Ken Thomas

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THE RADIOCHEMISTRY OF AMERICIUM AND CURIUM

University of California
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The Radiochemistry of Americium and Curium

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The Radiochemistry of Americium and Curium

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January 1960

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Foreword

The Subcommittee on Radiochemistry is one of a number of subcommittees working under the Committee on Nuclear Science of the National Research Council. Its members represent government, industrial, and university laboratories in the areas of nuclear chemistry and analytical chemistry.

The Subcommittee has concerned itself with those areas of nuclear science which involve the chemist, such as the collection and distribution of radiochemical procedures, the radiochemical purity of reagents, radiochemistry in environmental science and in nuclear medicine, and the role of radiochemistry in college and university programs.

This series of monographs has grown out of the need for compilations of radiochemical information, procedures, and techniques. The Subcommittee has endeavored to present a series that will be of maximum use to the working scientist. Each monograph presents pertinent information required for radiochemical work with an individual element or with a specialized technique.

Experts in the particular radiochemical technique have written the monographs. The U. S. Department of Energy has sponsored the printing of the series.

The Subcommittee is confident these publications will be useful not only to radiochemists but also to research workers in other fields such as physics, biochemistry, or medicine who wish to use radiochemical techniques to solve specific problems.

G. Davis O'Kelley, *Chairman*
Subcommittee on Radiochemistry

CONTENTS

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INTRODUCTION

This volume which deals with the radiochemistry of americium and curium is one of a series of monographs on radiochemistry of the elements. There is included a review of the nuclear and chemical features of particular interest to the radiochemist, a discussion of problems of dissolution of a sample and counting techniques, and finally, a collection of radiochemical procedures for the elements as found in the literature.

The series of monographs will cover all elements for which radiochemical procedures are pertinent. Plans include revision of the monograph periodically as new techniques and procedures warrant. The reader is therefore encouraged to call to the attention of the author any published or unpublished material on the radiochemistry of americium and curium which might be included in a revised version of the monograph.

The authors have reviewed briefly the chemistry of americium and curium, attempting to keep the emphasis on separations of these elements while including enough background information to give the reader some familiarity with the topic. Much thermodynamic and electrochemical data have been omitted; however, most of the original references have been given and may be consulted to obtain further information. Complete nuclear data such as cross sections, decay schemes, etc. are not included as this information is readily available in standard sources.

Referenced reports which are followed by (OTS) and their price may be obtained from the Office of Technical Services, Department of Commerce, Washington 25, D. C. The symbols "mf" and "ph" refer to microfilm and photostat. If no such symbol follows the listing of a report, the authors were unable to determine its present availability. The U.S. Atomic Energy Commission has made some arrangements for the sale of microcopies with the Microcard Foundation, P.O. Box 2145, Madison 5, Wisconsin and with Readex Microprint Corporation, 115 University Place, New York 3, N.Y. It is possible that these organizations may be able to supply microcopies of reports. The flyleaf of each volume of Nuclear Science Abstracts may be consulted for further information. Single copies of the 1958 Geneva Conference papers may be available for 25 cents from United Nations Bookstore, United Nations Headquarters, East 42nd Street and 1st Avenue, New York, N.Y. We are informed that single copies of the 1955 Geneva Conference papers are no longer available.

I. GENERAL REVIEWS (See Refs. 1 to 12)

II. ISOTOPES OF AMERICIUM AND CURIUM(13)

Isotope	Half-life	Type of Decay	Isotope	Half-life	Type of Decay
Am^{237}	~ 1.3 h	EC 99+%	Cm^{238}	2.5 h	EC < 90%, α > 10%
Am^{238}	1.9 h	EC	Cm^{239}	2.9 h	EC
Am^{239}	12 h	EC 99+%	Cm^{240}	26.8 d	α
Am^{240}	51 h	EC	Cm^{241}	35 d	EC 99+%, α 0.96%
Am^{241}	458 y	α	Cm^{242}	162.5 d	α
Am^{242m}	16.01 h	β^- 81%, EC 19%, no IT lim. 6%	Cm^{243}	35 y	α
Am^{242}	152 y(14)	β^- 90%, EC 10%	Cm^{244}	17.9 y	α
Am^{243}	7.95 x 10^3 y	α	Cm^{245}	8 x 10^3 y	α
Am^{244}	26 m	β^- 99+%	Cm^{246}	6.5 x 10^3 y	α
Am^{245}	1.98 h	β^-	Cm^{247}	> 4 x 10^7 y	α
Am^{246}	25.0 m	β^-	Cm^{248}	4.7 x 10^5 y	α 89%, spont. fission 11%
			Cm^{249}	64 m	β^-
			Cm^{250}	2 x 10^4 y	spont. fission

III. REVIEW OF AMERICIUM AND CURIUM CHEMISTRY

Introduction

The two elements, americium (Z = 95) and curium (Z = 96), which are the subjects of this review, probably represent the last of the heavy elements on which extensive macrochemistry in the usual sense (involving several milligram to gram quantities) is ever likely to be done.* The availability of americium and curium in the laboratories of the United States, United Kingdom, and the USSR has resulted in international contributions to the elucidation of their chemistry.

While much of the information on these elements was obtained with relatively short lived isotopes Am^{241} (α, $t_{1/2}$ = 458 years) and Cm^{242} (α, $t_{1/2}$ = 162.5 days) with the attendant radiation difficulties, the availability of longer lived isotopes in large quantities is approaching. In particular, approximately a gram of Am^{243} (α, $t_{1/2}$ = 7951 years) and Cm^{244} (α, $t_{1/2}$ = 17.9 years) will be separated in 1959-1960 in the United States. One can anticipate the formation of longer lived isotopes of curium by re-irradiation of Cm^{244} (see Table of Isotopes).

All of the chemical manipulations with even the longest lived isotopes of americium or curium require extreme caution and care. Only tracer scale experiments, i.e., $\leq 10^5$ counts/min, should be performed on the bench top since the total body burden (bone) is only 0.057 micro curies. Any macro-scale investigations must be carried out in enclosures such as glove boxes to prevent any physical dispersal of contamination. It is a tribute to the many workers in this field that relatively few accidents have ever occurred. There are no known cases of serious illness or death from americium or curium poisoning; however, prompt medical treatment is mandatory in the case of an accident, e.g. surgical excision and intravenous treatment with calcium EDTA are usually used following skin punctures which deposit the radioactive element. A report of a medical conference at the Argonne National Laboratory(17) summarizes medical experience in this field.

In the case of the common isotope of americium, Am^{241}, care is also required to avoid excessive hand exposure to the prominent ~ 60 kev gamma radiation. (Lead foil or x-ray glass is a useful absorber.) With large quantities of americium or curium, neutron exposure from (α, n) reactions becomes a problem.

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* The next higher element, berkelium (Z = 97), is in a particularly unfortunate situation. Isotopes capable of being formed by neutron irradiation of plutonium, e.g. Bk^{249} and Bk^{250},(15) are both short lived and have large destruction cross sections. To be sure, excellent but demanding work can and will be done on small quantities,(16) e.g. the absorption spectrum of Bk was examined on a submicrogram amount.

A. Americium

Americium, element 95, is the actinide homolog of europium. As a hydrated trivalent ion, americium has properties typical of a trivalent actinide or lanthanide. However, americium exhibits other valence states which may sometimes be used to effect separations. Americium has the valence states of (0), (III), (IV), (V), and (VI) and of these, only Am(III), (V), and (VI) are found in aqueous solution. (The rather complicated situation with respect to Am(IV) will be discussed later.) The ionic species for these valence states in aqueous acid media may be represented as Am^{+++}, AmO_2^{+} and AmO_2^{++}. Such a representation does not include waters of hydration or possible complexed forms. A more detailed discussion of the characteristics of the individual valence states is given below.

1. The Metallic State - Am(0)

Americium metal is more highly electropositive than uranium, neptunium, or plutonium and has been prepared only by the action of powerful reductants on anhydrous americium salts at high temperatures.(18) Two reactions which have been used successfully are: (1) Ba + AmF_3(18) and (2) La + AmO_2.(2) A double hexagonal close packed structure has been reported with a = 3.642 ± 0.005 Å and c = 11.76 ± 0.01 Å.(19) A face-centered cubic phase also exists.(2) Both the measured and calculated densities are in agreement: calc. = 11.87 ± 0.05;(19) exp. = 11.7 ± 0.3.(18) The atomic radius is 1.82 Å.(19) The vapor pressure of the metal over the temperature range 1103° - 1453° K may be represented by: $\log p_{mm} = 7.563 - 13{,}162/T$.(20) Thus, the vapor pressure of americium is considerably higher than that of plutonium.(21) This may have significance as a separation procedure.

Differing from some other actinide metals,(22) no sludge or "hydroxide" formation occurs as americium metal is allowed to dissolve in hydrochloric acid, that is, dissolution takes place completely according to the reaction $Am + 3\,H^{+} \rightarrow Am^{+++} + 1.5\,H_2$.(18,23) The heat of solution at infinite dilution of americium metal in hydrochloric acid is - 163.2 kcal/mole(24) and with some estimates for the entropy changes for such a reaction, the formal potential for the metal vs. the hydrated trivalent ion is + 2.32 volt.(7,24) Americium metal is therefore quite similar to a typical lanthanide metal and is the first actinide metal which shows such correspondence. Most of the studies on americium metal (on milligram scale) have been carried out at the University of California Radiation Laboratory at Berkeley by B. B. Cunningham and co-workers and the original literature should be consulted for specific information.(18,19,20,2

2. Non-Existence of Divalent Americium

Since americium is the homolog of europium and presumably has the $7s^2 5f^7 6d^0$ ($^8S_{7/2}$) structure, it had been assumed that americium should form a divalent state. However, work with the gaseous ions shows, in the case of Am and Am^+, that the energy difference between f^7 and f^6d is less than that for the analogous europium species.(25) Some early work(6) (tracer scale) did give certain indications of divalency but later experiments with macro quantities of americium produced no reduction product intermediate between Am(III) and Am(O).(5) Under conditions (either in solution or anhydrous) where one may quantitatively prepare Eu(II), Sm(II) or Yb(II), no corresponding reaction took place using americium. If one allows americium metal to react with a minimum of O_2 or H_2, one can obtain substances corresponding to the stoichiometry AmO and AmH_2. It has been shown, however, that the americium radius in such "compounds" is more metallic than ionic(5) and therefore should not be construed as evidence for divalent americium.

3. The Trivalent State - Am(III)

The trivalent state of americium is the one most often encountered in aqueous solution. As a simple hydrated ion, trivalent americium is very similar to a typical trivalent lanthanide ion. Those reagents which show specific behavior toward the lanthanide group will also undergo their characteristic reaction with trivalent americium. Like the lanthanides, trivalent americium has an insoluble fluoride, hydroxide, phosphate, oxalate, iodate, etc. While small differences in solubility probably exist between such insoluble lanthanide compounds and those of americium, only in two instances have these differences been examined in detail so as to achieve separation of americium from a lanthanide element.

By slow hydrolysis of dimethyl oxalate(26) in a solution containing both americium and lanthanum, americium oxalate is enriched in the precipitate relative to lanthanum. A typical oxalate precipitation by this method carries 95% of the americium and leaves 50% of the lanthanum in solution. Americium(III) oxalate, vacuum dried at room temperature, has the formula $Am_2(C_2O_4)_3 \cdot 7H_2O$. Its decomposition was studied on a thermal balance.(27) On heating <u>in vacuo</u>, water is lost stepwise, forming the anhydrous oxalate at 240°. On heating to 240° <u>in air</u>, anhydrous americium oxalate is formed which then decomposes on further heating. Decomposition, forming black AmO_2, begins at about 300° and is complete at ca 470°. The solubility of Am(III) oxalate under various conditions is given below.(28)

Some data have been obtained(28) on the solubilities of the double sulfates of americium and certain alkali metals. Three double sulfates of americium and potassium have been obtained. The compound having the composition $K_8Am_2(SO_4)_7$ which is precipitated at high concentrations of potassium sulfate has the lowest solubility, 3 mgs./liter.

TABLE I

AMERICIUM OXALATE SOLUBILITY

	Media	°C	Formal Solubility gm/l
Am(III) oxalate	0.1 M $H_2C_2O_4$ + 0.1 M HNO_3	22	1.8×10^{-3}
"	0.25 M HNO_3	20	2.5×10^{-1}
"	0.2 M $H_2C_2O_4$	25	1.8×10^{-2}

A second precipitation method which has been examined in detail involves the use of hydrofluosilicic acid(29) to separate americium and promethium. Under the experimental conditions used (see procedures), promethium fluoride precipitates while americium remains in solution. There are earlier reports(8) which describe the use of this reagent both as a precipitant and as an eluant for ion exchange columns.

Very little quantitative information is available on the complexing of americium. A thermodynamic (zero ionic strength) equilibrium constant of ca. 0.068 has been calculated for the reaction $AmCl^{++} \rightleftharpoons Am^{+++} + Cl^-$.(30) Further evidence for complexing of americium with chloride ion results from the K_D of 165 reported by Coleman, Hecht and Penneman(31) for americium in saturated LiCl and anion exchange resin. A procedure has been developed for the separation of americium or curium from trivalent lanthanides using the LiCl-anion resin system and will be discussed in the purification section.(32,33) Americium and curium are much less tightly bound to Dowex-50 cation exchange resin in 12-13 M HCl than the lanthanides(34,35) and this property is very valuable as a group separation.

Americium thiocyanate complexing is demonstrated by the absorption of americium on strong base anion exchange resin from an aqueous phase 5 M NH_4SCN.(36) Low molecular weight lanthanides are not strongly absorbed under these conditions and this system gives excellent lanthanum-americium separations. A K_D of > 5 was measured for americium in 3 M $LiNO_3$ toward anion resin.(37)

Other evidence for Am(III) complexing evolves from the electromigration studies of Yakovlev and Kosyakov.(38) Briefly, 70-90% anodic migration was observed for Am(III) in 10 M HCl, HNO_3 and H_2SO_4. Only 1% anodic migration was observed for 3.7 M $HClO_4$ systems. Approximately 100% anodic migration was noted for 50% K_2CO_3 and 78% migration was determined in 25% $NaC_2H_3O_2$.

With the exception of the work of Ward and Welch,(30) very little can be said about the exact species present in an aqueous media. Absorption on anion exchange resins does not really define an anionic species in the aqueous phase. This area of americium and curium chemistry is still vast and uncharted.

The majority of separations of americium (or curium) from various contaminants which involve either ion exchange or solvent extraction have dealt with the americium in the trivalent state. These will be discussed separately in the purification section.

4. The Tetravalent State - Am(IV)

Only three compounds have been identified which contain tetravalent americium. These are the dioxide, AmO_2(39,40) and two compounds with fluorine, AmF_4 and $KAmF_5$.(41) There is some question as to whether AmO_2 is a stoichiometric oxide. In an accurate determination of the specific activity of Am^{241} it was found that anhydrous $AmCl_3$ and $Am_2(SO_4)_3$ gave comparable results but that AmO_2 prepared at 890° would have to have the stoichiometry $AmO_{2.1}$(42) to give concordant results for the specific activity.

Tetravalent americium has never been observed in solution. The formal potential of Am^{+3} - Am^{+4} is -2.44 volt(43) from which one would presume rapid oxidation of water by tetravalent americium in aqueous acid solution. The formal potential of Am^{+4} - AmO_2^+ has been estimated as -1.04 volt.(5) Therefore the disproportionation of Am(IV) would be favored by ca. +1.4 volt or 17 kcal/mole. Some evidence for Am(IV) disproportionation has been obtained upon dissolution of AmO_2 in H_2SO_4(28) and $HClO_4$(44) and constitutes another path for the rapid disappearance of Am(IV) even if it should have a fleeting existence in solution.

5. The Pentavalent State - Am(V)

The existence of this valence state was discovered by Werner and Perlman(12,45) who prepared it by oxidation of Am(III) in potassium carbonate solution at 95° with hypochlorite ion. The pentavalent state of americium is obtained under such conditions in the form of an insoluble (< 5 mg/liter) double salt with the alkali carbonate. More elaborate experiments with rubidium and ammonium enabled the characterization of the hexagonal compounds $RbAmO_2CO_3$ and $NH_4AmO_2CO_3$(46) and orthorhombic $KAmO_2CO_3 \cdot 2(K_2CO_3)$.(46,47) A monoclinic double salt with sodium carbonate also exists.(46) Other oxidants such as ozone or persulfate have also been found effective. Other things being equal, ozone is preferred because no new cations or anions are introduced into the solution.

The precipitation of Am(V) is routinely used to purify americium from carbonate-soluble impurities such as lanthanum or curium. The oxidation of americium with ozone proceeds smoothly at 92° in 3 M K_2CO_3. The Am(V) is formed as a finely divided tan precipitate. Removal of the carbonate supernatant followed by washing the precipitate with dilute K_2CO_3 solution (water alone destroys the compound) will reduce the concentration of elements such as lanthanum by a factor of 10 or more per oxidation cycle.

It has been found recently that high ($\geq$ 3 M) concentrations of potassium carbonate are not necessary to achieve complete oxidation of trivalent americium to the pentavalent state. If one bubbles ozone through a slurry of trivalent americium hydroxide in ca. 0.03 M $KHCO_3$ at 92°, hexagonal $KAmO_2CO_3$ is obtained.(44) A strikingly different behavior is observed with 0.03 M $NaHCO_3$. Using sodium bicarbonate at 92°, one obtains hexavalent americium in the form of a mahogany colored, soluble complex.(44) The structure of this complex is yet unknown. This Am(VI) complex also is obtained by treating trivalent americium in 2 M Na_2CO_3 with ozone at room temperature.(44) If one continues to bubble ozone through the solution and then increases the temperature to ca. 90°, the insoluble sodium-Am(V) compound precipitates. In fact, this technique represents an excellent way to prepare the sodium-Am(V) compound free of Am(III).

