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**"Ten years of experience in extraction chromatographic processes
for the recovery, separation and purification of actinides elements"**

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I INTRODUCTION

Since about fifteen years the French Atomic Energy Commission has developed a program for the production of isotopes of actinides elements for french and international uses. An overview of the isotopes produced, the accumulated amounts since the beginning of the program and the method of preparation is presented Table I. Basically there is two types of programs.

I.1. Major programs

- (i) Involving the preparation of special targets, their irradiation by neutrons in nuclear reactors and the chemical treatment of the irradiated targets
 - . production of ^{233}U by irradiation and treatment of $^{232}\text{ThO}_2$ targets
 - . production of ^{238}Pu by irradiation and treatment of $^{237}\text{Np}/\text{Al}$ or $^{237}\text{NpO}_2/\text{MgO}$ targets
 - . production of ^{242}Pu , ^{243}Am , ^{244}Cm by irradiation and treatment of $^{239}\text{Pu}/\text{Al}$ targets or $^{242}\text{PuO}_2$ targets.
- (ii) Involving the milking of large amounts of parent material : production of ^{241}Am by chemical treatment of kilogram amounts of PuO_2 or Pu metal stocks rich in ^{241}Pu .
- (iii) Involving the chemical treatment of large volumes of alpha active liquid wastes : recovery of ^{241}Am .

I.2. Minor programs

Which correspond to productions of special isotopes either by milking of stocks of aged parent (^{228}Th , ^{229}Th , ^{234}U , ^{237}U , ^{239}Np , ^{240}Pu , ^{248}Cm) or by chemical treatment of small irradiated targets (^{242}Cm).

For the production and purification of all these isotopes chemical separations must be achieved ; in few cases these separations are easy to be performed due to the large difference in chemical properties of the two elements in presence, this is the case for the production of ^{239}Np ($^{239}\text{Np}(\text{IV})/^{243}\text{Am}(\text{III})$) separation or ^{240}Pu ($^{240}\text{Pu}(\text{IV})/^{244}\text{Cm}(\text{III})$) separation ; for the other isotopes produced difficult separations are needed :

- . recovery of traces of $^{233}\text{U}(\text{VI})$ in large amounts of $^{232}\text{Th}(\text{IV})$
- . recovery of traces of 228 , $^{229}\text{Th}(\text{IV})$ in large amounts of $^{233}\text{U}(\text{VI})$ (containing ^{232}U)
- . separation $^{238}\text{Pu}/^{237}\text{Np}$
- . separation $^{243}\text{Am}/^{244}\text{Cm}$.

At the beginning of the programs these separations were realized using liquid-liquid extraction (L.L.E.) techniques operated in mixer-settlers but ten years ago the extraction chromatographic technique was developed for preparative purposes and is now applied for all chemical separations needed for the production of actinides isotopes. That technique appears to be simple and flexible. It can be used for the production of μg to kilogram amounts of actinide isotopes. This paper focuses on the experience gained after ten years and describes some peculiar production of actinide isotopes solved by using extraction chromatographic techniques.

II EXTRACTION CHROMATOGRAPHY TECHNIQUE

More than ten years ago extraction chromatography technique was principally used in analytical laboratories for the separation of small amounts of metallic ions [1]. Its field of applications is now extended to process chemistry especially for nuclear applications [2] to [5]. The main advantages of extraction chromatography techniques can be compared with those of more conventional liquid-liquid extraction or ion exchange chromatography methods. Table II presents such a comparison; in spite of a lower capacity than that possessed by ion exchange chromatography, extraction chromatography seems preferable due to the large versatility of extracting functions available and the simple method which can be used for the recovery of actinide trapped in the extracting material. The main advantage of extraction chromatography vs liquid-liquid extraction lies in the simplicity of the device used to perform the separations. Of course the small exchange capacities of the columns used in extraction chromatography make that technique only ideal for the production of μgrams to kilograms amounts of actinides. For the production of tons amounts of actinides, extraction chromatography cannot compete with liquid-liquid extraction.

II.1. Extracting molecules and their uses

The choice of an extracting molecule suitable for extraction chromatography application depends on several criteria :

- . affinity for the actinide to be recovered
- . simple conditions for loading and elution are needed
- . impregnation conditions of the extracting molecule on the inert support
- . lowest molecular weight possible allowing the highest exchange capacity of the columns
- . low solubility in aqueous solutions.

Table III presents some characteristics of extracting molecules used in our laboratory meeting some or all the criteria described above.

The simplest molecule used is the TBP for which the behavior for the extraction of actinides ions is well known from liquid-liquid extraction (L.L.E.) data. The transposition of the knowledge from L.L.E. to L.L.C. is simple and easy. The high affinity of TBP for U(VI) and Pu(IV) present in acidic aqueous solutions makes L.L.E. technique using TBP extracting agent ideal for purification of uranium and plutonium. To obtain high distribution coefficients for trivalent actinides (Am(III) and Cm(III)) with TBP it is necessary to use highly salted aqueous solutions which induces liquid wastes difficult to manage, that is why a research of extracting molecules having a high affinity for trivalent actinides in acidic media was initiated. In a first step POX.11 (a phosphine oxide) whose properties are close to those of TOPO was studied. The use of POX.11 instead of TBP for the extraction of Am(III) allows a decrease of the concentration of the salting out reagent needed in aqueous solutions : 3.6. M instead of 7 to 8 M LiNO_3 . The main advantage of POX.11 vs TOPO lies in its liquid nature allowing simple method for loading the extracting molecule on the inert support. In a second step search for molecules able to extract Am(III) from nitric acid solutions without salting out reagent was pursued. For this application DHDECMP, an extracting molecule developed in the U.S.A. [6] [7] and $\varphi\varphi$ (a new molecule) were selected. At first the use of $\varphi\varphi$ in L.L.E. was considered difficult because of the solid nature of this compound involving difficulties for the homogeneous loading on the inert support, but it was found that the solvate between $\varphi\varphi$ and nitric acid is liquid and easy to impregnate on the stationary phase.

In the case of TnOAHNO_3 , preparation of the loaded material is easy : first liquid TOA is loaded on the support and when the column is filled with this material, a flow of nitric acid through the column converts the amine in its salt. The high affinity of TOAHNO_3 for tetravalent actinides from nitric acid solutions makes this extracting agent suitable for the purification of Pu(IV) or Np(IV).

The use of HD(DIBM)P, a highly sterically hindered extractant is restricted to the separation between Am(VI) and trivalent actinides or lanthanides. The selectivity of the separation is very high. The special properties of di-2-ethylhexylphosphorodithioic acid able to extract U(VI) in a synergetic combination with TBP from acidic solutions and to reduce Pu(IV), allow a very special separation U(VI)/Pu(IV) without the need to reduce plutonium to Pu(III) in the feed.

II.2. Inert support

The properties needed for the inert support used in L.L.C. are :

- commercial availability
- low prices
- high specific area
- hydrophobic properties
- highest specific gravity possible.

Three different inert supports were used : Celite 545, Gas Chrom Q (Applied Science Lab) and hydrophobic silica (Merck). Celite 545 was made hydrophobic by treatment with dimethyl dichlorosilane. The particule size distribution of Celite 545 and Gas Chrom Q is 110 to 140 μ and their specific area $\approx 1 \text{ m}^2.\text{g}^{-1}$. The highest specific gravity of the hydrophobic silica makes this product more attractive than the two others, this permit highest extracting capacities for the column per unit of volume.

