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I am submitting herewith a thesis written by Robert Len Shankle entitled "A Study of the Apparent Solubilities in Water of Americium Dioxide and Europium Sesquioxide." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.

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A STUDY OF THE APPARENT SOLUBILITIES IN WATER OF AMERICIUM DIOXIDE AND EUROPIUM SESQUIOXIDE

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Robert Len Shankle

December 1976

1306048

ACKNOWLEDGMENTS

The author wishes to express his deep appreciation for the leadership and advice given by Dr. Joseph R. Peterson, without whose guidance and patience this project would not have been completed.

Sincere appreciation is also extended to the other committee members, Dr. George K. Schweitzer and Dr. Milton H. Lietzke, for their kind advice and counsel.

Special thanks are given to Dr. Robert L. Fellows, Dr. John H. Burns, Dr. Richard G. Haire, Dr. Robert J. Silva, Mr. David Hobart, and all other personnel of the Transuranium Research Laboratory for their support, advice, and technical assistance.

The author is sincerely grateful to the University of Tennessee for a Teaching Assistantship during two years, to the Chemistry Division of Oak Ridge National Laboratory, as operated by Union Carbide Corporation, for providing all necessary equipment, laboratory space, and support work during the course of this study, and to the Energy Research and Development Administration for financial support.

Finally, the author wishes to express his deepest appreciation and thanks to Terre Shankle, whose patience, understanding, and love were the motivation for this work, which, like all other things, is dedicated to her.

ABSTRACT

The apparent solubilities of americium-241 dioxide and americium-243 dioxide in distilled water were measured. In order to obtain a preliminary estimate of the solubility, and to check the experimental procedure, the most common oxide form of the corresponding lanthanide, europium sesquioxide, was examined also. The Eu_2O_3 was prepared by calcination of the oxalate at 650 °C to insure the absence of formation of any refractory material. The americium-241 sample was initially present as a nitrate and was carried through an oxalate precipitation and calcination in air to obtain the dioxide. The americium-243 sample was initially present as the dioxide.

Excess amounts of each compound were contacted with a known volume of distilled water by means of a magnetic stirrer. Samples were periodically removed and filtered to remove any suspended material. The europium sample was mixed with a solution of 2-thenoyltrifluoroacetone (TTA), 1,10-phenanthroline, acetone, and water, and the fluorescence of the $Eu(TTA)_3$ complex at 612 nm was measured and compared with prepared standards. The americium samples were mounted on stainless steel plates, and their gross alpha activity was measured on a 2π-geometry alpha proportional counter that had been first standardized. When the specific activities and sample volumes were considered, solubilities were obtained.

A prediction based on the water solubilities of neighboring sesquioxides of about 1.5×10^{-6} M for the water solubility of Eu_2O_3 was experimentally verified. The apparent water solubility of $^{241}AmO_2$ was found to be 1.5×10^{-5} M, and likewise, for $^{243}AmO_2$, was 2.9×10^{-4} M.

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CHAPTER I

INTRODUCTION

A. Historical Background of Americium

Americium (Z=95) was the fourth synthetic member of the actinide series to be discovered, although it is the third transuranic element. The initial experimental work was done by Seaborg, Ghiorso, James, and Morgan at the Metallurgical Laboratory of the University of Chicago concurrently with their work on curium (Z=96), which actually was identified a few months prior to americium. It took about one year, during 1944 and 1945, for the complete distinction between the two elements to be made.[1]

Part of the problem in this initial work was a basic misconception of the expected behavior of the newly discovered transuranic elements. The first two synthetic elements, neptunium and plutonium, proved to have chemical properties that were similar to uranium, rather than being like rhenium and osmium, which by the then-current periodic concept should have been immediately above the two new elements in the periodic chart. The implication was that these new synthetic elements would constitute a "uranide" group, that is, uranium-like in properties. This delayed the discovery of americium and curium because the methods used for their detection were based on an expected similarity to plutonium.[2]

This misconception was cleared up in 1955 by Seaborg, who postulated that the elements beyond actinium actually constituted a

second "rare-earth" series that fitted in the periodic table directly below the lanthanides. This indicated that americium and curium should be chemically similar to europium and gadolinium, respectively, and when experiments were so designed, the next two "actinide" elements were soon discovered.[2]

Americium was initially produced according to the following nuclear reactions:

$$^{239}Pu\ (n,\gamma)\ ^{240}Pu\ (n,\gamma)\ ^{241}Pu \rightarrow\ ^{241}Am + \beta^{-}, \qquad (1)$$

where n is an incident neutron, γ is a resulting gamma ray, and β^{-} is an emitted beta particle. Seaborg and his co-workers were also able to make ^{241}Am by a charged particle reaction:

$$^{238}U\ (\alpha,n)\ ^{241}Pu \rightarrow\ ^{241}Am + \beta^{-}, \qquad (2)$$

where α is an incident alpha particle. The discoveries of americium and curium were first announced on November 16, 1945, with official naming coming in April, 1946. Element 95 was named americium (analogously to europium), and element 96 was named curium, after the Curies, as gadolinium had been named after J. Gadolin.[1]

B. Hazards to Human Health

Americium exists in thirteen known isotopic forms, having mass numbers (A) ranging from 237 to 246, with metastable energy states at A=242 and A=244. Of these, three isotopes, ^{241}Am, ^{242m}Am, and ^{243}Am, have half-lives long enough to be of significance to man. These

half-lives are 434 yr, 152 yr, and 7700 yr, respectively, with the other isotopes having half-lives on the order of hours.[3,4]

These three isotopes are primarily alpha emitters and as such, constitute serious radiological hazards if they are absorbed into the body. Americium, like most other transuranics, will tend to concentrate in the skeletal system when absorbed, where the most biological damage is therefore done. The biological half-life of americium, which is the time required for one-half of the nuclide to be removed from the body by both its own radioactive decay and by biological elimination, is approximately 200 yr and consequently, enough of the element will remain in the body to cause chronic alpha irradiation of the bones, producing bone cancer or other radiation damage.[5,6] Absorption of americium isotopes is therefore relatively dangerous. For example, taking ^{3}H as unity, ^{241}Am has a relative risk of 600 with regard to water-borne exposure. When air-borne exposure is considered, ^{241}Am is 3.3×10^{6} times as dangerous to the skeleton as is ^{3}H.[7] As such, careful containment when using ^{241}Am is usually required.[8]

Taking into consideration factors such as these, the United States Energy Research and Development Administration (ERDA) has issued standards for radiation protection for different radioactive sources.[9,10] The americium standards, expressed as both microcuries per milliliter (μCi/ml) and as molarity (M) are listed in Table I (p 4). These guidelines are for use in either a controlled area, such as the Oak Ridge National Laboratory (ORNL), or in an uncontrolled area, which is an unregulated zone. The numbers in Table I are based primarily on

TABLE I

CONCENTRATION GUIDELINES FOR Am IN AIR AND WATER ABOVE NATURAL BACKGROUND

Isotope[a]	Controlled Area		Uncontrolled Area	
	Air	Water	Air	Water
	μCi/ml (M)	μCi/ml (M)	μCi/ml (M)	μCi/ml (M)
^{241}Am(s.)	6E-12[b] (7.2E-18)	1E-04 (1.2E-10)	2E-13 (2.4E-19)	4E-06 (4.8E-12)
(ins.)	1E-10 (1.2E-16)	8E-04 (9.6E-10)	4E-12 (4.8E-18)	3E-05 (3.6E-11)
^{242m}Am(s.)	6E-12 (2.5E-18)	1E-04 (4.2E-11)	2E-13 (8.4E-20)	4E-06 (1.7E-12)
(ins.)	3E-10 (1.3E-16)	3E-03 (1.3E-09)	9E-12 (3.8E-18)	9E-05 (3.8E-11)
^{242}Am(s.)	4E-08 (2.0E-19)	4E-03 (2.0E-14)	1E-09 (5.1E-21)	1E-04 (5.1E-16)
(ins.)	5E-08 (2.6E-19)	4E-03 (2.0E-14)	2E-09 (1.0E-20)	1E-04 (5.1E-16)
^{243}Am(s.)	6E-12 (1.3E-16)	1E-04 (2.1E-09)	2E-13 (4.2E-18)	4E-06 (8.4E-11)
(ins.)	1E-10 (2.1E-15)	8E-04 (1.7E-08)	4E-12 (8.4E-17)	3E-05 (6.3E-10)
^{244}Am(s.)	4E-06 (2.9E-18)	1E-01 (7.2E-14)	1E-07 (7.2E-20)	5E-03 (3.6E-15)
(ins.)	2E-05 (1.4E-17)	1E-01 (7.2E-14)	8E-07 (5.8E-19)	5E-03 (3.6E-15)

a. s. = soluble, ins. = insoluble

b. 6E-12 is to be read as 6×10^{-12}

the exposure limits for man set by ERDA as given in Table II (p 6).[9] The dose equivalents are in rems, which are a measure of how biologically effective an absorbed dosage of radiation is. The assumption that air and water are the major transport routes of radionuclides has been researched and verified.[11]

C. Current Sources and Projected Amounts

Americium is currently prepared by one of two general methods. Either uranium or plutonium nuclei are bombarded with heavy ions using an accelerator, or a plutonium target is irradiated in a nuclear reactor. The latter method is the more widespread, since larger amounts can be produced more economically in this fashion.[12] Generally speaking, americium is produced by a series of neutron-induced reactions acting on a starting material, usually ^{232}Th or ^{238}U, which eventually produces plutonium isotopes that undergo beta-decay to form americium. This decay scheme is illustrated in Figure 1 (p 7). The nuclear transitions shown in the decay scheme are: (n,γ), incident neutron-emitted gamma ray; β^-, emitted beta particle; IT, internal transition; EC, electron capture. The numbers associated with the transitions are half-lives ($t_{1/2}$), with m, h, d, and y standing for minute, hour, day, and year, respectively.

The exact amount of americium produced in a reactor is a function of several parameters. Factors such as the neutron flux of the reactor, the length of the irradiation, the amount of target material, and the starting composition of the fuel will influence the level of

TABLE II

RADIATION PROTECTION STANDARDS FOR INTERNAL AND EXTERNAL EXPOSURES TO MAN

Type of Exposure	Exposure Period	Dose Equivalent (rem)
Whole body, head and trunk, gonads, lens of the eye, red bone marrow, active blood-forming organs	Year	5
	Calendar Quarter	3
Unlimited areas of the skin (except hands and forearms), other organs, tissues, and organ systems (except bone)	Year	15
	Calendar Quarter	5
Bone	Year	30
	Calendar Quarter	10
Forearms	Year	30
	Calendar Quarter	10
Hands and feet	Year	75
	Calendar Quarter	25

