

APPLICATION OF ION EXCHANGE RESINS TO THE
SEPARATION OF CARRIER FREE FISSION PRODUCTS

by

ALCÍDIO ABRÃO, M. J. NASTASI e ALMIR A. LARANJA

PUBLICAÇÃO I.E.A. N.º **101**

Agosto — 1965



INSTITUTO DE ENERGIA ATÔMICA
Caixa Postal 11049 (Pinheiros)
CIDADE UNIVERSITÁRIA "ARMANDO DE SALLES OLIVEIRA"
SÃO PAULO — BRASIL

APPLICATION OF ION EXCHANGE RESINS TO THE SEPARATION OF
CARRIER FREE FISSION PRODUCTS

by

Alcídio Abrão, M.J. Nastasi e Almir A. Laranja

Radiochemistry Division, Instituto de Energia Atômica
São Paulo, Brazil

Publicação IEA nº 101

Agosto - 1965

Comissão Nacional de Energia Nuclear

Presidente: Prof. Luiz Cintra do Prado

Universidade de São Paulo

Reitor: Prof. Luiz Antonio da Gama e Silva

Instituto de Energia Atômica

Diretor: Prof. Rômulo Ribeiro Pieroni

Conselho Técnico-Científico do IEA

Prof. Hélio Lourenço de Oliveira) pela USP
Prof. Walter Borzani	
Prof. Rui Ribeiro Franco) pela CNEN
Prof. Theodoreto H.I. de Arruda Souto)	

Divisões Didático-Científicas:

Div. de Física Nuclear: Prof. Marcello D.S. Santos

Div. de Engenharia de Reatores: Prof. Tharcísio D.S. Santos

Div. de Ensino e Formação: Prof. Luiz Cintra do Prado
(licenciado)

Div. de Radioquímica: Prof. Fausto Walter de Lima

Div. de Radiobiologia: Prof. Rômulo Ribeiro Pieroni

Div. de Metalurgia Nuclear: Prof. Tharcísio D.S. Santos

Div. de Engenharia Química: Prof. Kazimiers J. Brill

APPLICATION OF ION EXCHANGE RESINS TO THE SEPARATION OF
CARRIER FREE FISSION PRODUCTS

by

Alcídio Abrão, M.J. Nastasi e Almir A. Laranja

RESUMO

Estudou-se a separação de produtos de fissão de meias-vidas longas partindo-se de urânio natural irradiado utilizando-se um procedimento químico no qual consta o uso de resinas catiônicas e aniônicas. Foram separados, em sequência, os seguintes radioisótopos de fissão: Cs-137, Sr-89 e Sr-90 e Terras Raras na resina catiônica e Zr-95, Nb-95 e Ru-103, Ru-106, na resina aniônica.

O urânio é irradiado como pastilhas de U_3O_8 (5 g cada) durante 15 a 200 horas e observado um período de resfriamento de 8 meses. As pastilhas são dissolvidas com ácido nítrico e o urânio é extraído com TBP (30% em CCl_4). A solução aquosa (refinado) contendo os produtos de fissão é adicionado ácido oxálico e feita destilação até redução de volume para aproximadamente 5 ml. O resíduo é retomado com HCl 0,1M e as condições acertadas para que a solução resultante seja 0,4M em ácido oxálico. Esta é percolada numa coluna de resina catiônica (Dowex 50-X8, 100-200 mesh, forma H^+) ficando retidos Cs-137, Sr-89, Sr-90, e elementos de Terras Raras (predominantemente Ce-141, Y-90, Y-91, Ce-144, Pr-144 e Pm-147). A coluna é lavada com solução $H_2C_2O_4$ 0,4M - HCl 0,1M, após o que são eluídos Cs-137 com HCl 1M, Sr-89 - Sr-90 com HCl 1,5M e Terras Raras com HCl 6M.

O efluente da coluna catiônica contendo Zr, Nb e Ru, é per-

colado numa coluna de resina aniônica (Dowex 2-X8, 200-400 mesh) previamente condicionada com ácido oxálico.

Em seqüência são eluídos Zr-95 e Nb-95 com HCl 1M - $H_2C_2O_4$ 0,1M e Ru com HNO_3 3M.

Todos os radioisótopos são obtidos livres de carregador. A pureza radioquímica é verificada com o auxílio da técnica de espectrometria de raios gama.

RÉSUMÉ

On a étudié la séparation des produits de fission de demi-vies longues et moyennes à partir de l'uranium naturel irradié, au moyen de résines échangeuses d'ions.

On a obtenu, par ordre de séparation, les radioéléments suivants: Cs-137, Sr-89, Sr-90 et Terres Rares sur la résine cationique, et Zr-95, Nb-95 et Ru-103, Ru-106 sur la résine anionique.

On a irradié des pastilles d' U_3O_8 (5 g) par des périodes variant de 15 à 200 heures et on a observé un refroidissement de 8 mois. On dissout les pastilles avec de l'acide nitrique et on extrait l'uranium avec du TBP (30% en CCl_4).

