LMF-70

CWE
Thiessen

LMF-70
UC-48

705075

CHARACTERIZATION OF AN AEROSOL SAMPLE FROM THREE MILE ISLAND REACTOR AUXILIARY BUILDING

G.M. KANAPILLY
J.A. STANLEY
G.J. NEWTON
B.A. WONG
P.B. DeNEE

JANUARY 1981

INHALATION TOXICOLOGY RESEARCH INSTITUTE
LOVELACE BIOMEDICAL & ENVIRONMENTAL RESEARCH INSTITUTE
P.O. Box 5890 Albuquerque, NM 87115

Prepared for the Office of the Assistant Secretary for the Environment of the United States Department of Energy under Contract Number DE-AC04-76EV01013.

1007291

NO POSTAGE
NECESSARY
IF MAILED
IN THE
UNITED STATES

BUSINESS REPLY CARD

FIRST CLASS PERMIT NO. 8000 ALBUQUERQUE, NM

POSTAGE WILL BE PAID BY ADDRESSEE

Inhalation Toxicology Research Institute
Lovelace Biomedical and Environmental
Research Institute
P. O. Box 5890
Albuquerque, NM 87185

ATTN: Library

Lovelace Inhalation Toxicology
Research Institute

LMF REPORT SERIES

___ I wish to continue receiving the following LMF reports from the Lovelace Inhalation Toxicology Research Institute:

- ___ Nuclear Program
- ___ Coal Combustion & Gasification Program
- ___ Diesel Exhaust Program
- ___ Solar & Conservation Program
- ___ ALL REPORTS

___ I do not wish to receive any future LMF reports.

Name _____

Organization _____

_____

Address _____

_____

1007243

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or 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.

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

1507250

LMF-70

Category: UC-46

CHARACTERIZATION OF AN AEROSOL SAMPLE FROM THREE MILE ISLAND REACTOR AUXILIARY BUILDING

G. M. Kanapilly
J. A. Stanley
G. C. Newton
B. A. Wong
P. D. DeKee

Inhalation Toxicology Research Institute
Lovelace Biomedical and Environmental Research Institute
P. O. Box 5890
Albuquerque, NM 87115

January 1981

Prepared for the Office of the Assistant Secretary for the Environment of the United States
Department of Energy under Contract Number DE-AC04-76-VS1013.

1007225

TABLE OF CONTENTS

	Page
ACKNOWLEDGMENT	i
EXECUTIVE SUMMARY	1
INTRODUCTION	1
MATERIALS AND METHODS	2
Aerosol Sample	2
Dissolution	2
Analysis of Dissolved Activity	3
Determination of Gamma Activities	3
Scanning Electron Microscopy Energy Dispersive X-Ray Analysis	3
Alpha Spectroscopy	4
RESULTS	4
DISCUSSION	7
REFERENCES	9

LIST OF TABLES

		Page
Table 1.	Radionuclide Activity (pCi) in the IM1 Filter Samples as of 79305	3
Table 2.	Elemental Composition of the IM1 Aerosol Sample as Determined by Energy Dispersive X-Ray Analysis	6

LIST OF FIGURES

		Page
Figure 1.	A schematic of the flow through dissolution system	3
Figure 2.	Gamma spectrum of Segment 3 of the IM1 aerosol as determined in a coaxial Ge-Li detector	4
Figure 3.	Dissolution of radionuclides in a flow-through system expressed as fraction dissolved versus elapsed time (hours)	5
Figure 4.	Dissolution of radionuclides in a static system expressed as fraction dissolved versus elapsed time (hours)	5
Figure 5.	Scanning electron micrograph of original aerosol sample from Segment 3	6
Figure 6.	Scanning electron micrograph of aerosol particles from Segment 1 after dissolution experiment in the flow through system	6
Figure 7.	An alpha spectrum of the aerosol sample determined on an electroplated sample by using a surface barrier detector and pulse height analyzer	7

1007246

ACKNOWLEDGMENT

We would like to thank Drs. R. O. McClellan and B. [illegible] Bunker for valuable discussions and suggestions during the course of this study. We are indebted to Drs. M. G. Snipes, R. G. Gaudily and S. P. Weissman for their critical review of the manuscript. We thank Mr. Donald A. Ritter of General Public Utilities (GPU) Services Corporation for providing the air filter samples. We acknowledge Ms. Sally Burkin contributions in the [illegible] dissolution studies and the contributions of Mrs. Aurelia Day, Mr. Ken Aubert and Dr. R. A. Gaimette in the [illegible] spectroscopic analysis of the samples.