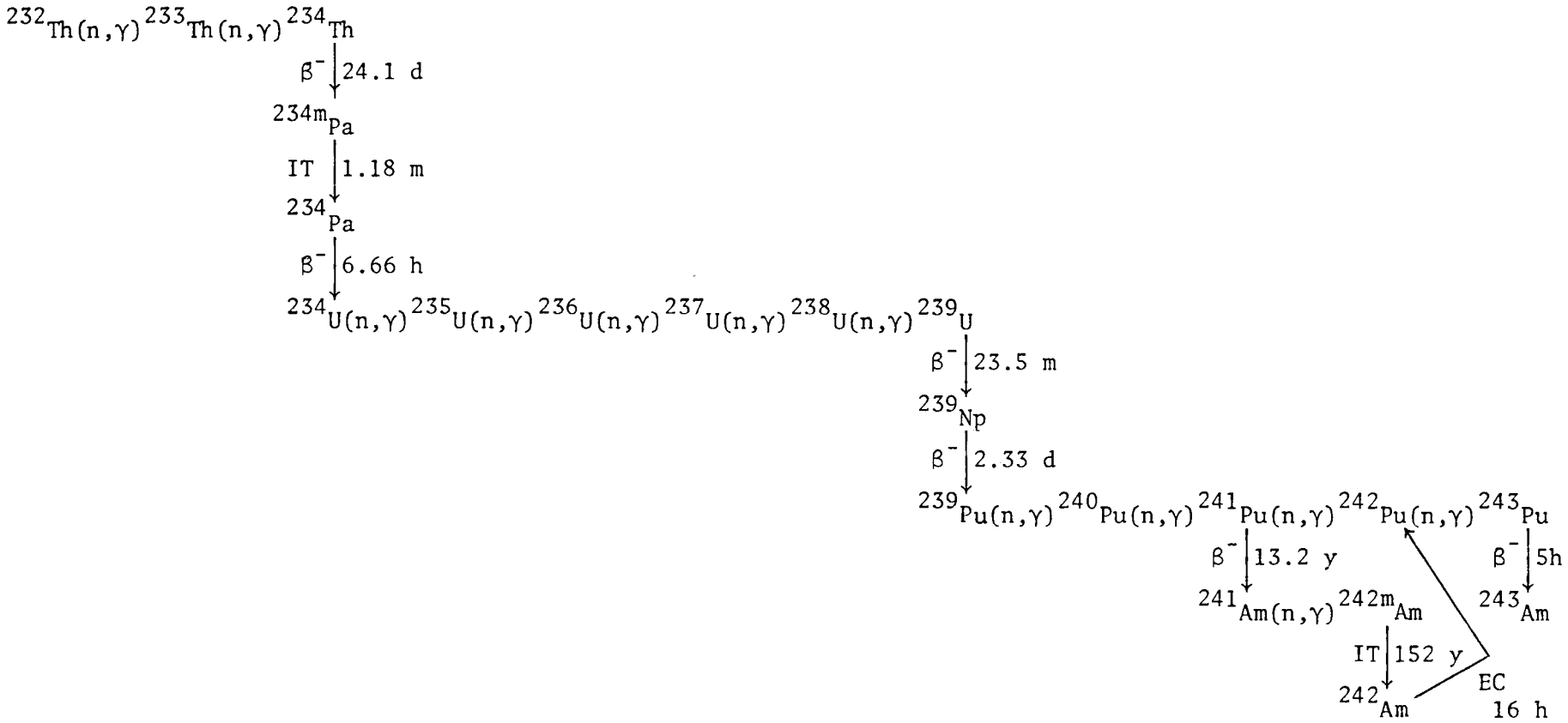


Figure 1. Method of americium formation in a nuclear reactor.

americium production. Presently, there are three basic reactor fuel types in use or projected for future use. These are for light water reactors (LWR), high-temperature gas reactors (HTGR), and liquid-metal fast breeder reactors (LMFBR). LWR fuels can either be Power Reactor-Uranium (PWR-U) or Power Reactor-Plutonium (PWR-Pu) fuels, and LMFBR fuels can either be Atomics International Follow-On (AIFO) or General Electric Follow-On (GEFO) fuels.[13]

The amount of radioactive waste that will be generated by the United States nuclear power industry has been estimated as a function of reactor fuel composition.[13,14] Predictions, just like the two considered here, usually differ because of different technical and political considerations (i.e., can it be done, and will it be allowed). The amount of americium that can be expected to be generated from a one metric ton charge of five different nuclear reactor fuels is indicated in Table III (p 9). Therefore, knowing how many total metric tons of waste are generated annually, one can determine the amount of americium produced over the next few years. The data from two independent estimations[13,14] are given in Appendix I (pp 48-49). Both studies predict a steady increase in the americium inventory, as illustrated in Figure 2 (p 10), which is based on the data of Blomeke.[13]

Whatever basis is used for the prediction of future nuclear waste levels, it is clear that the amount of waste will be increasing with time. For example, by the year 2000, not considering the radioactive decay of any of the nuclides, approximately 0.5 billion curies of americium will have been produced, with most of it being stored

TABLE III

CURIES OF Am IN THE HIGH-LEVEL WASTES GENERATED FROM A ONE METRIC TON CHARGE OF DIFFERENT REACTOR FUELS MEASURED AT THE TIME OF DISCHARGE

Isotope	µg/Ci	PWR-U	PWR-Pu	HTGR	AIFO	GEFO
^{241}Am	2.892E 05	159	1580	27.8	2260	1450
^{242m}Am	1.020E 05	9.14	227	0.459	113	111
^{242}Am	1.224E 00	9.14	227	0.459	113	111
^{243}Am	5.186E 06	18.2	514	7.28	54.1	56.9
-------- TOTAL --------		195	2548	36.0	2540	1730

TOTAL LWR (PWR-U & PWR-Pu). . . . 2743 Ci/2MT
Weighted Average[a]. . . . 2383 Ci/MT

TOTAL HTGR. . . . . 36.0 Ci/MT

TOTAL LMFBR (AIFO & GEFO) 4270 Ci/2MT
Weighted Average . . . . 2212 Ci/MT

a. Weighted as to percent of total amount

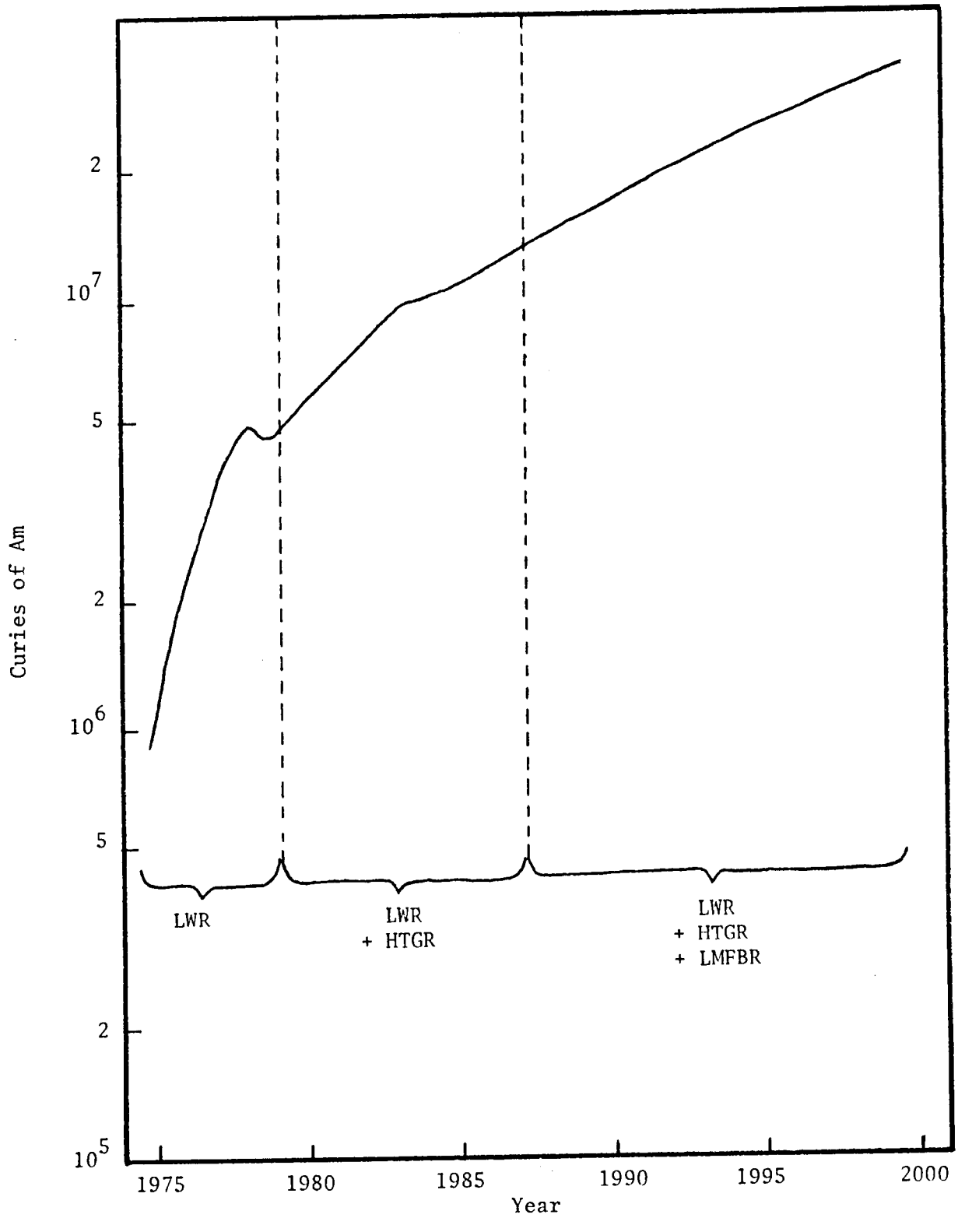


Figure 2. Curies of americium generated annually for 1975-2000.

underground.[15] Considering this large amount, the behavior of americium in the natural environment is of considerable importance.

D. Solubility Determinations

There are several classical approaches to the study of the solubility of solids in liquid media that conceivably could be applied to the AmO_2-water system studied here. A method of medium accuracy, as proposed by Reilly and Rae,[16] involves the approach to equilibrium from both supersaturated and unsaturated systems of the same materials. Analysis of the solvent from both determinations should give consistent values of the solubility. Another method, designed to accommodate large numbers of samples, calls for taking pairs of solvent-solute samples, heating both to a temperature insufficient to dissolve all of the solid, chilling one tube to crystallize out considerable solid, and then combining the two, with filtering, to form the solution for analysis.[17] Solubility may also be measured by allowing the solvent to percolate over the solute a sufficient number of times to allow a constant solution density to be reached.[18] These methods were not chosen for the present study because the relatively large amounts of solute required could not be tolerated. Methods suitable for the analysis of small samples were then considered.

Spectrophotometric determinations, such as flame photometry[19] and colorimetric analysis,[20] are sensitive enough to accommodate small amounts of samples. Flame photometry involves the aspiration of a sample solution into a flame and the measuring of the emitted spectral

lines from the sample. Emissions can result from the excitation caused by the flame (flame emission) or that from an external source (atomic absorption). Were it not for the radioactivity involved in the present work, this method would be useful for the americium determination, because of the relatively high optical density associated with its spectral lines.[21] However, this method would be limited by factors such as quenching effects in the solutions and by a possible lack of linearity in the calibration curves. These same arguments also apply to the absorption processes observed in a colorimetric determination.

Electrochemical methods may be applied to the solubility study of a substance dissociating into ions in solution. The solution may be analyzed conductometrically,[22] with the conductance of the solution falling to a minimum at the point where saturation of the solution occurs. This would allow the amount of solute in the solution to be determined directly. A measurement of the pH of a solution in which a hydrolysis product forms could also be made.[23] Studies such as this are usually concerned with, in actinide-water systems, the determination of the hydroxide ion concentration. Knowing this and the nature of the species that dissociated in solution, one could determine values of the actinide solubility.

Simple monomers, hydrolysis products, or other uncharged species such as polymeric forms, can be detected by means of an ultracentrifugation technique.[21] The centrifugation tends to separate out species in layers in the bottom of the centrifuge tube according to molecular weight. This molecular weight data can also give information regarding the degree of possible polymerization that has occurred.

In studying the actinides, plutonium has been investigated in aqueous solution quite extensively and has been shown to exist in several different forms, both ionic and nonionic, in solution.[21] To a lesser extent, neptunium has also been examined and found to show similarities to the Pu behavior. Assuming such a periodic similarity continues, the indication is that AmO_2 may possibly be present in aqueous solution in forms such as AmO_2, $Am(OH)_4$, $Am(OH)_3^+$, $Am(OH)_2^{2+}$, $Am_2(OH)_7^+$, $(AmO)_2^{4+}$, Am^{4+}, and possibly others.