Pentavalent americium (in non-complexing media) has the structure AmO_2^+. Evidence for this oxygenated ion has been drawn from several sources. Some studies have been made on correlations of fine structure in the visible spectra of uranium and transuranium (V) and (VI) ions.(48,49,50) Crystallographic studies on the insoluble (V) compounds of plutonium, neptunium and americium showed the MO_2^+ ion existed as a molecular entity.(51) The reversibility of the Am(V)-Am(VI) couple has been taken as further testimony to the analogous nature of Am(V) and Am(VI).(52) Studies of the asymmetric stretching frequencies of the $[O-M-O]^+$ and $[O-M-O]^{++}$ ions confirmed the doubly oxygenated linear (or nearly linear) configuration for these ions.(53)

As might be expected, the chemical properties of such a doubly oxygenated, singly charged ion differ markedly from those of trivalent Am^{+++}. Both the pentavalent AmO_2^+ and hexavalent AmO_2^{++} are fluoride-soluble and this property is useful in small scale separations from fluoride insolubles such as the lanthanides. However, an insoluble potassium double fluoride of Am(V) exists, $KAmO_2F_2$(54) but fairly high concentrations of KF are necessary to achieve precipitation.

The pentavalent state is unstable in acidities higher than 1 molar undergoing disproportionation with a fairly complex mechanism.(28,38,55,56,57,58) Originally, it was thought that the disproportionation followed a fairly simple kinetic experssion, viz: $-d[\mathrm{Am(V)}]/dt$(mole liter^{-1} hour^{-1}) $\cong$ 0.04 $[\mathrm{Am(V)}]^2[\mathrm{HClO_4}]^4$. However, more recent work(44) with the long lived Am^{243} has shown that the rate expression is more complicated and should be represented by an equation of the form $-d[\mathrm{Am(V)}]/dt = k_1[\mathrm{Am(V)}^2[\mathrm{HClO_4}]^2 + k_2[\mathrm{Am(V)}]^2[\mathrm{HClO_4}]^3$. The reproportionation of Am(VI) and Am(III) to form Am(V) has also been observed using Am^{243}.(44)

The pentavalent state of americium also can undergo self-reduction(59) with a zero-order rate in perchloric acid corresponding to ~ 2%/hour. The rate is somewhat variable in different media.(38,56,57,58) It must be emphasized that this rate applies only to the isotope Am^{241}, which hitherto has been used almost exclusively for studies on the chemistry of americium. The half-life of Am^{241} is 458 years, corresponding to a specific activity of 7.12 x 10^9 d/min/mg. The emitted alpha particles interact with the solution to produce materials, the net effect of which is to reduce Am(V) to Am(III). The rate of production of these radiolysis products is proportional to the total amount of alpha-emitter and determines the rate of self-reduction. Thus, pentavalent americium containing the longer lived Am^{243} will undergo considerably slower self-reduction. Hydrogen peroxide is one of the products of "radiation-fragment" recombination; therefore any solution containing a species which will complex or destroy peroxide will serve to slow the self-reduction of Am(V). The rate of self-reduction is much slower in HCl solutions,(49) or $\mathrm{Cl_2}$-satd. solutions.(5)

6. The Hexavalent State - Am(VI)

The general chemistry of the (V) and (VI) states of americium have some similarities, both states are fluoride-soluble and afford a quick separation from fluoride-insoluble contaminants. The hexavalent state was prepared initially by direct oxidation of the trivalent ion in dilute acid ($\leq$ 0.2 M $\mathrm{H^+}$) at 92° using ammonium persulfate.(60) Some precautions are necessary to achieve this oxidation;(5) the acid must be dilute because persulfate decomposes via an acid-catalyzed path(61) to produce peroxymonosulfuric acid which would rapidly reduce any hexavalent americium formed. Hexavalent americium is reduced by $\mathrm{Cl^-}$, $\mathrm{Br^-}$ or $\mathrm{I^-}$ in acid solution and environments of these ions cannot be tolerated.

Argentic ion and, to some extent, ceric ion, may also be used to achieve the oxidation of Am(III) to Am(VI).(60) Electrolytic oxidation gives a high yield in 6 M $\mathrm{HClO_4}$(58,60) but a three-compartment cell at 0°

must be used at lower acidities to obtain comparable yields.(62)

Oxidation of Am(V) to Am(VI) is most conveniently carried out with ozone, but ceric ion or argentic ion in hot, dilute acid have also been used.(60) To some extent, all of these methods suffer from the disadvantage of contaminating the resulting Am(VI) solution with the reduction products of the oxidant. Even dissolution of the Am(V) potassium carbonate precipitate in acid followed by ozone oxidation to Am(VI) still leaves potassium ion present which is often a disadvantage for work in perchlorate media. The electrolytic method often fails where the concentration of impurities is high.

Two rather new methods have been employed which may be used to generate Am(VI) directly. If ozone is bubbled through a slurry of $Am(OH)_3$ in dilute (ca. 0.03 M) $NaHCO_3$ at 92°, one obtains the hexavalent state in the form of a soluble complex as previously mentioned.(44) Subsequent, slow addition of acid to such a solution (in the presence of ozone) yields Am(VI) quantitatively in acid solution, with only a negligible contribution to the ionic strength from the sodium salt produced by neutralization.

The second method involves the <u>direct</u> oxidation of Am(III) to Am(VI) using ozone.(44) Direct oxidation in acid solution had not been successful with ozone.(5) A re-examination of the Am(III)-Am(IV) potentials in acidic and basic solution suggested conditions under which this oxidation should be favorable, i.e., neutral or slightly alkaline solutions. While the E^o value for the Am(III)-Am(IV) couple in 1 M H^+ is -2.44 volt, the E^o_B value should be about 2 volts more positive, about -0.4 or -0.5 volt (1 M OH^-).(1) This estimate depends primarily upon what is taken for the ratio of $Am(OH)_4/Am(OH)_3$ solubilities. Experimentally, it was found that at approximate neutrality, (pH = 6-9), oxidation of $Am(OH)_3$ takes place with ozone. Hypochlorite will also cause oxidation but no Am(VI) is observed after acidification, possibly due to reduction by chloride ion. The ozone method (which is most effective at 92°), takes about 1 hour for complete oxidation on a several milligram scale. Following the ozone treatment, one may slowly add acid (while continuing ozone flow) to obtain Am(VI).

The hexavalent state apparently shows some amphoteric behavior; when hydroxide is added to an acid solution of Am(VI) (constantly bubbling ozone to maintain oxidizing conditions), a dark brown precipitate forms about pH = 7 but <u>redissolves</u> to yield a light yellow solution at pH = 13-14. If an Am(VI) solution is made basic without ozone present, considerable reduction to Am(V) occurs.(44,60) No characteristic Am(VI) structure is observed on spectral studies of the basic solution but the "normal" Am(VI) absorption spectrum reappears on acidification. The spectrum of Am(VI) in bicarbonate or in carbonate solution is markedly different from its appearance in acid solution. This is somewhat at variance with the behavior of Am(III) whose spectrum is altered very little from acidic solution, to $Am(OH)_3$ slurry, to 6 M K_2CO_3 solution where Am(III) forms a soluble complex.

Sodium americyl acetate is the only solid compound of Am(VI) which has been examined carefully. It is isomorphous with the sodium acetate double salts containing hexavalent uranium, plutonium or neptunium.(60) The compound has the formula $NaAmO_2(C_2H_3O_2)_3$, is light yellow in color and has a solubility of 0.67 gm/l in 3 M $NaC_2H_3O_2$.(28) No solid oxide or fluoride of the (VI) state has been prepared.

The hexavalent state also undergoes self-reduction as in the case of Am(V); however, the rate of reduction of Am(VI) to Am(V) is more rapid than that of Am(V) to Am(III). The self-reduction rate of Am^{241}(VI) is ca. 1%/hour.(38,57,59) As with Am(V), this is essentially a zero order reaction, proportional only to the total alpha emitter present. This fairly rapid reduction rate with Am^{241} has interfered with precise studies on the (VI) state. The use of long-lived Am^{243} will allow more accurate elucidation of many facets of Am(VI) chemistry. The Am(V)-Am(VI) couple is reversible and Am(VI) is also reduced more rapidly than Am(V) by chemical reagents that will reduce both, e.g., H_2O_2.(28,58) Both nitrite(28) and chloride(5) reduce Am(VI) rapidly to Am(V) without reduction of Am(V).

7. Spectra of Am(III), Am(V) and Am(VI)

All of the aqueous valence states of americium have characteristic spectra. The various maxima are of such wave length as to allow all three solution valence states to be determined simultaneously. In Figures 1, 2, and 3, the spectra are shown and Table II lists the principal maxima and the molar extinction coefficients of each. The coefficients were determined in slightly different media and with different types of instruments. It is not surprising that slight discrepancies exist. Very significant changes in extinction coefficients are noted in higher concentrations of complexing acids such as HF, HCl, H_2SO_4 and HNO_3(5,28,38,58,57) and must be considered when using spectrophotometric techniques for americium determination. The intense Am(III) maxima at 5027 Å does not obey Beer's law at higher americium concentrations (apparently an instrumental effect).

It should be noted here that the actions of Am^{241} alpha radiation on solutions can cause complicating effects in ordinary spectra. The self-reduction of Am(V) and of Am(VI) has been mentioned. Even in the case of Am(III), radiolysis products affect the spectrum at short wave lengths (< 4000 Å).(63) Reduction of perchlorate ion has been observed in concentrated solutions.(28,44)

