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NUCLEAR SCIENCE SERIES

**The Radiochemistry
of the Transcurium Elements**

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The Radiochemistry of the Transcurium Elements

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**Subcommittee on Radiochemistry
National Academy of Sciences—National Research Council**

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FOREWORD

The Subcommittee on Radiochemistry is one of a number of subcommittees working under the Committee on Nuclear Science within the National Academy of Sciences - 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 establishment of specifications for radiochemically pure reagents, availability of cyclotron time for service irradiations, the place of radiochemistry in the undergraduate college program, etc.

This series of monographs has grown out of the need for up-to-date compilations of radiochemical information and procedures. The Subcommittee has endeavored to present a series which will be of maximum use to the working scientist and which contains the latest available information. Each monograph collects in one volume the pertinent information required for radiochemical work with an individual element or a group of closely related elements.

An expert in the radiochemistry of the particular element has written the monograph, following a standard format developed by the Subcommittee. The Atomic Energy Commission has sponsored the printing of the series.

The Subcommittee is confident these publications will be useful not only to the radiochemist but also to the research worker in other fields such as physics, biochemistry or medicine who wishes to use radiochemical techniques to solve a specific problem.

W. Wayne Meinke, Chairman
Subcommittee on Radiochemistry

INTRODUCTION

This volume which deals with the radiochemistry of the transcurium elements 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 element 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 the transcurium elements which might be included in a revised version of the monograph.

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The Radiochemistry of the Transcurium Elements

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I. GENERAL COMMENTS

The transcurium element group is composed of berkelium (Bk), atomic number 97; californium (Cf), number 98; einsteinium (Es), number 99; fermium (Fm), number 100; mendelevium (Md), number 101; and nobelium (No), number 102.

These elements are all synthetic; that is, they are all usually produced by multiple neutron capture or charged particle reactions on isotopes of elements of lower atomic number. Their discovery and production is described by Thompson.¹ With the inclusion of the as yet undiscovered element 103 they compose the second half of the actinide series in which the 5f electron shell is being completed. Their chemistry is extraordinarily similar to that of the lanthanides or rare earths. Excepting Bk (and possibly No), they exist solely as tripositive ions in aqueous solutions. Bk can be oxidized to the +4 state under conditions equivalent to those required for oxidation of Ce^{+3} to Ce^{+4} (≈ 1.6 v).

The chemical properties of any one of these elements are quite similar to those of the rest, so it is appropriate to speak of many of their chemical properties in collective terms. The radiochemical procedures can usually be divided into three parts:

1. The isolation of a tripositive lanthanide-actinide fraction.
2. Separation of the tripositive actinides from the lanthanides.
3. Separation of the actinides from each other.

The transcurium actinides have characteristic α decay energies (note that the light Pb-Bi isotopes may be confused with some transcurium nuclides) and short spontaneous fission half-lives. Because of these properties they can be identified and measured without being entirely separated from fission products, and hence some of the procedures do not provide for complete purifications.

The lightest transcurium element, Bk, is five atomic numbers beyond the last abundantly occurring natural element, uranium. The longer-lived isotopes of Bk are several mass numbers more than 238, so even this most easily produced transcurium element is several transmutation generations away from natural occurrence. Therefore these elements have not yet been available for study in larger than microgram quantities. Cunningham² and Thompson and Muga³ have reported the magnetic susceptibilities of the tripositive Bk and Cf ions as well as the solution absorption spectra in the range from about 5300 to 8700Å. Neither ion is strongly colored although Cf⁺³ displays two weak absorption peaks at 7800 and 8300Å. These studies are remarkable in that they were performed on submicrogram quantities of Bk and Cf. No such work has been possible on Es, Fm, Md, or No, and in fact almost no chemical studies, even at tracer levels, have been possible on Md and No because the half-lives of the observed isotopes are so short. It is clear that there is very little information about these elements except what is derived from tracer studies and comparisons with the chemistry of the lanthanides.

II. GENERAL REVIEWS OF THE CHEMISTRY OF THE TRANSCURIUM ELEMENTS

General reviews of the chemistry of the transcurium elements can be found in the following books and articles:

G. T. Seaborg, "The Transuranium Elements," Addison-Wesley Publishing Co., Inc., Reading, Mass., 1958. [Ref. 4.]

J. K. Katz and G. T. Seaborg, "Chemistry of the Actinide Elements," Methuen and Co., Ltd., London, 1957. [Ref. 5.]

S. G. Thompson, B. G. Harvey, G. R. Choppin, and G. T. Seaborg, J. Am. Chem. Soc. 76, 6229 (1954). [Ref. 6.]

B. B. Cunningham, J. Chem. Educ. 36 (January, 1959). [Ref. 2.]

S. G. Thompson and M. Louis Muga, "Methods of Production and Research on Transcurium Elements," Proc. U. N. Intern. Conf. Peaceful Uses Atomic Energy, 2nd, Geneva, 1958, 15/P/825. [Ref. 3.]

III. TABLE OF ISOTOPES OF THE TRANSCURIUM ELEMENTS

<u>Nuclide</u>	<u>$t_{1/2}$</u>	<u>Mode of Decay</u>
${}_{97}\text{Bk}^{243}$	4.5 h	EC, 99 + %; α , 0.15%
Bk^{244}	4.4 h	EC, 99 + %; α , $6 \times 10^{-3}\%$
Bk^{245}	4.98 d	EC, 99 + %; α , 0.11%
Bk^{246}	1.8 d	EC
Bk^{247}	$\approx 10^4$ y	α
Bk^{248}	16 h	β^- , 70%; EC, 30%
Bk^{249}	314 d	β^- , 99 + %; α $2.2 \times 10^{-3}\%$; SF, $6 \times 10^{-6}\%$
Bk^{250}	3.13 h	β^-
${}_{98}\text{Cf}^{244}$	25 m	α
Cf^{245}	44 m	EC, 70%; α , 30%
Cf^{246}	35.7 h	α ; SF, $2 \times 10^{-4}\%$
Cf^{247}	2.5 h	EC
Cf^{248}	350 d	α ; SF $> 1.5 \times 10^{-2}\%$
${}_{98}\text{Cf}^{249}$	360 y	α ; SF, $4 \times 10^{-4}\%$
Cf^{250}	10.9 y	α ; SF $\approx 0.15\%$
Cf^{251}	≈ 800 y	α
Cf^{252}	2.2 y	α , 97%; SF, 3%

III. TABLE OF ISOTOPES OF THE TRANSCURIUM ELEMENTS (Contd.)

Nuclide	$t_{1/2}$	Mode of Decay
Cf ²⁵³	17 d	β^-
Cf ²⁵⁴	56 d	SF \approx 100%
⁹⁹ Es ²⁴⁶	7.3 m	α , EC
Es ²⁴⁷		α
Es ²⁴⁸	25 m	EC, 99 + %; α , 0.3%
Es ²⁴⁹	2 h	EC, 99 + %; α , 0.13%
Es ²⁵⁰	8 h	EC
Es ²⁵¹	1.5 d	EC, 99 + %; α , 0.53%
Es ²⁵²	\approx 140 d	α
Es ²⁵³	20.03 d	α ; SF, 8×10^{-6} %
Es ²⁵⁴	480 d	α ; no β^-
	37 h	β^- , 99 + %; EC \approx 0.1%
Es ²⁵⁵	24 d	β^-
Es ²⁵⁶	short	β^-
¹⁰⁰ Fm ²⁴⁸	0.6 m	α
Fm ²⁴⁹	150 s	α
Fm ²⁵⁰	30 m	α , EC
Fm ²⁵¹	7 h	EC \approx 99%; $\alpha \approx$ 1%
Fm ²⁵²	22.7 h	α ; SF $< 4 \times 10^{-2}$ %
Fm ²⁵³	\approx 3.0 d	EC, 89%; α , 11%
¹⁰⁰ Fm ²⁵⁴	3.24 h	α ; SF, 5.50×10^{-2} %
Fm ²⁵⁵	21.5 h	α ; SF $< 4.5 \times 10^{-3}$ %
Fm ²⁵⁶	3-4 h	SF \approx 100%
¹⁰¹ Md ²⁵⁵	—	α + ?
Md ²⁵⁶	\approx 30 m	EC
¹⁰² No ²⁵³	\approx 10 s	α + ?

III. TABLE OF ISOTOPES OF THE TRANSCURIUM ELEMENTS (Contd.)

<u>Nuclide</u>	<u>$t_{1/2}$</u>	<u>Mode of Decay</u>
No ²⁵⁴	3 s	$\alpha + ?$
103 ²⁵⁶ — (tentative identification)	0.25 s	$\alpha + ?$

Abbreviations in the table above are as follows:

s = seconds, m = minutes, h = hours, d = days, y = years,

EC = electron capture, α = α particle emission, β^- = negatron emission, SF = spontaneous fission decay.

A more complete description of most of these nuclides can be found in the compilation by Strominger, Hollander, and Seaborg in Reviews of Modern Physics, Vol. 30, No. 2, Part II, pp. 585-904. The α particle energies, decay schemes, and genetic relationships are tabulated.