The exact nature of an AmO_2-water equilibrium system is therefore quite complex. Since both ionic and nonionic species are likely to exist in solution, and since the hazard to man associated with such a solution is dependent on the total amount of americium present in the system, be it ionic or nonionic, a method was chosen that would not be specific for either form, but rather would yield a value for the overall apparent solubility.[24] The method chosen, filtration followed by alpha analysis, was used in connection with a distilled water medium. This should allow at least a first approximation of the behavior of AmO_2 in a natural water system to be made. The apparent solubility in distilled water should represent a lower limit for the solubility of AmO_2 in a natural water system, where the presence of complexing agents is highly likely.

E. Problem Studied

The behavior of americium in contact with water, either in a nuclear waste burial ground or through an accidental release, is not

well known at present. Considering that water is one of the major pathways of radionuclides to man,[11] information relating to the solubility of americium in water would be useful.

Since the most common form of americium found in today's mixed oxide nuclear fuels is americium dioxide,[13,25] this form was chosen as the compound of interest. Two isotopes of americium, ^{241}Am ($t_{1/2}$=434 yr) and ^{243}Am ($t_{1/2}$=7700 yr), were studied separately to see if any isotope effect in their water solubilities exists. In order to determine a rough estimate for the americium solubilities and to evaluate the planned experimental methods, a preliminary experiment was run on the water solubility of the most common oxide of the corresponding lanthanide, europium sesquioxide (Eu_2O_3).

CHAPTER II

EXPERIMENTAL METHODS

A. Equipment

The fluorescence of the complex of europium with 2-thenoyltrifluoroacetone (TTA) was monitored using an Aminco-Bowman Spectrophotofluorometer, Model 4-8202, with spectra recorded on an Aminco-Bowman X-Y Recorder, Model 1620-827. Due to an equipment failure, an Electro Instruments Model 500 X-Y Recorder was substituted during the course of the experiment. The excitation light source was a xenon arc lamp, and an excitation wavelength of 390 nm was used.[26] The optimum slit widths used were: excitation source slit-open; cell excitation slit-open; cell emission slit-1 mm; monochromator slit-open; photomultiplier slit-2 mm. A standard 1 cm glass cuvette was used to hold the samples.

Weighings of Eu_2O_3, TTA, and 1,10-phenanthroline were made on a Sartorius 200 g capacity pan balance. A Cenco-Parmer 700 W crucible furnace and a Marshall tube furnace were used in the Eu and Am heatings, respectively, and were controlled by Variac rheostats. Class A volumetric pipettes and glassware were used in all additions to, or dilutions of, reagents. Standard alpha-containment gloved boxes, operated at reduced pressure and equipped with absolute filters, electric and water connections, and heater and thermocouple connectors were used in the preparation of the americium dioxide. The heating

apparatus used in the preparation of the $^{241}AmO_2$ is shown in Figure 3 (p 17).

The X-ray diffraction patterns of the Eu_2O_3 and AmO_2 samples were obtained using a General Electric XRD-6 X-Ray Diffraction Unit. The exposures were run at 45 kV and 13 mA for about 2 hours. The samples were sealed in quartz capillary tubes and mounted in a Norelco 57.3 mm diameter X-ray powder camera, Type No. 52057-B. The line positions on the exposed films were read by two independent workers and then averaged. Best fit lattice parameters were obtained by the method of least squares using the LCR-2 program.[27]

The americium samples were counted following filtering of a ∿1 ml aliquot through a Millipore 0.2 μm pore size paper filter and placing 10 or 15 μl portions of the filtrate on separate stainless steel planchets. The filtering apparatus is shown in Figure 4 (p 18). The planchets were dried under a heat lamp, flamed to remove any volatile material, and counted on a 2π-geometry α-proportional counter. A standard source of α-radioactivity was first run to determine the counter efficiency (about 50.5%).

B. Reagents

A series of standard solutions of Eu_2O_3 was prepared by progressive dilution of a 10^{-2} M Eu^{3+} solution. All sample volumes were transferred using micropipettes and volumetric glassware, with dilutions being made with a fluorescing solution that was abbreviated TAWP, for TTA (10^{-2} M), acetone:water (3:1 by volume), and 1,10-phenanthroline (0.158 wt %).[28]

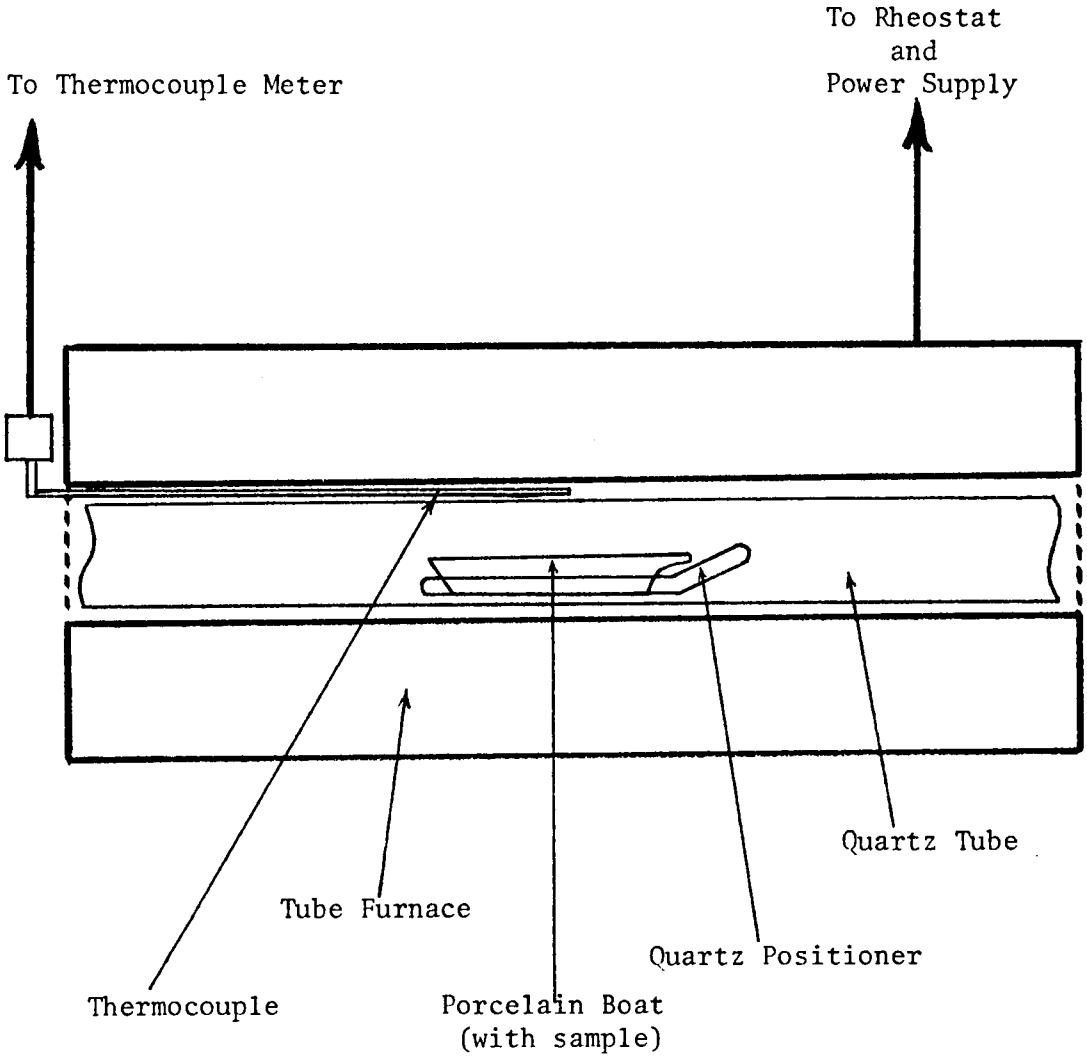


Figure 3. Heating apparatus for ^{241}Am sample.

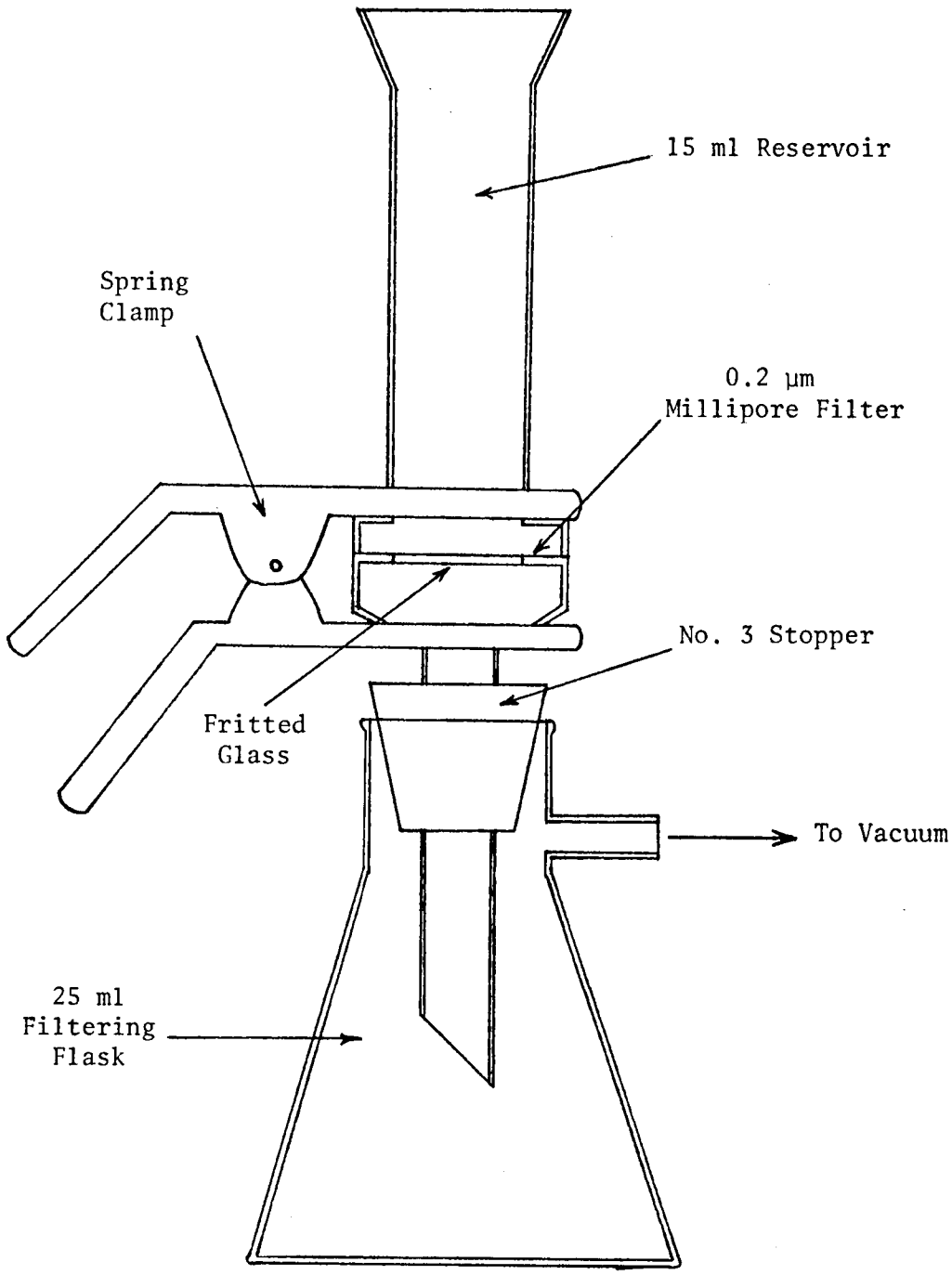


Figure 4. Americium filtering apparatus.