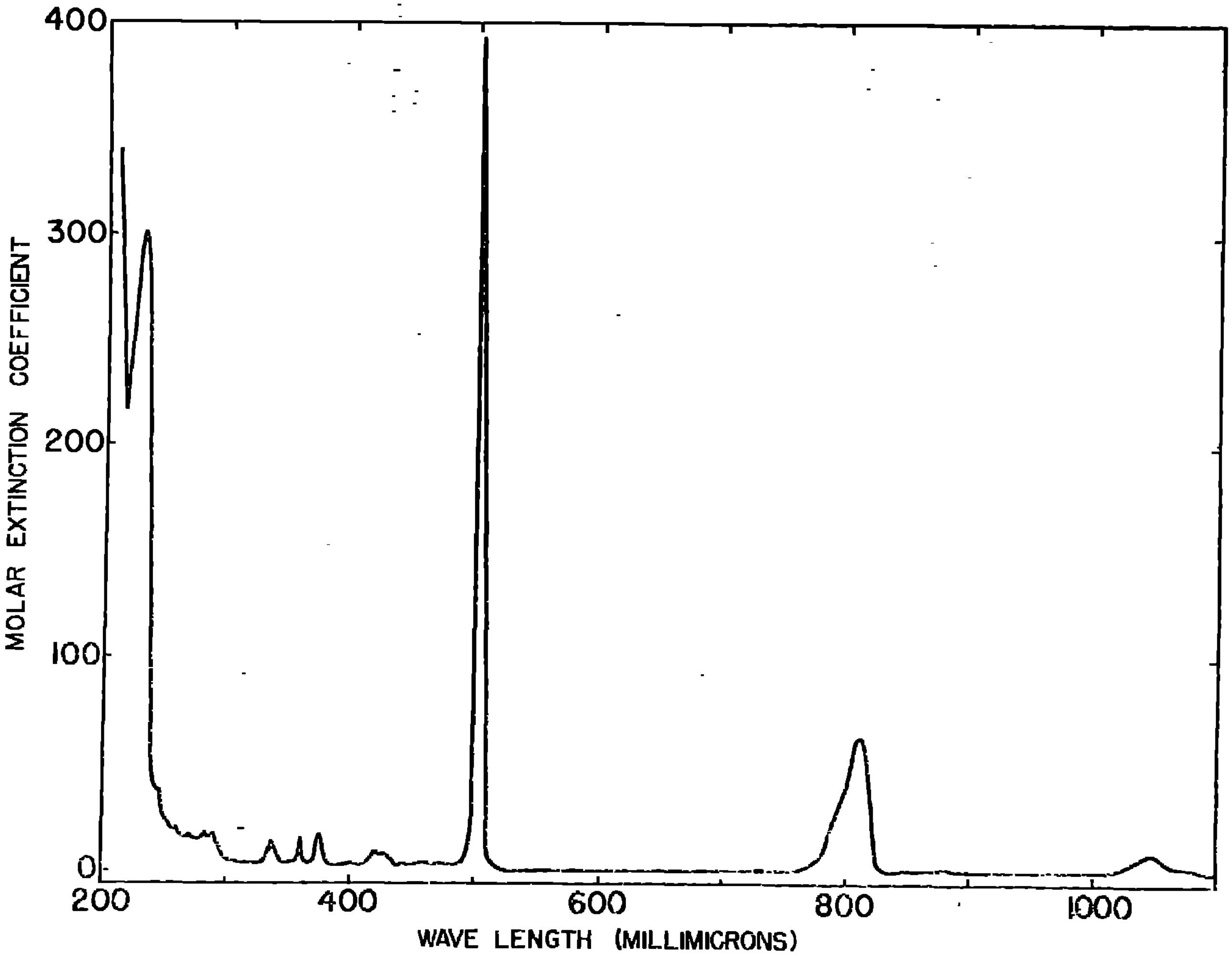

Fig. 1 Absorption Spectrum of AM (III) in 1M $HClO_4$

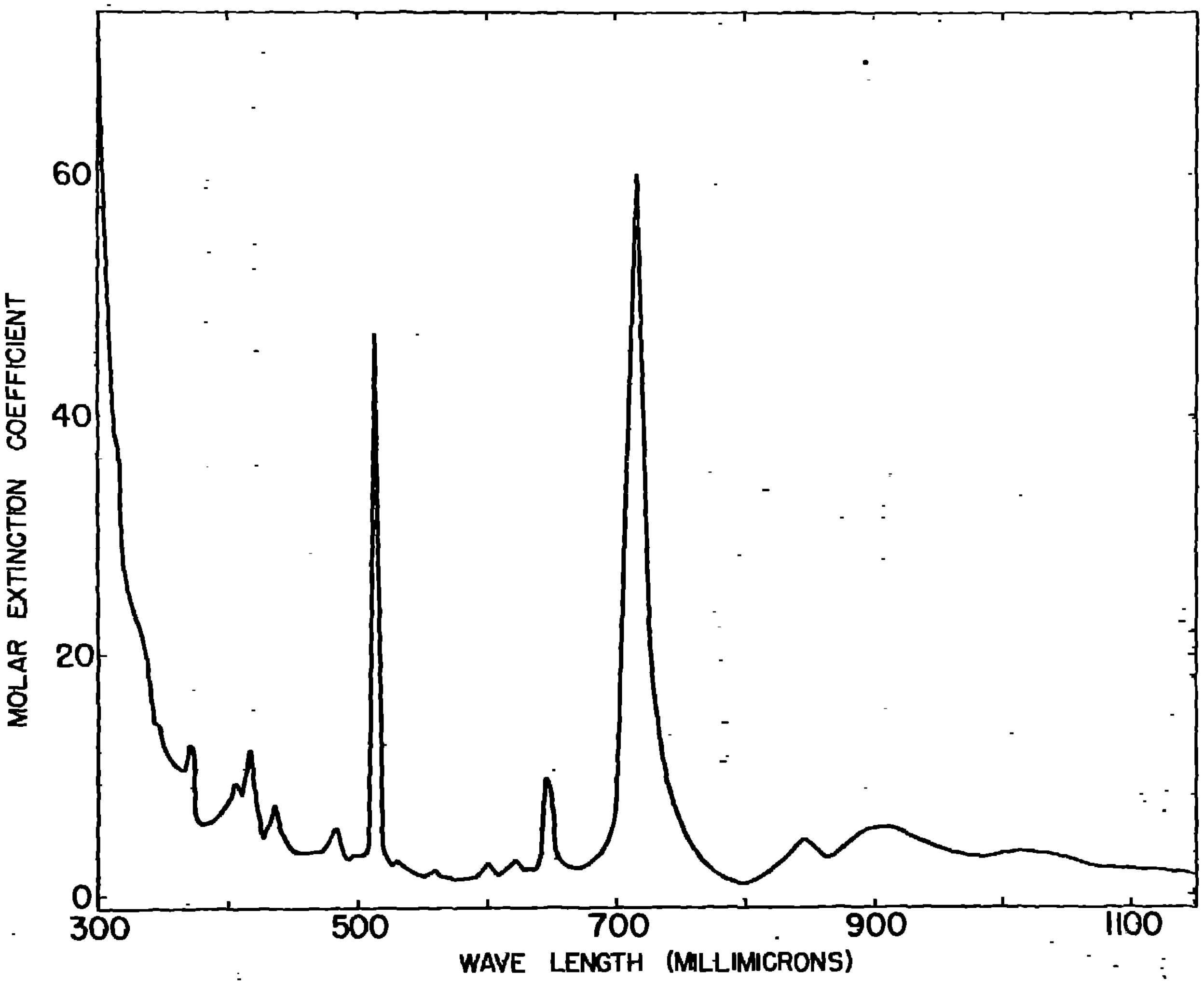

Fig. 2 Absorption Spectrum of AM (V) in 1M HClO$_4$

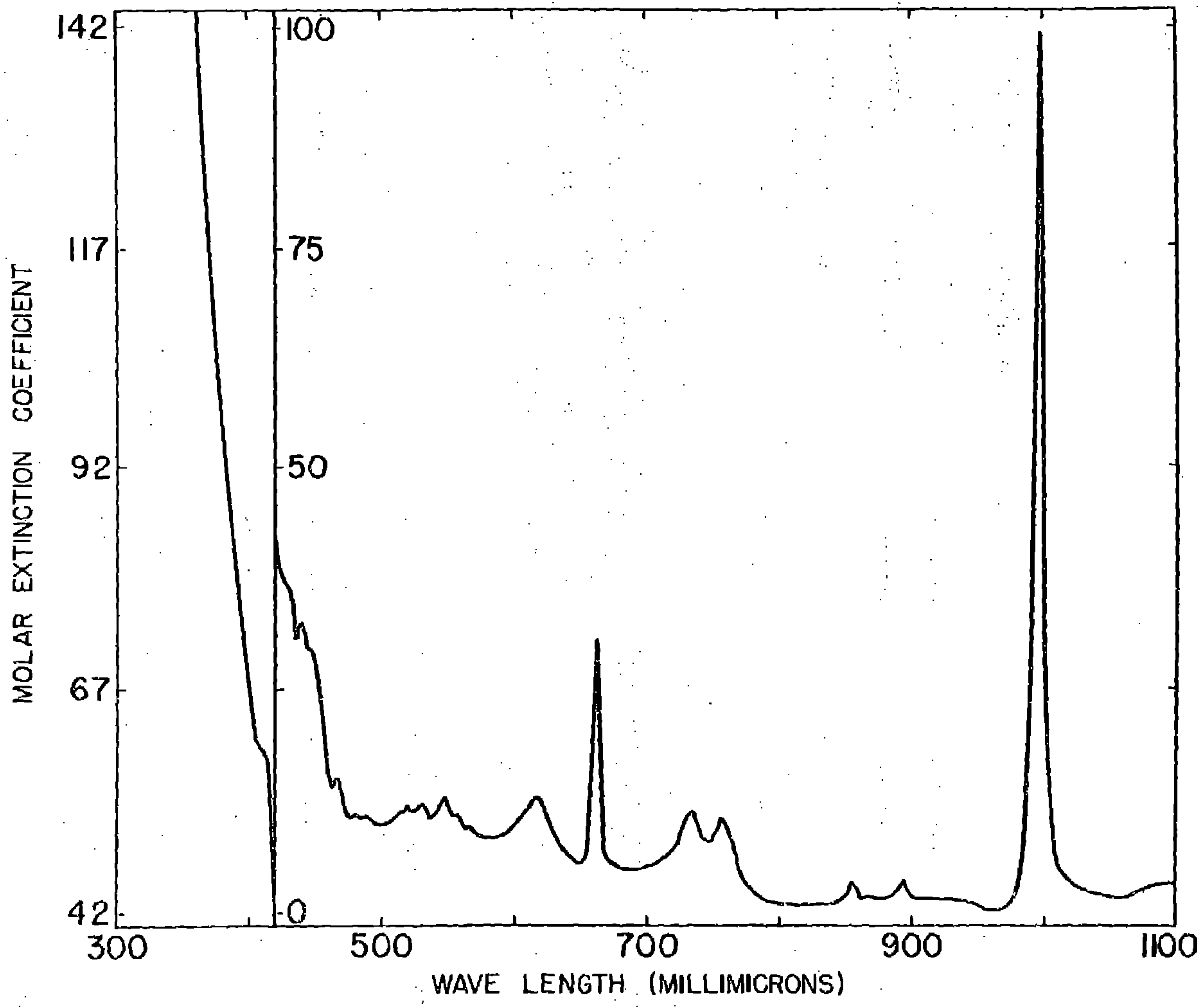

Fig. 3 Absorption Spectrum of Am (VI) in 1M $HClO_4$

TABLE II

ABSORPTION MAXIMA AND MOLAR EXTINCTION COEFFICIENTS FOR AMERICIUM

	Å	ε	Ref.	Media
Am(III)	5027	391	(63)	(a)
	5029	368	(44)	(b)
	5031	378	(38)	(c)
	5027	408	(44)	(e)
	8120	62.6	(44)	(b)
	8110	64.4	(38)	(c)
	8160	69.2	(62)	(f)
	8122	68.0	(44)	(e)
	8110	63.0	(57)	(g)
Am(V)	5131	45.6	(63)	(a)
	5140	44.1	(38)	(c)
	5140	44.4	(56)	(d)
	7151	59.3	(63)	(a)
	7180	59.6	(38)	(c)
	7150	56.4	(56)	(d)
	7190	62.5	(62)	(f)
	7167	54.5	(44)	(b)
	7150	55.0	(57)	(g)
Am(VI)	4085	60.2	(63)	(a)
	6630	30.5	(63)	(a)
	6660	24.6	(38)	(c)
	9950	63.8	(38)	(c)
	9960	83.3	(62)	(f)
	9945	87.7	(44)	(e)
	9947	86.4	(44)	(b)
	9920	75.0	(57)	(g)

Media:

(a) 0.1 M $HClO_4$
(b) 2.0 M $HClO_4$
(c) 0.1 M $HClO_4$
(d) 0.5 M HCl
(e) 0.03 M $HClO_4$; $\mu = 2.00$ with $LiClO_4$
(f) 1.0 M $HClO_4$
(g) 0.2 M $HClO_4$

8. Purification of Americium from Other Elements

Where available, detailed procedures of separation are given in the listing following this descriptive portion. However, since much of the information has not been written in the form of a specific procedure, a general survey of the results concerning purification is in order here. If one is faced with the separation of americium from non-alpha emitting contaminants, the alpha activity of americium itself will serve as a quantitative check on the procedure. The 60 kev gamma associated with Am^{241} is readily detected and is a convenient method for following americium in both a quantitative and qualitative manner. If other alpha-emitters are present, it is often necessary to utilize an alpha energy analyzer to discriminate the americium fraction of the activity.

Purification will be discussed below under three separate categories: (a) where americium is present in tracer quantities, (b) where americium is present in milligram quantities and is contaminated with ca. $\leq$ 100-fold impurities, and (c) where the americium is present in milligram to gram quantities but is contaminated with ca. $\geq$ 1000-fold excess of impurities. These distinctions are somewhat arbitrary of necessity and a technique which will be discussed for one scale might be just as suitable for another when considering a particular problem. Some chemical reasoning and intuition should allow a reasonable decision as to which techniques to employ.

(a) Tracer Scale Americium or Curium

Bismuth phosphate which was the historic co-precipitation reagent for plutonium will also carry americium from 0.1 - 0.3 M HNO_3. Impurities such as calcium and magnesium are not carried. Its use for the separation of americium from urine is discussed in the procedures.

With tracer quantities, lanthanum provides a convenient carrier for americium(III) or curium(III) in precipitation reactions. Quantitative oxidation of Am(III) to Am(VI) in dilute acid is obtained with persulfate(84) even at americium concentrations as low as 10^{-8} M. Such a technique can serve to separate americium and lanthanum, as well as americium from curium if the oxidation of americium were followed by addition of fluoride to precipitate curium/lanthanum trifluoride.(80,85,88) Lanthanum may also be separated from americium and curium by a 13 M HCl Dowex-50 resin column(34,35) or a 5 M NH_4SCN Dowex-1 resin column.(38)

Ion exchange techniques provide the most powerful tool to separate tracer (and macro) quantities not only of americium and curium but also the transcurium elements. As simple, hydrated cations in dilute mineral acids, trivalent americium and curium are tightly bound to cation resins such as Dowex-50. Distribution coefficients as large as 3.86×10^5 (resin/aqueous) have been measured for americium in 0.1 M $HClO_4$.(67)

The trivalent actinides elute ahead of the lanthanides from Dowex-50 resin in 13 M HCl(34,35) but there is little tendency for americium or curium to absorb onto anion resin from hydrochloric acid media. Several workers(68,69,70) have investigated the behavior of americium and curium in mineral acids toward Dowex-1 and Dowex-2. Their work shows that americium and curium are not significantly absorbed ($\leq$ 1 column volume) on these anion resins from 0.1 M to concentrated HCl, H_2SO_4 and HNO_3.

The absorption of Am(III) and Cm(III) on Dowex-1 from concentrated aqueous solutions of chloride,(32,33) nitrate(37) and thiocyanate(36,71) salts contrasts strongly with their lack of absorption from the corresponding acids. A clean separation of americium from lanthanum has been obtained using Dowex-1 and 5 M NH_4SCN.(36,71) For a single batch equilibration, separation factors of 30 for americium-lanthanum and 3 for americium-ytterbium were found in 5 M NH_4SCN and Dowex-1.(72) Surls and Choppin(73) report values for the distribution coefficients between 2 M NH_4SCN and Dowex-1 for 18 4f and 5f elements and also report distribution coefficients for americium and europium over a 1 - 4 M thiocyanate concentration range.

Several cation exchange systems particularly suited to tracer scale separations of americium and curium and transcurium elements have been utilized. Classically, buffered citrate solution was used,(6) but this reagent has been superseded by others giving better separation. From Dowex-50, the eluant 20% ethyl alcohol-satd. HCl(68) gives an excellent actinide-lanthanide group separation along with a somewhat better intra-actinide separation than 13 M HCl alone. A method for the recovery of americium and curium (and transcurium elements) from cyclotron targets has been studied by Chetham-Strode.(74) Briefly, this separation depends upon absorption of Am(III)-Cm(III) on cation resin from 1 M HCl. Washing with this eluant removes alkali metals, alkaline earths and silica. The americium and curium are then eluted from the column with 6 M HCl. Little separation of americium and curium is obtained but excellent resolution from the light and heavy lanthanides can be realized.

A great deal of information is available concerning the use of buffered ammonium lactate,(66,75,76) ammonium tartrate,(75,76) and ammonium glycolate.(77) However, ammonium alpha-hydroxyisobutyrate (pH $\cong$ 4) as an eluant from Dowex-50 has been used almost exclusively in recent years for intra-actinide separations.(78) Most of the work with alpha-hydroxyisobutyric acid has been done at 87°. Other recent studies(79 have shown similar separation factors can be obtained for americium, curium and californium at room temperature with lower cross linked resin.

The reagent ethylenediamine tetraacetic acid (EDTA) and cation resin systems show even higher separation factors for americium and curium(80) than the alpha-hydroxyisobutyric system. However, the alpha-hydroxyisobutyrate system is generally preferred, perhaps because the greater solubility of the particular metal complexes concerned and the employment of more rapid flow rates.(81) The compound pentasodium diethylenetriamine pentaacetate (DPTA) has been shown to form very tight complexes with thorium.(82) Other work indicates that DPTA complexes plutonium as expected and has certain advantages compared to EDTA for removal of plutonium from the body.(83) The possibilities of actinide separation using DPTA are yet to be explored.

Table III is a comparison of ammonium glycolate, ammonium lactate, ammonium alpha-hydroxyisobutyrate and EDTA in which the peak positions are normalized to curium. The free column volume has been subtracted from all positions. Elutions of lanthanide tracers showed essentially the same behavior relative to gadolinium(78,81) with americium eluting in about the same position as promethium. Hence, operation with these reagents is <u>not</u> useful as an <u>actinide-lanthanide</u> separation.

There are several solvent extraction techniques which have been used on the tracer level. The reagent thenoyltrifluoroacetone, TTA,(84,85) at

TABLE III

ACTINIDE PEAK POSITIONS WITH VARIOUS ELUANTS

Element	Glycolate(78) 87° (Dowex-50x12) (0.25 M)	Lactate(78) 87° (Dowex-50x12) (0.4 M)	Butyrate(78) 87° (Dowex-50x12) (0.4 M)	Butyrate(79) 25° (Dowex-50x4) (0.5 M)	EDTA(80) 25° (Dowex-50x12) (0.001 M)
Md	---	---	0.05	---	---
Fm	---	0.23	0.07	---	---
Es	---	0.33	0.13	0.13	---
Cf	0.6	0.41	0.20	0.19	0.18
Bk	0.70	0.65	0.45	0.37	---
Cm	1.00	1.00	1.00	1.00	1.00
Am	1.14	1.21	1.45	1.4	2.04

a concentration of 0.2 M in benzene will quantitatively extract americium and curium from an aqueous phase of pH = 4.0. Some separation from lanthanum is possible by operation at pH = 3.3; however, little or no separation of americium from curium can be attained at any acidity. This reagent is one best reserved for tracer levels of activity since the unsaturated TTA molecule is quite easily attacked by macro amounts of alpha radiation and the complex with americium does not have a high solubility.(71,86) This reagent does allow a convenient tracer scale separation of americium from plutonium since tetravalent plutonium is completely extracted at much higher (ca. 0.1 M) levels of acidity. A procedure has been developed(87) for quantitative tracer separation of americium and plutonium. Another, slightly modified, TTA system for the separation of americium and yttrium tracer has been reported.(88) This was accomplished by extracting both americium and yttrium from an aqueous phase initially pH = 5 into 0.5 M TTA in xylene. The americium was then stripped from the organic phase with an equal volume of 3% EDTA at pH = 6.47. Two back extractions removed 74% of the original americium with no detectable yttrium.

Considerable work has been done with the reagent tributyl phosphate (TBP). This ester is much more resistant to radiation than TTA and is more often used with macro amounts than at the tracer level. There are several experimental parameters to consider such as TBP concentration, acid and salt concentration of the aqueous phase, etc. Peppard and co-workers(89) studied the distribution coefficients of lanthanides and actinides from 12.0 M HCl and 12.0 and 15.6 M HNO_3 into undiluted TBP. Other work(90) describes the counter-current separation of americium and curium from nitric acid solutions into TBP.

The extraction of americium with acidic esters of orthophosphoric acid has been reported.(91) The distribution ratio of americium into the organic phase can reach values of 10^3 from aqueous phases of dilute acidity and fractional values for the formal concentration of the ester in the organic phase.

The extraction of Am(III) from 1 M NH_4SCN into TBP(44) has been used on the milligram scale (see purification section) for americium purification. This system would also be useful with tracer quantities.

Welsh(92) studied the extraction of americium(III) from aqueous nitrate solution by tributyl phosphate. The extraction is favored by high nitrate ion concentration and high TBP concentration in the organic phase; it is retarded by high aqueous acidity. The extraction of americium is greatly influenced by highly charged cation nitrates, e.g., into 35% TBP, 2.5 M aluminum nitrate, $K_a^o = 142$, while from 5 M $NaNO_3$, $K_a^o = 3$.

The solvent extraction techniques mentioned all involve trivalent americium. Reduction of Am(VI) tracer occurs so easily that use of this valence state on a tracer level is not recommended. Both cation and anion resins reduce Am(VI) to Am(V);(44,62) however, Dowex-50 has been used to separate Am(III) from Am(V) without reduction of Am(V).(62)

(b) Milligram Scale Separations

Methods, such as ones involving oxidation of Am(III) to Am(V) or Am(VI), which are excellent for the separation of americium on the milligram scale from only milligram amounts of impurities are often found unsuitable at higher impurity levels. Many times a concentration step must be performed for volume reduction and separation of milligram amounts of americium from bulk impurities other than lanthenum. A trivalent lanthanide-actinide fraction may usually be concentrated by a suitable combination of fluoride or oxalate precipitations. Most transition elements form soluble complexes with these anions and are removed. Several such procedures have been reviewed.(3,87)

Concentration by extraction from nitrate media using TBP has been mentioned above and is a useful technique. Coleman(44) has found that 40% TBP extracts americium from 1 M NH_4SCN with a K_a^o of ~ 100; if the concentration of NH_4SCN is 1 M or less, lanthanum has a K_a^o about a factor of 10 less than that for americium. (With thiocyanate generally, the presence of high acidity or strong oxidizing agents must be avoided.)

Experience on the isolation of ≥ 25 mgs of americium from gram amounts of impurities is summarized in recent reports. Hall and Herniman(55) report a procedure for the separation of 25 mg of americium from 2 gm of plutonium and 0.5 gm each of uranium and iron. Plutonium and uranium were removed by solvent extraction. Americium oxalate was then precipitated and metathesized to the sulfate. A series of oxidation-reduction cycles separated the residual plutonium. Final purification involved the use of a 12 M HCl-Dowex-50 ion-exchange column.

The separation of 50 mg of Am^{241} from gram amounts of plutonium, bismuth, iron and sub-gram amounts of lanthanum and other impurities was described by Milham.(83) The procedure consisted essentially of precipitating the combined hydroxides using ammonia, dissolution of the precipitate in concentrated HCl followed by passage through Dowex-2 resin which absorbed iron and plutonium. The effluent was diluted to 4 M HCl and passed through a second Dowex-2 column which absorbed bismuth. Lanthenum and americium were separated using Dowex-50-concentrated HCl.

Naito(84) carried out the isolation of ca. 50 mg of americium from gram quantities of impurities. After precipitation methods for concentration and partial purification, the use of both the 13 M HCl-Dowex-50 and the 5 M NH_4SCN-Dowex-1 ion-exchange methods are described, giving detailed analyses of various impurities after each step.

Weigel(86) was faced with the problem of recovering about 100 mgs of americium from very impure waste solutions. He attempted to extract the americium with TTA and experienced precipitate formation, but was eventually able to recover most of the americium by other techniques. (The disadvantages of TTA for macro quantities of americium have been mentioned earlier.)

Once an americium fraction has been enriched to the point where americium is the major constituent, any of the several techniques mentioned in the previous section can be used. In addition to methods which work at tracer levels, methods involving precipitation of carrier-free americium and oxidation-reduction techniques become feasible.