1007241

CHARACTERIZATION OF AEROSOLS SAMPLED FROM THREE MILE ISLAND UNIT 2 AND REACTOR AUXILIARY BUILDING

G. H. Beaverly, J. A. Worley, S. J. Baker, L. A. Wade and P. G. Weber

EXECUTIVE SUMMARY

The accident which occurred at the Three Mile Island Unit Two Nuclear Generating Plant on March 28, 1979 resulted in contamination of the containment and auxiliary buildings. Analyses were performed on both "as-sampled" (1) radiochemical composition and (2) dissolution characteristics of material collected on filters during a series of continuous air sampling in the auxiliary building. The work was done to help characterize the environment in which cleanup operations are being performed. Scanning electron microscopy along with scanning electron microscopy were employed to determine the chemical and isotopic composition of the aerosol. The major radioisotopes found on the filter were ^{90}Sr, ^{90}Y, ^{134}Cs and ^{137}Cs. Dissolution behavior of the aerosol in a synthetic sump water (borate containing NaOH) was determined using both static and flow-through systems. In both systems, rapid dissolution of greater than 90% of both $^{90-90}Sr$ and $^{134-137}Cs$ was found. Only slight differences in the dissolution rates of Sr and Cs were observed. Scanning electron microscopy analysis showed the presence of nanometer size particles as well as larger particles ranging up to 30 μm. The major matrix elements were Fe, Cu, Si, Mg, Al and Ca, except for Al and Si, all matrix elements dissolved in the 1.0 mole dissolution studies. Although the radioactivities were associated with a refractory matrix, it is observed rapid dissolution in water justifies classification as Class B aerosols.[1] Knowledge of radiochemical classification can be used in evaluation of dosimetry data and predictions of core distribution after irradiation exposure to TMI aerosols. The techniques used in this study are applicable to other aerosols of unknown composition.

INTRODUCTION

The Three Mile Island nuclear accident of March 1979 resulted in the contamination of the containment and auxiliary buildings. During the cleanup operations of the auxiliary building, airborne radioactive fission products were encountered. The potential inhalation of these aerosols by workers and others involved in the cleanup prompted the characterization of the aerosol. In addition, knowledge of the characteristics of the aerosol could provide some information on the source of the release. Thus, the quantities, distributions and decay kinetics of the radioactive isotopes were the primary data sought. Data on elemental composition, size characteristics, and other physicochemical properties of the aerosol were also desirable.

The dissolution behavior of an inhaled aerosol is one of the major factors that determine its retention, translocation and resulting dose distribution.[1] Since the nature of the aerosol from the auxiliary building of the Three Mile Island (TMI) was not known, there was no basis for predicting its dissolution in the lung since inhalation deposition. An important variable affecting the dissolution rates is the solvent. A solvent prepared and extensively for previous dissolution studies of several radionuclides in a variety of chemical forms is a synthetic sump water[2-4] simulation. The U.S. dissolution of many aerosols in this solvent were quite relatively comparable to their U.S. dissolution in the lungs of animals.[3,4] Therefore, a series of dissolution studies on the aerosol were conducted using this solvent. Other auxiliary studies for characterizing the aerosol included scanning electron microscopy (SEM) analysis, energy dispersive x-ray analysis (EDXA) and alpha and gamma spectroscopy.

100 246

MATERIALS AND METHODS

Aerosol Sample

The aerosol sample, which TMI personnel supplied, was obtained by filtering about 10^9 cc of air from the auxiliary building on a 2 inch diameter, glass fiber filter during a period of about 8 days. According to the information supplied by personnel from the GPU Service Corporation, the isotopic concentrations were approximately 20% ^{137}Cs, 20% ^{134}Cs, 60% ^{89}Sr, 2-4% ^{90}Sr-^{90}Y, 2-4% ^{140}Ba-^{140}Ca and 1% of ^{58}Co and ^{60}Co. The sample appeared to be a thick, black deposit. Presumably, this material contained normal room aerosol, combustion aerosol and other unknown aerosols.