The preparations of the standard solutions are summarized in Table IV (p 20).

All reagents used in this work were of reagent-grade purity and were used without further purification or treatment, unless otherwise noted.

C. Procedure

The basic procedure used in both the preliminary europium work and the subsequent study of the americium system was to contact, by means of stirring, a known excess of the particular oxide with distilled water. The excess was necessary to insure the formation of a saturated solution. Samples were periodically withdrawn from the reaction vessels with filtering (so as to avoid minute particles suspended in the supernatant liquid) and then were analyzed.

It was not known whether the Eu_2O_3 obtained from the supplier was high-fired (prepared at high temperature) or low-fired. Since high-firing would likely produce a less soluble refractory compound, the Eu_2O_3 was dissolved in concentrated HNO_3[29] and then reprecipitated as the oxalate by adding oxalic acid. The resulting $Eu_2(C_2O_4)_3$ was then calcined to Eu_2O_3 in air at approximately 650 °C, the lowest temperature possible for a complete oxalate-to-sesquioxide conversion.[30] A sample of the Eu_2O_3 as obtained from the supplier, American Potash and Chemical Corporation, was also run for comparison.

The two Eu_2O_3 samples were placed in separate vessels containing distilled water and were contacted by means of magnetic stirrers and

TABLE IV

PREPARATION OF STANDARD Eu^{3+} SOLUTIONS

$[Eu_2O_3]$, M	Preparation of 25 ml Standard
10^{-2}	0.0880 g Eu_2O_3 dissolved in conc. HCl, then diluted with TAWP
10^{-4}	0.250 ml 10^{-2} M diluted with TAWP
10^{-5}	0.025 ml 10^{-2} M diluted with TAWP
10^{-6}	0.250 ml 10^{-4} M diluted with TAWP
10^{-7}	0.025 ml 10^{-4} M diluted with TAWP
10^{-8}	0.250 ml 10^{-6} M diluted with TAWP

stirring bars.[31] The vessels used were Pyrex flasks that, when covered, were placed in a secondary vessel for the purpose of temperature control. The secondary vessel used was a vacuum desiccator, and the temperature was maintained at a room temperature of 24 ± 2 °C. The pH was intermittently monitored using pHydrion paper and was found to be consistently ∿5. The experimental setup is shown schematically in Figure 5 (p 22).

An X-ray diffraction analysis of the untreated Eu_2O_3 was run for verification of the starting compound. The results agreed well with reported literature values.

A 5 ml sample of supernatant liquid was withdrawn from the europium system through a glass tube packed with Pyrex wool, which served as a coarse filter. After vacuum filtering the sample through a Buchner funnel of double filter paper (Whatman #50, crystalline pore size), 1 ml of the sample was transferred into a 25 ml volumetric flask and diluted with a fluorescing solution that was 10^{-2} M TTA, 0.158 wt % 1,10-phenanthroline, and 3:1 in acetone:distilled water.[28] The fluorescence of the $Eu(TTA)_3$ complex at 612 nm[32] was then measured and compared to standard solutions of Eu^{3+} that were prepared identically to the samples, except that the Eu_2O_3 solid was initially dissolved in concentrated HCl.

The ^{241}Am was obtained from the Oak Ridge National Laboratory (ORNL) Chemical Technology Division as a nitrate solution. The ^{243}Am was obtained from the ORNL Chemistry Division as the solid dioxide.

The $^{241}Am(NO_3)_3$ was treated with oxalic acid as previously described for the Eu_2O_3. The resulting oxalate was filtered through ashless filter paper (Whatman #50) and left overnight to dry. The dried

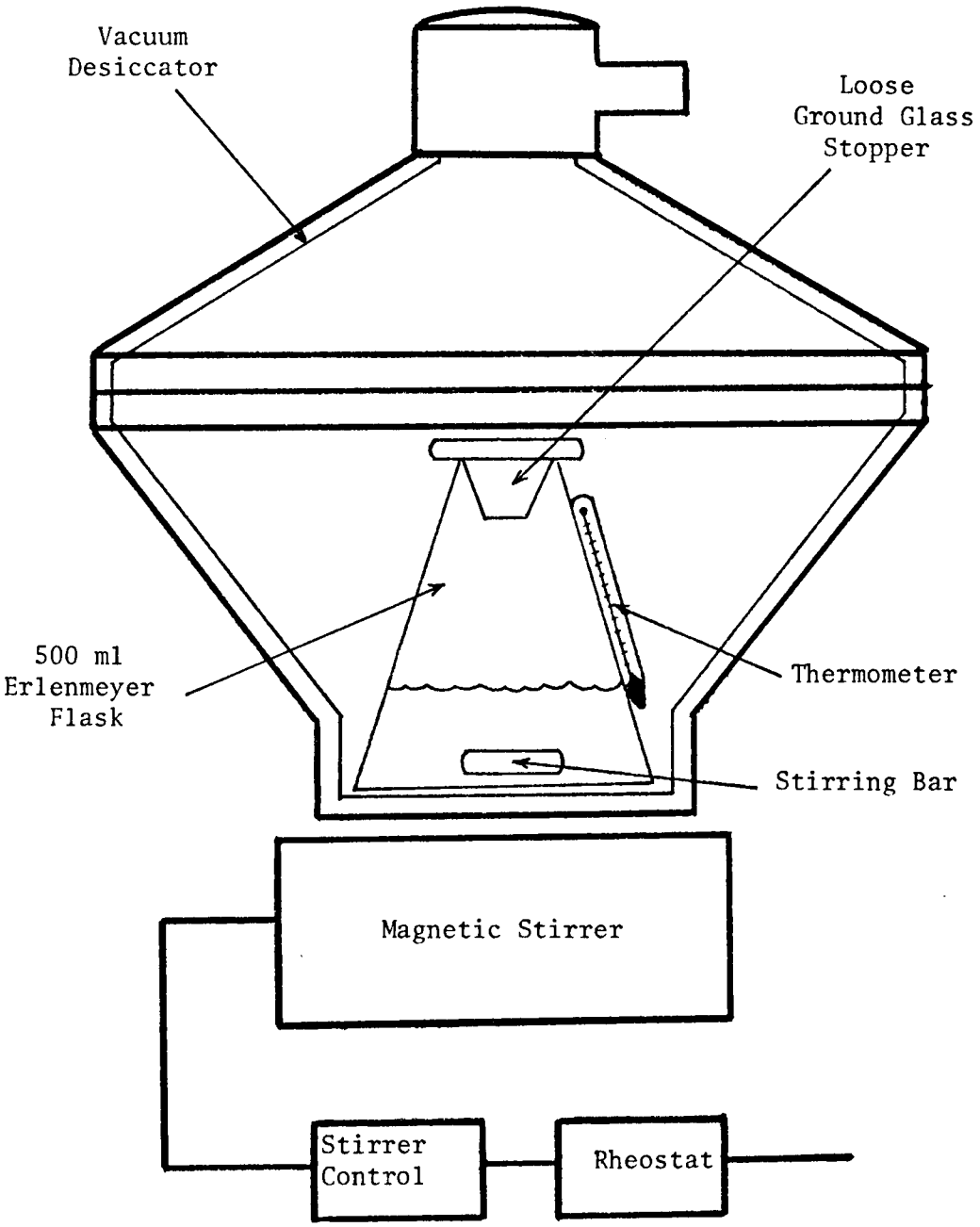


Figure 5. Europium stirring apparatus.

sample was then transferred to a Coors ceramic boat and placed in a tube furnace for conversion of the oxalate to the dioxide by heating at 600 °C in air (see Figure 3, p 17). Heating for two hours produced the desired change. The X-ray diffraction data obtained from a sample of each of the Am dioxides are listed in Appendix II (pp 50-55).

The two Am dioxides were then put into separate distilled water media, consisting of tall beakers and covers, and mixed using magnetic stirrers. This work was done in a standard alpha-containment gloved box due to the activity of the Am samples. Samples were periodically withdrawn with filtering through 0.2 μm pore diameter filters, and aliquots were mounted and dried on stainless steel plates for gross alpha counting and gamma pulse-height analysis. The gamma analyses, which were run by the ORNL Analytical Chemistry Division, were done as checks on the isotopic purity of the mounted samples. Approximately 95% purity of the samples was obtained. The gross alpha counts were corrected for background and converted to disintegrations per minute (dpm) by dividing by the counter efficiency. The dpm were converted to mass by dividing by a specific activity for the samples that had been weighted according to the average percentages of ^{241}Am and ^{243}Am present in the samples. Mass values were converted into the corresponding number of moles, which were divided by the sample volumes to yield the water solubilities in molarity (M).

CHAPTER III

EXPERIMENTAL RESULTS

A. Behavior of Eu_2O_3 in Aqueous Solution

The Eu_2O_3 as obtained from the supplier was verified by the results of X-ray powder diffraction analysis. The observed lines and calculated lattice parameters are shown in Appendix II, Table II-A (pp 51-52). A summary of the calculations is shown in Table II-D (p 55).[33,34,35,36,37]

The results of the study of the Eu_2O_3 (both high- and low-fired) are summarized in Table V (p 25). From these data it can be seen that the equilibrium in the Eu_2O_3-water system (the untreated Eu_2O_3) was reached at a time between 550 hrs and 990 hrs of elapsed contact time. The data are reproduced from the recorder chart in Figure 6 (p 26). Fluorescence in the low-fired system was first observed at 333 hrs, sooner than the original, untreated Eu_2O_3, and approached the same equilibrium value as the suspected high-fired system.

Best fits for the standard and sample data were determined with a simple regression program available with the Tektronix 4051 programmable calculator in the ORNL Transuranium Research Laboratory (TRL). The 10^{-6} M, 10^{-7} M, and 10^{-8} M Eu_2O_3 standards gave a peak height at 612 nm of 4.5 cm, 1.5 cm, and 0.1 cm, respectively. The average value of the 990 hr and 1540 hr samples was 0.7 cm. When these data were processed, the following best-fit equation was generated:

$$\text{Peak Height (cm)} = 0.35573 + (4213581)\ [Eu_2O_3]\ , \qquad (3)$$

TABLE V

Eu FLUORESCENCE AS A FUNCTION OF TIME

Elapsed Hrs.	612 nm Fluorescence?	Comments
24	no	Cloudiness appeared in the solution, due apparently to fragmentation of Eu_2O_3.
125	no	Drop of solution examined under magnification with narrow light beam. No Tyndall effect observed; no colloid indicated.
550	no	Low-fired Eu_2O_3 started to stir along with this system.
990	yes	Peak less than 10^{-7} M standard seen.
1540	yes	Peak less than 10^{-7} M standard seen.
2200	yes	Larger-than-expected peak seen due to formation of an unfilterable suspension of Eu_2O_3 seen under magnification.
333[a]	yes	Small ($<<10^{-7}$ M standard) peak seen.
1650[a]	yes	Peak less than 10^{-7} M standard seen.
1970[a]	yes	Peak less than 10^{-7} M standard seen.

a. For the low-fired system.

