

ION EXCHANGE PROPERTIES OF VANADIUM FERROCYANIDE

II. DYNAMIC EXPERIMENTS

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The ion exchange properties of vanadium ferrocyanide under static conditions have been studied in a preceding paper¹. It was found that heavy alkali metals (mainly cesium) are sorbed selectively on this sorbent. In this paper we have studied the dynamic behaviour of this sorbent for the isolation and separation of the heavy alkali metals, with reference mainly to the isolation of ¹³⁷Cs from a solution of fission products.

EXPERIMENTAL

The experiments were carried out with the vanadium ferrocyanide (molar ratio V:Fe = 1:1), which had been prepared by the reaction of vanadyl chloride with ferrocyanic acid, as described earlier¹.

Columns 0.6 cm in diameter and 10 cm high were used, and their lower part was fitted with a sinter plate and tap. The effective filling was 0.5 to 1 g of the sorbent, particle size 100–200 mesh. The column was carefully washed with water and then with 0.1 M HNO₃ before use for the experiments, which consisted of a tracer method using ¹³⁷Cs, ⁸⁶Rb, ⁹⁰Sr, ⁹⁰Y, ¹⁴⁴Ce, ⁹⁵Zr, and ¹⁰⁶Ru as radioactive indicators.

The procedure in sorption and elution experiments was such that the respective radioisotope (carrier-free or in weighable amounts) was sorbed from 0.1 M HNO₃, the column was then carefully washed with 0.1 M HNO₃ and the sorbed element was eluted by means of an elution agent (HNO₃, NH₄NO₃, NaNO₃). In both sorption and elution studies every tenth fraction was collected, then dried and its activity measured. The activity of the fraction was plotted graphically against the number of fractions (elution and sorption fractions). The overall amount of the sorbed (or eluted) element was determined by comparing the activity of the bulked eluate (after correcting for the samples taken) with a standard. The capacity for Cs, Rb, Sr and Ce was determined from the breakthrough curves. The procedure included passing a 0.1 M solution of the above-named isotopes in 0.1 M HNO₃ over 0.5 g of the sorbent and determining the activity of the fractions emerging from the column. The maximum capacity of the element sorbed under dynamic conditions was determined by graphical integration of the break-through curves, after correcting for the free volume of the column.

To isolate ¹³⁷Cs from a solution of fission products (cooled for about one year) 5 ml of a stock solution of the fission products was passed through a sorbent-filled

column (0.5 g, height 4 cm). After sorption the column was washed with 3 *M* HNO₃ in order to remove the other fission products (Sr, Y, Ce, Eu, Zr, Ru), which could also have been adsorbed. In this way all the fission products except cesium were washed out from the column. Cesium was then eluted by means of a 10 *M* HNO₃ solution. Its purity was determined by γ -spectra measurements on a 200-channel pulse height analyser (Intertechnique).

Reagents used were all of reagent-grade purity.

RESULTS AND DISCUSSION

The experiments were divided into several steps. First, the quantitative character of the sorption and elution of heavy alkali metals was tested (Rb and Cs) on a column filled with vanadium ferrocyanide.

The sorption of cesium and rubidium alone, and their subsequent elution by nitric acid and ammonium nitrate of various concentrations are illustrated in Figs. 1a, 1b and 2.

It can be seen from these figures that the sorption of cesium and rubidium from 0.1 *M* HNO₃ is quantitative although the elution from the column differs. Whereas cesium is hardly eluted even by a 10 *M* ammonium nitrate solution, rubidium is already slightly eluted by 1 *M* NH₄NO₃, up to 50% is eluted by 3 *M* NH₄NO₃, and with 6 *M* NH₄NO₃ rubidium is eluted nearly quantitatively. These results agree with the static experiments¹, where the values of observed selectivity coefficients K_{Cs/NH_4} and K_{Rb/NH_4} differed greatly ($\alpha_{Cs/Rb} = 1.1 \cdot 10^2$), and they may be significant for the separation of both elements as will be shown below.