À la solution aqueuse contenant les produits de fission on ajoute de l'acide oxalique et ensuite on réduit le volume à 5 ml environ, par distillation.

Le résidu est repris par l'acide chloridrique 0,1M et l'acidité est ajustée à 0,4 M en acide oxalique. Cette solution est passée sur une colonne de résine cationique (Dowex 50-X8 100-200 mesh sous la forme H^+) où sont retenus le Cs-137, le Sr-89, le Sr-90 et les éléments des Terres Rares (en particulier Ce-141, Y-90, Ce-144, Pr-144 et Pm-147).

On lave la colonne avec une solution $H_2C_2O_4$ 0,4M HCl 0,1M

et ensuite on élue le Cs-137, Sr-89, Sr-90 et les Terres Rares avec de l'acide chloridrique 1M, 1,5M et 6M respectivement.

L'effluent de la résine cationique qui contient le Zr, Nb et Ru est passée sur une colonne de résine anionique (Dowex 2-X8, 200-400 mesh) préparée préalablement avec de l'acide oxalique.

Sont élués par ordre, le Zr-95 et le Nb-95 avec de l'acide chloridrique 1M et $H_2C_2O_4$ 0,01M, et le Ru avec de l'acide nitrique 3M. Tous les radioéléments sont obtenus sans entraîneurs. La pureté radiochimique est vérifiée au spectromètre à rayons gamma.

SUMMARY

A radiochemical procedure for separation of medium and long half-lived fission products radioisotopes is described. The procedure was designed for the recovery of carrier free fission products in irradiated uranium. The radioisotopes Cs-137, Sr-89, Sr-90 and the Rare Earths were separated with a cationic resin, while Zr-95, Nb-95 and Ru-103, Ru-106 were sequential separated using an anionic resin.

Pellets of U_3O_8 were neutron irradiated during 15 or 200 hours and cooling time of 8 months or more was observed. The pellets were dissolved in nitric acid and the uranium was extracted with TBF- CCl_4 . To the raffinate, oxalic acid was added, and then distilled to approximately 5 ml. The residue was taken in 0.1M HCl and the acidity adjusted to be 0.4M in oxalic acid. The fission products mixture was passed through a Dowex 50-X8, H-form cationic resin, where Cs-137, Sr-89, Sr-90, and the Rare Earths radioisotopes (Ce-141, Ce-144, Pr-144, Y-90, Y-91, and Pm-147) were sorbed. The column was washed with 0.4M $H_2C_2O_4$ - 0.1M HCl and then Cs-137, Sr-89 and Sr-90, and Rare Earths elements were eluted with hydrochloric acid of 1.0, 1.5 and 6.0 molarity, respectively.

The cationic column effluent, containing Zr-95, Nb-95 and

Ru-103, Ru-106, was percolated in a Dowex 2-X8 anionic column previously conditioned with oxalic acid. Zirconium-95, followed by Nb-95 was eluted with 1.0M HCl - 0.01M $H_2C_2O_4$ and finally Ru-103, Ru-106 was eluted with 3.0M HNO_3 .

The radiochemical purity was verified by gamma-ray spectrometry.

INTRODUCTION

Sequential separation methods using ion exchange resins have been reported. Wish and Rowell⁽¹⁾ utilized hydrochloric and nitric acid as eluents for a sequential separation of uranium, neptunium and plutonium. Also Wish⁽²⁾ described a method for the separation of neptunium, plutonium, uranium, zirconium, niobium, and molybdenum isotopes in mixed fission products. These fission products were absorbed on Dowex-2 anionic resin from concentrated hydrochloric acid and then eluted with hydrochloric acid, hydrochloric-hydrofluoric mixture, and nitric acid.

This paper describes a radiochemical procedure developed for the sequential separation of medium and long half-lived fission products radioisotopes. The procedure was designed for the recovery of carrier free fission products in natural irradiated uranium. The procedure is simple and provide nearly quantitative recoveries and high precision for the following radioisotopes Ru-103, Ru-106, Zr-95, Nb-95, Cs-137, Sr-89, Sr-90, Ce-141, Ce-144, Pr-144, Y-90, Y-91 and Pm-147. These fission products radioisotopes of great interest and representing the major components of a 8 months or more aged fission mixture were sequential separated using a scheme including cationic and anionic ion exchange resin columns. Radiocesium, radiostrontium and the rare earths fission radioisotopes were bound to the cationic resin while ruthenium, radiozirconium and its daughter niobium were sorbed on the anionic resin column. Each column was eluted with appropriate

eluents allowing the individual radioisotope separation, the rare earths elements being separated in one group.

A completely satisfactory separation scheme was achieved after investigating various eluents for these elements from columns of both cationic and anionic resins.