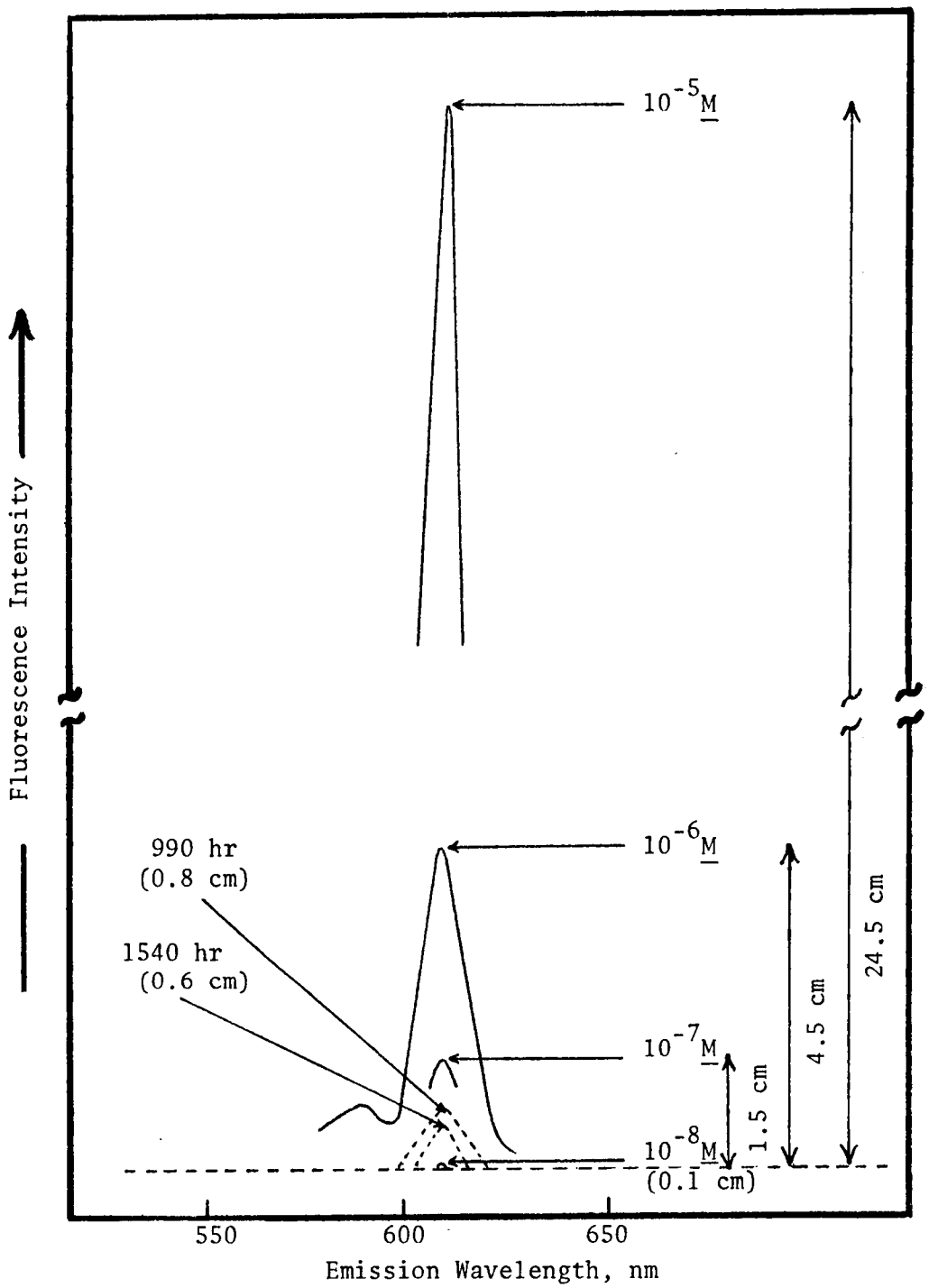


Figure 6. Fluorescence intensity of europium standards and samples.

where $[Eu_2O_3]$ is given in moles per liter. Substitution of the sample value of 0.7 cm gave a value of 8×10^{-8} M, which, when corrected for being a 25 ml dilution, gave a value of 2×10^{-6} M for the solubility of Eu_2O_3 in water. This corresponds to a solubility of 7×10^{-5} g Eu_2O_3/100 ml solution.

Rechecks of earlier Eu_2O_3 samples gave virtually the same peak heights as were initially found. This indicated that the system, once complexed by the TTA, was stable with time, with essentially no precipitation occurring.

B. Behavior of AmO_2 in Aqueous Solution

The $^{241}AmO_2$ and $^{243}AmO_2$ were verified by the results of X-ray powder diffraction analysis. The observed lines and calculated lattice parameters are shown in Appendix II, Tables II-B and II-C (pp 53-54). A summary of the calculations is shown in Table II-D (p 55).[33,34,35,36,37]

Soon after the systems were begun stirring, both exhibited a color change from the black of the dioxide form to a dark brown. The change was more noticeable in the $^{243}AmO_2$ system, due probably to the fact that a larger amount of $^{243}AmO_2$ was initially introduced into the vessel, and because of radiolysis effects that will be discussed later. The color of the $^{243}AmO_2$ system persisted slightly even through the filtration using the 0.2 μm pore diameter filter paper. The absence of a large particle size colloidal suspension and the presence of a solution was indicated by the fact that no particulate matter or Tyndall effect were observed under 40X magnification of one filtered sample of each of the two AmO_2-water systems.

Several quality control steps were carried out in the counting procedure to insure accuracy. The activity of a flamed versus an unflamed plate was investigated, the activities of washes of the mounting pipettes and filtering apparatus were determined, and the relative isotopic purity of the sample plates was measured. Flaming of the stainless steel plates resulted in counting rates that were ∿5% lower than the counting rates of the unflamed plates. Activity left in the pipettes and filtering apparatus amounted to about 0.5% and <5%, respectively, of the gross alpha counting rate.

Relative isotopic purities of the samples were determined by gamma pulse-height analysis as run by the Analytical Chemistry Division at ORNL. A summary of the results of these analyses is shown in Table VI (p 29). It can be seen that the samples were reasonably isotopically pure, with the major isotopic contamination coming from the short-lived daughter of ^{243}Am, neptunium-239, which, being a beta-gamma emitter, would not affect the alpha counting rates. Portions of the gamma spectra for typical ^{241}Am and ^{243}Am sample plates are shown in Figures 7 and 8 (pp 30-31), respectively.

The results of the study of the AmO_2 systems are shown in Table VII (p 32) and Figure 9 (p 33). The measurements were made at the ambient temperature of the gloved box, 17 ± 2 °C. From these data (excluding those noted) and the isotopic purity data, it can be seen that the average value for the apparent water solubility of the $^{241}AmO_2$ is 1.5×10^{-5} M, and, for $^{243}AmO_2$, 2.9×10^{-4} M. These figures represent 4.1×10^{-4} g/100 ml and 8.0×10^{-3} g/100 ml, respectively.

TABLE VI

Am SAMPLE PURITY AS DETERMINED BY GAMMA PULSE-HEIGHT ANALYSIS

Isotope/Sample	^{241}Am Counts[a,d]	^{243}Am Counts[b,d]	% ^{241}Am	% ^{243}Am	Other Isotopes[c]
241/1	94737	5964	94.1	5.9	^{239}Np[e]
241/2	51835	5006	91.2	8.8	^{239}Np[e]
243/1	3277	131436	2.4	97.6	^{239}Np
243/2	1034	82769	1.2	98.8	^{239}Np

a. Measured peak = 59.6 keV, from 85.5% α-transition.

b. Measured peak = 75.0 keV, from 87.9% α-transition.

c. ^{239}Np present as 2.3 d α-daughter of ^{243}Am. Not relevant to % calculations because not an α-emitter.

d. Peak counts determined by taking n channels as the peak, then subtracting the immediately preceeding and following n/2 channels as background.

e. Peaks due to ^{237}Np, the 2.2×10^6 yr α-daughter of ^{241}Am, were not observed.

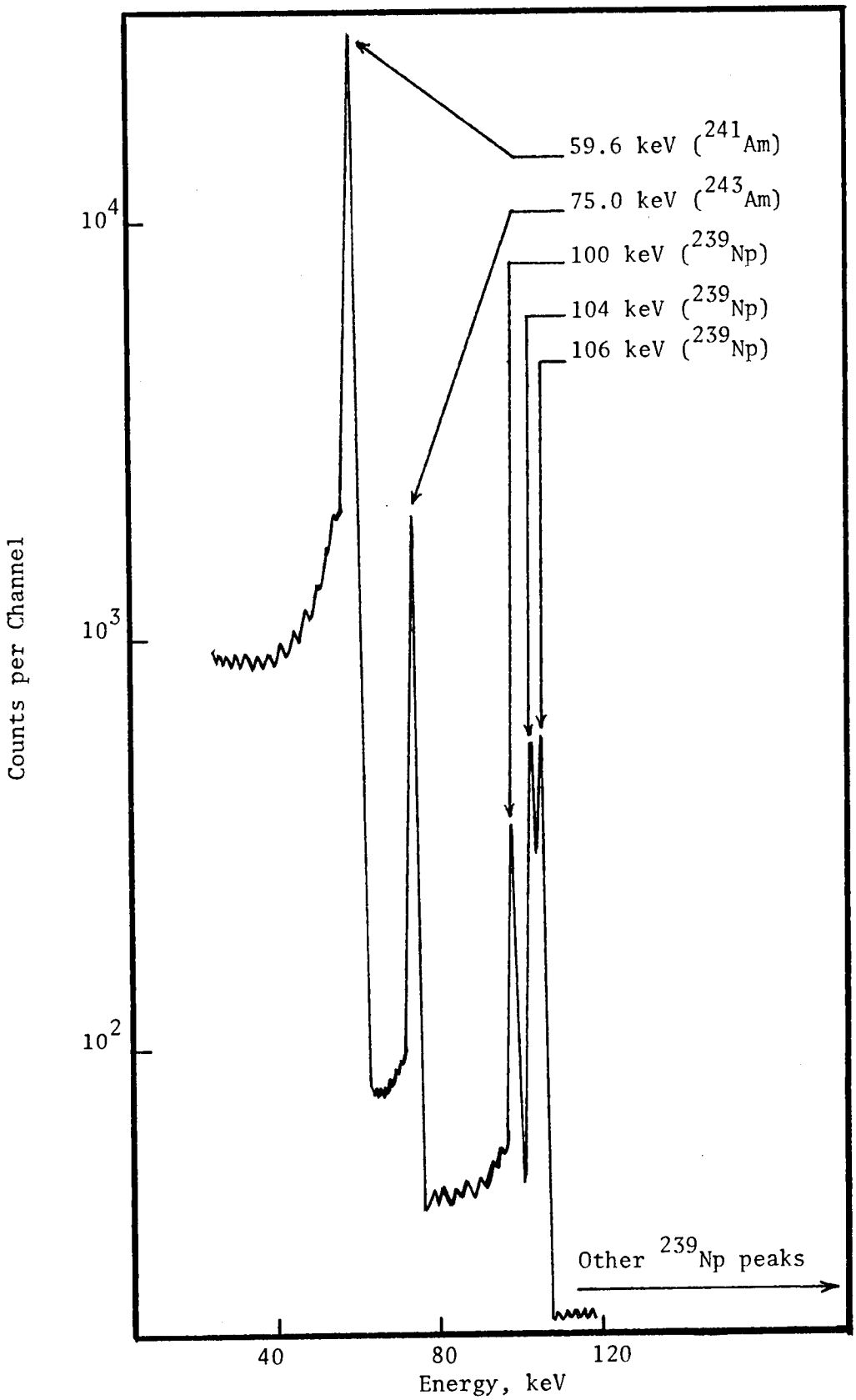


Figure 7. Partial gamma spectrum of a typical ^{241}Am sample.

