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Radiometric Method for the Determination of Uranium in Soil and Air

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RADIOMETRIC METHOD FOR THE DETERMINATION OF URANIUM IN SOIL AND AIR: Single-Laboratory Evaluation and Interlaboratory Collaborative Study

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FOREWORD

Protection of the environment requires effective regulatory actions that 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 that 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 for exposure assessment through 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 study of a method for measuring uranium in soil and air. 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 studies also allow each participating laboratory to critically evaluate its capabilities in comparison with 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.

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Director
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ABSTRACT

Results of a single-laboratory evaluation and an inter-laboratory collaborative study of a method for determining uranium isotopes in soil and air samples are presented. The method is applicable to 10-gram soil samples and to both glass fiber and polystyrene (Microsorban) air filter samples. Sample decomposition is accomplished with a nitric-hydrofluoric acid dissolution. After a solvent extraction step to remove most of the iron present, the uranium is isolated by anion exchange chromatography and electrodeposition. Alpha spectrometry is used to measure the uranium isotopes.

Two soil samples, a glass fiber air filter sample, and a polystyrene air filter sample were used to evaluate the method for uranium concentrations ranging from a few tenths to about one hundred disintegrations per minute per sample. Tracer recoveries for the single-laboratory evaluation averaged 78%, while the tracer recoveries for the collaborative study averaged 66%. Although the precision of the collaborative study results did not approach counting statistics errors, the measured uranium concentrations for these samples agreed to within 5% of the reference concentrations when the uranium concentration was greater than one disintegration per minute per gram of soil or one disintegration per minute per air filter.

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Acknowledgement is also given to the following laboratories which provided materials used in this study: Environmental Measurements Laboratory, New York, N. Y.; Environmental Monitoring and Support Laboratory, U.S. EPA-Las Vegas, Nevada; and the Radiological and Environmental Sciences Laboratory, Idaho Falls, Idaho.

INTRODUCTION

With the increased operations of nuclear power plants and with projections that even greater production of nuclear energy will be necessary to meet future energy demands (Lee, et al., 1977), the determination of uranium in environmental samples is becoming more important. Production of nuclear energy involves many processes which could be sources of unacceptable releases of uranium or other radioactive materials into the environment, including uranium mining, uranium milling, conversion of uranium to uranium hexafluoride, enrichment, fuel fabrication, reactor power plant operations and fuel reprocessing. Additional sources of releases may also occur during transportation and waste management of the radioactive materials.

The objective of this study was to choose and evaluate a method which could be recommended for measuring uranium isotopes in environmental soil and air samples. Fluorometric procedures (ASTM, 1977a; Danielsson et al., 1973) are most commonly used for the determination of small concentrations of natural uranium; however, such measurements are only indicative of uranium-238 due to its extremely low specific activity. In many cases, uranium-234 is not in equilibrium with uranium-238 in soils and ores (Sill, 1977; NCRP, 1975), and environmental samples may be enriched in uranium-235. The concentrations of these isotopes should be measured. Isotopic data are of considerable help in understanding both biological and geological processes and are also necessary to assess the lung dose resulting from exposure to uranium-containing materials.

In addition to being an isotopic method, the recommended method would have to be applicable to a wide variety of soil samples found in the United States and to air samples collected on polystyrene or glass fiber filters. The method would also have to produce results of sufficient accuracy and precision, be free from interferences, be cost-effective, and be applicable for routine analyses.

SUMMARY

This report presents the results of a single-laboratory evaluation and interlaboratory collaborative study of a candidate method for the determination of uranium in air and soil. The method was chosen on the basis of a literature search and a preliminary laboratory evaluation of currently available methods. Reference soil samples and both glass fiber and polystyrene air filter samples were analyzed in a single-laboratory evaluation done at Mound Facility to show that criteria previously established for the method were met. After the single-laboratory evaluation, a copy of the procedure (Appendix I) and the reference samples were sent to fourteen other laboratories for analysis by the present method. Uranium-232 tracer which had been standardized at Mound was also supplied to the laboratories so that all laboratories would be using the same tracer. Eight laboratories had submitted results after about a 7-month period, and a statistical evaluation of the collaborative study was carried out.

CONCLUSIONS

The requirments set forth in the criteria for the method (defined in next section) were satisfied by the present procedure for the determination of uranium isotopes in soil and air. Chemical recoveries averaged 78% for the single-laboratory evaluation at Mound and 66% for the multilaboratory collaborative study. Uranium activities in the range of a few tenths of a disintegration per minute (dpm) were measured and, when the uranium concentrations were greater than one dpm per gram of soil or one dpm per air filter, the average deviation from the reference concentration was about 5%. The relative standard deviations of the collaborative results among the laboratories averaged about 10% for concentration levels exceeding one dpm per gram of soil or one dpm per filter. Plutonium, americium, polonium and thorium tracers (30 to 300 dpm) were used to show that these elements did not interfere with the uranium analysis.

The single-laboratory and interlaboratory evaluations showed that the present method provides a relatively simple and accurate means of determining uranium in soil and air samples.

CRITERIA

Criteria for the present method were established based on a literature review of published methods for determining uranium in soil and air samples and the environmental data obtained using these methods.

The criteria were as follows:

1. The method will be a radiometric method yielding isotopic information, rather than a chemical method giving only total uranium.

2. The method will be applicable to up to 10 grams of a wide variety of soil samples found in the U.S. and shall also be applicable to air samples collected on polystrene or glass fiber filters.

3. The method will be capable of determining highly insoluble forms of uranium.

4. The method will reflect cost effectiveness by emphasizing simplicity of equipment, reagents and procedures.

5. The chemical yield of the method will be 50% or better.

6. The sensitivity of the method with 10-gram soil samples or air filter samples will be 0.10 dpm/g or dpm/filter, respectively.

7. Plutonium, americium, polonium, and thorium tracers will be used in testing the method to give assurance that isotopes of these elements do not interfere with the uranium analysis.

8. The single-laboratory relative standard deviation of the method, not including the counting statistics error, will be $\sim$5% or better.

9. The accuracy of the method will be dependent upon the accuracy of the tracer activity U-232, which is expected to be about 1.5%, the accuracy in the measurement of the amount of tracer added, and the counting errors.

CHOICE OF METHOD

Three methods are commonly used for the initial decomposition of environmental samples: acid leach, acid dissolution, and fusion. Since the acid dissolution and fusion methods provide more rigorous decomposition of the sample matrix than the acid leach method, it was decided to omit the acid leach method from further consideration. A recent comparison of acid dissolution and fusion methods for the analysis of plutonium in soil (Whittaker and Grothaus, 1979) has strongly indicated that the two methods are equivalent, even for highly refractory forms of plutonium. This study showed that the acid dissolution method was less time-consuming and more economical than the fusion method; therefore, an acid dissolution method, similar to that used for the measurement of plutonium in soil (USAEC, 1974), was chosen for the present method.

A method for the measurement of uranium isotopes in water has been recently developed at Mound Facility (Bishop et al, 1978) through an Interagency Agreement with the EPA's Environmental Monitoring and Support Laboratory-Las Vegas (EMSL-LV). Several of the analytical techniques used in the uranium-in-water method were found to be applicable to the measurement of uranium isotopes in soil and air samples. After sample decomposition by an acid dissolution procedure, the uranium could be concentrated by coprecipitation with iron hydroxide and isolated by anion exchange chromatography in a hydrochloric acid medium, prior to electrodeposition onto a stainless steel slide for alpha pulse height analysis. However, soil and air samples usually contain a great deal more iron than water samples, making it necessary to remove the bulk of this iron before the ion exchange separation to prevent overloading of the anion exchange column with ferric ions. Extracting the hydrochloric acid sample solution with isopropyl ether (Morrison and Freiser, 1957) before passing this solution through the ion exchange column was found to be an effective way to remove most of the iron from the sample solution.

PREPARATION OF REFERENCE MATERIALS

Two air filters and two soil samples were prepared as reference materials for the single-laboratory evaluation and the collaborative study. The first simulated air sample, referred to as Sample 1, was prepared by pipeting 250 λ of a

diluted uranium-236 standard solution onto a 70-mm diameter glass fiber filter and drying in an oven at 120°C. Based on the standardization of the U-236 standard solution by the National Bureau of Standards (NBS), the activity deposited onto each prepared filter was 1.33 dpm. The uncertainty of the calibration of the standard solution was reported by the NBS to be 0.94 percent. A second simulated air sample, referred to as Sample 3, was prepared by placing 40.0 mg of a standard diluted pitchblende ore between the layers of a rectangular Microsorban filter (100 mm x 125 mm) and sealing the filter in a plastic bag. When these samples were analyzed, both the plastic bag and the filter were ignited to ensure that no sample would be lost by removing the filter from the plastic bag. The diluted pitchblende ore was obtained from the EPA's EMSL-LV and had a uranium-238 concentration of about 560 dpm/g. The diluted ore was prepared by the Radiological and Environmental Services Laboratory, U. S. Department of Energy, Idaho Falls, Idaho by diluting an extensively characterized primary unaltered pitchblende ore in secular equilibrium with a background soil (Sill, 1977).