Hydrochloric acid was preferred among various recommended eluents for elution of cesium, strontium and rare earths from cationic column, by simply changing the HCl molarity.

Although the elution of anionic resin presented more difficulties, an acceptable elution scheme was found. From many possible eluents for zirconium and niobium, specially hydrofluoric acid alone or in mixture with other inorganic acid^(3,4) or organic solvents, a 1.0M HCl - 0.01M oxalic acid⁽⁵⁾ was preferred. With this mixture zirconium was eluted first, followed by niobium. Ruthenium was the last radioisotope eluted from anionic column and the simplest eluent for it was found to be 3M HNO₃.

Good results were obtained when the proposed scheme was applied to the separation of these radioisotopes in aged irradiated natural uranium.

EXPERIMENTAL PART

Reagents

- Nitric acid: 8M, 4M and 3M.
- 30% tributylphosphate in CCl₄.
- Oxalic acid: 0.1M, 0.4M and 1.0M.
- Hydrochloric acid: 0.1M, 1.0M, 1.5M and 6.0M.
- Eluent mixtures: 0.1M HCl - 0.4M oxalic acid and 1.0M HCl - 0.01M oxalic acid.
- Dowex 50-X8 cationic resin, 100-200 mesh.
- Dowex 2-X8 anionic resin, 200-400 mesh.

Counting Equipment

A single pulse height gamma ray analyser, model 1820A, Nuclear Chicago Corp., with a well type Na(Tl) scintillation crystal and Nuclear Chicago model 181 Scaler with mica window Geiger tube were used.

Irradiated Uranium

Two sources of irradiated material has been used:

a) natural uranium as U_3O_8 of nuclear grade purity. Pellets of 5 grams each were irradiated during 15 hours in a 10^{13} n/cm²/sec. neutron flux at the S. Paulo swimming-pool reactor. The irradiated pellets were dissolved in 8M HNO_3 , the acidity adjusted to 1M HNO_3 by dilution with deionized water, and the Te-132 was separated by an alumina column for I-132 production⁽⁶⁾. The uranyl nitrate solution containing the fission products others than Te, Mo, Tc, was saved and stored for cooling. Eight months or more aged mixture was used for the sequential fission products separation.

b) the same material was irradiated during 200 hours special ly for the fission products separation, observing a cooling time of 8 months or more. The sintered U_3O_8 pellets were enclosed into stainless steel capsules and machine opened with remote control in a hot cell. The pellets were dissolved with hot 4M HNO_3 .

Solvent Extraction of Uranium

The uranyl nitrate saved from the I-132 production, or provenient from the dissolution of 200 hours irradiated U_3O_8 pellets, containing the fission products radioisotopes had its free acidity adjusted to approximately 2M HNO_3 . The uranyl nitrate solution was extracted with equal volume of 30% TBP in CCl_4 . The mixture was mixed well during 3 minutes, the layers allowed to

settle and the organic phase removed. Two more extractions were made and residual TBP was washed out with equal two volumes of pure CCl_4 . The wash solutions were discarded. The aqueous phase (raffinate) was saved for the fission products separation. For the TBP extraction a glass apparatus (fig. 1) operated with vacuum was used. The organic phase was carefully drained and kept for posterior recovery of uranium.