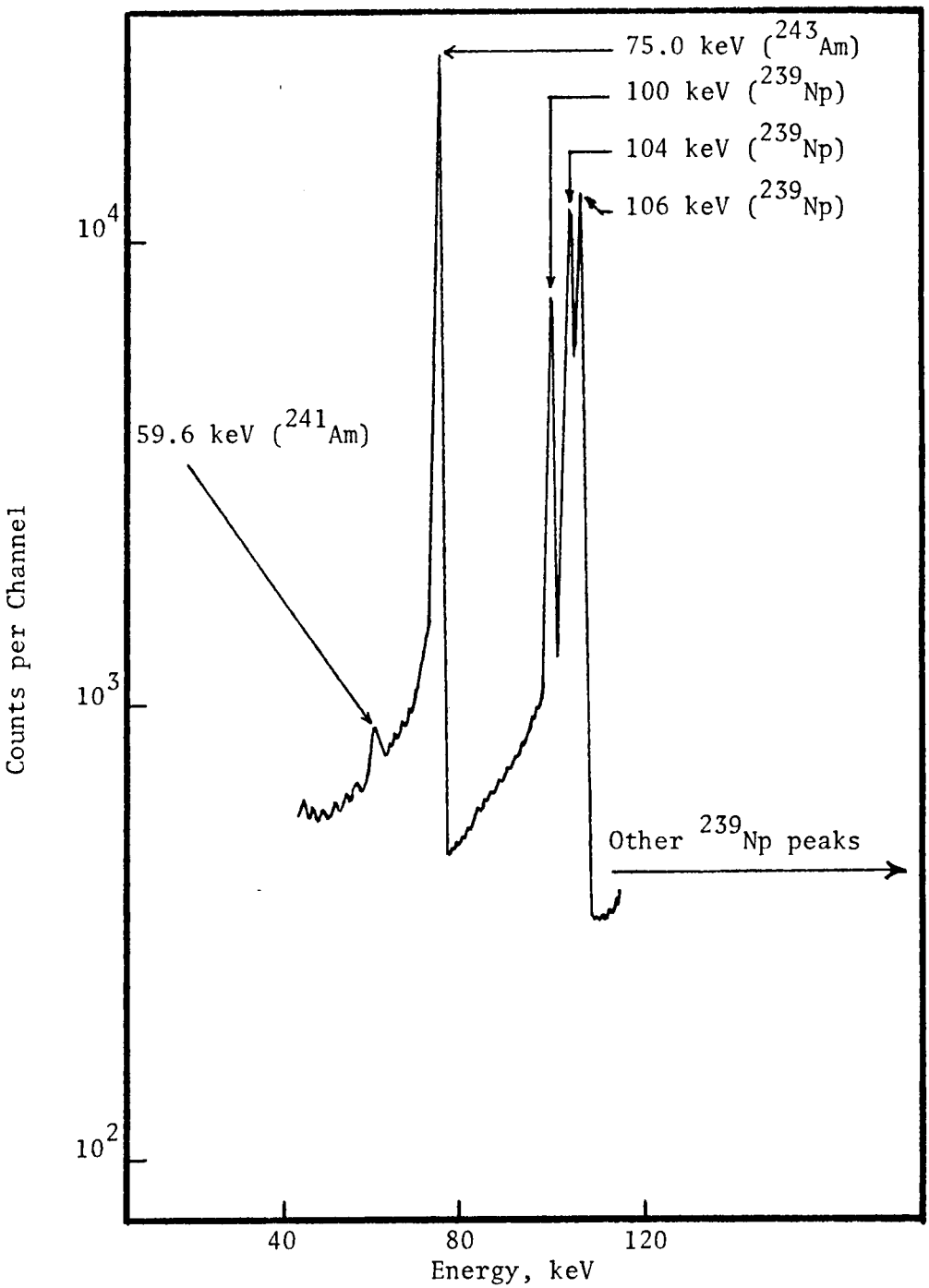


Figure 8. Partial gamma spectrum of a typical ^{243}Am sample.

TABLE VII

RESULTS OF AMERICIUM DIOXIDE SOLUBILITY STUDY

Sample	Elapsed Time, h	Total α, cpm[a]	Total Moles AmO_2[b]	Sample Volume, µl	Total Solubility, M
$^{241}AmO_2$	310	183429 ± 856[c]	1.9×10^{-10}	10	1.9×10^{-5}
	430[d]	298686 ± 1094	3.1×10^{-10}	10	3.1×10^{-5}
	478	160538 ± 802	1.6×10^{-10}	10	1.6×10^{-5}
	528	158422 ± 796	1.6×10^{-10}	15	1.1×10^{-5}
	622	169452 ± 824	1.7×10^{-10}	15	1.2×10^{-5}
$^{243}AmO_2$	475	254432 ± 1008	3.3×10^{-9}	10	3.3×10^{-4}
	595[d]	601914 ± 1552	7.8×10^{-9}	10	7.8×10^{-4}
	643	210688 ± 918	2.7×10^{-9}	10	2.7×10^{-4}
	693[d]	809444 ± 1800	1.1×10^{-8}	15	7.0×10^{-4}
	787	311906 ± 1116	4.1×10^{-9}	15	2.7×10^{-4}

a. cpm/0.505 = dpm.

b. Specific activity of ^{241}Am sample calculated to be 7.064×10^6 dpm/µg, based on sample analysis showing 92.7% ^{241}Am (7.587×10^6 dpm/µg) and 7.3% ^{243}Am (4.242×10^5 dpm/µg). Specific activity of ^{243}Am sample calculated to be 5.531×10^5 dpm/µg, based on sample analysis showing 98.2% ^{243}Am and 1.8% ^{241}Am.

c. Error limits are 2 standard deviations in triplicate determinations.

d. High values, not considered in averages, were due to the apparent failure of the filter and the resulting passage of particular matter into the solution.

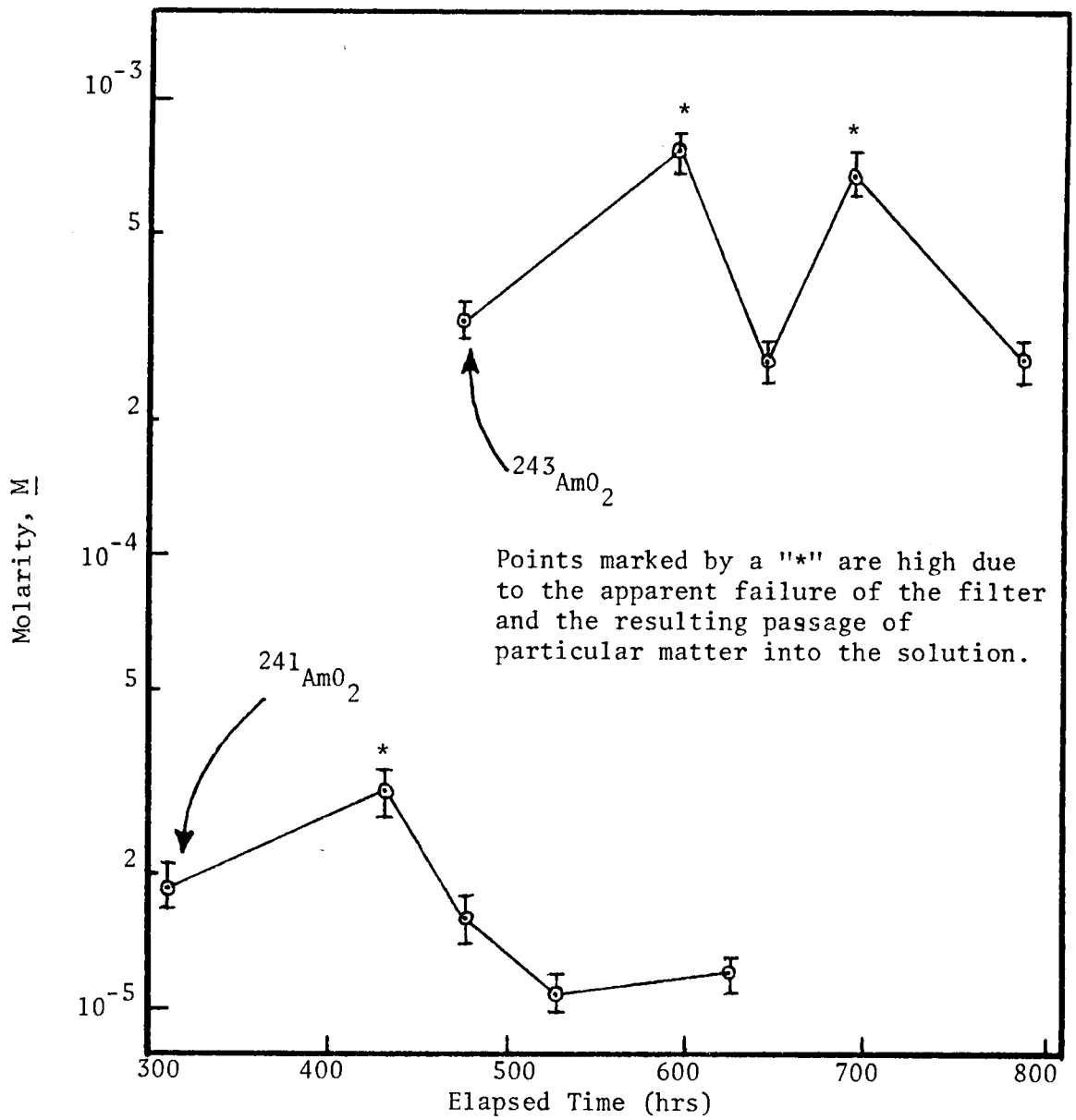


Figure 9. Apparent water solubility of $^{241}AmO_2$ and $^{243}AmO_2$ as a function of time.

CHAPTER IV

DISCUSSION OF RESULTS

A. Eu_2O_3 Water Solubility

The initial assumption that the Eu_2O_3 as obtained from the manufacturer was prepared at a temperature greater than 650 °C has been experimentally verified. As seen in the experimental results of the Eu fluorescence study, the fluorescence peak of the $Eu(TTA)_3$ complex was observed sooner in the treated (low-fired) system than in the untreated system. However, since both systems approached the same equilibrium value of 7×10^{-5} g/100 ml, it can be deduced that the temperature used in the initial preparation of Eu_2O_3 was not much greater than 650 °C. A much greater temperature would have pushed the first observable fluorescence of the system beyond the observed 990 hrs and would likely have resulted in equilibrium being reached at a much later time. Unfortunately, verification of the actual preparation conditions is not possible, since the manufacturer, American Potash and Chemical Corporation, is no longer in business.

The experimentally determined value of 2×10^{-6} M for the water solubility of Eu_2O_3 is in good agreement with an interpolated value of 1.5×10^{-6} M. Using the data of Fullam and Roberts[31] (as verified by Meloche[23] and Moeller[38]) and of Linke,[39] a plot of lanthanide sesquioxide solubility in water as a function of atomic number (see Moeller[40]) was prepared. This graph is shown as Figure 10 (p 35).

