

9. DISSOLUTION AND ANALYSIS OF THE EPIGENETIC  
FRACTION OF CALCRETE BY NEUTRON  
ACTIVATION ANALYSIS

The object of this analysis was to determine the distribution of trace elements within the epigenetic calcite-carnotite fraction of the calcretes, which contain about 10 to 50 per cent  $\text{CaCO}_3$  (Table 27). Both calcite and carnotite are epigenetic minerals which were precipitated from aqueous solution. Along with these minerals, elements in trace quantities were simultaneously precipitated.

Calcretes of the Langer Heinrich formation have, in places, high uranium contents, in some instances over  $15 \times 10^3$  ppm and as little as 20 ppm in others. Neutron activation analysis of samples with such high uranium concentration is further complicated due to the errors introduced from fission products and crowding of the spectrum with  $^{239}\text{Np}$  peaks.

Therefore it was found necessary to selectively remove uranium. The method adopted for this was reversed phase liquid chromatography using TBP absorbed onto Kel-F, as outlined in Table 11 and based on the method given in

Table 9.

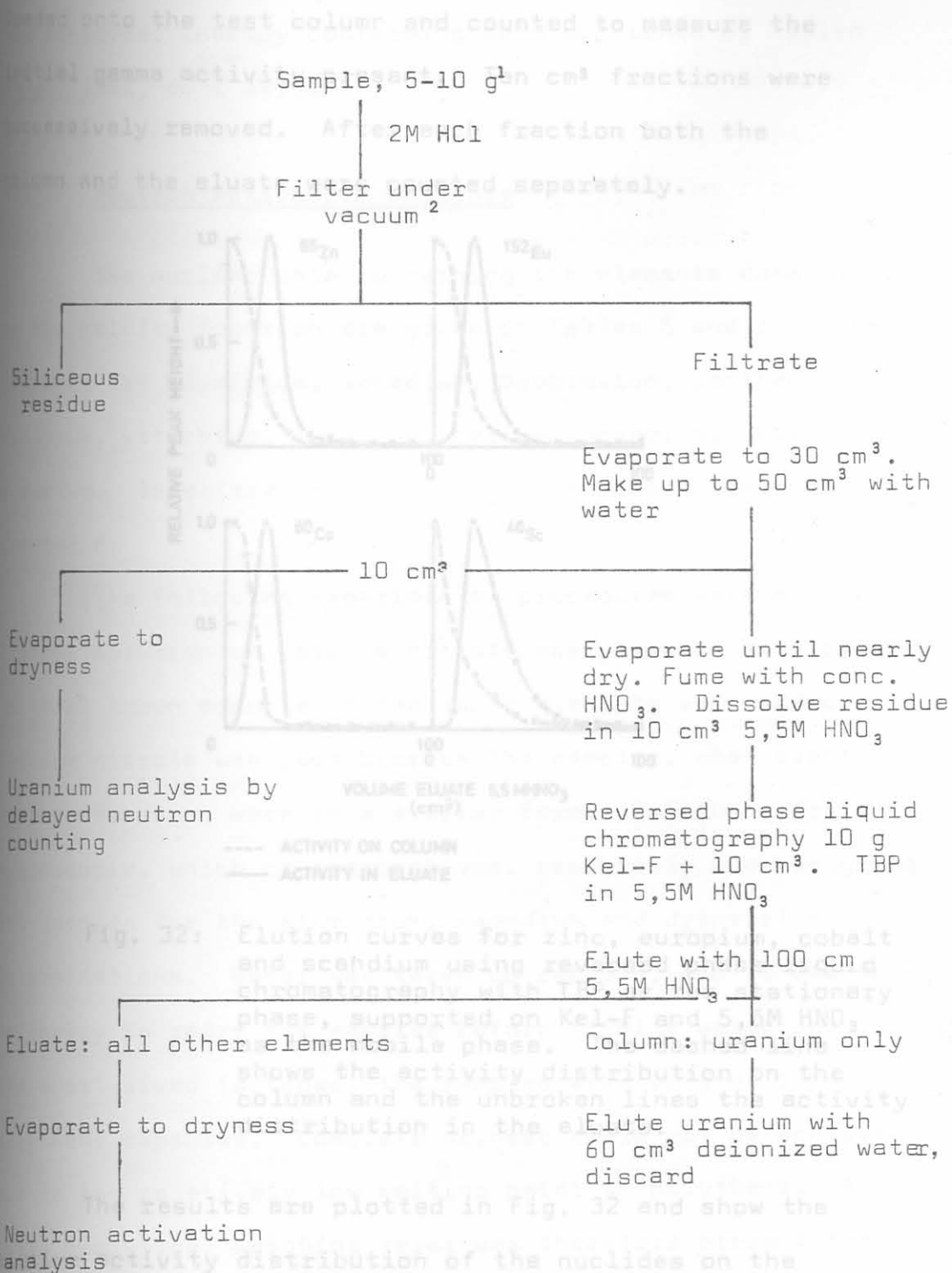
In order to ascertain whether there were significant losses of some trace elements during the separation procedure, radioactive tracers of europium, cobalt, scandium and zinc were made for test purposes (Table 10).