Nitric Acid Elimination

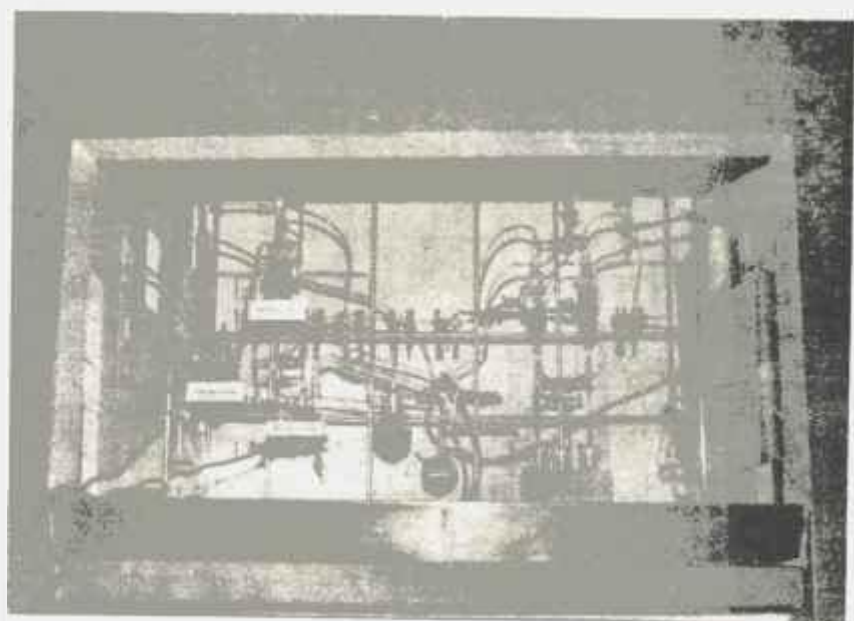
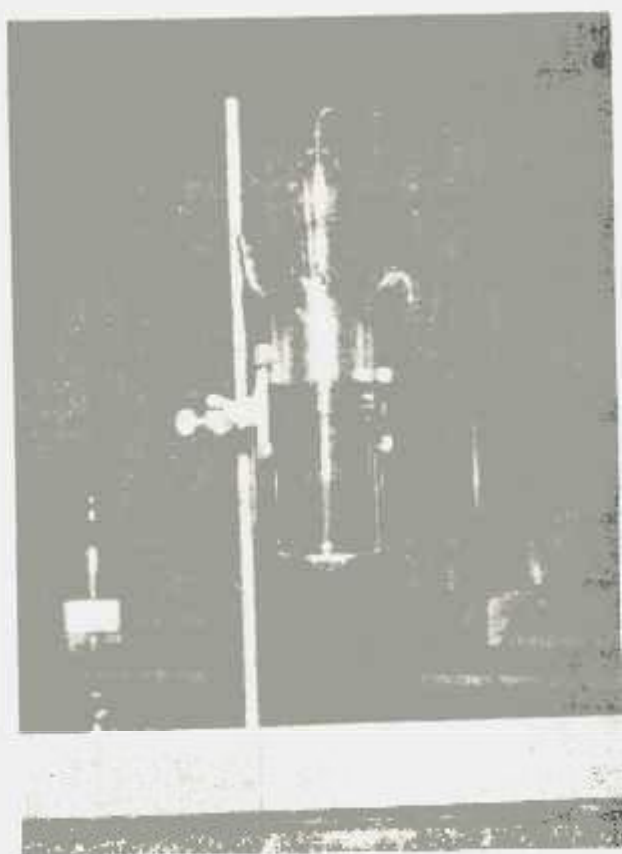
The aqueous phase containing the fission products (raffinate) was drained into a 250 ml distillation flask. To the raffinate 1.0M oxalic acid was added until an excess of approximately 25% in respect to the nitric acid present and this mixture was distilled until a residual volume of about 5 ml. The addition of reagents and all operations were remote controlled (fig. 1).

The residue containing the excess of oxalic acid was took in 0.1M HCl and the volume adjusted in order to have a final 0.3 to 0.4M $\text{H}_2\text{C}_2\text{O}_4$ acidity. If necessary, after the hydrochloric acid addition the solution was warmed for the complete dissolution of crystalized oxalic acid.

Cationic Resin Column Operation

A 80 mm i.d. glass column, provided with teflon stopcorck, containing 6 ml. of Dowex 50-X8, 100-200 mesh, cationic ion exchange resin, was first conditioned in the H^+ - form and then washed with 100 ml. of 0.4M oxalic acid solution.

The $\text{HCl-H}_2\text{C}_2\text{O}_4$ fission products solutions was allowed to pass through the cationic resin with a flow rate of about 1 ml./min. under gravity flow conditions. Cesium, strontium and rare earths radioisotopes were held by the resin and zirconium, niobium and ruthenium passed in the effluent. The effluent was saved for posterior separation of zirconium, niobium and ruthenium. After



loaded, the resin was washed with 100 ml. of 0.1M HCl - 0.4M $H_2C_2O_4$ mixture for the complete removal of zirconium, niobium and ruthenium. The washing solution was flowed with the same velocity as the influent. Wash was discarded into the waste flask solution.

Cs, Sr, and R.E. Sequential Elution

The eluent for the cationic column was hydrochloric acid. Radiocesium was first eluted with 80 ml. of 1.0M HCl with a flow rate of about 0.8 ml./min. Then, radiostrontium was eluted with 100 ml. of 1.5M HCl. Finally the rare earths radioisotopes as a group were eluted with 90 ml. of 6M HCl.

Figure 2 shows the sequential elution of the fission products held on the cationic resin. In the elution curve the activity of each 3 ml. fraction was plotted. Cesium-137 and rare earths radioisotopes fractions were gamma counted at the photopeak energy, while the mixture of Sr-89 plus Sr-90 was beta counted.

Anionic Resin Column Operation

A similar glass column with the same dimensions used for the cationic resin was prepared for the anionic species, having 6 ml. of Dowex 2-X8, 200-400 mesh. The resin, previously in the Cl-form, was conditioned with 100 ml. of 0.4M oxalic acid.

The effluent solution provenient from the cationic resin was passed down through the column, the anionic zirconium, niobium and ruthenium oxalates being held by the resin. The solution was percolated with an average flow rate of about 0.3 ml./min. The column was washed with 30 ml. of 0.1M HCl-0.4M $H_2C_2O_4$ mixture. The washing solution, containing negligible activity, was discarded into the waste disposal flask.