IV REVIEW OF FEATURES OF TRANSCURIUM ELEMENT CHEMISTRY MOST INTERESTING TO RADIOCHEMISTS

IV. A. Coprecipitation and Precipitation Chemistry

The tripositive actinides display such marked similarity to the lanthanides that one of the latter (usually Ce or La) is ordinarily used as a carrier during precipitation steps. They all form insoluble fluorides from strong ($\approx 3\text{--}5\text{M}$) acid, oxalates from less strong acids ($\approx 1\text{--}2\text{M}$), phosphates in slightly acidic solutions ($\approx 0.1\text{M}$), and hydroxides or hydrated oxides in basic solutions. These hydrated oxides are insoluble in dilute carbonates, but they readily dissolve in excess (40%) carbonate or many of the complexing anions of organic acids such as citrate.

While there are several other ions which coprecipitate as insoluble oxyfluorides at lower acid concentrations, the precipitation of fluorides from $\approx 3\text{M}$ HCl or HNO_3 uniquely carries Sc^{+3} , Y^{+3} , the tripositive lanthanides and actinides, thorium, and the alkaline earths. The alkaline earth

group is left in solution when the remainder of these elements are precipitated as hydrated oxides from carbonate-free solutions. Holdback Sr^{++} enhances the separation achieved with any single precipitation step.

Of course, the transcurium elements do not carry appreciably on acid sulfides, lead chromate, barium sulfate, or silver chloride.

Bk^{+4} coprecipitates with zirconium phosphate, zirconium iodate and ceric iodate, and insoluble hydroxides.⁷

IV.B. Complex Ions and Chelate Formations

The order of the complexing power of different anions is fluoride > chloride > nitrate > perchlorate for mononegative anions, and carbonate > oxalate > sulfate for dinegative anions. The complex/chelate formation is of utmost importance in ion exchange separations since the $+3$ ions are so strongly adsorbed on cation resin that special measures are required for their rapid elution. Complex ions are formed with organic substances, and citrate, tartrate, lactate, α -hydroxyisobutyrate, EDTA, TTA, acetate, and thiocyanate are known to form moderately strong complexes. For instance, the dissociation constant of the EDTA complex of Cf is listed as $10^{-19.09 \pm 0.2}$ by Fuger.⁸

IV.C. Extraction Behavior

The only rapid extraction separation for the transcurium elements involves the extraction of Bk^{+4} away from Bk^{+3} , Cm^{+3} , and Cf^{+3} into di(2-ethylhexyl) orthophosphoric acid-heptane from HNO_3 solutions. The ratio of extraction coefficients for the $+4$ state is more than 10^6 times that for the $+3$ state.⁹ Procedure 6 (Section VII of this report) is based on this extraction.

Cf, Es, Fm, and Cm can be separated from each other and from the lanthanides with appropriate extractions into di(2-ethylhexyl) phosphoric acid, 2-ethylhexyl phosphoric acid, or diphenyl phosphoric acid from aqueous HCl solutions.¹⁰ These extractions are effective with macro concentrations of Cf.¹¹

The extractions of the lanthanides and actinides into tri-n-butyl phosphate are discussed by Best *et al.*,¹² and a purification of Bk with this reagent is described by Hulet.¹³

Magnussen *et al.*,¹⁴ have reported the extraction coefficients of several of the transcurium elements from 0.1M ammonium chloroacetate buffer into TTA-toluene solutions. The data fit the equation

$$K = \frac{E(H^+)^3}{(HT)^3(f_{HT})^3},$$

where E is the extraction coefficient, HT is the TTA concentration in the organic layer, and f_{HT} is the TTA activity coefficient in the organic phases given by $f_{HT} = 1 - 0.24 (HT)^{0.48}$. The data are listed in Table I, corrected to benzene solvent by Poskanzer and Foreman¹⁵ who subtracted 0.2 pH unit from the pH_{50} value obtained in toluene and recalculated K.

Table I. Extraction coefficients (K) of the transcurium elements for extraction from 0.1M ammonium chloroacetate into TTA-toluene solutions.

Ion	K	pH for 50% Extraction (Benzene)
Bk ⁺³	$\approx 1.5 \times 10^{-7}$	3.0
Cf ⁺³	8×10^{-8}	3.1
E ⁺³	6×10^{-8}	3.1
Fm ⁺³	8×10^{-8}	3.1

The lanthanides extract under nearly the same conditions, i.e., pH_{50} for La is ≈ 4.0 and pH_{50} for Lu is ≈ 3.0 , so lanthanide-actinide separations are not readily feasible. Group separations from ions of the alkaline earth group, the +4 Zr-Hf family, and the oxygenated ions can be performed by pre-extracting Zr, Hf, Pa, Np, Pu, etc. from a solution adjusted to pH 2, discarding the organic phase, then adjusting the pH to 4.5 and extracting the lanthanides and actinides. This step has not been reported in any of the currently used procedures.

IV.D. Ion Exchange Chemistry

The great similarity between the various transcurium elements has intensified interest in and work on their ion exchange behavior. With the exception of No, the transcurium elements have been identified by their relative elution positions from cation exchange resin. While separation procedures have been devised which do not make use of ion exchange operations, they are not presently in general use.

In order to compare data from various sources, the ion-exchange-column eluate volumes have been reduced to units of "free column volumes." This volume, abbreviated FCV, is characteristic of a particular resin bed loading and can be derived for any column by finding the elution position of unadsorbed materials such as organic dyes, etc. The FCV is about 55% of the volume of the column bore.

IV.D.1 Separations of the actinides and lanthanides The chloride and thiocyanate complexes of the actinides are stronger than the corresponding complexes of the lanthanides. When mixtures of lanthanides and actinides are eluted from strong base cation resins such as Dowex-50 or Zeo-Carb 225 with 12M HCl or $2\text{M NH}_4\text{CNS}$, the actinides are eluted before the lanthanides and group separations are obtained. Figure 1 indicates the relative elution positions from Dowex-50 AG with 20% ethyl alcohol saturated with HCl gas at 20°C .^{6, 16} Similar separations are obtained with the same eluant from Zeo-Carb 225 resin. Figure 2 shows the relative elution positions from Dowex-50 using $1.8\text{M NH}_4\text{CNS}$ eluate.¹⁷

The complexes of the actinides in very strong complexing agents such as 13M HCl , 10M LiCl , and $2\text{M NH}_4\text{CNS}$ are such that anionic species are formed. Similar anionic species of the lanthanides are not as probable under the same conditions, so group separations are possible using these complexing agents and anion exchange resin.¹⁸

Figure 3 shows the relative elution positions of the actinides from Dowex-1 anion resin with 13M HCl .⁶ Similar or better separations have