The weight of sample dependent on the  $\text{CaCO}_3$  content. A 0.45 mm Sartorius membrane filter, type SM126, was used.

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TABLE 11: PROCEDURE FOR THE CHROMATOGRAPHIC SEPARATION OF URANIUM FROM CALCRETES



## NOTES:

- The weight of sample used was dependent on the CaCO<sub>3</sub> content.
- PVC, 0,45 mm Sartorius membrane filter, type SM128, was used.

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The radioactive sample was dissolved in 5,5M  $\text{HNO}_3$ , loaded onto the test column and counted to measure the initial gamma activity present. Ten  $\text{cm}^3$  fractions were successively removed. After each fraction both the column and the eluate were counted separately.

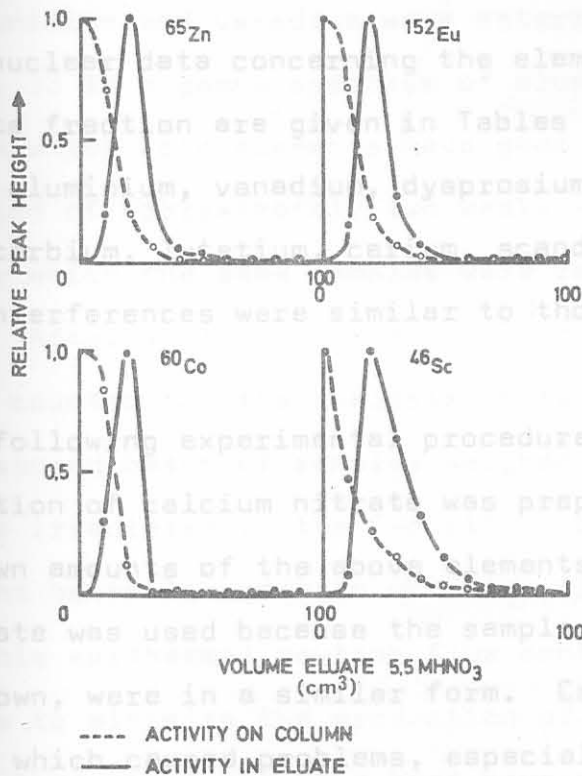


Fig. 32: Elution curves for zinc, europium, cobalt and scandium using reversed phase liquid chromatography with TBP as the stationary phase, supported on Kel-F and 5,5M  $\text{HNO}_3$  as the mobile phase. The dashed line shows the activity distribution on the column and the unbroken lines the activity distribution in the eluate.

The results are plotted in Fig. 32 and show the relative activity distribution of the nuclides on the column and in the eluate in terms of eluate volume. After 100  $\text{cm}^3$  of 5,5M  $\text{HNO}_3$ , no nuclides were detected on the column or in the eluate. The conclusions were, firstly, that there was no retention of those elements on the column,

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and secondly, that a very good separation from the uranium was achieved, thereby confirming data published by Hamlin et al (1961, p. 1 549).

### 9.1 Neutron Activation Analysis

The nuclear data concerning the elements determined in the calcite fraction are given in Tables 8 and 10. The elements are aluminium, vanadium, dysprosium, lanthanum, samarium, ytterbium, lutetium, cerium, scandium, cobalt and europium. Interferences were similar to those described in Chapter 8.

The following experimental procedures were adopted.

A stock solution of calcium nitrate was prepared as a standard. To this, known amounts of the above elements were added. Calcium nitrate was used because the samples, when eventually evaporated down, were in a similar form. Calcium nitrate is hygroscopic, which caused problems, especially when weighing the samples for the aluminium, vanadium and dysprosium determinations. Water was taken up rapidly, and it was found necessary to redry the samples before finally weighing. For the short-lived isotopes, the samples were weighed into polythene capsules. Complete dryness could not be achieved due to the relatively low melting point of polythene. A small analytical weighing error was therefore present for aluminium, vanadium and dysprosium. As far as the remaining elements were concerned, the samples were weighed into quartz ampoules which could be heated to higher temperatures, thereby driving off the moisture.



