164
3-9-81
JWS

①

Dr. 2379

R-2573

Y-2237

UCC-ND

**NUCLEAR
DIVISION**

**UNION
CARBIDE**

MASTER

**DETERMINATION OF PLUTONIUM IN AIR
AND SMEAR SAMPLES**

E. R. Hinton, Jr.
W. O. Tucker

February 1981

OPERATED BY
UNION CARBIDE CORPORATION
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Printed in the United States of America
Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

NTIS price codes
Printed copy: A02
Microfiche copy: A01

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Date of Issue: February 27, 1981
Distribution Category: UC-4

Y-2237

DETERMINATION OF PLUTONIUM IN AIR AND SMEAR SAMPLES

E. R. Hinton, Jr.
W. O. Tucker

Plant Laboratory Department
Product Certification Division

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Oak Ridge Y-12 Plant

P. O. Box Y, Oak Ridge, Tennessee 37830

Prepared for the Department of Energy
Under US Government Contract W-7405-eng-26

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ABSTRACT

A method has been developed for the determination of plutonium in air samples and smear samples that were collected on filter papers. The sample papers are digested in nitric acid, extracted into 2-thenoyltrifluoroacetone (TTA)-xylene, and evaporated onto stainless steel disks. Alpha spectrometry is employed to determine the activity of each plutonium isotope. Each sample is spiked with plutonium-236. All glassware used in the procedure is disposable. The detection limits are 3 and 5 dpm (disintegrations per minute) for air and smear samples, respectively, with an average recovery of 87%.

CONTENTS

SUMMARY	4
INTRODUCTION	5
PLUTONIUM IN AIR AND SMEAR SAMPLES	6
Development of Procedure	6
Sample Digestion	6
Extractions	7
Planchet Preparation	8
Counting Equipment	9
Results and Discussion	10
REFERENCES	13
APPENDIX. DETERMINATION OF PLUTONIUM IN AIR AND SMEAR SAMPLES	14

SUMMARY

This report discusses the development of a procedure for the determination of plutonium on filter papers from air- and smear-sampling operations. A nitric acid digestion procedure, utilizing 4-oz bottles which were uniformly heated in a specially designed carbon block, has been developed. Three organic extraction systems were examined, and a system using 0.5 *M* 2-thenoyltrifluoroacetone (TTA) in xylene was chosen for separation of the plutonium. The extraction is carried out in the same bottle as the digestion.

The TTA containing the extracted plutonium is evaporated onto a stainless steel disk in preparation for counting in an alpha spectrometer. The recovery for each sample is determined by use of a plutonium-236 (^{236}Pu) spike, added before digestion. Calculations consist of resolving the alpha spectrum to determine the net activity of ^{239}Pu , ^{240}Pu and ^{238}Pu and correcting for appropriate dilutions and recovery.

The procedure has the advantages of using disposable glassware and allowing the rapid analysis of a large number of samples. For batch analyses, the time required to analyze a sample is approximately 30 min. The detection limit is 3 dpm (disintegrations per minute) for air samples and 5 dpm for smear samples with an average recovery of 87%.

INTRODUCTION

The Plant Laboratory of the Oak Ridge Y-12 Plant^(a) has the responsibility of analyzing both air and surface-smear samples for trace quantities of plutonium. These samples are taken to insure that plutonium contamination levels on incoming uranium components are within established, safe limits for handling and processing within the Y-12 Plant.

The earliest samples of this type were processed in the laboratory by using a modified version of an existing procedure for plutonium. This procedure, as applied to smear and air samples, consisted of a perchloric (HClO_4)-nitric (HNO_3) acid digestion of the sample paper and electroplating onto a 2-in.-diameter nickel disk. Both plutonium and uranium were electroplated onto the disk. An alpha spectrum was then obtained by means of a silicon surface-barrier detector and was resolved to yield results for uranium and plutonium. Both smear and air samples were taken on Whatman No. 41 paper^(b) (4-in.-diameter paper for smears and 1-in.-diameter for air). The dissolution was done in 150-mL beakers, which were washed and reused. Glassware from the two types of samples could not be mixed because of cross-contamination. Even though the smear samples had, at most, a few thousand disintegrations per minute of plutonium they could easily contaminate the air samples which were generally less than 10 dpm.

The use of HClO_4 in the dissolution was undesirable because of the limited HClO_4 hood space available and, also, because of safety considerations. In addition, the electroplating step became a problem because of the time required (50 min) and the limited number of electroplating cells available.