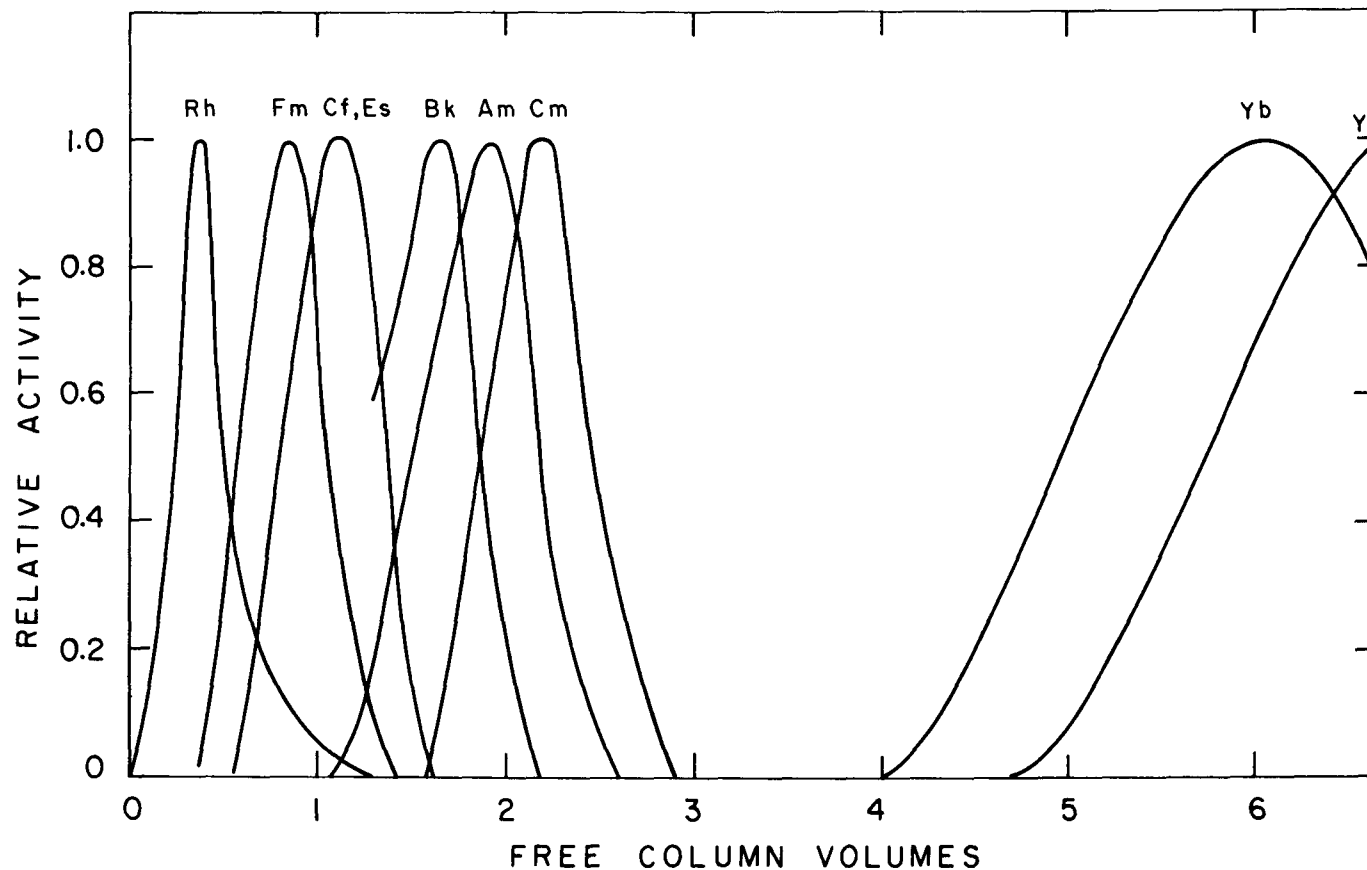


Fig. 1. Relative elution positions of transplutonium actinides, Y, Yb, and Rh from Dowex-50 AG with 20% ethyl alcohol saturated ($\approx 12.5M$) with HCl. The transplutonic elements appear as a group between 0.3 and 3 free column volumes.

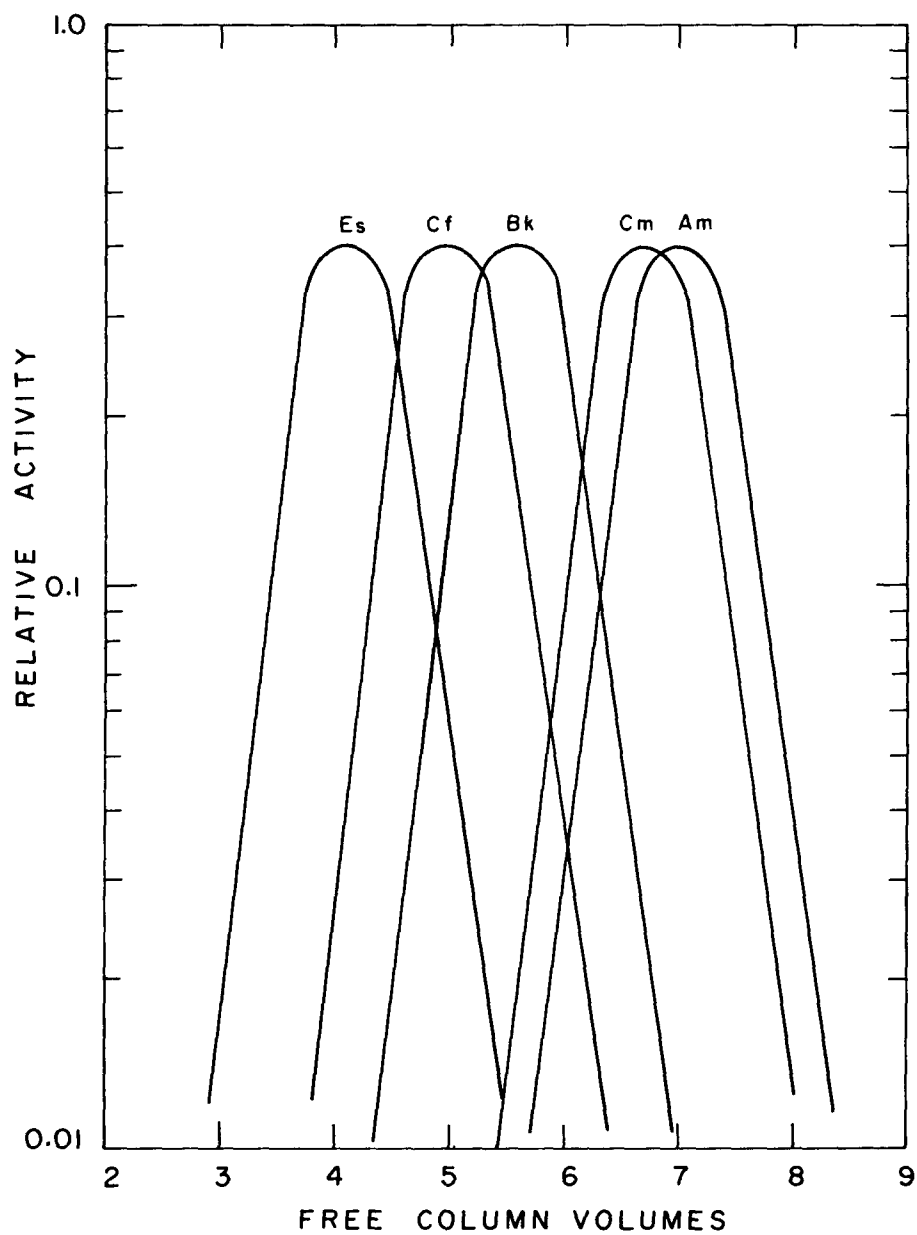


Fig. 2. Relative elution positions of the transplutonium actinides from Dowex-50 with 1.8M ammonium thiocyanate at 87°C.

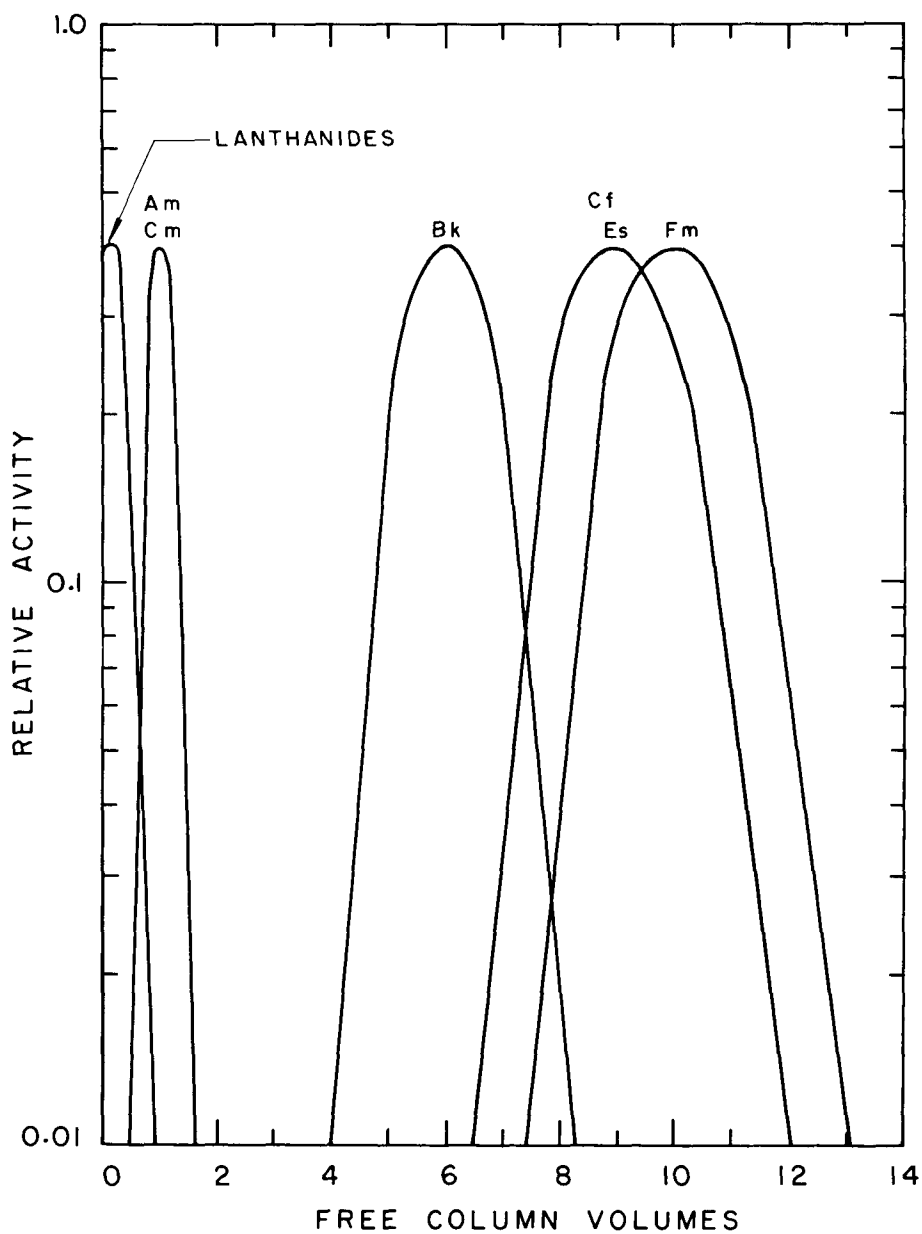


Fig. 3. Relative elution positions of the lanthanides and transplutonium actinides from Dowex-1 with 13M HCl at room temperature.