Zirconium, Niobium and Ruthenium Sequential Elution

Radiozirconium, followed by radioniobium was eluted with the same 1.0M HCl - 0.01M $H_2C_2O_4$ eluent solution⁽³⁾: A total

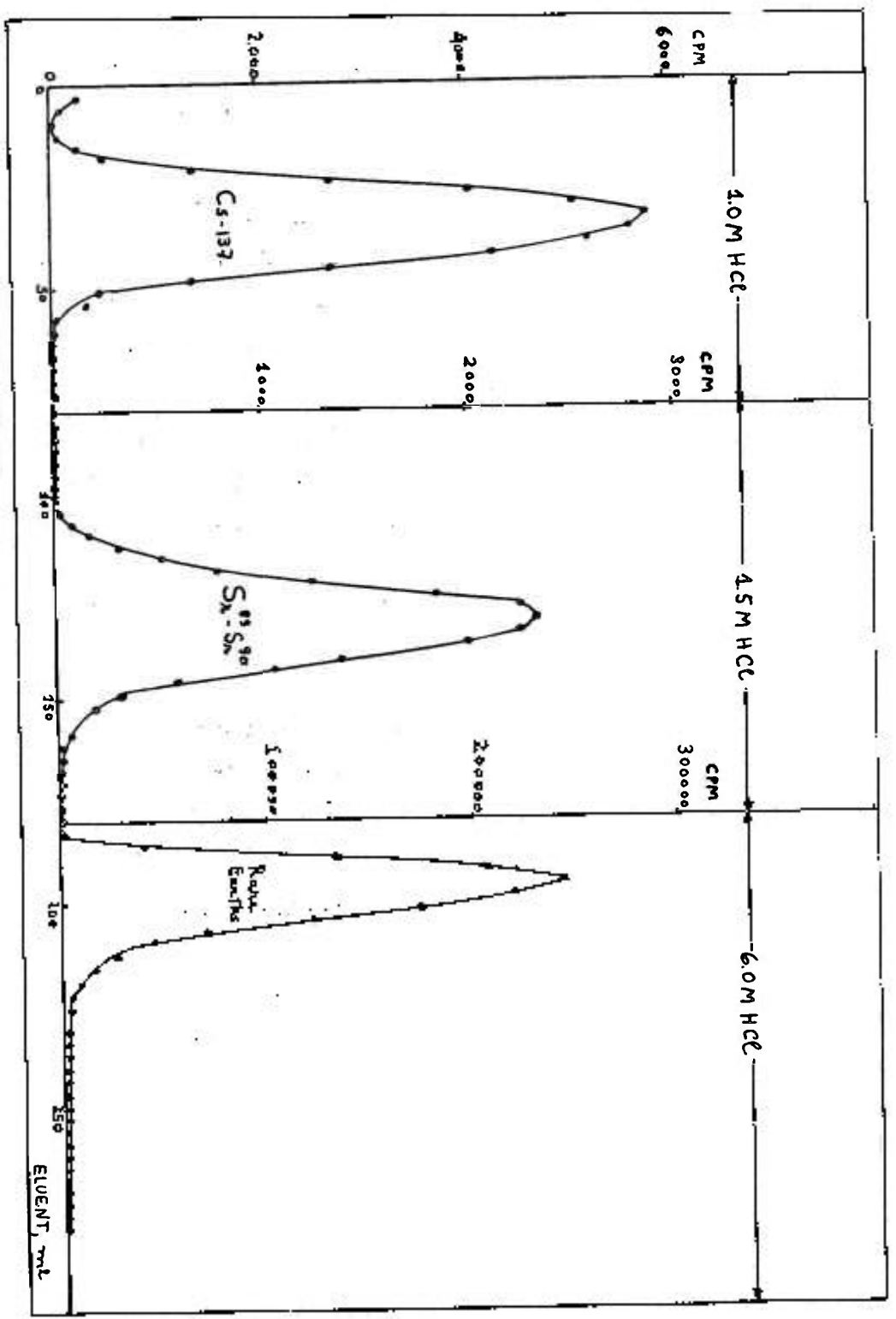


Fig. 2 - Elution Curves for Cs^{137} , Sr^{89-90} , and Rare Earths - Cationic Resin

volume of 200 ml. was used for elution of both radioisotopes. Zirconium required about 50 ml. for complete elution, while niobium presented a elution peak broader than the zirconium one. (fig. 3)

Finally radoruthenium was eluted with 80 ml. of 3.0M HNO_3 .

Figure 3 shows the sequential elution curve for zirconium, niobium and ruthenium on anionic column. All 3 ml. fractions were gamma counted at the correspondent photopeak energy.

RESULTS AND DISCUSSION

The procedure here described does not make use of concentrated acids (HCl , HNO_3 , or HCl-HF mixture). This is advantageous considering for instance the corrosion effects in the hot cell or decomposition of the resin.

Elution curves for Zr-95 and Nb-95 in the proposed method showed to be symmetrical. This was not the case when concentrated HCl alone or HCl-HF mixtures were used⁽²⁾.

