing the barium sulfate into a 250-ml Erlenmeyer flask and add 4 ml concentrated sulfuric acid and 3 drops concentrated nitric acid.

7.4.2 Heat the solution on a covered hot plate until the sulfuric acid fumes and then more strongly over a blast burner until the barium sulfate has dissolved completely and the brown color from the filter has been destroyed. If necessary, add an additional 1 ml of concentrated sulfuric acid to obtain complete dissolution. (Do not permit evaporation of any significant quantity of sulfuric acid or part of the barium sulfate will reprecipitate in a high-temperature modification that is not readily soluble in the subsequent aluminum nitrate dissolution. Subsequently, the barium sulfate particles will become coated with the water-immiscible organic solvent in the extraction process and will transfer to the organic phase giving a pseudo-extraction effect.)

7.4.3 Add 1 drop of a 1:1 mixture of concentrated nitric and 72% perchloric acids to the hot solution to oxidize the last of the organic matter.

7.4.4 Immediately set the flask off to cool to room temperature.

7.4.5 After the flask has cooled, add 60 ml of the reprecipitating solution and 1 ml of 25% potassium metabisulfite.

7.4.6 Set the flask on the uncovered hot plate.

7.4.7 When the cake has disintegrated, add 1 ml of a filtered 20% solution of ferrous ammonium sulfate in 0.9M sulfuric acid and boil the solution for 2 minutes. (This will complete the reduction of hexavalent plutonium that will have been produced in the perchloric acid oxidation.)

7.4.8 Filter the barium sulfate while still hot on another GA-6 Metricel filter and wash with a few milliliters of 0.09M sulfuric acid.

7.4.9 Discard the filtrate and wash solution.

7.5 DISSOLUTION OF BARIUM SULFATE[10]

7.5.1 Place the filter containing the barium sulfate in a 250-ml Erlenmeyer flask.

7.5.2 Add 2 ml of concentrated nitric acid and 4 ml of 72% perchloric acid. CAUTION: Wet ashing organic material with perchloric acid can be extremely hazardous. It is mandatory that the analyst be thoroughly familiar with these hazards and accepted safety precautions.

7.5.3 Heat the flask on a hot plate until the refluxing perchloric acid reaches the top of the flask. (By this time, the filter will have been oxidized and the barium sulfate will have been dissolved completely. Certain soil samples, however, may not clear up completely because of the presence of other elements, but any remaining precipitate will dissolve subsequently in the aluminum nitrate. Longer boiling with perchloric acid should be avoided because of increased oxidation of both cerium and plutonium in the sample, making complete reduction by sodium nitrite more difficult. If not reduced subsequently, quadrivalent cerium carries through the extraction and causes severe interference in the electrodeposition, and the recovery of plutonium is less complete.)

7.5.4 Remove the flask from the hot plate for 1 minute.

7.5.5 Combine 50 ml of the acidic 2.2M aluminum nitrate solution and 1 ml of 25% sodium nitrite solution and pour into the flask rapidly while swirling the flask continuously.

7.5.6 Heat the solution just to the boiling point. (This will redissolve any traces of barium sulfate that might have reprecipitated.)

7.5.7 Allow the solution to cool to room temperature.

7.6 EXTRACTION OF PLUTONIUM[10]

7.6.1 Organic extraction of plutonium.

7.6.1.1 Pour the solution into a 250-ml separatory funnel and add 50 ml of 30% Aliquat-336 (NO_3) in xylene.

7.6.1.2 Rinse the walls of the flask with 25 ml of the 2.2M acidic aluminum nitrate solution and add 5 ml of 25% sodium nitrite.

7.6.1.3 Transfer the rinse to the separatory funnel, and swirl the separatory funnel just enough to distribute the blue color of the nitrous acid through the aqueous phase and allow to stand for 2 minutes.

7.6.1.4 Shake vigorously for 3 minutes, preferably on a mechanical shaker, but not hard enough to cause formation of stable emulsions.