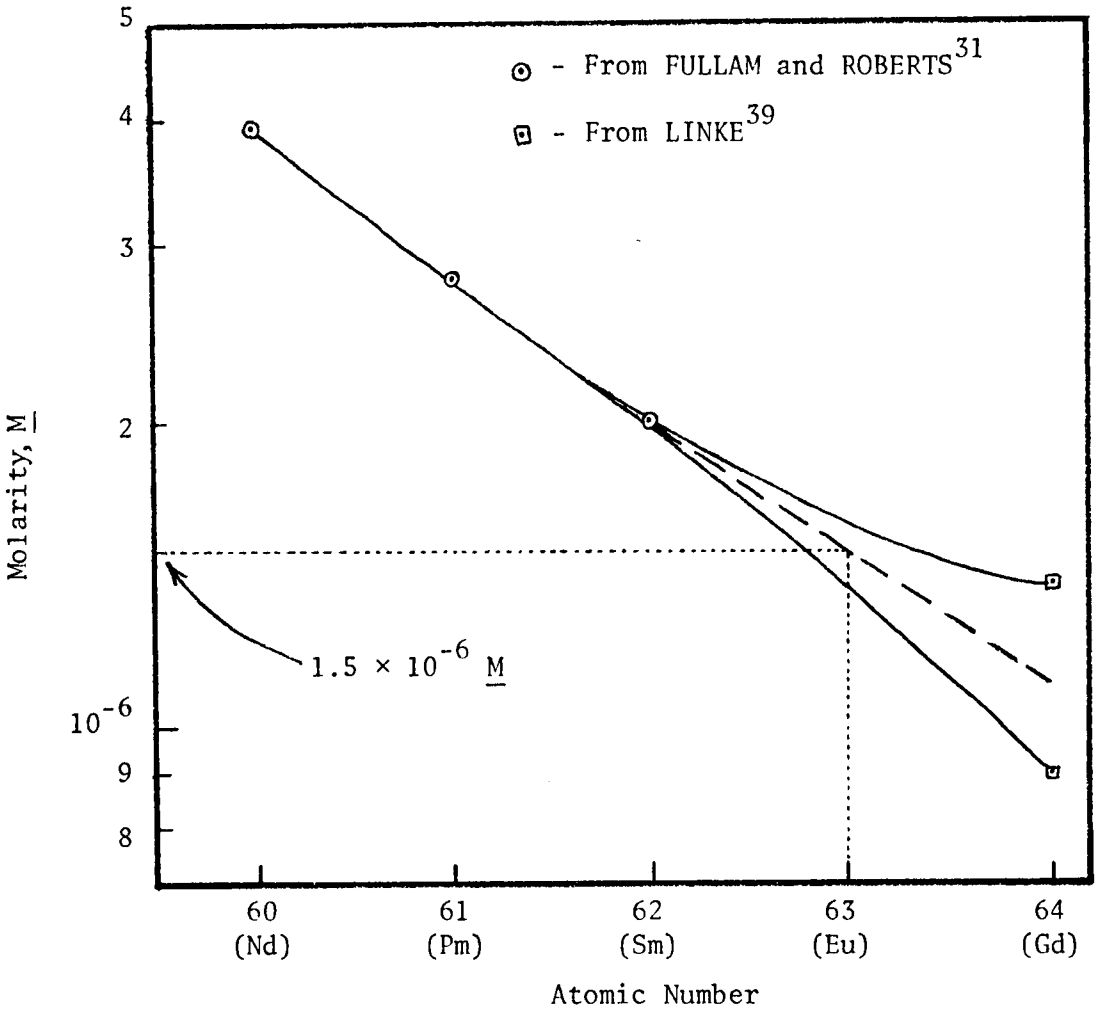


Figure 10. Water solubilities of some rare-earth sesquioxides.

In a manner similar to the present experimental procedure, Fullam and Roberts[31] found that the water solubilities of the sesquioxides of Nd, Pm, and Sm were 3.9×10^{-6} M, 2.8×10^{-6} M, and 2.0×10^{-6} M, respectively. Linke[39] reported two different experimental values of 1.4×10^{-6} M and 0.9×10^{-6} M for the water solubility of Gd_2O_3. Taking the average value for the Gd_2O_3 solubility, i.e., 1.15×10^{-6} M, a smooth curve resulted from which the solubility of Eu_2O_3 in water was estimated to be about 1.5×10^{-6} M, or 5×10^{-5} g/100 ml.

Because of the good agreement between this estimated value and the experimentally determined one, it is assumed by the author that the nature of the Eu_2O_3, once in solution, is similar to the experimentally determined composition of the Nd, Pm, and Sm sesquioxide solutions.[31] It was found by thermogravimetric and X-ray diffraction analyses that the composition of the equilibrium solutions was such that the principal component present was, generally, $Ln_2O_3 \cdot 3H_2O$, a hydrated lanthanide (Nd, Pm, or Sm) sesquioxide. This indicates that not much dissociation of the Eu_2O_3 occurred in the water medium. Since essentially no ionic species were formed (indicated by the lack of $Ln(OH)_3$) the solubility product expression, $K_{sp} = [Eu^{3+}]^2 [O^{2-}]^3$, would probably not be valid. It can therefore be stated that Eu_2O_3 is present in water solution as $Eu_2O_3 \cdot 3H_2O$ and is soluble to the extent of 7×10^{-5} g/100 ml of solution.

The major sources of error associated with the Eu_2O_3 study were in the volumetric glassware used and the accuracy to which the charts could be measured. The error in the 1000 µl pipettes used in the

preparation of the Eu_2O_3 standards and samples was estimated to be ∿1%. The error in the 25 ml volumetric flask used was ∿2%. Another source of error was in determining the peak height of the fluorescence peak, since the peaks were smoothed to get a reproducible peak point. The baseline was found by connecting the straight portions of the recorded spectrum immediately before and after the peak. The peak-to-baseline height, which was proportional to the europium concentration, was measured to ± 0.1 cm. This results in a possible error of ∿15% when the sample data values are considered, making the probable Eu_2O_3 value $2 \pm 0.3 \times 10^{-6}$ M.

B. AmO_2 Water Solubility

The color change observed in the two systems was probably caused to a large extent by the radiolysis of the water medium by the ionizing radiation of the samples. When the radiation, either α, β, or γ, encounters an electron in one of the water molecules, energy is transferred to the electron.[41,42] If enough energy is transferred, the bonds of the molecule may be broken,[42,43] and free radicals may be formed. In this case, water molecules are disrupted into H· and ·OH radicals, which can lead to the formation of hydrogen peroxide, H_2O_2. This strong oxidizing agent can affect the system, altering the solubility observed. This is especially true if any foreign matter is present in the system. Although a detailed elemental analysis of the compounds is not available, it is known that the $^{243}AmO_2$ contained traces of iron in it. This suggests that an oxide, or other compound or complex, of iron may have been formed in the $^{243}AmO_2$ reaction vessel and consequently caused the formation of the brown color.

The experimental results obtained here do not agree with the assumption that the compound containing the more radioactive species, in this case ^{241}Am, would be the more soluble.[44] However, there are factors, such as power density and, to a lesser extent, chemical history,[45] that might explain the discrepancy. With regard to sample history, it is not known exactly how the $^{243}AmO_2$ was prepared. Due to time limitations, it was only structurally verified before introduction into the water medium. The possible differences in preparation between the $^{243}AmO_2$ and the $^{241}AmO_2$ may account, to a small degree, for the observed differences in the water solubility of the two compounds.

The biggest difference between the two samples, however, is their different power densities, the amount of power generated per unit mass of nuclide. The difference is due to the presence of more ^{239}Np, the 2.3 day half-life α-daughter of ^{243}Am, in the ^{243}Am system than in the ^{241}Am system. When it is considered that the power densities of ^{241}Am, ^{243}Am, and ^{239}Np are 0.1115, 0.00642, and 586 watts/g, respectively,[46,47] the difference in solubility observed here becomes more understandable. The larger amounts of ^{239}Np present in the $^{243}AmO_2$ solution may be sufficient to heat the solution enough to increase the solubility of the dioxide.

The uncertainty of the exact nature of the americium in solution must be recalled here. The americium species actually present in the solution systems may be different, or the same but in dissimilar proportions, as a result of the disparity in power densities. Due to the complexity of these systems, there may be other, currently unknown

factors responsible for the difference in behavior observed here. This reemphasizes that the present AmO_2 solubilities are, at best, apparent solubilities.

Different sources of error are present in this determination. Pipetting technique caused a difference in the counting rates of ∿5% to be observed between different plates of the same sample. In the calculations, errors were due to the statistical fluctuations in the counting rates of the samples. Also, since the values used for the specific activities of the samples were based on experimentally determined half-lives, the errors in these determinations (∿4% for ^{241}Am and ∿0.5% for ^{243}Am) were present in the final values. Considering these experimental errors and those already mentioned regarding sample quality control in Chapter III, Part B, a reasonable estimate of the total error in the solubility values would be ± 10%.

No values for water solubilities of americium or other actinide compounds were found in the literature. As such, a comparison like the one made in the Eu_2O_3 study is not possible. A comparison with the Eu_2O_3 value could be made, but due to the great differences in the systems (different oxide form, radioactive versus nonradioactive species), such a comparison would not be very useful.

When considering the experimentally found solubilities of the americium dioxides, it would be interesting to consider how much americium one is actually referring to in regard to current safety guidelines (see Table I, p 4). When compared to these standards, it is found that americium dioxide is much more soluble in water than the

current allowable amounts. For example, $^{241}AmO_2$ is >3 x 10^5 times and >7 x 10^6 times more soluble in water than is currently allowed for soluble ^{241}Am in a controlled and uncontrolled area, respectively. The experimental $^{243}AmO_2$ water solubility also exceeds the ^{243}Am guidelines by similar amounts. It is evident from these figures that extreme care must be exercised whenever any americium waste is disposed of. The need for proper and complete segregation of all americium wastes from sources of water, be it groundwater or rainwater, is absolutely critical for achieving success in any organization's nuclear waste disposal program.

C. Proposed Studies

Finally, there are several observations that should be considered for further study. In the Eu_2O_3 work, since the temperature of preparation apparently affected the time required for fluorescence to be observed, a study of Eu_2O_3 samples prepared at different calcination temperatures of the oxalate would be useful. Also, as a verification that the difference in the 990 hr and 1540 hr peak heights is due to experimental error, the time of the experiment could be extended to see if the final observed values for the solubilities were indeed the true equilibrium values.

The main aspect needing further investigation in the americium systems is to determine the solubility of $^{243}AmO_2$ that has been prepared identically to the $^{241}AmO_2$. This study should also include in it a procedure for purifying the compounds used, thereby eliminating, or minimizing, the extra heating effect produced by the daughter

radioactivities. Special attention should be paid to the apparent high values of solubility that periodically occurred in this work, with consideration being given to the possibility that factors other than particulate matter or accumulated errors, such as small temperature changes, might cause the fluctuations. The length of the study should also be extended to check on the stability of the system, i.e., to see if true equilibrium is ever reached.

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APPENDIXES

APPENDIX I

AMERICIUM INVENTORY PREDICTIONS

The predicted amounts of americium that will be produced during the period 1975-2000 are shown, with values of total metric tons (MT) of waste produced and total curies (Ci) of Am produced being employed. The cases of light water reactors (LWR), high-temperature gas reactors (HTGR), and liquid-metal fast breeder reactors (LMFBR) are considered. Table I-A (p 48) is based on the data of Blomeke,[13] and Table I-B (p 49) comes from WASH-1139.[14]

TABLE I-A

PROJECTED Am INVENTORY FOR 1975-2000 (FROM BLOMEKE[13])

Yr	LWR		HTGR		LMFBR		TOTAL	
	Total MT	Am,Ci	Total MT	Am,Ci	Total MT	Am,Ci	MT	Am,Ci
75	400	9.5E 05	0	0	0	0	400	9.5E 05
76	1100	2.6E 06	0	0	0	0	1100	2.6E 06
77	1700	4.1	0	0	0	0	1700	4.1
78	2032	4.8	0	0	0	0	2032	4.8
79	1955	4.7	4	1.4E 02	0	0	1959	4.7
80	2395	5.7	7	2.4	0	0	2402	5.7
81	3039	7.2	8	2.8	0	0	3047	7.2
82	3509	8.4	37	1.3E 03	0	0	3546	8.4
83	4052	9.7	66	2.4	0	0	4118	9.7
84	4195	9.8	98	3.5	0	0	4293	9.8
85	4752	1.1E 07	169	6.1	0	0	4921	1.1E 07
86	5229	1.3	239	8.6	0	0	5468	1.3
87	5689	1.7	321	1.2E 04	5	1.1E 04	6015	1.4
88	6355	1.5	406	1.5	7	1.6	6768	1.5
89	6999	1.7	492	1.8	77	1.7E 05	7568	1.7
90	7650	1.8	590	2.1	175	3.9	8415	1.9
91	8158	1.9	683	2.5	306	6.8	9147	2.0
92	9000	2.1	764	2.8	492	1.1E 06	10256	2.3
93	9536	2.3	858	3.1	710	1.6	11104	2.4
94	10092	2.4	955	3.4	1038	2.3	12085	2.6
95	10478	2.5	1040	3.7	1470	3.3	12988	2.8
96	10736	2.6	1116	4.0	2073	4.6	13925	3.0
97	11194	2.7	1193	4.3	2689	6.0	15076	3.3
98	10837	2.6	1261	4.5	3450	7.6	15548	3.4
99	11180	2.7	1333	4.8	4270	9.5	16783	3.6
00	11042	2.6	1415	5.1	5123	1.1E 07	17580	3.8
					--- Total ---		198244	4.4E 08[a]

a. Radioactive decay is not considered in this total.