Approximately 100 mg samples were used for all determinations.

Initially the polythene capsules were irradiated in the pneumatic facility of the reactor for two minutes, allowed to decay for one minute, and counted for five minutes. Aluminium and vanadium were determined by this method. Fig. 33 is a gamma spectrum of aluminium and vanadium from which both elements have good relative intensities. A period of approximately two weeks was allowed to elapse, after which the same samples were reirradiated for ten minutes. After a decay period of 70 to 120 minutes the samples were counted for the analysis of dysprosium. (Fig. 34).

The second batch of samples weighed into quartz ampoules were irradiated in the C-position of the poolside rack for eight hours in order to obtain a flux with the lowest possible epithermal neutron flux contribution. This was done to minimize the production of fission products from uranium that might not have been completely removed in the extraction process. The samples were counted after four days for lanthanum, samarium, ytterbium and lutetium (Fig. 35) and finally after 13 days for cerium, iron, scandium, cobalt and europium (Fig. 36).

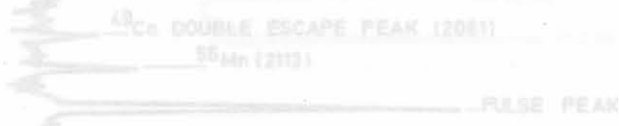


Fig. 33: Gamma-ray spectrum for the analysis of aluminium and vanadium in the epigenetic calcite fraction.

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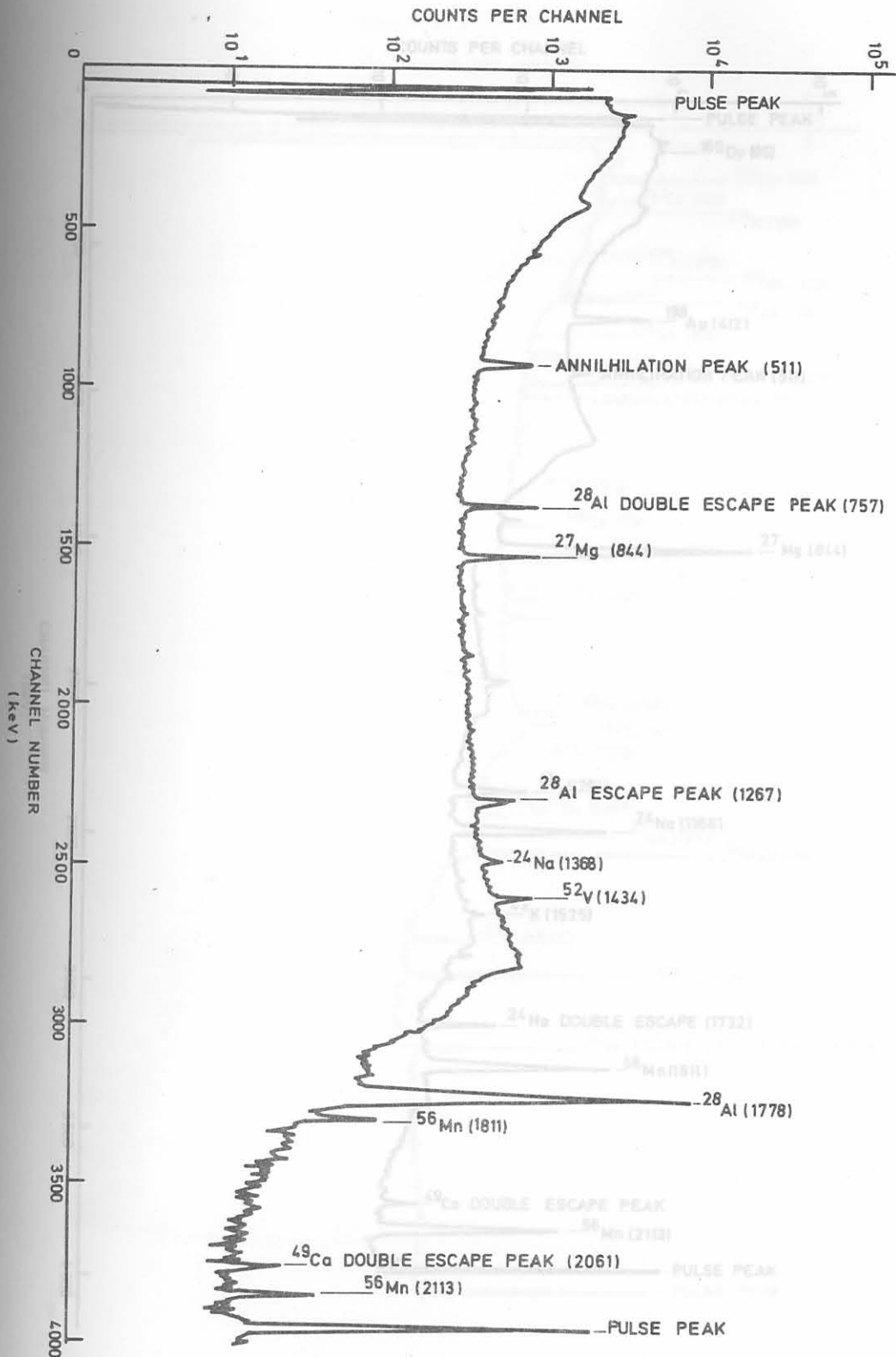