The elution of sorbed cesium by nitric acid is similar, to some extent, to the elution of these elements with ammonium nitrate. Cesium is only slightly eluted by nitric acid, the efficiency of elution increasing with increasing concentration of acid, up to 10 *M* HNO₃, when the cesium is eluted from the column nearly quantitatively (> 98%). This elution is evidently connected with the oxidative properties and with

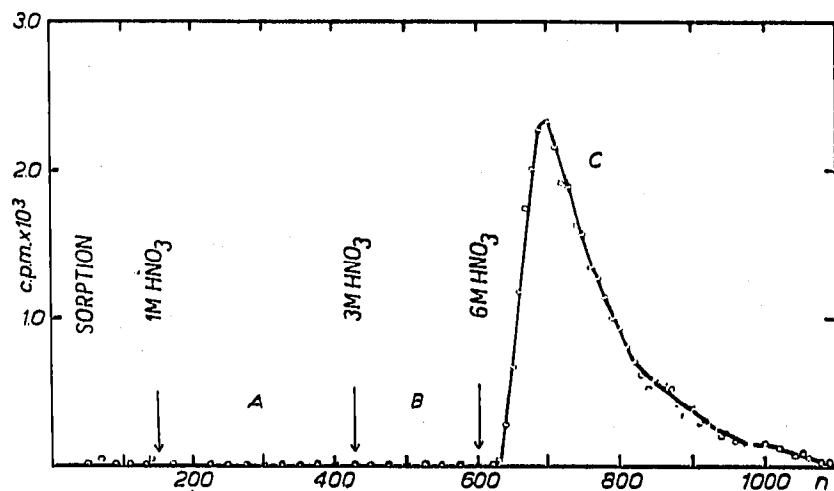


Fig. 1 (a). Elution of ⁸⁶Rb with various concentrations of nitric acid. Rubidium sorbed from 0.1 *M* HNO₃. A = elution with 1 *M* HNO₃; B = elution with 3 *M* HNO₃; C = elution with 6 *M* HNO₃. 0.5 g of the sorbent, 3.6 cm bed, drop interval: A = 7.5 sec; B = 12 sec; C = 8 sec. Drop size: A = 0.014 ml; B = 0.014 ml; C = 0.014 ml. In the case of C 99.9% of Rb was eluted.

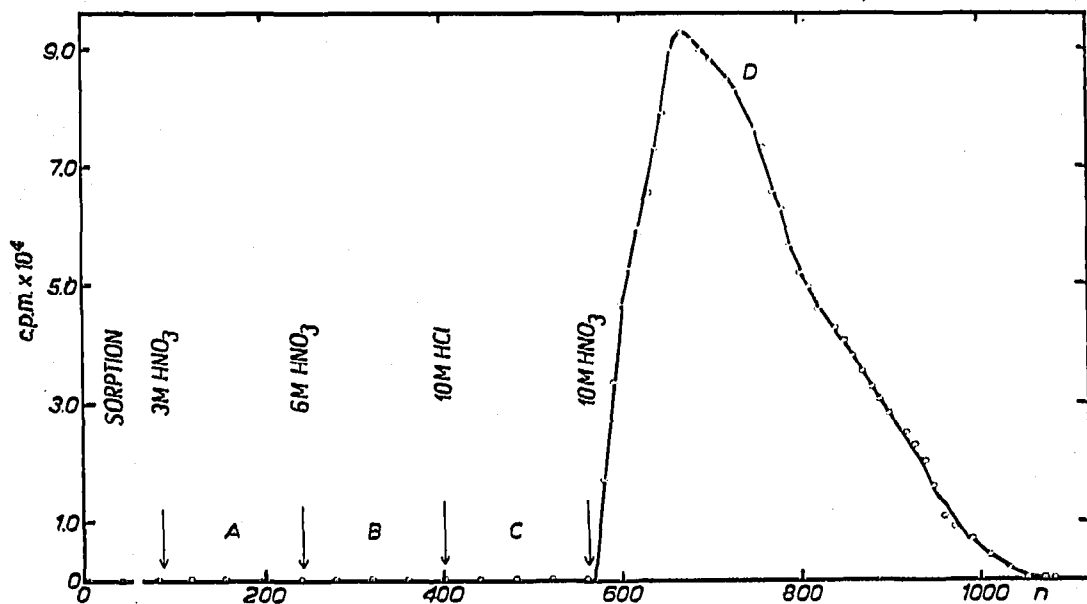


Fig. 1 (b). Elution of ^{137}Cs with acid of various concentrations. ^{137}Cs sorbed from $0.1 M \text{HCl}$, 0.5 g sorbent, 3.0 cm bed. A = elution with $6 M \text{HNO}_3$, drop interval 12 sec ; B = elution with $10 M \text{HCl}$, drop interval 15 sec ; C = elution with $10 M \text{HNO}_3$, drop interval 12 sec ; drop size 0.016 ml . In case C 98.5% of ^{137}Cs was eluted.