7.6.1.5 Allow the solution to stand for 10 minutes.

7.6.1.6 Discard the aqueous phase.

7.6.1.7 Swirl the separatory funnel and let the solution stand for another 2 minutes.

7.6.1.8 Discard the additional aqueous phase that separates due to drainage. (This will ensure maximum elimination of the large quantity of barium and aluminum present.)

7.6.2 First acid scrub of the organic phase to strip the tervalent actinides and lanthanides.

7.6.2.1 Shake for 2 minutes with three successive 10-ml portions of 8M nitric acid. After each of the three scrubs, allow the phases to separate for 2 minutes and drain and discard the lower aqueous layer. (This will remove the last traces of barium, aluminum, tervalent actinides and lanthanides, particularly cerium.)

7.6.3 Second acid scrub of the organic phase to strip thorium.

7.6.3.1 Shake for 3 minutes with three successive 50-ml portions of 10M hydrochloric acid. After each scrub allow the phases to separate for 2 to 3 minutes and drain and discard the lower aqueous layer. If levels of thorium higher than normal are present in the soil (>130 µg/10g), increase the number of hydrochloric acid scrubs.

7.6.4 Acid extraction of plutonium.

7.6.4.1 Shake vigorously for 2 minutes with 50 ml of a solution containing 5 ml of 72% perchloric acid and 2 g of oxalic acid.

7.6.4.2 Allow to stand for at least 2 minutes for adequate phase separation.

40-60 keV 75 .1μm

7.6.4.3 Drain the aqueous phase into a 250-ml Erlenmeyer flask and save.

7.6.4.4 Shake the organic phase vigorously for 2 minutes with 25 ml of distilled water.

7.6.4.5 Allow to stand for at least 2 minutes for adequate phase separation.

7.6.4.6 Drain the aqueous phase into the same 250-ml Erlenmeyer flask used in step 7.6.4.3.

7.7 ELECTRODEPOSITION[4,12]

7.7.1 Add 4 ml of a 5% solution of sodium hydrogen sulfate monohydrate in 1:1 sulfuric acid and 5 ml of concentrated nitric acid to the 250-ml Erlenmeyer flask.

7.7.2 Evaporate the solution to near dryness on an uncovered hot plate to volatilize perchloric and sulfuric acids. Add nitric acid as necessary throughout the evaporation (especially if the solution darkens) to ensure complete oxidation of all organic matter. CAUTION: Wet ashing with perchloric acid can be extremely hazardous. It is mandatory that the analyst be thoroughly familiar with these hazards and accepted safety precautions.

7.7.3 Continue heating on the uncovered hot plate, until the sulfuric acid has volatilized completely. During the last stages of this evaporation, it will be necessary to gently flame the sides of the flask with the blast burner to prevent condensation of the acid. Remove from the heat and cool to room temperature to crystallize the salts. (Upon cooling, the salts must be dry with no visible droplets of acid on the sides of the flask. If significant acid is allowed to remain in this step the pH during electrodeposition will be too low and the plutonium recovery will be reduced.)

7.7.4 Add 2 ml of a 6M hydrochloric acid – 0.3M sulfuric acid solution and heat on an uncovered hot plate to dissolve the salts. Continue heating until the dense fumes of sulfuric acid first appear and immediately remove from the hot plate and cool. Dissolve the sample by adding 5 ml of the pre-adjusted electrodeposition solution and warming. Transfer the solution to the electrodeposition cell using an additional 5 ml of the electrodeposition solution in small increments to rinse the flask.

7.7.5 The solution should be ready for electrodeposition without any

further adjustment. (Three drops of thymol blue indicator added to the solution in the cell should yield a definite reddish-pink color. If the solution has a straw-yellow hue add 1.8M sulfuric acid dropwise to a definite reddish-pink end point.)

7.7.6 Lower the platinum anode into the solution until the bottom edge of the anode is about 2 mm above the shoulder of the cell. (If set too deeply, gas bubbles will be trapped and cause fluctuation of the current.)

7.7.7 Turn on the current and adjust to 1.2 amps.

7.7.7.1 As the solution warms the current will increase and must be readjusted to 1.2 amps when it rises above this value.