On the several milligram scale, americium is conveniently purified from carbonate-soluble impurities (such as La(III), Cm(III)) by oxidation of Am(III) to the insoluble Am(V) carbonate from potassium carbonate (the conditions are described in the Am(V) section). Dissolution of the Am(V) precipitate in dilute acid can be followed by ozone oxidation to Am(VI), subsequent addition of fluoride ion will precipitate the lanthanide-like fluoride-insolubles leaving Am(VI) in solution. The americium may be subsequently recovered by adding a reducing agent to the Am(VI) supernatant solution (still containing excess fluoride) and precipitating americium trifluoride. Trivalent americium fluoride may be dissolved in 1 M HNO_3-satd. H_3BO_3 or metathesized to the hydroxide by treatment of the fluoride precipitate with 0.1 M KOH for 1 hour at ca. 90°. Alternatively, Am(III) can be oxidized to Am(VI) in dilute acid with persulfate (for details see section on Am(VI)) and the fluoride precipitation carried out. One may recycle the americium in such an operation as necessary to obtain the desired degree of purity.

Ion-exchange operations on the milligram scale are subject to some limitations. Considerably more cross-contamination generally occurs between adjacent elements (e.g., americium and curium) and it should be emphasized that the separation factors given in Table III are for peak positions. Furthermore, the gas evolution caused by the alpha radiation associated with milligram quantities often causes plugging of the column from bubbles. This in turn necessitates more rapid flow rates which may downgrade the effectiveness of the separation. Nevertheless, most of the ion-exchange techniques mentioned in the previous section have been used successfully on the milligram scale.

(c) Milligrams to Grams of Americium with Multifold Levels of Impurities

Unfortunately (or perhaps, fortunately), chemists have often had to consider the problem of recovering americium (or curium) from solutions wherein the actinide is present only as a "barely detectable" spectroscopic impurity. It has certainly not been uncommon to encounter several gallons of highly salted "solution," perhaps ca. 15 M in total cation and density ~ 1.6. Such "solutions" usually have the color, viscosity and transparency of split pea soup and invariably have a suspicious sludge on the bottom of the container. Nevertheless, there may be americium contents ranging from several milligrams to several grams which somehow must be recovered. Glum as the prospect may seem, it is possible to recover the americium from such miserable media in reasonable yield with only slight wear and tear on the personnel concerned. Isolation of curium from similar media would be expected to be about as efficient.

There have been several schemes described which lend themselves to treatment of such extremely impure americium solutions. Probably the bulk of this work has been oriented toward the recovery of americium from various plant residues which are by-products from the purification of plutonium. Since americium is formed in reactors by the reactions $Pu^{239}(n,\gamma)Pu^{240}(n,\gamma)Pu^{241} \xrightarrow{\beta^-} Am^{241}$, this americium isotope is continually encountered in plutonium processing raffinates.

Obviously, some preliminary step must lead toward the concentration of an actinide-lanthanide fraction which may be followed by more specific chemistry. Successful carrying of Pu(III) and Am(III) with calcium oxalate from solutions containing high concentrations of magnesium, aluminum and calcium nitrates (total cation concentration up to 10 N) has been reported on a plant scale.(35)

If the concentration of total cation is high, solvent extraction with TBP is widely used in concentrating the americium. The impurity itself acts as the salting agent to insure high extraction coefficients. A routine method has been reported(71) using 30% TBP in Gulf BT (Gulf BT is a kerosene type diluent sold by the Gulf Refining Company). This was used to extract americium from a dilute acid aqueous phase (ca. 0.1 M) and heavily salted with alkaline earths, aluminum and sodium nitrates. Distribution coefficients of 6 to 10 were obtained for this system. With many impurities, the use of a higher pH must be avoided since precipitation followed by emulsification can occur. Little or no separation from lanthanides was obtained and considerable amounts of other impurities were also extracted, but it served well as a convenient concentration step for the americium. The americium was recovered from the organic phase by stripping with water.

An oxalate precipitation was then made which further concentrated the lanthanides, alkaline earths and americium from other metals. The oxalate cake was metathesized to the hydroxide by treating with 0.1 M NaOH for 1 hour at 90°, yielding a dense, readily filterable precipitate. By batch-wise washing the hydroxide precipitate with 2 M NH_4NO_3, the alkaline earths were leached away with little loss of americium. Following this, the americium and lanthanides were separated by ion exchange.

Another report(96) describes the recovery and separation of americium and plutonium from solutions of typical composition: Pu = 100 mg/liter; Am = 2 mg/liter and total cation (impurity) = 10 N. If the solution is made 1.6 - 2.2 M in H^+ and contacted with 37% TBP, only plutonium is extracted. After treatment of the plutonium-depleted aqueous residues with base to bring the acidity to 0.13 M, americium and lanthanides are extracted with 37% TBP.

The separation of americium from such concentrates has been reported by ORNL and LASL. One ORNL concentrate(97) consisted of about 10 g of Am^{241} with 3 kg of lanthanum and smaller amounts of corrosion products. Two separation techniques were used on this material:

(1) Elution of americium from a 25% loaded Dowex-50 resin column with 0.15 M citric acid--0.10 M diammonium citrate--0.3 M ammonium nitrate, pH = 3.3, gave a product containing 99% of the americium with a La/Am ratio of 1/100 or less in one fourth of a column volume. Approximately 9 g of americium was purified by this method.

(2) Elution with 12.8 M hydrochloric acid from a 20 to 30% loaded Dowex-50 column gave 90% of the americium in two column volumes of product with a La/Am ratio of about 1/4. About 1 g of americium was purified by this method. (Note: Use of concentrated HCl in conjunction with grams of americium and kilograms of lanthanides requires many liters of 13 M HCl to evaporate. This has deleterious effects on metal process equipment.) Later, a solvent extraction process for the separation of americium from large quantities of the light rare earths was demonstrated on a pilot plant scale.(98) The process utilizes the preferential extraction of americium into 100% TBP from 17 M nitric acid. Americium is enriched in the TBP by a factor of 10 compared to lanthanum.

At LASL, separation of americium from such americium-lanthanum concentrates utilized displacement analysis with 0.1% citrate pH = 8 and Dowex-50 resin. With multigram amounts, a series of head-to-tail bands develop which may be cleanly separated.(71,99) It has been replaced by the 5 M NH_4SCN-Dowex-1 system which is much superior.(71,94)

A combination procedure using Dowex-1 and NH_4SCN to separate americium from rare earths, iron, aluminium, manganese and chromium is outlined below. An impure mixture of americium, lanthanum, iron, etc. is absorbed from dilute acid on Dowex-50. Passage of 1 M NH_4SCN through the column removes iron readily. The column is stripped with 5 M NH_4SCN and the solution is fed directly onto a Dowex-1 column. Elution is continued with the 5 M NH_4SCN until the rare earths are eluted. (Presence of rare earths in the effluent is conveniently tested by addition of oxalate ion or ammonia.) If bulk rare earths are present, ~ 20 ml of Dowex-1/gram of rare earth is needed.

Chromium(III) apparently reaches equilibrium slowly in thiocyanate solutions. It has been found(44) that when Cr(III) is removed from Dowex-50 cation-exchanger with 5 M NH_4SCN it is not absorbed on Dowex-1 anion-exchanger if the chromium solution is not allowed to stand. If the Cr(III) is allowed to stand in 5 M NH_4SCN it is then strongly absorbed on Dowex-1. Naito(94) suggests passage of 2 M NH_4SCN through the Dowex-1 column to remove manganese and aluminum prior to stripping americium from the column with 0.1 M HCl.

It has been mentioned(32,33) that the actinides are absorbed on Dowex-1 anion resin from highly concentrated LiCl. There are two reported procedures which utilize this separation. Separation of 1 gram of americium from 100 grams of lanthanum using saturated lithium chloride (20 molal) and Dowex-1 resin at room temperature was reported.(71) The americium is bound to the resin while the lanthanum is washed through. Crane and Higgins(32) isolated thousand-curie quantities of curium^{242} by using 10 M LiCl-dilute HCl at 80° as eluant from Dowex-1. A lanthanide-actinide separation using hot (87°C) 8 M LiCl - 0.1 M HCl and Dowex-1 was studied.(33) The lanthanides come thru the column first; and some separation of americium and curium is obtained. The americium or curium may be readily desorbed by stripping with HCl. However, operation with these reagents and macro quantities of alpha-emitter often suffers from the disadvantages of increased neutron hazard from the (α,n) reaction on lithium and the syrupy consistency of concentrated LiCl solutions.

A method developed at the Canadian Chalk River Project by Butler and Merritt(100) has been used to separate grams of americium from kilograms of fairly pure plutonium. The bulk of the plutonium was separated by precipitation of the peroxide. A hydroxide and fluoride precipitation followed by anion and cation columns with HCl brought the americium to 99.9% purity.

Some studies(101) have been done using molten bismuth to extract americium from molten plutonium, however, the conditions described did not give a high yield purification of americium-plutonium. An earlier report(102) describes vacuum fractionation of americium from plutonium and curium from americium using differences in volatility. Although the experimental conditions described were somewhat difficult to maintain, this type of separation may have advantages under some conditions.

B. Curium

Curium, element 96, is the actinide homolog of gadolinium. The single valence of +3 in aqueous solution makes this aspect of curium chemistry much simpler to consider. Two other states, (0) and (IV) can be attained under anhydrous conditions. A more detailed discussion of these valence states is given below.

1. The Metallic State - Cm(0)

Curium metal has been prepared by reduction of CmF_3 with barium metal vapor.(103) Curium is appreciably less volatile than americium.(44,102) The properties of the metal were studied with great difficulty because of the radiation. The intense alpha and gamma radiation accompanying Cm^{242} (162.5 day half-life; 7.4×10^{12} α/min/mg) render any manipulations with this isotope extremely hazardous. The gamma radiation also blackens x-ray film and necessitates the use of extremely small (< 0.5 microgram) amounts which decreases the accuracy of crystallographic measurements. Within the last few years, milligram amounts of 17.9 year Cm^{244} have become available and already some of the early Cm^{242} work has been repeated and extended using the longer-lived isotope.

2. The Trivalent State - Cm(III)

The trivalent state of curium is the only one encountered in solution. As a trivalent ion, curium is similar to trivalent americium (and hence to trivalent lanthanides) and exhibits essentially the same behavior toward group reagents. Fluoride, hydroxide, oxalate, etc. are all quantitative precipitants. A thermodynamic constant of ~ 0.070 has been determined for the reaction $CmCl^{++} = Cm^{+++} + Cl^-$.(30)

The exclusively trivalent state of curium in aqueous solution can be helpful in separations. However, if one must purify curium from another exclusively trivalent "lanthanide-like" impurity, a method such as ion exchange must be employed. Group separation of actinides (trivalent) from lanthanides has been described in detail; anion resin, LiCl;(32,33) cation resin, 13 M HCl;(34,35) cation resin, 20% ethyl alcohol - saturated HCl.(68) Although probably not useful for Cm^{242} in macro amounts because of the effects of alpha activity, NH_4SCN, Dowex-1(36,71) would undoubtedly prove to be a good method for the separation of curium from the lanthanides.

For the separation of americium and curium, several ion exchange techniques discussed in the tracer americium section are applicable. These are citrate, tartrate, lactate, and α-hydroxyisobutyrate.

Oxidation-reduction cycles can be used in a solution containing americium and curium, e.g., the americium can be oxidized to the (V) or

(VI) state, the curium remaining trivalent throughout.(65) The concentration of Cm^{242}/ml is a critical factor in the oxidation of Am(III) to Am(VI). It was found that Cm^{242} concentrations > 0.5 mg/ml prevented the persulfate oxidation of Am(III) to fluoride-soluble Am(VI).(65) On lowering the Cm^{242} concentration to 0.16 mg/ml, quantitative oxidation to Am(VI) was obtained. Similar experience was reported by Crane and Perlman.(104)

The oxidation of Am(III) to insoluble Am(V) in potassium carbonate has been used by several workers(8,44,63) as a separation from curium. It seems less sensitive to the alpha activity of Cm^{242}. Concentrations ranging up to 0.32 mg/ml were used in 2 M, 3 M and saturated K_2CO_3 solution with the Am(V) precipitate containing 0.2 - 2% of the curium after a single precipitation.(65)

A convenient small-scale separation for americium and curium involves treatment of a slurry of the mixed trivalent hydroxides in 0.03 M $NaHCO_3$ with ozone at 92°.(44) The americium is oxidized to the soluble Am(VI) complex; the curium hydroxide is unchanged and may be separated by centrifugation and dissolved in any desired acid. Decontamination factors from americium of 2-3 per cycle can be obtained by this technique.

3. Spectrum of Cm(III)

The recent discovery(105) of prominent absorption peaks in the near u.v. spectrum of aqueous Cm(III) using Cm^{244} has analytical uses. The spectrum is given in Figure 4. The three major peaks obey Beer's Law and may be used for quantitative determinations.

4. The Tetravalent State - Cm(IV)

Only two compounds have been studied which contain tetravalent curium, the dioxide, CmO_2(106) and CmF_4.(107) These are prepared only under stringent conditions using oxygen or elemental fluorine. Such compounds were found to be isostructural with oxides and fluorides of the other tetravalent actinides. Attempted dissolution of these compounds resulted in the oxidation of water and the immediate appearance of Cm(III).

5. Separations of Curium from Other Elements

Detailed procedures will be given in the following section. The general methods were mentioned under trivalent curium.

Solvent extraction techniques with TBP have been applied. For a gross removal of lanthanides and actinides, TBP extraction from salted solutions is effective. A distribution coefficient of ca. 100 was reported(108) for curium into undiluted TBP from an aqueous phase 7.2 M $NaNO_3$ and 0.4 M HNO_3.

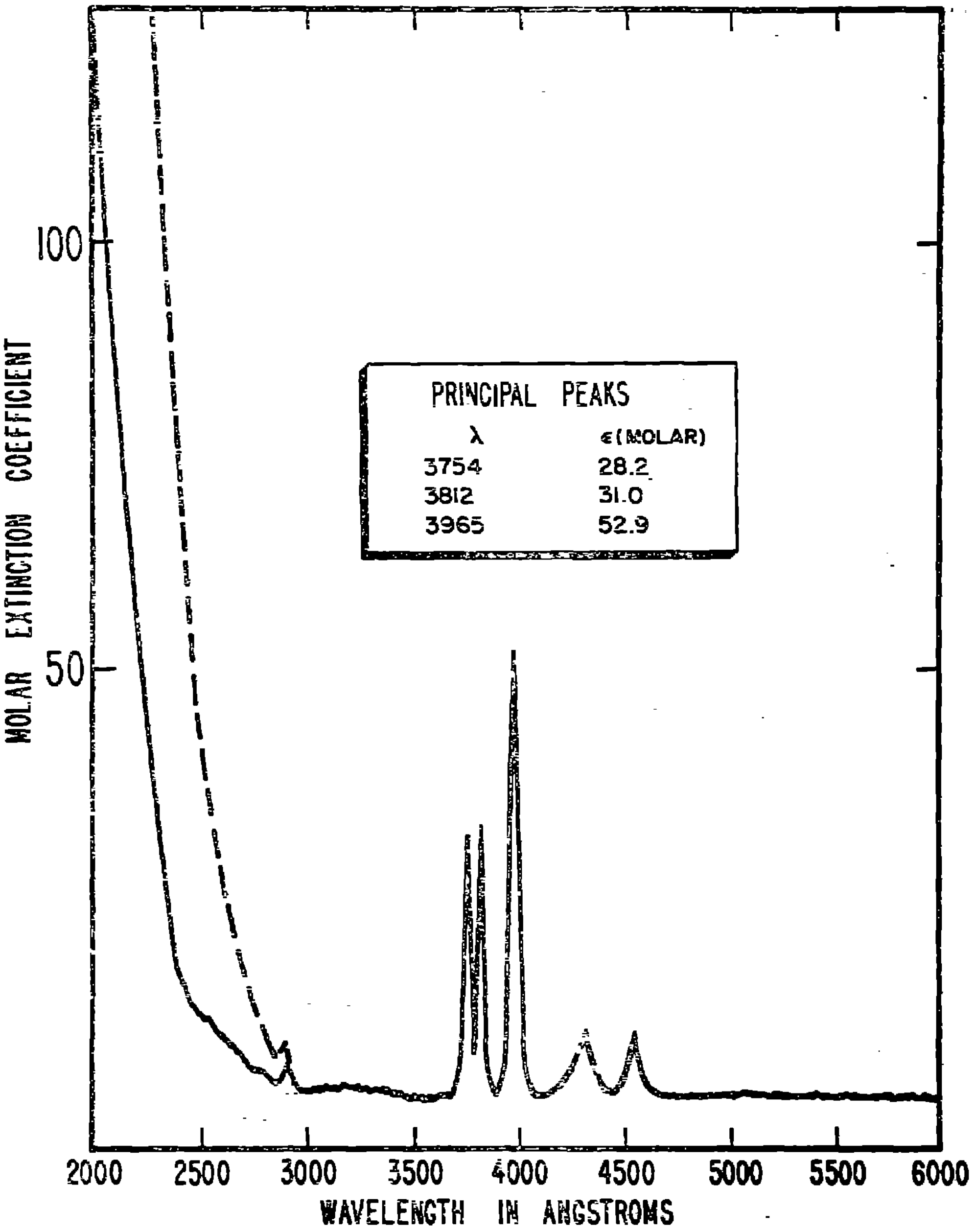

Fig. 4 Absorption Spectrum of Aqueous Cm III — 98.7 Hours

IV. COUNTING TECHNIQUES

Alpha emitting isotopes can be determined by the usual counting techniques and an excellent general discussion is given elsewhere.(109) Where several alpha emitters are present, use of an alpha energy analyzer is necessary.