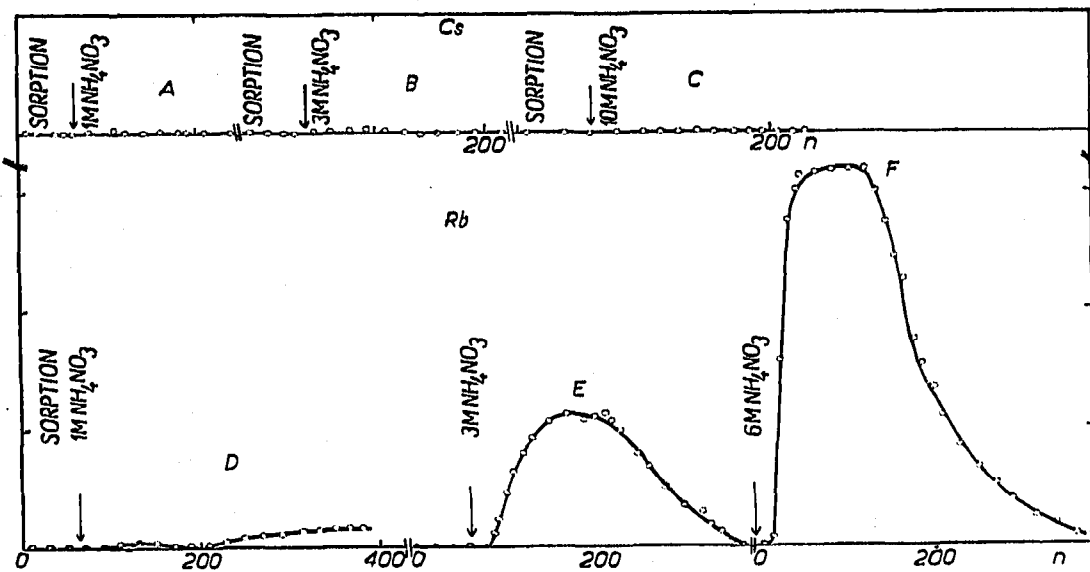


Fig. 2. Elution of ^{137}Cs and ^{86}Rb with ammonium nitrate of various concentrations. Sorption from $0.1 M \text{HNO}_3$. Cesium. A = eluted with $1 M \text{NH}_4\text{NO}_3$; B = $3 M \text{NH}_4\text{NO}_3$; C = $10 M \text{NH}_4\text{NO}_3$, 0.5 g of sorbent, 3.0 cm bed, drop interval: A = 8 sec ; B = 12 sec ; C = 10 sec . Drop size: 0.012 ml . Rubidium. Sorbed from $0.1 M \text{HNO}_3$. D = eluted with $1 M \text{NH}_4\text{NO}_3$, 0.5 g of sorbent, 5.0 cm bed, drop interval 7.5 sec , drop size 0.011 ml ; eluted 6.6% ^{86}Rb . E = eluted with $3 M \text{NH}_4\text{NO}_3$, 0.5 g sorbent, 5.0 cm bed, drop interval 8.0 sec , drop size 0.011 ml ; eluted 57.8% ^{86}Rb . F = eluted with $6 M \text{NH}_4\text{NO}_3$, 0.5 g of sorbent, 4.3 cm bed, drop interval 12 sec , drop size 0.017 ml ; eluted 98.3% of ^{86}Rb .