The total β and γ activity on the filter was about 0.8 [illegible]. The filter was divided into four segments (Table 1) with approximately 40% activity on each of segments 1 and 2 and 10% activity on each of segments 3 and 4. Segments 1 and 2 were used in the dissolution studies. Segment 3 was used for electron microscopic analysis and the fourth segment for determining isotopic composition by radiochemical analysis.

Table 1

Radionuclide Activity (nCi) in the TMI Aerosol Filter Samples as of 7/30/79 (11/1/79)

Sample	^{137}Cs	^{134}Cs	^{90}Sr-^{90}Y	^{89}Sr
Segment 1	657	167	124	440
Segment 2	634	164	120	424
Segment 3	157	37	23	105
Segment 4	219	54	41	146
Total	1666	412	308	1112

Dissolution

Two different dissolution systems, a flow-through system and a static system, were used in this study.[2] In the flow-through system, the solvent was directly in contact with the particles. This dynamic dissolution system provides estimates of early dissolution rates. The static dissolution system was a simpler system better adapted for long-term dissolution studies.

In both dissolution systems, the samples were sandwiched between two Nuclepore® filters (100 nm pore diameter) and secured in a filter holder. The flow-through filter holder was a 47 mm polypropylene filter holder (Millipore, Inc.). A Dorsett® filter holder[3] with both filter faces open to the solvent was used in the static system.

The solvent used in this study was a synthetic ultrafiltrate containing DTPA (SUF - DTPA). The pH, ionic concentration, precipitating and chelating capacity of this solvent were designed to be similar to that of semi-ultrafiltrate.[2,3] The solvent pH was maintained between 7.3 and 7.4 by exposing it to 5% CO_2 in air. Both dissolution studies were conducted at 37°C by maintaining the dissolution systems in a water bath.

A schematic of the flow-through system is shown in Figure 1. The solvent in a lucite reservoir was pressurized with 5% CO_2 in air. The maintenance of a 0.5 ml/min flow rate required a pressure of 1.5 to 2.5 psig. A Gelman® filter cartridge with pore diameter of 0.2 μm was used as a prefilter for the solvent. The eluent fractions were collected at 20 minute intervals during the first day and then at 30 minute intervals by using a fraction collector.

1001249

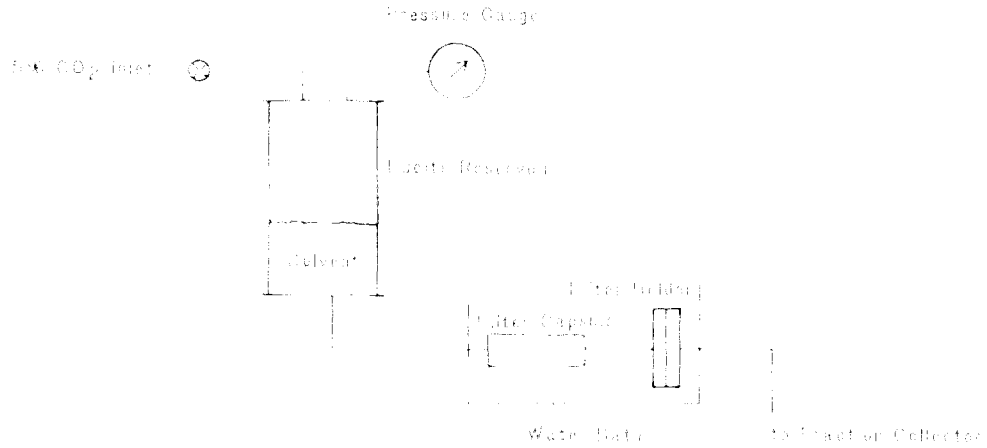

Figure 1. A schematic design of the flow-through dissolution system used to study the [illegible] dissolution of radioactive ions present on an air filter sample collected in the auxiliary building at the [illegible] facility.

In the static system, the filter assembly was placed in 100 ml of solvent in a 500 ml container, sealed with a lid and then placed in the water bath. Solvent changes were made at 2, 4, and 18 hours and then every 24 hours. The solvent was changed by removing the filter assembly from the solvent and placing it in fresh solvent.

[illegible]

Gamma activity dissolved in the flow-through system was determined by counting the fractions directly in a Beckman Autogamma Counter (Model [illegible]) with a NaI crystal detector. Ten milliliter aliquots of the static system samples were counted in the same detector. Total dissolved beta activities were determined by counting 100 [illegible] aliquots prepared on planchets in a Beckman Wide Beta II [illegible] proportional counter.

