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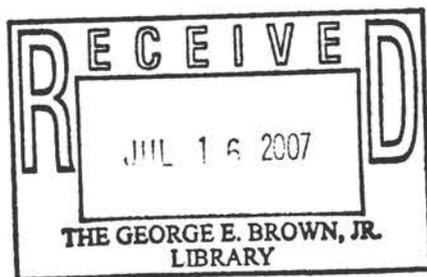
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# The Radiochemistry of Francium

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January 1960



**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, the problems of stockpiling uncontaminated materials, the 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

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# The Radiochemistry of Francium\*

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January 1960

## I. INTRODUCTORY REMARKS - THE GREAT NUCLEAR INSTABILITY OF FRANCIUM

The principal isotope of the alkali element, francium, is actinium K discovered in 1939 by Mlle. M. Perey<sup>1-3</sup> among the decay products of actinium. Perey showed that alpha emission occurred in 1.2 percent of the radioactive disintegrations of actinium and gave rise to a beta emitter with the properties of a heavy alkali element and a half life of 21 minutes. Following the system of nomenclature used in the natural radioelements, she chose the name actinium K for this radioelement. Later when it became clear from her extensive studies of the nuclear origin and the chemical characteristics of this radioelement that she had made the first unchallengeable identification of an isotope of element 87, she accepted the honor of naming the element and chose francium.

A number of isotopes of francium have been prepared by reactions of artificial transmutation. The identification of these isotopes has come about chiefly by the investigation of the complex mixture of radioactivities produced

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\*This report was prepared at the request of the Subcommittee on Radiochemistry of the Committee on Nuclear Science of the National Research Council as a contribution to a proposed master file on the radiochemistry of all the elements.

when thorium is bombarded with high energy protons. One isotope<sup>4</sup>, the 4.8 minute  $\text{Fr}^{221}$ , is a member of the decay chain of  $\text{U}^{233}$ . From a glance at Table 1, it is

Table 1. The Isotopes of Francium

Isotope	Half life	Type of decay	Energy of $\alpha$ -particles (Mev)	Method of Preparation
$\text{Fr}^{223}$ (AcK)	21 min	$\beta$	--	Daughter $\text{Ac}^{227}$ in $\text{U}^{235}$ decay family
$\text{Fr}^{222}$	14.8 min	$\beta$	--	Th + p
$\text{Fr}^{221}$	4.8 min	$\alpha$	6.33(84%) 6.12(16%)	Member $\text{U}^{233}$ decay family
$\text{Fr}^{220}$	27.5 sec	$\alpha$	6.69	Member $\text{Pa}^{228}$ decay family
$\text{Fr}^{219}$	0.02 sec	$\alpha$	7.30	Member $\text{Pa}^{227}$ decay family
$\text{Fr}^{218}$	$5 \times 10^{-3}$ sec (est.)	$\alpha$	7.85	Member $\text{Pa}^{226}$ decay family
$\text{Fr}^{212}$	19.3 min	$\alpha$ 44% K 56%	6.342(24%) 6.387(39%) 6.411(37%)	Th + p

seen that none of the artificially-prepared isotopes is of longer life than actinium K. A number of authors<sup>5-7</sup> have examined the trends in nuclear stability throughout the entire heavy element region above lead and have arrived at the following conclusions about the nuclear stability of francium isotopes: there is no possibility that a stable isotope will be found; there is a slight possibility that a nuclear species with a somewhat longer life than AcK will eventually be identified but the chances even of this are not high; it appears likely that francium will remain the most unstable of the first 100 elements.

It follows then that the macroscale chemistry of francium cannot be investigated and that the chemistry of francium is identical with the radiochemistry of the element. The radiochemist is interested in the radiochemistry of francium for three chief reasons.

1. The separation of actinium K from natural or artificial sources of actinium as a preliminary to the investigation of the radiochemical or

biological properties of a pure solution of this activity or for an investigation of its radiations.

2. The quantitative removal of actinium K from an actinium source and quantitative measurement of its disintegration rate as a method of assay of the strength of an actinium source. This application is of some importance because of the difficulty of the calibration of actinium sources by other methods.<sup>8</sup>

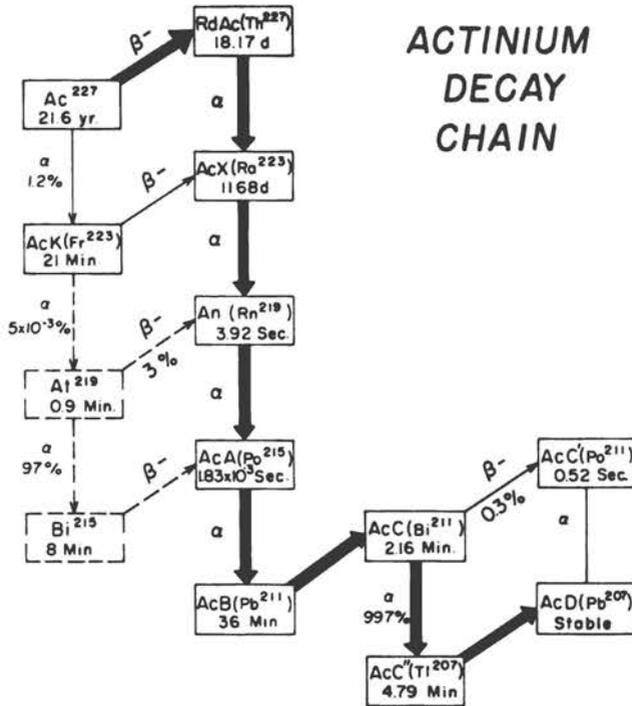
3. The separation of francium isotopes from targets bombarded with charged particle beams. In the past the principal type of nuclear reaction study has involved the bombardment of thorium targets with high energy protons in synchrocyclotrons. In the near future there will be interest in the isolation of francium from targets of mercury, thallium, lead, and bismuth bombarded with highly accelerated ions of such heavier elements as carbon, nitrogen, oxygen, neon and argon.

## II. THE ACTINIUM DECAY CHAIN AND THE RADIATIONS OF ACTINIUM K.

Since actinium K will remain the most widely used isotope of francium, it is necessary to consider its radiations in some detail. Because of its short half life it is necessary in any work with AcK to consider its genetic relationships with actinium and with the other members of the actinium decay chain.

Figure 1 shows the course of the actinium decay chain. Only 1.2 percent of the disintegrations of  $\text{Ac}^{227}$  produce atoms of AcK which puts a severe limitation on the amount of AcK which one can isolate. Some pertinent intensity figures are summarized in Table 2. Actinium K also undergoes alpha branching<sup>9</sup> to produce  $\text{At}^{219}$  but this branching is so slight that for ordinary radiochemical purposes it can be completely neglected. The chief decay is by the emission of energetic beta particles with an endpoint energy of 1.15 Mev. These energetic beta particles are easily counted in an ordinary GM counter or proportional counter using standard corrections for back scattering, self absorption, self scattering, etc. In addition, actinium K does emit some characteristic gamma rays as summarized in Table 3. Details on the measurement of these gamma rays can be found in references a and c cited in the table.

# ACTINIUM DECAY CHAIN



NU-18331

Fig. 1. The decay chain of actinium. The main path of the decay is shown in bold arrows.

Table 2. Some Useful Intensity Figures

One milligram  $\text{Ac}^{227} = 1.62 \times 10^{11}$  disintegrations/minute =  
73 millicuries  $\text{Ac}^{227} = 0.87$  millicuries AcK (at equilibrium).

One millicurie  $\text{Ac}^{227} = 2.22 \times 10^9$  disintegrations/minute =  
12 microcuries or  $2.66 \times 10^7$  disintegrations/minute of AcK  
(at equilibrium).

1000  $\beta^-$  disintegrations/minute of AcK will decay to form 1.25  
 $\alpha$  disintegrations/minute of AcX alpha activity (plus an equi-  
valent number of  $\alpha$  disintegrations of An, AcA and AcC). This  
alpha activity will then decay with an 11.7 day half life.

One metric ton of natural uranium in an undisturbed ore sample  
contains 0.2 milligrams  $\text{Ac}^{227}$  and  $3.8 \times 10^{-10}$  grams AcK.