the influence of nitric acid on the sorbent since the use of the same concentration of hydrochloric acid causes only 0.2% elution. Rubidium can be eluted with only 6 *M* HNO₃, and is washed out from the column nearly quantitatively. Comparison of the behaviour of cesium and rubidium on elution with nitric acid suggests that nitric acid could possibly be used to separate rubidium from cesium. Experiments carried out under dynamic conditions with cesium and rubidium alone have confirmed the results of the static experiments, showing the possibility of using the sorbent in question for sorption even from acid media (Cs 6 *M*, Rb 3 *M* HNO₃), the practicality of separating Rb from Cs, and the use of the sorbent to isolate cesium from solutions containing high concentrations of ammonium salts. It has also been found that the sorbed cesium and rubidium may be washed out from the column in yields as high as 100%. By elution of the cations with 10 *M* HNO₃ no observable defects in the mechanical properties of the columns were observed. Interruption of the bed in the column and deterioration of flow properties are found only if 10 *M* nitric acid is left in the column for a prolonged time. For experiments with the same column it would be necessary to wash out the 10 *M* HNO₃: this must be done step-wise with 6 *M*, 3 *M* and finally 1 *M* HNO₃. Columns from which cesium has already been eluted can be used for subsequent sorption only at a higher acidity (1 *M* HNO₃). Elution with ammonium salts has no influence on the mechanical properties of the column.

An important factor in the practical application of a sorbent is its maximum capacity. From Fig. 4, a capacity of 2.40 mequiv. Cs/g and 1.27 mequiv. Rb/g was determined graphically with 0.1 *M* HNO₃. The capacity for Cs agrees with the results from the static experiments, where a value of 2.36 mequiv./g of the sorbent in 0.12 *M* HNO₃ was found¹.

On the basis of the sorption and elution experiments with ¹³⁷Cs and ⁸⁶Rb alone, as well as on the static experiments¹, an attempt was made to separate Rb and Cs from each other. The first attempt to separate the two elements by elution with nitric acid in different concentrations led to negative results since 6 *M* HNO₃ washed out some cesium together with the rubidium. Therefore, the elution of Rb with ammonium

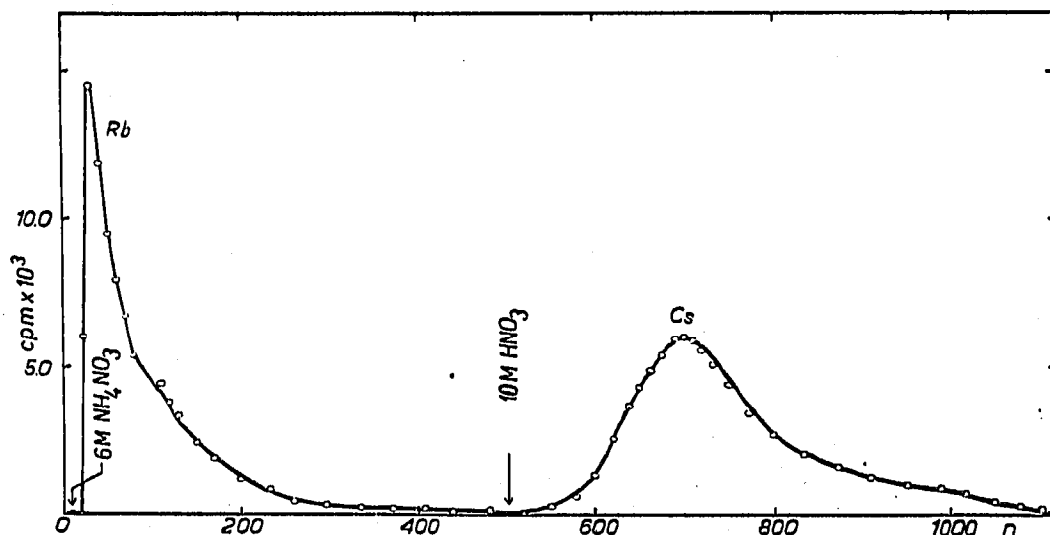


Fig. 3. Separation of weighable amounts of rubidium from cesium. Sorbed 2.65 mg of Cs + 1.71 mg of Rb from 0.1 *M* HNO₃, 0.5 g sorbent, 5.2 cm bed, drop interval: Rb elution 7 sec, Cs elution 10 sec. Drop size: 0.018 ml. Eluted: 98.9% of Rb and 98.5% of Cs.