7.7.7.2 After 15 to 30 minutes the current will stabilize and electrolysis can be allowed to continue at 1.2 amps without attention for a total electrolysis time of 1.5 to 2.0 hours.

7.7.8 Without cutting off the current, add 10 ml of 1.5M ammonium hydroxide and continue the electrolysis for 1 minute.

7.7.9 Lift the anode out of the cell and then switch off the current.

7.7.10 Discard the solution in the cell.

7.7.11 Rapidly flood the cell three times with a solution of 1% ammonium nitrate in 0.15M ammonium hydroxide.

7.7.12 Disassemble the cell.

7.7.13 Quickly wash the planchet with a stream of alkaline ethyl alcohol. Touch a piece of filter paper to the edge of the planchet to absorb the film of alcohol.

7.7.14 Write the sample number on the bottom of the planchet. Place the planchet in a cupped planchet and heat for 10 minutes on an uncovered hot plate.

7.7.15 Count the sample in an alpha spectrometer to resolve the isotopes of plutonium. For samples containing less than 1 dpm/g of plutonium a minimum of 1.5×10^3 counts should be collected for the plutonium-236 tracer. For higher levels, count for 1000 minutes or until 10^4 counts have been collected in each of the plutonium-236 and the plutonium-239 and/or plutonium-238 energy regions.

NOTE: Protactinium-231 quantitatively follows plutonium through this procedure and if it is present in the soil its peak will be found at 100 to 130 keV lower energy than the plutonium-239 peak in the alpha spectrum. Under normal

conditions these peaks should be completely resolved. If not, graphically plot the two peaks and resolve by extrapolation.

8. QUALITY ASSURANCE PROGRAM

For any analytical procedure, a rigorous quality assurance program must be followed to ensure accurate and precise results. Such a program must include the evaluation of all variables in the final calculation for their degrees of uncertainty and for any significant systematic errors. Precautions must be taken to eliminate any cross contamination between samples, especially if high- and low-level samples are run concurrently. Standard samples should be analyzed both to check out initial capabilities and to provide for a continuing quality control program.

8.1 The internal laboratory precision of the method is evaluated by considering the uncertainties in all the variables in the final calculation. These include the counting uncertainties associated with counting the sample and the standards for calibration, uncertainties associated with pipettings and tracer dilutions and weighing the original sample, and any uncertainty in the timing of the 2π count during the calibrations. All uncertainties should be evaluated and, if significant, propagated to the final result. Variability between laboratories is expected to be greater than that for a single laboratory due to the variability in NBS standards used for calibration, slight differences in calibration procedures, etc. The interlaboratory precision of the method can be adequately estimated only on the basis of collaborative testing. Systematic errors in the method will be minimized by calibrating all pipets, volumetric flasks, and balances used for the tracer calibration and sample analysis, and by calibrating the 2π counter timing mechanism. The systematic error introduced by the $\pm 1\%$ uncertainty in the NBS standard and the error in the backscatter correction factor cannot be compensated for.

8.2 Cross contamination of samples may be avoided with good housekeeping and by either segregating apparatus used for high- and low-level samples, or by carefully decontaminating glassware and platinumware between analyses.

Contamination of stock reagents must be avoided. This can best be accomplished by employing intermediate containers to which small portions of the stock reagents can be transferred before adding to the sample. The excess reagent is then discarded and the intermediate container rinsed before reuse. Reagent blanks using the same reagents, tracer, glassware, platinumware, electrodeposition equipment and detector must be run initially and periodically thereafter to determine the radiochemical background for the method and ascertain that contamination of these items has not occurred.

8.3 PREPARATION OF STANDARD SOILS[8] (optional)

Standard soil samples prepared as outlined below should be analyzed in triplicate to evaluate the initial capabilities of a laboratory and periodically thereafter to provide for a continuing quality control program.

8.3.1 From the desired geographical area, select two or three times as much soil (approximately 5400 g) as the total quantity of standards to be prepared. Dry for 24 hours at about 110° C.