As both an alpha and gamma emitter, Am^{241} can be determined by counting either type of radiation. A method has been reported(110) for absolutely calibrating such counting instruments. A detailed procedure for gamma counting americium is given in the following section.

Platinum is used classically for counting discs but these are expensive unless cleaned and re-used. However, 3 - 5 mil stainless steel (for nitrate solutions) and tantalum discs are in general use. These may be discarded after one use. Metal plates have the advantage that they can be heated inductively. Glass microscope cover glasses are used in some laboratories. Since they are of soft glass, they must be flamed with caution.

V. COLLECTION OF DETAILED RADIOCHEMICAL PROCEDURES

PROCEDURE 1

GAMMA COUNTING PROCEDURE FOR AM^{241}

Source: J. Bubernak, M. S. Lew, G. M. Matlack, Anal. Chem., 30, 1759 (1956).

This procedure was developed for the determination of $americium^{241}$ in the presence of plutonium. It takes advantage of the fact that the gamma to alpha activity ratio for $americium^{241}$ is many times greater than it is for plutonium. It cannot be used in the presence of fission products or where there has been an enrichment of the uranium daughters of plutonium, particularly 6.8 day U^{237}.

Counter Calibration. Greatest sensitivity is obtained with a well-type scintillating crystal, such as Harshaw 7F8 NaI(Tl) crystal, coupled to a 2 inch multiplier phototube (Dumont 6292). The phototube output, after going through a pre-amplifier such as the Model 205-B, Atomic Instrument Co., is led into a scaler whose trigger sensitivity is set at 10 millivolts. Under these conditions and with an $americium^{241}$ sample prepared as described below, a specific activity of about 2×10^6 gamma counts per minute per microgram of americium is found when the high voltage for the phototube is set in the vicinity of 1000 volts. The exact voltage will vary from one phototube to another. The specific activity of plutonium at this voltage is approximately 80 counts per minute per microgram. For maximum stability it is desirable to set the voltage so that the lower cut-off point of the counter lies in the valley between the 59.6 kev gamma peak of americium^{241} and that at 28 kev (the unresolved combination of the 26 kev gamma and the escape peak at 31 kev). This adjustment may be made, without the aid of a pulse-height analyzer, by inserting an americium sample in the well, and determining a "plateau" curve for the counter, using the phototube high voltage as the variable. Plotting the differential of this curve yields the gamma spectrum of the americium sample versus phototube voltage, from which the voltage for the desired cut-off point may be determined.

Calibrate the counter with known amounts of pure plutonium and pure americium, preparing the samples as described under "Procedure". The plutonium standard must also be alpha counted in order to obtain the plutonium alpha to gamma activity ratio, which is used when samples containing both americium and plutonium are gamma counted.

Procedure. The procedure given below is for samples which contain both americium and plutonium. If only americium is present, Steps 1, 4 and 5 may be omitted.

1. Determine the total alpha activity of the sample by counting a suitable aliquot in a 2 π-proportional alpha counter. It may be necessary to dilute the sample before performing this step.
2. Transfer 2 milliliters of the sample or diluted sample to a 13 x 100 millimeter test tube, being careful not to leave any drops on the side walls. If it is expected that 2 milliliters will give an excessively high gamma count rate, use a smaller aliquot, then add sufficient 1 M nitric acid to make the volume 2.0 ± 0.1 milliliters. Stopper the tube with a cork.
3. Place the tube in the well of a Type 7F8 Harshaw NaI(Tl) crystal, and gamma count for a suitable length of time.
4. If plutonium is present, assume that the total alpha activity found in Step 1 is from plutonium and compute the corresponding gamma activity from the plutonium alpha-gamma activity ratio.
5. Subtract this from the total gamma activity to obtain the americium gamma activity. Even if most of the alpha activity is americium, the assumption made in Step 4 will introduce an error which is never greater than 0.2 percent.

PROCEDURE 2

DETERMINATION OF AMERICIUM IN PLUTONIUM PRODUCT SOLUTIONS

Source: H. R. Schmidt, HW-25927, (1952), $1.80 (ph OTS), $1.80 (mf OTS), based on work by

H. W. Miller, HW-22267, (1951), $0.10 (OTS), and

A. Chetham-Strode, Jr., HW-25205, (1952), $1.80 (ph OTS), $1.80 (mf OTS).

Principle and Limitations. Americium is determined in the presence of large amounts of plutonium by oxidizing the plutonium quantitatively to the fluoride-soluble plutonyl state and subsequently precipitating americium trifluoride with cerium fluoride carrier. In samples of high plutonium to americium ratios, significant amounts of the plutonyl ion are carried with the americium by mechanisms of adsorption and occlusion. The cerium-americium fluoride is therefore dissolved with zirconium and reprecipitated from a solution of greatly reduced plutonium concentration.

The entire procedure is carried out in the presence of a small amount of dichromate, which serves as a holding oxidant for the plutonium.

Reducing agents in the sample interfere with the determination and must be eliminated.

Procedure. Pipet an aliquot containing 1 x 10^6 total alpha d/m into a 3 ml. centrifuge cone and dilute to 2 ml. with 2 M HNO_3. Transfer the cone to a water bath and heat for 15 min. at 85-95°C.

Add four drops (250 µl) of 0.1 M ceric sulfate in 1 M H_2SO_4 and digest for 15 min. at 85-95°C. Remove the cone and cool to room temperature.

Add 10 drops (500 µl) of 27 M HF which has been previously treated with $Cr_2O_7^=$ and stored in a platinum container. Digest the precipitate for 5 min. at room temperature, centrifuge, and discard the supernate.

To the precipitate add one drop of 0.05 M $Cr_2O_7^=$, 3 drops of 0.1 M $ZrO(NO_3)_2$, and 2 ml. of 2 M HNO_3. Stir until the precipitate dissolves. Reprecipitate the fluorides by the addition of 10 drops of the dichromate-treated HF. Digest 5 min. and centrifuge as before.

Wash the precipitate three times with a 1 M HNO_3 - 1 M HF solution previously treated with a few drops of dichromate. Slurry the precipitate with a few drops of the wash liquid and transfer to a platinum disc for counting.

PROCEDURE 3

DICHROMATE PROCEDURE FOR AMERICIUM

Source: J. Bubernak and G. M. Matlack, CMB-1, Los Alamos
Scientific Laboratory

This procedure has been used for samples which contained sufficient reducing agents to interfere with the method where cerium is used both as the oxidizing agent and carrier.

1. Transfer the sample, not more than 200 microliters, into a 3 milliliter centrifuge cone (Pyrex), and dilute to 1 milliliter with 2 M nitric acid.

2. Add two drops of lanthanum carrier (lanthanum nitrate solution containing 3 milligrams of lanthanum per milliliter), and 1 drop of 1 M potassium dichromate.

3. Stir well with platinum wire stirring rods, remove the stirring rods, then place the centrifuge cone in a boiling water bath. Remove after 25-30 minutes and place the centrifuge cone in cold water to cool to room temperature.

4. Add 3 to 4 drops of 20 M hydrofluoric acid, stir well, and allow to stand for 5 minutes. (The hydrofluoric acid should contain sufficient dichromate to give a faint yellow color, in order to counteract any reducing agents in the hydrofluoric acid.)

5. Centrifuge for 5 minutes, then remove the supernatant.

6. Wash the precipitate with 1 milliliter of 1 M nitric acid - 1 M hydrofluoric acid mixture containing a small amount of dichromate. Centrifuge 5 minutes and discard supernatant.

7. Repeat Step 6.

8. Slurry the precipitate with 1 M nitric acid, transfer quantitatively to a clean platinum plate. Evaporate to dryness, then heat to a dull red. Count in a 2 π proportional alpha chamber.

PROCEDURE 4

THE DETERMINATION OF Pu(IV) AND Am(III) IN NITRIC ACID SOLUTION

Source: T. Bruce, AECL-CRDC-805, (1958), $0.50 (AECL)

Limitations. The method is not suitable for solutions having very high Pu/Am ratios or vice versa. Uranium will not interfere but a correction is necessary for the alpha activity of uranium in the americium sources. Occasional checks, using solutions of known plutonium and americium content, are necessary.

Reagents.

(a) Zirconium solution: Dissolve 1.8 grams of zirconium oxychloride in 500 ml. of 0.1 M HCl. Centrifuge and decant the supernatant into a bottle. The zirconium concentration is about 1 mg/ml.

(b) Phenyl arsonic acid: Prepare a saturated solution. The solubility of this compound is about four grams per 100 ml at room temperature.

(c) Wash solution: 10 ml of saturated phenyl arsonic acid solution made up to 100 ml with one molar nitric acid solution.

Method.

Step I: Accurately pipette an aliquot of solution, containing about 10^5 counts of alpha activity, into a 2 ml centrifuge tube. Rinse the pipette twice with molar nitric acid solution. Add one drop of zirconium carrier solution and dilute to one ml with molar nitric acid solution. Mix thoroughly and add two drops of saturated phenyl arsonic acid solution. Let stand for about five minutes to allow the precipitate to settle, then place the centrifuge tube in a boiling water bath for five minutes to coagulate the precipitate. Cool and centrifuge for several minutes. Transfer the supernatant to a 2 ml volumetric flask and wash the precipitate once with 10 drops of wash solution. Centrifuge and transfer the wash to the 2 ml volumetric flask.

Step II: Make the supernatant solution up to exactly 2 ml. Accurately pipette an aliquot of the supernatant, containing less than 300 μgms of uranium, on a stainless steel source tray. Rinse the pipette twice with dilute nitric acid solution. Add sufficient concentrated ammonium hydroxide to neutralise the nitric acid. Evaporate to dryness, then decompose the salts with gentle heat. Ignite and count the source with an alpha counter.

Step III. Slurry the precipitate with a few drops of water and transfer to a stainless steel source tray. Rinse the centrifuge tube and transfer pipette several times with water. Neutralize the nitric acid with concentrated ammonium hydroxide. Evaporate to dryness then heat gently to decompose the ammonium nitrate and zirconium chelate. Ignite and count the source with an alpha counter.

Calculations.

Symbols: C sup = cpm per source of supernatant,
A sup = aliquot of supernatant in microlitres,
A_o = aliquot of original solution in microlitres,
U = micrograms of uranium per source multiplied by 0.75,
Cppt = cpm per source of precipitate.

Americium: $(\text{C sup} - \text{U}) \times \frac{2{,}000}{\text{A sup}} \times \frac{1{,}000}{A_o}$ = cpm americium per ml of original solution.

Plutonium: $\text{Cppt} \times \frac{1{,}000}{A_o}$ = cpm plutonium per ml of original solution.

PROCEDURE 5

CHEMICAL PROCEDURES USED IN BOMBARDMENT WORK AT BERKELEY

Source: W. W. Meinke, AECD-3084, Decl. 1951, $0.20 (OTS)

Element separated: Americium
Target material: $(NH_4)_2PuF_6$ ~ 10 mg
Type of bbdt: 60" and 184"
Procedure by: K. Street
Time for sep'n: ~ 1.5 hr.
Equipment required: 50 ml beaker, 15 and 5 ml centrifuge cones, 2 mm by 5 cm cation exchange resin column

Yield: Better than 50%

Degree of purification: Eliminates all other activities except Cm by factor of ~ 10^6. Decontamination from Pu ~ 10^8.

Advantages: It works.

Procedure:

(1) Scrape target material into beaker and dissolve in 1 ml 16 M HNO_3 and 0.5 ml sat. H_3BO_3.

(2) Wash into 15 ml cone, add 0.2 mg La^{+++} and ppt with 15 M NH_4OH.

(3) Centrifuge, wash, and dissolve in 10 M HNO_3 + 0.03 M Fe^{+++}. Add $NaBiO_3$ and heat at ~ 70° for 5 min. Dilute to 3 M in H^+ and add H_3PO_4 to 1 M. Centrifuge and transfer supnt to clean cone.

(4) To supnt add "preoxidized HF" to 1 M, centrifuge and wash ppt.

(5) Slurry ppt and transfer to 5 ml cone. Dissolve ppt (LaF_3) in 1 drop sat H_3BO_3 and 2 drops conc. HNO_3. Add ~ 0.5 mg Ba^{++} holdback, ppt with conc. NH_4OH, and wash.

(6) Repeat steps (3), (4), and (5), adding ~ 0.5 mg Zr^{++++} after dissolving ppt in HNO_3 at start of step (3).

(7) Dissolve in 2 drops 0.5 M $HClO_4$ and transfer to 5 ml cone containing 25 λ resin. Stir for 5 min, centrifuge and remove supnt.

(8) Transfer both batches of resin to a 2 mm x 5 cm ion exchange column that has been washed with ~ 13.5 M HCl. Elute with 13.5 M HCl at a flow rate of ~ 1 ml/cm²/min. Am comes off at 3/4 to 1 ml.

Remarks:

If target material has been heated excessively it may be necessary to fume with H_2SO_4 in order to dissolve it.

Preoxidized HF is prepared by adding small amount of $KMnO_4$ to HF until color persists.

PROCEDURE 6

CHEMICAL PROCEDURES USED IN BOMBARDMENT WORK AT BERKELEY

Source: W. W. Meinke, AECD-3084, Decl. 1951, $0.20 (OTS)

Element separated: Curium
Target material: $(NH_4)_2PuF_6$ ~ 10 mg
Type of bbdt: 60" and 184"

Procedure by: K. Street
Time for sep'n: 1.5 to 24 hr.
Equipment required: 50 ml beaker, 15 and 5 ml centrifuge cones, 2 mm x 5 cm cation exchange resin column + 1 mm x 10 cm cation exchange column.

Yield: Better than 50%

Degree of purification: Eliminates all other activities by a factor of ~ 10^6. (Am to varying degree)

Procedure:

(1) Scrape target material into beaker and dissolve in 1 ml 16 M HNO_3 and 0.5 ml sat. H_3BO_3.

(2) Wash into 15 ml cone, add 0.2 mg La^{+++} and ppt with 15 M NH_4OH.

(3) Centrifuge, wash, and dissolve in 10 M HNO_3 + 0.03 M Fe^{+++}. Add $NaBiO_3$ and heat at ~ 70° for 5 min. Dilute to 3 M in H^+ and add H_3PO_4 to 1 M. Centrifuge and transfer supnt to clean cone.

(4) To supnt add "preoxidized HF" to 1 M, centrifuge and wash ppt.

(5) Slurry ppt and transfer to 5 ml cone. Dissolve ppt (LaF_3) in 1 drop sat H_3BO_3 and 2 drops conc. HNO_3. Add ~ 0.5 mg Ba^{++} holdback, ppt with conc. NH_4OH, and wash.

(6) Repeat steps (3), (4), and (5), adding ~0.5 mg Zr^{++++} after dissolving ppt in HNO_3 at start of step (3).

(7) Dissolve in 2 drops 0.5 M $HClO_4$ and transfer to 5 ml cone containing 25 λ resin. Stir for 5 min, centrifuge and remove supnt.

(8) Transfer both batches of resin to a 2 mm x 5 cm ion exchange column that has been washed with ~ 13.5 M HCl. Elute with 13.5 M HCl at a flow rate of ~ 1 cm^2/min. Am comes off at 3/4 to 1 ml.

(9) Elution with 13.5 M HCl brings off Am and Cm at about the same time, however, Am is eluted slightly ahead of Cm and consequently one can obtain samples rich in Am and samples rich in Cm.

(10) For further separation of Cm from Am it is necessary to run an elution with 0.25 M ammonium citrate at pH 3.05.* Time of elution varies considerably with batch of resin used and requires from 12 to 24 hr for a good separation.

Remarks:

If target material has been heated excessively it may be necessary to fume with H_2SO_4 in order to dissolve it.

Preoxidized HF is prepared by adding small amount of $KMnO_4$ to HF until color persists.

PROCEDURE 7

SEPARATION OF Am FROM Cm BY SOLVENT EXTRACTION

Source: D. F. Peppard and G. W. Mason (to be published),
Argonne National Laboratory, Lemont, Illinois (1959)

This method utilizes the extractability of Am(VI) into a solution of HDEHP(DEP) (di(2-ethyl hexyl) orthophosphoric acid) in toluene in the presence of trivalent species such as Cm(III). It is recommended that this procedure be reserved for macro amounts of americium since Am(VI) tracer is sometimes difficult to maintain in an oxidized condition. The distribution coefficient, K_a^0, for Am(VI) is ca. 1000. The efficiency of the process is > 99% with respect to recovery of americium.

1. The sample of Am - Cm is evaporated to dryness in a steam bath, then taken up in 5-10 ml of 0.1 M HNO_3. The solution is made 0.1 M with respect to $(NH_4)_2S_2O_8$, and warmed to 80°C for 20-30 min., following which it is cooled in an ice bath for 3-4 min., then immediately extracted as follows:

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*Editors' Note:

Separation with α-hydroxy-isobutyrate would also be adequate.

2. The aqueous phase is contacted twice for 3-5 min. intervals with separate equal volumes of pre-oxidized 0.3 M DOF in heptane. Pre-oxidation of the solvent is accomplished by agitation with an equal volume of 0.1 M HNO_3 + 0.1 M $(NH_4)_2S_2O_8$ for approximately 30 min. just prior to use.

3. The two organic fractions are separately scrubbed twice for 30 sec per contact with 0.1 M HNO_3 + 0.1 M $(NH_4)_2S_2O_8$. The volume of scrub should be 1-4 to 1-3 the volume of organic.

