

Purification of Ac^{227} by Solvent Extraction

By

C. T. Rhee

Chemistry Division

Atomic Energy Research Institute, Korea

(Received May 25, 1964)

溶媒抽出法에 의한 Ac^{227} 의 精製

原子力研究所

李 鎭 澤

(1964 5. 25 수리)

要 約

Ac^{227} 을 溶媒抽出法에 의하여 그의 崩壊系列元素로부터 分離하는 迅速한 方法을 考察해 보았다. HDEHP 및 TBPO 로 二段階抽出過程을 거침으로서 追跡子用으로 充分한 純度를 가진 Ac^{227} 을 얻을 수 있으며 이들 過程中에 일어날 Ac^{227} 의 損失程度도 推定해 보았다. Ac^{227} 으로부터 Th^{227} 의 milking 도 兼하여 實驗하였다.

Abstract

A rapid method of daughter free Ac^{227} tracer preparation was studied. Through two stage extraction by HDEHP and TBPO, essentially daughter free Ac^{227} tracer can be prepared. Possible loss of Ac^{227} activity during the process was estimated. Milking of Th^{227} from Ac^{227} was also studied.

Introduction

Ac^{227} which is a daughter element of U^{235} and also produced artificially by the neutron irradiation of Ra^{226} is the main isotope of actinium element to be used as a long lived actinium tracer. However, since it decays not only in a complicated series of five α emission and three β emission (shown in Table I) but also with emission of very weak β particle (~ 40 Kev) which was considered for a number of years as to be "rayless" since no radiation could be detected, it is desirable to be purified frequently from its daughter radiation to meet the purpose of tracer experiments. The main daughter to be separated out are 18d Th^{227} , 11d Ra^{223} and possibly 36m Pb^{211} . Although there are many works published for this purpose such as conventional

precipitation method ^{(1) (2)}, ion exchange method ^{(3) (4)} ⁽⁵⁾ or solvent extraction method, ^{(6) (7) (8)} these procedures are generally tedious and time consuming work for simple tracer preparation. The author tried to study some simple procedure for the purification of Ac^{227} tracer using solvent extraction technique and found the result with Di-(2-ethyl hexyl) ortho phosphoric acid (HDEHP) and Tri-*n*-butyl phosphine oxide (TBPO) are satisfactory for the practical use.

Experiment

Reagents and radioisotopes used.

TBPO supplied by Tama Chem. Co. Japan was used without further purification. HDEHP supplied by Wako, Japan was further purified as previous work ⁽⁹⁾. Toluene and other chemicals were all analytical grade.

Ac²²⁷, Pu²³⁹ and Am²⁴¹ were imported from RCC, irradiation at the Institute. England. Cm²⁴² was prepared from Am²⁴¹ through pile

Table 1. Decay series of Ac²²⁷.

	Ac ²²⁷ 21 y	Th ²²⁷ 18 d	Ra ²²³ 11 d	Rn ²¹⁹ 3.9 s	Po ²¹⁵ 1.8x 10 ⁻³ s	Pb ²¹¹ 36 m	Bi ²¹¹ 2.6 m	Tl ²⁰⁷ 4 m	Pb ²⁰²
β^-									
α	4.94 (1.2%)	6.036 Others	5.712 Others	6.813 Others	7.36	6.617 6.273			
β	0.04 (98.8%)					1.39 0.5	1.44		
γ	0.03 Other	0.236 Other	0.269 Other	0.272 Other		0.829 Other	0.351 Other	0.87	

Table 2. Operation conditions.