8.3.2 Grind the sample lightly in a mortar and pestle, using just enough pressure to break up the clods of soil but not enough to grind the small pieces of rock and sand that are inevitably present.

8.3.3 Heat the entire sample in a disposable aluminum foil pan in a muffle furnace at 400° C for 3 hours to oxidize organic material.

8.3.4 Sieve using a 200-mesh (74-μm opening) U.S. Standard Sieve. Discard the rocky residue not passing through the sieve.

8.3.5 Blend the entire batch of prepared soil overnight.

8.3.6 Resieve about 600 g of the -200-mesh stock soil through a combination of 200-mesh and 325-mesh (44-μm opening) sieves until about nine tenths of the material has passed a second time through the 200-mesh sieve. (This is to ensure absence of larger or irregular particles to facilitate resieving of the final spiked material.)

8.3.7 Remove the 200-mesh sieve and continue shaking the 325-mesh sieve until little more of the fine material passes through.

8.3.8 Place approximately 100 g of the -200, +325-mesh fraction into a 250-ml platinum dish. Combine and save the remaining fractions of the 600 g of -200-mesh stock soil in the two screens and pan.

8.3.9 Add small portions of distilled water to the soil in the platinum

dish and stir thoroughly until a smooth paste is obtained.

8.3.10 Add 1 ml of a standard solution containing about 5×10^4 dpm/ml of plutonium-239 in 2M nitric acid dropwise with continuous stirring from a calibrated silicone-treated pipet. Mix each drop of the radioactive solution thoroughly throughout the wet soil with a heavy glass stirring rod before adding the next drop.

8.3.11 Heat the mud under an infrared lamp while stirring thoroughly and continuously until the mass becomes immobile. (This is to prevent separation of any liquid phase that could evaporate to form areas of higher concentrations or "hot spots" of activity.) Break the soil into small pieces with the stirring rod. Save the soil clinging to the stirring rod and any escaping soil particles for the subsequent determination of plutonium-239 losses.

8.3.12 Dry the sample at 110° C for several hours and then muffle the sample at 700° C for 4 hours.

8.3.13 In the following grinding and screening operations, it is mandatory that all of the spiked soil be accounted for in order to make the necessary correction for plutonium-239 losses. Perform these operations on a large sheet of glazed paper to recover any lost soil. Take the necessary precautions to avoid inhaling any radioactive dust or contaminating the laboratory area.

8.3.14 Grind the dried material with a mortar and pestle until it passes entirely through the 200-mesh sieve. Collect the sieved material in the pan provided with the sieve. (It will be necessary to tap the screen sharply against the bench top to keep the sieve from glazing over with the fine powder obtained on grinding.)

8.3.15 Add enough of the same unspiked -200-mesh stock soil to give a total of 1800 ± 1 g and blend overnight to ensure homogeneity.

8.3.16 To determine the quantity of plutonium-239 activity not included in the soil sample, quantitatively transfer all of the residual spiked soil left on the stirring rod, mortar and pestle, screen pan and the glazed paper to the residual material in the platinum dish used to prepare the spiked soil. Use nitric and hydrofluoric acids, as well as a rubber policeman, if necessary, to rinse the stirring rod and mortar and pestle. Rinse the screen and pan with distilled water.

8.3.17 Add a few milliliters of 48% hydrofluoric acid and 500 dpm of calibrated plutonium-236 working tracer to the platinum dish.

8.3.18 Evaporate to dryness.

8.3.19 Analyze the residue as described in Section 7.

8.3.20 Subtract the activity remaining in the dish from the activity added and divide by the total weight of the prepared soil.

8.3.21 When prepared as directed, the sample contains about 28 dpm/g of plutonium-239. Smaller concentrations can be prepared either by using a smaller quantity of the plutonium initially or by blending weighed quantities of the higher standard with additional weighed quantities of the same -200-mesh soil used to prepare the original standard. When samples are prepared with concentrations below a few dpm/g, the soil should be obtained from at least 2 feet below the surface of undisturbed ground to minimize corrections that must be made for the radionuclides present from global fallout.