The first reference soil sample, referred to as Sample 2, was blended at the EMSL-LV and analyzed by Mound and EMSL-LV. Uranium concentrations of the isotopes U-238 and U-234 in dpm/g were, respectively, 1.91 ± 0.06 and 2.78 ± 0.08 from Mound's analyses and 1.89 ± 0.07 and 2.77 ± 0.05 from the analyses done at EMSL-LV using their method. The second reference soil sample, referred to as Sample 4, was prepared by physically hand-mixing 2 grams of a standard pitchblende ore (Sill, 1977) with 100 grams of a soil of a known uranium content, and then blending this mixture with about 500 additional grams of the same soil. The blending was carried out in a Patterson/Kelly twinshell blender for a total of about 96 hours. The soil of known uranium content was obtained from Environmental Measurements Laboratory, U. S. DOE, New York, N. Y. During the blending of the soil, duplicate 5-gram samples were taken for analysis at approximately 30 hours, 48 hours and at the end of the sample period, and the measured average concentrations of U-238 and U-234 in dpm/g for these samples were, respectively, 20.30 and 20.14 (30 hrs), 20.81 and 20.51 (48 hrs), and 21.30 and 20.86 (96 hrs).

SINGLE-LABORATORY EVALUATION

A single-laboratory evaluation of the present method was performed at Mound Facility in order to determine if the criteria that had been established for the method had been met before proceeding with the interlaboratory collaborative study. The reference materials described in the previous section were used to evaluate the method, and the results of the single-

TABLE 1. SINGLE-LABORATORY EVALUATION CONCENTRATIONS AND RECOVERIES FOR SAMPLE 1 (Glass Fiber Filter)[a]

Sample	U-238 (dpm/filter)	U-234 (dpm/filter)	U-236 (dpm/filter)	Recovery %
1A	0.184	0.227	1.38	93
1B	0.249	0.293	1.44	101
1C	0.193	0.207	1.28	85
1D	0.200	0.214	1.40	77
Avg.	0.207 ± 0.029	0.235 ± 0.039	1.38 ± 0.07	89 ± 10
Ref.			1.32 ± 0.03	

TABLE 2. SINGLE-LABORATORY EVALUATION CONCENTRATIONS AND RECOVERIES FOR SAMPLE 2 (Reference Soil)

Sample	U-238 (dpm/gram)	U-234 (dpm/gram)	U-235 (dpm/gram)	Recovery %
2A	1.78	2.69	0.109	62
2B	1.87	2.66	0.087	75
2C	1.90	2.81	0.097	73
2D	1.90	2.76	0.091	77
2E	1.93	2.77	0.099	79
2F	1.90	2.83	0.100	71
2G	1.92	2.64	0.093	78
2H	2.01	2.86	0.103	58
2I	1.99	2.89	0.089	86
2J	1.94	2.79	0.102	75
2K	1.90	2.81	0.100	83
2L	1.89	2.76	0.096	66
Avg.	1.91 ± 0.06	2.77 ± 0.08	0.098 ± 0.007	74 ± 8

[a]Errors in Tables 1 through 4 represent one standard deviation.

TABLE 3. SINGLE-LABORATORY EVALUATION CONCENTRATIONS AND RECOVERIES FOR SAMPLE 3 (Microsorban Filter)

Sample	U-238 (dpm/filter)	U-234 (dpm/filter)	U-235 (dpm/filter)	Recovery %
3A	23.1	48.5	1.91	91
3B	22.2	41.4	1.86	67
3C	23.0	47.5	2.00	91
3D	21.8	40.3	1.82	89
3E	23.7	29.2†	1.48†	86
3F	19.5	41.5	1.85	86
3G	22.3	44.2	1.85	77
3H	23.0	40.2	1.88	90
3I	25.5	46.5	1.99	83
Avg.	22.7 ± 1.6	43.8 ± 3.4	1.90 ± 0.07	84 ± 8

†Rejected by ASTM test.

TABLE 4. SINGLE-LABORATORY EVALUATION CONCENTRATIONS AND RECOVERIES FOR SAMPLE 4 (Diluted Pitchblende Ore)

Sample	U-238 (dpm/gram)	U-234 (dpm/gram)	U-235 (dpm/gram)	Recovery %
4A	20.32	20.39	1.02	88
4B	20.02	19.86	1.03	42
4C	20.32	19.90	1.02	88
4D	21.39	21.20	1.18	25
4E	21.25	20.92	1.05	80
4F	21.30	20.77	1.42†	70
Avg.	20.77 ± 0.61	20.51 ± 0.55	1.06 ± 0.07	66 ± 26
Ref.	20.54 ± 0.23	20.54 ± 0.23	0.89 ± 0.02	

†Rejected by ASTM test.

laboratory evaluation of these samples are summarized in Tables 1 through 4. Reference values for Samples 1 and 4 were calculated from the concentrations of the standard materials used in the preparation of these samples and are given in Tables 1 and 4. Since reference values were not known for Samples 2 and 3, the average uranium concentrations determined in the single-laboratory evaluation for these samples were used as reference concentrations in the subsequent collaborative study. An ASTM-recommended criterion (ASTM 1977a), which is discussed in the next section of this report, was used for rejection of outliers.

Four duplicate analyses were performed on a soil sample of known uranium concentration, obtained from Environmental Measurements Laboratory, New York, to test the present procedure for interferences from other radionuclides. The following tracers were added for these analyses: Po-210 (87 dpm) and U-236 (10 dpm); Pu-236 (93 dpm), Am-241 (258 dpm) and U-236 (10 dpm); Th-228 (38 dpm) and U-236 (10 dpm); and for one duplicate determination no tracers were added to ensure that there were no alpha peaks in the areas of interest. The final spectra from these analyses showed that no plutonium and thorium could be detected (<0.1%), while only very small peaks were observed for polonium (<0.3%) and americium (<1%).

INTERLABORATORY COLLABORATIVE STUDY

Fourteen laboratories agreed to participate in a multilaboratory collaborative study of the present method, and they were sent the procedure to be used, the reference materials, specific collaborative study instructions (Appendix 2), and U-232 tracer solution, which had been standardized at Mound. After about 7 months, 8 of the 14 laboratories had completed their analyses, while the other 6 laboratories were unable to participate in the study because of other commitments. Each laboratory was randomly assigned a number from 1 to 8 and their results are listed in Tables 5 through 8. Each of these tables also gives the averages of the replicate results, $\bar{X}$; the experimental standard deviations, S_i; the ratios of the average value to the known value, $\bar{X}/X_{Ref}$; and the uranium tracer recovery for each of the analyses. Since Mound and EPA personnel decided in previous studies (Bishop et al., 1978, 1979) that determinations which had chemical recoveries less than 20% were unacceptable, data listed in these tables with such low recoveries were rejected as questionable and omitted from further consideration. Outliers were rejected on the basis of an ASTM-recommended criterion for rejection (ASTM 1977b).

TABLE 5. COLLABORATIVE STUDY RESULTS FOR SAMPLE 1 (Glass Fiber Filter - Reference Concentration: U-238 = 0.21 dpm/filter; U-234 = 0.24 dpm/filter; U-236 = 1.32 dpm/filter)[a]

Lab	U-238[b] (dpm/filter)	$\bar{X} \pm S_i$ (dpm/filter)	$\frac{\bar{X}}{X_{Ref}}$	U-234[b] (dpm/filter)	$\bar{X} \pm S_i$ (dpm/filter)	$\frac{\bar{X}}{X_{Ref}}$	U-236[b] (dpm/filter)	$\bar{X} \pm S_i$ (dpm/filter)	$\frac{\bar{X}}{X_{Ref}}$	Recovery %
1	0.17±0.01	---[c]	0.81	0.10±0.01	---	0.42	1.32±0.03	---	1.00	80
2	--- ---	---	---	1.18±0.18* 0.51±0.07	---	2.13	--- ---	---	---	17 51
3	0.14±0.03 0.21±0.04	0.17±0.05	0.81	0.13±0.03 0.38±0.05	0.25±0.18	1.04	1.22±0.09 1.50±0.10	1.36±0.20	1.03	71 58
4	0.70±0.07 1.69±0.09	1.20±0.70†	5.71	0.66±0.07 1.64±0.09	1.15±0.69†	4.79	0.76±0.07 1.31±0.08	1.04±0.39†	0.79	63 81
5	--- ---	---	---	--- ---	---	---	1.23±0.04 1.19±0.06	1.21±0.03	0.92	80 84
6	0.36±0.03 0.26±0.02	0.31±0.07	1.48	0.49±0.04 0.32±0.02	0.40±0.12	1.67	1.25±0.06 1.31±0.05	1.28±0.04	0.97	44 76
7	0.26±0.05 0.20±0.03	0.23±0.04	1.10	0.20±0.05 0.20±0.03	0.20±0.00	0.83	1.28±0.12 1.20±0.08	1.24±0.06	0.94	30 64
8	0.075±0.023 0.041±0.014	0.058±0.024	0.28	0.007±0.007 0.046±0.015	0.027±0.028	0.12	1.60±0.14 1.24±0.10	1.42±0.25	1.08	69 79

[a]Where S_i is the experimental (within laboratory) standard deviation; $\bar{X}$ is the average of replicate results; and X_{Ref} is the reference concentration (dpm/filter). This also applies to Tables 6 through 8.