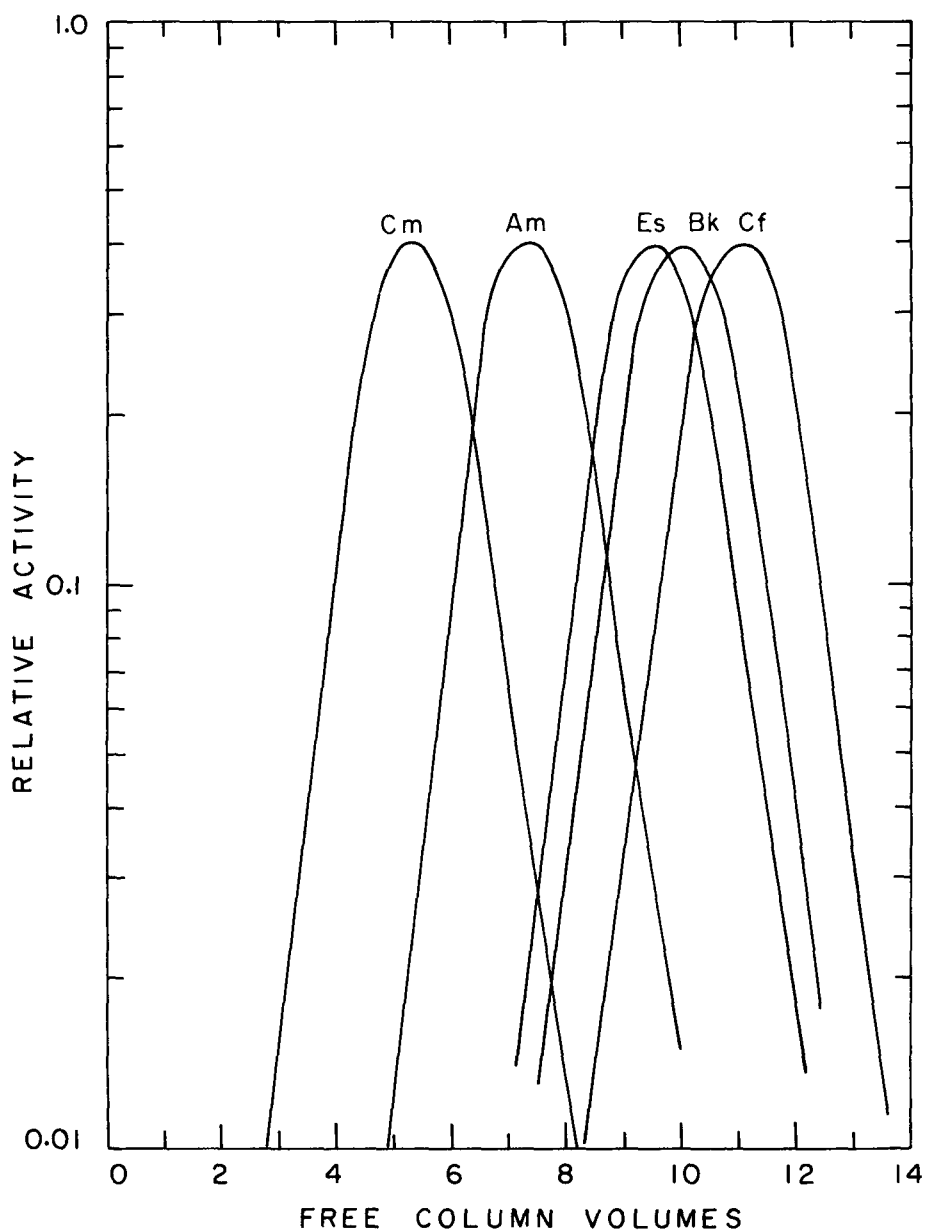


Fig. 4. Relative elution positions of the transplutonium actinides from Dowex-1 with 2.0M ammonium thiocyanate at 87°C.

been reported using the same eluant and Amberlite IRA-400.¹⁹ Figure 4 shows the relative elution positions from the same resin using 2M NH_4CNS . Lithium chloride solutions of about 10M give adsorptions and elutions equivalent to 13M HCl .

When the transcurium actinides are eluted from cation resins like Dowex-50 AG(4% cross-linked) with 0.1M to 6M HCl , very little separation between the actinides and lanthanides is obtained, but separations from most other cations can be effected. Procedure 7 (Section VII of this report) by Phillips and Gatti²⁰ uses a "cleanup" column operated primarily to remove impurities of Ca, Fe, and Al. Columns operated at 87°C are assembled as shown in Fig. 5. Trichloroethylene is boiled and its vapor is conducted

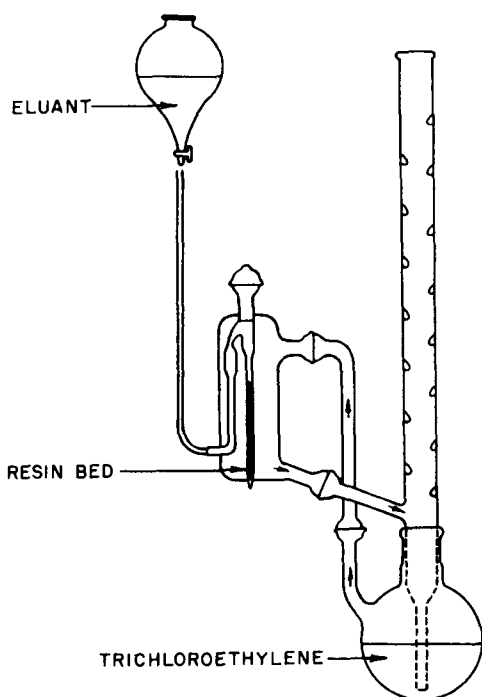


Fig. 5. Column apparatus for elutions at 87°C . Trichloroethylene is boiled in the flask, the vapors conducted through the column jacket around the resin bed, and the condensed vapor returned to the flask.

around the column into a condenser and back to the boiling flask, thus providing heat exchange at 87°C . Higher column temperatures are less practical because of the formation of vapor bubbles in the solutions and resin bed; however, with adequate care, temperatures to 100°C can be used.

IV. D. 2 Separations of the transcurium elements from each other. While separations of the transcurium elements from each other are obtained with relatively concentrated HCl and NH_4CNS , no element is separated cleanly from its neighbor.

The most convenient and frequently used method for separation of these elements from each other has been to elute them from cation resin with chelating organic acid anions. Several acid anions including those of citric, glycolic, tartaric, lactic, and α -hydroxyisobutyric acid have been used successfully as eluants.²¹ While some advantage is obtained in separation factors if α -hydroxyisobutyrate is used, the general features of the elution are the same with any of the eluants. Figure 6 is a typical elution curve of the actinides from Dowex-50 (12% cross-linked) with ammonium α -hydroxyisobutyrate. Similar elutions are reported at room temperature from the same resin (4% cross-linked)¹⁶ and at 77°C from Zeo-Carb 225.²²

Table II indicates the elution positions of the actinides and lanthanides from cation resin with α -hydroxyisobutyric acid. The data are normalized to $\text{Cm} = 1.00$. Data have been summarized from Choppin *et al*,²¹ Smith and Hoffman,¹⁶ and Milsted and Beadle.²²

Since the elution position of a particular element depends on the competition between the resin and a solution phase chelate, the position can be varied at will by adjusting the parameters that determine the chelate concentration. These are the pH of the solution of weak acids which form chelating anions, and the total acid concentration. Figure 7 shows the effect of varying the pH of solutions of ammonium α -hydroxyisobutyric acid. The effect of a change of α -hydroxyisobutyric acid concentration can be calculated by assuming K_d will be unchanged when the anion concentration is the same and the ionization constant of the acid is 1.1×10^{-4} .