The gamma spectrum of each elution fraction (3 ml.) was recorded for the radiochemical purity control of each radioisotope separated. In some cases the presence of contaminants was not detected directly by gamma ray spectrometry of the separated radioisotope; the contaminant was separated with the aid of isotopic carrier by standard radiochemical procedures and gamma counted.

Cesium

The elution of cesium showed, from 3 to 20 ml., a slight residual contamination due to Zr-95-Nb-95 mixture. Radiochemically pure cesium was recovered from 20 to 50 ml. portion of the elution curve (fig. 2) in each run. No contamination due to radiostrontium and radoruthenium was found in this recovered cesium eluate.

Strontium

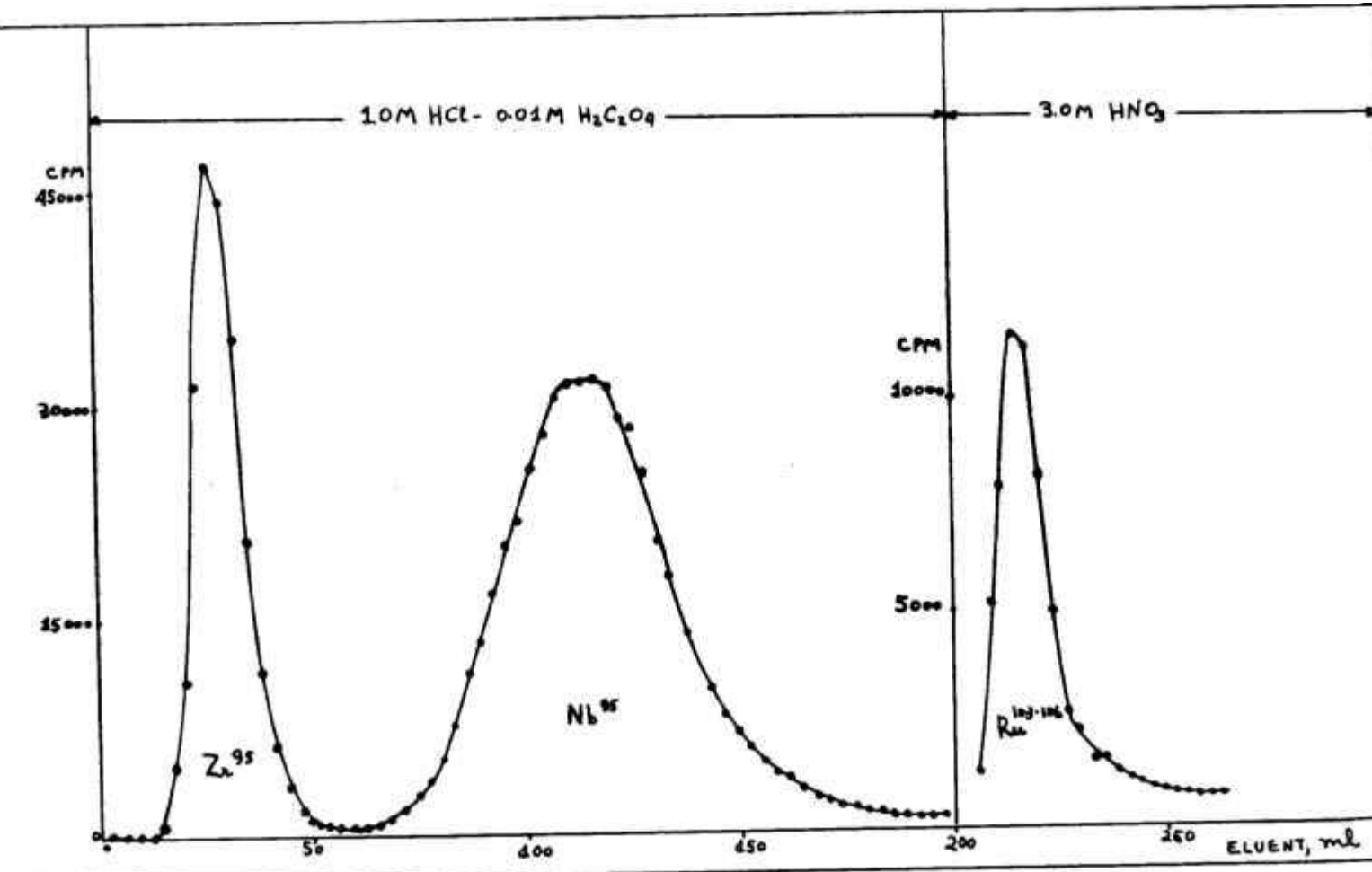


Fig. 3 - Elution Curves for Zr⁹⁵, Nb⁹⁵, and Ru¹⁰³⁻¹⁰⁶ .. Anionic Resin

All fractions of the radiostrontium eluate were analysed by gamma spectrometry. Contamination due to any gammaemitters was not found. In one run of a series of experiments, less than 0.1% of the total Zr-95-Nb-95 pair was found as contamination in the Sr-89-Sr-90 eluate collected in the 105-155 ml. range (fig. 2). The contamination due to Zr-95 and Nb-95 radioisotopes was easily eliminated in the Sr-89-Sr-90 eluate by passing this solution directly through a silica-gel column (0.8 cm x 3 cm). The radiostrontium repurified was completely free of Zr-95-Nb-95 activity.