[b]The error given here is the error associated with one-sigma counting statistics. This statement also applies to Tables 6 through 8.

[c]When only one uranium concentration was determined, or if one value was rejected, no average or standard deviation is tabulated. This also applies to Tables 6 through 8.

*Rejected because uranium tracer recovery was less than 20%.

†Rejected by ASTM test.

TABLE 6. COLLABORATIVE STUDY RESULTS FOR SAMPLE 2 (Reference Soil - Reference Concentration: U-238 = 1.91 dpm/gram; U-234 = 2.77 dpm/gram; U-235 = 0.098 dpm/gram)

Lab	U-238 (dpm/gram)	$\bar{X} \pm S_i$ (dpm/gram)	$\frac{\bar{X}}{X_{Ref}}$	U-234 (dpm/gram)	$\bar{X} \pm S_i$ (dpm/gram)	$\frac{\bar{X}}{X_{Ref}}$	U-235 (dpm/gram)	$\bar{X} \pm S_i$ (dpm/gram)	$\frac{\bar{X}}{X_{Ref}}$	Recovery %
1	1.86±0.03 1.92±0.03	1.89±0.04	0.99	2.71±0.04 2.75±0.03	2.73±0.03	0.99	--- ---	---	---	85 89
2	1.67±0.05 2.08±0.08	1.88±0.29	0.98	2.78±0.08 2.96±0.10	2.87±0.13	1.04	---	---	---	70 45
3	1.94±0.06 1.82±0.06	1.88±0.09	0.98	2.64±0.07 2.68±0.09	2.66±0.03	0.96	0.109±0.009 0.110±0.010	0.110±0.001	1.12	40 28
4	1.75±0.05 1.76±0.04	1.76±0.01	0.92	2.52±0.06 2.53±0.06	2.53±0.01	0.91	0.077±0.006 0.102±0.007	0.090±0.018	0.92	76 78
5	1.85±0.03 1.87±0.03	1.86±0.02	0.97	2.70±0.04 2.74±0.04	2.72±0.03	0.98	0.109±0.005 0.103±0.005	0.106±0.004	1.08	68 70
6	1.84±0.03 1.86±0.03	1.85±0.02	0.97	2.65±0.04 2.68±0.04	2.67±0.02	0.96	0.068±0.004 0.083±0.005	0.076±0.011	0.78	67 69
7	1.48±0.03†	---	0.78	2.27±0.05	---	0.80	0.072±0.005	---	0.62	74
8	1.72±0.08 2.21±0.11	1.97±0.35	1.03	2.47±0.11 3.49±0.17	2.98±0.72	1.08	0.077±0.008 0.089±0.010	0.083±0.009	0.85	88 60

†Rejected by ASTM test.

TABLE 7. COLLABORATIVE STUDY RESULTS FOR SAMPLE 3 (Microsorban Filter - Reference Concentration: U-238 = 22.7 dpm/filter; U-234 = 43.8 dpm/filter; 1.90 dpm/filter)

Lab	U-238 (dpm/filter)	$\bar{X} \pm S_i$ (dpm/filter)	$\frac{\bar{X}}{\bar{X}_{Ref}}$	U-234 (dpm/filter)	$\bar{X} \pm S_i$ (dpm/filter)	$\frac{\bar{X}}{\bar{X}_{Ref}}$	U-235 (dpm/filter)	$\bar{X} \pm S_i$ (dpm/filter)	$\frac{\bar{X}}{\bar{X}_{Ref}}$	Recovery %
1	22.2±0.2 21.4±0.2	21.8±0.6	0.96	44.2±0.4 42.4±0.4	43.3±1.3	0.99	--- ---	---	---	99 107
2	23.2±1.0 24.9±1.5*	---	1.02	31.1±1.2 39.0±2.1*	---	0.71	--- ---	---	---	34 17
3	22.7±0.5 24.1±0.5	23.4±1.0	1.03	43.7±0.9 46.0±0.8	44.9±1.6	1.03	2.16±0.11 2.58±0.10	2.37±0.30	1.25	31 42
4	18.7±0.5 23.4±0.6	21.1±3.3	0.93	33.9±0.8 43.9±1.0	38.9±7.1	0.89	1.50±0.10 1.88±0.11	1.69±0.27	0.89	81 77
5	21.6±0.3 19.0±0.3	20.3±1.8	0.90	39.0±0.6 23.6±0.3	31.3±10.9	0.72	1.50±0.06 1.02±0.05	1.26±0.34	0.66	73 70
6	22.4±0.5 24.9±0.4	23.7±1.8	1.04	46.1±1.0 41.7±0.6	43.9±3.1	1.00	1.93±0.10 1.65±0.06	1.79±0.20	0.94	30 72
7	19.2±0.5 20.7±1.0*	---	0.85	36.4±0.9 38.2±1.7*	---	0.83	1.71±0.11 1.74±0.20*	---	0.90	53 15
8	19.9±2.8* 20.4±1.1	---	0.90	35.4±5.0* 33.7±1.8	---	0.77	1.03±0.26* 1.46±0.13	---	0.77	17 60

*Rejected because uranium tracer recovery was less than 20%.

TABLE 8. COLLABORATIVE STUDY RESULTS FOR SAMPLE 4 (Diluted Pitchblende Ore: U-238 = 20.54 dpm/gram; U-234 = 20.54 dpm/gram; U-235 = 0.89 dpm/gram)

Lab	U-238 (dpm/gram)	$\bar{X} \pm S_i$ (dpm/gram)	$\frac{\bar{X}}{X_{Ref}}$	U-234 (dpm/gram)	$\bar{X} \pm S_i$ (dpm/gram)	$\frac{\bar{X}}{X_{Ref}}$	U-235 (dpm/gram)	$\bar{X} \pm S_i$ (dpm/gram)	$\frac{\bar{X}}{X_{Ref}}$	Recovery %
1	22.00±0.24 19.99±0.21	21.00±1.42	1.02	21.36±0.23 19.65±0.21	20.51±1.21	1.00	--- ---	---	---	92 94
2	19.24±1.14* 21.74±0.63	---	1.06	20.39±1.20* 21.56±0.63	---	1.05	--- ---	---	---	13 52
3	20.97±0.55 22.22±0.55	21.60±0.88	1.05	20.44±0.54 21.66±0.53	21.05±0.86	1.02	1.56±0.07 1.45±0.06	1.51±0.08	---	63 72
4	10.91±0.42†	---	---	10.81±0.42†	---	---	0.63±0.05	---	---	24
5	20.22±0.32 18.77±0.81*	---	0.98	20.29±0.32 18.46±0.80*	---	0.99	--- 1.07±0.08*	---	---	46 6
6	19.84±0.31 20.49±0.25	20.17±0.46	0.98	19.50±0.31 20.31±0.25	19.91±0.57	0.97	0.92±0.03 0.95±0.02	0.93±0.02	0.89	51 85
7	16.43±0.30†	---	---	16.55±0.031†	---	---	0.96±0.03	---	0.91	76
8	17.68±2.91* 21.14±2.48*	---	---	18.07±2.97* 20.16±2.37*	---	---	0.96±0.20* 1.53±0.21*	---	---	7 9

*Rejected because uranium tracer recovery was less than 20%.

†Rejected by ASTM test.

For this rejection criterion, with n observations listed in order of increasing magnitude by $x_1 \leq x_2 \leq x_3 \leq \ldots \leq x_n$, if the largest value x_n is in question, then T_n is calculated as follows:

$$T_n = (x_n - \bar{x})/s \qquad (1)$$

where:

T_n = test criterion

$\bar{x}$ = arithmetic average of all n values

s = the estimate of the population standard deviation based on the sample data

Alternately if x_1 rather than x_n is the doubtful value, the criterion is as follows:

$$T_1 = (\bar{x} - x_1)/s \qquad (2)$$

If the T_n or T_1 value exceeds the critical value, the measurement in question may be rejected. Critical values of T for various levels of significance are given in the ASTM reference (ASTM 1977b). A 5% two-sided level of significance was employed in deciding whether or not to reject a given measurement in the present study.