No. fraction	1	2	3	4	5	6	7	8	9	10
Phase										
Aqueous (N. HCl)	3.12x 10 ⁻⁴	1.09x 10 ⁻³	2.26x 10 ⁻³	3.63x 10 ⁻³	5.00x 10 ⁻³	6.24x 10 ⁻³	7.06x 10 ⁻³	8.07x 10 ⁻³	8.67x 10 ⁻³	9.09x 10 ⁻³
Organic (% HDEHP)	20	20	30	30	50	50				

Extraction

Craig type discontinuous counter current solvent extraction apparatus (supplied by Tajiri Co., Japan) was used for the check of the distribution of various activities in Ac²²⁷ sample. The number of equilibrating cells (10 ml) was limited to ten in the present study. The gradient in the acidity of aqueous solutions was prepared in the extractor train. After filling up all equilibrating cells with 0.01 N HCl, five successive portions of 10 ml distilled water were sent through the train under usual operation of mixing, settling, overflowing. On the otherhand, the gradient in the solvent concentration (six portions of 5 ml) was obtained by mere manual dilution. The calculated gradient conditions are shown in Table 2.

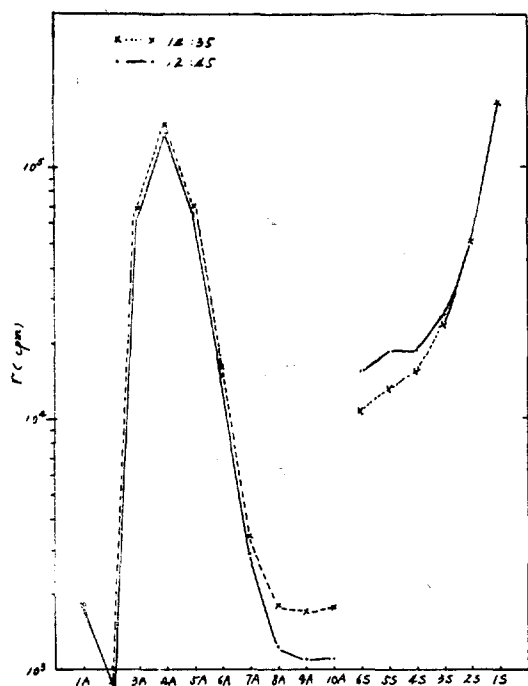
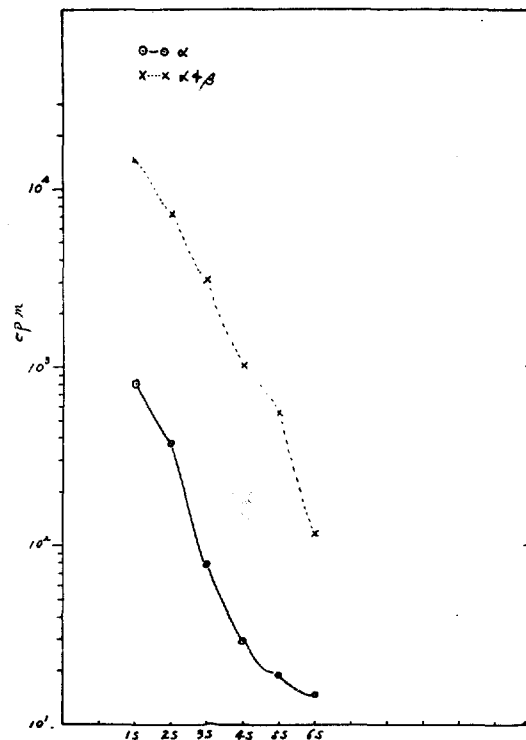
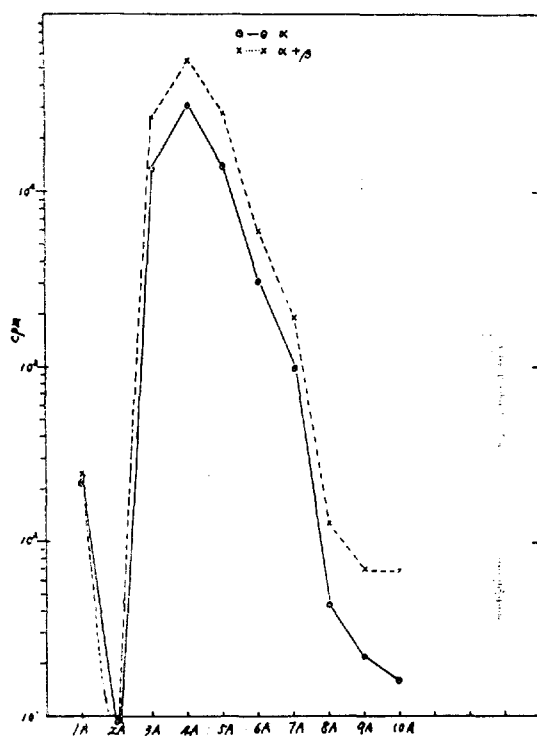
The aqueous solution of Ac²²⁷ tracer was added to the acid solution of the first cell prior to the extraction operation and the organic fractions of a given number were supplied to the first cell one by one successively. Extraction and transfer-cycles were repeated after the completion of the six organic supply until the last organic fraction was withdrawn from the last cell.