Rare Earths

The rare earths radioisotopes Y-90, Y-91, Ce-141, Ce-144, Pr-144, Pm-147, were eluted together in one group. The useful volume colume was collected in the 180-220 ml. range in the elution curve. (fig. 2) In all experiments this group of radioisotopes was free of extraneous contamination.

Zirconium and Niobium

Concerning to the elution of the anionic resin a constant contamination of radioruthenium appeared in all Zr-95 and Nb-95 fractions. This contamination amounted to less than 5% of the total radioruthenium in the original irradiated uranium. Therefore, following the elution curve for the Zr-95 and Nb-95 (fig:3) we found that from 0 to 15 ml. only radioruthenium was present. From 15 to 50 ml. range, correspondent to the recovered Zr-95 eluate, the Ru/Zr ratio diminished gradually until no ruthenium was detected by direct gamma spectrometry analysis. From 50 to 70 ml. range ruthenium appeared again, that is, the Ru/Zr ratio increased again, and, consequently radioruthenium was detected in the gamma spectra for the correspondent elution fractions.

The same situation was found with respect to Nb-95.

The contamination due to radioruthenium in the recovered eluate for Zr-95 and Nb-95 was analysed by adding isotopic carrier

for ruthenium and reducing to the elemental form with metallic magnesium. The separated ruthenium was gamma counted at the photo-peak. The procedure for the separation of radioruthenium is described in the appendix.

Ruthenium

In almost all experiments the eluted ruthenium fractions were contaminated with about 0.8% of the total Zr-95-Nb-95 mixture in the original irradiated uranium. Even in the useful recovered eluate of ruthenium (40 ml.) Zr-95 and Nb-95 were detected by gamma spectrometry, directly. The presence of Zr-95-Nb-95 pair was confirmed by percolating the ruthenium eluate in a small silicagel column. A 0.8 cm i.d. glass column was prepared by pouring 2 ml. of distilled water-washed silica-gel. After percolating the ruthenium eluate, the column was washed with dilute nitric acid and rinsed with water. The silica-gel was transferred to a plastic vial and the gamma spectrum was recorded. The effluent of the silica-gel column was a high radiochemically pure ruthenium.

If desired, Zr-95-Nb-95 pair could be eluted from the silica-gel column with dilute hydrofluoric acid or oxalic acid.

APPENDIX

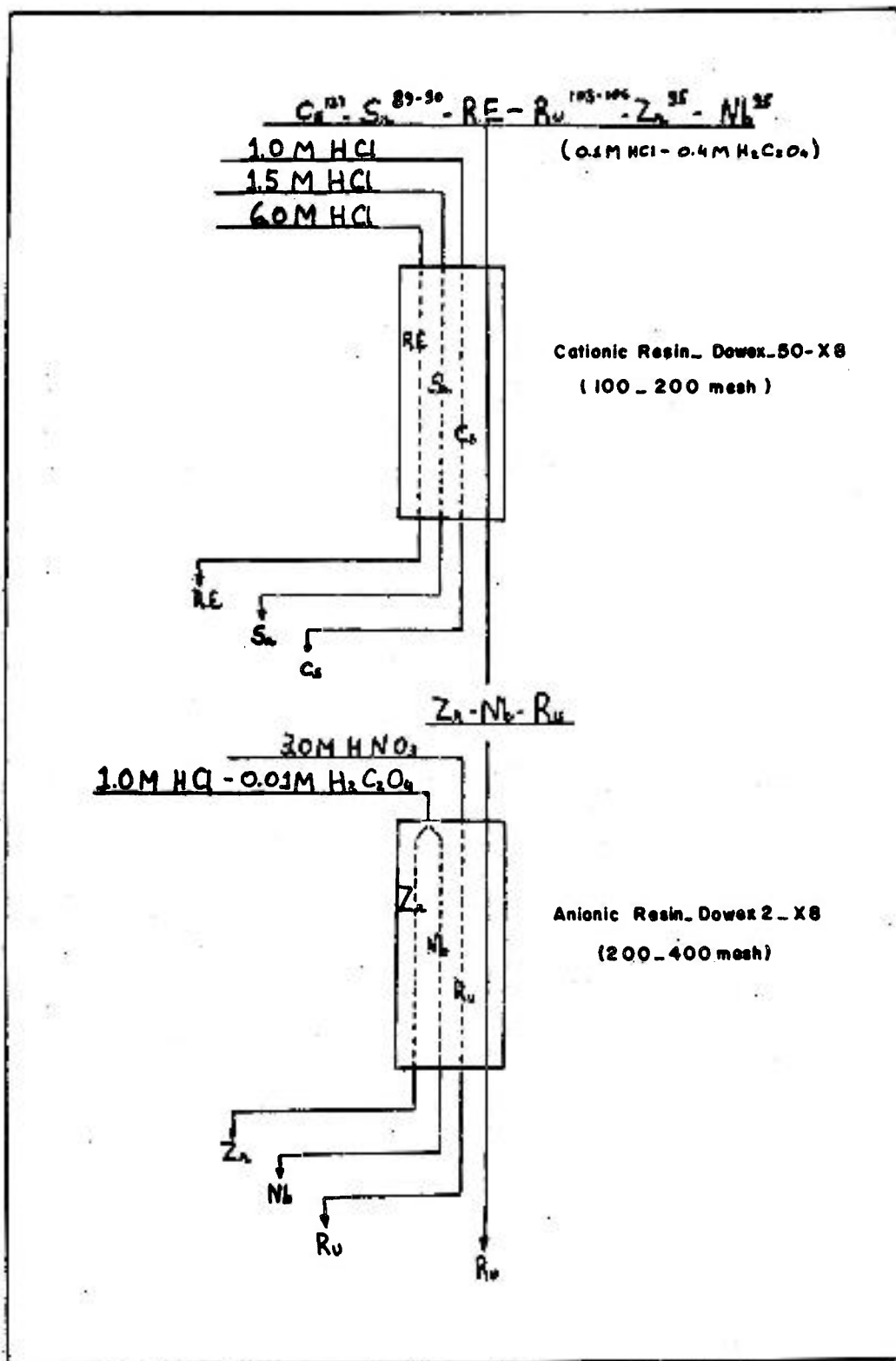
Separation of Ruthenium⁽⁷⁾ in Zr-95 and Nb-95 Eluates