Undissolved activity remaining on the filter or total sample or segment four of the filter sample were analyzed by dissolving the activity in 2 M HCl at [illegible]. After dilution, aliquots were counted in the Wide Beta II counter and the Autogamma counter. The filter retained < 1% activity, although some black residue was still present.

The [illegible] activities in the original aerosol sample and in the dissolution fractions were determined by precipitating ^{90}Y presumably at pH [illegible] and counting the associated beta emission. Total Sr was precipitated from the remaining solution at pH 10.

[illegible]

Gamma activities in the aerosol sample were determined by counting for 17 hours in a coaxial Ge-Li detector with an active surface area of 15 cm^2 and a resolution of 1.4 keV at 622 keV. After the dissolution studies, the filter samples were also counted in this Ge-Li detector system to determine the remaining gamma activity.

[illegible]

Samples were transferred onto polished carbon stubs by pressing the carbon stub against the sample on the filter. Duplicate carbon stub samples were obtained from the same aerosol filter and were observed in a [illegible] Model [illegible] scanning electron microscope (SEM). Energy dispersive x-ray analysis (EDXA) of selected areas was performed by using a Li-drifted Si detector (Kevex

Model 78) and Kevex Model 5100 multichannel analyzer. Micrographs were also obtained by using the secondary electron imaging mode of the SEM. All micrographs were taken using 25 kV accelerating voltage and about 1 pa beam current.

Alpha spectrometry

An aliquot of the original aerosol sample in 2 M HCl solution was evaporated to dryness, redissolved in 3 M HCl and the iron was removed by ethyl ether extraction. The actinides were then electroplated on stainless steel discs from a $NaHSO_4$ - Na_2SO_4 buffer at pH 2.[10] The alpha activities were determined in a 128-channel pulse height analyzer with a resolution of 14.8 keV per channel. The detector was a 300 mm^2 surface barrier silicon detector (Princeton Gamma Tech). The duration of alpha counting and analysis was 19 hours.

RESULTS

A gamma spectrum of the aerosol sample is shown in Figure 2. All four segments had identical gamma peaks with the same ratios of ^{134}Cs to ^{137}Cs. The amounts of the major radioactivities present in the different segments and the total aerosol filter are shown in Table 1. The activities of ^{134}Cs and ^{137}Cs were determined directly from gamma spectroscopy and the activities of ^{90}Sr-^{90}Y and ^{89}Sr on Segment 4 by radiochemical methods. The ^{89}Sr activity was calculated by subtracting ^{90}Sr-^{90}Y activity from the total observed ^{89}Sr and ^{90}Sr-^{90}Y activity. The activities of ^{90}Sr-^{90}Y and ^{89}Sr in the other three segments were calculated from the ^{137}Cs activity in each segment and the ratios of ^{90}Sr-^{90}Y/^{137}Cs and ^{89}Sr/^{137}Cs observed in Segment 4.