II.3. Preparation and characteristics of the stationary phases

Impregnations of the stationary phase with the extracting molecule are carried out as follows : a certain mass of material is placed in contact with a solution of extractant in hexane or acetone, the solvent is then evaporated under reduced pressure by means of a Buchi Rotavapor rotary evaporator. Impregnation levels in mass in the final mixtures are respectively : TBP (27 %), POX 11 (30 %), DHDECMP (30 %), $\varphi\varphi$ (30 %), TOA (25 %), HD(DIBM)P (30 %), HD₂EHDTP + TBP (30 %). Batches of mixture can be prepared at the 3 kg scale. Table IV presents the exchange capacities of the different stationary phases used, for the extraction of actinide at different oxidation states from nitrate solutions.

II.4. Chromatographic equipment

The chromatographic equipment includes :

- plexiglass columns packed with the stationary phase impregnated with the extractant
- Prominent proportioning pumps
- storage tanks for various solutions
- gauge for in-line detection at the outlet of the column.

The column is filled by successive additions and repeated packings of the dry stationary phase. Once the packing is completed and the top cover cemented, the column is placed in the glove-box or the hot cell, where it undergoes pre-equilibrium designed to produce the chemical conditions required for fixation and to expel the air.

Two kinds of gauges are used for in-line selection at the outlet of the column :

- small Geiger-Muller tube for detection of ^{241}Am (60 keV)
- cerium doped glass scintillator for alpha detection.

Depending on the amount of actinide to be extracted the size of column varies from 100 g to 9 kg of stationary phase contained. The most used columns contain 2.8 kg of stationary phase and possess a Φ : 82 mm and a height h : 700 mm, their void volume is about 1.5 liters. Degradation of the column can occur by washing or radiolytic damage of the extractant. The columns the most sensitive to these phenomena are those loaded with DHDECMP used for the extraction of americium 241. Columns loaded with D_2EHDTp are sensitive to oxydation by nitric acid media, thus it is necessary to add an anti-nitrite agent ($\text{NH}_2\text{SO}_3\text{H}$) in the feed. Used columns can be eliminated as alpha solid waste after removal of the solution contained.

III SEPARATION AND PURIFICATION OF ACTINIDES ISOTOPES BY EXTRACTION CHROMATOGRAPHY

Instead of an overall description of a special process for the production of an actinide isotope we will describe in the present chapter some peculiar points corresponding to different processes :

- treatment of irradiated targets
- recovery of actinides from alpha active wastes
- recovery of decay products from aged actinide stocks.

III.1. Treatment of irradiated targets

III.1.1. Neptunium 237 irradiated targets

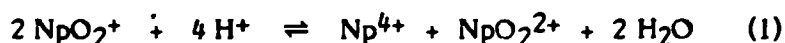
This program was initiated in France in 1969 in order to prepare plutonium 238 batteries suitable for nuclear pacemakers. That production of plutonium 238 was based on the irradiation of Np/Al or NpO_2/MgO targets in nuclear reactors, the chemical treatment of the irradiated targets after six months of cooling with a double aim : recovery of plutonium 238 and of neptunium 237 for recycling. The overall process was based on liquid-liquid extraction technique operated in mixer-settlers after the dissolution of the targets in nitric acid solutions [8]-[10].

In 1975 we started to test extraction chromatography as an alternative for the L.L.E. process. Here we will focus on two experiments concerning the difficult separation between plutonium and neptunium. Such a separation can be achieved by two systems based on :

- Valence adjustment, Pu(IV)/Np(V) then selective extraction of Pu(IV) by TOAHNO_3 columns
- Valence adjustment, Np(IV)/Pu(III) then selective extraction of Np(IV) by TOAHNO_3 columns.

(i) Pu(IV)/Np(V) separation on TOAHNO₃ column

In nitric acid media the most stable oxidation states for plutonium and neptunium are Pu(IV) and Np(V), it is thus possible to perform the separation by selective extraction of Pu(IV). Such a separation faces with a difficulty : the Np(V) trend to disproportionate according to



If in nitric acid of moderate concentration reaction (1) is shifted to the left, in the presence of an extracting agent having affinities for Np^{4+} , NpO_2^{2+} or for both, reaction (1) is shifted to the right, thus the neptunium is coextracted with the plutonium(IV).

To minimize this phenomenon and thus the efficiency of the Pu(IV)/Np(V) separation the feed must be adjusted to a low nitric acidity (1 M) compatible with hydrolytic properties of Pu(IV). A dissolution liquor of an NpO_2/MgO irradiated target of total volume = 23 l : $\text{Np(V)} = 11 \text{ g.l}^{-1}$, $\text{Pu(IV)} = 0.6 \text{ g.l}^{-1}$ was adjusted to $\text{HNO}_3 = 1 \text{ M}$ and then injected on a TOAHNO₃/Gas chrom Q column containing 1015 g of stationary phase ($\Phi = 60 \text{ mm}$, $H = 700 \text{ mm}$) with a flow rate equal to 2.5 l.h^{-1} . After washing the column with $\text{HNO}_3 = 2 \text{ N}$ at 2.5 l.h^{-1} , plutonium 238 was eluted with a solution of following composition : $\text{H}_2\text{SO}_4 = 1 \text{ M}$, $\text{HNO}_3 = 0.2 \text{ M}$.

Forteen grams of ^{238}Pu were recovered in one cycle, ^{237}Np was free of ^{238}Pu , decontamination factor F.D. Pu(Np) was only moderate ≈ 20 but acceptable for a first cycle of Pu/Np separation, decontamination of ^{238}Pu from fission products was high.

(ii) Np(IV)/Pu(III) separation on TOAHNO₃ column

Separation between neptunium 237 and plutonium 238 can be achieved after reduction to Np(IV) and Pu(III) by selective extraction of Np(IV). Such a separation is difficult to perform with high concentration of plutonium 238 in solution because of the intense radiolysis leading to the destruction of the excess of reductor used and thus to the oxidation of plutonium to Pu(IV). Such a process can be used for final purification of neptunium 237 contaminated with traces of plutonium 238. Recently the purification of 300 grams of neptunium 237 contaminated with 17.5 ppm of plutonium 238 (due to the large difference in the half lives of these isotopes the alpha contribution of plutonium 238 was 30 %) was realized using the following procedure.

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Feed The concentration of neptunium in the feed was 100 g.l^{-1} in 6 M HNO_3 , the reduction of neptunium to Np(IV) and plutonium to Pu(III) was done by addition of $\text{N}_2\text{H}_5\text{NO}_3$ to 1.5 M and a warming of the solution to 80°C during two hours. Thus after cooling the solution was adjusted to 0.1 M in ferrous sulfamate ($\text{Fe}(\text{NH}_2\text{SO}_3)_2$) freshly prepared under nitrogen by dissolution of iron in sulfamic acid. The presence of ferrous sulfamate in the feed allows the maintenance of plutonium as Pu(III). The presence of small amount of iron(III) in the feed, induces a small oxidation of plutonium to Pu(IV) and thus a decrease in the performance of the separation.

The feed is then injected on a TOAHNO_3 column containing few percent of octanol 2 in order to decrease a little the distribution coefficient of tetravalent actinide and thus improve the quality of the separation.

Washing The column loaded with Np(IV) was washed by $\text{HNO}_3 = 3 \text{ M}$ to remove plutonium and iron ions present in the void volume.

Elution The elution of Np(IV) was performed with a solution: $\text{HNO}_3 = 0.1 \text{ M}$; $\text{H}_2\text{SO}_4 = 0.75 \text{ M}$ due to the complexing properties of SO_4^{--} ions. In the purified neptunium the concentration of plutonium was 0.24 ppm . The decontamination factor for the entire process was $\text{F.D.Np(Pu)} = 73$ which is a good performance for this low level of ^{238}Pu contamination.