The objective of this work, therefore, was to establish an alternative procedure which would eliminate the use of HClO_4 , the electroplating step, and the problem of cross-contamination of glassware. Accuracy, precision, recovery efficiency, and sample-processing time were major considerations also.

(a) Operated by the Union Carbide Corporation, Nuclear Division, for the Department of Energy.

(b) H. Reeve Angel & Co., Inc.

PLUTONIUM IN AIR AND SMEAR SAMPLES

DEVELOPMENT OF PROCEDURE

Sample Digestion

In order to decompose the filter papers (Whatman 41, ashless) used in the smearing process and in the air-monitoring system, a digestion procedure was developed using 4-oz narrow-mouth glass bottles and hot HNO_3 as the oxidant. The glass bottles provided a completely disposable system in which both digestion and extraction could be accomplished. It was felt that HNO_3 , without the aid of HClO_4 , could be used to digest the filters with little change in the quality of the digestion, thus eliminating the hazards and special hoods associated with the use of HClO_4 . Normally, three evaporations to dryness with concentrated HNO_3 resulted in thin white residues in the bottles and could be accomplished in 2.5 to 3 h.

Initially, uniform heating of the samples was provided by a sand bath, heated on a hot plate. The sand bath, however, was messy and did not provide sufficiently uniform heating of the samples. In order to overcome the problems associated with nonuniform heating, three carbon blocks (9-in. X 9-in. X 4-in.) were cut and six holes (2-in.-diameter X 3-in.-depth) were bored—at approximately 20° angles in each block—to contain the bottles. The 2-in.-diameter holes were oversized by 0.125 in. in order to compensate for expansion of the glass during heating. This arrangement provided uniform heat to the samples and increased the surface area of the liquid in the bottles to facilitate evaporation. Figure 1 illustrates the digestion system in operation.

Figure 1. CARBON-BLOCK SAMPLE DIGESTION SYSTEM.

194901

Extractions

Several methods^{1,2} are available for separating uranium and plutonium from various media. However, a method was needed which could be easily adapted to a large number of samples. Since uranium and plutonium form extractable chelates and ion-associated systems, solvent extraction—which is fast, simple, and efficient—appeared to be the best approach to the problem.

Complexes involving plutonium (IV) tend to be the most stable, have the highest extraction efficiencies, and are next followed by complexes involving plutonium (VI). The plutonium (V) system tends to be highly unstable, while plutonium (III) does not extract.^{1,2}

Since partition coefficients are usually higher in HNO_3 systems than in hydrochloric acid (HCl) or sulfuric acid (H_2SO_4), most extractions are carried out from HNO_3 solutions.¹ This parameter blended easily with the HNO_3 digestion as previously described.

Three extraction systems, methyl isobutyl ketone (MIBK),³ tri-n-octylphosphine oxide (TOPO)-xylene,⁴ and TTA,⁵ are commonly used. Experiments were focused upon these three systems to find the one with the best characteristics and which was most easily adapted to this laboratory.

Preliminary experiments found the MIBK extraction system to be lacking on several points. In order to use MIBK as an extraction system for plutonium, the plutonium must be in the (VI) oxidation state. Since the HNO_3 digestion left the plutonium in the (IV) state, further oxidation with dichromate¹ was needed. This additional step added too much time to the analysis. It was also necessary to use a salting agent aluminum nitrate [$\text{Al}(\text{NO}_3)_3$] to force the plutonium into the solvent, and the MIBK had to be purified with a HNO_3 -potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) wash to remove reductants. Because of these factors, an MIBK extraction system offered no immediate advantage over electroplating.

Experiments with 0.1 M TOPO in xylene [$\text{C}_6\text{H}_4(\text{CH}_3)_2$] were tried with partial success. Extractions were made from 1 M HNO_3 solutions; and, although both uranium and plutonium could be extracted, the recovery for plutonium was approximately 50% versus approximately 85% for uranium.

A major problem with the TOPO extraction was the lack of surface tension of the TOPO solution on metal planchets. Flat, stainless steel planchets were used with the sample evaporation equipment (described later); and the TOPO tended to run to the edges of the planchet. The planchet had to be dried for approximately 30 min before flaming which added time to the procedure. When flamed, the TOPO residues badly flaked, causing loss of the sample. Watch glasses that were used instead of metal planchets alleviated these problems somewhat; however, because of breakage, the watch glasses could not be flamed but, rather, were baked in a muffle oven at 650°C for 30 min. Even then, the breakage problem was not completely eliminated.