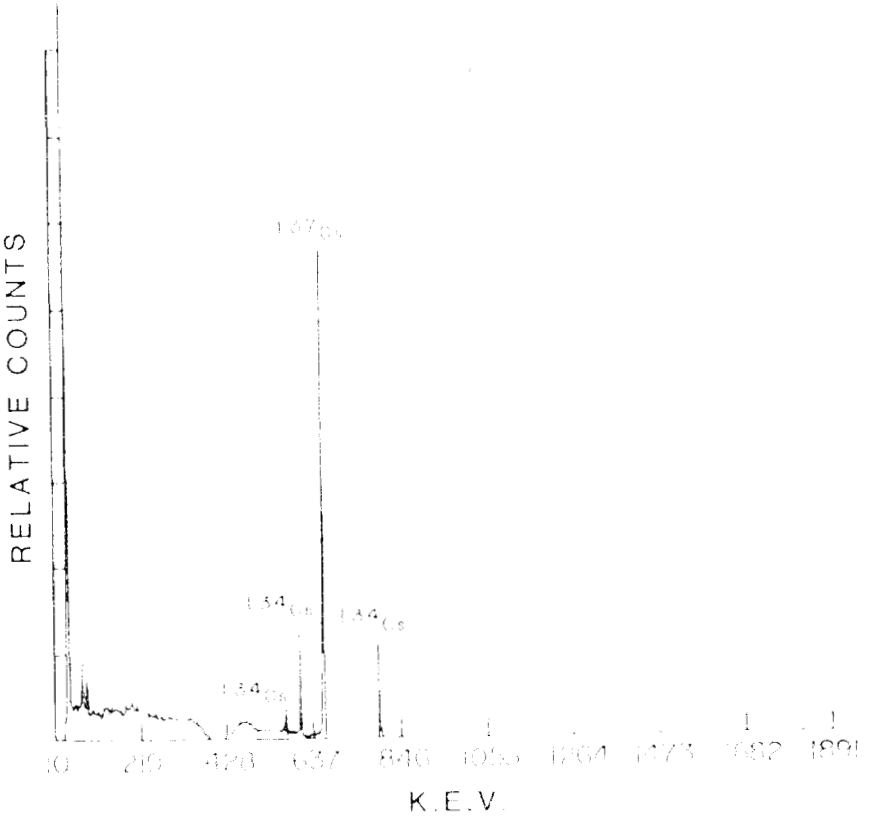

Figure 2. Gamma spectrum of Segment 4 of the 1m aerosol as determined with a coaxial Ge-Li detector.

1007251

The dissolution data obtained in the flow-through and static systems are summarized in Figures 3 and 4, respectively, as fractions of undissolved activity remaining on the filter versus elapsed time. Total gamma activity was directly determined on the filters before the samples were subjected to dissolution. The initial total beta activities on these filters were calculated from the ratio of total beta counts in the Wide Beta II counter to ^{137}Cs in segment 4 and the ^{137}Cs count on segment 1 (flow-through system) and segment 2 (static system). The undissolved fractions were calculated on the basis of beta counts. The ^{90}Sr-^{90}Y activity, both initial and those in the solutions were determined radiochemically. Summation of all dissolved radioactivites and those remaining on the filter provided estimates of initial amounts of radioactivities within a few percent of those activities shown in Table 1.

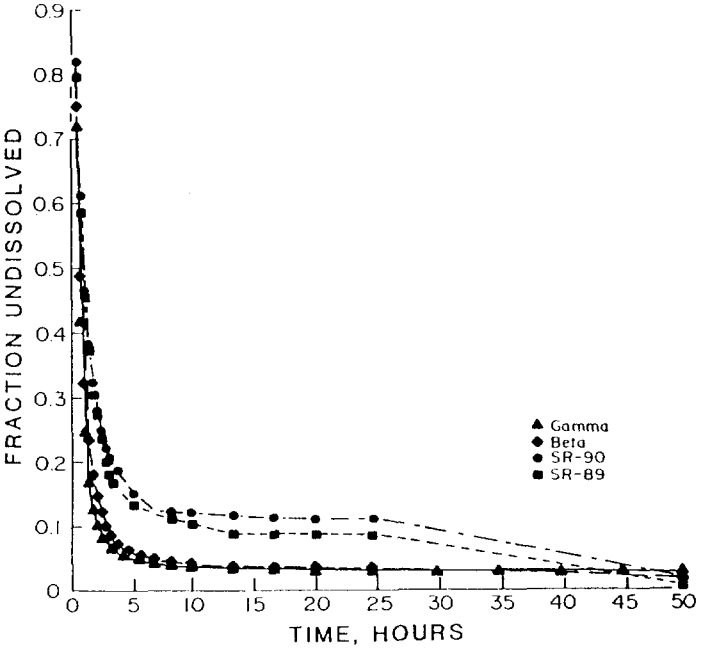

Figure 3. Dissolution of radionuclides in a flow-through system expressed as fraction dissolved versus elapsed time.

