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PART II: ANALYTICAL METHODS

7. CHROMATOGRAPHIC SEPARATION, PURIFICATION AND
SOURCE PREPARATION OF THORIUM, PROTACTINIUM
AND URANIUM FROM GEOLOGICAL MATERIALS

TABLE 7: NUCLEAR DATA FOR NATURALLY OCCURRING ISOTOPES
 OF THORIUM, PROTACTINIUM AND URANIUM

The relative abundances of some of the naturally occurring isotopes of the elements thorium, protactinium and uranium are used for dating purposes and in particular in Pleistocene geochronology (Rosholt, 1970, p. 173).

Table 7 gives the necessary nuclear data of the respective isotopes used in this study which are all long-lived and alpha emitters. In alpha spectrometry the separation of the elements from geological materials and from each other are a prerequisite in applying this technique to age

determinations because ^{230}Th and ^{234}U peaks overlap and thin sources are required.

Analytical methods and procedures for the separation of metal ions have received considerable attention over the past three decades. Numerous techniques were developed which predominantly involved anion exchange and reversed phase liquid chromatography. The most satisfactory system for the separation of thorium, protactinium and uranium was found to be anion exchange in the chloride form. Each separated fraction obtained from geological materials was found unsuitable for analysis due to the presence of contaminants, which therefore necessitated the use of subsequent purification processes to be applied to each element. Thorium was selectively absorbed onto anion exchange resin in the nitrate form. Reversed phase liquid chromatography, using strong base anion exchange resin in the chloride form, is efficient in separating these elements due to the remarkably different adsorption characteristics.

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chromatography was applied in different forms to both protactinium and uranium.

TABLE 7: NUCLEAR DATA FOR NATURALLY OCCURRING ISOTOPES OF THORIUM, PROTACTINIUM AND URANIUM

Element	Isotope	Half-life (years)*	α -Energy (MeV)*
Th	^{230}Th	8×10^4	4,68
Pa	^{231}Pa	$3,25 \times 10^4$	5,06
U	^{238}U	$4,51 \times 10^9$	4,20
	^{235}U	$7,1 \times 10^8$	4,40
	^{234}U	$2,47 \times 10^5$	4,77

*Lederer et al (1968)

No attempt was made to recover the elements quantitatively through the various stages of separation. Known amounts of isotopic spikes for the respective elements were added in order to determine the chemical yields. Analysis of the separated fractions was done by alpha spectrometry which required a source for each element to be prepared by electrodeposition.

7.1 Experimental Procedure for the Separation of Thorium, Protactinium and Uranium from Synthetic, and in Some Instances, Actual Samples

Anion exchange chromatography, using strong base

resins in the chloride form, is efficient in separating these elements due to the remarkably different adsorption charac=

teristics of their anionic chloride complexes.

Elution curves for the separation of thorium, protactinium and uranium are given in Fig. 16 and were derived from the experimental procedures.

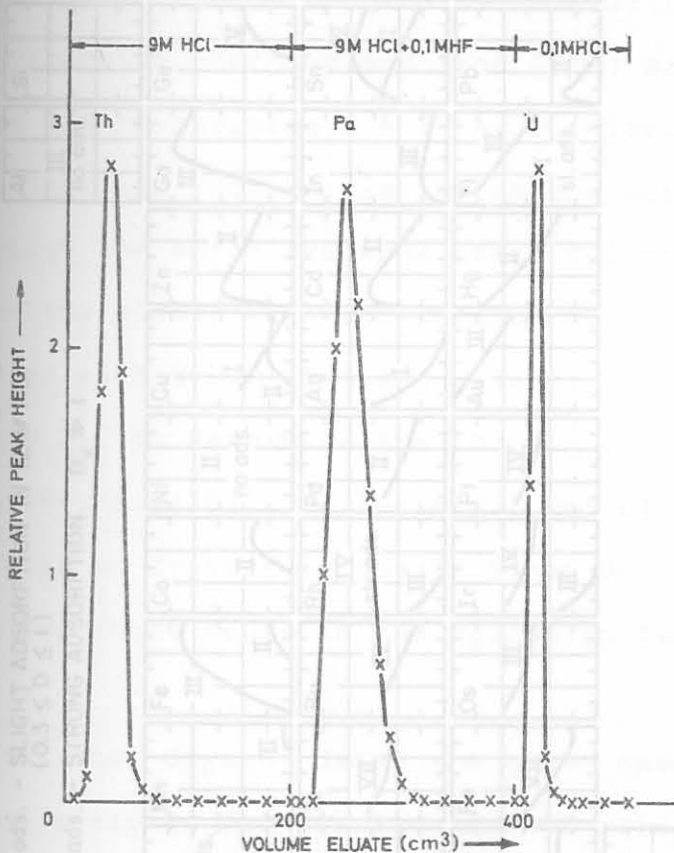


Fig. 16: Elution curves for thorium, protactinium and uranium from strong base anion exchange resin using Bio Rad AGI-X8 in the chloride form.

Fig. 17 summarizes the adsorption of the elements at different hydrochloric acid molarities, which are given as a function of the log of the distribution coefficient (Kraus and Nelson, 1956, p. 118).