Glass stoppered five and ten ml measuring cylinders were used for the batch extraction by manual five minutes shaking and centrifugal phase separation. All experiments were carried out at room temperature, 17°~20°C.

Radiochemical assay. γ activity of liquid sample was measured by well type NaI (TI) scintillation detector connected with Nuclear Chicago Model 181 A scaler. α spectrum of plated sample was taken with α solid detector (C-4-25-0.2, supplied by RCA victor, Canada) connected with RCL 256 multi channel analyzer. The standard activities for the energy calibration were Pu²³⁹, Am²⁴¹ and Cm²⁴². Since the solid detector had been used more than one year the resolution power dropped to 8% for the 5.15 Mev peak of Pu²³⁹. TGC-2 thin end window detector (1.8 mg/cm²) connected with Nuclear Chicago Model 181 A scaler and NMC Model PC-3 A 2 π proportional counter were used for α or β counting. For α or β counting, aliquot amount of aqueous sample was taken on stainless steel plate and dried by infrared lamp and high frequency induction heater. Organic sample was changed to aqueous sample by back extraction of the activity into aqueous phase through acidity change and/or dilution of the organic phase with inert diluent.

Results and Discussion

1). Counter current extraction. The measured γ activities are shown in Fig 1. They were counted twice with a time interval of two hours. The aqueous fractions are numbered as 1 A and 10 A for the first and last cells respectively. The organic fractions are num-

Fig1. Distribution of γ activity.Fig3. Distribution of α & β Activity.Fig2. Distribution of α & β Activity.

bered as 1S, 2S... successively from the first effluent. The counted γ activities in 1A to 2A and 1S to 2S were not changed during the said intervals but those of 3A to 10A were increased and those of 3S to 6S were decreased. The rate of increasing or decreasing were pronounced in the range of 8A to 10A and 5S to 6S. The distribution of α and $\alpha+\beta$ activities are shown in Fig 2 and 3. The ratio of $\alpha+\beta$ to α is getting increased from 8A reaching maximum at 3S and decreasing again up to 1S. From these results and those published data of distribution ratio⁽¹⁰⁾, it was assumed that Ra^{223} is accumulated in 3A to 7A, Th^{227} and Ac^{227} are concentrated in 3S to 1S, and Pb^{211} is distributed in 8A to 4S. Actually it is hard to study the behavior of Bi^{211} & Tl^{207} from these results because of their short half-life and also accumulation from Pb^{211} during the experimental period. The activities in 1A to 2A possibly indicate presence of some impurities other than daughter activity of Ac^{227} . Thus it was found that Ra activity can be eliminated completely by extraction of Ac^{227} with 20% NDEHP from 0.01N HCl solution. All Th^{227} and some part of Pb^{211} may possibly be extracted together. Since the distribution

ratio of Th is so large ($\sim 10^4$)⁽¹⁰⁾ at any acidity it is very easy to eliminate the Th activity from Ac^{227} merely by back extraction of the Ac^{227} from the co-extracted HDEHP phase.

2). **Back extraction of Th^{227} .** It was hard to make good plate for taking spectrum of Th fraction since the distribution ratio is so large that back extraction to aqueous phase was quite impossible without making some modification. Thus, it was necessary to study also the problem of back extraction of Th^{227} . The result and various conditions tested for the back extraction of Th^{227} from 20% HDEHP in toluene are shown in Table 3. It was found that the Th activity can be back extracted almost quantitatively from HDEHP phase by oxalic acid aqueous solution of 0.7M concentration.