III.1.2. Plutonium 239 irradiated targets [11], [12]

This program was initiated for the production of americium 243 and curium 244 isotopes. The Pu/Al targets containing initially 400 g of fissile material were irradiated with an integrated flux of 11.28 n.cm^{-2} . Chemical treatment started after three years of cooling time.

The overall process is operated by L.L.C. after dissolution of the targets in nitric acid which is realized using 88 liters . The highly radioactive solutions contain 350 Ci.l^{-1} of β, γ emitters and 44 g of ^{242}Pu ; 8.35 g of ^{243}Am and 7.44 g of ^{244}Cm .

The first step of the process lies in the recovery and purification of the plutonium 242 , which is realized by extraction chromatography using a TOAHNO_3 column or a TBP column. To prevent clogging of these columns by fission products precipitates, the feed is filtrated through a small column containing a bed of silica. After washing of the column with nitric acid solution the elution of the plutonium 242 is realized with a sulfonitric solution (TOAHNO_3 column) or a hydroxylammonium nitrate reducing solution (TBP column).

The largest difficulty associated with that treatment lies :

- In the separation of trivalent actinides (^{243}Am , ^{244}Cm) from trivalent lanthanides present in the solution in large quantities (≈ 140 g).
- In the separation Am/Cm. The difficulties have been solved by L.L.C. using a TALSPEAK like system, where TBP extractant was used instead of HDEHP. Thus in this system the selectivity of the separation is only due to the DTPA present in aqueous solution.

All the lanthanides possess a higher affinity than Am(III) and Cm(III) for TBP column from $\text{LiNO}_3 = 8 \text{ M}$, $\text{HNO}_3 = 0 \pm 0.05 \text{ M}$, $\text{DTPA} = 0.1 \text{ M}$, $\text{pH} = 1.2$ solution, the separation factor $\alpha = D_{\text{Ln}^{3+}} \cdot D_{\text{Am}^{3+}}^{-1}$ is large for the light lanthanides and is close to 1.4 for Tb and heavier Ln(III). To achieve a good separation (Am, Cm) from Ln, it is necessary to perform several cycles.

Separation between americium 243 and curium 244 is based for the first step on the same procedure. Figure 1 presents the separation between 1.51 g of curium 244 and 1.75 g of americium 243 using a TBP column and a Talspeak like system.

Final purification of americium 243 is performed by selective extraction of Am(VI) on a HD(DiBM)P column using a process identical with that described below for the purification of americium 241. That process appears very simple and flexible, easy to operate in the difficult conditions found in hot cells. Until now about 100 g of americium 243 and ≈ 90 g of curium 244 of high purities have been successfully produced.

III.2. Recovery of actinides from alpha aqueous wastes

In 1978 a program was initiated with the goal of producing large amounts of americium 241 used to prepare neutron sources (americium 241-beryllium or americium-lithium) for oil industry. The first source of americium 241 found in the C.E.A. consisted in alpha aqueous liquid wastes :

- "Masurca" waste resulting from the reprocessing of certain irradiated fuels and from criticality analyses. Cadmium was added to the solution for safety reasons and then its initial volume of about 400 m^3 was reduced to 4 m^3 by distillation
- Waste coming from the reprocessing of fabrication scrap from fabricating (U, Pu) O_2 fuels intended for fast breeder reactors. The annual volume of this waste solution amounts to some tens of m^3 .

The americium 241 contents of these wastes were respectively 108 mg.l⁻¹ and 28 mg.l⁻¹. As the uranium content of the "Masurca" waste was high (12 g.l⁻¹) it appears that L.L.C. wasn't suitable for its recovery prior to recovery of higher actinides. Thus conventional L.L.E. using TBP organic solution in mixer-settlers was used. The neptunium 237 and plutonium 239 were recovered by ion exchange chromatography using an anionic resin (IRA 400) prior to the recovery of americium 241 by extraction chromatography. In order to decrease the concentration of the salting out reagent necessary to obtain high distribution coefficient of Am(III), di-nhexyloctoxymethylphosphine oxide (POX.11) [13] was selected as extracting agent. A moderate concentration of LiNO₃ = 3.6 M was found sufficient to obtain high K_DAm(III) (≈5.10³ml.g⁻¹) for a nitric acid concentration of 0.1 M. The POX.11 nevertheless has the disadvantage of extracting Fe(III) with rather slow kinetics, which in the case of the "Masurca" waste gives rise to a sharp drop in K_DAm(III). The addition of EDTA to aqueous solution in equal concentration to Fe(III) (0.2 M) helps to avoid its extraction and to restore all the extractive properties of the POX.11 for Am(III). This is due to the selective formation of the complex FeY⁻ (with YH₄ = EDTA) whose formation constant log(FeY⁻) = 25.1 [14] is much higher than that of the americium(III) complex = log (AmY⁻) = 18.0 [15]).

Experiments were realized to determine the exchange capacity of POX.11 vs Am³⁺, simulations of Am³⁺ by Nd³⁺ was also used in order to decrease the irradiation of the chemist working in a glove-box. Figure 2, presents studies of saturation of a POX.11 column by Am(III) or by Nd(III) nitrates. In each case the breakthrough is obtained for a stoichiometric ratio POX.11/M(III) close to 4 indicating that the extracted complex possesses the following formula: M(NO₃)₃ (POX.11)₄. That result was confirmed either by the study of POX.11 (30 %)/SiO₂ mixture saturation in test tubes or by the saturation of a POX.11 dodecane solution. Such a stoichiometry is very unusual because for trioctylphosphine oxide (TOPO) trivalent actinides or lanthanides are extracted as M(NO₃)₃.(TOPO)₃. The POX.11 possesses a high affinity for U(VI) and Pu(IV), for these ions stoichiometries are similar to those obtained with TOPO = UO₂(NO₃)₂ (POX.11)₂ and Pu(NO₃)₄ (POX.11)₂.

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During the chemical treatment of the "Masurca" waste rather large POX.11 column was used containing 9 kilograms of POX.11 (30 %)/SiO₂ stationary phase. A feed of 685 liters of total volume was treated, the decontamination factor of the effluent in americium 241 was 250; americium 241 (17 g) was recovered by elution with 20 liters of nitric acid (concentration factor = 34) with 89 % yield and its decontamination vs Cd²⁺ and Fe³⁺ was close to 130 [16].

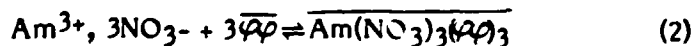
The major drawbacks encountered in the use of POX.11 process for the recovery of americium 241 from alpha liquid wastes lies in the rather complicated feed adjustment: presence of LiNO₃ 3.6 M as salting-out reagent and of EDTA to complex Fe(III) present in the feed. That is why new molecules able to extract trivalent americium from nitric acid media without need of salt and possessing high affinity and selectivity for trivalent actinides were considered. The first molecule investigated is di-n-hexyldiethylcarbamoyl-methylenephosphonate (DHDECMP) well studied for L.L.E. in the U.S.A. [5].

Distribution coefficient of Am(III) between nitric acid solutions and DHDECMP (30 %)/SiO₂ stationary phase were measured at low nitric acid concentration $K_{DAm^{3+}} = 0.9 \text{ ml.g}^{-1}$ (HNO₃ = 0.1 M) and $K_{DAm^{3+}}$ maximum = 26 ml.g⁻¹ is obtained for HNO₃ = 6 M. It is thus possible to extract trivalent americium from moderate volumes of 5 to 6 M HNO₃ (due to the relatively low value of $K_{DAm^{3+}}$ maximum) and to perform the elution with water.