The elution curve for thorium was produced in the following manner. Thorium is not adsorbed throughout the total hydrochloric acid concentration range. This also applies to the alkali metals, alkaline earths, rare earths etc. Other elements such as uranium, protactinium, titanium, zirconium, hafnium and iron (III) are strongly adsorbed at high molarities. A 9M hydrochloric acid solution containing thorium, lanthanum and europium was passed through the anion exchange resin column. Ten cm³ portions of the eluate were collected. Five cm³ of each were titrated with 0,01M EDTA and xylenol orange indicator at pH 3,0 to 3,5 to determine the thorium concentration (Strelow, 1959, p. 1201). A further 2 cm³ of each portion was evaporated to dryness in quartz tubes and the residue irradiated for three hours in the hydraulic facility of SAFARI-1.

After four days of decay the gamma spectrum of each fraction was analyzed for thorium and the rare earths. Nuclear data for the isotopes used are given in Table 8.

The elution data are presented in Fig. 18, from which it was noted that thorium and the rare earths were co-eluted.

Rapid elution of protactinium was accomplished with a 9M hydrochloric acid - 0,1M hydrofluoric acid mixture. In addition, uranium IV and VI can also be separated in this manner. Oxidation of all the uranium to the VI state was essential prior to loading the sample solution onto the column. (Kraus et al, 1956, p. 2694). The adsorption characteristics of elements from hydrochloric acid-hydrofluoric acid mixtures are given in Fig. 19.

TABLE 8: NUCLEAR DATA FOR RADIONUCLIDES PRODUCED BY THERMAL NEUTRONS

Element	Target Isotope	Isotopic Abundance ¹ (%)	Thermal Neutron Activation Cross Section (Barn) ¹	Product Isotope	Half-life ²	γ -Ray Photo-peak measured ³ (keV)
Th	²³² Th	100	7,4	²³³ Pa	27 d	312
La	¹³⁹ La	99,9	9,6	¹⁴⁰ La	40,22 h	1 595
Eu	¹⁵¹ Eu	47,8	3 100	¹⁵² Eu	12 y	1 408
U	²³⁸ U	99,3	2,73	²³⁹ Np	2,35 d	277
Fe	⁵⁸ Fe	0,33	1,2	⁵⁹ Fe	45 d	1 099
	⁵⁴ Fe	5,82	2,8	⁵⁴ Mn	303 d	835
As	⁷⁵ As	100	4,5	⁷⁶ As	26,5 h	559
Zr	⁹⁴ Zr	17,4	0,075	⁹⁵ Zr	65 d	724
				⁹⁵ Nb	33 d	766
Hf	¹⁸⁰ Hf	35,2	12,6	¹⁸¹ Hf	42,5 d	482
Ce	¹⁴⁰ Ce	88,5	0,54	¹⁴² Ce	33 d	145

¹ Chart of the Nuclides² Lederer et al (1968)³ Adams and Dams (1969)

europium from strong base anion exchange
 chloride form.
 during the course of this investigation it was found
 have large distribution coefficients for hydrochloric
 acid molarities below four in hydrochloric acid-hydrofluoric
 acid mixtures. In this work 9M hydrochloric acid - 0,1M
 hydrofluoric acid mixture was used to elute protactinium
 because the distribution coefficient of protactinium in this

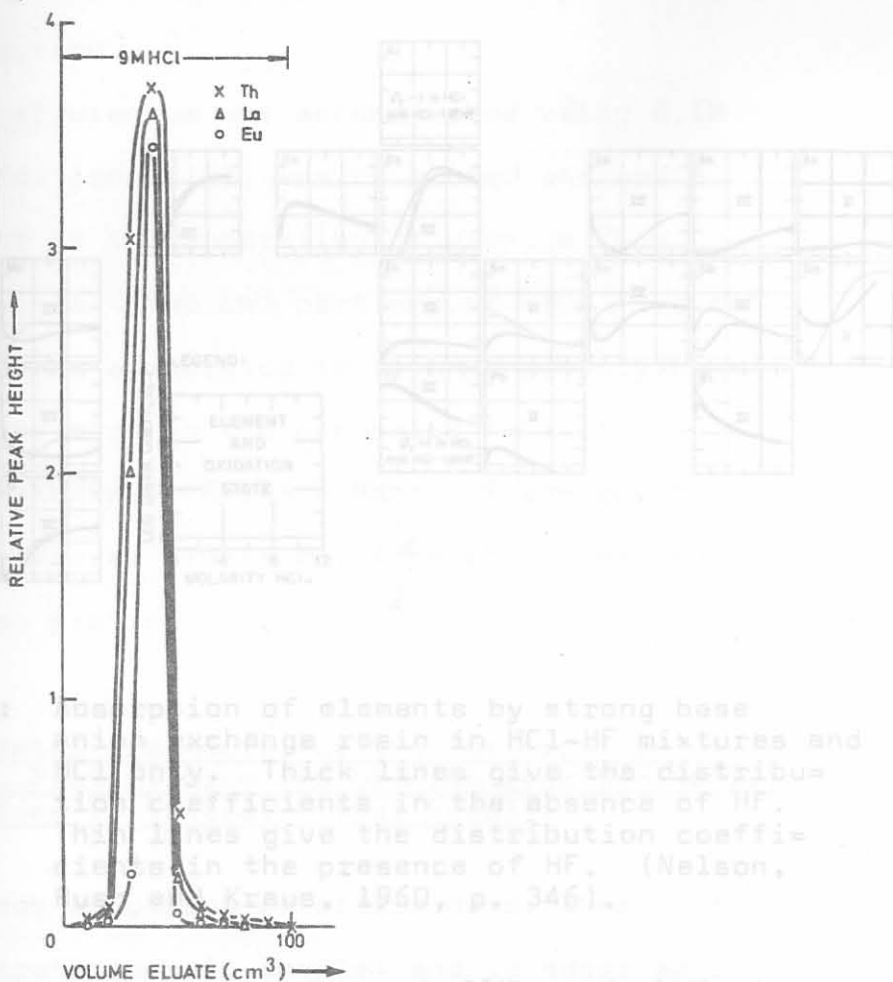


Fig. 18: Elution curves for thorium, lanthanum and europium from strong base anion exchange resin using Bio-Rad AGI-X8 in the chloride form.