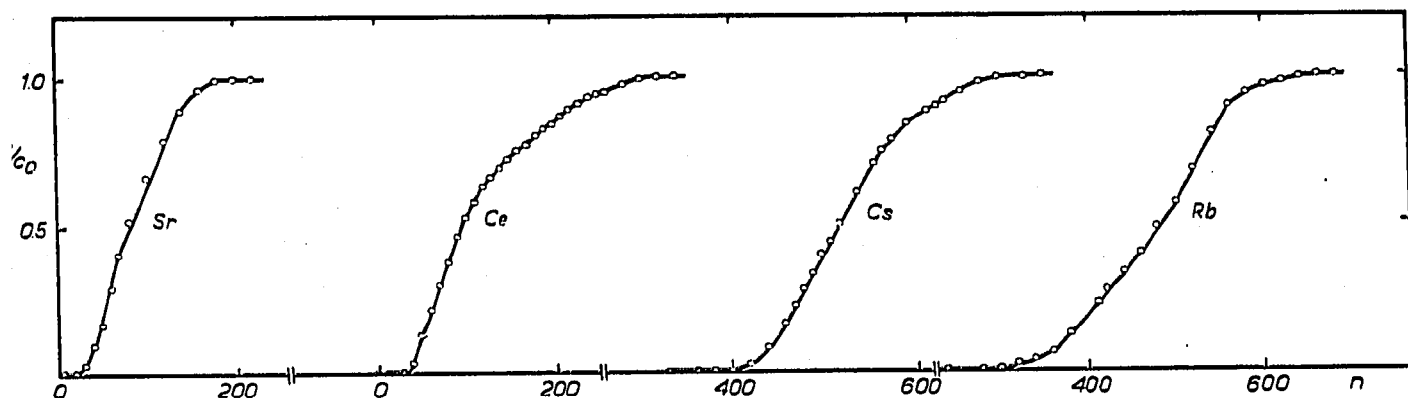


Fig. 4. Break-through curves for Sr, Ce, Rb and Cs. Sorption in all cases from $0.1 M HNO_3$, $0.5 g$ of sorbent. Sr: $5 \cdot 10^{-3} M$ solution of Sr^{2+} , $3.5 cm$ bed, drop interval $20 sec$, drop size $0.026 ml$. Ce: $5 \cdot 10^{-3} M$ solution of Ce^{3+} , $3.5 cm$ bed, drop interval $21 sec$, drop size $0.022 ml$. Rb: $0.1 M$ solution of Rb^+ , $1.0 cm$ bed, drop interval $18 sec$, drop size $0.013 ml$. Cs: $0.1 M$ solution of Cs^+ , $6 cm$ bed, drop interval $12 sec$, drop size $0.023 ml$.

nitrate and cesium with nitric acid was tested. Both elements have been separated successfully in carrier-free and weighable amounts, as shown in Fig. 3.

For Rb elution $6 M NH_4NO_3$ was used; cesium was then eluted with $10 M HNO_3$. The yields as well as the purity of fractions (determined by spectrometric measurements) were satisfactory. In practice, the column must be washed carefully with $0.1 M HNO_3$ after Rb elution, and before Cs elution with HNO_3 , in order to remove