Table 3. Back extraction of Th^{227} from 20% HDEHP-Tol.

Back extractor	Concentration(M)	Activity(cpm)	% Back extracted
H_2O	0.01	org 58,056	1.2
		aq 736	
		org 106,629	
		aq 5,468	
NaOH	0.1M	org 32,964	4.8
		aq 12,009	
		org 85,205	
		aq 215	
Oxalic acid	0.0001	org 94,050	3.9
		aq 3,956	
	0.001	org 96,172	9.7
		aq 9,245	
	0.01	org 95,544	9.4
		aq 9,967	
	0.3	org 9,163	90.6
		aq 79,343	
	0.5	org 3,122	96.7
		aq 99,944	
	0.7	org 1,450	99.1
		aq 94,311	

3). **α -Spectrum.** Aliquot amount of the original sample of Ac^{227} was dissolved in 0.01 N HCl and extracted with 20% HDEHP in toluene, back extracted with same volume of 2N HNO_3 and, finally, the Th activity in organic phase was back extracted with 0.8 M oxalic acid aqueous solution. This oxalic acid solution was dried and ignited to destroy the oxalate. This was dissolved in 1M HNO_3 . The spectrum of the original sample, aqueous phase in the first extraction and the Th fraction were taken and are shown in Fig

4, 5, and 6. As being expected Fig 6 shows pure Th^{227} activity and the weak Ac^{227} peak in Fig 4 was

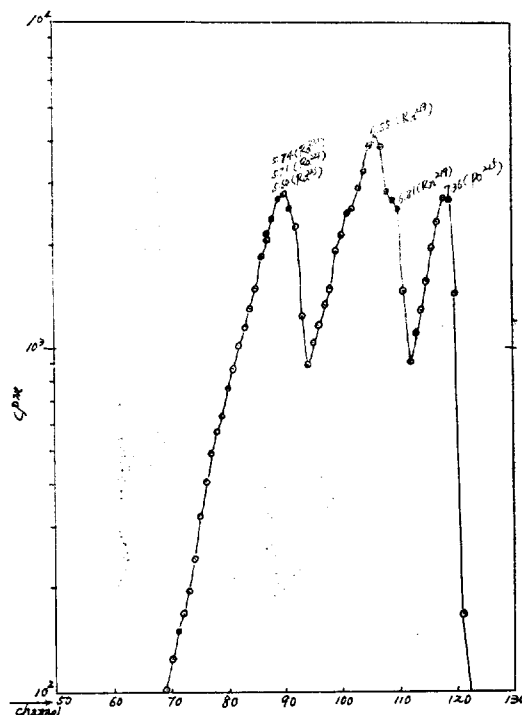


Fig4. α -Spectrum of Original Sample.

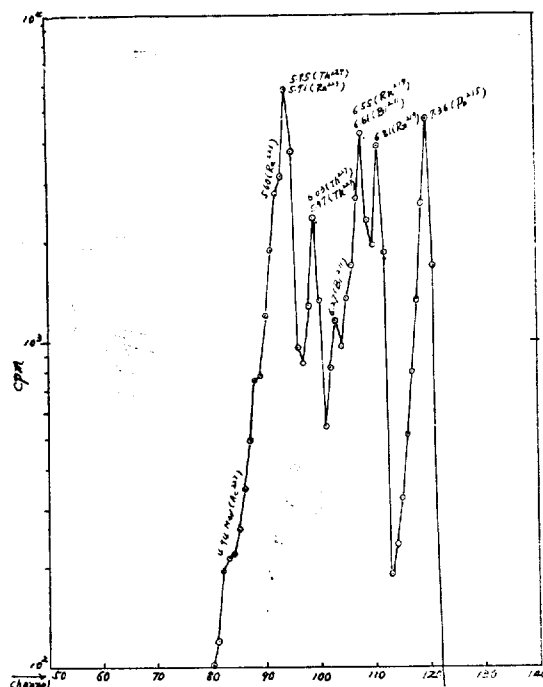


Fig5. α Spectrum of Ra^{223} Fraction. (4 hours later from Separation)