system is nearly zero. The elution curve for protactinium (Fig. 16) was determined using the gamma-emitting ^{233}Pa isotope (Table 8). A sharp separation from both thorium and uranium is shown.

During the course of this investigation it was found that ^{231}Pa was completely lost during the separation process whereas the spike ^{233}Pa was recovered with good yield. The

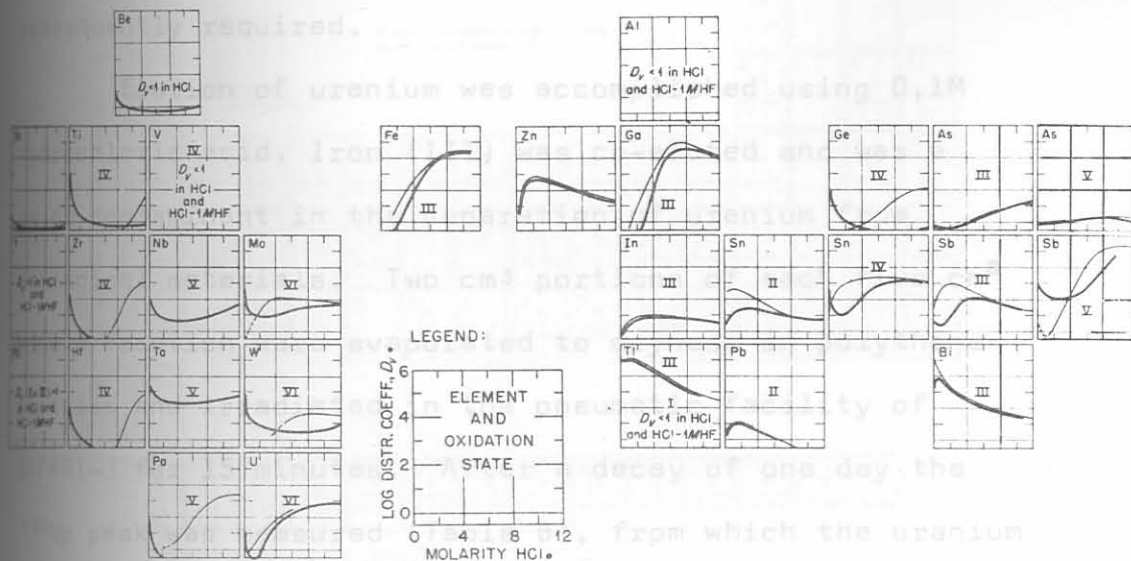


Fig. 19: Absorption of elements by strong base anion exchange resin in HCl-HF mixtures and HCl only. Thick lines give the distribution coefficients in the absence of HF. Thin lines give the distribution coefficients in the presence of HF. (Nelson, Rush and Kraus, 1960, p. 346).

reason for the anomalous behaviour of ^{231}Pa and ^{233}Pa is probably due to both species being in different chemical forms. Since ^{233}Pa is synthetically produced, it would be in the form of an anionic chloride complex, whereas naturally occurring ^{231}Pa may be in the form of a complex oxide species in a highly oxidizing environment (Ahrland *et al*, 1973, p. 470). To ensure that both isotopes were in identical chemical states, the following procedure was adopted.

Carnotite was separated by heavy media using TBE (1, 1, 2, 2, tetrabromoethane, SG = 2,96) and the Franz Isodynamic Magnetic Separator to remove magnetic impurities. The carnotite was initially digested and fumed with concentrated hydrofluoric acid. Successive fumings with concentrated

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perchloric and hydrochloric acids respectively were subsequently required.

Elution of uranium was accomplished using 0,1M hydrochloric acid. Iron (III) was co-eluted and was a major contaminant in the separation of uranium from geological materials. Two cm³ portions of each five cm³ eluate fraction were evaporated to dryness in polythene capsules and irradiated in the pneumatic facility of SAFARI-1 for 15 minutes. After a decay of one day the ²³⁹Np peak was measured (Table 8), from which the uranium elution curve was plotted (Fig. 16).

7.2 Experimental Procedure for the Purification of Thorium, Protactinium and Uranium from Synthetic, and in Some Instances, Actual Samples

In aqueous solutions of nitric acid, thorium forms a stable hexanitrate anionic complex and is adsorbed on strong base anion exchange resin in the nitrate form. Adsorption is best in 8M nitric acid with very few other elements being co-adsorbed (Fig. 20) (Buchanan and Faris, 1960, p. 365). Selectivity of this method is good as thorium can be separated from most elements, including anions.