4. The Am is then re-extracted by contacting the organic layer with 6.0 M HNO_3 containing a trace of H_2O_2.

5. It is important to wash both the original aqueous (Cm solution) and the final re-extract (Am in 6.0 M HNO_3) thoroughly with heptane directly after the extraction is completed to completely remove traces of HDEHP.

PROCEDURE 8

THE OXIDATION OF AMERICIUM TO THE SEXAVALENT STATE

Source: M. Ward and G. A. Welch, J. Chem. Soc., 1954, 4038

In most of the experiments the percentage of sexavalent americium was followed by making use of the fact that, unlike trivalent americium, it is not coprecipitated on lanthanum fluoride. In a typical experiment in which 99% oxidation was obtained, the americium solution (containing 2×10^5 α d/m) was pipetted into a 3-ml centrifuge tube, and made 0.3 M* with respect to nitric acid, the final volume being 1 ml. One drop of 10% silver nitrate* and 8 drops of 5% ammonium persulfate solution were added and the mixture was heated in boiling water for 4 min. A further 8 drops of 5% ammonium persulfate were added and the tube heated for a further 2 min. Lanthanum carrier (0.5 mg) was added as nitrate solution and the unoxidized americium coprecipitated on lanthanum fluoride by the addition of ammonium fluoride solution. The ammonium fluoride was treated with argentic nitrate just before use to prevent any reduction of the americium by impurities in the fluoride. The lanthanum fluoride was centrifuged out, then washed twice, and its americium content determined by alpha-counting.

*Editors' Note:

We recommend 0.1 M HNO_3 for the oxidation and do not believe the silver nitrate catalyst is necessary in this oxidation. See Procedure 7.

PROCEDURE 9

AMERICIUM - CURIUM PURIFICATION

Source: R. W. Hoff, E. K. Hulet, and G. H. Coleman,
Ernest O. Lawrence Radiation Laboratory, Livermore,
California (1959)

This procedure was developed to purify tracer quantities of isotopes of americium and curium from a mixture of fission products and lighter actinides. No attempt was made to produce appreciable separations of americium and curium from each other. The isotopes to be determined were generally Am^{241}, Am^{242m}, and Cm^{242}. In the case of curium, purity requirements were such that a nearly massless sample be produced with less than 10^5 β d/m from an original sample of approximately 10^{14} fissions. The determination of Am^{242m} required additional decontamination from fission product beta activity. Samples containing 10^8 atoms of Am^{242m} isolated from a 1.5-day old fission mixture containing 10^{14} fissions showed 16-hour beta decay over 2-3 half-lives. The chemical yield of the procedure, exclusive of volatilization of the sample in the final step, was approximately 75 percent. The yield of the volatilization step can be varied but was generally of the order of 50 percent. The separation time for two persons to run twelve samples is approximately eight hours.

Step 1: If the isotopes to be determined are Am^{241}, Am^{242m}, and Cm^{242}, chemical yield tracers of isotopically pure Am^{243} and Cm^{244} are added in the proper amounts to the unknown solution. Care should be taken that the Am^{241}/Am^{243} and Cm^{242}/Cm^{244} alpha activity ratios favor the lower energy alpha particle (heavier mass isotope) in each case to aid in resolution of the alpha pulse analysis data.

Step 2: If the unknown solution (usually 25 ml. or less) is < 6 M HCl, add an equal volume 12 M HCl plus a few drops 16 M HNO_3. Let stand for 10 minutes. Pour the solution on a 6 cm. x 6 mm. (diam.) Dowex 1 X 10 ion exchange column which has been washed with 12 M HCl containing a few drops of 16 M HNO_3. Collect the eluate in a 40 ml. cone and wash column with 12 M HCl containing a few drops 16 M HNO_3.

Step 3: To the eluate and wash, add 1 1/2-2 drops $La(NO_3)_3$ carrier solution (10 mgs. La^{+3}/ml.) plus 0.5 ml. Zr^{+4} carrier solution (10 mg./ml.). Cool in an ice bath and precipitate a hydroxide with NH_4OH. Digest, centrifuge, and wash precipitate with dilute NH_4OH, then H_2O.

Step 4: Dissolve the hydroxide with 2-3 ml. 6 M HCl, transfer to a 20 ml. lusteroid cone, and dilute to 10 ml. volume with H_2O. Add excess conc.

HF, digest with stirring at 90° C. to precipitate LaF_3. Centrifuge and wash precipitate with 2 M HCl-2 M HF.

Step 5: Dissolve precipitate in 3 ml. saturated H_3BO_3-6 M HCl mixture. Transfer to a 12 ml. glass centrifuge cone. Precipitate $La(OH)_3$ with NH_4OH, digest, centrifuge, and wash precipitate twice with H_2O.

Step 6: Dissolve the precipitate with HCl gas and saturate the solution. Load the solution (~3 drops) on a 5 cm. x 3 mm. (diam.) Dowex 50 X 12 colloidal form ion exchange column which has been washed with 13 M HCl solution. Allow the loading solution to pass into the resin. Elute the column with a further volume of 13 M HCl at a rate of 1.5 min./drop (air pressure is generally required to reach this flow rate), collecting three drops per culture tube. Combine tubes 4, 5, and 6 into a 12 ml. cone. Evaporate to dryness.

Step 7: Repeat the column elution by adding 3 drops 13 M HCl to the dry material in the cone and loading this solution onto another Dowex 50 column as per step 6.

Step 8: Upon evaporating the combined tubes 4, 5, and 6 to a small volume after the second column elution, transfer and evaporate the solution on a tungsten filament. The counting sample is produced by volatilizing the material in a vacuum onto a one-inch diameter platinum plate.

NOTES:

1. The volatilization is necessary to obtain good resolution in the alpha particle pulse analysis and is also an aid in obtaining reproducible results in the beta counting.

2. Some interference in the beta counting of Am^{242m} will be encountered from the growth of the Np^{239} daughter of the alpha decay of Am^{243}. One can readily correct for this growth of Np^{239} activity, subsequent to its removal during the chemical procedure.

3. Although americium-curium separations found using this procedure are slight, appreciable separations can occasionally occur in the 13 M HCl Dowex 50 column step. Thus, tracers for both elements must be added if one is to determine chemical yields of each element accurately.

PROCEDURE 10

SEPARATION OF Am AND Cm FROM FISSION PRODUCTS AND OTHER ACTINIDE ELEMENTS

Source: W. T. Carnall, Argonne National Laboratory, Lemont,
Illinois (1959)

This report summarizes procedures used at ANL to separate Am and Cm from highly neutron-irradiated Al-Pu alloys.

Following dissolutions of the alloy in strongly basic solution, the slurry is centrifuged to separate the bulk of Al, as soluble $NaAlO_2$, from the solid residue containing the heavy elements. This residue is then dissolved in concentrated HCl and eluted through an anion exchange resin which retains Pu and some transition element fission products, but passes the heavier actinides and a large fraction of the fission products.

The eluate from the anion column is evaporated to dryness, taken up in dilute acid, and passed through a cation exchange resin. Under these conditions the heavy elements are retained on the column, along with various fission product nuclides. On elution with conc. HCl, three bands of activity are developed; the first and third in order of elution are characterized by β-γ active fission products. The center, α-peak contains the heavy element fraction.

The heavy elements can subsequently be resolved either by ion exchange or solvent extraction techniques. In both cases the Am and Cm are either separated in a combined fraction or as highly cross contaminated individual fractions; however a high degree of resolution from other actinides is obtained.

Final separation of Am and Cm is accomplished by one of the two following procedures. Both require prior oxidation (see Procedure 7) of Am(III) to Am(VI) in the presence of Cm(III); in one case the Am(VI) is solvent extracted away from the Cm, in the other case fluoride is added to the system resulting in the selective pptn of Cm(III).

With the solvent extraction procedure it is possible to obtain Am of high purity from a mixture of Am and Cm; however this technique will not strip the last traces of Am from an impure Cm fraction. The fluoride cycle is applicable to the preparation of pure fractions of both Am and Cm.

Since the samples of Am and Cm encountered at ANL are principally Am^{243}($t_{\frac{1}{2}}$ = 7951 y) and Cm^{244}($t_{\frac{1}{2}}$ = 17.6 y), assay is normally made by α-counting based on α-pulse analysis. However for small amounts of Am^{243} in a Cm^{244} sample, a more precise analysis can be obtained by solution absorption spectra. This is because the energies of the α-particles emitted by Am^{243} are significantly less than those from Cm^{244}. Thus upon α-pulse analysis, a small percentage of the α-particles from Am^{243} are lost in the Cm^{244} tail. Coupled with this, Am(III) has a particularly strong absorption band at 502.3 mμ which does not conflict with any of the Cm bands. Thus one should be able to detect 6.43×10^{-3} mg Am^{243}/ml or 2.76×10^{6} d/m/ml by spectral means.

PROCEDURE 11

SEPARATION OF ISOTOPES INCLUDING AMERICIUM AND CURIUM FROM A NEUTRON IRRADIATED PLUTONIUM-ALUMINUM ALLOY

Source: M. Jones, R. P. Schuman, J. P. Butler, G. Cowper, T. A. Eastwood and H. G. Jackson, Phys. Rev., 102, 203 (1956).

See Also: W. M. Manning, M. H. Studier, H. Diamond and P. R. Fields, US Patent 2,859,095 (1958).

J. P. Butler, T. A. Eastwood, H. G. Jackson, T. L. Collins, M. E. Jones, F. M. Rourke, R. P. Schuman (compiled by R. P. Schuman), KAPL-1781, (1957), $1.00 (OTS).

Essentially similar procedures for separating heavy elements from a neutron irradiated plutonium-aluminum alloy were used by Argonne National Laboratory, Lawrence Radiation Laboratory (formerly University of California Radiation Laboratory), Atomic Energy of Canada, Limited, and Knolls Atomic Power Laboratory. The scheme is outlined below:

(a) The aluminum cladding (~ 25 g) was dissolved in 175 ml of 5 M NaOH, 3.5 M $NaNO_3$ solution in a stainless steel vessel fitted with a stainless steel reflux condenser. Towards the end of the reaction the mixture was boiled to ensure complete solution. The solution was centrifuged and the insoluble residue washed with KOH solution.

(b) The insoluble residue was dissolved in 13 M HCl-0.3 M HNO_3. The lanthanide and actinide elements were then precipitated first as fluorides and, after dissolution in H_3BO_3-HNO_3 mixture, finally as hydroxides. The hydroxides were dissolved in 9.5 M HCl-0.1 M HNO_3.

(c) The plutonium was removed by passing the acid solution through anion-exchange resin column.[111] Dowex - 1, 8% cross-linked, 100-200 mesh was used in a column 0.8 cm^2 in area and 5 cm long; the flow rate was 1 cm per min.

(d) The transplutonium elements were separated from fission-product lanthanide elements by cation exchange using Dowex 50, 12% cross-linked (0.82 cm^2 by 20 cm long). The particle size was selected by grading the hydrogen form of the resin in an up-flow of water and the fraction with a settling rate between 0.75 and 1.2 cm per min was used. The elution was then done with conc. HCl at a flow rate of 0.3 cm/min.

(e) Individual actinide elements were separated from each other by cation exchange.[112] The trans-curium isotopes were separated from the bulk of the curium on a Dowex 50 column 0.78 cm^2 in area, 8.0 cm long at 87°C using ammonium lactate* (0.4 M, pH = 4.58) as the eluant. The final separation of trans-curium actinides was done in a column of area 0.031 cm^2, 5 cm long using white Dowex 50, 12% cross-linked, settling in water at a rate of 0.30-0.60 cm/min, with ammonium lactate (0.4 M, pH = 4.18) as eluant. To obtain pure samples of einsteinium and fermium, one or more of steps (b) to (e) were repeated when necessary.

PROCEDURE 12

PROCEDURE FOR THE SEPARATION OF TRACER AMOUNTS OF TRANSPLUTONIUM ELEMENTS FROM FISSION PRODUCTS

Source: D. C. Hoffman, J. W. Barnes, H. L. Smith, W. R. Daniels, J-11, Los Alamos Scientific Laboratory

The following procedure was devised to separate the transplutonium elements from day-old fission product samples containing 10^{15} to 10^{16} fissions. These elements are carried with yttrium or lanthanum fluoride and hydroxide precipitates which are subsequently dissolved and the HCl solutions passed through several anion resin columns to remove U, Np, Pu, and most of the remaining fission products (in particular, Zr and Te). An ethanol-HCl elution from a cation resin column[113] is used to remove the lanthanides. Final separation of the individual transplutonics is accomplished by elution from a cation resin column with ammonium α-hydroxy-isobutyrate.[114]

Reagents

Y carrier: 10 mg Y/ml [added as $Y(NO_3)_3 \cdot 6\ H_2O$ in H_2O]

La carrier: 5 mg La/ml [added as $La(NO_3)_3 \cdot 6\ H_2O$ in H_2O]

Zr carrier: 10 mg Zr/ml [added as $ZrO(NO_3)_2$ in 1 M HNO_3]

Te carrier: 10 mg Te/ml [added as Na_2TeO_3 in 1 M HCl]

*Editors' Note:

Ammonium α-hydroxy-isobutyrate is now used.

Sr carrier: 10 mg Sr/ml [added as $Sr(NO_3)_2 \cdot 4\ H_2O$ in H_2O]

NH_4OH: conc

HCl: 0.1 M, 0.5 M, 3 M, conc

10 M solution I: 0.1 ml conc HNO_3 per 15 ml 10 M HCl

HF: conc

$HF-HNO_3$: equal volumes of 2 M solutions

HF-HCl: solution 0.006 M in HF and 0.1 M in HCl

HNO_3: conc

H_3BO_3: saturated solution

Phenolphthalein indicator solution

Ethanol-HCl elutriant: 20% ethanol - 80% conc HCl (by volume) saturated with HCl gas at room temperature. (If a cold solution is passed through a resin column, bubbles will form, disturbing the resin bed.) This solution should be prepared just prior to use.

Ammonium α-hydroxy-isobutyrate elutriant:

The stock solution of α-hydroxy-isobutyric acid is prepared (usually 0.5 or 1 M), and kept refrigerated to inhibit possible mold formation. The compound may be obtained from Fairmount Chemical Company, Newark, New Jersey. From the stock solution, small quantities are withdrawn and partially neutralized with ammonium hydroxide to obtain elutriant of the desired pH. The pH of the elutriant should be chosen so as to elute the activities in a convenient volume, considering the column volume and the speed with which the separation must be made. If 0.5 M isobutyrate is used, the peak position in FCV (free column volume units) may be estimated directly from Table I and Fig. 1. If stronger or weaker acid is used, the pH corresponding to a given anion activity (as shown in Fig. 2) must be calculated, using the relationship

$$K_1 = \frac{(H^+)(A^-)}{(HA)} \simeq \frac{10^{-pH}(A^-)}{(M_{HA}) - (A^-)}$$

or

$$10^{-pH} \simeq \frac{K_1\ [(M_{HA}) - (A^-)]}{(A^-)}$$

where $K_1 \simeq 10^{-3.8}$

(M_{HA}) = molarity of α-hydroxy-isobutyric acid

(A^-) = anion activity (isobutyrate) read from Fig. 2

Anion exchange resin: Bio-Rad* AG 1-X10, 100-200 mesh for large columns and 200-400 mesh for the small column. The resin is stored as a slurry in H_2O

Cation exchange resins: Bio-Rad AG 50-X4, 400 mesh or finer. The resin is prepared by washing in succession with H_2O, NH_4OH, H_2O and three times with conc HCl. For the ethanol-HCl columns, the resin is stored as an HCl slurry. For the slurry in H_2O, the resin should be washed an additional three times with H_2O.

Dowex 50 cation resin is used for the butyrate column, from 2-8% DVB (% divinylbenzene which is proportional to cross-linkage), depending on individual preference and what is available. Time required for attainment of equilibrium and volume required for elution increase with percentage DVB of the resin. The data in the accompanying graphs were taken with 4% resin. The resin should be very fine, 400 mesh or finer; or if wet-graded, that fraction which settles at a rate of 0.1-0.5 cm/min. If the resin has not been specially treated by the supplier, it should be washed thoroughly with 6 M ammonium thiocyanate, 6 M ammonium hydroxide, water, and hydrochloric acid, then stored as the ammonium form in water. (If no resin can be found that achieves a good separation at room temperature, 12% DVB Dowex 50 may usually be used successfully with a column heated to 80-90° C.)

Ion exchange columns: The column tip is plugged with glass wool or sand. A slurry of resin is introduced and allowed to settle, and the supernate discarded. The resin is washed by passing several ml of elutriant through the column. (Just prior to use, the butyrate column is slurried with the elutriant and allowed to settle again.) A uniformly deposited bed of resin, free from air bubbles or channels, is essential to a successful elution. The free column volume is approximately equal to half the apparent volume of the resin bed.

Equipment

Centrifuge

Block for holding centrifuge tubes

Fisher burner

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* Specially purified and graded resins may be obtained from Bio-Rad Laboratories, 32nd and Griffin Avenue, Richmond, California. For some reason, resins vary from batch to batch in their ability to achieve various separations, so it is recommended that several samples of resin be tried before discarding the method.

Glass stirring rods

Pt wire stirring rods

Transfer pipettes and syringes

Vacuum trap for withdrawing supernates (optional)

40-ml conical centrifuge tubes

3-ml conical centrifuge tubes

15-ml polyethylene test tubes

Ion exchange columns (fabricated by fusing a length of glass tubing to a centrifuge cone and drawing out the tip)

6-cm x 2-mm I.D. glass columns

14-cm x 2-mm I.D. glass columns

12-cm x 8-mm I.D. glass columns

Procedure

Step 1. To an aliquot of the sample in a 40-ml centrifuge tube, add 2 drops each of Zr, Te and Sr carriers and 1 drop of Y carrier. Using phenolphthalein indicator, add NH_4OH to precipitate the $Y(OH)_3$. Centrifuge, discard the supernate, and wash the precipitate twice with 0.5-1.0 ml H_2O.