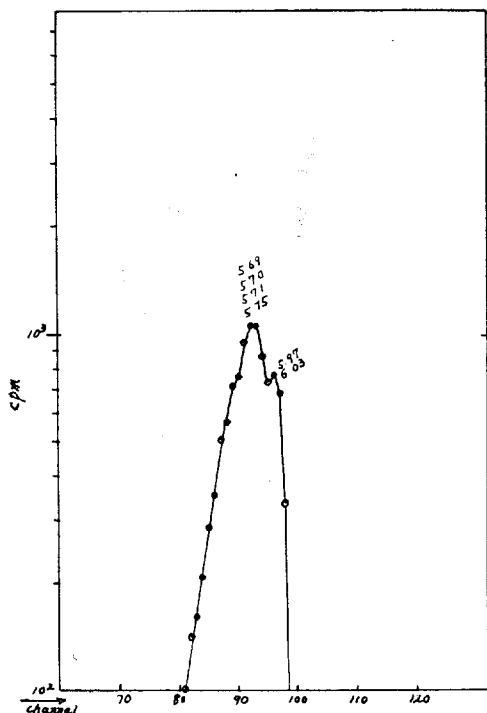


Fig6. α spectrum of Th^{227} fraction (4 hours later from separation)

disappeared in Fig 5. Bi^{211} peak could not be found in Fig 5. but this cannot be the verification of the quantitative co-extraction of Bi^{211} or Pb^{211} with Ac^{227} since the spectrum was taken four hours later after the separation.

4). **Purification by TBPO.** To study the possibility of separation of the Ac^{227} from Pb^{211} activity, the original sample was treated as shown in Fig 7.

An aliquot amount of original sample was dried up under infra red lamp and dissolved in 2.5c. c. of 0.01N HCl. This was extracted with 2.5c. c. of 20% HDEHP-toluene and the organic phase was scrubbed with 2.5c. c. of 1N HCl. One drop of the aqueous phase was plated on stainless steel plate (plate ①). The aqueous phase was extracted again with 2.5c. c. of 5% TBPO-toluene. Again, one drop of this aqueous phase was plated (plate ②). The β and $\alpha+\beta$ activities of plate ① and ② were measured by the same end window G. M. counter and gas flow 2π proportional counter, respectively, and the results are shown in Table 4.