Table 3. Decay Characteristics of Fr<sup>223</sup>(AcK)

		Reference
Half life	21 minutes	
Energy of main $\beta^-$ particle	1.15 Mev 1.2 Mev	a b,c
Energy and abundance of gamma radiations	49.8 kev 40% 80 kev 24% 215 kev 3% 310 kev 0.8%	a (see also c)
Energy of $\alpha$ -particle	5.34 Mev	d
Abundance of $\alpha$ -particle	$5 \times 10^{-3}\%$	e

- a. E. K. Hyde, Phys. Rev. 94, 1221 (1954).  
 b. M. Perey and M. Lecoïn, J. phys. et radium 10, 439 (1939); Nature 144, 326 (1939).  
 c. M. Lecoïn, M. Perey, M. Riou et J. Teillac, J. physique et Radium 11, 227 (1950).  
 d. J. P. Adloff, Comp. Rend. 240, 1421 (1955); M. Perey and J. P. Adloff, J. phys. et radium 17, 545 (1956).  
 e. E. K. Hyde and A. Ghiorso, Phys. Rev. 90, 267 (1953).

One method of calibrating the counting efficiency of a beta counter for AcK activity is described by Hyde<sup>10</sup> as follows. "A sample of radiochemically pure carrier-free AcK was evaporated in the center of a one-inch diameter platinum disc. An asbestos washer was placed on the disc and a clean platinum collector disc was placed above a few millimeters away. A torch was touched to the bottom disc for one second to bring the platinum to a red glow and the francium was volatilized to the collector foil, leaving behind any traces of Ac<sup>227</sup>, AcX or RdAc present at that time. This instant was taken as zero time. The counting rate of the volatilized francium sample was followed and extrapolated back to zero time. Several hours later the alpha disintegration rate of the sample was carefully measured in an alpha counter (52 percent geometry for platinum backed samples). One-fourth of this alpha activity was ascribed to the 11.7 day AcX daughter of AcK and by straightforward calculations the absolute value of the initial disintegration rate of AcK at time zero was calculated. 1000 disintegrations of 21 minute AcK produces 1.25 disintegrations of 11.68 day AcX. This method of standardization substitutes the lesser

uncertainties of alpha counting for the greater uncertainties of absolute beta counting. For further certainty the identity and purity of the alpha spectrum can be checked by pulse height analysis of the linearly amplified pulses of an alpha ionization chamber designed for alpha energy determinations.

An initially pure sample of AcK will show a straight line decay (when plotted on semi-log paper) with a half life of 21 minutes for about 3 half lives but will eventually turn over into a long lived component ("tail") contributed by the daughter activities. The alpha particles of the AcX, actinon and AcA can be blocked from the beta counter by placing a few milligrams of aluminum absorber over the sample but the energetic beta particles of AcB and AcC" are not removed. These activities grow to a counting rate a few tenths of a percent of the original counting rate of Actinium K. When the counting rate of the daughter activities becomes an appreciable fraction of the AcK counting rate it is necessary to repurify the AcK or to isolate a new sample from the actinium source. Hence in most experimental studies one starts with an actinium source, spends somewhere between 10 and 40 minutes isolating and purifying an AcK sample and then has about a two hour period in which to carry out experiments.

### III. TOPICAL REVIEW OF THE RADIOCHEMISTRY OF FRANCIUM

#### A. Coprecipitation Behavior

Francium is the heaviest member of the alkali group of metals and resembles most closely the element cesium. Many of the chemical techniques for the isolation of francium have been adapted from cesium procedures. The radiochemist should keep in mind the possibility of adapting any recently discovered information on the chemical separation of cesium for the same purpose in its higher-mass homologue.

Francium presumably exists in aqueous solution as a large singly-charged ion with little tendency to form complex ions. Like the other alkali elements francium remains in solution when other elements are precipitated as hydroxides,

carbonates, fluorides, sulfides, chromates, etc. One method of francium purification consists simply in the removal of all foreign radioactivities by the successive precipitation of a series of insoluble scavenger precipitates following which the radiations of francium are sought in the residual solution.

Francium does coprecipitate with some insoluble salts however. Our knowledge of this behavior comes largely from the work of M. Perey<sup>3,11</sup> and can be summarized as follows.

Cesium perchlorate.  $\text{CsClO}_4$ . If several milligrams of cesium chloride are added to a small volume of chilled francium solution and a concentrated solution of sodium perchlorate is added, the perchlorate of cesium, insoluble in alcohol, precipitates with 60 percent of the francium. Actinium C" (thallium) also precipitates.

Glendenin and Nelson<sup>12</sup> published a radiochemical procedure for cesium, based on the precipitation of cesium perchlorate, which can be adapted to the coprecipitation of francium. They applied their method to the isolation of fission product cesium from uranium. They precipitated added cesium carrier as the perchlorate from cold perchloric acid. The insolubility of the compound was enhanced by the addition of alcohol. To eliminate certain other radioactive contaminants such as zirconium, niobium, molybdenum, tin, antimony and tellurium, ferric hydroxide was thrown down as a by-product precipitate. Rubidium if present was removed by a preliminary precipitation of cesium silicotungstate from 6 N HCl which left the rubidium unprecipitated. A procedure incorporating the precipitation of cesium perchlorate is described in Section IV.

A carrier-free method of isolation of cesium is described by these same authors.<sup>13</sup> Cesium activities are coprecipitated on ammonium perchlorate from cold perchloric acid with absolute ethanol. This procedure could also be used for francium. A by-product ferric hydroxide precipitate removes contaminating activities. In the final solution the  $\text{NH}_4^+$  ion and  $\text{ClO}_4^-$  ions are destroyed with aqua regia leaving pure cesium. A disadvantage of this procedure is that any sodium or rubidium initially present is not removed.

Cesium picrate.  $C_6H_2(NO_2)_3OCs$ . Cesium picrate formed by the addition of a solution of picric acid in 50 percent alcohol to a solution containing cesium carrier and francium activity will carry 50 percent of the francium.

Cesium iodate.  $CsIO_3$ . A precipitate of cesium iodate will remove a part of the francium traces from an aqueous solution.

Cesium and rubidium tartrate. The experimental conditions are important in this case. When cesium tartrate is precipitated from an acetic acid solution of small volume a part of the francium is removed with the precipitate. In a dilute acetic acid solution in the presence of potassium some potassium tartrate precipitates but it carries neither the francium nor the cesium. It does however carry actinium C", an isotope of thallium.

Alkali chloroplatinates.  $M_2PtCl_6$ . Francium coprecipitates with the chloroplatinates of cesium, rubidium, and potassium which are insoluble in a mixture of water and alcohol while those of sodium and lithium are soluble. The potassium compound is more soluble than those of rubidium or cesium. Francium coprecipitates nearly quantitatively.

Cesium chlorobismuthate.  $Cs_2B_1Cl_5 \cdot 5 H_2O$ . Quantitative coprecipitation of francium.

Cesium chloroantimoniate.  $Cs_2SbCl_5 \cdot 2.5 H_2O$ . Ninety percent of the francium coprecipitates.

Cesium chlorostannate.  $Cs_2SnCl_6$ . Nearly complete coprecipitation. When cesium chlorostannate is precipitated from a dilute solution of francium, cesium and rubidium, the rubidium remains in solution while the francium coprecipitates with the cesium.

Cobaltinitrites.  $Cs_2Na [Co(NO_2)_6]$ . In an acetic acid solution the double salt of cesium and sodium is sparingly soluble and removes francium from solution.