Step 2. Dissolve the precipitate in a minimum amount of 3 M HCl and transfer to a polyethylene test tube. Add 2 drops conc HF per ml of solution. (If the solution contains a large amount of Fe or U add HF to decolorize the solution, then 2 drops per ml in addition.) Let the solution stand for five minutes, centrifuge, discard the supernate, and wash the precipitate with 0.5 ml of the 2 M HF-2 M HNO_3 solution.

Step 3. Dissolve the fluoride precipitate by adding 1 drop saturated H_3BO_3, stirring, and then add 2 ml conc HCl. Transfer the solution to a 40-ml glass centrifuge tube. Add 2 drops Sr carrier and then boil the solution briefly. Precipitate the $Y(OH)_3$ with NH_4OH, centrifuge, discard the supernate, and wash the precipitate twice with 0.5-1.0 ml H_2O.

Step 4. Dissolve the precipitate in 3 ml 10 M HCl. Add 1 drop conc HNO_3. Transfer the solution to a 5-cm x 2-mm AG 1 anion resin column which has been washed with several column volumes of 10 M solution I. Push through with pressure. After adding 1 drop each of Zr and Te carriers, pass the solution through two additional 10-cm x 8-mm anion columns which have also been treated with 10 M solution I. Wash the centrifuge tube and then all three columns in succession with two 3-ml portions of 10 M solution I. (The small column contains the Pu, which can be determined by the procedure described in LA-1721.)*

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* Collected Radiochemical Procedures, (Radiochemistry Group J-11), J. Kleinberg, Ed., LA-1721, 2nd Ed. (1958), $2.50 (OTS).

Step 5. Add NH_4OH to the combined 10 M solution I fractions to precipitate $Y(OH)_3$. Centrifuge, discard the supernate, and wash the precipitate twice with 0.5 ml H_2O.

Step 6. Dissolve the precipitate in a minimum amount of 0.1 M HCl and pass the solution through a 1-cm x 2-mm AG 50 cation resin column which has been previously washed with several column volumes of 0.1 M HCl. Wash the column with 1 ml of 0.1 M HCl, then 2 ml of the 0.006 M HF-0.1 M HCl solution, and finally 1 ml 0.5 M HCl.*

Step 7. Using a transfer pipet and a minimum of H_2O, transfer the cation resin from the 1-cm column to the top of a 12-cm x 2-mm Dowex 50 resin column which has been previously washed with several column volumes of the ethanol-HCl elutriant. After the resin has settled, withdraw the excess H_2O and wash out the column above the resin with a small portion of ethanol-HCl. Elute the activity with the 20% ethanol-HCl solution using sufficient pressure to give approximately 1 drop every 45 seconds. Collect the desired fraction† in a 40-ml centrifuge tube. (See Fig. 3)

Step 8. Place the tube containing the sample in an oil or steam bath and evaporate to approximately 0.5 ml, using a stream of air over the solution if rapid evaporation is desired. Add a drop of lanthanum nitrate solution (5 mg La/ml), and transfer the sample to a 3-ml centrifuge cone. The final solution should consist of 1.5 ml of 2-4 M HCl.

Step 9. Precipitate $La(OH)_3$ with gaseous ammonia or carbonate-free ammonium hydroxide. Centrifuge, discard supernate, and wash the precipitate with 0.5 ml of water.

Step 10. Dissolve the precipitate in a few drops of 0.1 M HCl and equilibrate this solution with a quantity of resin which is small with respect to the size of the column. For example, if a 15-cm column is being used, 2-4 mm of the resin may be withdrawn with 0.1 M HCl and used for the equilibration. Transfer the slurry carefully to the column reservoir and allow to settle. Withdraw the supernatant liquid and discard.

Step 11. Introduce carefully several ml of the elutriant, so as not to disturb the active band at the top of the column. Apply slight air pressure, if necessary, to produce a flow rate of a drop every 1-3 minutes. (Pressure may be applied with a 10-ml syringe fitted with a rubber stopper,

---

* The small cation column was used as an alternative to equilibrating and washing the resin in a test tube and then transferring the resin to the top of the column. It seemed to be more rapid, give better decontamination and necessitate less direct handling of the rather "hot" solution.

† Essentially no separation of Am and Cm was observed in these ethanol-HCl elutions.

or, more conveniently, from a pressure reduction valve attached to a source of compressed air.)

Step 12. Collect the effluent dropwise on platinum plates or in 1-ml beakers. Assay all fractions and combine the drops which comprise a peak. If additional chemistry is necessary, the butyrate may be destroyed by evaporating the solution to dryness, then destroying residual organic matter with nitric and perchloric acids.

TABLE I

Separation Factors with Ammonium α-hydroxy-isobutyrate

(Cm = 1.0)

Element	Relative Peak Position
Es	0.13
Cf	0.19
Bk	0.37
Cm	1.00
Am	1.39
Lu	0.011
Yb	0.016
Tm	0.022
Er	----
Ho	0.039
Y	0.069
Dy	0.076
Tb	0.14
Gd	0.22
Eu	0.34
Sm	0.7
Pm	1.1
Nd	2.3
Ce	3.4

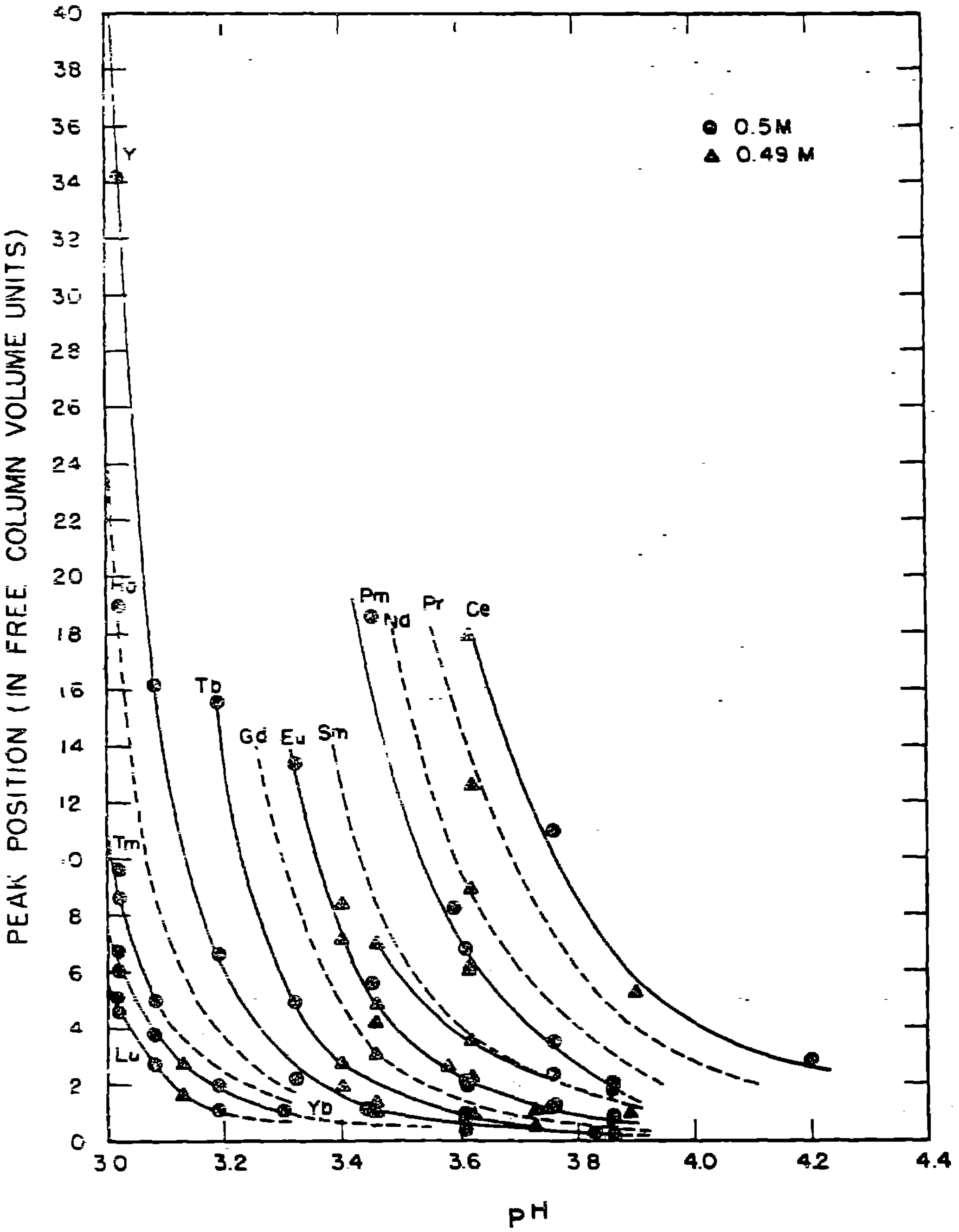

Fig. 1

Lanthanide Elution Positions vs. pH with 0.5 M

α-hydroxy-isobutyric Acid

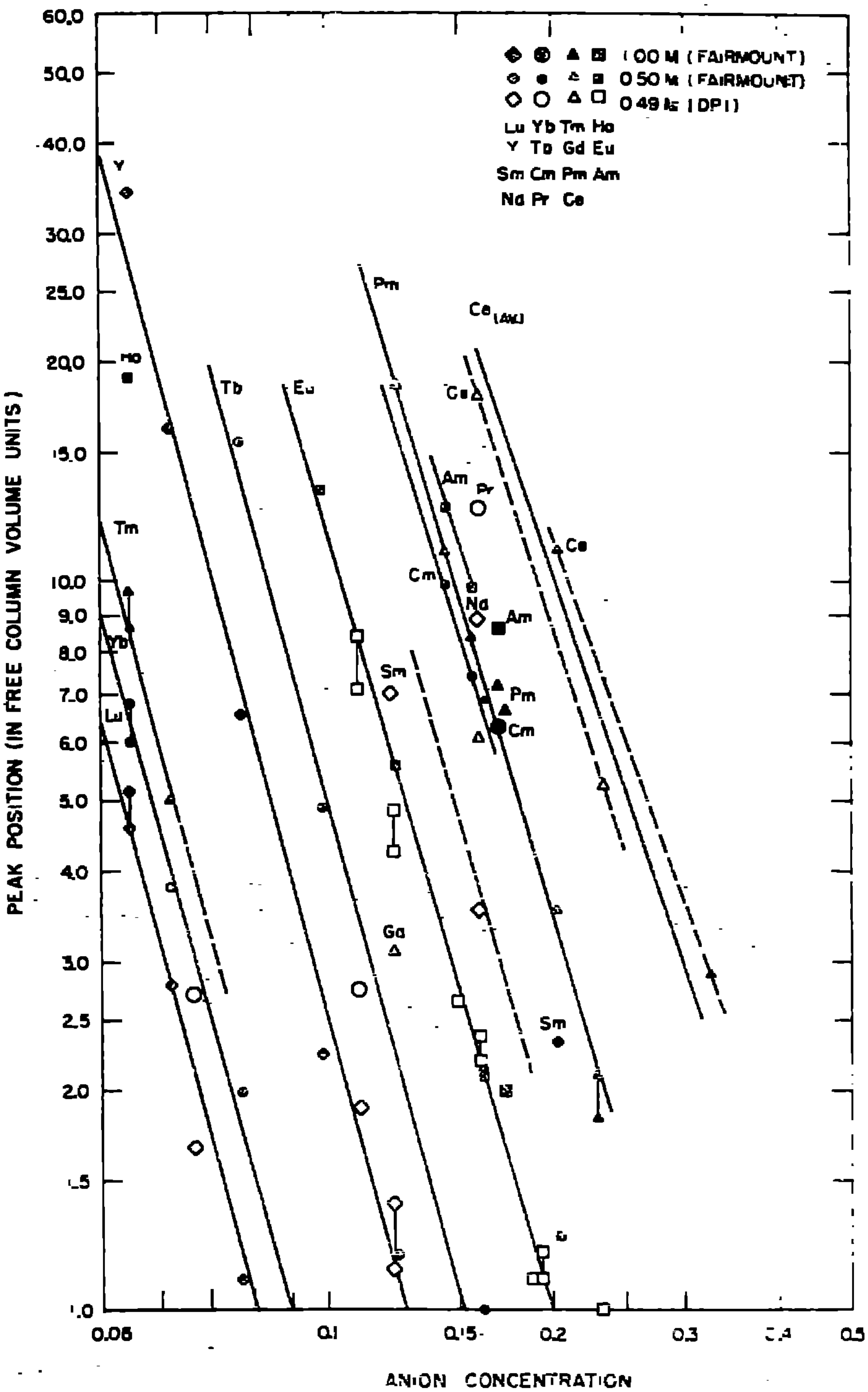

Fig. 2 Lanthanide and Actinide Elution Positions vs. α-hydroxy-isobutyrate Anion Concentration

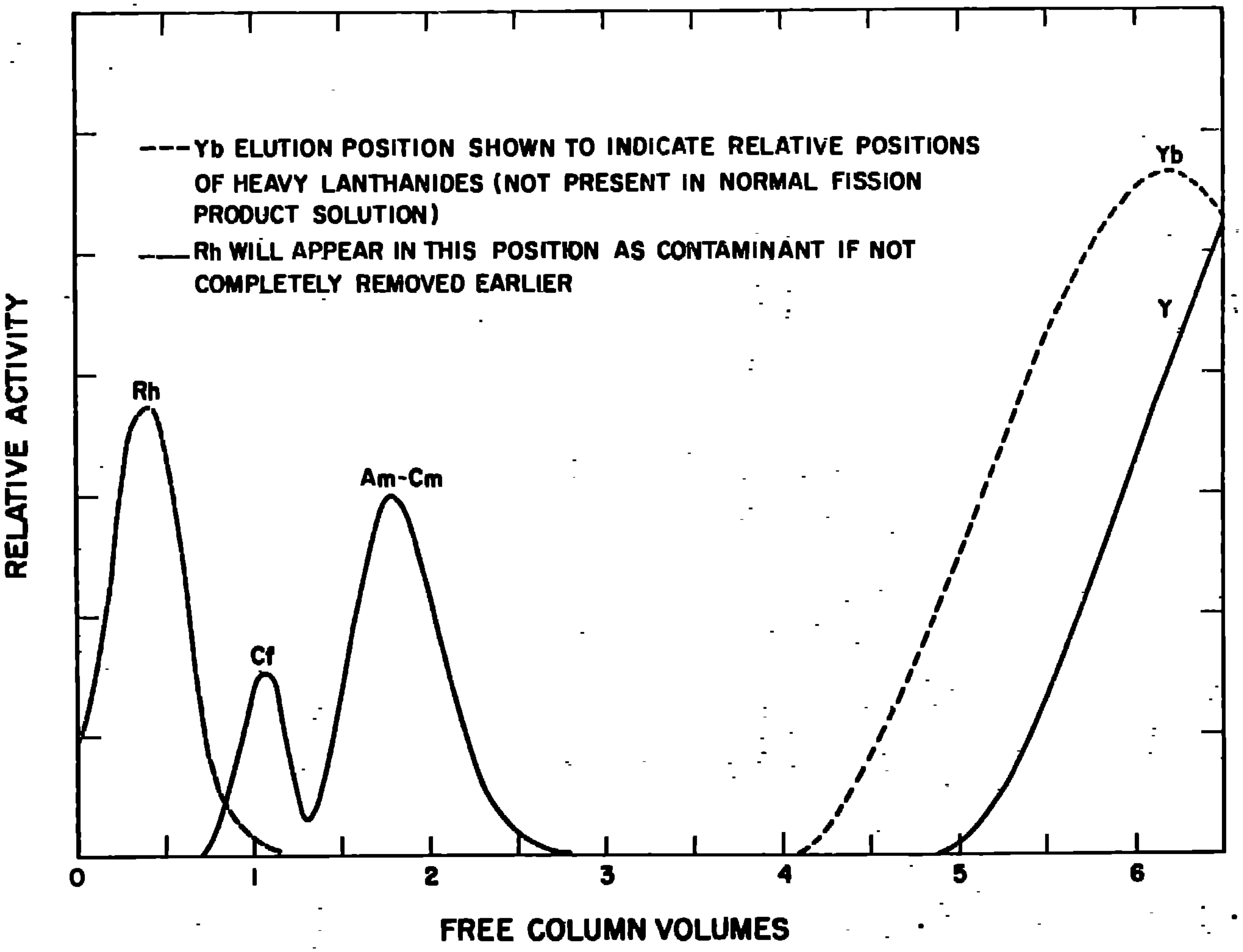

Fig. 3 20% Ethanol-Saturated HCl Elutions from AG 50-X4 Cation Resin

PROCEDURE 13

SEPARATION OF AMERICIUM AND PROMETHIUM

Source: R. S. Pressly, ORNL-2202, TID-4500, (1957), \$1.80 (ph OTS), \$1.80 (mf OTS).

See Also: S. G. Thompson, L. O. Morgan, R. A. James, and I. Perlman, "The Transuranium Elements," NNES IV-14B, McGraw-Hill Book Company, Inc., New York, N. Y., 1949, pp 1339-1361.

A method for the separation of promethium from americium has been developed. Americium remains soluble while promethium fluoride is selectively precipitated from a solution of 3 M hydrofluosilic acid upon heating.