9. CALCULATION OF RESULTS[3,5]

9.1 CALIBRATION OF THE 2π ALPHA COUNTER

9.1.1 The counting efficiency of the 2π counter is determined by counting an NBS certified americium-241 source electrodeposited on a platinum disk.

9.1.2 The 2π counting efficiency ($E_{2\pi}$) is calculated as:

$$E_{2\pi} = \frac{C_1}{(a_1)(t)(1.023)} \qquad (9.1.2)$$

in which C_1 = the net counts of the americium-241 source

a_1 = the certified activity of the americium-241 source (dpm)

t = the duration of the count (min)

1.023 = the backscatter factor correcting the counting efficiency of a source on platinum to that on stainless steel

9.2 STANDARDIZATION OF THE PLUTONIUM-236 TRACER

9.2.1 The purified plutonium-236 stock tracer is standardized by counting evaporated sources on the 2π counter and an electrodeposited source on the alpha spectrometer. The 2π count, which represents total activity, is corrected by multiplying by the plutonium-236 fraction of the total activity as determined by alpha spectrometry.

9.2.2 The activity concentration (AC in dpm plutonium-236 per ml) of the stock tracer is calculated from:

$$AC = \frac{(C_{2\pi})(f_6)}{(E_{2\pi})(v)(t)} \qquad (9.2.2)$$

in which $C_{2\pi}$ = the net counts of the evaporated source on the 2π counter

$E_{2\pi}$ = the counting efficiency of the 2π counter

v = the volume of stock tracer used to prepare the evaporated source (ml)

t = the duration of the count for the evaporated source on the 2π counter (min)

f_6 = the ratio of the net counts in the plutonium-236 energy region to the net counts in the entire 3 to 8 MeV energy region in the alpha spectrum of the electroplated tracer source

9.2.3 The plutonium-236 activity (T in dpm) added to the sample to trace the plutonium recovery through the analysis is calculated as:

$$T = (AC)(D)(V)(e^{-\lambda t}) \qquad (9.2.3)$$

in which AC = the activity concentration of the stock tracer solution (dpm plutonium-236 per ml)

D = the dilution factor in preparing the working tracer from the stock tracer

V = the volume of working tracer added to the sample (ml)

$e^{-\lambda t}$ = the decay correction for plutonium-236 for the time interval between the date of tracer calibration and date of sample analysis

9.3 CALCULATION OF PLUTONIUM CONCENTRATIONS IN THE ALIQUOT OF SOIL TAKEN FOR ANALYSIS

9.3.1 The concentration of plutonium-239 or plutonium-238 in the aliquot of soil taken for analysis (X_i in dpm/g) is calculated from:

$$X_i = \frac{(C_i)(T)}{(C_6)(W)} \qquad (9.3.1)$$

in which C_i = the net sample counts in the plutonium-239 or plutonium-238 energy region of the alpha spectrometer

C_6 = the net sample counts in the plutonium-236 energy region of the alpha spectrometer

T = the activity of plutonium-236 tracer added to the sample (dpm)

W = the weight of the soil aliquot taken for analysis (g)

9.3.2 The above calculation assumes that the plutonium-236 tracer used in the analysis is sufficiently free from plutonium-238 and plutonium-239 activities (<0.1%) to cause negligible interference in the plutonium determinations. Older supplies of plutonium-236 (pre-1974) may contain appreciable amounts of plutonium-238 and/or plutonium-239 (up to 1% or 2%) and should not be used. If the poorer grade tracer is used, a freshly purified portion must be assayed for plutonium-236, plutonium-238, and plutonium-239 by alpha spectrometry and the necessary corrections for adding plutonium-238 and plutonium-239 to the sample with the tracer must be made.