Figure 3 presents an experiment related to the separation of americium 241 from fission products ¹³⁴, ¹³⁷Cs and ¹⁰⁶Ru and from inactive contaminants contained in a real waste. During the loading step fission products and inactive contaminants escaped from the column. After the washing of the column by a small volume of HNO₃ = 5 M, the americium 241 is eluted with three void volumes of the column. Americium 241 was recovered with a yield of 98 % and after conversion to AmO₂, its purity was found 85 % which is a very good performance for only one cycle. Adaptation of DHDECMP process to the purification of large amounts of americium 241 (50 grams) was realized but the lives of the columns were found to be limited because of the washing and radiolytic damage of the DHDECMP.

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Another molecule able to extract trivalent americium from nitric acid solution was studied: the diphenyl di-n-butyl carbamoyl methylene phosphine oxide ($\overline{\text{PP}}$). High distribution coefficients of Am^{3+} were obtained from nitric acid solutions with a maximum for $\text{HNO}_3 = 2.5 \text{ M}$. The extraction reaction is:



The usefulness of that molecule for the recovery of americium 241 from nitric acid solutions by L.L.C. was demonstrated in an experiment where a nitric acid solution ($\text{HNO}_3 = 2 \text{ M}$) containing $13,4 \text{ mg.l}^{-1} \text{ }^{241}\text{Am}$ was loaded on a small column containing 1 g of $\overline{\text{PP}}$ (30 %)/ SiO_2 stationary phase. Four hundreds voids volume of the column were decontaminated with F.D. (Am^{3+}) = 388. Americium 241 can be eluted from the $\overline{\text{PP}}/\text{SiO}_2$ column, after washing by water, with a K_2CO_3 solution.

III.3. Recovery of decay products from aged actinide stocks

III.3.1. Recovery of americium 241 from aged plutonium metal or PuO_2 stocks

The recovery of americium 241 from alpha active wastes is a rather complicated method due to the large volumes involved and their low concentration in americium. A more attractive way to produce hundreds of grams amounts of americium 241 is to treat aged stocks of plutonium metal or plutonium dioxide initially rich in ^{241}Pu . The first step of the process consists in the dissolution of the starting material on 300 g scale in nitric medium (containing F^- ion) under reflux conditions in a tantalum dissolver. After filtration the solution is injected on a TBP column for $\text{Pu}(\text{IV})$ extraction, americium 241 escapes from the column.

After washing of the column with 5 M nitric acid, the plutonium is eluted as $\text{Pu}(\text{III})$ with a hydroxylamine nitrate solution and then converted in PuO_2 . The raffinate containing the ^{241}Am is then adjusted to the following conditions: $\text{H}^+ = 0 + 0.05$, $\text{Al}(\text{III}) = 1.8 \text{ M}$, $\text{DTPA} = 0.1 \text{ M}$ and loaded on a TBP column in order to decontaminate americium 241 from impurities (Pu , inactive metallic ions) and to reduce the volume of the americiated solution. After a washing of the TBP column with 8 M LiNO_3 solution, americium is eluted with 2 M nitric acid. Final purification of americium 241 is performed with a method described in Figure 4. The first step consists in the precipitation of $\text{Am}(\text{OH})_3$, which is redissolved after filtration, in concentrated K_2CO_3 solution.

The addition of $K_2S_2O_8$ allows the precipitation of americium(V), potassium double carbonate. After precipitation, the precipitate is taken up with an oxidizing acidic solution containing $K_2S_2O_8$ and Ag ions acting as catalyst in the oxidation of Am(V) to Am(VI) by $S_2O_8^{--}$ ions. After warming to 50°C americium is totally converted to Am(VI) (a spectrometric measurement is performed prior loading the solution into the L.L.C. column). The adjusted Am(VI) feed is then injected on a bis (2,6 dimethyl 4-heptyl)phosphoric (HDDiBMP) acid column previously treated by an oxidizing solution ($S_2O_8^{--}$ and Ag(II) ions) until persistence of the dark color of Ag(II) ions in the effluent. Extraction of Am(VI) is apparent on the column by a greenish band. After washing of the column by an oxidizing solution americium is eluted with a reducing solution ($N_2H_5NO_3 = 0.5 M$, $HNO_3 = 1 M$).

Such a process is applied successfully on a 50 to 60 g. of ^{241}Am scale. The yield of the purification lies on the range 85 to 97 % for routine experiment. Americium 241 purity of 98.5 % was measured by calorimetry after transformation into AmO_2 .

Laboratory experiments were performed in order to determine the stoichiometry of the extracted americium(VI) compound and thus the exchange capacity of the HD(DiBM)P columns. Figure 5 presents the curve obtained on the study of the saturation of a small HD(DiBM)P column with Am(VI), the concentration of ^{241}Am in the effluent is measured in line with a small Geiger-Muller detector. The break through is obtained for an HD(DiBM)P/Am(VI) ratio equal to 4, thus if HA stands for HD(DiBM)P the formula of the extracted americium(VI) compound is $= AmO_2A_2(HA)_2$. The same stoichiometry was found for U(VI) extracted complex.

Using this process, about 500 g. of high purity ^{241}Am have been produced.

III.3.2. Recovery of uranium 234 from aged plutonium 238 stocks

In aged plutonium 238 dioxide, uranium 234 accumulates. Due to the very different half lives of these isotopes ($t_{1/2} = 87,7$ years for plutonium 238 and $2.44 \cdot 10^5$ years for uranium 234) the recovery of high nuclear purity uranium 234 necessitates very efficient separation process.

Ten grams of plutonium 238 on the dioxide form were processed for uranium 234 recovery according to the following scheme :

- (i) Dissolution of PuO₂ in HNO₃ acid with F⁻ ion acting as catalyst.
- (ii) Precipitation of the bulk of plutonium 238 as oxalate, ²³⁴U(VI) remains in the mother liquor.
- (iii) Change of medium by Pu(IV), U(VI) coextraction with TBP and back extraction with the addition of alpha bromocapric acid to the organic phase towards HNO₃ = 1 N aqueous solution.
- (iv) Extraction chromatography on HD₂EHDTP (20 %), TBP (10 %)/Gas Chrom Q column.

The extraction chromatographic separations between ²³⁸Pu and ²³⁴U were performed using a column containing 20 g of stationary phase. During the loading step of the feed, extraction of ²³⁴U(VI) is realized by the synergetic mixture : di 2 ethyl hexyl phosphorodithioic acid (HA)/tributyl phosphate. The extracted complex which formula is : UO₂A₂.TBP possesses an intense yellow color [17]. The di 2 ethyl hexyl phosphorodithioic acid possesses reductive properties vs Pu(IV) thus plutonium 238 escapes from the column as blue Pu(III). A fraction of the column (at the top) is destroyed by this reaction.

After washing of the column with a solution of composition HNO₃ = 1 N, NH₂SO₃H = 0.1 M, ²³⁴U(VI) is eluted with a 0.4 M (NH₄)₂C₂O₄ solution. Forty six milligrams of uranium 234 were recovered and after two cycles of extraction chromatographic separations the alpha contribution of plutonium 238 in the purified uranium 234 was only 1.27 %.

Decontamination factors for extraction chromatographic separations were respectively : cycle 1 F.D. U(Pu) = 517 ; cycle 2 F.D. U(Pu) = 452. For the entire process F.D. U(Pu) = 4.5.10⁷ was obtained and the uranium 234 recovery yield was 75 %.