When a laboratory had made only one determination or when one of the duplicates had been rejected, the one acceptable value was used as the laboratory average. The average value for each laboratory was used to calculate the grand average value for the collaborative study. Uranium-235 concentrations reported by the laboratories were divided by 0.844 because only 84.4% of the total alpha branches from uranium-235 are included in a well-resolved spectrum of natural uranium (Sill, 1977). The laboratory calculations were checked to ensure that this correction had not been made previously.

In general, the procedure evaluated at Mound was followed by the participating laboratories, but a few minor deviations were made. Since Laboratory 5 did not have the necessary counting equipment and since the alpha pulse height analysis system at Laboratory 4 was being repaired, the slides from these laboratories were counted at Mound and the resulting spectra were sent back to these laboratories to be analyzed as described in the procedure. Laboratory 1 used silver slides, rather than the stainless steel slides recommended in the procedure. The only laboratory that deviated considerably from the procedure was Laboratory 2. This laboratory used an ammonium oxalate procedure for electrodeposition rather than the ammonium sulfate procedure

given in the present method. Three out of the eight determinations reported by Laboratory 2 had tracer recoveries of less than 20% and had to be rejected, while the average uranium-232 recovery for this laboratory was only 37%. Previous experience at Mound has indicated that an ammonium sulfate procedure generally gives better yields than an ammonium oxalate procedure.

DISCUSSION OF RESULTS

A summary of the collaborative study results is given in Table 9. In this table, the grand averages or the average collaborative study concentrations ($\bar{X}_c$) and the standard deviations (S_d) of the individual laboratory averages are presented for the uranium isotopes measured for each sample. These statistics were calculated as follows (Youden and Steiner, 1975):

$$\bar{X}_c = \frac{\Sigma \bar{X}_i}{n} \tag{3}$$

$$S_d = \left(\frac{\Sigma (\bar{X}_i - \bar{X}_c)}{n-1} \right)^{\frac{1}{2}} \tag{4}$$

where:

$\bar{X}_i$ = average of duplicate results for laboratory i for the given sample

n = number of laboratories providing results for the given sample

The precision standard deviation or the combined within-laboratory standard deviation, S_r, and the standard deviation of the systematic errors or the precision of the method between laboratories, S_b, are also given in Table 9. The precision standard deviation is estimated according to Youden's Formula (3) (Youden and Steiner, 1975) as follows for duplicate determinations:

$$S_r = (\Sigma d^2/2n)^{\frac{1}{2}} \tag{5}$$

where:

d = the absolute difference between the duplicates

TABLE 9. SUMMARY OF RESULTS FOR URANIUM-IN-SOIL AND AIR COLLABORATIVE STUDY*

Sample	Isotope	Tabulated Quantity					
		$\bar{X}_c$	S_d	S_r	S_b	$\bar{X}_{Ref} \pm S_{Ref}$	% Difference
1	U-238	0.19	0.09 (47%)	0.05 (26%)	0.07 (33%)	0.21 ± 0.03	9.5
1	U-234	0.25	0.18 (72%)	0.11 (44%)	0.16 (64%)	0.24 ± 0.04	4.2
1	U-236	1.31	0.08 (6.1%)	0.15 (12%)	---	1.32 ± 0.03	0.8
2	U-238	1.87	0.06 (3.2%)	0.17 (8.9%)	---	1.91 ± 0.06	2.1
2	U-234	2.68	0.21 (7.8%)	0.28 (10%)	0.07 (2.6%)	2.77 ± 0.08	3.2
2	U-235	0.090	0.016 (18%)	0.010 (11%)	0.014 (16%)	0.098 ± 0.007	8.2
3	U-238	21.6	1.7 (7.9%)	1.9 (8.8%)	1.0 (4.6%)	22.7 ± 1.6	4.9
3	U-234	37.9	5.7 (15%)	6.1 (16%)	3.7 (9.8%)	43.8 ± 3.4	13
3	U-235	1.70	0.40 (24%)	0.28 (16%)	0.35 (21%)	1.90 ± 0.07	11
4	U-238	20.95	0.74 (3.5%)	1.0 (4.8%)	0.22 (1.0%)	20.54 ± 0.23	2.0
4	U-234	20.66	0.65 (3.1%)	0.92 (4.5%)	0.00 (0%)	20.54 ± 0.23	0.6
4	U-235	1.01	0.37 (37%)	0.06 (6.0%)	0.37 (37%)	0.89 ± 0.02	13

*The tabulated quantities are defined as: $\bar{X}_c$ - collaborative study average concentration, S_d - standard deviation of the laboratory averages, S_r - precision standard deviation or combined within-laboratory averages, S_b - standard deviation of the systematic errors, $\bar{X}_{Ref} \pm S_{Ref}$ - reference concentration and standard deviation of the reference concentration.

n = the number of collaborating laboratories reporting duplicates

The standard deviation of the systematic error, S_b, is computed from the other two standard deviations according to Youden's Formula (4) (Youden and Steiner, 1975):

$$S_b^2 = S_d^2 - S_r^2/2 \qquad (6)$$

Also given in Table 9 are the reference concentrations and estimated errors of these concentrations. Reference values for Samples 2 and 3 were obtained from the single-laboratory evaluation. The "% difference" given in Table 9 is the percent difference between the reference value and the average reported value.

From the comparison of the average collaborative study uranium concentrations with the reference values shown in Table 9, there appears to be good agreement of the data for all four samples. To determine whether the average collaborative study concentrations agree with the reference values, the t-test was used. Two equations were used in applying the t-test. The first relationship applies to a situation in which the average of the measured value and the average of the reference value each shows a significant standard deviation; this equation is as follows (Walpole and Myers, 1972):

$$t = \left| \bar{X}_c - \bar{X}_{Ref} \right| \Big/ \left(\frac{S_d^2}{n_c} + \frac{S_{Ref}^2}{n_{Ref}} \right)^{\frac{1}{2}} \qquad (7)$$

where:

t = test criterion

$\bar{X}_c$ = average of collaborative test results

$\bar{X}_{Ref}$ = average reference value

S_d = estimated standard deviation of collaborative test results

n_c = number of collaborating laboratories

S_{Ref} = estimated standard deviation of reference concentration

n_{Ref} = number of determinations made in obtaining the reference value

The second relationship applies to a situation in which the error in the reference value is considered to be negligible; or, in other words, the reference value is considered to be the true mean. This equation is as follows (Youden and Steiner, 1975):

$$t = \frac{|\bar{X}_c - R| \, (n_c)^{\frac{1}{2}}}{S_d} \qquad (8)$$

where:

R = the reference value considered to be the true mean

Other quantities are defined as in equation (7)

The calculated values of t for the four reference samples and the data used to calculate these values are given in Table 10. Critical values of t (t_{crit}), determined for a 5% level of significance, are also given for comparison to the calculated t values. When t is less than t_{crit}, it can be said that the two means agree. It can be seen in Table 10 that all results from the collaborative study agree with the reference values, except the U-234 determination in Sample 3. It should be pointed out that three of the duplicate results reported by the laboratories for Sample 3, which are given in Table 7, show large variations in duplicate values for this determination, and relatively poor precision was obtained for the U-234 concentration of Sample 3 in the single-laboratory evaluation given in Table 3. Since only 40 mg of diluted pitchblende ore was added to the Microsorban air filter, a homogeneity problem may be suspected; however, the U-238 results show better precision than the U-234 results. It would be expected that U-238 and U-234 activities would be in equilibrium for Sample 3 but, instead, the U-234 activity is about a factor of two greater than the U-238 activity. This is evidence that the naturally occurring uranium series had been altered in the preparation of this sample and may help explain why the U-234 concentration appears to be less homogeneous than the U-238 concentration. Blank determinations of the polystyrene filters and plastic bags in which the samples were sent to the participating laboratories showed that the unexpected U-234/U-238 ratio was not caused from these materials. Although the reason for the discrepancy between the reference value and

TABLE 10. t-TEST FOR SYSTEMATIC ERRORS IN COLLABORATIVE STUDY RESULTS*

Sample	Isotope	Tabulated Quantity[a]					
		$\bar{X}_c \pm S_c$	$\bar{X}_{Ref} \pm S_{Ref}$	n_c	n_{Ref}	t	t_{crit}
1	U-238	0.19 ± 0.09	0.21 ± 0.03	5	4	0.47	2.57
1	U-234	0.25 ± 0.18	0.24 ± 0.04	6	4	0.13	2.45
1	U-235	1.31 ± 0.08	1.32 ± 0.03	6		0.31	2.57
2	U-238	1.87 ± 0.06	1.91 ± 0.06	7	12	1.40	2.16
2	U-234	2.68 ± 0.21	2.77 ± 0.08	8	12	1.16	2.31
2	U-235	0.090 ± 0.016	0.098 ± 0.007	6	12	1.17	2.45
3	U-238	21.6 ± 1.7	22.7 ± 1.3	8	9	1.48	2.16
3	U-234	37.9 ± 5.7	43.8 ± 3.4	8	8	2.51	2.20
3	U-235	1.70 ± 0.40	1.90 ± 0.07	6	8	1.21	2.57
4	U-238	20.95 ± 0.74	20.54 ± 0.23	5		1.24	2.78
4	U-234	20.66 ± 0.65	20.54 ± 0.23	5		0.41	2.78
4	U-235	1.01 ± 0.37	0.89 ± 0.02	4		0.65	3.18

[a]The tabulated quantities are defined in the text.

collaborative study value is not apparent, it is probably related to the reference sample, rather than the analytical method used in the preparation of the collaborative study.