TABLE I-B

PROJECTED Am INVENTORY FOR 1975-2000 (FROM WASH-1139[14])

Yr	LWR		HTGR		LMFBR		TOTAL	
	Total MT	Am,Ci	Total MT	Am,Ci	Total MT	Am,Ci	MT	Am,Ci
75	250	6.9E 05	3	1.1E 02	0	0	253	6.9E 05
76	930	2.6E 06	2	7.2E 01	0	0	932	2.6E 06
77	1310	3.6	2	7.2	0	0	1312	3.6
78	1710	4.7	2	7.2	0	0	1712	4.7
79	1660	4.6	2	7.2	0	0	1662	4.6
80	1740	4.8	2	7.2	0	0	1742	4.8
81	2300	6.3	2	7.2	0	0	2302	6.3
82	3000	8.2	7	2.5E 02	0	0	3007	8.2
83	3700	1.0E 07	12	4.3	4	1.7E 04	3716	1.0E 07
84	4300	1.2	21	7.6	6	2.6	4327	1.2
85	4800	1.3	34	1.2E 03	6	2.6	4840	1.3
86	5600	1.5	44	1.6	7	3.0	5651	1.5
87	6200	1.7	65	2.3	7	3.0	6272	1.7
88	7000	1.9	100	3.6	7	3.0	7107	1.9
89	8100	2.2	136	4.9	7	3.0	8243	2.2
90	8900	2.4	177	6.4	25	1.1E 05	9102	2.5
91	9900	2.7	219	7.9	32	1.4	10151	2.7
92	11000	3.0	271	9.8	64	2.7	11335	3.0
93	11900	3.3	323	1.2E 04	130	5.6	12353	3.3
94	13000	3.6	365	1.3	230	9.8	13595	3.7
95	14000	3.8	417	1.5	360	1.5E 06	14777	4.0
96	14900	4.1	468	1.7	540	2.3	15908	4.3
97	15800	4.3	510	1.8	770	3.3	17080	4.7
98	16800	4.6	562	2.0	1050	4.5	18412	5.1
99	17500	4.8	604	2.2	1370	5.9	19474	5.4
00	18300	5.0	646	2.3	1750	7.5	20696	5.8
					--- Total ---		215961	5.9E 08[a]

a. Radioactive decay is not considered in this total.

APPENDIX II

X-RAY DIFFRACTION DATA

X-ray diffraction data for compounds studied in this work are given as follows: Eu_2O_3 in Table II-A (pp 51-52), $^{241}AmO_2$ in Table II-B (p 53), $^{243}AmO_2$ in Table II-C (p 54), and a summary of experimental lattice parameters in Table II-D (p 55).

TABLE II-A

Eu_2O_3 X-RAY DIFFRACTION DATA[a]

h k l	Observed 2θ	Calculated 2θ[b]	Calculated 2θ[c]
2 1 1	19.84	20.00	19.89
3 1 0	25.47	25.91	25.80
2 2 2	28.19	28.43	28.33
4 0 0	32.82	32.95	32.84
4 1 1	34.83	35.01	34.91
4 2 0	36.64	36.97	36.87
3 3 2	38.65	38.84	38.75
4 2 2	40.46	40.64	40.55
1 3 4	42.27	42.38	42.29
5 2 1	45.59	45.70	45.60
4 4 0	47.10	47.28	47.19
4 3 3	48.71	48.83	48.74
6 0 0	50.22	50.35	50.26
6 1 1	51.83	51.83	51.74
1 4 5	54.55	54.70	54.62
6 2 2	55.95	56.10	56.02
1 3 6	57.46	57.48	57.40
4 4 4	58.67	58.83	58.75
5 4 3	60.18	60.17	60.09
0 4 6	61.39	61.49	61.41
6 3 3	62.79	62.79	62.72
6 4 2	64.00	64.08	64.00
7 3 0	65.71	65.35	65.28
6 5 1	67.82	67.86	67.79
8 0 0	69.13	69.10	69.03
8 1 1	70.34	70.33	70.26
8 2 0	71.45	71.55	71.48
6 5 3	72.75	72.76	72.69
8 3 1	75.17	75.16	75.09
6 6 2	76.38	76.34	76.28
8 4 0	78.69	78.70	78.65
8 3 3	79.70	79.88	79.82
2 4 8	81.00	81.04	80.99
6 5 5	82.21	82.21	82.15
1 5 8	84.42	84.53	84.48
7 6 3	86.74	86.84	86.79
8 4 4	88.05	87.99	87.94
8 5 3	89.15	89.14	89.10
8 6 0	90.36	90.29	90.25
10 1 1	91.67	91.45	91.41

TABLE II-A (Continued)

h	k	l	Observed 2θ	Calculated 2θ[b]	Calculated 2θ[c]
2	6	8	92.57	92.60	92.56
3	4	9	93.68	93.75	93.72
10	2	2	94.89	94.91	94.87
7	6	5	96.19	96.07	96.03
8	5	5	98.51	98.39	98.36
8	6	4	99.61	99.55	99.53
10	3	3	100.92	100.72	100.70
10	4	2	101.93	101.90	101.87
8	7	3	103.24	103.08	103.06
10	5	1	105.35	105.46	105.44
8	8	0	106.45	106.65	106.64
10	4	4	108.77	109.07	109.06
10	5	3	110.28	110.30	110.29
8	7	5	112.79	112.77	112.77
10	6	2	114.00	114.03	114.03
8	8	4	116.62	116.58	116.58
1	8	9	117.92	117.87	117.88
12	2	0	119.23	119.18	119.19
10	7	1	120.34	120.51	120.52
12	2	2	121.95	121.86	121.87
9	8	3	123.46	123.22	123.24
11	6	1	125.87	126.02	126.05
12	4	0	127.48	127.46	127.49
0	8	10	130.40	130.42	130.46
6	7	9	132.01	131.95	131.99
10	8	2	133.52	133.52	133.57
9	8	5	135.13	135.13	135.18
12	4	4	140.86	140.27	140.34
4	8	10	143.88	144.02	144.10
1	9	10	145.99	146.03	146.12
2	6	12	148.20	148.15	148.25
1	8	11	150.32	150.41	150.52

a. $\lambda = CuK\bar{\alpha} = 1.54178$ Å.

b. Without Nelson-Riley extrapolation.

c. With Nelson-Riley extrapolation.

TABLE II-B

$^{241}AmO_2$ X-RAY DIFFRACTION DATA[a]

h	k	l	Observed 2θ	Calculated 2θ[b]	Calculated 2θ[c]
1	1	1	28.81	28.77	28.73
2	0	0	33.42	33.35	33.30
2	2	0	47.76	47.78	47.84
3	1	1	56.89	56.82	56.78
2	2	2	59.40	59.60	59.56
4	0	0	70.03	70.03	70.00
3	3	1	77.35	77.41	77.38
4	2	0	79.66	79.81	79.79
4	2	2	89.19	89.30	89.28
5	1	1	96.41	96.39	96.37
4	4	0	108.64	108.49	108.48
5	3	1	116.07	116.14	116.14
6	0	0	118.78	118.80	118.80
6	2	0	130.31	130.27	130.28
5	3	3	140.34	140.34	140.36
6	2	2	144.25	144.19	144.22

a. $\lambda = CuK\bar{\alpha} = 1.54178$ Å.

b. Without Nelson-Riley extrapolation.

c. With Nelson-Riley extrapolation.

TABLE II-C

$^{243}AmO_2$ X-RAY DIFFRACTION DATA[a]

h	k	l	Observed 2θ	Calculated 2θ[b]	Calculated 2θ[c]
1	1	1	28.80	28.71	28.88
2	0	0	33.41	33.28	33.44
2	2	0	47.84	47.77	47.92
3	1	1	56.75	56.69	56.82
2	2	2	59.76	59.46	59.59
4	0	0	69.98	69.87	69.98
3	3	1	77.39	77.22	77.32
4	2	0	79.60	79.62	79.71
4	2	2	89.12	89.07	89.14
5	1	1	96.23	96.13	96.18
4	4	0	108.46	108.16	108.19
5	3	1	115.77	115.76	115.77
6	0	0	118.38	118.40	118.40
6	2	0	129.70	129.76	129.72
5	3	3	139.52	139.69	139.60
6	2	2	143.33	143.47	143.36

a. $\lambda = CuK\bar{\alpha} = 1.54178$ Å.

b. Without Nelson-Riley extrapolation.

c. With Nelson-Riley extrapolation.

TABLE II-D

EXPERIMENTAL LATTICE PARAMETERS FOR Eu_2O_3, $^{241}AmO_2$, AND $^{243}AmO_2$

Compound	Calculated a_o, Å[a]	Calculated a_o, Å[b]
Eu_2O_3[c]	10.869 ± .005[d]	10.874 ± .006[d]
$^{241}AmO_2$[e]	5.373 ± .002	5.374 ± .002
$^{243}AmO_2$[e]	5.385 ± .003	5.387 ± .002

a. Without Nelson-Riley extrapolation.

b. With Nelson-Riley extrapolation.

c. Literature values for Eu_2O_3 = 10.866 ± .005 Å[33] (unidentified error limit) and 10.869 Å[34,35] (no error limits reported).

d. Error limits are 2 standard deviations.

e. Literature value for $^{241,243}AmO_2$ = 5.377 ± .004 Å[36,37] (unidentified error limit).

VITA

Robert Len Shankle was born in Humboldt, Tennessee on May 8, 1951. He graduated from Humboldt High School in May 1969 and enrolled at the University of Tennessee at Martin in September 1969. During his undergraduate studies, he participated in the Cooperative Education Program in Chemistry, being employed by E. I. duPont de Nemours and Co., Inc. at the Savannah River Plant in Aiken, South Carolina for seven work quarters. During this time, he co-authored two papers on nuclear fuel solvent extraction. He returned to school and was president of the local chapter of the Student Affiliates of the American Chemical Society during his senior year. After graduating in June 1974 with a B.S. in Liberal Arts, he returned to the Savannah River Plant as a Graduate Summer Technical Student, the first of two such summer appointments.

In September 1974, he entered graduate school at the University of Tennessee at Knoxville. He held the position of Graduate Teaching Assistant in the Department of Chemistry until June 1976, when he became a Graduate Research Assistant, supported by the U. S. Energy Research and Development Administration. The Master of Science in Chemistry degree was awarded in December 1976.

He is the son of C. B. and Mary Frances Shankle of Humboldt, Tennessee. In June 1974, he married Terre Anne Strube of Dyersburg, Tennessee.