Fig. 33: Gamma-ray spectrum for the analysis of aluminium and vanadium in the epigenetic calcite fraction.

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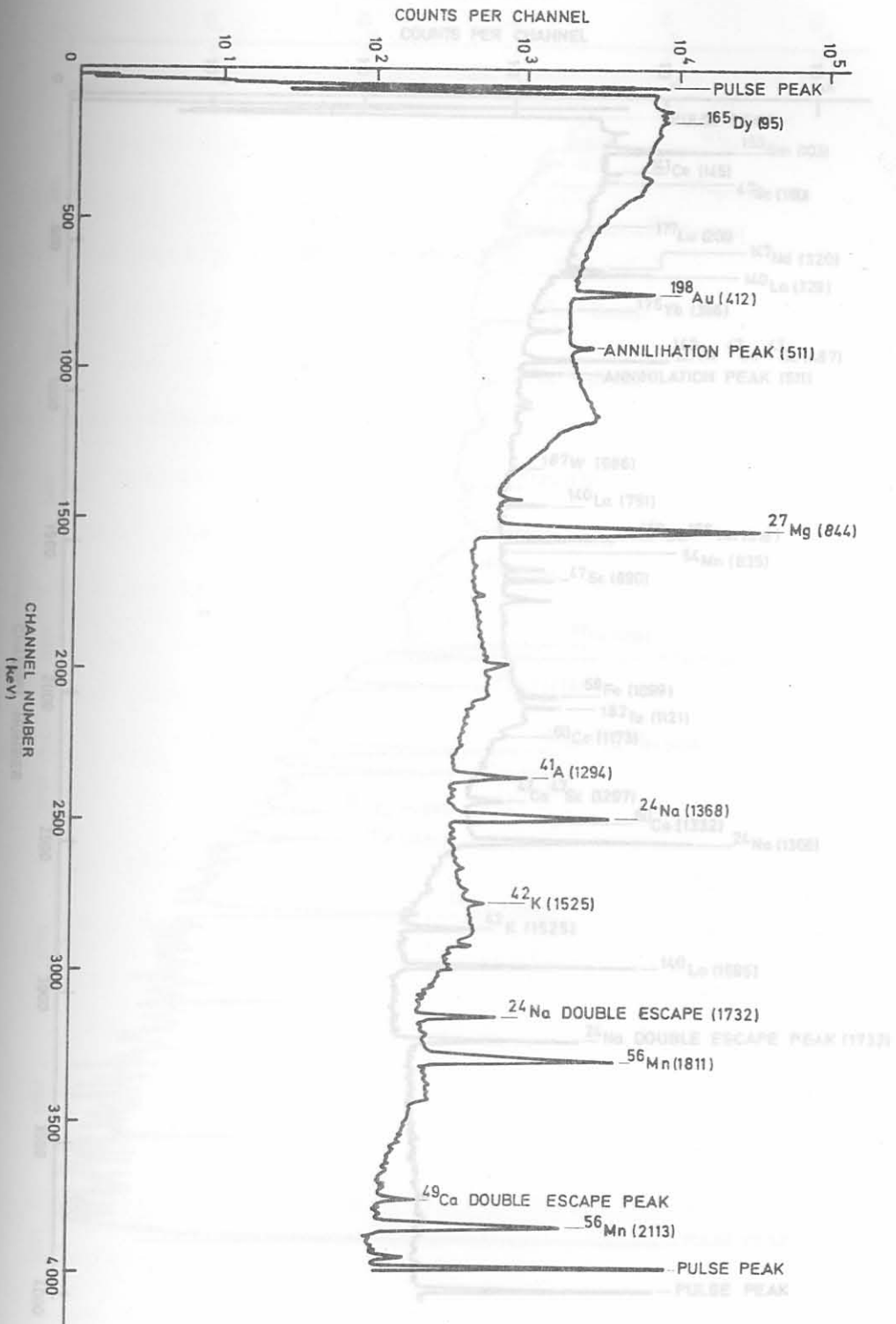