The spacing between the heavier members of the series, Md and Fm, is much less than the spacing between Cf and Bk for constant pH and concentration of eluant. Although nearly equal spacing has been attained for rare-earth separations in columns utilizing continuously variable eluants,²³

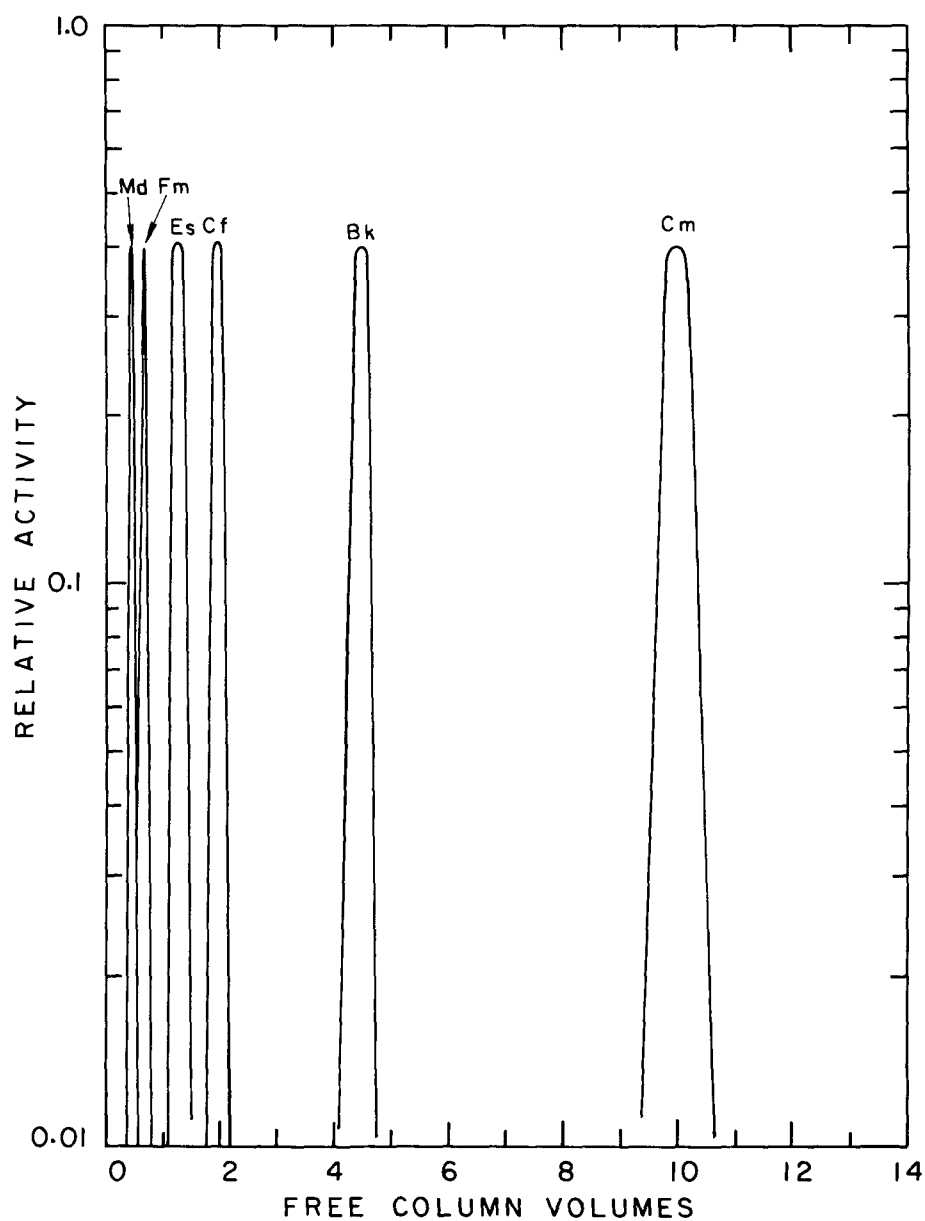


Fig. 6. Relative elution positions of curium and the transcurium actinides from Dowex-50 12% cross-linked resin with pH 4.2 ammonium α -hydroxyisobutyrate at 87°C.

Table II. Elution positions of actinides and lanthanides from cation exchange resin with α -hydroxyisobutyric acid.

Element	Dowex-50 4% at 25°C	Zeo-Carb 225 at 77°C	Dowex-50 12% at 87°C
Md	--	--	0.050
Fm	--	--	0.069
Es	0.13	--	0.13
Cf	0.19	0.21	0.20
Bk	0.37	--	0.45
Cm	1.00	1.00	1.00
Am	1.39	1.38	1.4
Lu	0.11	--	0.015
Yb	0.016	--	0.020
Tm	0.22	--	0.026
Er	--	--	0.037
Ho	0.039	--	0.055
Y	0.069	--	0.06
Dy	0.076	--	0.078
Tb	0.14	--	0.14
Gd	0.22	--	0.28
Eu	0.34	--	0.39
Sm	0.7	--	0.71
Pm	1.1	--	1.2
Nd	2.3	--	2.1
La	--	--	--
Ce	3.4	--	3.5

there are no reports that this has been accomplished with the transcurium elements.

The flow rate at which a column is operated affects the apparent width of the elution peaks. Figure 8 shows the effect for Dowex-50 12% resin, graded to settle at 0.5 to 0.25 cm/min in water, when the eluate is 0.4M lactic acid and the column is operated at 87°C. The curve is displaced toward greater half-widths at the same flow rate when coarser resin is used. A limiting half-width of about 5 or 6% is found with the finest resin and slowest flow rates.

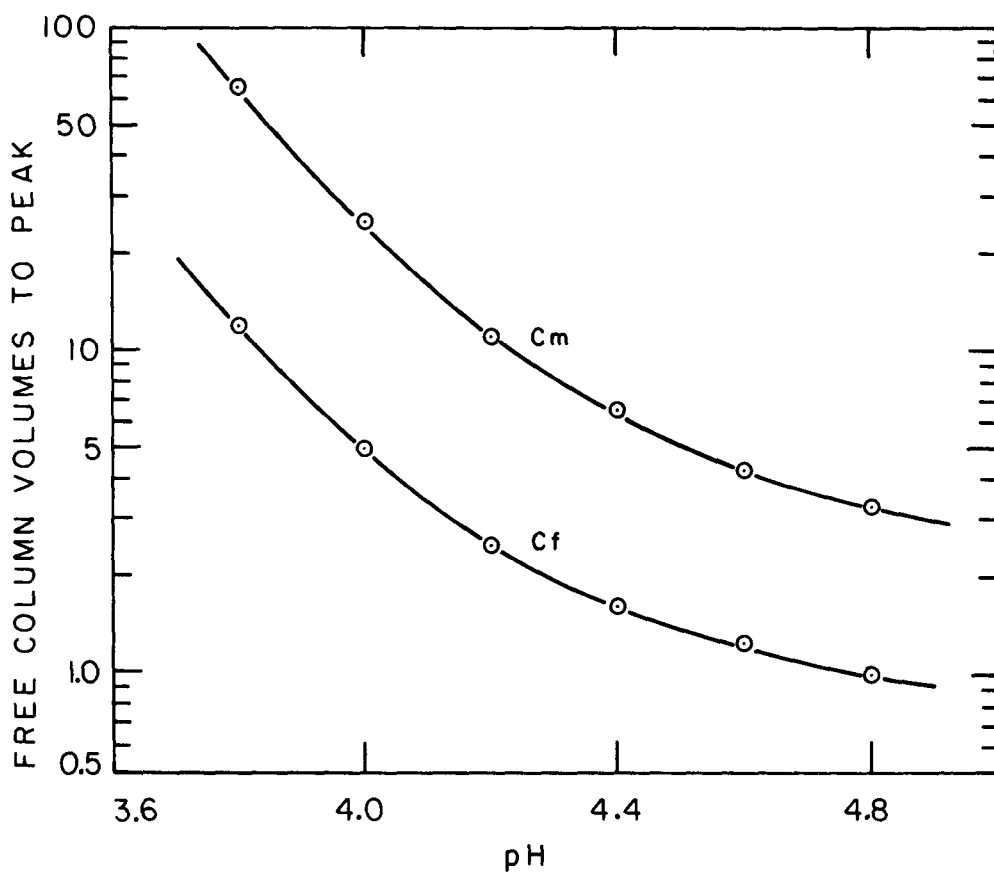


Fig. 7. The peak position of Cf and Cm as a function of pH for 0.4M ammonium α -hydroxyisobutyrate and Dowex-50, 12% cross-linked resin. The peak position of other lanthanides and actinides can be predicted from this curve and the table in the text.