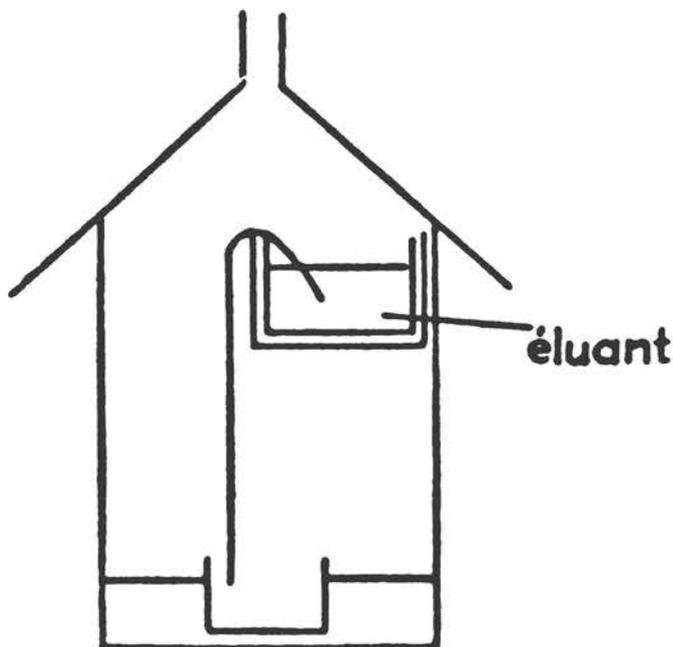
Cesium silicotungstate.  $Cs SiO_2 \cdot 12 WO_3 \cdot n H_2O$ . Francium precipitates quantitatively with this compound. Similar heteropoly acid salts such as silicomolybdate, phosphotungstate etc. are also good carriers for francium.

$Cs_3Bi_2I_9$ . Evans<sup>14</sup> has published a cesium fission product isolation method based upon the precipitation of this double salt from cold acetic acid solution. Probably this procedure could be adapted to francium isolation. A preliminary precipitation of a mixed hydroxide and carbonate precipitate is used to remove many interfering activities.

Silicotungstic acid. From many standpoints the best compound for the coprecipitation of francium is silicotungstic acid precipitated from concentrated or saturated hydrochloric acid.<sup>15</sup> This carrier is to be distinguished from its cesium salt. The free acid is insoluble in strong hydrochloric acid and removes francium quantitatively and selectively from solution. This carrier has the virtue that it can be instantly dissolved in a little water and then reprecipitated by addition of an excess of hydrochloric acid. The francium can be cleanly separated from the silicotungstic acid carrier by dissolving it in a little water, and passing it through a short column of Dowex 50 cation exchange resin. The francium is adsorbed while the unionized silicotungstic acid passes through. The francium can then be quickly eluted from the resin with a little concentrated hydrochloric acid. Detailed procedures based on the use of this carrier are given in Section IV of this report.

#### B. Filter Paper Chromatography

Adloff and Perey<sup>16,17</sup> have developed a rapid method for the separation of AcK from Ac based on filter paper chromatography. A very simple technique of descending chromatography was selected. The experimental apparatus is sketched in Fig. 2. Schleicher paper about one centimeter wide and 15 centimeters long was used. The eluant was a 10 percent solution of ammonium carbonate. A drop of solution containing the radioelements is evaporated near the top of the paper at the position "zero" about 2.5 centimeters from the end of the paper strip. This upper end of the paper is dipped into the eluant. The eluant is sucked up by the paper. A liquid front forms and moves down the paper entraining the radioelements selectively as it passes through the position zero. The elution is speeded if an atmosphere of saturated water vapor is maintained



MU-18339

Fig. 2. Simple chromatography apparatus used by Adloff.<sup>16</sup>

around the paper particularly if the temperature is raised to 60°C. At this temperature the liquid front travels 8-12 centimeters in 15 minutes.

Ammonium carbonate was chosen as the eluant since actinium, radioactinium, actinium X and actinium B are isotopes of elements whose hydroxides or carbonates are insoluble; hence these activities are moved little or none from position zero. The AcK and the AcC" ( $Tl^{207}$ ) move rapidly down the paper, reaching a position some 8-12 centimeters below the zero point in 15 minutes. These eluted activities can then be extracted from the paper band by simple washing with water or a weakly acid solution. By boiling this solution, the excess of ammonium carbonate is destroyed leaving a carrier free solution of AcK and AcC". All reagents must be of high purity. Some procedures using the chromatography separation as a final step are given in Section IV.

If the actinium parent source contains only a small amount of rare earths or none at all, it is possible to put the actinium directly on the paper and

to elute the actinium K from it very quickly. With good technique the complete time of separation may be reduced to as little as 6 minutes.

Fouarge and Meinke<sup>18</sup> have suggested another chromatographic technique. They recommend that the actinium source be adsorbed on top of an 8 centimeter long column of cellulose mixed with zirconium oxide in the weight proportions 2.5 to 0.25. Some  $H_2O_2$  should be added to the actinium solution before adsorption. The elution is done with phenol (liquified by equilibration with 2 N HCl). The actinium K elutes from the column within a few minutes. The volume of the solution containing the francium is only 2-5 milliliters. There is some contamination with  $Ac^{227}$  which can be removed with an additional decontamination step consisting of the precipitation of  $BaSO_4$  or  $BaCrO_4$ . The purpose of the  $ZrO_2$  and the  $H_2O_2$  is to reduce the elution of radioactinium.

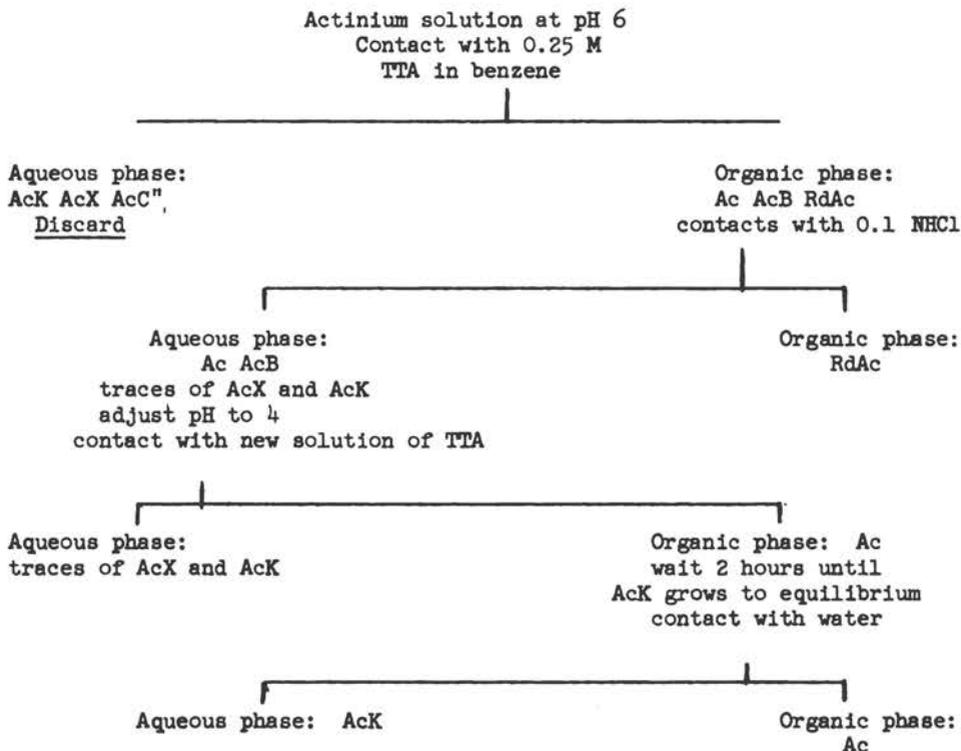
### C. Use of $\alpha$ -Thenoyltrifluoroacetone in the Purification of Actinium K

The  $\beta$ -diketone,  $\alpha$ -thenoyltrifluoroacetone, (called TTA for convenience) is widely used as a complexing agent in radiochemistry. In benzene solution it forms extractable complexes of many elements, particularly those elements existing as highly-charged ions in aqueous solution. The extractability of these complexes is sensitively dependent on the acidity of the system because of the appearance of the hydrogen ion concentration to the nth power in the equation,



Francium does not form a complex with TTA but all the other members of the actinium decay chain with the exception of actinium X do form extractable complexes if the pH is suitably adjusted.

The outline of a procedure for isolating actinium K from actinium is given by Adloff<sup>16</sup> as follows.



This method does not work at all well if the actinium source contains a great quantity of rare earth elements because the solubility of the TTA complexes in benzene is rather limited. There are some other disadvantages. For example, it takes several minutes of stirring before the complex is formed and extracted. Also the extraction coefficients lie in the range of 20 to 100 and are not so large that a clean separation can be made in a single extraction.