9.4 CALIBRATION OF THE ALPHA SPECTROMETER AND CALCULATION OF THE PLUTONIUM RECOVERY

9.4.1 The absolute counting efficiency of the alpha spectrometer (E_s) must be determined in order to evaluate the plutonium recovery through the analytical procedure. Americium-241 electroplated in the same manner as the samples should be used for this purpose. The spectrometer counting efficiency may be calculated from:

$$E_s = \frac{(r_s)(E_{2\pi})}{r_{2\pi}} \qquad (9.4.1)$$

in which r_s = the net counting rate of the electroplated source over the entire energy region on the alpha spectrometer (cpm)

$r_{2\pi}$ = the net counting rate of the same source on the 2π counter (cpm)

$E_{2\pi}$ = the counting efficiency of the 2π counter

9.4.2 The plutonium recovery through the analysis (Y) is calculated from:

$$Y = \frac{R_6}{(T)(E_s)} \qquad (9.4.2)$$

in which R_6 = the net counting rate in the plutonium-236 energy region of the alpha spectrum of the sample (cpm)

9.5 PROPAGATION OF UNCERTAINTIES

9.5.1 The uncertainties associated with the plutonium-236 tracer calibration and the soil analysis are estimated from the 2σ or 95% confidence level (95% C.L.) uncertainties of all appropriate radioactivity counts, weighings, pipettings, dilutions and measurements of counting times.

9.5.2 The 2σ or 95% C.L. uncertainty in a net radioactivity count, $C = G - B$, is:

$$\pm 2\sqrt{G + B}$$

in which G = the gross number of counts collected
B = the expected number of background counts during the same time interval

The uncertainties in the other variables are determined experimentally by replicate calibrations.

9.5.3 For linear addition or subtraction of independent variables, uncertainties are propagated by taking the square root of the sum of the squares of the individual uncertainties.

9.5.4 For linear multiplication and division of independent variables, the fractional uncertainty in the final result is obtained by taking the square root of the sum of the squares of the fractional errors in each of the independent variables.

10. SAMPLE CALCULATIONS

10.1 CALIBRATION OF THE 2π ALPHA COUNTER

10.1.1 The NBS certified americium-241 standard (3.23×10^5 dpm ± 1%) was counted on the 2π alpha counter for 10.00 ± 0.02 minutes. The total number of

counts collected was 1,564,612 ± 2,500 at the 95% C.L. (2σ).

10.1.2 The 2π counting efficiency calculated from equation 9.1.2 is:

$$E_{2\pi} = \frac{1{,}564{,}612 \pm 2{,}500^{*}}{(3.23 \times 10^{5})(10.00 \pm 0.02)(1.023)}$$

$$= 0.474 \pm 0.001$$

10.2 STANDARDIZATION OF THE PLUTONIUM-236 TRACER

10.2.1 The first evaporated source of 1.029 ± 0.002 ml of the stock plutonium-236 tracer gave 61,124 ± 494 net counts for a 250.0 ± 0.0 minute count on the 2π counter. The electroplated tracer counted for 250 minutes on the alpha spectrometer yielded 51,460 net counts in the plutonium-236 energy region and 62 net counts in the rest of the 3 to 8 MeV energy region, giving a correction factor (f_6) of

$$\frac{51{,}460}{51{,}460 + 62} \pm 2\left(\frac{(51{,}460)(62)}{(51{,}460 + 62)^{3}}\right)^{\frac{1}{2}}$$

or 0.999 ± 0.000 to be applied to the 2π count.[5]

10.2.2 The activity concentration (AC) of the plutonium-236 tracer calculated from equation (9.2.2) is:

$$AC = \frac{(61{,}124 \pm 494)(0.999 \pm 0.000)}{(0.474 \pm 0.001)(1.029 \pm 0.002)(250.0 \pm 0.0)}$$

$$= 501 \pm 4 \text{ dpm plutonium-236 per ml at the 95\% C.L.}$$

10.2.3 The second evaporated source yielded an activity concentration value of 495 ± 4 dpm plutonium-236 per ml.

10.2.4 Averaging the two values, the activity concentration of the stock tracer is:

AC = 498 ± 3 dpm plutonium-236 per ml at the 95% C.L.