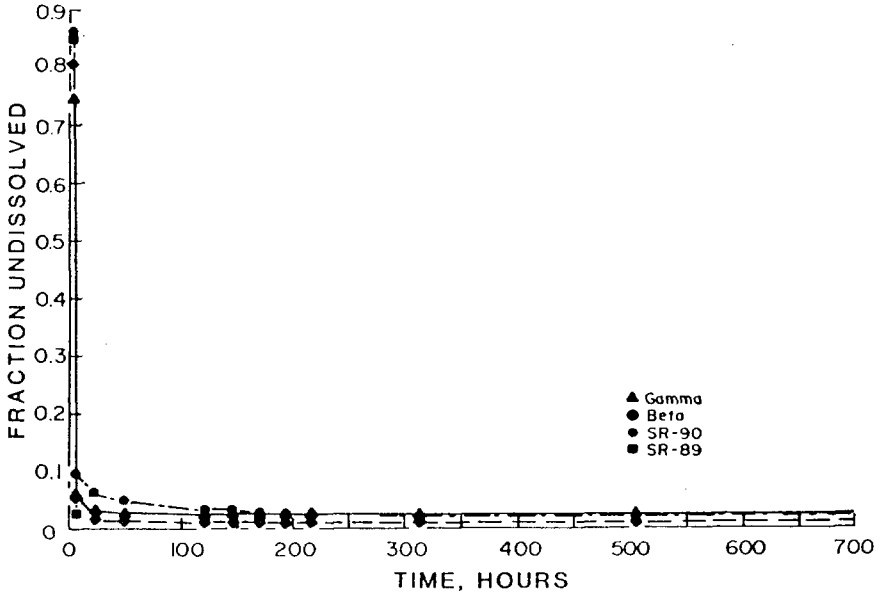

Figure 4. Dissolution of radionuclides in a static system expressed as fraction dissolved versus elapsed time.

1007252

Scanning electron micrographs of particles from Segment 3, which represents the original aerosol sample, and those from Segment 1 after dissolution in the flow-through system are shown in Figures 5 and 6, respectively. Average elemental composition of a large number of particles from Segment 3 and 1 are shown in Table 2.

An alpha spectrum of the original aerosol is shown in Figure 7. Based on ^{137}Cs counts, this sample represented about 4% of the total sample. The total activity of ^{239}Pu, ^{238}Pu or ^{241}Am, and ^{236}Pu in this sample is 0.50 dpm. On this basis, an estimate of total actinide alpha activity on the original aerosol was calculated to be 13 dpm.

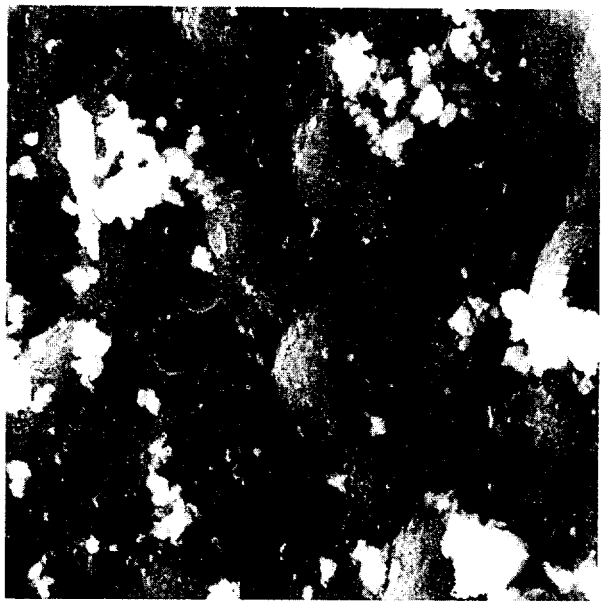

Figure 5. Scanning electron micrographs of original aerosol sample from Segment 3 of the TMI filter. Magnification 3000 X.

Figure 6. Scanning electron micrograph of aerosol particles from Segment 1 of the TMI filter after dissolution experiment in the flow-through system. Magnification 3000 X.

Table 2

Elemental Composition of the TMI Aerosol Filter Sample as Determined by Energy Dispersive X-Ray Analysis

Element	Weight (%)	Atomic (%)	Standard Deviation
Segment 3 Before Dissolution			
Mg	7.2	9.6	2.9
Al	16.2	19.3	1.6
Si	27.1	31.1	1.5
S	17.3	17.4	1.1
Ca	18.0	14.4	0.93
Fe	14.3	8.2	1.0
Segment 1 After Dissolution			
Al	63.8	64.8	7.9
Si	36.2	35.3	3.2

