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Rapid Separation of Carrier-Free ^{95}Zr from ^{95}Nb Using MnO_2 Column

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NOTE

Rapid Separation of Carrier-Free ^{95}Zr from ^{95}Nb Using MnO_2 Column

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Summary

An efficient and simple method is presented for the radiochemical separation of ^{95}Zr from ^{95}Nb in a carrier-free state. ^{95}Zr is desorbed quantitatively from the MnO_2 column using a 3 *M* HNO_3 + 0.05 *M* HF solution. By following the recommended procedure, a decontamination factor higher than 10^5 is achieved. The radionuclidic purity of the separated ^{95}Zr has been ascertained by gamma-ray energy measurements as well as by a radiochemical method. The entire procedure takes less than 20 min.

^{95}Nb is the daughter of ^{95}Zr, and the separation of these two isotopes in a carrier-free state poses a difficult problem in many radiochemical separations. No satisfactory scheme for the carrier-free separation of ^{95}Zr from ^{95}Nb was found to have been proposed, though some reports are available for the milking of ^{95}Nb from the ^{95}Zr parent (*1*, *2*). Solvent

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extraction procedures using thenoyl trifluroacetone (*3–6*) and tri-*n*-butyl phosphine oxide (*7*) are rapid and provide good decontaminations, but the recovery of the activities is not quantitative. Precipitation (*8*) as $BaZrF_6$ and coprecipitation (*8*) with LaF_3 are quick but the subsequent purification using mandelic acid is rather slow. Moreover, about 0.5% of the niobium activity was always found to accompany the zirconium fraction, even after final purification. Ion exchange elution techniques have been recommended for such separations (*8*), but they are mostly time consuming and unsuitable for carrier-free separations. Radiochemical separation of Zr from Nb with salicyl hydroxamic acid, reported recently (*9*), merits mention here. A decontamination factor of the order of 5×10^4 was realized. The very poor chemical yield of Zr (only 50–60%) was attributed to losses in the purification steps. Our present study reveals that a better yield as well as a better decontamination factor could be achieved for Zr by using adsorption on MnO_2. The results of this investigation are reported here. This one-step method offers the advantages of speed, clean separation, adaptability to remote control, and can be used with high levels of radiation where ion exchange procedures generally fail. The radionuclidic purity of the separated ^{95}Zr has also been confirmed.

EXPERIMENTAL

Adsorber

MnO_2 used in the column experiments was prepared according to the procedure described by Bigliocca et al. (*10*). The MnO_2 precipitate was dried at 60°C, crushed, and sieved. Only 25–100 mesh particles were used in these experiments in order to get a reasonable flow rate.

Tracer

The beta active nuclides ^{95}Zr and ^{95}Nb, which were in radioactive equilibrium, were obtained in the form of an oxalate complex in weak oxalic acid solution from the Isotope Division of this establishment.

Countings

A 5.1×3.8 cm well-type NaI(Tl) detector connected to a single channel analyzer, two $\pi\beta$ proportional counter, and a 2-cc Ge(Li) detector coupled with a 400 channel analyzer were used for gross gamma-

TABLE 1

Radiochemical Separation of ^{95}Zr from ^{95}Nb Using MnO_2 Column

Experiment No.	% Adsorption of ^{95}Zr–^{95}Nb on MnO_2 column	% Recovery of ^{95}Zr with 3 *M* HNO_3 + 0.05 *M* HF solution	% ^{95}Nb left over on MnO_2 column	Decontamination factor for Zr from Nb ($\times 10^5$)
1	99.5	96.1	100	1.5
2	99.9	97.4	100	1.8
3	99.7	98.2	100	1.6