However, the last step of this procedure is attractive. Once an actinium sample is highly purified and extracted into benzene as the TTA-complex it is a simple matter to wait for the actinium K to grow into the equilibrium amount and then to back extract the actinium K into distilled water. This washing out of the actinium K is essentially instantaneous. If the ratio of the benzene to water is kept high (perhaps 10 to 1) the back extraction of the actinium is kept to a minimum. An increase in the TTA concentration of the benzene is also very helpful in this respect.

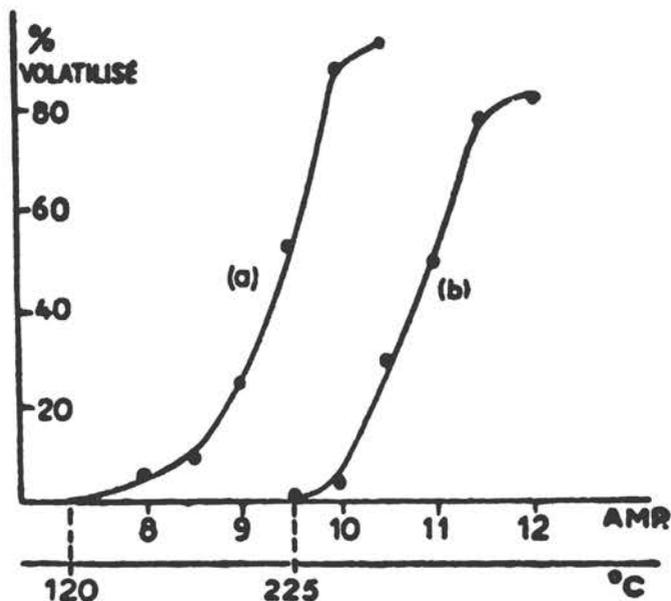
One could devise a procedure in which the preliminary removal of radio-actinium and actinium X is done not by a series of TTA extractions but by other methods. The TTA extraction step could be reserved for the final separation of actinium K.

#### D. Volatility of Francium

During the course of a study of  $\text{Fr}^{221}$  and other members of the decay chain of  $\text{U}^{233}$ , Hagemann et al.<sup>19</sup> noticed that francium was distilled from a platinum backing when this was heated to a dull red heat. Similar behavior was noted with cesium tracer. Hyde<sup>15</sup> made thin plates of francium (plus cesium carrier) by heating a platinum disc upon which the francium had been evaporated and collecting it on a cool platinum disc a few millimeters away. This volatilization step is incorporated in procedure 4 of Section IV.

Adloff<sup>16</sup> subjected the volatilization of francium to much closer study to determine the exact temperature range in which francium was distilled. He evaporated a francium solution upon a platinum filament through which a known electric current could be passed at will. A platinum-rhodium thermocouple was used to calibrate the temperature of the filament as a function of the current and other experimental variables. A water-cooled copper foil was mounted a few millimeters above the filament to collect the volatilized radioactivity. The whole apparatus was mounted in a bell jar which could be evacuated to permit study of the volatilization in a vacuum.

Adloff<sup>16</sup> isolated actinium K from an actinium-lanthanum mixture by the precipitation procedure given in variation two of Procedure 5 of Section IV below. The final solution was evaporated to dryness, taken up in a drop of hydrochloric acid or ammonia, and evaporated on the filament. His apparatus included a GM counter which could be used to measure the actinium K activity on the filament before and after each passage of current through the filament. Figure 3 shows the type of results obtained. Francium begins to volatilize in air at  $225^\circ \pm 50^\circ\text{C}$  and in vacuum at  $110^\circ \pm 15^\circ\text{C}$ . At temperatures well above these threshold values francium is volatilized rapidly and quantitatively.



MU-18340

Fig. 3. Volatilization of francium from an electrically heated platinum filament. Francium evaporated on the filament as a chloride solution. (a) In vacuum (b) in air.

The volatilization takes less than one minute and the volatilized activity appears to be quantitatively condensed on the cooled collector foil. Adloff established that actinium X (a radium isotope) did not volatilize to any detectable extent below  $300^{\circ}\text{C}$ . It is rather certain that actinium and radio-actinium, if present, would be left on the heated filament. On the other hand, actinium B and particularly actinium C'' (a lead isotope and a thallium isotope respectively) are rather volatile at the temperatures required to distill francium.

#### E. Ion Exchange

Kraus, Phillips, Carlson and Johnson<sup>20</sup> have reported a systematic study of the ion exchange properties of hydrous oxides with particular reference to radiochemical separations. They report some interesting results for the alkali elements. Cation exchangers prepared from acidic oxides (e.g. zirconium phosphate, tungstate or molybdate) when largely in the hydrogen form were

found to have remarkable selectivity for the various alkali metals. Adsorbability increases sharply with atomic number and is extremely high for cesium in acidic solutions. Under these conditions, cesium is so strongly adsorbed that it may be isolated essentially uniquely from all other elements in the Periodic Table.

The behavior of francium was not tested but it seems highly likely that this method could be applied to francium with excellent results.

#### F. Methods of Preparing Actinium Free of Radioactinium and Actinium X

An examination of the procedures given in Section IV shows that a recurring problem in the isolation of actinium K from actinium is the preliminary removal of radioactinium and actinium X from the actinium source. We note in the actinium decay chain (see Fig. 1) that the immediate daughters of actinium are 18.17 day  $RdTh$  and 11.68 day  $AcX$ . If these two descendants are quantitatively removed from the actinium, considerable time will pass before the radioactivity of these nuclides will grow back into the actinium source to an amount comparable to the equilibrium amount of  $AcK$ . Also all the other shorter-lived products down the chain from  $AcX$  can grow back into the actinium source only at a rate controlled by the growth of radioactinium and actinium X. In the meantime the actinium K grows quickly to its equilibrium value within two hours.

It greatly simplifies the radiochemical problem and shortens the required time of purification if actinium K has to be separated only from actinium. Hence it is worth considering the possible methods of separating actinium cleanly from thorium and radium. These methods are only mentioned here. Details on thorium and actinium radiochemistry can be found elsewhere.<sup>21,22</sup>

#### Separation of Actinium and Thorium

By precipitation methods. Cerium (IV) can be precipitated under oxidizing conditions by the dropwise addition of ammonia. Cerium (IV) hydroxide is much more insoluble than actinium hydroxide and can be selectively precipitated

in the presence of actinium and rare earths. The radioactinium coprecipitates with the ceric hydroxide.

By extraction of thorium into organic solvents. Undiluted tributyl phosphate extracts thorium tracer from an aqueous solution very thoroughly. For 3 M  $\text{HNO}_3$  solutions the  $K_{\text{aqueous}}^{\text{TBP}}$  is about 30, for 6 M  $\text{HNO}_3$  solutions it is about 100. Other solvents such as di-2-ethyl hexyl phosphoric acid and tri-n-octylphosphine oxide has an even higher extraction power for thorium. Actinium can be made to extract into these solvents, but it is easy to choose conditions under which the actinium extraction is entirely negligible. For references and further details see reference 21.

By extraction of the TTA complex of thorium. Hagemann<sup>23</sup> has studied the extraction of the  $\alpha$ -thenoyltrifluoroacetone complex of thorium and actinium from an aqueous solution into a 0.2 M solution of  $\alpha$ -thenoyltrifluoroacetone in benzene. In the pH range 1 and higher the extraction of thorium is about 99 to 1 into the benzene phase. The extraction of actinium is negligible below pH 3, rises rapidly to 99 percent extraction at pH 5 and remains at the value for higher pH. Hence by adjusting the acidity to the pH range 1-3 thorium can be extracted cleanly away from actinium.

By anion exchange. Thorium forms a negatively charged nitrate complex in nitric acid solution over a wide range of nitric acid concentration. This complex is readily adsorbed on synthetic anion exchange resins such as Dowex A2 or De Acidite FF. Maximum adsorption occurs near 7 M  $\text{HNO}_3$ . Details can be found in the literature.<sup>21,24-26</sup> Actinium shows no such behavior. An extremely simple and quantitative separation can be made by putting the actinium source in 7 M  $\text{HNO}_3$  solution, and passing it through a short column of Dowex 2 or De Acidite FF resin packed into a glass tube above a glass wool plug.