IV CONCLUSIONS

Extraction chromatography technique was developed in the last ten years for actinides recovery, separations and purifications. Due to the large variety of organic extracting ligands available, that technique can be applied successfully to solve difficult actinides separations. The processes developed for the recovery and purification of microgram to kilogram amounts of actinides isotopes are easy to operate either in glove boxes or in hot cells. Nevertheless there is still some difficulties to solve : especially the extraction of trivalent americium from nitric acid solutions for which if some opportunities exist : uses of DHDECMP or φφ, their performances are not really ideal. More research is needed in this area.

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TABLE I
ISOTOPES PRODUCED OR RECOVERED

| ELEMENT | ISOTOPE | METHOD OF PRODUCTION | Scale of production since the beginning of the program |
|-------------------|-------------------|--|--|
| T H O R I U M | ^{228}Th | $^{232}\text{U} \alpha \text{ } ^{228}\text{Th}$ milking of large amounts of aged ^{233}U rich in ^{232}U | 10 μg |
| | ^{229}Th | $^{233}\text{U} \alpha \text{ } ^{229}\text{Th}$ milking of large amounts of aged ^{233}U | mg |
| U R A N I U M | ^{233}U | Irradiation of ^{232}Th by neutrons Chemical treatment of irradiated $^{232}\text{ThO}_2$ targets | hundreds of grams |
| | ^{234}U | $^{238}\text{Pu} \alpha \text{ } ^{234}\text{U}$ milking of large amounts of aged $^{238}\text{PuO}_2$ | grams |
| | ^{237}U | $^{241}\text{Pu} \alpha \text{ } ^{237}\text{U}$ milking of aged plutonium rich in ^{241}Pu isotope | μCi |
| N E P T U N I U M | ^{237}Np | Recovered in special campaigns in the reprocessing plant devoted to treatment of irradiated nuclear fuels | 10 kg |
| | ^{239}Np | $^{243}\text{Am} \alpha \text{ } ^{239}\text{Np}$ milking of aged $^{243}\text{AmO}_2$ | μg |
| P L U T O N I U M | ^{238}Pu | Irradiation of $^{237}\text{Np}/\eta$ Chemical treatment of irradiated Np/Al or NpO_2/MgO targets | kg |
| | ^{240}Pu | $^{244}\text{Cm} \alpha \text{ } ^{240}\text{Pu}$ milking of aged $^{244}\text{CmO}_2$ | 10 of mg |
| | ^{242}Pu | Irradiation of ^{239}Pu targets/ η chemical treatment of irradiated Pu-Al targets | hundreds |
| A M E R I C I U M | ^{241}Am | $^{241}\text{Pu} \beta^- \text{ } ^{241}\text{Am}$ Milking of aged PuO_2 or Pu metal stocks - Chemical treatment of alpha active liquid wastes | kilogram |
| | ^{243}Am | Irradiation of ^{239}Pu or ^{242}Pu by neutrons Chemical treatment of Pu-Al or PuO_2 irradiated targets | 100 g |
| C U R I U M | ^{242}Cm | Irradiation of ^{241}Am by neutrons Chemical treatment of irradiated AmO_2 targets | 10 mg |
| | ^{244}Cm | Irradiation of ^{239}Pu or ^{242}Pu by neutrons - Chemical treatment of irradiated Pu-Al or PuO_2 targets | 100 g |
| | ^{248}Cm | $^{252}\text{Cf} \alpha \text{ } ^{248}\text{Cm}$ Milking of aged ^{252}Cf stock | 10 of μg |

| METHOD CHARACTERISTICS | EXTRACTION CHROMATOGRAPHY | ION EXCHANGE CHROMATOGRAPHY | LIQUID-LIQUID EXTRACTION |
|---|---|---|--|
| Versability of extracting functions | large | mean | very large |
| Exchange capacity | mean (adjustable) | large | mean (adjustable) |
| Extracting device | simple (1 column + 1 pump) | simple (1 column + 1 pump) | complex (mixer-settlers + pumps) |
| Number of plates | large | large | small |
| Sensitivity of performance to operating conditions | small | small | large |
| Recovery of the actinide trapped in the extracting material | simple A diluent washing of the column allows the recovery of the extractant and of the actinide | very difficult A possible method is to calcine the resin and to dissolve ashes in acid | simple Technique of solvent washing |
| Elimination of alpha contaminated material | easy (quasi solid waste) | easy (solid waste) | difficult (large volumes of alpha organic liquid wastes) |

TABLE II Comparison of extraction chromatography, resin chromatography and liquid-liquid extraction techniques for actinides separations

| N° | FORMULA | ABBREVIATION | STATE | MOLECULAR (weight) | TYPE OF APPLICATION |
|----|--|----------------------|--------|--------------------|--|
| ① | $\begin{array}{c} \text{C}_4\text{H}_9\text{O} \\ \\ \text{C}_4\text{H}_9\text{O}-\text{P}-\text{O} \\ \\ \text{C}_4\text{H}_9\text{O} \end{array}$ | TBP | liquid | 266 | $\left. \begin{array}{l} {}^{238}\text{Pu(IV)}/{}^{237}\text{Np(V)} \\ {}^{243}\text{Am}/{}^{244}\text{Cm} \end{array} \right\}$ |
| ② | $\begin{array}{c} \text{C}_6\text{H}_{13} \\ \\ \text{C}_6\text{H}_{13}-\text{P}-\text{O} \\ \\ \text{C}_7\text{H}_{15}-\text{O}-\text{CH}_2 \end{array}$ | POX.11 | liquid | 346 | ${}^{241}\text{Am(III)}/\text{transition elements}$ |
| ③ | $\begin{array}{c} \text{C}_6\text{H}_{13} \quad \text{O} \\ \quad \quad \quad \\ \text{C}_6\text{H}_{13} \quad \text{P} - \text{CH}_2 - \text{C} - \text{N} \begin{array}{l} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{array} \\ \quad \quad \quad \\ \text{O} \quad \quad \quad \text{O} \end{array}$ | DHDECMP | liquid | 363 | ${}^{241}\text{Am(III)}/\text{transition elements}$ |
| ④ | $\begin{array}{c} \text{C}_6\text{H}_5 \quad \text{O} \\ \quad \quad \quad \\ \text{C}_6\text{H}_5 \quad \text{P} - \text{CH}_2 - \text{C} - \text{N} \begin{array}{l} \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\ \text{C}_4\text{H}_9 \end{array} \\ \quad \quad \quad \\ \text{O} \quad \quad \quad \text{O} \end{array}$ | $\varphi\varphi$ | solid | 371 | ${}^{241}\text{Am(III)}/\text{transition elements}$ |
| ⑤ | $\begin{array}{c} \text{C}_8\text{H}_{17} \\ \\ \text{C}_8\text{H}_{17}-\text{NH}^+, \text{NO}_3^- \\ \\ \text{C}_8\text{H}_{17} \end{array}$ | TOAHNO ₃ | solid | 416 | ${}^{237}\text{Np(IV)}/{}^{238}\text{Pu(III)}$ |
| ⑥ | $\begin{array}{c} \text{((CH}_3)_2\text{-CH-CH}_2)_2\text{-CH-O} \\ \\ \text{((CH}_3)_2\text{-CH-CH}_2)_2\text{-CH-O} - \text{P} - \text{O} \\ \\ \text{OH} \end{array}$ | HD(DIBM)P | liquid | 350 | ${}^{241}\text{Am(VI)}/\text{Gd(III), Ln(III)}$ |
| ⑦ | $\begin{array}{c} \text{C}_8\text{H}_{17}-\text{O} \\ \\ \text{C}_8\text{H}_{17}-\text{O} - \text{P} - \text{S} \\ \\ \text{SH} \end{array}$ | D ₂ EHDTP | liquid | 354 | ${}^{234}\text{U(VI)}/{}^{238}\text{Pu(IV)}$ |