To test the suitability of the method the following procedure was followed. A granite sample was dissolved and loaded onto an anion exchange resin column in the nitrate form. Two cm³ portions of the eluted ten cm³ fractions were evaporated in quartz ampoules and irradiated in the hydraulic facility for two hours. After a decay of

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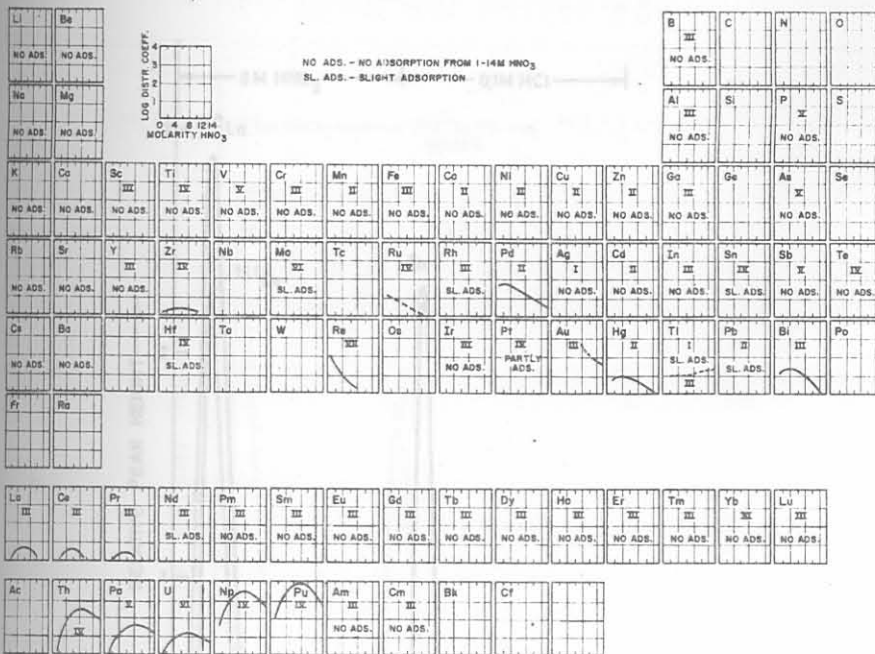


Fig. 20: Absorption of elements by strong base anion exchange resin in nitric acid. (Buchanan and Faris, 1960, p. 365).

two days the samples were counted. From the data, elution

curves for lanthanum, cerium and thorium were drawn (Fig. 21) which show a sharp separation between the rare earths and thorium.

These were produced by the irradiation of an iron foil (Table 8). ⁷⁵As was a contaminant and was therefore reversed phase liquid chromatography having a stationary phase of tributyl phosphate (TBP) supported by Kel-F powder mounted on a gamma spectrometer and in 5.5M nitric acid. ⁵⁹Fe, ⁵⁴Mn and ⁷⁶As were quantitatively eluted. As uranium (²³⁸U) was selectively extracted into the TBP phase from a 5.5M nitric acid solution. Impurities such as iron (III) were quantitatively eluted with the nitric acid. Uranium was eluted with distilled water. To test the efficiency of the separation, the isotopes ⁵⁹Fe, ⁵⁴Mn and ⁷⁶As were used as tracers. Elution curves for the rare earths and thorium using Fig-Rad AGI-XB in the nitrate resin are shown in Fig. 21. A sharp separation

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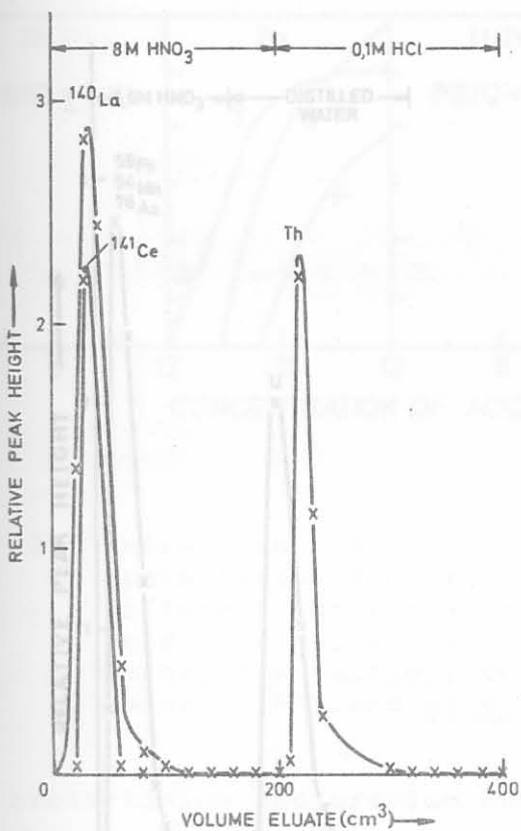


Fig. 21: Elution curves for the rare earths and thorium from strong base anion exchange resin using Bio-Rad AGI-X8 in the nitrate form. Liquid chromatography with tributylphosphate as the supporting substance and nitric acid and distilled

tracers. These were produced by the irradiation of an iron foil (Table 8). ^{75}As was a contaminant and was therefore studied simultaneously. Ten cm^3 portions of the eluate were counted on a gamma spectrometer and in 5.5M nitric acid ^{59}Fe , ^{54}Mn and ^{76}As were quantitatively eluted. As uranium (^{238}U) is not a gamma emitter it would not be counted directly. Two cm^3 fractions of the eluted portions were evaporated in polythene capsules and irradiated for 15 minutes: After a decay of one day the samples were counted. Elution curves for the system are shown in Fig. 22. A sharp separation (Ahrlund et al, 1973, p. 578).