An additional objective of the present study was to determine if the precision of the measured uranium concentrations approached the precision expected from counting statistics. The standard deviations expected from counting statistics errors were calculated from the total counts and total counting time of each duplicate determination which were supplied by the participating laboratories. They are given in Table 11, along with the standard deviation of the uranium concentrations determined in each sample. It can be seen that the errors calculated from the collaborative study do not approach the error expected from counting statistics. The average collaborative study error for determinations of uranium activities above 1.0 pCi/g was found to be about 10%, which is a factor of 3 higher than the error expected from counting statistics. Standard deviations for reference samples with the highest uranium concentrations and lowest counting errors were found to be about 3%, and this might be considered the lower limit for the precision of the present method. The errors shown in Table 11 for the determination of uranium in air (Samples 1 and 3) were somewhat higher than the errors for the determination of uranium in soil (Samples 2 and 4), but this would be expected since the counting errors for the air samples were also higher.

Some comments about the collaborative study were provided by a few of the participating laboratories. One laboratory commented that the procedure was not long or time-consuming, while another laboratory indicated that even though the procedure was good overall, they felt that it was very lengthy, especially since only uranium isotopes are separated and analyzed. It was pointed out by one of the participants that the uranium added to the Microsorban air filters of Sample 3 appeared to differ from one filter to its duplicate. Two suggestions for possible changes in the procedure were expressed. These were to substitute an ammonium iodide solution (100 mg per 10 ml 6M HCl) for the hazardous hydriodic acid used in the anion exchange separation, and to add the uranium tracer before ignition of the Microsorban filters.

The single-laboratory and multilaboratory evaluations of the present procedure showed that the method provides a relatively simple, cost effective, and accurate means of determining uranium isotopes in soil and air samples for uranium concentrations of greater than a few tenths of a disintegration per minute.

TABLE 11. OVERALL STANDARD DEVIATION OF COLLABORATIVE STUDY RESULTS AND STANDARD DEVIATIONS EXPECTED FROM COUNTING STATISTICS ERRORS*

Sample Number	Isotope	Average Uranium Concentration (dpm/g or dpm/filter)	Std Dev of Data (dpm/g or dpm/filter)	Std Dev Expected From Counting Statistics (dpm/g or dpm/filter)
1	U-238	0.19	0.09 (47%)	0.02 (11%)
1	U-234	0.25	0.18 (72%)	0.03 (12%)
1	U-235	1.31	0.08 (6.1%)	0.06 (4.6%)
2	U-238	1.87	0.06 (3.2%)	0.04 (2.1%)
2	U-234	2.68	0.21 (7.8%)	0.05 (1.9%)
2	U-235	0.090	0.016 (18%)	0.005 (5.6%)
3	U-238	21.6	1.7 (7.9%)	0.6 (2.8%)
3	U-234	37.9	5.7 (15%)	0.9 (2.4%)
3	U-235	1.70	0.40 (24%)	0.09 (5.3%)
4	U-238	20.95	0.74 (3.5%)	0.38 (1.8%)
4	U-234	20.66	0.65 (3.1%)	0.38 (1.8%)
4	U-235	1.01	0.37 (37%)	0.04 (4.0%)

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APPENDIX 1
TENTATIVE METHOD FOR THE DETERMINATION OF URANIUM ISOTOPES IN SOIL AND AIR SAMPLES

This appendix is a reprint of a procedure of the same title by Vito R. Casella, Carl T. Bishop, Antonia A. Glosby, and Charles A. Phillips of Mound Facility in Miamisburg, Ohio. The report was prepared December 12, 1977, for the U. S. Environmental Protection Agency under Contract No. EPA-78-D-X0143. Mound Facility is operated by Monsanto Research Corporation for the U. S. Department of Energy under U. S. Government Contract No. EY-76-C-04-0053. The procedure was prepared by Mound Facility for distribution to participants in the interlaboratory collaborative study and was designated as report number MLM-MU-77-72-0001.

PREFACE

The analytical procedure described in this document is a tentative method for the determination of uranium isotopes in soil and air samples. It is being collaboratively tested according to an interagency agreement between the U. S. Environmental Protection Agency (EPA) and the U. S. Department of Energy (DOE). Data from the collaborative test will be examined and information on the precision and accuracy of the method will be obtained. A final report describing the results of the collaborative study will be prepared.

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1. SCOPE AND APPLICATION

1.1 General Considerations

This procedure applies to the determination of uranium isotopes in soil or air filter samples. It has been applied to soils from various parts of the U.S. and to both fiber glass and polystyrene air filters. Analysis of soils for uranium at levels greater than 0.01 dpm/g can be performed using this method for 10 gram samples. Although 10 g samples are recommended, it can be applied to samples of up to 50g of soil.

The method described in this procedure can be carried out by an experienced technician under the supervision of a chemist who fully understands the concepts involved in the analysis. It involves relatively simple operations, but it should be utilized only after satisfactory results are obtained by the analyst when replicate standard samples are analyzed.

1.2 Minimum Detectable Activity

The minimum detectable concentration of a given uranium isotope is dependent upon the size of the sample analyzed and the minimum detectable activity (MDA) of the isotope. In a given laboratory situation this will also depend upon the observed blank values (cf. Section 3). The MDA is defined as that amount of activity which in the same counting time, gives a count which is different from the background count by three times the standard deviation of the background count.

The MDA can be calculated from some typical parameters that might be expected from the method described in this procedure. Suppose a sample is counted for 1000 minutes using a silicon surface barrier detector with a 25% counting efficiency, the background in the energy region of interest is 5 counts in 1000 minutes, and the chemical recovery of the uranium tracer is 80%. From the definition of the MDA,

the sample count would have to be seven (ca. 3 x $\sqrt{5}$) in 1000 minutes, and to achieve this count under the stated conditions would require 0.034 d/m of activity. Thus, a typical MDA for a given uranium isotope by this procedure would be 0.03 d/m.

1.3 Sensitivity

Using the minimum detectable activity computed in the last section and considering a 10 gram soil sample, the lowest concentration of uranium-238, as mg U-238/g of soil, that could be detected by this method would be:

0.034 d/m / (0.739 d/m/mg x 10g) = 0.0046 mg/g.

The lowest concentration of U-238 detectable per air filter is the same as the MDA, i.e. 0.046 mg/filter.

The sensitivity of this isotopic method can be compared (Bishop, 1977) to methods which determine total uranium concentrations fluorometrically. Although fluorometric methods are comparable in sensitivity to counting methods for U-238 (natural uranium), fluorometric methods could not detect other uranium isotopes which are readily detectable by counting methods. This is because the isotopic method can be used to detect much smaller masses of these other uranium isotopes which have high specific activities. The long lived isotopes of uranium along with some of their properties of interest to this procedure are given in Table 1.

PROPERTIES OF URANIUM ISOTOPES
OF INTEREST IN ENVIRONMENTAL SAMPLES

Isotope	Half-Life (Years)	Specific Activity (dis/min/μg)	Alpha Energies in MeV (Abundance)
U-232	72	4.75×10^{7}	5.32 (68%), 5.27 (32%)
U-233	1.62×10^{5}	21,000	4.82 (83%), 4.78 (15%)
U-234	2.47×10^{5}	13,730	4.77 (72%), 4.72 (28%)
U-235	7.1×10^{8}	4.76	4.58 (8%), 4.40 (57%) 4.37 (18%)
U-236	2.39×10^{7}	141	4.49 (76%), 4.44 (24%)
U-238	4.51×10^{9}	0.739	4.20 (75%), 4.15 (25%)

1.4 Precision and Accuracy

The precision of the method has not yet been evaluated, but based on experience with a similar procedure for uranium in water, the precision is expected to approach that of counting statistics errors. The accuracy is expected to be within the limits propagated from counting statistics and the uncertainty in the specific activity of the tracer used.

2. SUMMARY

The present procedure involves a nitric acid-hydrofluoric acid dissolution, coprecipitation of uranium with iron hydroxide, an ether extraction if the sample contains iron as a major constituent, separation of uranium by anion exchange, and electrodeposition of the uranium followed by alpha pulse height analysis.