The Zr-95 or Nb-95 eluate was concentrated by evaporation to about 5 ml. and two ml of isotopic carrier for ruthenium were added (23 mg Ru, as RuCl_3), followed by addition of 12M NaOH until the solution became alkaline and then 2 ml. more were added. Then 15 ml. of saturated NaIO_4 were added and the solution was boiled. (In this point sometimes a precipitate occurred; if it was the case, ignore the precipitate and follow the procedure. The use of KIO_4 instead of NaIO_4 avoided the occurrence of this precipitate.) Then 5 ml. of

alcohol were added for precipitation of ruthenium oxide and the mixture was maintained a few minutes in the steam bath. The precipitate was centrifuged and the supernatant discarded. The precipitate was washed twice with 2M NaOH and then dissolved with 5 ml. of hot 6M HCl. The solution was neutralized by addition of 12M NaOH and an excess of 2 ml. was added, followed by addition of 10 ml. of saturated NaIO_4 and the solution warmed. The solution was then neutralized with concentrated HNO_3 and then RuO_4 was extracted with pure CCl_4 (freshly distilled). The CCl_4 extraction was repeated twice more. The separated organic phase was washed with 25 ml. of water acidified with two drops of concentrated nitric acid. Ruthenium was stripped from the organic phase with two portions of 10 ml. of 6M NaOH. To this alkaline solution containing the ruthenium 0.5ml. of ZrCl_2 solution (10 mg. of Zr) was added. The mixture was centrifuged, the supernatant was transferred into a centrifuge tube, and the precipitate discarded. To the supernatant 5 ml. of alcohol were added, the tube warmed in steam bath and then centrifuged. The supernatant was discarded and the precipitate was twice washed with NaOH 2M after what it was dissolved with 5 ml. of hot 6M HCl. Finally elemental ruthenium was precipitated with metallic magnesium. The mixture was boiled, cooled, and then centrifuged. The supernatant was discarded. The reduced ruthenium was washed with water and weighed. The chemical yield for ruthenium was 40%. The recovered ruthenium was gamma counted at the photopeak energy for determination of radioruthenium contamination in the Zr-95 and Nb-95 fractions.

REFERENCES

- (1) Wish, L., Rowell, M., U.S. Naval Radiological Defense Laboratory, Tech. Rept. USNRDL-TR-117 (1956).
- (2) Wish, Leon, Anal. Chem., 31, 326 (1959).
- (3) Geiger, Eric L., Anal. Chem. 31, 806 (1959).
- (4) Dixon, E.J. and Headridge, J.B., Analyst, 89, 185 (1964).
- (5) Wacker, R.E. and Baldwin, W.H., USAEC Report ORNL 637, March, 1950.
- (6) Radioisotopes Production at "Instituto de Energia Atômica", Radiochemistry Division.
- (7) Loveridge, B.A., and Thomas, A.M., AERE-C/R-2828.



Scheme of Sequential Fission Products Elution.