1. To approximately 100 ml of 8.0 M HNO_3 solution of Pm^{147} (~ 0.5 curies/ml), H_2SiF_6 solution is added until the mixture is 3.0 to 3.3 M H_2SiF_6.

2. The solution is heated slowly to boiling and boiled slowly for approximately 20 min. The H_2SiF_6 decomposes to give hydrofluoric acid and silicon fluoride. Both are volatile and the excess of each is removed. Americium is more strongly complexed by $SiF_6^{=}$ than is Pm^{147}. The Pm^{147} precipitates as PmF_3.

3. The granular precipitate settles rapidly and the supernatant liquid is centrifuged to remove the precipitate. The precipitate is washed with 50 ml of H_2O and the water rinse is added to the supernatant liquid.

4. Fifty milliliters of saturated boric acid solution is added to the centrifuge tube to slurry out the precipitate into the beakers containing the bulk of the precipitate. The slurry is agitated and heated to approximately 80°C.

5. Fifty milliliters of 16 M HNO_3 is added, and the precipitate is heated to boiling; the precipitate is dissolved and a small amount of SiO_2 is precipitated.

6. The SiO_2 is centrifuged out and the solution is saved. The volume is reduced to ~ 100 ml by boiling. The solution is now 8.0 M HNO_3 and 0.44 M H_3BO_3.

7. Steps 1 through 6 are considered a cycle. This procedure is repeated through approximately eight cycles to decontaminate to the desired factor of ~ 200 alpha counts per millicurie.

8. To precipitate PmF_3 and AmF_3, HF is added to the H_2SiF_6 supernatant until the solution is 3.0 M. After three cycles approximately 15% of the americium is left with the Pm^{147} product and 85% of the americium is in the H_2SiF_6 supernatant waste.

PROCEDURE 14

ELECTRODEPOSITING AMERICIUM

(a) Source: Roy Ko, Nucleonics, 14, 74 (1956)

Assemble electrolysis cell using 22-mm diameter stainless steel, platinum, or copper disk cathode.

Add 4 ml of solution of 0.20 M HCOOH, 0.15 M $HCOONH_4$.

Add americium solution not exceeding 400 microliters.

Place platinum anode stirrer 10 mm above cathode and rotate at approximately 200 rpm.

Electrolyze at 80-100 ma for 1-2 hr.

At end of electrolysis, siphon out solution with current on. Rinse with dilute NH_4OH and then with acetone.

Dissassemble cell and ignite disk to redness over bunsen flame.

(b) Source: G. N. Yakovlev, P. M. Chulkov, V. B. Dedov, V. N. Kosyakov, and Y. P. Sobolev, J. Nuc. Energy, 5, 159 (1957).

The electrolysis of neutral solutions of $PuCl_3$, $AmCl_3$ and $CmCl_3$ from 50% ethyl alcohol, 45% acetone, 5% water was successful at a current density of 0.2 ma/cm².

(c) Source: H. Diamond, R. Barnes and P. Fields, private communication, reported in ANL 5054 (1953), $6.30 (ph OTS), $3.00 (mf OTS).

The americium was electrodeposited on a tantalum cathode from 0.2 M K_2CO_3 solution.

(d) Source: W. G. Smith and J. M. Hollander, Phys. Rev., 101, 746 (1956)

W. G. Smith, W. M. Gibson and J. M. Hollander, Phys. Rev., 105, 1514 (1957)

The hydrochloric acid solution was evaporated to dryness and the americium activity dissolved in 0.5 ml of NH_4HSO_4 (pH = 3.6) plating solution, from which the activity was electroplated upon a 10-mil platinum wire.

Similar experiments are described in:

AEC-TR-3497, G. I. Khlebnikov and E. P. Dergunov, Atomnaya Energ., 4, 376 (1958).

V. B. Dedov and V. N. Kosyakov, Proc. Int'l. Conf. Peaceful Uses of Atomic Energy, 7, 369 (1956).

PROCEDURE 15

THE DETERMINATION OF AMERICIUM IN URINE

Source: M. F. Milligan, E. E. Campbell, B. C. Eutsler,
Jean McClelland, and W. D. Moss. LASL LA-1858 (2nd
Edition), p 18, (1958), $4.00 (OTS).

Abstract

The method is based on the coprecipitation of americium with bismuth phosphate from a nitric acid solution of urine salts at a pH of 1.7. The bismuth phosphate is dissolved in 6N HCl and the americium coprecipitated a second time with lanthanum fluoride. The precipitate is slurried onto a stainless steel plate and counted with a low-background proportional alpha counter. Thorium, plutonium, curium, actinium, and neptunium are carried through this determination. Quantities of the order of 0.5 d/m of americium can be detected by this method.

Reagents

Concentrated Nitric Acid - HNO_3 70%, sp. gr. 1.42.

n-Octyl Alcohol (primary) - $CH_3(CH_2)_6CH_2OH$, practical.

Boiling Chips - Carborundum, 20 mesh.

Saturated Sulfur Dioxide Water - Bubble sulfur dioxide (SO_2) gas, technical, gently through 500 ml of distilled water for 2 hours.

Bismuth Nitrate Solution - Dissolve 231.2 g of bismuth nitrate [$Bi(NO_3)_3 \cdot 5H_2O$ - AR] in 660 ml of conc. nitric acid and dilute to 1 liter with distilled water. The solution contains 0.1 g Bi/ml.

Concentrated Phosphoric Acid - H_3PO_4 (orthophosphoric acid) 85%, sp. gr. 1.71.

50% Sodium Hydroxide Solution - 50 g of sodium hydroxide (NaOH - AR, pellets) dissolved in 50 ml of distilled water.

1N Nitric Acid - Add 64 ml of conc. nitric acid to approximately 500 ml of distilled water in a 1 liter volumetric flask. Mix, cool, and make up to 1 liter with distilled water.

Concentrated Hydrochloric Acid - HCl 36%, sp. gr. 1.19.

Lanthanum Nitrate Solution

Purification of Lanthanum Nitrate

Reagents

Lanthanum Nitrate - $La(NO_3)_3 \cdot 6H_2O$ - AR.

Ammonium Hydroxide - NH_4OH 30%, sp. gr. 0.90.

Concentrated Nitric Acid - HNO_3 70%, sp. gr. 1.42.

Barium Nitrate - $Ba(NO_3)_2$ - AR.

Sodium Sulfate Solution - Place 5 g of sodium sulfate (Na_2SO_4 -

AR) in a 100 ml volumetric flask, dissolve in distilled water, and dilute to 100 ml with distilled water.

<u>Potassium Permanganate</u> - $KMnO_4$ - AR.

<u>20% Sodium Hydroxide Solution</u> - Place 40 g of sodium hydroxide ($NaOH$ - AR, pellets) in approximately 100 ml of distilled water and dissolve. Mix, cool, and make up the volume to 200 ml.

<u>Methyl Orange Indicator</u> - Dissolve 0.1 g of methyl orange (orange III, tropeolin D, sodium p-dimethylaminoazobenzene sulfonate) in 100 ml of distilled water. pH range: red, 3.1 - orange yellow, 4.4.

<u>Ammonium Nitrate</u> - NH_4NO_3 - AR.

<u>TTA Solution</u> - Dissolve 50 g of 2-thenoyltrifluoroacetone [$C_8H_5O_2SF_3$, "TTA", 4, 4, 4-trifluoro-1-(2-thienyl)-1, 3-butanedione] in toluene ($CH_3C_6H_5$ - reagent grade) in a 1 liter volumetric flask and make up to volume with toluene. Store in a brown glass bottle in the dark.

<u>Procedure</u>

1. Dissolve 5 g of lanthanum nitrate in 200 ml of distilled water in a 400 ml beaker.
2. Add 50 ml of ammonium hydroxide to the beaker and stir.
3. Transfer the solution to four 90 ml centrifuge tubes. Rinse the beaker with distilled water and add the washings to the tubes to give equal volumes. Centrifuge at 2000 rpm for 5 minutes. Discard the supernatant fluid.
4. Add conc. nitric acid, with stirring, to Tube 1 until the precipitate is just dissolved. Transfer the clear solution to Tube 2. Rinse Tube 1 with 2 to 3 ml of conc. nitric acid and add to Tube 2. Stir and add conc. nitric acid, with a medicine dropper, if necessary, until the precipitate is just dissolved. Transfer the solution to Tubes 3 and 4 in the same manner. Transfer the combined solutions in Tube 4 to two clean 90 ml centrifuge tubes. Divide the solution to give equal volumes. Rinse Tube 4 with conc. nitric acid and add the washings to the two tubes of solution.
5. Add distilled water to each tube to give a volume of 40 ml in each. Add ammonium hydroxide to each tube until a precipitate just forms.
6. Add 40 mg of barium nitrate and 1 ml of sodium sulfate solution to each tube, mix, and let stand for 30 minutes.
7. Centrifuge at 2000 rpm for 5 minutes. Pour the supernatant solution into two clean 90 ml centrifuge tubes.
8. Add 10 ml of distilled water to each tube, shake to wash the precipitate, and centrifuge again at 2000 rpm for 5 minutes. Add the washings to the two tubes of supernatant solution. Discard the residue.

9. Add 25 ml of ammonium hydroxide to each tube. Mix, centrifuge at 2000 rpm for 5 minutes, and discard the supernatant solution.

10. Dissolve each precipitate in 5 ml of conc. nitric acid and heat to boiling.

11. Add 20 mg of potassium permanganate to each tube.

12. Neutralize the solutions with 20% sodium hydroxide to a pH of 8 using Hydrion paper for the indicator.

13. Place the tubes in a water bath or sand bath at 60° to 90°C for 1 hour. (A drying oven may be used for this.)

14. Add enough conc. nitric acid to give a pH of 6 to 7 with Hydrion paper. Cool the tubes with tap water and centrifuge at 2000 rpm for 5 minutes. Pour off the supernatant solution into one clean 90 ml centrifuge tube. Discard the dark precipitate.

15. Dilute the combined solutions to 50 ml with distilled water and add 30 ml of ammonium hydroxide. Centrifuge at 2000 rpm for 5 minutes. Discard the supernatant solution. The precipitate should be nearly white at this step. If the precipitate is a dark brown, dissolve in conc. nitric acid, heat to boiling, and centrifuge at 2000 rpm for 5 minutes. Discard any precipitate that remains and proceed with Step 15.

16. Dissolve the precipitate in 2 to 3 ml of conc. nitric acid and dilute to 30 ml with distilled water. Neutralize the solution with ammonium hydroxide using methyl orange as the indicator. The indicator will change from red to orange at a pH between 3.1 and 4.4.

17. Add 5 g of ammonium nitrate. Stir until dissolved. It may be necessary to let the solution stand for a few minutes until the ammonium nitrate dissolves.

18. Transfer the solution to a 125 ml Squibb separatory funnel. Rinse the tube with 10 ml of distilled water and add to the solution in the funnel. Add 10 ml of TTA solution and shake for 25 minutes with an automatic wrist-action shaker.

19. Let the solutions stand until the phases separate (approximately 5 minutes).

20. Drain the aqueous solution into a clean 90 ml centrifuge tube and add 20 ml of ammonium hydroxide. Drain the TTA solution and discard.

21. Centrifuge at 2000 rpm for 5 minutes. Discard the supernatant solution.

22. Add 10 ml of distilled water to the precipitate in the tube. Mix to wash the precipitate, centrifuge for 5 minutes at 2000 rpm, and discard the wash solution.

23. Dissolve the precipitate in 2 to 3 ml of conc. nitric acid and transfer quantitatively to a 100 ml volumetric flask with distilled water. Dilute the solution in the flask to 100 ml and mix.

24. Weigh three planchets accurately on an analytical balance. Number the planchets and record the weights. Place 1 ml of the lanthanum solution (Solution I) on each planchet. Dry the planchets under an infrared lamp. Flame the planchet to red heat with a burner. Let cool to room temperature and weigh. Calculate the concentration of La^{+3} assuming that the material weighed is lanthanum oxide (La_2O_3).

Weight of dried planchet - weight blank planchet = g La_2O_3

$$\text{g } La_2O_3 \times 1000 \times \frac{277.8}{325.4} = \text{mg } La^{+3}/\text{ml Sol. I}$$

$$\text{g } La_2O_3 \times 853.7 = \text{mg } La^{+3}/\text{ml Sol. I}$$

25. Place a calculated number of milliliters (see below) of Solution I in a 100 ml volumetric flask and dilute to 100 ml with distilled water. Solution II should contain 1 mg La^{+3} per milliliter.

$$\frac{(100 \text{ ml} \times 1 \text{ mg } La^{+3}/\text{ml Sol. II})}{\text{mg } La^{+3}/\text{ml Sol. I}}$$

$$= \frac{100 \text{ mg } La^{+3}}{\text{mg } La^{+3}/\text{ml Sol. I}}$$

= ml of Sol. I to be diluted to 100 ml to give Sol. II

$= 1 \text{ mg } La^{+3}/\text{ml}$

Concentrated Hydrofluoric Acid - HF 48%.

Dilute Hydrofluoric Acid - Add approximately 1 ml of hydrofluoric acid to 100 ml of distilled water in a Bakelite beaker.

Procedure

1. Two morning and two evening voidings of urine are collected by the employee and sent to the laboratory. The total sample is mixed in a 2 liter beaker and 1 ml of antifoam (octyl alcohol), 1 g of boiling chips, and approximately 200 ml of conc. nitric acid are added.

2. The sample is covered with a Speedyvap and taken to dryness at a low heat on a hot plate. (If expedient, high heat may be used to bring the sample to dryness.) Samples may burn violently as they go to dryness. This does not affect the recovery.

3. The ash is completely oxidized (to a white ash) by repeated evaporation with small portions of conc. nitric acid (5 to 10 ml portions).

4. When the ash is completely white, dry, and cool, add 5 ml of conc. nitric acid and 25 ml of distilled water and boil for 1 minute. Transfer the solution to a 90 ml centrifuge tube.

5. Fifteen milliliters of distilled water is added to the beaker, brought to a boil, and added to the solution in the centrifuge tube. This rinsing is repeated with another 15 ml portion of distilled water, giving an approximate volume of 55 to 60 ml in the centrifuge tube.

6. Centrifuge at 2000 rpm for 5 minutes.

7. Carefully transfer the supernatant solution to a 150 ml beaker containing 2 ml of saturated sulfur dioxide water. This transfer must be carefully effected since any insoluble material will be carried through the entire procedure. The sulfur dioxide is added to ensure reduction of any americium present to the trivalent state.

8. Adjust the pH of the acid salt solution in the beaker to 1.7 by adding 50% sodium hydroxide solution dropwise. Stir the solution with a magnetic stirrer while adding the hydroxide. The Beckman pH meter, Model H-2, is used to determine the pH.

9. Transfer the solution in the beaker to a second 90 ml centrifuge tube quantitatively and place the tube in a constant-temperature oil bath at 80° to 84°C. Stir mechanically at a moderate speed for 10 to 15 minutes.

10. Add 1 ml bismuth nitrate solution and 1 ml of conc. phosphoric acid to the solution and continue stirring in the oil bath for 1 hour.*

$$Bi^{+3} + PO_4^{-3} \longrightarrow Bi\,PO_4$$

11. Remove from the oil bath (wipe excess oil off the tubes) and centrifuge at 2000 rpm for 5 minutes.

12. Discard the supernatant solution and break up the bismuth phosphate precipitate with a fine stream of distilled water. Transfer the precipitate to a 40 ml centrifuge cone with repeated washings until the volume is approximately 30 ml.

13. Centrifuge at 2000 rpm for 5 minutes and discard the supernatant carefully.

14. Rinse down the 90 ml centrifuge tube with 2 ml of conc. hydrochloric acid and 2 ml of distilled water.

15. Add this dilute hydrochloric acid washing to the precipitate and dissolve the precipitate with gentle swirling. If the precipitate does not dissolve readily, add conc. hydrochloric acid dropwise until solution is complete.

16. To the dissolved precipitate add 0.2 ml of lanthanum nitrate solution and 1 ml of conc. hydrofluoric acid. If the solution is turbid, add conc.

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* It is obvious that the final pH, after the addition of bismuth nitrate and phosphoric acid, is not 1.7. Experimentation has shown that the pH adjustment to 1.7 before this addition gives the highest percentage yield of americium.

hydrochloric acid dropwise until it clears. Let stand for 5 minutes (not longer than 10 minutes) to ensure complete precipitation.

$$La^{+3} + 3F^{-} \longrightarrow LaF_3 \downarrow$$

17. Centrifuge at 2000 rpm for 5 minutes and discard the supernatant fluid.

18. Shake the lanthanum fluoride precipitate with 15 to 20 ml of dilute hydrofluoric acid wash solution and centrifuge at 2000 rpm for 5 minutes.

19. Discard the supernatant and invert the cone quickly on several thicknesses of Kleenex. Drain for 15 to 20 minutes. The liquid must drain thoroughly from the tube since any residual hydrofluoric acid will attack the stainless steel plate.

20. Quantitatively transfer the precipitate to a 7/8 in., 10 mil stainless steel plate by slurrying with distilled water.

21. Dry the plate at low heat on an electric hot plate covered with an asbestos pad.

22. Flame the dried plate to red heat with a burner and count the alpha activity with a low-background proportional counter for 120 minutes. (The low levels of americium encountered necessitate this long counting time.)

23. Report the results as d/m/sample:

$$\frac{c/m}{\text{efficiency of counter}} = d/m/\text{sample}$$

The efficiency of the alpha counters used at LASL is assumed to be 50%.

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