After adding uranium-232 tracer, organic matter is removed from the sample by heating. Subsequently, the sample is decomposed by a nitric acid-hydrofluoric acid digestion, and the uranium is coprecipitated by making this solution basic with ammonium hydroxide (carbonate free). The hydroxide precipitate is dissolved in 8 M hydrochloric acid, which is extracted with isopropyl ether to remove the bulk of the iron present. For samples with relatively low iron concentrations, such as air filters containing little particulate matter, this extraction can be omitted.

The 8 M hydrochloric acid solution is passed through an anion exchange resin column. Uranium, polonium and bismuth will be adsorbed on the resin while thorium and radium will pass through the column. Plutonium and any unextracted iron are also retained by the resin, but are eluted with 6 M HCl containing hydrogen iodide. The iodide ion reduces plutonium (IV) to plutonium (III) and reduces the iron (III) to iron (II), and neither of these ions are retained by the ion exchange resin in 6 M HCl. The uranium is eluted from the column with 1.0 M HCl, while any zinc adsorbed on the column will remain. Electrodeposition of the uranium onto a stainless steel slide is performed, and the slide is counted by alpha pulse height analysis using a silicon surface barrier detector.

When uranium-232 is used as a tracer, the other isotopes of uranium listed in Table 1 can be detected in the alpha spectrum of an unknown sample. From the alpha energies given in Table 1, it can be seen that the alpha energy of uranium-232 is at least 0.50 MeV higher than the energy of any other uranium isotope. Thus, there should be little interference from tailing of the uranium-232 into the lower energy alpha peaks. If a sample contained both uranium-233 and uranium-234, it would be very difficult to resolve these two peaks since their principal alpha energies differ by only 0.05 MeV. The other uranium peaks can be resolved if the resolution is good.

3. INTERFERENCES

3.1 The only possible alpha activity that may come through the chemistry of the procedure is protactinium-231 (Edwards, 1968). Protactinium-231 has the following alpha energies in MeV, the abundance being given in parantheses: 5.06 (10%), 5.02 (23%), 5.01 (24%), 4.95 (22%) and 4.73 (11%). Thus, from Table 1, it can be seen that this protactinium-231 could possibly interfere with the determination of uranium-233 or uranium-234.

3.2 In determining very low levels of uranium isotopes in environmental samples, detector backgrounds and laboratory blanks must be accurately determined. Blank determinations must be made in order to ascertain that the contamination from reagents, glassware and other laboratory apparatus is negligible compared to the sample that is being analyzed. A blank determination should be made in exactly the same way a sample determination is made. For accurate analyses blank determinations should be consistent, and should be an order of magnitude lower than activities obtained when analyzing samples.

4. APPARATUS

4.1 Instrumentation

4.1.1 Alpha Pulse Height Analysis System - A system consisting of a silicon surface barrier detector capable of giving a resolution of 50 keV or better with samples electrodeposited on flat mirror finished

stainless steel slides is used. The resolution here is defined as the width of the alpha peak in keV, when the counts on either side of the peak are equal to one-half of the counts at the maximum of the peak. The counting efficiency of the system should be greater than 15% and the background in the energy region of each peak should be less than 10 counts in 1000 minutes.

4.1.2 Electrodeposition Apparatus - A direct current power supply, 0-12 volts and 0-2 amps, is required for the electrodeposition described in this procedure. A disposable electrodeposition cell is also recommended. An apparatus similar to that shown in Figure 1 has been used in the present procedure. In the present procedure, the cell itself is surrounded by water, but the water is not circulated. The electrodeposition can be carried out without the water cooling. The cathode is a stainless steel slide with a polished mirror finish. The diameter of the slide is 1.91 cm (3/4 in.) and the thickness is ca. 0.05 cm (0.02 in.). The exposed cathode area during electrodeposition is 2 cm^2.

The anode is a 1 mm diameter platinum wire with an 8 mm diameter loop at the end above the cathode.

4.2 Laboratory Equipment

4.2.1 Balance - top loading, capacity 1200 g, precision $\pm$ 0.1 g.

4.2.2 Balance - analytical, capacity 160 g, precision $\pm$ 0.1 mg

4.2.3 Hot plate - magnetic stirrer and stirrer bar.

4.2.4 Centrifuge - capable of handling 100 ml or larger centrifuge bottles.

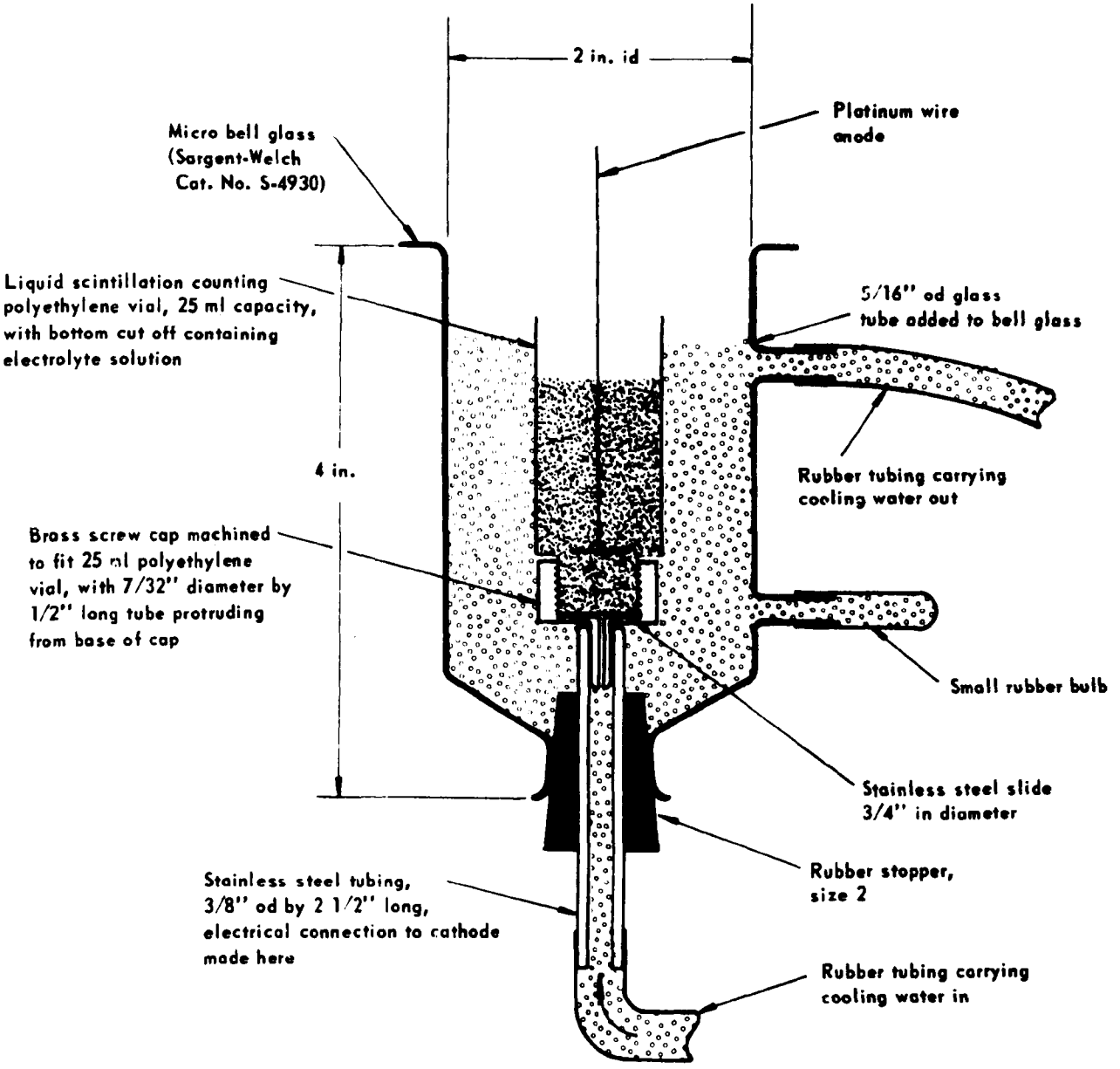

Figure 1. Water Cooled Electrodeposition Apparatus

4.3 Labware

4.3.1 Graduated cylinders - 25 ml to 100 ml.

4.3.2 Beakers - glass, 100 ml to 250 ml.

4.3.3 Beakers - teflon, 250 ml with teflon covers.

4.3.4 pH paper - pH range 2 to 10.