1007253

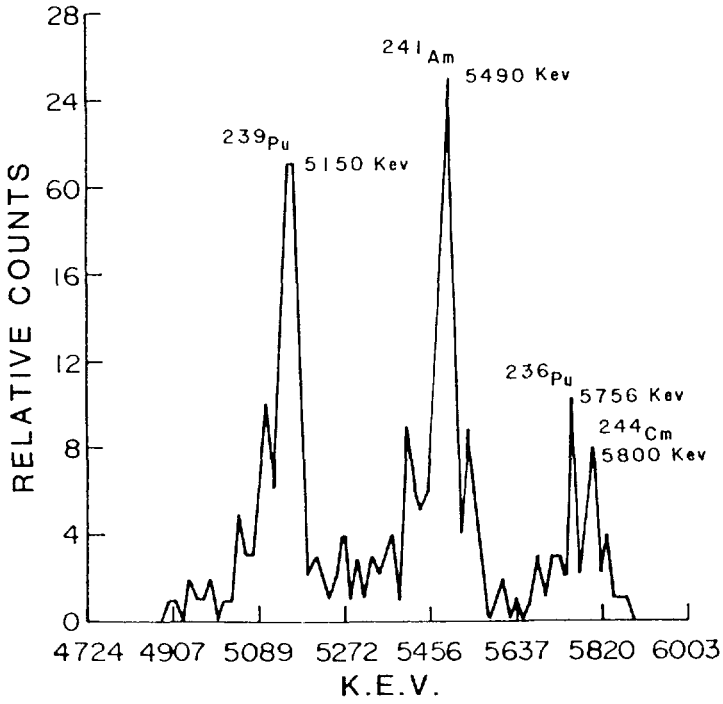

Figure 7. An alpha spectrum of the TMI aerosol sample determined on an electroplated sample by using a surface barrier detector and pulse height analyzer.

DISCUSSION

Analysis of the gamma spectrum (Fig. 2) indicated that ^{137}Cs and ^{134}Cs were the primary gamma-emitting radionuclides on the filter. The data supplied by GPU suggested the presence of small quantities of ^{140}Ba, ^{140}La and ^{60}Co. Since the gamma spectrum (Fig. 2) was obtained about a month after the aerosol was collected, it was expected that no ^{140}Ba or ^{140}La would be observed. The energy peaks at 1168 and 1365 keV, from ^{134}Cs, could have been interpreted by TMI personnel as that of ^{58}Co and ^{60}Co. It is noteworthy that there was no indication of any lanthanide isotopes, such as ^{144}Ce, present in the sample.

The quantities and proportions of ^{134}Cs, ^{90}Sr-^{90}Y and ^{89}Sr (Table 1) were similar to the estimates provided by GPU. All data indicated that the major radionuclides were ^{134}Cs, ^{137}Cs, ^{89}Sr and ^{90}Sr-^{90}Y. If there were other beta-emitting lanthanides, they would have been noticeable during the repeated counting of the ^{90}Y fractions obtained during the radiochemical analysis of ^{90}Sr-^{90}Y. The half-time of decay of the ^{90}Y fraction indicated no major, long-lived lanthanide isotopes. The observed actinide radionuclides (Fig. 7) were unexpected. Although the alpha activity was only 13 dpm in the total aerosol sample, it is a significant observation that there were actinide nuclides present in the aerosol. Since the physicochemical behavior of lanthanide and actinides are similar, there may have been minute but undetectable amounts of gamma- and beta-emitting lanthanide radionclides also present in the original aerosol.

The presence of major isotopes of alkali and alkaline earth elements, which are generally water soluble, but not other fission products such as ^{144}Ce and ^{91}Y in detectable quantities suggest that the major release mechanism was probably one of dissolution in water and then dispersion in the auxiliary building. In addition, the presence of the small amount of insoluble actinide suggests other possible mechanisms of particle release as a minor contributing factor. The elemental analysis (Table 2) suggests that the aerosol consisted of nonradioactive materials. Comparison of the composition before and after dissolution suggests that only Al and Si were insoluble and the other elements were present as soluble materials. The radionuclides were

1007254

present as minor components in a heterogeneous matrix consisting of Fe, Ca, S, Mg, Al, Si and carbonaceous material. The aluminum and silicon represented 43% of the total inorganic mass. It should be noted that the EDXA was incapable of determining C, O_2, H_2, etc. The filter sample was black both before and after dissolution which suggested the presence of soot or other carbonaceous materials.