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between iron and uranium was achieved.

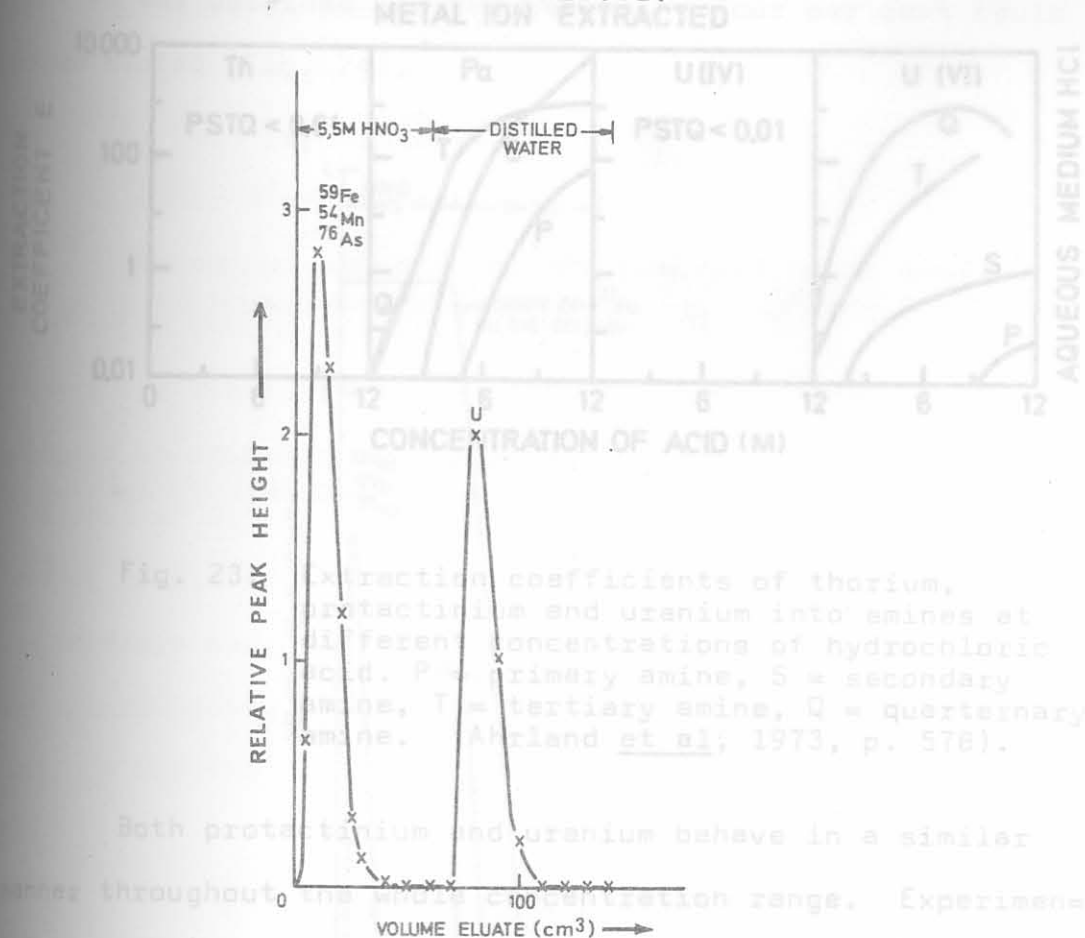


Fig. 23: Extraction coefficients of thorium, protactinium and uranium into amines at different concentrations of hydrochloric acid. P = primary amine, S = secondary amine, T = tertiary amine, Q = quarternary amine. (Ahrlund et al, 1973, p. 578).

Both protactinium and uranium behave in a similar manner throughout the whole concentration range. Experimentally this fact was substantiated here and showed that the

Fig. 22: Elution curves for iron, manganese, arsenic and uranium using reversed phase liquid chromatography with tributylphosphate as the supporting substance and nitric acid and distilled water as the mobile phases.

Contaminants of protactinium were titanium, zirconium

Protactinium was purified using a modified version of the reversed phase liquid chromatographic method proposed by Stronski (1969) to separate thorium, protactinium and uranium.

A quarternary amine, aliquat-336, was used as the stationary phase supported on teflon powder, and the mobile phase was concentrated hydrochloric acid. Fig. 23 shows the variations in extraction coefficient of thorium, protactinium and uranium with increasing concentrations of hydrochloric acid (Ahrlund et al, 1973, p. 578).