#### Separation of Actinium and Radium

By precipitation methods. Actinium rare earth mixtures may be precipitated as hydroxides with carbonate-free ammonia. Radium stays in solution. There is some contamination of the precipitate with actinium X so that it is usually

necessary to dissolve the precipitate in dilute acid and reprecipitate it several times.

By extraction of actinium into organic solvents. By proper adjustment of the salt concentration in the aqueous phase, actinium can be caused to extract into some organic solvents leaving radium behind in the aqueous phase. For example actinium is well extracted by undiluted tributyl phosphate from an aqueous solution saturated with ammonium nitrate and 0.3 Molar in nitric acid. A more powerful salting effect is achieved with saturated aluminum nitrate.

By extraction of the TTA complex of actinium. At a pH of 5 or higher small amounts of actinium are extracted into a 0.2 Molar solution of  $\alpha$ -thenyltrifluoroacetone in benzene.<sup>23</sup> Radium is not extracted. Because of the limited solubility of the complex compound in benzene this method does not work well if the actinium is contaminated with much inert rare earth material.

#### IV. COLLECTION OF DETAILED PROCEDURES FOR ISOLATION AND PURIFICATION OF FRANCIUM

##### Procedure 1. Carrier Free Method for the Isolation of Francium from Thorium Cyclotron Targets Based on Coprecipitation with Silicotungstic Acid.

Source: E. K. Hyde, J. Amer. Chem. Soc. 74, 4181 (1952).

The following procedure is based on the fact that silicotungstic acid is insoluble in concentrated hydrochloric acid and that trace amounts of francium will coprecipitate with the free acid. The francium is then separated from the silicotungstic acid by a simple ion exchange method.

Small bombarded strips of thorium metal foil (approximate dimensions 0.5 x 1.5 x 0.005 inches) are dropped into a 50-ml. centrifuge cone and quickly put into solution with 5 ml. of hot concentrated hydrochloric acid containing a few drops of 0.2 M solution of ammonium fluosilicate. (The fluosilicate catalyzes the dissolution of the thorium.) This solution is diluted with 15 ml. of ice-cold concentrated hydrochloric acid which has been presaturated with hydrogen chloride gas. A small amount of insoluble material is centrifuged down and removed. The clear solution is stirred vigorously and three drops of

### Procedure 1 (Cont'd.)

a 0.4 M solution of silicotungstic acid are added. A white crystalline precipitate of free silicotungstic acid forms and is centrifuged down. This precipitate is washed twice with 15 ml. of concentrated hydrochloric acid which has been saturated with hydrogen chloride gas and after centrifugation and decantation of the bulk of the hydrochloric acid the remaining drops of excess hydrochloric acid are carefully removed by pipet. The precipitate is dissolved in 1.0 ml. of redistilled water. A column of Dowex-50 cation exchange resin with the approximate dimensions 1 cm. x 4 mm. is prepared previous to the bombardment from 250-500 mesh resin in the ammonium form as shown in Fig. 4. This column is carefully rinsed with redistilled water. The 1.0 ml. of solution containing the francium and the silicotungstic acid is pipetted on top of the column and drawn through the column by suction at the rate of about 0.5 ml. per minute. The column is rinsed with 1-2 ml. of redistilled water at the same rate. The non-ionic silicotungstic acid passes through the column without sticking. A white precipitate with solution properties distinct from the normal form of silicotungstic acid may form in the solution which passes through the column. The francium adsorbs strongly on the column. This adsorption is a strong function of acid concentration and the success of this step depends on freeing the silicotungstic acid precipitate sufficiently from hydrochloric acid that the acid concentration in the 1.0 ml. of solution is  $< 0.5$  M. The column is inserted in a second 15-ml. side-arm tube and the francium is rapidly desorbed by pulling 500  $\mu$ l. of clean concentrated hydrochloric acid through the column in a period of 2-3 minutes. The resulting 500  $\mu$ l. solution is a pure carrier-free solution of francium uncontaminated with any radioactivity except that of cesium fission products which are not separated. Rubidium fission product activities are separated.

A small amount of solid matter will appear in this final solution unless the glass vessels used are very clean, the resin is carefully rinsed to remove the excess ammonium ion used in regeneration, the distilled water is of high

## Procedure 1 (Cont'd.)

purity and the hydrochloric acid is freshly prepared from redistilled water and hydrogen chloride gas. This entire procedure is quite rapid, can be completed in 30 minutes or less and has given excellent results in repeated use. On the few occasions when slight radioactive contaminants were encountered, the difficulty was traced to the small amount of insoluble matter formed in the dissolution step which sometimes is hard to remove completely by centrifugation. When 10-15 minutes more time may be spent on purification, a precipitation of  $\text{Th}(\text{OH})_4$  using calcium hydroxide as the precipitant may be introduced between the silicotungstic acid precipitation and the ion exchange step. The  $\text{Th}(\text{OH})_4$  helps to ensure separation of this solid matter and many possible contaminants (notably traces of protactinium) coprecipitate with it.

After the initial precipitation and hydrochloric acid washing of the silicotungstic acid, the solid is dissolved in 1 ml. of water. One mg. of thorium ion is added and precipitated as the hydroxide by the addition of approximately 100-200 mg. of solid calcium hydroxide. After centrifugation, the clear supernatant solution is transferred to a clean 15-ml. centrifuge cone and saturated with gaseous hydrogen chloride to reprecipitate the silicotungstic acid. After centrifugation, the supernatant hydrochloric acid is completely removed, the acid is dissolved in 1.5 ml. of pure water and adsorbed on the Dowex-50 column as described above.

Check experiments showed that recovery of cesium (as stand-in for francium) was > 96% through this procedure. A small amount of calcium (~0.1 mg.) appears in the final francium fraction when this procedure is followed. If this is undesirable, the manganese dioxide by-product precipitate discussed in section 6 below may be substituted.

### Notes on the Carrier-Free Silicotungstic Acid Method.

The details of the carrier-free silicotungstic acid procedure were worked out using 37 year  $\text{Cs}^{137}$  tracer as a stand-in for francium and some findings

Procedure 1 (Cont'd.)

concerning the chemical yield and the effects of other ions on the yield may be mentioned.

(1) Free silicotungstic acid precipitated from a concentrated hydrochloric acid solution of  $\text{Cs}^{137}$  tracer carries more than 98% of the cesium activity.

(2) If the silicotungstic acid carrying cesium tracer from a concentrated hydrochloric acid solution is dissolved in pure water and reprecipitated by adding concentrated hydrochloric acid, the cesium is again coprecipitated quantitatively. These reprecipitations may be carried out repeatedly.

(3) Sodium ion interferes with the coprecipitation of cesium. When  $\text{Cs}^{137}$  tracer in 0.5 ml. of 6 N sodium hydroxide was added to 10 ml. of concentrated hydrochloric acid and hydrogen chloride gas passed in, a precipitate of sodium chloride formed. When silicotungstic acid was precipitated from the clear hydrochloric acid solution after removal of the solid sodium chloride, only 15-30% yield of the initial  $\text{Cs}^{137}$  was obtained. None of the missing  $\text{Cs}^{137}$  was found with the sodium chloride. This result is important since it means that sodium ion must be absent from the solution and that a by-product precipitate such as  $\text{Fe}(\text{OH})_3$  cannot be used in the isolation procedure if sodium hydroxide is used to precipitate the iron. This was verified in an experiment in which silicotungstic acid was precipitated from concentrated hydrochloric acid to carry  $\text{Cs}^{137}$  tracer. The precipitate was dissolved in pure water. One mg. of ferric ion as ferric chloride was added and precipitated with sodium hydroxide. The supernate was added to 15 ml. of concentrated hydrochloric acid and the solution was saturated with hydrogen chloride. After removal of a sodium chloride precipitate, 0.4 M silicotungstic acid was added to precipitate the free heteropoly acid. Only 10% of the  $\text{Cs}^{137}$  was found on this precipitate.