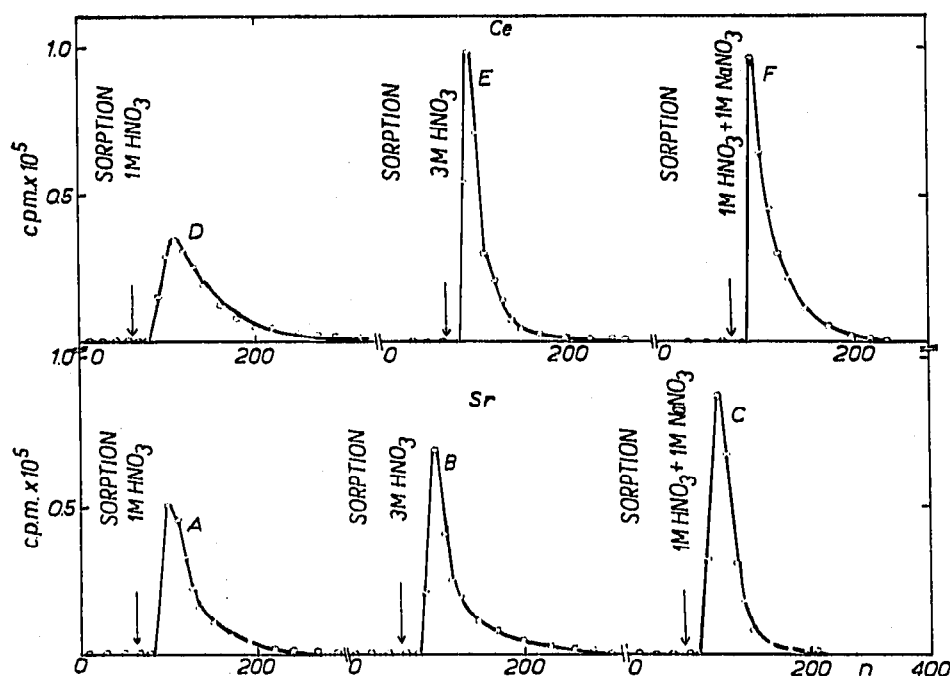


Fig. 5. Elution of ^{90}Sr and ^{144}Ce with nitric acid of various concentrations. Sorption in all cases from $0.1 M HNO_3$. Elution of ^{90}Sr : A = $1 M HNO_3$, $0.5 g$ of sorbent, $4.9 cm$ bed, drop interval $12 sec$, drop size $0.02 ml$. Eluted: 97.5% of ^{90}Sr . B = $3 M HNO_3$, other values the same as for A, drop interval $11 sec$. Eluted: 98.5% of ^{90}Sr . C = $1 M HNO_3 + 1 M NaNO_3$, other values as for A, drop interval $16 sec$, drop size $0.02 ml$. Eluted: 98.8% of ^{90}Sr . Elution of ^{144}Ce : D = $1 M HNO_3$, $1 g$ of sorbent, $5.2 cm$ bed, drop interval $5 sec$, drop size $0.03 ml$. Eluted: 87.4% of ^{144}Ce . E = $3 M HNO_3$, other values the same as for D. Eluted: 100% of ^{144}Ce . F = $1 M HNO_3 + 1 M NaNO_3$, $1 g$ of sorbent, $6.0 cm$ bed, drop interval $20 sec$, drop size $0.031 ml$. Eluted: 98.1% of ^{144}Ce .

ammonium salts, which owing to their decreased solubility in strong HNO_3 would, if they were allowed to remain, cause blockage of the column bed.

In the next stage of our work, the sorption and elution of the other fission products (Sr, Ce, Ru, Zr) was studied and the best conditions for the isolation of ^{137}Cs from a solution of the fission products were determined.

The sorption and elution of carrier-free ^{90}Sr and ^{144}Ce by nitric acid or mixtures of HNO_3 and NaNO_3 is illustrated in Fig. 5. The results show that there is practically quantitative sorption of ^{90}Sr and ^{144}Ce (Ce 99.9 %, Sr 99.0 %) from 0.1 M HNO_3 . With a concentration of 0.5 M HNO_3 cerium is already eluted to the extent of 24.8 %, with 1 M HNO_3 87.4 %, and with 3 M HNO_3 100 %. When a mixture of $\text{NaNO}_3 + \text{HNO}_3$ is used, a mixture of their 1 M solutions will elute 98 % of the cerium sorbed.

The behaviour of strontium is similar. 1 M nitric acid will elute 97.5 % of strontium sorbed on the column, 3 M HNO_3 98.5 %, and when a mixture of 1 M $\text{HNO}_3 + 1 M$ NaNO_3 is used, 98.8 % of the ^{90}Sr is eluted from the column. From experiments with the sorption and elution of ^{90}Sr and ^{144}Ce it follows that nitric acid is the most suitable eluant for separating cesium from strontium and the rare earths.