4.3.5 Automatic pipettes - with disposable tips, volumes between 100λ and 1000λ.

4.3.6 Centrifuge bottles - 250 ml.

4.3.7 Ion exchange columns - approximately 1.3 cm ID, 15 cm long with 100 ml reservoir.

4.3.8 Pipettes - glass, Class A.

4.3.9 Disposable pipettes - 2 ml glass eye-dropper type, with rubber bulb.

4.3.10 Dropping bottles.

4.3.11 Watch glasses.

4.3.12 Polyethylene washing bottles.

4.3.13 Glass stirring rods

4.3.14 Safety glasses or goggles.

4.3.15 Rubber gloves.

4.3.16 Crucible tongs - platinum tipped.

4.3.17 Beaker tongs.

4.3.18 Spatulas.

4.3.19 Heat lamp-mounted on ring stand for drying slides.

5. STANDARDS, ACID, REAGENTS

5.1 Standards

5.1.1 Standardized uranium-232 solution.

5.2 Acids

Reagent grade, meeting American Chemical Society (ACS) specifications; diluted solutions prepared with distilled deionized water.

5.2.1 Nitric acid - concentrated (16 M).

5.2.2 Hydrochloric acid - concentrated (12 M, 8 M, 6 M, 1.0 M, 0.5 M.

5.2.3 Sulfuric acid - concentrated (18 M), 1.8 M.

5.2.4 Hydrofluoric acid - concentrated (48% solution).

5.2.5 Hydriodic acid - concentrated (48% solution).

5.3 Reagents

Reagent grade, meeting ACS specifications; solutions prepared with distilled deionized water.

5.3.1 Ferric chloride - in 0.5 M HCl containing 10 mg of iron per ml of solution.

5.3.2 Ammonium hydroxide - concentrated (15 M), 1.5 M, 0.15 M.

5.3.3 Anion exchange resin - Bio Rad AG1-X4 (100-200 mesh) chloride form. (Available from Bio Rad. Laboratories, 3rd and Griffin Avenues, Richmond, California, 94804). A column is prepared by slurrying this resin with 8 M HCl and pouring it onto a column of inside diameter approximately

1.3 cm. The height of the column of resin should be about 10 cm.

5.3.4 Sodium hydrogen sulfate solution ca. 5% in 1 M H_2SO_4; dissolve 10 g of the $NaHSO_4 \cdot H_2O$ in 100 ml of water and then carefully add 100 ml of 2 M H_2SO_4.

5.3.5 Preadjusted electrolyte - 1 M ammonium sulfate adjusted to pH 3.5 with 15 M NH_4OH and 18 M H_2SO_4.

5.3.6 Thymol blue indicator, sodium salt (available from Fisher Scientific Company) - 0.04% solution.

5.3.7 Ethyl alcohol - made slightly basic with a few drops of 15 M NH_4OH per 100 ml of alcohol.

6. CALIBRATION AND STANDARDIZATION

6.1 Standardization of the Uranium-232 Tracer Solution

If a standard uranium-232 solution is not available, a freshly purified sample of uranium-232 could be standardized by mixing a known amount of another standard solution such as uranium-236, with a known amount of the solution to be standardized, mixing thoroughly and electroplating the mixture. From an alpha pulse height analysis of the mixture the specific activity of the uranium-232 solution could be determined. Alternately, a freshly purified solution of uranium-232 could be standardized by 2π counting. Weighed aliquots of the solution free of hydrochloric acid could be evaporated on platinum or stainless steel slides and counted with a 2π proportional counter. The efficiency of the 2π proportional counter can be accurately determined with a National Bureau of Standards alpha-particle standard. When using these standards, corrections for resolving time and backscattering must be made if necessary.

6.2 Determination of Alpha Spectrometer Efficiency

Determination of the alpha spectrometer counting efficiency is not necessary to get an accurate concentration of the uranium isotopes in the sample being analyzed, since the counting efficiency of the electroplated sample is the same for the tracer uranium isotope and for the unknown uranium isotope. This efficiency cancels out when the concentration of the unknown uranium isotope is calculated (cf. Section 8.1).

A determination of the alpha spectrometer counting efficiency is required to calculate the uranium recovery of a particular analysis. To determine this efficiency requires that one count an alpha particle source of known alpha particle emission rate under the same conditions that the samples are counted. The alpha particle counting efficiency is then calculated as illustrated in Section 8.2.

7. STEP BY STEP PROCEDURE FOR ANALYSIS

7.1 Acid Dissolution

7.1.1 Weigh a representative 10.0 ± 0.1 grams of 100 mesh soil sample or the glass fiber filter(s) and transfer to a casserole. If a Microsorban (polystrene) filter(s) was used, place the filter(s) into a 150-ml or 250-ml Pyrex beaker and cover with a watch glass.

7.1.2 Add an appropriate quantity of uranium-232 tracer. If the activity is expected to be less than 1 dpm/g, or is unknown, add 10 dpm of tracer. For higher levels add as much uranium-232 tracer as the estimated activity of uranium in the sample. If a Microsorban filter(s) was used, add the uranium-232 tracer after Step 7.1.3.

7.1.3 Heat the casserole containing the soil sample or glass fiber filter(s) at 600°C for four hours in a muffle furnace; remove, and cool. If a Microsorban filter(s) was used, place the Pyrex beaker in a muffle furnace at 200°C for 1 hour. Increase the temperature at 1 hr intervals to 300°C, 400°C and 550°C. Muffle for 2 or 3 hrs at 550°C or until only a brown powdery ash remains. Remove and cool.

7.1.4 Transfer the sample to a 250-ml Teflon beaker, rinsing the casserole with 10 ml portions of 16 M HNO_3 to a final volume of 60 ml of nitric acid. For Microsorban filter(s) rinse the beaker with 5 ml portions of 16 M HNO_3 to a final volume of 30 ml of nitric acid.

7.1.5 Carefully add 30 ml of 48% hydrofluoric acid (20 ml for Microsorban filters), cover with a teflon watchglass and heat on a hotplate with frequent stirring for about 1 hr. Remove from the hotplate and cool. (CAUTION: HF is very hazardous. Wear rubber gloves, safety glasses or goggles, and a laboratory coat. Avoid breathing HF fumes. Clean up all spills and wash thoroughly after using HF).

7.1.6 Carefully add 30 ml (20 ml for Microsorban filters) each of 16 M HNO_3 and HF (48%) and digest with some stirring for an additional hour.

7.1.7 Remove from the hotplate and cool to room temperature. Slowly add 20 ml of 12 M HCl and heat on a hotplate with some stirring until the solution has evaporated to a liquid volume of approximately 10 ml.

7.1.8 Add 50 ml of distilled water and digest on a hot plate with stirring for 10 minutes to dissolve the soluble salts.

7.1.9 Cool and transfer the total sample into a 250-ml centrifuge bottle with a minimum of distilled water from a wash bottle. If any insoluble residue is present, the sample should be centrifuged and the supernate should be transferred into another centrifuge bottle. This residue should be washed with 10 ml of 1.0 M HCl which is added to the supernate. Discard the insoluble residue. Proceed to section 7.2, Coprecipitation.

7.2 Coprecipitation

7.2.1 Add 20 mg of iron as $FeCl_3$ in 0.5 M HCl to the centrifuge bottle and stir. (This step is usually not necessary for soil samples containing iron).

7.2.2 Add 15 M NH_4OH (CO_3^{2-} free) while stirring to precipitate the iron. Continue adding 15 M NH_4OH to raise the pH to 9-10 as determined by pH paper, then add 5 ml in excess.

7.2.3 Centrifuge for approximately 5 minutes, decant and discard the supernate.

7.2.4 Dissolve the precipitate with a minimum of 12 M HCl and add 8 M HCl to a volume of about 50 ml. Transfer the solution to a 250-ml separatory funnel using two 5-ml rinses of 8 M HCl and proceed to Section 7.3, Ether Extraction.

7.3 Ether Extraction

7.3.1 Add 60 ml of isopropyl ether to the separatory funnel and shake the solution for two minutes. Allow the phases to separate and then transfer the aqueous phase (lower phase) to a second separatory funnel. Add 5-ml of 12 M HCl to the aqueous phase.

7.3.2 Repeat this ether extraction two more times. The bulk of the iron is removed as evidenced by the appearance of a yellow color in the organic phase. (If the sample has a very high concentration of iron, additional extractions may be necessary.)

7.3.3 Transfer the aqueous phase to a 150-ml beaker, boil for 15 min, and proceed with Section 7.4, Anion Exchange Separation.

7.4 Anion Exchange Separation

7.4.1 Condition the anion exchange resin column (prepared as described in Section 5.3) by rinsing the column with 4 column volumes of 8 M HCl.

7.4.2 Transfer the sample from Step 7.3.3 to the conditioned anion exchange resin.

7.4.3 After the sample has passed through the column, elute any unextracted iron (and plutonium if present) with 6 column volumes of 6 M HCl containing 1 ml of concentrated HI per 50 ml of 6 M HCl (freshly prepared).