Preliminary experiments with 0.5 *M* TTA-xylene extractions from 1 *M* HNO₃ solutions gave excellent recoveries of plutonium (85%-90%), although uranium extraction was < 1%. Since plutonium was the prime element of interest for analysis, a decision was made to employ TTA in the extraction; and, for those samples requiring uranium analysis, a quick fluorometric analysis could be provided on the aqueous phase of the extraction system. An existing TOPO procedure used in the laboratory was modified for use in this method. The complete method can be found in the **Appendix**.

Planchet Preparation

A method for Y-12 Plant planchet preparation was adapted from one used at the Oak Ridge National Laboratory.⁶ Figure 2 presents an illustration of the system. Disposable Pasteur pipettes are heated and drawn into fine capillaries. Thermometer clamps hold the pipettes in

Figure 2. PLANCHET PREPARATION SYSTEM.

194902

a vertical position and centered over 1.25-in.-diameter X 0.030-in.-thick stainless steel planchets, resting upon 1.25-in.-diameter steel washers. Heat is provided by a hot plate with a surface temperature of approximately 200°C. The hole in the washer beneath the planchet produces an approximately 0.5-in.-diameter "cool" spot in the center of the planchet. As liquid slowly drips from the capillary, it pools in the cool area; and the solvent evaporates at the edge of the pool. When the solvent evaporates, an approximately 0.5-in. spot containing the plutonium remains. With the system shown in figure 2, approximately 20 samples per hour can be prepared.

Counting Equipment

The completed planchets are counted, using a 8192-channel Tracor Northern^(c) TN-1700 multichannel analyzer and EG&G-ORTEC^(d) 600-mm² silicon surface-barrier detectors. The multichannel analyzer is equipped with a TN-1204 four-input multiplexer which allows simultaneous counting of four samples, with each sample being stored into a quarter of the analyzer memory. The detector efficiency is approximately 10%, with a sample-to-detector distance of 0.60 in. Figure 3 shows the counting system.

Figure 3. MULTICHAMBERED ALPHA SPECTROMETER.

194900

(c) Tracor, Inc., subsidiary.

(d) EG&G Instruments subsidiary.

The counting is done in vacuum chambers which are evacuated to $< 50\text{-}\mu\text{m}$ mercury during the count period. Two chambers are connected to a single vacuum pump which can evacuate them to $50\text{-}\mu\text{m}$ mercury in approximately 3 min. The count periods are 15 and 30 min for the smear and air samples, respectively. The TN-1700 analyzer system is equipped with a Data General Nova II^(e) computer which allows the operator to set up "regions of interest" and integrate the counts in each plutonium alpha peak. Regions are set for ^{239}Pu - ^{240}Pu , ^{238}Pu , and ^{236}Pu . Then, following each analysis, the total counts in each peak are shown on the analyzer display as each region is selected by the operator.

RESULTS AND DISCUSSION

In order to evaluate the digestion procedure, six 4-in.-diameter filters containing 468 dpm from ^{239}Pu - ^{240}Pu were digested with concentrated HNO_3 in 4-oz bottles. The samples were then electroplated onto nickel planchets and alpha counted, which resulted in an average recovery of $59\% \pm 11\%$ [95% confidence level (cl)] compared with $66\% \pm 4\%$ (95% cl) obtained with the earlier method. The data indicated there was no significant loss in the quality of the digestion when using the new procedure.

Several advantages over the old digestion system are gained with the new one. The HClO_4 is not required; this therefore eliminates the need for special hoods and also eliminates the safety hazards associated with its use. The bottles used are less expensive than Pyrex^(f) beakers. Cross-contamination between low-level air samples and higher level smear samples is eliminated because new bottles are used once and then salvaged. This also reduces the possibility of contaminating other areas with plutonium, e.g., the glassware washing area.

The ability to analyze low levels of plutonium in the presence of high levels of uranium was a major consideration in the development of the method. The use of TTA as the extracting medium worked well in this respect. Since TTA extracted $< 1\%$ of the uranium present, there was little interference between uranium and ^{239}Pu - ^{240}Pu . Planchets prepared from TTA gave alpha spectra having well-defined peaks with only a small amount of tailing to the low-energy side of the peaks, as can be seen in figure 4. By comparing figure 5 (containing an alpha spectrum obtained with TOPO) with figure 4, the differences in peak quality are quite evident.

Prior to the implementation of the extraction procedure, a sample recovery was calculated from data obtained from control samples that were analyzed along with regular samples. Although this method worked, more accurate data can be obtained by spiking each individual sample with an internal standard. For this, ^{236}Pu was selected because of its availability in a pure form. The use of ^{236}Pu as an internal standard for smear analyses works well; however, it is not an optimum spike for air filter analyses. Tailing of the ^{236}Pu

(e) Data General, Corp.