(4) Ammonium ion may not be used in the by-product scavenge precipitation of thorium hydroxide because of the precipitation of ammonium chloride and ammonium silicotungstate when the supernate is later saturated with hydrochloric acid. This introduces ammonium chloride into the final francium fraction and

Procedure 1 (Cont'd.)

also drastically reduces the coprecipitation of francium. (In check experiments using  $\text{Cs}^{137}$  as a stand-in for francium losses of  $> 90\%$  were observed.) In other applications such as those given below any ammonium salts originally present should be destroyed in a preliminary step such as by evaporation with aqua regia.

(5) The separation factor of rubidium from cesium was shown to be greater than 300 by a determination of the amounts of 19 day  $\text{Rb}^{86}$  and 13 day  $\text{Cs}^{136}$  present in the final cesium-francium fraction from a thorium target.

(6) Manganese dioxide may be precipitated instead of  $\text{Th}(\text{OH})_4$  as a by-product scavenger precipitate between the initial precipitation of silicotungstic acid and the final ion exchange separation. This is done as follows: The silicotungstic acid precipitate is dissolved in 1.5 ml. of water. One drop of a 56% solution of  $\text{Mn}^{++}$  and one drop of 1 M potassium permanganate are added to precipitate manganese dioxide. After 2 minutes, this is centrifuged off and discarded. The supernatant solution is pipetted into a 15-ml. centrifuge cone containing 8 ml. of cold hydrochloric acid. Gaseous hydrochloric acid is passed into the solution to bring down the silicotungstic acid. After centrifugation, the acid is dissolved in four drops of pure water and again precipitated by adding 5 ml. of cold hydrochloric acid saturated with gaseous hydrogen chloride. This precipitate is separated by centrifugation, carefully freed of excess hydrochloric acid and dissolved in 1.0 ml. of redistilled water in preparation for the ion exchange step described above. Recovery of cesium or francium is essentially quantitative.

(7) The presence of thorium does not interfere with the quantitative coprecipitation of cesium.

(8) In the ion exchange step the column procedure described is to be preferred to a batch procedure in which the resin is stirred with the water solution of  $\text{Cs}^{137}$  to effect adsorption and with a concentrated hydrochloric acid solution to effect desorption. In repeated trials of batch procedures, yields were erratic and low (20-70%).

Procedure 1 (Cont'd.)

On the other hand, nearly quantitative adsorption and desorption of  $\text{Cs}^{137}$  tracer was found using the column shown in Fig. 4. For example,  $\text{Cs}^{137}$  tracer in 1.0 ml. of 0.5 M hydrochloric acid was adsorbed on the column and rinsed with 2.0 ml. of pure water in a period of only 3 minutes. It was desorbed with 1.0 ml. of concentrated hydrochloric acid in a period of only 3 minutes. More than 97% of the original activity was found in the first 500  $\mu\text{l}$ . of final hydrochloric acid solution.

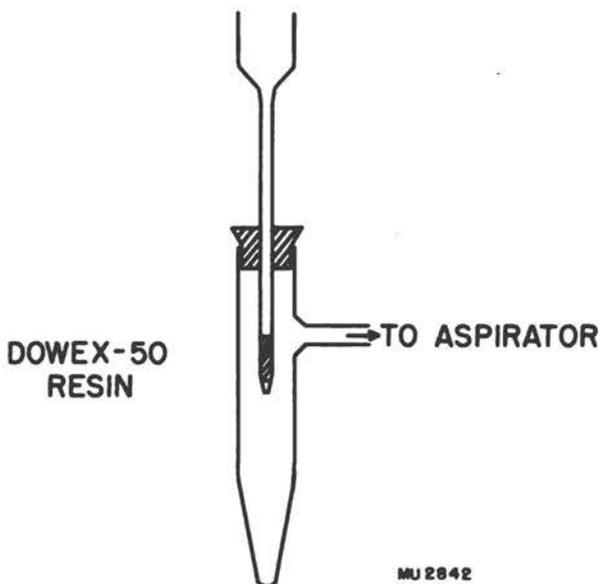


Fig. 4. Simple ion exchange column for separation of francium from silicotungstic acid.

(9) It was thought desirable to ascertain the coprecipitation behavior of radium with silicotungstic acid since some of the barium salts of the heteropoly acids are isomorphous with the free acids. In check experiments using  $\text{Ra}^{226}$  tracer less than 0.2% coprecipitation was observed. This was borne out by the use of the method in thorium bombardments. No radium activities were ever found in the final francium fraction although as much as 0.01% would easily have been observed.

Procedure 2. Application of the Carrier-Free Silicotungstic Acid Method to the Isolation of Actinium K from Actinium. Source: E. K. Hyde, J. Amer. Chem. Soc. 74, 4181 (1952).

The carrier-free silicotungstic acid method (Procedure 1 above) is a very simple and effective method for the isolation of AcK ( $\text{Fr}^{223}$ ) from  $\text{Ac}^{227}$ . In this case the sample of  $\text{Ac}^{227}$  is simply placed in saturated hydrochloric acid solution and a few drops of 0.4 M silicotungstic acid is added to bring down the AcK. The precipitate is washed and subjected to the ion exchange step described above. The AcK samples may be prepared in a carrier-free condition ready for counting within one half-life (21 minutes) of the time of separation from actinium. The actinium is left in the hydrochloric acid solution so that a fresh sample of AcK may be removed later simply by adding more silicotungstic acid.

This application has been checked starting with an actinium sample of  $2.6 \times 10^7$  dis./min.  $\text{Ac}^{227}$ . The decay of the AcK samples so isolated was followed with a Geiger counter to establish the 21 minute half-life. Then these samples were counted in an alpha counter to measure the exact amount of the  $\alpha$ -emitting daughters of AcK. The  $\alpha$ -particle energies were measured in a 48 electronic channel differential pulse analyzer connected to an ionization chamber to prove that the  $\alpha$ -activities present were AcK and its daughters and no others. The absence of RdAc  $\alpha$ -particles was specifically verified. From these data, with proper allowance for the 1.2%  $\alpha$ -branching of  $\text{Ac}^{227}$  and for decay since time of separation, etc., it was possible to calculate the chemical yield of AcK. This yield was quantitative within the experimental error of 5%.

Adloff\* reports some difficulty in applying this method to a source of actiniferous lanthanum containing a high proportion of rare earths. Apparently some rare earth material precipitates in the silicotungstic acid fraction and the mixed precipitate is contaminated with some actinium X. In most cases this contamination was removed if the silicotungstic acid was dissolved in a little water and reprecipitated with hydrochloric acid saturated with HCl gas.

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\* J. P. Adloff, Theses, Universite Strasbourg, 1958.

## Procedure 2 (Cont'd.)

Adloff also reports that if AcK is repeatedly milked from the same actinium solutions by addition of more silicotungstic acid after suitable growth periods the amount of actinium K removed in later milkings may be 25 or more percent below the initial amount. The exact cause of this declining yield was not determined.

Procedure 3. Isolation of Fr<sup>221</sup> from its Ac<sup>225</sup> Parent by the Silicotungstic Acid Precipitation Method. Source: E. K. Hyde, J. Amer. Chem. Soc. 74, 4181 (1952).

The 4.8 minute isotope of Fr<sup>221</sup> may be isolated from its 10 day parent Ac<sup>225</sup> which in turn is isolated from the decay products of U<sup>233</sup> or is prepared by the cyclotron bombardment of thorium. The shortness of the half-life requires that the isolation procedure be as brief as possible. If one first carefully purifies the actinium parent, the number of possible contaminating radioactivities is quite limited and a single precipitation of silicotungstic acid and a single hydrochloric acid wash give a nearly quantitative separation of the Fr<sup>221</sup> from its parent. If one can tolerate a small amount of inert solid matter in the final francium solution, the ion exchange step can be replaced by the following.

The precipitate is dissolved in 500  $\mu$ l. of distilled water and stirred with 1 or 2 ml. of ethyl ether. In the three phase system produced, the bottom layer consists of a liquid compound of silicotungstic acid and ether, the uppermost phase is ethyl ether and the intermediate phase is a water solution of francium. This method is not as satisfactory as the ion exchange method since a small part of the silicotungstic acid remains in the aqueous phase, but is useful when the most rapid separation is necessary and a small amount of inert solid matter may be tolerated.

Procedure 4. The Cesium Silicotungstate-Cesium Perchlorate Method for the Isolation of Francium from Bombarded Thorium Targets. Source: E. K. Hyde, J. Amer. Chem. Soc. 74, 4181 (1952).