7.4.4 Rinse the column with an additional two column volumes of 6 M HCl.

7.4.5 Elute the uranium with six column volumes of 1.0 M HCl.

7.4.6 Evaporate the sample to about 20 ml and add 5 ml of 16 M HNO_3.

7.4.7 Evaporate the sample to near dryness.

7.5 Electrodeposition

7.5.1 Add 2 ml of a 5% solution of $NaHSO_4 \cdot H_2O$ in 1 M H_2SO_4 to the sample.

7.5.2 Add 5 ml of 16 M HNO_3, mix well and evaporate to dryness, but do not bake.

7.5.3 Dissolve the sample in 5 ml of the preadjusted electrolyte (cf. Section 5.3), warming to hasten the dissolution.

7.5.4 Transfer the solution to the electrodeposition cell using an additional 5-10 ml of the electrolyte in small increments to rinse the sample container.

7.5.5 Add three or four drops of thymol blue indicator solution. If the color is not salmon pink, add 1.8 M H_2SO_4 (or 15 M NH_4OH) until this color is obtained.

7.5.6 Place the platinum anode into the solution so that it is about 1 cm above the stainless steel slide which serves as the cathode.

7.5.7 Connect the electrodes to the source of current, turn the power on, and adjust the power supply to give a current of 1.2 amps. (Constant current power supplies will require no further adjustments during the electrodeposition.)

7.5.8 Continue the electrodeposition for a total of 1 hr.

7.5.9 When the electrodeposition is to be terminated, add 1 ml of 15 M NH_4OH and continue the electrodeposition for 1 min.

7.5.10 Remove the anode from the cell and then turn off the power.

7.5.11 Discard the solution in the cell and rinse the cell 2 or 3 times with 0.15 M NH_4OH.

7.5.12 Disassemble the cell and wash the slide with ethyl alcohol that has been made basic with NH_4OH.

7.5.13 Touch the edge of the slide to a tissue to absorb the alcohol from the slide.

7.5.14 Dry the slide, place it in a box, and label for counting. (The sample should be counted within a week, since uranium-232 daughters grow into the sample and possibly interfere with the determination of certain other uranium activities.)

7.6 Alpha Pulse Height Analysis

7.6.1 Count the samples for at least 1000 minutes or longer if the detector efficiency is less than 15%, if the tracer recovery is low, or if the unknown uranium activity is low.

7.6.2 Check the alpha pulse height analysis spectrum for peaks at the uranium-233, uranium-234, uranium-235, uranium-236 and/or uranium-238 alpha energies (see Table 1) and determine the total counts in each peak. Where two isotopes are close in energy, complete resolution may not be possible. (This is the case with uranium-236 and uranium-235, for example.)

7.6.3 Make the necessary background corrections. (The background should be determined by a 4000 minute or longer count.)

7.6.4 Make a blank correction for each peak, if necessary.

8. CALCULATION OF RESULTS

8.1 Calculations of Uranium Concentrations

By integrating the appropriate energy peak along with the uranium-232 tracer peak, the concentrations of the corresponding uranium isotope can be determined (cf. Table 1). This concentration is calculated as follows:

$$X_i = \frac{C_i \times A_t}{C_t \times W_s} \qquad (8.1)$$

where X_i = the concentration of the unknown uranium isotope in d/m/g of soil or d/m/ filter.

C_i = the net sample counts in the energy region corresponding to the uranium isotope being measured.

A_t = the activity of the uranium-232 tracer added to the sample in d/m.

C_t = the net sample counts in the uranium-232 tracer energy region of the alpha spectrum.

W_s = the weight in grams of the soil sample taken for analysis; W_s is omitted from this formula (W_s=1) when the sample is an air filter.

8.2 Calculation of Alpha Spectrometer Efficiency

The absolute counting efficiency of the alpha spectrometer, ε, must be determined in order to calculate the uranium recovery of the analytical procedure.

To determine this efficiency requires a standard source of a known alpha particle emission rate:

$$\varepsilon = R_s/R_\alpha \qquad (8.2)$$

where R_s = the net counting rate of the standard source in the energy region of the alpha emitter of interest in counts per minute.

R_α = the absolute alpha particle emission rate of the alpha emitter of interest in alpha disintegrations per minute.

8.3 Calculation of Uranium Recovery of the Chemical Analysis

The uranium recovery efficiency E (%) expressed in percent is given by:

$$E(\%) = \frac{C_t \times 100\%}{t \times A_t \times \varepsilon} \qquad (8.3)$$

where t=the counting time in minutes and the other terms are as defined in Sections 8.1 and 8.2.

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APPENDIX 2
COLLABORATIVE STUDY INSTRUCTIONS

URANIUM IN SOIL AND AIR

(January 1978)

1. Use the procedure "Tentative Method for the Determination of Uranium Isotopes in Soil and Air Samples" by V. R. Casella et. al., December 2, 1977.

2. If you have not analyzed samples using a procedure similar to the one to be used in the collaborative study, a few known samples should be analyzed before analyzing the collaborative study samples.

3. Special reagents that you might not have on hand, such as the ion exchange resin, will be furnished by Mound if you desire. Contacts are given below.

4. Additional amounts of any sample are available if required. Contacts are given below.

5. All samples should be analyzed in duplicate. For sample 78-4, analyze five gram aliquots rather than ten grams.

6. Uranium concentrations may be as low as 0.5 dis/min/g or 0.5 dis/min/filter. Laboratory blanks should be determined in your laboratory to be certain that they are not a problem at these uranium concentrations.

7. Use the uranium-232 tracer, U-10, for this study. Data on this tracer is attached to these instructions. Using 500λ of this tracer gives 10.4 dis/min of U-232.

8. When analyzing the Microsorban samples, do not remove the filter from the plastic bag in which it is contained; ignite the filter and bag together when beginning the analysis.

9. The water cooled electrodeposition apparatus shown in Figure 1 of the procedure is only an illustration. Water cooling is not required, and any apparatus producing a suitable slide for alpha pulse height analysis is satisfactory.

10. Samples should be counted for 1000 minutes or at least long enough to accumulate 200 counts in an unknown alpha peak.

11. Report your results on the data sheet attached. Individual counting data is requested so that the counting statistics error can be resolved from other experimental errors.

APPENDIX 3
DATA ON URANIUM-232 TRACER

Isotope: U-232 I.D. No.: U-10

Date Prepared: 11/28/77

Specific Activity: 20.2 dis/min/gram (±2%)(on date prepared)

Density: 1.031 g/cm^3 at 20°C

Acid Medium: 1 M HNO_3

Source: U.S. ERDA - Health and Safety Laboratory, purified by ion exchange and standardized at Mound Facility.

Half Life: 72 years

Approximate Volume in Glass Ampoule: 6 ml

Opening Instructions: The constriction of the glass ampoule has been previously scored and reinforced with a blue ceramic band. It can readily be broken without a file. The small polyethylene bottle with the long narrow neck, enclosed with the ampoule, may be used to remove the tracer from the opened ampoule and for weighing the amount of tracer added to each sample.

Prepared At: Mound Facility
Monsanto Research Corporation
Miamisburg, Ohio 45342

APPENDIX 4
LABORATORIES PARTICIPATING IN THE URANIUM IN SOIL AND AIR COLLABORATIVE STUDY

Allied Chemical Corporation
Idaho Falls, Idaho

Argonne National Laboratory
Argonne, Illinois

Arkansas Department of Health
Little Rock, Arkansas

Eberline Albuquerque Laboratory
Albuqueque, New Mexico

LFE Environmental Analysis Laboratories
Richmond, California

Ohio State University
Columbus, Ohio

Reynolds Electrical and Engineering Co., Inc.
Las Vegas, Nevada

U. S. Energy Research and Development Administration
Environmental Measurements Laboratory
New York, New York

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

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16. ABSTRACT

Results of a single-laboratory evaluation and an interlaboratory collaborative study of a method for determining uranium isotopes in soil and air samples are presented. The method is applicable to 10-gram soil samples and to both glass fiber and polystyrene (Microsorban) air filter samples. Sample decomposition is accomplished with a nitric-hydrofluoric acid dissolution. After a solvent extraction step to remove most of the iron present, the uranium is isolated by anion exchange chromatography and electrodeposition. Alpha spectrometry is used to measure the uranium isotopes.

Two soil samples, a glass fiber air filter sample, and a polystyrene air filter sample were used to evaluate the method for uranium concentrations ranging from a few tenths to about one hundred disintegrations per minute per sample. Tracer recoveries for the single-laboratory evaluation averaged 78 percent, while the tracer recoveries for the collaborative study averaged 66 percent. Although the precision of the collaborative study results did not approach counting statistics errors, the measured uranium concentrations for these samples agreed to within 5 percent of the reference concentrations when the uranium concentration was greater than one disintegration per minute per gram of soil or one disintegration per minute per air filter.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Uranium Quantitative analysis Quality assurance Soil and air		68F 77B 99B, E

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