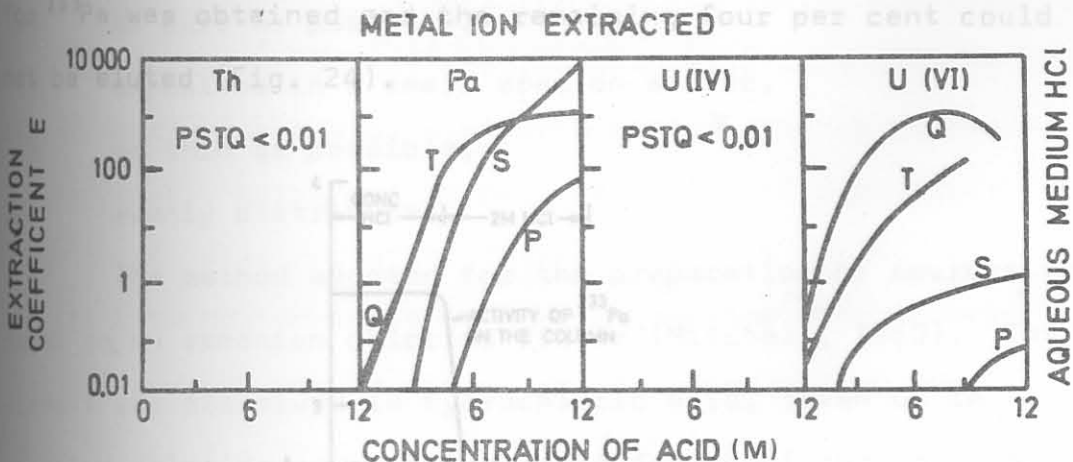


Fig. 23: Extraction coefficients of thorium, protactinium and uranium into amines at different concentrations of hydrochloric acid. P = primary amine, S = secondary amine, T = tertiary amine, Q = quarternary amine. (Ahrland et al, 1973, p. 578).

Both protactinium and uranium behave in a similar manner throughout the whole concentration range. Experimentally this fact was substantiated here and showed that the method of Stronski must be viewed with caution. Therefore for the purification of protactinium by this technique no uranium may be present in the initial solution.

Contaminants of protactinium were titanium, zirconium and hafnium, and in order to test whether these elements could be separated, the following procedure was adopted. The isotopes ^{95}Zr , ^{95}Nb (a decay product of ^{95}Zr), ^{181}Hf and ^{233}Pa were used as tracers (Table 8). Five cm^3 portions of eluate were counted on a gamma spectrometer. In concentrated hydrochloric acid protactinium was extracted into the aliquat-336 and sharp separation between protactinium and the contaminants was achieved. A recovery of 96 per cent

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for ^{233}Pa was obtained and the remaining four per cent could not be eluted (Fig. 24).

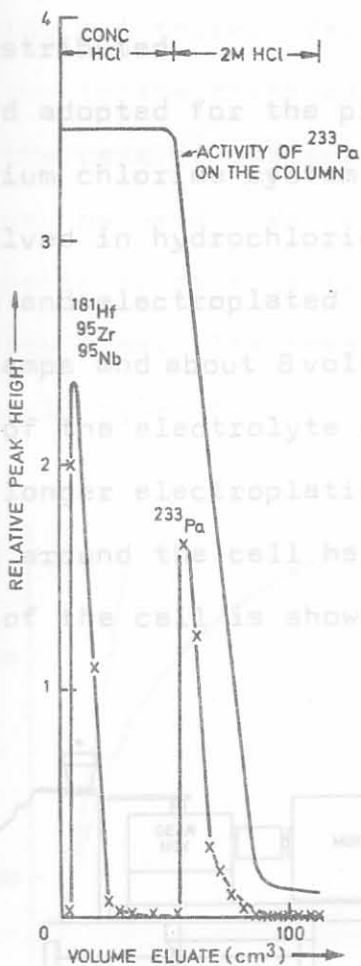


Fig. 24: Elution curves for zirconium, niobium, hafnium and protactinium using reversed phase liquid chromatography with aliquat-336 as the stationary phase, teflon as the supporting substance and hydrochloric acid as the mobile phase.

7.3 Source Preparation of Thorium, Protactinium and Uranium from Synthetic Samples.

Four basic requirements are necessary in preparing sources suitable for α -spectrometry. The source material must be thorium, protactinium and uranium.

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- (a) as pure as possible,
 (b) deposited in a small area on a disc,
 (c) as thin as possible,
 (d) evenly distributed.

The method adopted for the preparation of sources was based on an ammonium chloride system (Mitchell, 1960). The element was dissolved in hydrochloric acid, taken up in ammonium chloride and electroplated for about two hours at a current of 0,5 amps and about 8 volts dc. Due to excessive heating problems of the electrolyte at a high current, the low amperage and longer electroplating time were chosen. Water circulating around the cell helped to dissipate the heat. A drawing of the cell is shown in Fig. 25.

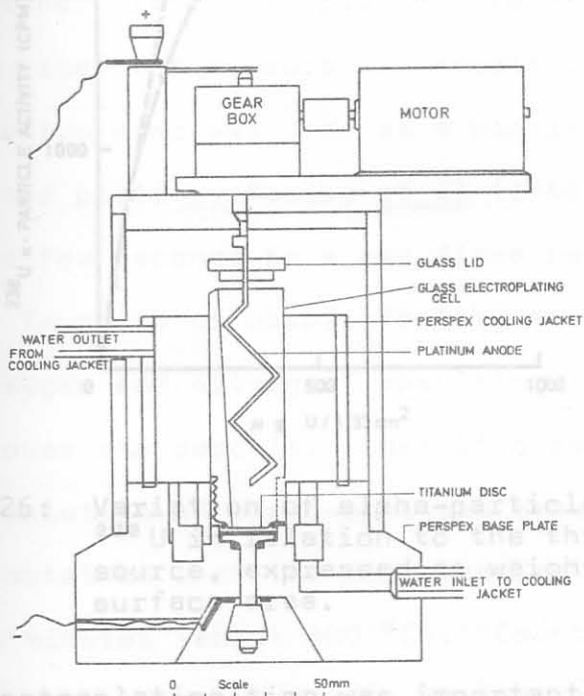


Fig. 25: A drawing of the electroplating cell used for the preparation of sources of thorium, protactinium and uranium.