10.3 CALCULATION OF PLUTONIUM-239 AND PLUTONIUM-238 CONCENTRATION IN THE ALIQUOT OF SOIL TAKEN FOR ANALYSIS

10.3.1 A 1.002 ± 0.002 ml aliquot of working plutonium-236 tracer (stock tracer diluted 1.029 ± 0.002 to 49.8 ± 0.01) was added to 10.0 ± 0.1 g of

*To avoid confusion, experimentally observed values were not rounded off in all equations. The calculated results, however, have been rounded off to the appropriate number of significant figures for the given situation.

the -10-mesh fraction of the soil sample and the analysis was performed 65 days after the calibration of the stock tracer ($e^{-\lambda t} = 0.958$). A 1134-minute spectrometer count of the sample yielded the following data.

Energy Region	Gross Counts	Background Counts	Net Counts $\pm 2\sigma$
Plutonium-236	1953	10	1943 ± 89
Plutonium-239	1394	6	1388 ± 75
Plutonium-238	215	8	207 ± 30

10.3.2 The amount of plutonium-236 tracer added (T in dpm) is calculated from equation (9.2.3).

$$T = (498 \pm 3)\left(\frac{1.029 \pm 0.002}{49.8 \pm 0.01}\right)(1.002 \pm 0.002)(0.958)$$
$$= 9.88 \pm 0.07 \text{ dpm plutonium-236}$$

10.3.3 The plutonium-239 and plutonium-238 concentrations in the -10-mesh fraction taken for analysis are calculated from equation (9.3.1).

$$X_9 = \frac{(1388 \pm 75)(9.88 \pm 0.07)}{(1943 \pm 89)(10.0 \pm 0.1)}$$
$$= 0.71 \pm 0.05 \text{ dpm plutonium-239 per g}$$

$$X_8 = \frac{(207 \pm 30)(9.88 \pm 0.07)}{(1943 \pm 89)(10.0 \pm 0.1)}$$
$$= 0.11 \pm 0.02 \text{ dpm plutonium-238 per g}$$

10.4 CALIBRATION OF THE ALPHA SPECTROMETER AND CALCULATION OF THE PLUTONIUM RECOVERY

10.4.1 The electroplated americium-241 source (step 6.1.4) yielded 206,741 ± 909 net counts in the 3 to 8 MeV energy range for a 100.0 ± 0.0 minute count on the alpha spectrometer. A 100.0 ± 0.0 minute count of the same source on the 2π counter yielded 465,093 ± 1,363 net counts.

10.4.2 The counting efficiency of the spectrometer (E_s) is calculated from equation (9.4.1).

$$E_s = \frac{(2067 \pm 9)(0.474 \pm 0.001)}{(4651 \pm 14)}$$
$$= 0.211 \pm 0.001$$

10.4.3 The plutonium recovery for the analysis of the soil sample calculated from equation 9.4.2 is:

$$Y = \frac{(1943 \pm 87)/1134}{(9.88 \pm 0.07)(0.211 \pm 0.001)}$$

$$= 0.82 \pm 0.04$$

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15. SUPPLEMENTARY NOTES

16. ABSTRACT This report presents the results of a single-laboratory evaluation and an interlaboratory collaborative test of a method for measuring plutonium in soil. The method employs potassium fluoride and potassium pyrosulfate fusions to decompose a 10-gram sample, barium sulfate precipitations, solvent extraction and electrodeposition to isolate the plutonium, and alpha spectrometry to measure the plutonium. The method is appended to the report.

The single-laboratory evaluation demonstrated that the overall within-laboratory precision of the method can approach the precision of nuclear counting statistics alone. The interlaboratory collaborative test showed the coefficient variation representing differences between laboratories to be approximately 10% for concentration levels exceeding 1 disintegration per minute per gram.

Also discussed are several problem areas associated with environmental actinide analyses. These include the difficulties which may be anticipated in requiring monitoring laboratories to adopt a specific complex method of this type. Suggestions are presented for improving agreement between laboratories by establishing criteria for analytical results rather than requiring specific methodology.

This report covers a period from January 1, 1974, to September 30, 1976, and work was completed as of December 31, 1976.

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