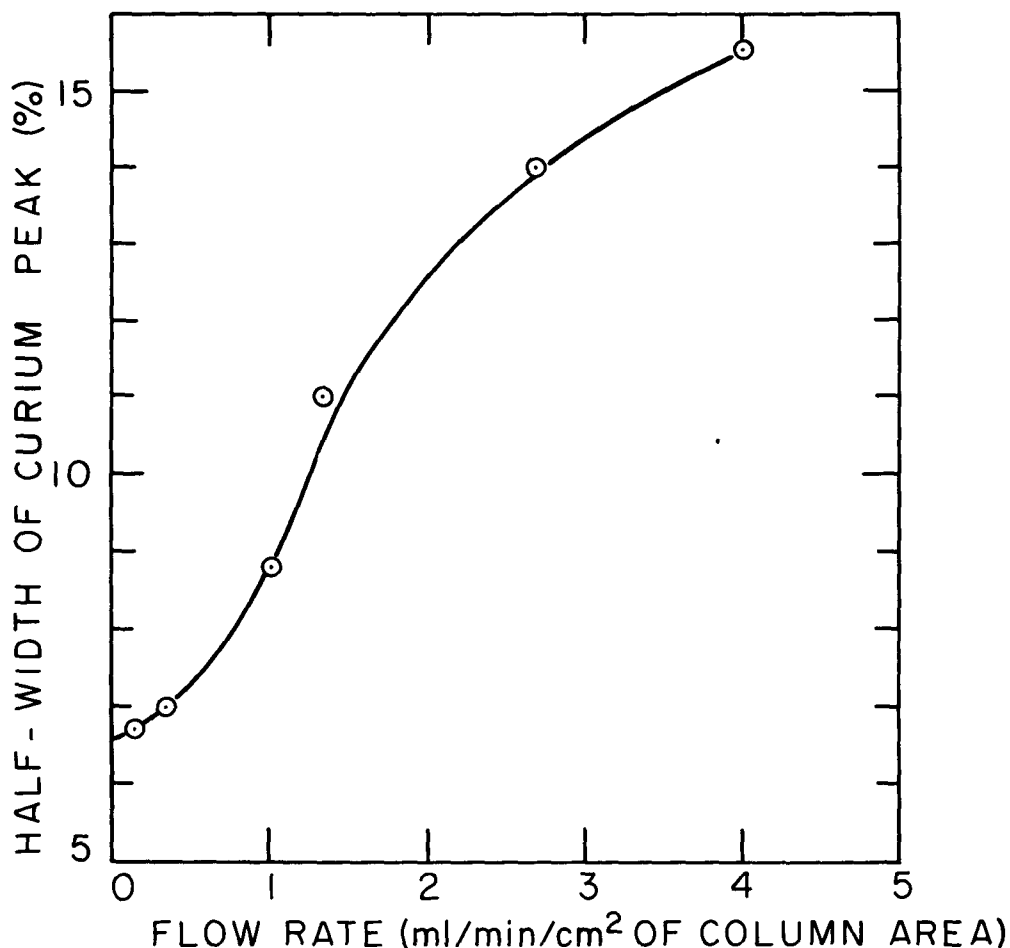


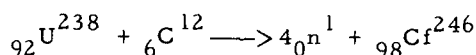
Fig. 8. Full width at half maximum (half-width) of the elution peak of curium from Dowex-50 12% cross-linked resin with 0.4M ammonium lactate at 87°C on one particular column. Similar curves would be obtained with other eluants and other columns, but the resin particle size, temperature of operation, length-to-diameter ratio of the resin bed, technique, and the presence or absence of carriers or mass impurities all affect the absolute value of half-width at any flow rate.

V. DISSOLUTION OF SAMPLES AND SPECIAL PROBLEMS RELATED TO HANDLING THE TRANSCURIUM ELEMENTS

The transcurium elements are all unstable with respect to a particle emission. Spontaneous fission is also a disintegration mode so that considerable numbers of neutrons may be emitted by some samples and targets. These facts make the handling of microgram or larger quantities of some transcurium elements very difficult and potentially hazardous. Most chemical operations must be carried on in gloved boxes, and in many instances

remote-control handling equipment is required even after the samples are free of fission product contamination. For instance, 1 microgram of Cf^{252} emits $\approx 2 \times 10^8$ neutrons/min and presents about a tolerance working dose of neutrons at a distance of 1 meter. Laboratories equipped to handle the transcurium elements should have α -particle and neutron survey meters as well as the usual β - γ survey meters.

The transcurium elements are produced in at least three different kinds of target. The neutron-deficient isotopes are produced by heavy-ion bombardments of uranium or plutonium by reactions such as



in which the product atoms are collected on "recoil catchers" separate from the bombarded target material. The techniques and difficulties are discussed by Thompson and Muga³ and Ghiorso and Sikkeland.²⁴ Briefly, when the chemistry is done, the target or catcher foil is dissolved in the appropriate strong acid solution and the appropriate separations are performed. When the transcurium elements are produced in this way no special handling equipment, such as glove boxes, may be needed although it may be needed for target preparation if transplutonium elements are bombarded. The target itself is seldom dissolved or handled when the recoil technique is used. Since the recoil atoms retain positive charges when stopped in helium gas, they can be electrostatically collected as thin samples and sometimes their decay characteristics can be studied without chemistry, however, some of the Pb and Bi isotopes have similar α -decay half-lives and particle energies so that identification by α particle measurements alone may be unreliable. The experiments done by Ghiorso, Sikkeland, Walton, and Seaborg leading to the discovery of element 102 (nobelium) are classic in the sense that every advantage has been taken of these nonchemical separation techniques. If chemistry is done on such electrostatically collected material, the collector plates are simply washed with concentrated HCl and the transcurium elements are removed without dissolution of the plate.

The second source of transcurium elements is the debris from thermonuclear explosions. Es and Fm were first discovered in filtered samples of the cloud produced by a multi-megaton thermonuclear explosion in which they had been produced by multiple neutron capture in U^{238} . The filter was dissolved by repeatedly digesting it in concentrated HNO_3 and finally destroying the last traces of organic material by fuming the residue in concentrated $HClO_4$. The fuming perchloric acid was then diluted with more than 10 times its volume of $6N$ HCl , and a separation procedure similar to Procedure 2 (Section VII) was performed on aliquots of this solution. The major massive impurities in such a solution are Ca, Fe, Na, and Al. This kind of sample usually has so little radiation that special handling equipment is unnecessary.

The last and most generally encountered source of the transcurium elements is uranium, plutonium, americium, or curium that has been exposed to large integrated neutron doses in a reactor. The production rates and chemical techniques are discussed by Thompson and Muga.³ The sample is usually produced in an aluminum-clad "slug" of an oxide or metal alloy of target material. Dissolution is accomplished by removing the aluminum in $6M$ $NaOH$ - $2M$ $NaNO_3$ solution, filtering or centrifuging the insoluble residue containing the transcurium elements away from the aluminate solution, and finally dissolving this residue with strong mineral acid (usually HCl , or occasionally HCl with a trace of HF and HNO_3). These operations are performed by remote control in shielded equipment since the target materials and intermediate isotopes undergo fission while the transcurium elements are being formed. The complete separations, including the isolation of a rare-earth fraction and the separation of the lanthanide and actinide fractions, are usually included in the "cave" operation. Procedure 1 in Section VII is typical.

VI. COUNTING PROCEDURES AND SOURCE PREPARATIONS

Counting samples of the transcurium elements are usually prepared "mass-free" or "thin" because there are no stable carriers, of course, and

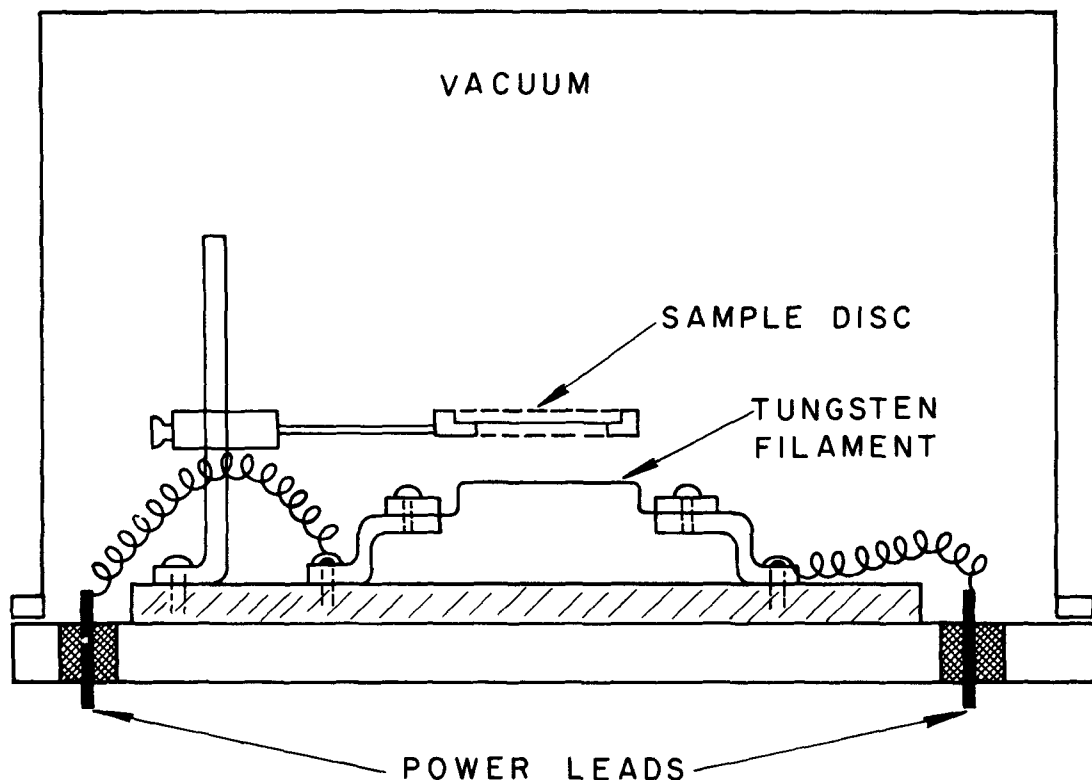


Fig. 9. Schematic diagram of vacuum volatilizer. Carrier-free solutions are evaporated on the tungsten filament, the system is evacuated, and the transcurium elements are volatilized onto the counting disc by passing a short-duration high-current pulse through the tungsten filament.

because some of the most useful measurements involve the α particles which have short ranges. The sample is usually prepared either by evaporating a drop or several drops of column eluate on a plate of platinum or other metal and then performing the counting operations, or by evaporating the pure carrier-free solution onto a tantalum or tungsten filament approximately 5 mm wide, 30 to 50 mm long, and 0.1 mm thick. This filament is placed between electrodes in a vacuum jar a few millimeters away from a $7/8$ -inch platinum counting disc, as indicated in Fig. 9, and the transcurium element salts (usually oxides) are volatilized onto the counting disc by allowing more than 10 amp of current to flow through the filament for a few tenths of a second. This current raises the filament temperature above 1400°C and effectively vaporizes all the transcurium material. Very thin uniform counting

plates can be prepared in this way; however, the active material will recoil off the plates at an appreciable rate unless they are heated to about 500°C in air.