(f) Registered trade name of Corning Glass Works.

194851

Figure 4. ALPHA SPECTRUM OBTAINED FROM 2-THENOYLTRIFLUORO-ACETONE-XYLENE EXTRACTION OF SAMPLE CONTAINING URANIUM AND PLUTONIUM.

194852

Figure 5. ALPHA SPECTRUM OBTAINED FROM TRI-N-OCTYLPHOSPHINE OXIDE-XYLENE EXTRACTION OF SAMPLE CONTAINING URANIUM AND PLUTONIUM.

peak tends to overlap the ^{238}Pu peak, and this results in counts that are biased high for ^{238}Pu . The use of ^{242}Pu would eliminate this problem since the energy of its alpha peak is lower than that of the ^{239}Pu - ^{240}Pu peak. Interferences with ^{242}Pu by uranium could be eliminated by washing the TTA extract with dilute HNO_3 . However, the availability of ultrapure ^{242}Pu is very limited.

Twelve smear control filters were analyzed using the complete procedure. Each filter contained 13,194-dpm uranium, 468-dpm ^{239}Pu - ^{240}Pu , and 321-dpm ^{236}Pu . Fluorescence analyses for uranium was also performed on the aqueous layer of each sample. Recoveries are shown in table 1. The recoveries of ^{239}Pu - ^{240}Pu and ^{236}Pu are in excellent agreement. Compared with electroplating, the TTA extraction method shows an increase of 20% in recovery efficiency of ^{239}Pu - ^{240}Pu .

Table 1
RECOVERIES OF PLUTONIUM-239 AND PLUTONIUM-240,
PLUTONIUM-236, AND URANIUM-235 OBTAINED FROM
2-THENOYLTRIFLUOROACETONE (TTA)-XYLENE
EXTRACTION AND URANIUM-235 BY
FLUORESCENCE MEASUREMENTS

^{235}U TTA (%)	^{235}U Fluorescence (%)	^{239}Pu - ^{240}Pu TTA (%)	^{236}Pu TTA (%)
0.14	104	88	93
0.33	109	74	80
0.00	93	86	79
0.19	108	88	90
0.78	116	95	95
0.12	103	80	88
0.17	71	83	78
0.54	82	89	90
0.17	91	93	97
0.45	97	95	80
0.56	82	91	89
0.00	84	72	69
Average			
0.25 ± 0.16 (95 cl)	95 ± 9 (95 cl)	86 ± 5 (95 cl)	86 ± 5 (95 cl)

A final test of 135 "real" samples spiked with 160-dpm ^{236}Pu were analyzed with the procedure, which resulted in an average recovery of $86\% \pm 17\%$ (standard deviation) for ^{236}Pu . The detection limit is 3 dpm for air samples and 5 dpm for smear samples when they are counted for 30 and 15 min, respectively.

REFERENCES

1. I. M. Kolthoff, P. J. Elving, and E. B. Sandell, Eds., *Treatise on Analytical Chemistry*, vol. 9, part 11, (John Wiley and Sons, Inc., New York, 1962).
2. H. Sorantin, "Determination of Uranium and Plutonium," *Verlag Chemie*, Weinheim, Germany (1975).
3. R. A. Schneider and K. M. Harmon, *Analytical Technical Manual, U. S. Atomic Energy Report HW-53368*, Hanford Atomic Products Operation, Richland, Wash. (1957).
4. J. C. White, Union Carbide Corporation, Nuclear Division, Oak Ridge Y-12 Plant, Oak Ridge, Tenn., and W. J. Ross, Oak Ridge National Laboratory, Oak Ridge, Tenn., Private Communication (1961).
5. F. L. Moore and J. E. Hudgens, Jr., *Analytical Chemistry*, **29**, 1767 (1967).
6. T. Scott, Oak Ridge National Laboratory, Oak Ridge, Tenn., Private Communication (1980).