TABLE III Extracting molecules and their uses in actinide separations

- ① tri-n butylphosphate
- ② di-n-hexyloctoxymethylphosphine oxide
- ③ di-n-hexyl diethyl carbamoylmethylene phosphonate
- ④ di phenyl di-n-butyl carbamoyl methylene phosphine oxide
- ⑤ tri-n-octylammonium nitrate
- ⑥ bis(2,6 dimethyl 4 heptyl)phosphoric acid
- ⑦ di-2-ethyl hexyl phosphoro dithioic acid

| STATIONARY PHASE | EXTRACTED COMPOUND | EXCHANGE CAPACITY m.mole.g ⁻¹ |
|---|--|---|
| TBP (27 %) | $\left\{ \begin{array}{l} \text{UO}_2(\text{NO}_3)_2 \cdot (\text{TBP})_2 \\ \text{Pu}(\text{NO}_3)_4 \cdot (\text{TBP})_2 \\ \text{Am}(\text{NO}_3)_3 \cdot (\text{TBP})_3 \end{array} \right.$ | 0.507 0.507 0.338 |
| POX II (30 %) | $\left\{ \begin{array}{l} \text{UO}_2(\text{NO}_3)_2 (\text{POX.11})_2 \\ \text{Pu}(\text{NO}_3)_4 (\text{POX.11})_2 \\ \text{Am}(\text{NO}_3)_3 (\text{POX.11})_4 \end{array} \right.$ | 0.433 0.433 0.216 |
| DHDECMP (30 %) | $\text{Am}(\text{NO}_3)_3 (\text{DHDECMP})_3$ | 0.275 |
| PO (30 %) | $\text{Am}(\text{NO}_3)_3 (\text{PO})_3$ | 0.269 |
| TOA (25 %) | $\text{Np}(\text{NO}_3)_6(\text{TOAH})_2(\text{TOAHNO}_3)_2$ | 0.177 |
| HD(DIBM)P (30 %) | $\text{AmO}_2(\text{D}(\text{DiBM})\text{P})_2 (\text{HD}(\text{DiBMP}))_2$ | 0.214 |
| D ₂ EHDTP (20 %) (HA) TBP (10 %) | $\left\{ \text{UO}_2\text{A}_2\text{-TBP} \right.$ | 0.282 |

TABLE IV Exchange capacities of the different stationary phases used

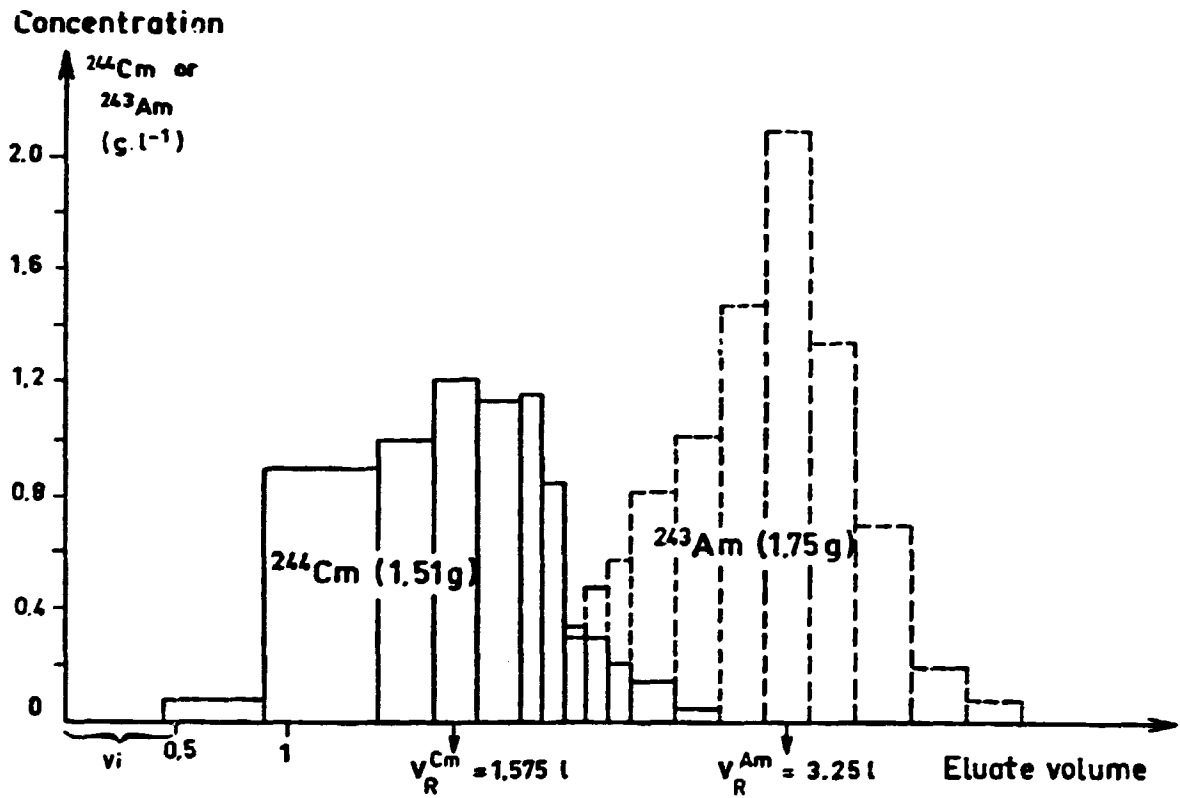


Figure 1 Separation $^{243}\text{Am}/^{244}\text{Cm}$ by extraction chromatography on a TBP/Gas Chrom Q column

FEED = DTPA = 0.1 M, Al^{3+} = 0.5 M, LiNO_3 7 M

SCRUB = LiNO_3 8 M

ELUTION = LiNO_3 8 M DTPA 0.1 M, pH 1.20

Column TBP (25 %) Gas Chrom Q, $m = 500$ g, $L = 64$ cm, $\phi 4,2$ cm
Flow rate = 1.2 l.h^{-1}