Small bombarded strips of thorium metal (approximate dimensions 0.5 x 1.5 x 0.005 inches) are dropped into a 15-ml. centrifuge cone containing 5 ml. of hot concentrated hydrochloric acid to which has been added a few drops of 0.2 M ammonium fluosilicate to serve as a dissolution catalyst. The thorium dissolves within a few seconds. The solution is diluted to 20 ml. with 15 ml. of ice-cold 6 M hydrochloric acid containing four drops of cesium chloride carrier solution (10 mg. cesium per ml.). The centrifuge cone is placed in an ice-bath and stirred for 1 to 2 minutes while 1 ml. of 1/8 M silicotungstic acid is added. The cesium silicotungstate is centrifuged down and the supernate discarded to active waste. The precipitate is washed twice with 5 ml. of cold 6 N hydrochloric acid, and these washings are discarded. The precipitate is then dissolved in 6 N sodium hydroxide. Five ml. of 70% perchloric acid is carefully added (safety glasses or face mask), and the solution is evaporated by swirling the tube over a burner until copious white fumes of perchloric acid are evolved. After cooling, the solution is diluted to 10 ml. and centrifuged to remove a precipitate of silica and tungstic acid. The supernatant solution is again evaporated to dense white fumes of perchloric acid by careful swirling over a burner. It is then cooled and 15 ml. of absolute ethyl alcohol is added. The solution is stirred for 1 minute and centrifuged to bring down the cesium perchlorate precipitate. The supernatant solution is disposed of at once since it contains ethyl perchlorate, which is extremely explosive when heated. The cesium perchlorate is washed twice with 5 ml. of ice cold absolute ethyl alcohol. The final washed precipitate is dissolved in a small amount of distilled water.

For the study of the  $\alpha$ -particle characteristics of francium isotopes where thin samples are highly desirable, very thin samples may be prepared on platinum disks from the final francium solution by the following volatilization procedure. An aliquot of the solution is evaporated on a platinum plate. A

#### Procedure 4 (Cont'd.)

second platinum catcher plate is inverted above the first using an asbestos washer to maintain a separation of a few millimeters. By touching the bottom plate for a fraction of a second with a gas-oxygen flame, the cesium and francium are deposited on the catcher plate in an extremely thin film.

Transfer of more than 90% of the francium is effected if the amount of cesium in the sample is quite small. This volatilization technique is useful not only for preparation of thinly spread plates, but also for preparation of a francium fraction completely free of an emanation daughter at a precisely measured time.

NOTE - This procedure is not to be preferred to Procedure 1.

#### Procedure 5. Classical Methods of Separation of Actinium K from Actinium or from Mixed Actinium-Rare Earth Sources by Precipitation Techniques.

##### Variation one - Actinium source in equilibrium with all its descendents.

Source: M. Perey, Theses, Universite Paris, 1946. See also Comptes Rendus 214, 797 (1942).

(1) With the actinium in aqueous solution as the chloride add a slight excess of sodium carbonate and bring solution to a boil. The hydroxides of actinium and of any unseparated rare earth elements are precipitated carrying down AcX (Ra<sup>223</sup>), RdAc (Th<sup>227</sup>), AcB (Pb<sup>211</sup>), and AcC (Bi<sup>211</sup>). The AcK (Fr<sup>223</sup>) and AcC" (Tl<sup>207</sup>) are left in the filtrate together with traces of the other nuclides.

(2) Acidify filtrate with hydrochloric acid and bring to a boil to destroy excess carbonate.

(3) Add a few milligrams of lanthanum and barium chlorides. Add K<sub>2</sub>CrO<sub>4</sub> and ammonia. The lanthanum and barium are precipitated as the chromates carrying down AcC" and traces of actinium and AcX. Filter.

(4) The filtrate containing the radiochemically pure AcK can be concentrated by evaporation.

Procedure 5 (Cont'd.)

Variation two - Actinium source in equilibrium with all its descendants.

Source: J. P. Adloff, Theses, Universite de Strasbourg, 1958.

The plan in this procedure is purify the actinium thoroughly from the long-lived radioactinium and actinium X daughters. Then the actinium is allowed to come to equilibrium with AcK (about two hours) after which a simple separation of actinium and AcK is effected by precipitation of the actinium.

(1) Start with the actinium-rare earth source in aqueous solution. Add cerium IV carrier. Add just enough  $\text{NH}_4\text{OH}$  to precipitate cerium IV hydroxide. Maintain oxidizing conditions in the solution. Filter or centrifuge. The ceric hydroxide removes the RdAc ( $\text{Th}^{227}$ ) from solution. This step may be repeated once to twice to insure complete removal of the RdAc. Some loss of actinium occurs by coprecipitation.

(2) Add a few milligrams of barium chloride to the filtrate. Add carbonate-free ammonia to precipitate the actinium-rare earth hydroxides. Filter. Barium and AcX are left in the filtrate together with AcK and AcC". Unfortunately the precipitate is usually contaminated with a portion of the AcX activity and it is necessary to repeat this step at least 6 times.

(3) Dissolve the final precipitate of actinium, now thoroughly cleaned of its radioactinium and actinium X daughters, and permit about two hours to pass while the AcK grows into equilibrium.

(4) Reprecipitate the actinium either with an excess of ammonia or ammonium carbonate. Filter.

(5) The filtrate contains AcK with some traces of AcX and AcC". The final purification may be done in two ways.

(6a) Precipitate barium carbonate to remove the remaining AcX from the solution.

(6b) Alternatively barium chromate may be precipitated as follows. Boil the filtrate and add hydrochloric acid to remove all traces of the ammonium carbonate. Add several drops of a saturated solution of potassium chromate.

### Procedure 5 (Cont'd.)

Then add some barium chloride and lanthanum chloride and finally some ammonia just to the point of alkalinity. The mixed precipitate of lanthanum chromate and barium chromate removes from solution any traces of actinium or actinium X which may be in the solution. Actinium C'' is also removed, which is an advantage not shared by the barium carbonate method of part 6a.

#### Variation three - Actinium source purified from its long-lived descendents.

Source: J. P. Adloff, Theses, Universite Strasbourg, 1958.

We assume in the beginning that the actinium source has been separated from its long-lived descendents RdAc and AcX by some method such as that outlined in variation two.

(1) Suspend the actinium-rare earth mixture in a solution of ammonium carbonate containing some added lead and barium.

(2) After the radioactive equilibrium Ac-AcK has been achieved separate the precipitate by centrifugation or filtration.

(3) The filtrate contains AcK and an appreciable amount of AcX. Precipitate barium carbonate once or several times to remove this AcX. It is also a good precaution to make one precipitation of lanthanum carbonate or hydroxide to remove traces of actinium which pass into solution by mechanical entrainment or by partial solubility.

(4) Evaporate the final solution to dryness and heat gently to remove ammonium salts.

Procedure 6. Separation of Actinium K from Actinium by Paper Chromatography.

Adapted from J. P. Adloff, Thèses, Université de Strasbourg, 1958.

Variation one - Preliminary removal and partial purification of actinium K by coprecipitation methods.

(1) Start with an actiniferous lanthanum solution in equilibrium with its long-lived daughters. Add ammonium carbonate to precipitate actinium and rare earths. Filter or centrifuge.

(2) Add lead, barium and lanthanum carriers to the filtrate and precipitate a mixed carbonate compound to strip residual actinium, AcK and RdAc from the solution. Filter or centrifuge.

(3) Repeat step (2) once or twice.

(4) Evaporate the filtrate to a small volume and pipet it onto the position "zero" 2.5 centimeters from the end of a strip of Schleicher paper about one centimeter wide and 15 centimeters long.

(5) Insert the paper in the apparatus shown in Fig. 2 with the upper end dipping into the eluant, a 10% solution of ammonium carbonate. Maintain an atmosphere of saturated water vapor within the beaker at a temperature of 60°.

(6) Let the chromatogram develop for 15 minutes. The AcK and AcC" will travel together down the paper to a position about 8 centimeters below position zero. The Ac, AcX and RdAc contaminants, if present, will remain near position zero.