No special counting equipment is used for detection of β , electron-capture, or α particles. Most tracer work is done with the transcurium elements by utilizing the fact that isotopes of these elements have unique α -particle energies. A particular process or bombardment can be traced by introducing known amounts, measured in terms of counts per unit time, of a specific longer-lived isotope (e.g., Cf^{252} or Cf^{254} to trace all Cf isotopes) and submitting the recovered samples to a pulse-height analysis to determine the ratio of α counts of several isotopes. An α pulse-height analyzer is a valuable and nearly indispensable piece of counting equipment for work with the transcurium elements.

The high spontaneous-fission decay rates are utilized in counting samples of the transcurium elements. Spontaneous fission counters are easily constructed by taking advantage of the fact that the specific ionization produced by fission fragments in a counting gas is higher than that produced by α particles. Large electrical pulses are obtained from fission fragments by modifying standard α -particle counters to operate with lower collector voltages. Satisfactory operation is usually obtained with the collector between $1/5$ and $1/2$ the voltage at which an α plateau is found. The gas flow proportional counters used for both α - and β -particle counting are especially useful because their collector voltages can usually be varied with ease. Semiconductor detectors and gas scintillation counters can also be used for detecting fission fragments and α particles.

VII. SPECIFIC SEPARATION PROCEDURES

Procedure 1

This procedure is for separation of an impure transcurium element fraction from a pile-irradiated plutonium or americium slug.²⁵ The process is designed to be performed on a 50-g aluminum slug containing 0.1 to 1.0 g of target material. Am and Cm are also purified.

The slug is placed in a dissolver pot surrounded by an oil bath heated to 80°C with an electric immersion heater. Then 800 ml of solution 6M in NaOH and 2M in NaNO₃ is added. The aluminum violently reacts and goes into solution (no heat required after reaction starts). The insoluble material is allowed to settle and the supernate is withdrawn through a sintered stainless steel filter stick. The precipitate is washed twice with 50-ml portions of 2N NaOH saturated with NH₃ gas, and then washed with 100 ml of H₂O. The washed precipitate is dissolved by adding 50 ml of 12M HCl - 0.1M HNO₃ and digesting. After the residue is dissolved, 50 ml of 11M LiCl is added and the solution is evaporated to 50 ml.

The solution is transferred to a 4-cm-diam × 20-cm-long Dowex-1 10% cross-linked resin column which is heated to 80°C with a water jacket. (Free column volume is ≈ 150 ml.) The evaporator container and column walls are washed with two 50-ml portions of 10M LiCl which are allowed to run through the column at the rate of about 2 ml/min. An additional 300 ml of 10M LiCl is passed through the column to elute the lanthanides, alkaline earths, and alkali metal ions. The transplutonium actinides are next eluted with 200 ml of 6N HCl. Plutonium remains on the column.

The 6N HCl is diluted to 600 ml and passed through a Dowex-50 12% resin bed 4 cm in diam and 20 cm long. The column is then washed with 300 ml of 2M NH₄Cl which removes Cr, Ni, and several other impurities and converts the resin to the NH₄⁺ form. The actinides are then eluted with 0.4M α-hydroxyisobutyric acid adjusted to a suitable pH. The desired elements are collected in four or five "cuts" selected on the basis of the ele-

Procedure 1 (Continued)

ments desired for further work and the number of FCV's predicted from Fig. 7 and the pH. The FCV is ≈ 150 ml. The transcurium element fraction thus obtained may be pure enough to be processed without remote-control equipment and is usually further purified by a procedure similar to Procedures 2 and 3 following

Procedure 2

This procedure was devised to separate the transplutonium elements from day-old fission product samples containing 10^{15} to 10^{16} fissions.²⁶ These elements are carried with yttrium or lanthanum fluoride and hydroxide precipitates, which are subsequently dissolved in HCl, the resultant solution is passed through several anion resin columns to remove U, No, Pu, and most of the remaining fission products (in particular, Zr and Te). An ethanol-HCl elution from a cation resin column is used to remove the lanthanides.

To prepare the ion exchange columns, the column tips are 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 eluant through the column. A uniformly deposited bed of resin, free from air bubbles or channels, is essential to a successful elution.

1. To an aliquot of the sample in a 40-ml centrifuge tube, add 2 drops each of 10 mg/ml Zr, Te, and Sr carriers and 1 drop of 10 mg/ml Y carrier. Using phenolphthalein indicator, add NH_4OH to precipitate the $\text{Y}(\text{OH})_3$. Centrifuge, discard the supernate, and wash the precipitate twice with 0.5-1.0 ml H_2O

2. Dissolve the precipitate in a minimum amount of 3M 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 enough HF to de-

Procedure 2 (Continued)

colorize the solution, then 2 drops per ml in addition.) Let the solution stand for 5 minutes, centrifuge, discard the supernate, and wash the precipitate with 0.5 ml of 2M HF - 2M HNO_3 solution.

3. Dissolve the fluoride precipitate by adding 1 drop saturated H_3BO_3 , stirring, and then adding 2 ml conc HCl. Transfer the solution to a 40-ml glass centrifuge tube. Add 2 drops of 10 mg/ml Sr carrier and then boil the solution briefly. Precipitate the $\text{Y}(\text{OH})_3$ with NH_4OH , centrifuge, discard the supernate, and wash the precipitate twice with 0.5-1.0 ml H_2O .

4. Dissolve the precipitate in 3 ml 10M HCl. Add 1 drop conc HNO_3 . Transfer the solution to a 5-cm \times 2-cm Dowex-1 AG anion resin column which has been washed with several column volumes of 10M HCl solution containing 0.1M HNO_3 . Push through with pressure. After adding 1 drop each of 10 mg/ml Zr and Te carriers, pass the solution through two additional 10-cm \times 8-cm anion columns which have also been treated with 10M HCl containing 0.1M HNO_3 (the small column contains Pu if present in the initial solution).

5. Add NH_4OH to the combined 10M HCl solution to precipitate $\text{Y}(\text{OH})_3$. Centrifuge, discard the supernate, and wash the precipitate twice with 0.5 ml H_2O .

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

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 \times 2-cm 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-

Procedure 2 (Continued)

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 (usually drops 6-25) in a 40-ml centrifuge tube. (See Fig 1 for typical elution positions.)

This solution will be free of most contaminants, however, the column separation can be repeated for complete separation of the lanthanide activities. The pure activities can be separated from each other with Procedure 3.

Note: Several variations of steps 6 and 7 are reported by different workers. Some prefer loading the resin slurry onto the resin bed of the column in step 7. Others prefer to run the solution from step 6 directly into the long column and to follow it with 10 to 20 column volumes of 2M HCl, then the alcoholic HCl. The 2M wash moves the transcurium elements down the column about 10% of the length and they are less perturbed by the shrinkage and accidental stirring of the resin than otherwise.

Procedure 3

This procedure is for separating the actinides from each other in solutions free of lanthanides, other mass impurities, and radioactivities. It is similar to the procedure of Thompson *et al.*⁶ except that it uses a hydroxyisobutyric acid instead of lactic acid, and consequently gives better separations.²⁷

1 Preparation of resin eluant and equipment.

A. Dowex-50 12% cross-linked resin, 200-400 mesh spheres (obtained from Bio-Rad Labs., 32nd and Griffin Ave., Richmond, Calif.), is further graded for size by selecting the fraction that settles between 0.5 and 0.25 cm/min from water.

B. The graded resin is washed alternately with 12M HCl and NH_4OH and finally stored in the ammonium form.

Procedure 3 (Continued)

C. The eluant is prepared from commercial α -hydroxyisobutyric acid diluted to 0.4M with the pH adjusted between 3.8 and 4.4 to give the desired elution time-peak separation. (See Fig. 7.) Phenol may be added until the solution is 0.01M to prevent the growth of mold.

D. Apparatus is set up as in Fig. 5. The column bore is 2 mm in diam and about 10 cm long over the capillary region. The tip is plugged with glass wool. The column is heated to the boiling point of trichloroethylene and the bore is filled with distilled water, then small amounts of resin slurry are added to the column and allowed to settle into the bore until a settled bed 5 cm in height is obtained. The excess distilled water is removed and several ml of eluant is added to further remove trace impurities. Just prior to using the column, the eluant reservoir is lowered, the top of the column is washed with distilled water, and a drop or two of distilled water is allowed to run into the column

2 An HCl or HNO_3 solution containing the actinide element mixture is evaporated to near dryness in a 5-ml centrifuge cone, and diluted with ≈ 0.1 ml of hot 0.05M HCl . This solution is transferred to the resin bed and allowed to run through. The cone and sides of the column above the resin bed are washed with $50\text{ }\mu\text{l}$ of 0.05M HCl solution which is allowed to run into the resin. The washing procedure is repeated.