Fig. 35: Gamma-ray spectrum after four days' decay

Fig. 34: Gamma-ray spectrum for the analysis of dysprosium in the epigenetic calcite fraction.

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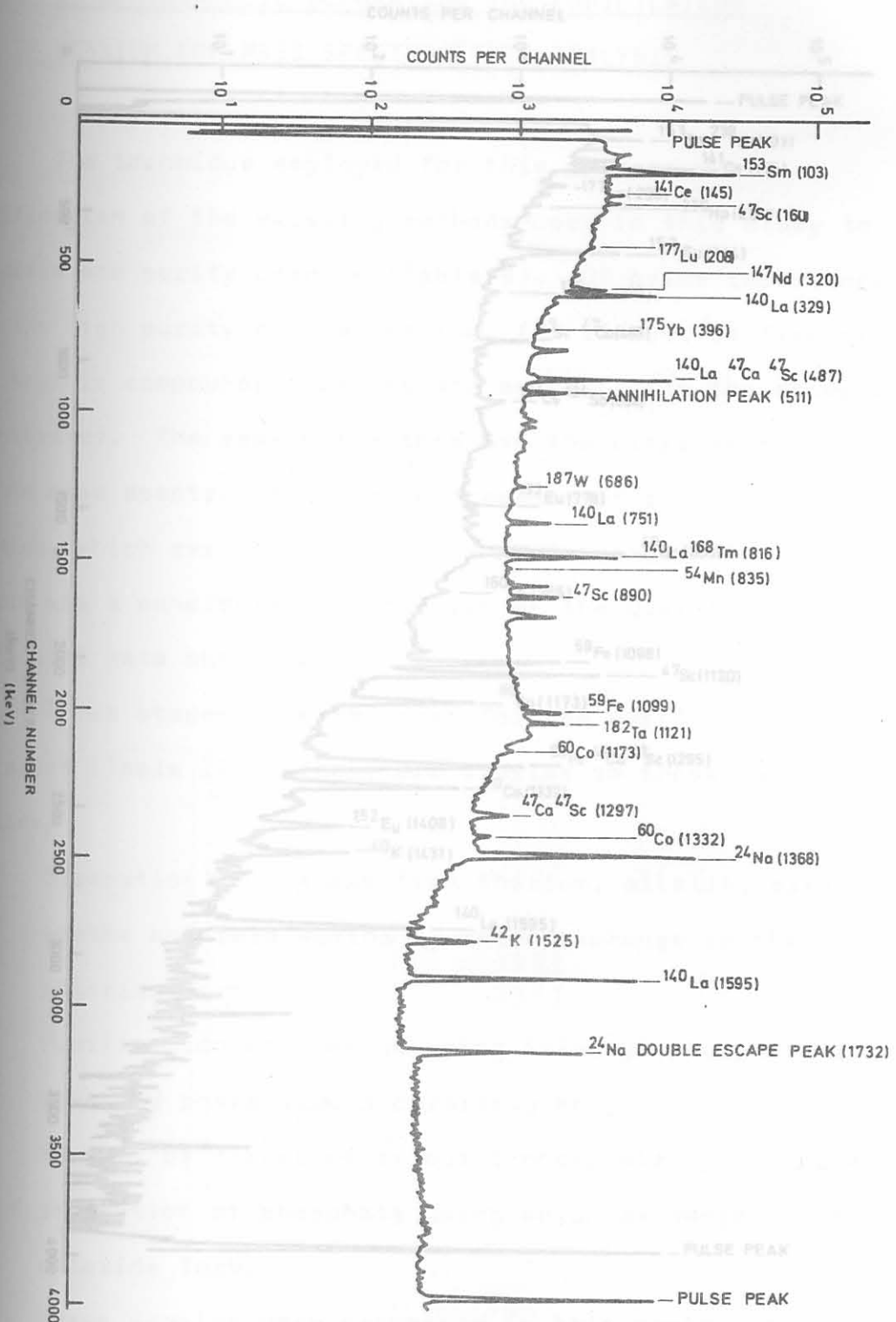
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Fig. 35: Gamma-ray spectrum after four days' decay for the analysis of lanthanum, samarium, ytterbium and lutetium in the epigenetic calcite fraction.