(7) If the position of the AcK peak is known sufficiently well from previous calibration runs with AcK or Cs<sup>137</sup> tracer cut out the proper portion of the paper. The AcK activity can then be leached quickly from the paper by simple washing. The total time taken from the initial separation of the AcK from the actinium can be made as short as 30 minutes.

If the position of the peak is not known sufficiently well or if this is meant to be a calibration run, dry the entire paper rapidly and place it before a suitable beta counter fitted with a collimator slit a few millimeters wide. The activity can then be measured as a function of distance along the strip by

## Procedure 6 (Cont'd.)

taking short counts at several points. The resulting radiochromatogram locates the francium peak. Its identity can be checked by determining the decrease in the counting rate at the peak as a function of time.

Note 1. Calibration runs can be made with  $Cs^{134}$  or  $Cs^{137}$  tracer.

Note 2.  $AcC''$  is not separated from  $AcK$  in this method. If it is important to remove the  $AcC''$  it can be done in two ways. The first is simply to wait for the decay of the 4.76 minute  $AcC''$ . A more rapid and more satisfactory method is to introduce a precipitation step specifically for this purpose immediately before the chromatography.

(a) Make a single precipitation of lead, barium and lanthanum with carbonate (step 2 above) and bring the filtrate to a boil rapidly to destroy excess ammonium carbonate.

(b) Adjust the pH to 2-3 with dilute acetic acid. Add a few milligrams of lead chloride. Pass in  $H_2S$  to precipitate lead sulfide. This precipitate removes all of the  $AcC''$  and part of the residual  $AcX$ . Filter.

(c) Concentrate the filter to a small volume and transfer to the chromatographic paper. Proceed as in (4) above.

Note 3. If one has need of fresh  $AcK$  samples for a series of experiments it is desirable to remove the bulk of the  $AcX$  from the original actinium source by a precipitation of the actiniferous lanthanum with carbonate-free ammonia. Then one can go back to this actinium source repeatedly at one or two hour intervals to get a new supply of actinium K. In one hour 87.5 percent of the equilibrium amount has reformed in the actinium. If this is done, a single precipitation of actinium-lanthanum carbonate suffices because the amount of  $AcX$  to be found in the supernate is small and it is possible to proceed immediately to the chromatography. The elimination of the additional cleanup precipitations reduces the total time of the  $AcK$  purification and hence increases substantially the strength of the samples.

Procedure 6 (Cont'd.)

Variation two - Elution of actinium K from an actinium source directly deposited on the chromatographic paper.

(1) A sample of actiniferous lanthanum very rich in actinium is purified from its long-lived derivatives by the method outlined in steps 1 and 2 of Procedure 5, variation 2. Alternate purification methods based on solvent extraction, the extraction of the  $\alpha$ -thenoyltrifluoroacetone complex of actinium, or ion exchange can be used.

(2) Concentrate the solution containing the actinium to a small volume and transfer it to the "zero" position of the chromatographic paper.

(3) Wait one or two hours until the AcK grows back almost to its equilibrium value.

(4) Insert the paper in the apparatus of Fig. 2 with the upper end dipping in the 10 percent ammonium carbonate solution. Maintain an atmosphere of saturated water vapor at 60°C.

(5) Permit the elution to proceed for 6 to 15 minutes. Almost all of the actinium K is moved several centimeters from the actinium deposit in 6-8 minutes.

(6) The portion of the paper containing the francium is washed with water to form the final solution. AcC" is not separated from the AcK.

Note 1. This method has the distinct advantage of reducing to a very few minutes the total time between the separation of AcK from its actinium parent and its final purification. Hence the strength of the francium activity from a given actinium parent source is increased.

Note 2. This method is not applicable to an actinium source containing a large amount of rare earth material.

Procedure 7. Extraction of Actinium K into Nitrobenzene in Presence of Sodium Tetraphenyl Boron.

Source<sup>\*</sup>: R. Muxart, M. Levi and M. G. Bouilssieres, Compt. Rendu. 249, 1000, 1959.

In this article it is stated that actinium K can be extracted into nitrobenzene from an aqueous solution adjusted to pH9 and 0.05 molar in sodium tetraphenyl boron. 99% of the francium is extracted. If radium is present in tracer amounts, 90% of it is also extracted. However, if the sodium salt of ethylenediamine tetra-acetic acid (EDTA) is present to a concentration of one percent, the extraction of the radium is suppressed, while that of francium remains quantitative. The authors state that actinium K can be separated from all members of the Ac<sup>227</sup> decay chain with the exception of actinium-C" (Tl<sup>207</sup>). The actinium K can be removed from the nitrobenzene by contacting the organic phase with two volumes of 1 N hydrochloric acid.

In the reported experiments, a chloride solution containing actinium K and actinium X was prepared. Sodium borate was added until the pH was 9. The solution was then made 0.05 molar in sodium tetraphenyl boron. Before it was added this reagent was purified by contact with aluminum hydroxide and by filtration. The solution was then stirred three minutes with an equal volume of nitrobenzene.

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## REFERENCES

1. M. Perey, *Compt. Rendu.* 208, 97 (1939).
2. M. Perey, *J. Phys.* 10, 435 (1939).
3. M. Perey, *Theses, Université Paris* (1946).
4. F. Hagemann, et. al. *Phys. Rev.* 79, 435 (1950).
5. I. Perlman, A. Ghiorso and G. T. Seaborg, *Phys. Rev.* 77, 28 (1950).
6. E. K. Hyde, *J. Phys. Chem.* 58, 21 (1954); *J. Chem. Educ.* 36, 15 (1959).
7. J. P. Adloff, *Thèses, Université de Strasbourg* (1958).
8. See particularly the papers of M. Perey on this subject. *Comptes. Rendus.* 214, 797 (1942); *ibid* 241, 953 (1955); *J. Chim. Phys* 43, 269 (1946).
9. E. K. Hyde and A. Ghiorso, *Phys. Rev.* 90, 267 (1953).
10. E. K. Hyde, *Phys. Rev.* 94, 1221 (1954).
11. M. Perey, pp 131-41, *Nouveau Traite de Chimie Minerale, Tome III, Massoneest Cie Editeurs, Paris* (1957).
- 11a. M. Perey, *Bull. Soc. Chim. France* 779 (1951).
12. L. E. Glendenin and C. M. Nelson, *National Nuclear Energy Series, Plutonium Project Record, Vol. 9B. "Radiochemical Studies; The Fission Products," Paper 283 (McGraw-Hill Book Company, Inc.) New York, N.Y., 1951.*
13. L. E. Glendenin and C. M. Nelson, *Ibid. Paper 285.*
14. H. B. Evans, *ibid. Paper 284.*
15. E. K. Hyde, *J. Amer. Chem. Soc.* 74, 4181 (1952).
16. J. P. Adloff, *Thèses, Université Strasbourg, 1958.*

17. M. Perey and J. P. Adloff, *Comptes Rendus* 236, 1163-5 (1953); *ibid.* 239, 1389-91 (1954). See also Proceedings of the XVI<sup>e</sup> Congrès International de Chimie Pure et Appliquée, Section de Chimie Minérale, Paris, 1957. pp. 333-336.
18. J. Fouarge and W. W. Meinke, Nuclear Chemical Research Progress Report, University of Michigan, Department of Chemistry.
19. F. Hagemann et al., *Phys. Rev.* 79, 435 (1950).
20. K. A. Kraus, H. O. Phillips, T. A. Carlson and J. S. Johnson, Proceedings of the Second U.N. International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958. Volume 32, 3 1958.
21. E. K. Hyde, "The Radiochemistry of Thorium", University of California Radiation Laboratory Report, UCRL-8703, April, 1959. This is a companion monograph in this same radiochemical series.
22. E. K. Hyde, "Radiochemical Separations Methods for the Actinide Elements", Proceedings of the U.N. International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1955. United Nations, New York.
23. F. Hagemann, *J. Amer. Chem. Soc.* 72, 768 (1950).
24. J. Danon, *J. Amer. Chem. Soc.* 78, 5953 (1956).
25. D. J. Carswell, *J. Inorg. Nucl. Chem.* 3, 384 (1957).
26. L. R. Bunney et al., *Analytical Chem.* 31, 324 (1959).