The maximum capacity of the sorbent for Sr and Ce was determined in order to test the possibility of its use for the isolation of rare earths, and possibly alkaline earths, which would seem to be practicable according to the experiments with carrier-

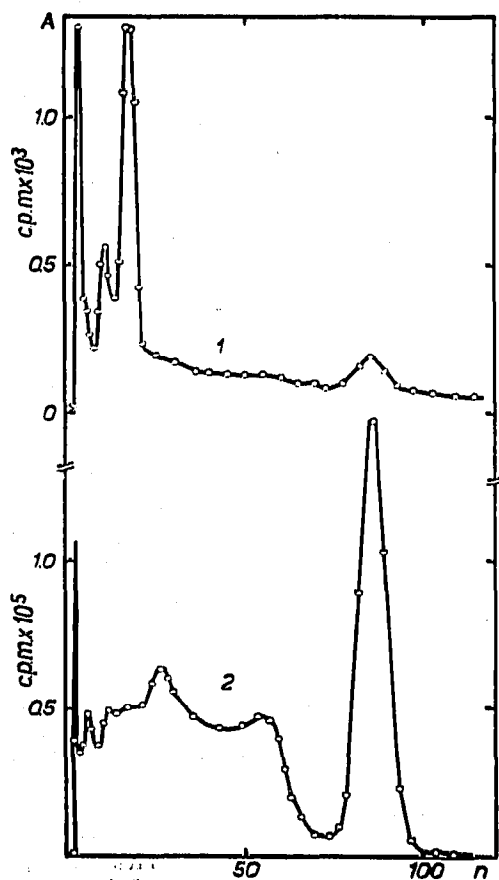


Fig. 6. γ -Spectrum of ^{137}Cs separated from a fission products mixture by sorption on vanadium ferrocyanide. 1 = initial mixture; 2 = purified cesium; A = activity expressed in c.p.m.; n = number of channels.

free amounts. The results are shown in Fig. 4. The capacity per g of the sorbent determined for Sr was $1.84 \cdot 10^{-2}$ mmoles and $2.4 \cdot 10^{-2}$ mmoles for Ce, which is very low when compared to the capacity for cesium.

From these results it was concluded that this sorbent is not suitable for the isolation of strontium and cerium. Experiments on the elution of ^{95}Zr - ^{95}Nb and $^{100}\text{RuNO}_3^+$ have shown that after sorption from 1 M HNO_3 solutions and careful washing with 0.1 M HNO_3 most of the activity passes out from the column during the washing. The rest of the total activity ($\sim 10\%$) is then washed out with 3 M HNO_3 . It may be therefore concluded that Sr, Ce, Ru and Zr may be separated from cesium (rubidium) by elution with 3 M HNO_3 , or with a mixture of nitric acid and ammonium nitrate.

All these conditions were verified by the isolation of ^{137}Cs from a solution of fission products (neutron irradiated uranium after one year of cooling), ^{137}Cs being isolated by means of the experimental procedure described in the experimental part. The γ -spectrum of cesium before and after isolation is shown in Fig. 6, which shows that all the radiochemical impurities, ^{144}Ce , $^{152+154}\text{Eu}$, ^{95}Zr , ^{100}Ru which were present in the initial sample have been separated from the cesium, and that practically radiochemically pure ^{137}Cs had been obtained (the test for contamination with ^{90}Sr was carried out by radiochemical analysis).

CONCLUSIONS

It has been found that vanadium ferrocyanide is a suitable selective sorbent with a good capacity for the isolation of Rb and Cs, especially from acid solutions.

This sorbent may be used for isolation of the cesium even in the presence of ammonium salts.

Rubidium may be separated from cesium on vanadium ferrocyanide.

The sorption of the other fission products (Sr, Ce, Ru, Zr) is limited and the separation of Rb and Cs from fission products is therefore possible.

The separation of ^{137}Cs from the fission products produced a radiochemically pure ^{137}Cs .

SUMMARY

The use of vanadium ferrocyanide for the separation and isolation of heavy alkali metals under dynamic conditions has been studied. The capacity of this sorbent for Cs, Rb, Sr, and Ce has been determined, and the conditions for maximum sorption and elution of these elements were also determined. The application of vanadium ferrocyanide to the isolation of ^{137}Cs from a solution of fission products was tested.

REFERENCES

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