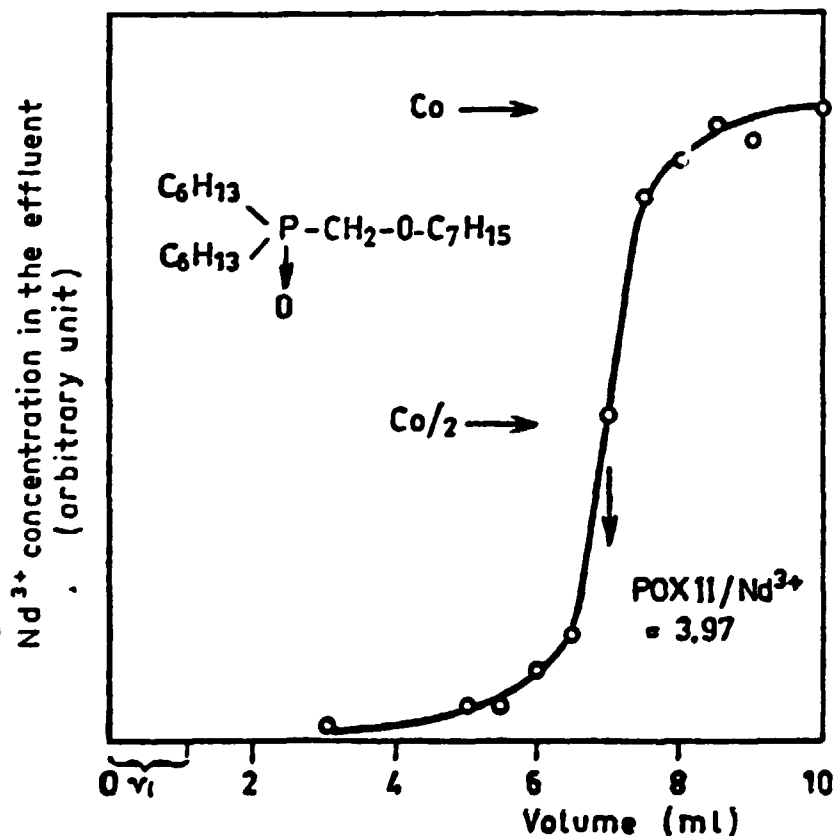
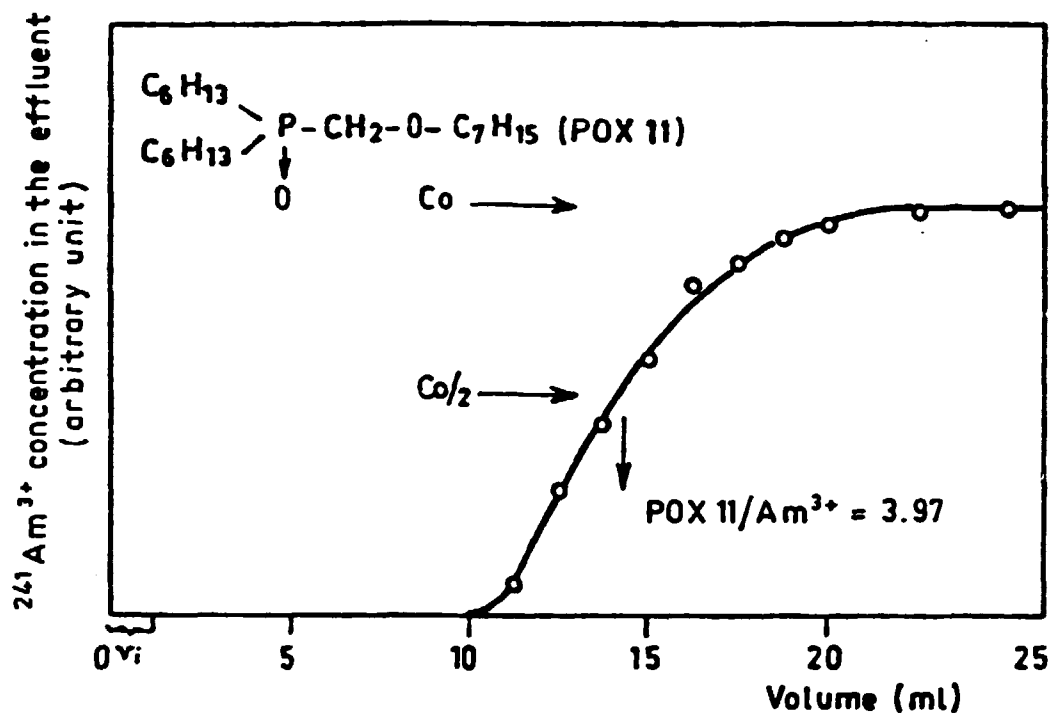


Figure 2 Saturation of POX.11/SiO₂ column with ²⁴¹Am and Nd

Columns = 1 g POX.11 (29,7 %)/SiO₂ ϕ = 5 mm, H = 80 mm,
 Void volume = 1,37 ml (Am^{3+}), 1,1 ml (Nd^{3+})

Aqueous phase =

[LiNO₃] = 3,6 M, [HNO₃] = 0,1 M, [Am^{3+}] = 3,81 g.l⁻¹ or [Nd^{3+}] = 5 g.l⁻¹

Flow rates = 15,1 ml.h⁻¹ (Am^{3+}), 1,25 ml.h⁻¹ (Nd^{3+})

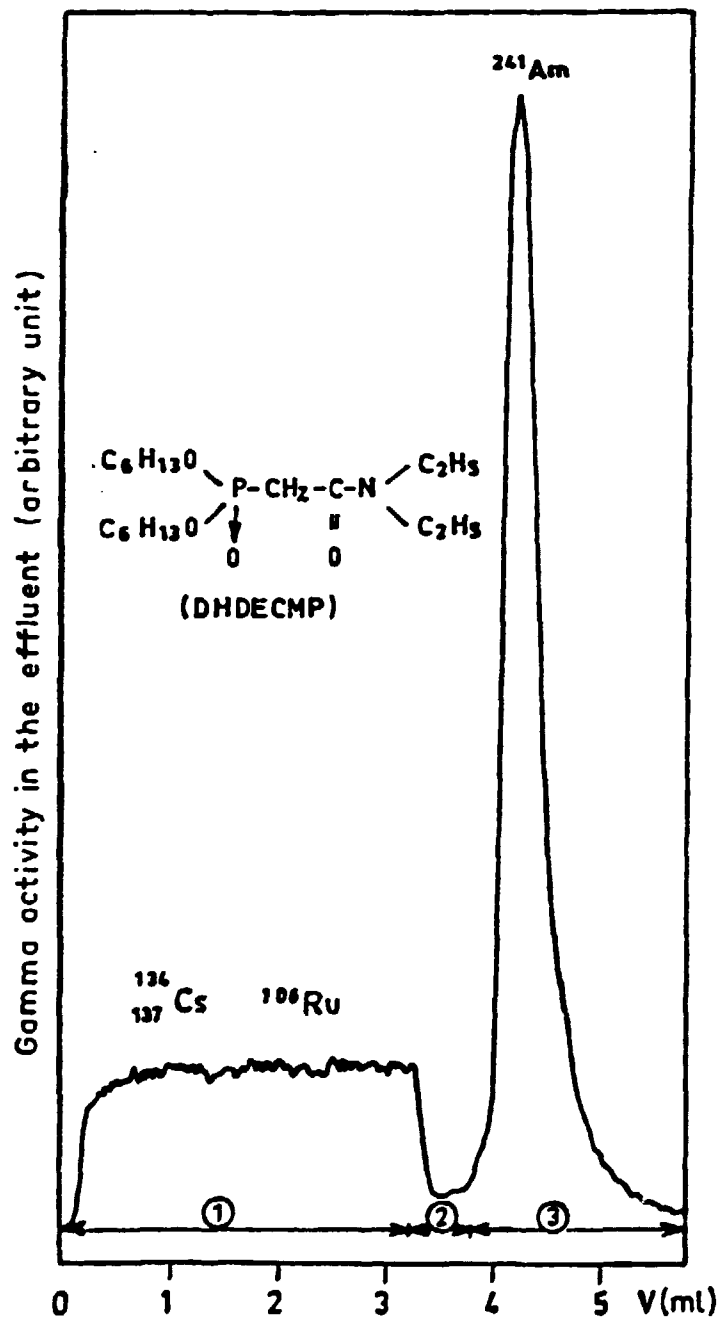


Figure 3 Purification of americium 241 from an industrial waste by extraction chromatography using a DHDECMP/SiO₂ column