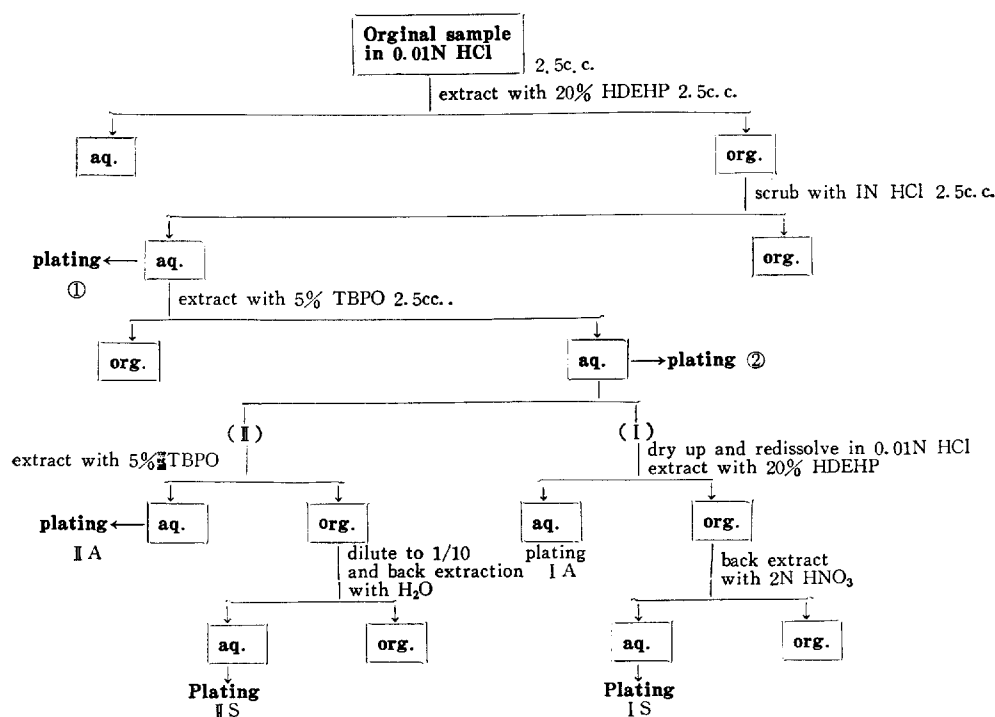


Fig7. Schematic diagram of HDEHP & TBPO extraction.

Table 4. β & $\alpha + \beta$ activities of plate (1) and (2).

Activity Plate	cpm	
	by G. M.	by Gas flow
(1)	174	2356
(2)	2	561

From these results it is understood that the Pb^{211} activity can be eliminated as a factor of 2.1×10 through the extraction procedure of 5% TBPO-toluene and the activity in plate ② is nearly daughter free Ac^{227} .

Two 1c.c. portions of the aqueous phase from which plate ② was made were taken, (I) and (II). Sample (I) was dried up under infra red lamp and dissolved in 1c.c. of 0.01N HCl and extracted with 1c.c. of 20% HDEHP-toluene. 50 λ of the aqueous phase was plated (IA) and the activity in organic phase was back extracted with 1c.c. of 2N HNO_3 to make good plate and 50 λ of this aqueous phase was plated (IS). On the other hand, 0.5c.c. of sample (II) was extracted with same volume of 5% TBPO-toluene and 50 λ of this aqueous phase was plated (IIA). The organic phase was diluted to 5c.c. with toluene and was back extracted with 5c.c. of distilled water and 0.5c.c. of this aqueous phase was plated (IIS). Those activities in plate (IS), (IA), (IIS) and (IIA) were measured to check the possible loss of Ac^{227} through these procedures. The 2π proportional counter was used for counting and the results are shown in Table 5.

Table 5. Distribution ratio of Ac^{227}

Plate	cpm	Distribution ratio※
IS	2.204	22
IA	104	
IIS	46	3.9×10^{-2}
IIA	1.191	

Thus, it was estimated that the Ac^{227} loss during the two extraction stage is less than $10\% \left(\frac{1}{22} + 3.8 \times 10^{-2} < 0.1 \right)$

(※ The distribution ratio was defined as the ratio of counted activity of organic phase to that of aqueous phase under equal volume base.)

Conclusion

Present study shows that Ac^{227} can be recovered more than 90% as daughter free state by extraction with 20% HDEHP in toluene from 0.01N HCl solution and re-extraction with 5% TBPO in toluene after back extraction with 1N HCl from the HDEHP phase. This procedure is very simple and the whole process will not take more than half an hour. Thus, this procedure seems very suitable for rapid preparation of daughter free Ac^{227} tracer and milking of Th^{227} from aged Ac^{227} activity.

References

- 1). D.E. Hull *et al*, *J. Am. Chem. Soc.* **57** 593 (1935).
- 2). "Gmelins Handbuch der Anorganischen Chemie" 8th ed. system number 40. pp 24-29 (1942).
- 3). C.K. McLane *et al*, Paper 19.6 of "The Trans-uranium element" *National Nuclear Energy Series*, Div. IV. Volume 14B (1949).
- 4). F. Hagemann *et al*, ANL-4215 (1948).
- 5). H.C. Andrews *et al*, ANL-4176 (1948).
- 6). F. Hagemann, *J. Am. Chem. Soc.* **72**, 768 (1950).
- 7). Henry G. Petrow *et al*, *Anal. Chem.* **33**, 1301 (1961).
- 8). *ibid*, *ibid* **35** 747 (1963).
- 9). C.T. Rhee, *AERI. C/R-3* (1963).
- 10). T. Ishimori, *et al*, *JAERI* 1047 (1963).