When α -particles pass through the source material they may suffer an energy loss, giving rise to a tailing effect on the low energy side of a peak. This is caused by the deposit being too thick. Variation of α -particle activity in relation to the thickness of the deposit is given in Fig. 26. For the case of uranium, sources with no more than $60 \mu\text{g U/cm}^2$ can be used. Values greater than this cause the relationship to diverge from linearity, which is a function of energy loss. The ideal situation, where there is no energy loss, is given by the dashed line in Fig. 26.

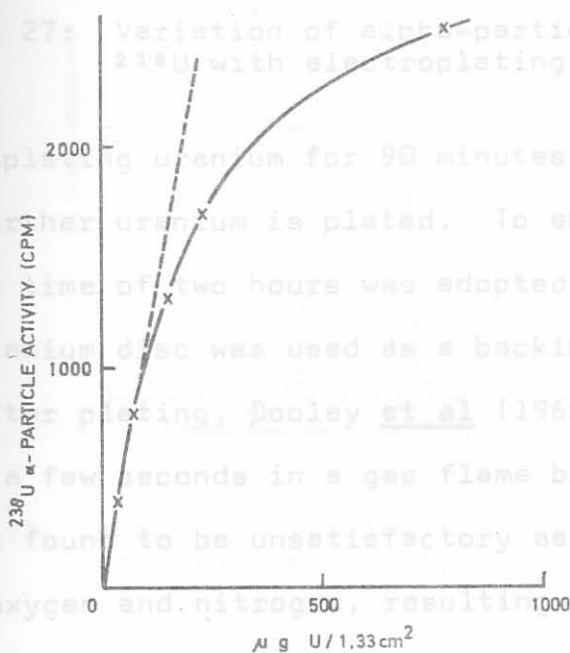


Fig. 27: Variation of alpha-particle activity of ^{238}U with electroplating time.

After electroplating uranium for 90 minutes the curve flattens out and no further uranium is plated. To ensure maximum deposition, a time of two hours was adopted.

A titanium disc was used as a backing for the source material. After plating, Dooley et al (1966, p. 1369) heated the disc for a few seconds in a gas flame before use. This technique was found to be unsatisfactory as titanium reacts readily with oxygen and nitrogen, resulting in the formation of a coating over the deposit. Loss of α -particle energy

Fig. 26: Variation of alpha-particle activity of ^{238}U in relation to the thickness of the source, expressed as weight of U per unit surface area.

As electroplating time was important to ensure a good yield, a plot of α -particle activity versus electroplating time showed the minimum time required for maximum deposition

of target material (Fig. 27). Data were recorded using an interlinked IBM computer, and processing was done manually by adding together the pulses in each channel over the required MeV range.

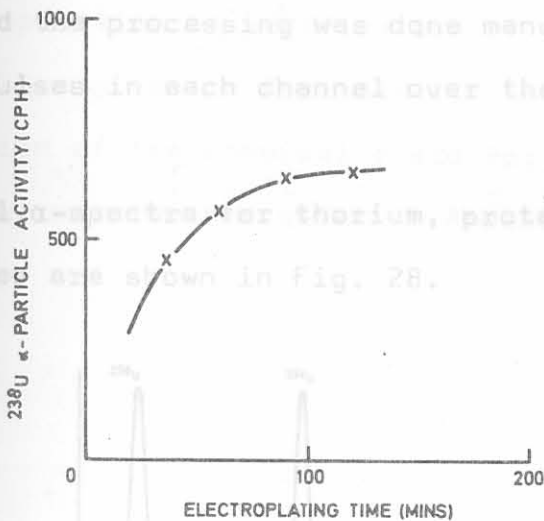


Fig. 27: Variation of alpha-particle activity of ^{238}U with electroplating time.

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A titanium disc was used as a backing for the source material. After plating, Dooley *et al* (1966, p. 1369) heated the disc for a few seconds in a gas flame before use. This technique was found to be unsatisfactory as titanium reacts easily with oxygen and nitrogen, resulting in the formation of a coating over the deposit. Loss of α -particle energy and poorer resolution of the α -spectrum resulted. Good results were obtained when the disc was heated on a hot plate for two minutes (about 400°C). Counting was done on a detector system consisting of a surface barrier silicon detector (Princeton Model PD-15-20-300) located in a vacuum chamber. A Tennelec power supply, preamplifier, amplifier and a biased amplifier were coupled to a Intertechnique 400

multichannel analyzer (Model SA 40B) for the spectral analysis. Data were recorded using an interlinked IBM typewriter, and the processing was done manually by adding together the pulses in each channel over the required MeV range.

Typical α -spectra for thorium, protactinium and uranium isotopes are shown in Fig. 28.