Column = 1 g DHDECMP (30 %)/SiO₂, $\phi = 5$ mm, H = 80 mm

- Aqueous Phases
- ① alpha active waste free from U and Pu (HNO₃ = 5 N)
 - ② HNO₃ = 5 M
 - ③ H₂O flow rate 2 ml.h⁻¹

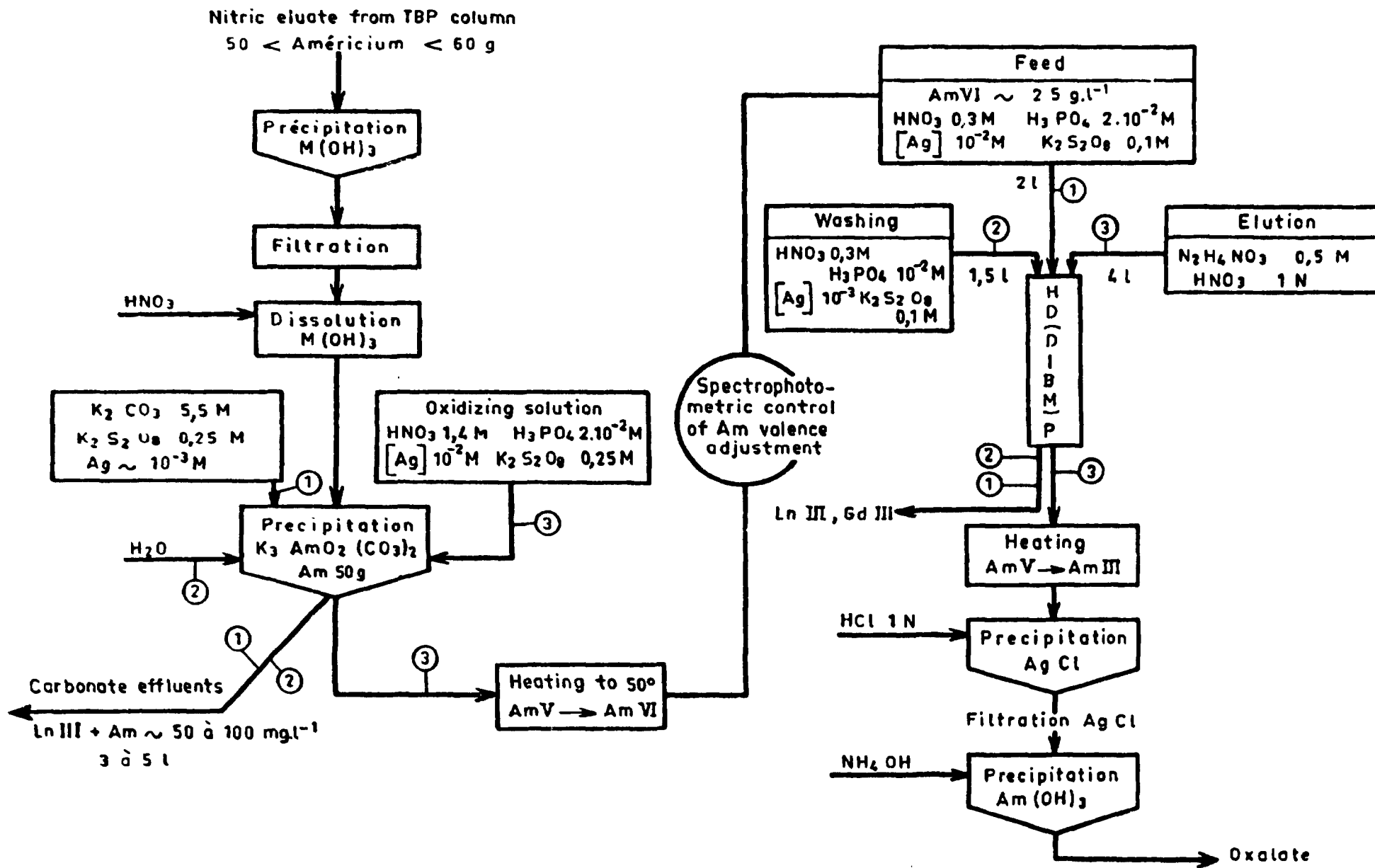


Figure 4 Recovery of americium 241 from aged plutonium stocks
 Final purification process for americium 241

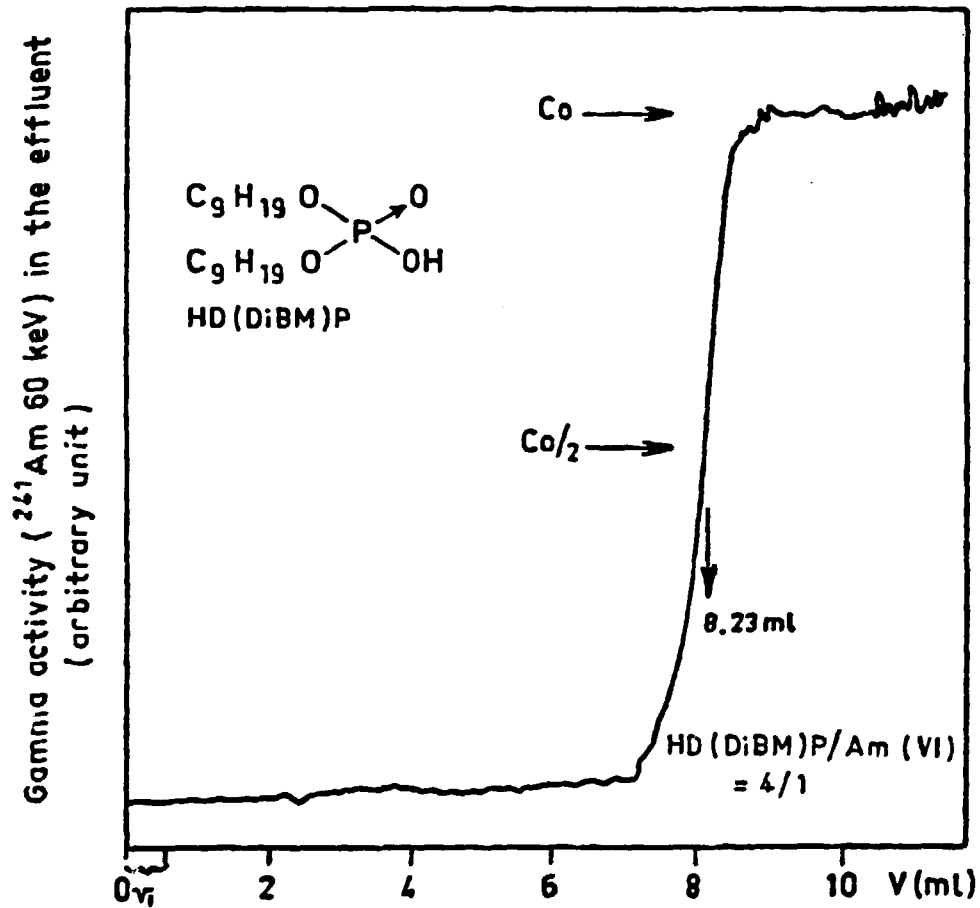


Figure 5 Saturation of HD(DiBM)P/SiO₂ column with ²⁴¹Am(VI)

Column = stationary phase = 0.500 g of HD(DiBM)P (29,56 %)SiO₂

Aqueous [NaNO₃] = 2 M, [HNO₃] = 0.1 M, [K₂S₂O₈] = 0.2 M,
Phase [Ag] = 2.10⁻²M, [Am(VI)] = 3.27 g.l⁻¹

Flow rate = 6 ml.h⁻¹

60 keV ²⁴¹Am detection by in-line Geiger Muller gauge