APPENDIX

DETERMINATION OF PLUTONIUM IN AIR AND SMEAR SAMPLES

1. Place the sample containers in the hood. Assign each sample to a 4-oz bottle, and write the sample number on the bottle.
2. Open each sample container (inside the hood and one at a time), and remove the filter paper. Place each paper into its numbered bottle.
3. Add 25-mL concentrated HNO_3 to each sample.
4. Add a 160-dpm ^{236}Pu spike to each sample.
5. Place the samples on a hot plate with a setting of HIGH (approximately 510°C).
6. Heat the samples on high heat until the solution turns orange and begins to fume.
7. Remove the samples from the hot plate, and place in carbon heating blocks which have been equilibrated to MEDIUM (approximately 260°C).
8. Heat for 45 min, then adjust the heat to HIGH. Heat on HIGH until the samples are dry (approximately 1 h). When dry, no visible fumes should be evolving from the bottles.
9. Remove the bottles from the blocks, and slowly add 15-mL concentrated HNO_3 to each bottle. Place the bottles back into the carbon block, and heat on high heat until dry.
10. Repeat step 9 with 10-mL concentrated HNO_3 .
11. When dry, the residues should be white. Any residues that are still yellow should be repeated through step 10.
12. Remove the bottles from the carbon block, allow them to cool, and add 5 mL of 1 *M* HNO_3 .
13. Place the samples on a hot plate on medium heat until condensation rinses the walls of the bottles. Add 1-mL of 1 *M* hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) to each sample, and digest on the hot plate for 10 min.
14. Remove the samples from the hot plate, and add 2 mL of 1 *M* sodium nitrite (NaNO_2)—that must be prepared fresh daily—to each sample. The addition of NaNO_2 will cause the samples to bubble and to evolve brownish-yellow fumes.
15. After the fumes have ceased to evolve from the bottles and the bottles are cool to the touch, add 5 mL of 0.5 *M* TTA in xylene to each sample.

16. Shake for 10 min on a shaker. Let the TTA layer (top layer) separate from the aqueous layer.
17. Remove the aqueous layer with a capillary pipette, and salvage into the appropriate salvage bottle.
18. Using a 1-mL Eppendorf pipette, transfer 1 mL of the TTA to a drawn capillary; and evaporate the TTA onto a 1.25-in.-diameter stainless steel planchet warmed on a hot plate (approximately 175°-200°C). Rinse each capillary with 1 mL of 0.5 M TTA onto the planchet.
19. Flame each planchet just until it reaches a dull red glow, and remove from the burner.
20. Write each sample number on a glassine bag, and place the appropriate planchet in the bag.
21. In the alpha spectrometer, count each smear sample planchet for 15 min and each air sample planchet for 30 min.
22. Determine the net counts in the ^{239}Pu - ^{240}Pu , ^{238}Pu , and ^{236}Pu alpha peak.
23. Calculate the ^{236}Pu recovery for each sample as follows:

$$R = \frac{C \cdot D}{T \cdot E \cdot S} \quad (1)$$

where:

R is the recovery,
 C is the net ^{236}Pu count,
 D is a dilution factor ($D = 5$),
 T is the count time,
 E is the detector efficiency, and
 S is the dpm of the ^{236}Pu spike added ($S = 160$).

24. Calculate the disintegrations per minute of ^{239}Pu - ^{240}Pu and ^{238}Pu using the following:

$$A = \frac{N \cdot D}{T \cdot E \cdot R} \quad (2)$$

where:

A is the activity (dpm) of the isotope of Pu being considered,
 N is the net counts from that isotope, and
 T, E, and R are defined as in equation (1).

Distribution

Department of Energy - Oak Ridge

Hickman, H. D.
Poteat, R. M.

Lawrence Livermore National Laboratory

Arnold, W. F.

Los Alamos National Laboratory

Hoyt, H. C.

Oak Ridge Gaseous Diffusion Plant

Armstrong, R. C.
Stief, S. S.
Wilcox, W. J., Jr.

Oak Ridge National Laboratory

Hopkins, C. C.
Scott, T.

Oak Ridge Y-12 Plant

Andrew, R. E.
Barkman, J. R.
Bernander, N. K.
Briscoe, O. W.
Cole, S. II.
Dodson, W. H./Googin, J. M.
Dorsey, J. G.
Fraser, R. J.
Hinton, E. R., Jr., (5)
Hopper, C.
Keith, A.
Kite, H. T.
Mills, J. M., Jr.
Tucker, W. O. (5)
West, C. M.
White, J. C.
Y-12 Central Files (master copy)
Y-12 Central Files (route copy)
Y-12 Central Files (Y-12 RC)
Y-12 Central Files (5)

Paducah Gaseous Diffusion Plant

Bewley, H. D.

Rockwell International - Rocky Flats

Nelson, R. C.

Sandia National Laboratories - Livermore

Spencer, W. J.

Union Carbide Corporation - New York

Tinsley, S. W.

In addition, this report is distributed in accordance with the Category UC-4, Chemistry, as given in the *Standard Distribution for Unclassified Scientific and Technical Reports*, DOE/TIC-4500.