The sizes of the aerosol particles were estimated from the electron micrographs (Figs. 5 and 6). Respirable-sized particles as well as larger particles ranging up to 10 μm were observed. Although the relative number density of the particles in the electron micrograph after dissolution (Fig. 6) was less than that before dissolution (Fig. 5), there was no apparent size-dependent, preferential dissolution of particles from the filter. Therefore, it is not possible from our study to deduce the size distribution of the soluble fraction which contained the radionuclides. However, it is reasonable to conclude that at least a fraction of the radionuclides were associated with the respirable-size particles.

The dissolution data (Figs. 3 and 4) show rapid dissolution of > 90% of all isotopes. The Cs isotopes appear to dissolve almost entirely in both dissolution systems. Less than 2% of the Cs isotopes could be detected on the filters after the dissolution experiments. The data show that within 5 hours, more than 95% of the Cs isotopes dissolved in both systems. The total beta dissolution rates were somewhat slower than the dissolution rates of the Cs isotopes. It should be remembered that the total beta activity was the sum of ^{89}Sr, ^{90}Sr-^{90}Y, ^{134}Cs and ^{137}Cs beta activities. The ^{90}Sr-^{90}Y dissolution rates suggest that a slightly higher fraction, 5 to 10% of the activity, was relatively insoluble compared with Cs. This undissolved fraction of the Sr was present in both dissolution systems.

The International Commission on Radiological Protection (ICRP) has grouped specific chemical forms of radionuclides into three classes (D, W, and Y) to describe their expected patterns of retention in different portions of the respiratory tract.[8] The three classes, days (D), weeks (W), and years (Y) describe both the expected clearance by mechanical and dissolution/absorption pathways. These classifications have been derived for single radionuclides in known chemical forms based on available *in vivo* and *in vitro* data. However, the ICRP solubility classification scheme does not include predictions for heterogenous mixtures such as the one present on the sample analyzed here.

Results from the *in vitro* dissolution tests performed on this sample demonstrate that most of the radionuclides present dissolved very quickly (within 5 hr) in the SUF plus DTPA solvent. Although an exact correspondence between *in vitro* and *in vivo* dissolution characteristics has not been established for these radionuclides in this form and mixture, it seems reasonable to assume that a similar rapid dissolution would occur *in vivo*. Thus, based on this assumption and the observed *in vitro* dissolution characteristics of the present sample, it is appropriate to evaluate observed air concentrations with respect to derived air concentrations (DAC) by classifying the radionuclides as class D materials.

This study has demonstrated the applicability of the above techniques for characterizing airborne radionuclides of unknown physical and chemical composition. The data may be useful in determining the body burden of these radionuclides from bioassay data and helping to estimate the dose distributions resulting from inhalation of the aerosol.

1007255

REFERENCES

1. Morrow, P. E., D. V. Bates, B. R. Fish, T. F. Hatch and T. T. Mercer, "Deposition and Retention Models for Internal Dosimetry of Human Respiratory Tract," Health Phys. 12: 173-207, 1966.

2. Kanapilly, G. M., O. G. Raabe, C. H. T. Goh and R. A. Chimenti, "Measurement of *In Vitro* Dissolution of Aerosol Particles for Comparison to *In Vivo* Dissolution in the Lower Respiratory Tract After Inhalation," Health Phys. 24: 497-507, 1973.

3. Kanapilly, G. M., O. G. Raabe and H. A. Boyd, "A Method for Determining the Dissolution Characteristics of Accidentally Released Radioactive Aerosols," in Proceedings of the Third International Congress of IRPA, pp. 1237-1242, Washington, DC, USAEC Document, CONF-73907, 1973.

4. Kanapilly, G. M. and C. H. T. Goh, "Some Factors Affecting the *In Vitro* Rates of Dissolution of Respirable Particles of Relatively Low Solubility," Health Phys. 25: 225-237, 1973.

5. Miglio, J. M., B. A. Muggenburg and A. L. Brooks, "A Rapid Method for Determining the Relative Solubility of Plutonium Aerosols," Health Phys. 33: 444-457, 1977.

6. Kanapilly, G. M. and G. J. Newton, "A New Method for the Separation of Multicurie Quantities of ^{90}Y from ^{90}Sr," Int. J. Applied Rad. and Isotopes 22: 567-575, 1971.

7. Kressin, I. K., "Electrodeposition of Plutonium and Americium for High Resolution Alpha Spectrometry," Anal. Chem. 49: 842-846, 1977.

8. "Limits for Intakes of Radionuclides by Workers," ICRP Publication 30, Part I, pp. 63-116, 1978.

1007256