3. The centrifuge cone is washed with $50\text{ }\mu\text{l}$ of eluant which is then transferred to the column and allowed to run into the column. The first drop to fall from the column after this is "drop 1" of the elution.

4. The bore of the column above the resin is filled with hot eluant carefully so as to avoid stirring the resin bed, and the eluant reservoir is lifted to provide the desired flow rate (see Fig. 8). Satisfactory separations are obtained with flow rates of $1/2$ to 1 drop per minute.

5. Each drop is collected on a platinum plate which is dried under a heat lamp and heated to red heat in an induction heater to remove the last

Procedure 3 (Continued)

traces of organic material. Plates are ready to count.

The approximate elution positions can be predicted from the curve in Fig. 7 and from Table II, assuming a 3-drop free column volume; however, slight variations in eluant and resin make it desirable to "calibrate" each column with a tracer of some transplutonium actinide before separations are attempted. If carriers are included in the solution the same procedure can be followed, but the column size should be adjusted to provide 0.4 cm^2 of column area for each milliequivalent of carrier, and the length of the column should be at least 10 times the diameter.

Procedure 4

This procedure separates the actinides from the lanthanides.⁶ Dowex-1 resin is used with an HCl solution containing the actinide elements, lanthanide activities, and about 1 mg lanthanum carrier.

A. Dowex-1 8% cross-linked resin, 200-400 mesh spheres, is size-graded by selecting the fraction that settles from 0.15 to 0.25 cm/min in water. The graded resin is washed alternately with 12M HCl and NH_4OH and is stored in the chloride form after a final HCl wash.

B. Eluant is prepared by saturating commercial analytical grade HCl with HCl gas. Immersing the bottles in room-temperature tap water helps dissipate the heat. The final concentration of acid at 20-22°C will be about 13M .

C. The column is prepared by attaching a section of 3-mm-diam capillary tubing to a 15-ml centrifuge cone, packing the tip with glass wool, and filling the bore to a height of 5 cm with the resin. The column should be alternately washed with eluant and water before use. The final wash is made with eluant.

1. The solution to be purified is evaporated to $\approx 30 \mu\text{l}$ with an air jet in a 5-ml centrifuge cone. The cone is placed in an ice-water bath

Procedure 4 (Continued)

and the solution saturated with HCl from a gas cylinder.

2. The solution is transferred to the top of the column. The first drop to fall after this is called "drop 1." The cone is rinsed with 30 μ l of eluant which is transferred to the column. This wash is then repeated. One milliliter of eluant is carefully placed on top of the column and drops are collected through drop 12. The flow rate can be maintained at about 3 minutes per drop with a hypodermic syringe and rubber stopper.

3. After drop 12 has fallen, the eluant is removed above the resin, a 15-ml centrifuge cone is placed under the column, and 1 ml of 10M HCL is placed on top of the resin. This is passed through the resin and elutes the transcurium elements. Am, Cm, and the lanthanides are found in drops 1-12. U and Pu (in the IV or VI oxidation state) remain on the resin and may be subsequently removed.

Procedure 5

This procedure²⁷ is for purification of Md recoils produced by a particle bombardment of Es²⁵³. It is typical of the catcher foil chemical techniques. Other actinide targets and products are similarly handled.

The target consisted of $\approx 10^9$ atoms of Es²⁵³ electroplated on a 1/32-in. \times 1/4-in. area of larger 0.002-in. -thick gold foil. A 48-Mev α beam was allowed to pass through the gold target foil and "knock off" the Md atoms onto a 0.0001-in. -thick gold "catcher" foil.

1. The catcher foil was dissolved in aqua regia, and the gold extracted with an equal liquid volume of ethyl acetate for \approx 1 min.

2. The aqueous phase was passed through a 2-mm-diam \times 1-cm-long bed of Dowex-1 anion resin heated to 87°C (see Fig. 9), at a rate of about five 30- μ l drops per minute. The original volume plus 5 drops containing the actinide elements was collected and evaporated with a jet of hot air.

Procedure 5 (Continued)

3. Tracer Es^{253} was added and the solution was passed through a 2-mm-diam by 5-cm-long bed of Dowex-50 \times 12 ammonia-form cation resin heated to 87°C. The adsorbed actinides were selectively eluted with a 0.4M solution of α -hydroxyisobutyric acid which had been adjusted to pH \approx 4.0 with ammonium hydroxide. The eluant was passed through the column at a flow rate of approximately four 20- μ l drops per minute. The Md fractions were collected in drops 8-13, Fm in drops 15-19, Es in drops 27-31, and Cf in drops 39-47.

Procedure 6

This procedure is for oxidation and extraction of Bk from a solution containing lanthanides and actinides.⁹ No carriers are used.

1. The solution is evaporated to near dryness two or three times with 16M HNO_3 . After the last evaporation, the sample is diluted and KBrO_3 is added to make the solution 10M in HNO_3 and 1M in KBrO_3 (Note 1). The volume of the solution is measured in milliliters (called V in the following).

2. V ml of 0.15M HDEP (Note 2)-heptane solution is washed three times with V ml of freshly prepared 10M HNO_3 - 1M KBrO_3 , for 3 minutes each time. The aqueous phases are discarded.

3. The solution from step 1 is contacted with the organic phase from step 2 for 3 minutes and the phases are separated.

4. The organic phase from step 3 is washed twice for 3 minutes with V ml of freshly prepared 10M HNO_3 - 1M KBrO_3 . The wash solutions are discarded.

5. The washed organic phase from step 4 is back-extracted for 3 minutes into V ml of freshly prepared 10M HNO_3 - 1.5M H_2O_2 solution. The organic phase is discarded.

6. The aqueous phase from step 5 is washed, first with V ml of 0.15M

Procedure 6 (Continued)

HDEP — heptane for 3 minutes, and then with V ml of heptane for 3 minutes. The organic phases are discarded, the aqueous phase contains $\approx 97\%$ of the Bk, decontaminated by factors of $\approx 10^4$ from all other lanthanides and actinides except Ce, and by factors of $\approx 10^6$ from Cm and Cf. (Note 3.)

Notes

1. 0.1M KBrO_3 may be substituted at all points calling for 1M KBrO_3 with little or no decrease in yield.

2. HDEP is di(2ethylhexyl) orthophosphoric acid, $\left[\text{C}_8 \text{H}_{17} \text{O} \right]_2 \text{PH}(\text{OH})$, and is available in impure form from the Victor Chemical Works. It is purified by the procedures reported by D.C. Stewart and H.W. Crandall, J. Am. Chem. Soc. 73, 1377 (1951).

3. Cunningham and Wallmann¹¹ have used a procedure similar to this for extracting submicrogram quantities of Bk from Cf and Cm. Solution volumes were reduced to submicroliter quantities.

Procedure 7

This procedure is for removal of macro impurities from tracer trans-curium samples.¹⁷

1. A jacketed column for operation at 87°C is prepared. Dowex-50 AG 4% cross-linked resin (settling rate 0.5 to 0.25 cm/min) is used in the H^+ form (HCl wash last), and prepared otherwise as in Procedure 3, steps 1A and 1B. The column bore is 3 mm in diam and the tip consists of a platinum rod fused to the glass capillary and bored out with a No. 64 drill. This tip delivers uniform 13- μl drops.

2. The solution to be purified is prepared so as to be 0.1M in HCl and then allowed to pass through the column. The column walls are rinsed with several 100- μl portions of 0.1M HCl.

3. About 1 ml of 2M HCl is carefully introduced above the resin bed

Procedure 7 (Continued)

and forced through the resin at the rate of about 6 drops per minute until 50 drops have been collected.

4. The remaining 2M HCl is withdrawn and 1 ml of 6M HCl is added and forced through the resin at the rate of 6 drops per minute until 30 or 40 drops are collected. The transcurium elements elute close together around drop 80 (counting from the beginning, including the 50 drops from step 3). Other cations elute as indicated in Table III.

Procedure 7 (Continued)

Table III. Order of elution of cations from resin column in Procedure 7.

Cations ^a	Drop No.	Free Column Volumes (after first)
Au } Pd } Pt }	≈ 7	
Bi	13	
Cd	16	
Pb	17	
Li } Mo }	22	2.6 of 2M HCl
Cu	24	
Fe	26	
Na	28	
Be	30	
Mg } Rb } Ni }	37	
Ca	53	2.8
Al } Sr }	64	3.6
Ba	70	4.0
Actinides and Lanthanides	75-85	4.4 - 5.1
Zr	96	5.9

^a The oxidation state of these ions was not specified. Where questions exist, it can be assumed that the oxidation state most stable and soluble in 2N HCl is the one indicated. The column specified will handle 0.1 to 0.2 mg of macro impurities, and peak half-widths (full widths at half maxima) generally run 6-8% under the conditions specified. These data have not all been reduced to free column volume units because several of the ions (Au, Pd, Pt, Bi, Cd, and Pb) move appreciably in 0.1N HCl and their elution position will depend on the volume of the solution from which the material is adsorbed. The positions of the actinides and lanthanides are not similarly affected.

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