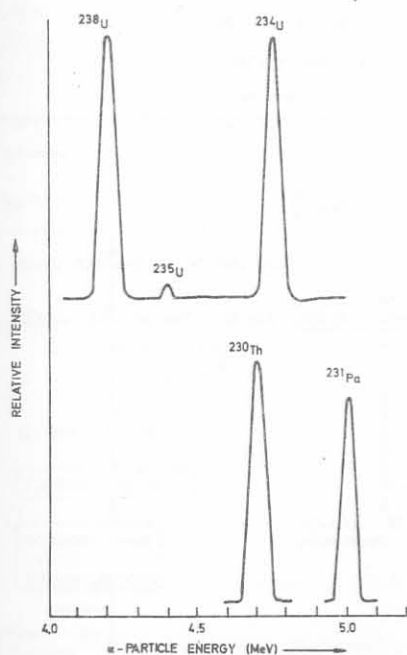


Fig. 28: Alpha spectra for thorium, protactinium and uranium isotopes.

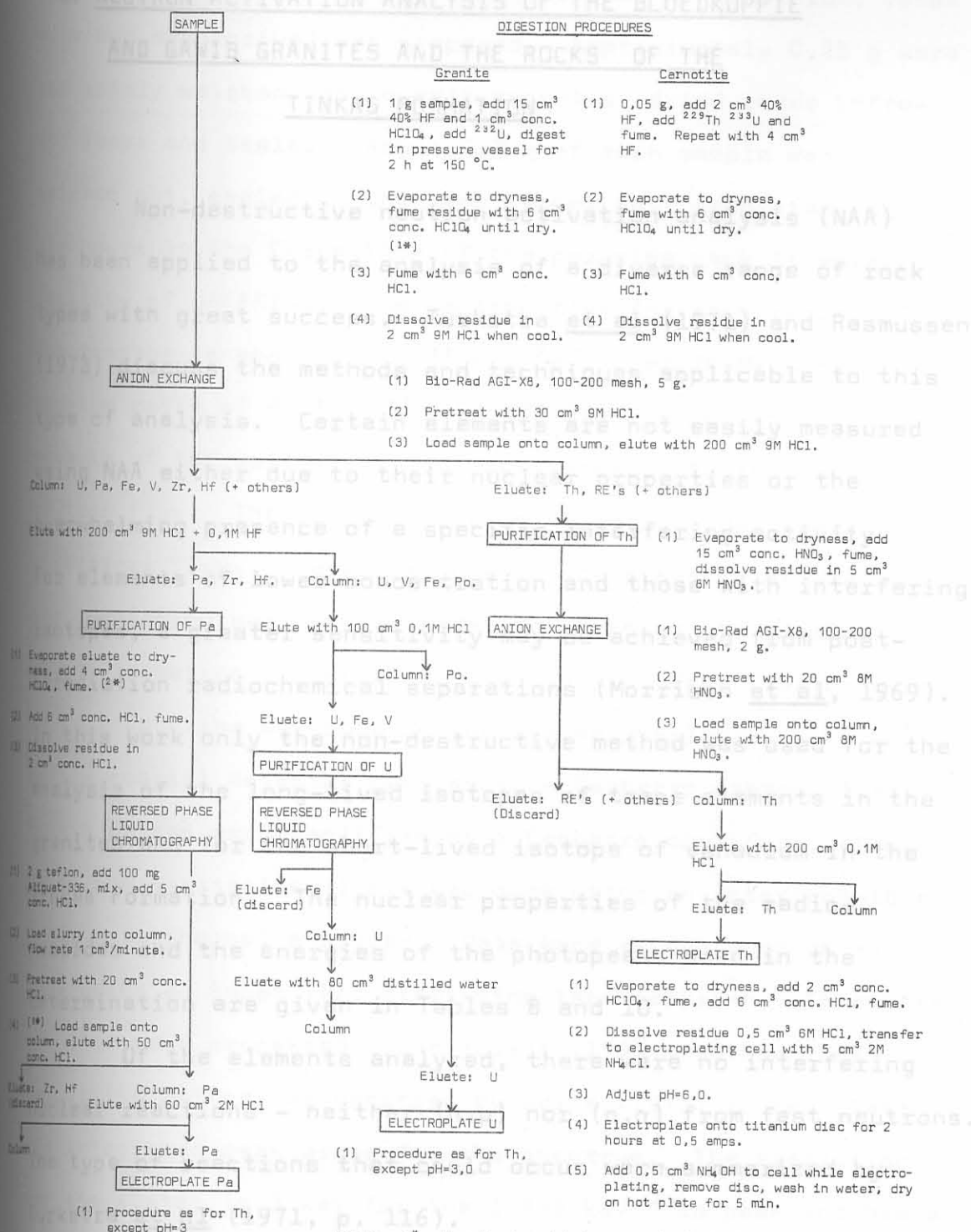
7.4 Chromatographic Separation Scheme

Two rock types, granite and calcrete, were analyzed in this scheme. In the former only uranium was separated on a whole-rock basis, whereas in the latter, carnotite was selectively separated by heavy media as described in Section 7.1. Table 9 gives the detailed procedure for the

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TABLE 9: PROCEDURE FOR THE CHROMATOGRAPHIC SEPARATION OF THORIUM, PROTACTINIUM AND URANIUM FROM GEOLOGICAL MATERIALS



NOTES: 1* - When the term 'dry' appears in the text it means that the residue must not be baked but allowed to remain slightly moist. This statement applies generally.
2* - Removes all traces of HF, which does not allow extraction into Aliquat-336.
3* - Monitor sample at each stage for radioactivity as a quality control.