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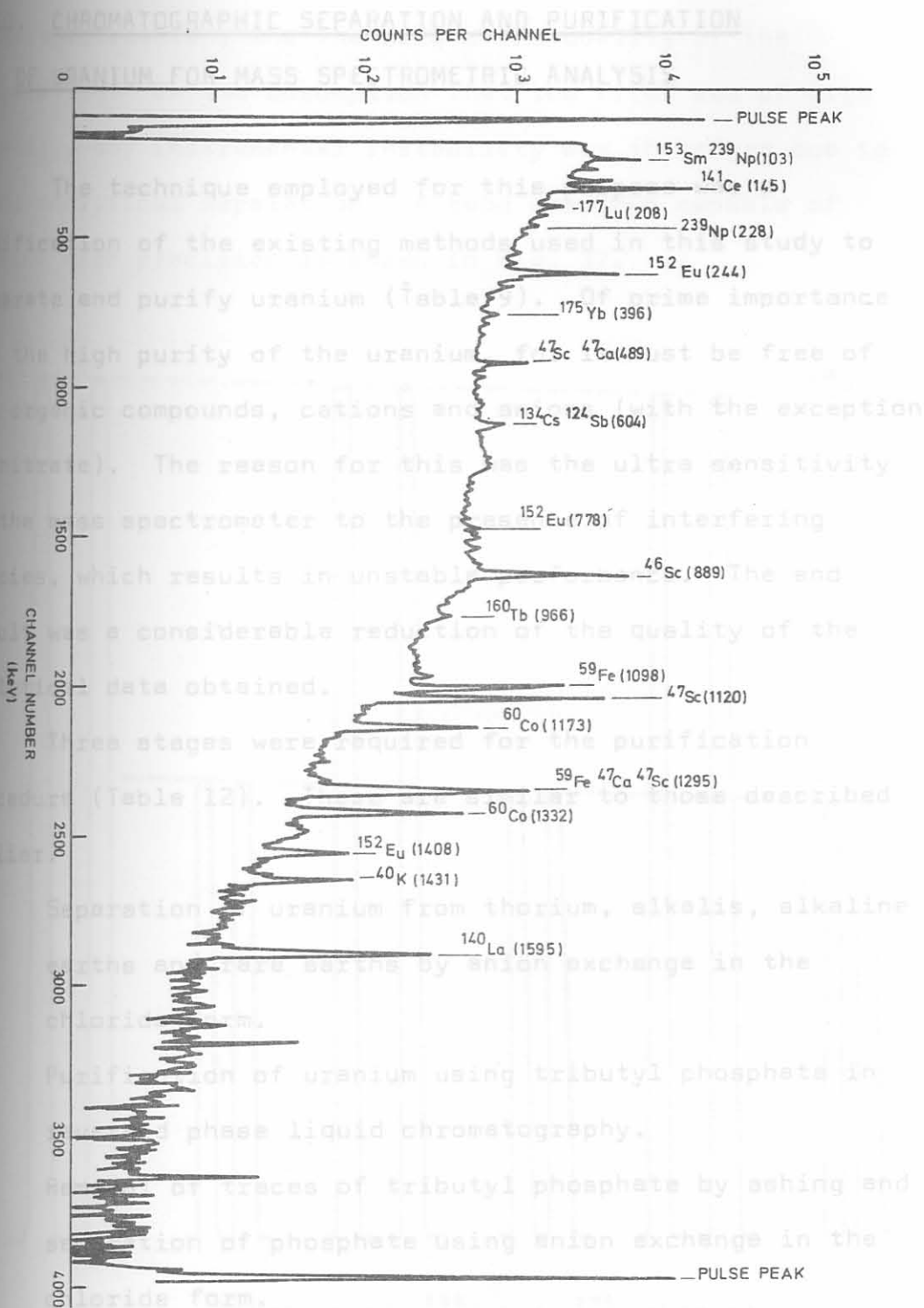


Fig. 36: Gamma-ray spectrum after 13 days' decay for the analysis of cerium, iron, cobalt, scandium and europium in the epigenetic calcite fraction..