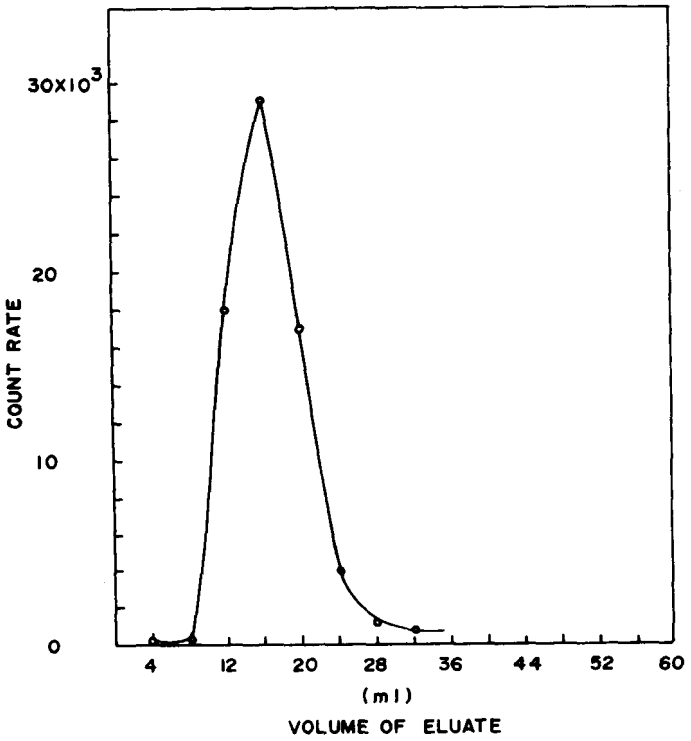

FIG. 1. Elution curve for ^{95}Zr separated from ^{95}Nb with 3 *M* HNO_3 + 0.05 *M* HF solution. Column dimensions: 10 × 1 cm. MnO_2 particles size: 25–100 mesh.

ray countings, beta counting, for the determination of Nb contamination in eluted Zr fraction, and for gamma-ray spectral analysis, respectively.

Radiochemical Procedure

A 10 × 1 cm column of MnO_2 was used in all column adsorption experiments. The column was equipped with 2 plugs of glass wool at the top and the bottom to retain the adsorber. A known aliquot of a ^{95}Zr–^{95}Nb equilibrium mixture which gave around 10^5 counts per minute, gamma radioactivity (gamma cpm), was heated to near dryness and fumed 2–3 times with a little $HClO_4$ to destroy the oxalic acid content of the tracer. Then it was taken up in a small volume of 3 *M* HNO_3 and loaded onto the MnO_2 column, followed by washing with sufficient nitric acid solution of the same concentration. Table 1 indicates that both Zr and Nb are well adsorbed at this acidity. The adsorbed ^{95}Zr activity was then eluted with a solution of 3 *M* HNO_3 + 0.05 *M* HF at a flow rate of 0.5 ml/min. Eluate was collected in 4 ml portions in counting tubes by using a fraction collector, and then counted. A typical elution curve is given in Fig. 1. A portion of the eluate was concentrated and the gamma-ray energy spectrum was taken using a 2-cc Ge(Li) detector.

RESULTS AND DISCUSSION

Experiments carried out to determine the adsorbability of ^{95}Zr and ^{95}Nb with MnO_2 clearly indicated that in 3 *M* HNO_3 medium it is almost 100%. A 3 *M* HNO_3 + 0.05 *M* HF solution used here selectively elutes only zirconium, and niobium is left undisturbed on the column itself. With 20–25 ml of the eluant, more than 95% of the zirconium activity could be easily stripped off the column. The gamma-ray spectra of the loaded ^{95}Zr–^{95}Nb tracer and that of the eluate recorded using a Ge(Li) detector half an hour after separation are shown in Fig. 2. The 0.765 MeV gamma-ray peak of ^{95}Nb is completely absent in the spectrum of the effluent. This gamma-ray spectral analysis of the eluate leads us to infer that this separation provides good radionuclidic purity.

The retention of ^{95}Zr on the MnO_2 column and the recovery by the HNO_3–HF mixture were calculated by comparing the area under the 0.725-MeV photopeak of ^{95}Zr. Covell's method (*11*) was used for peak area calculation. Results of three typical elution experiments are compiled in Table 1.

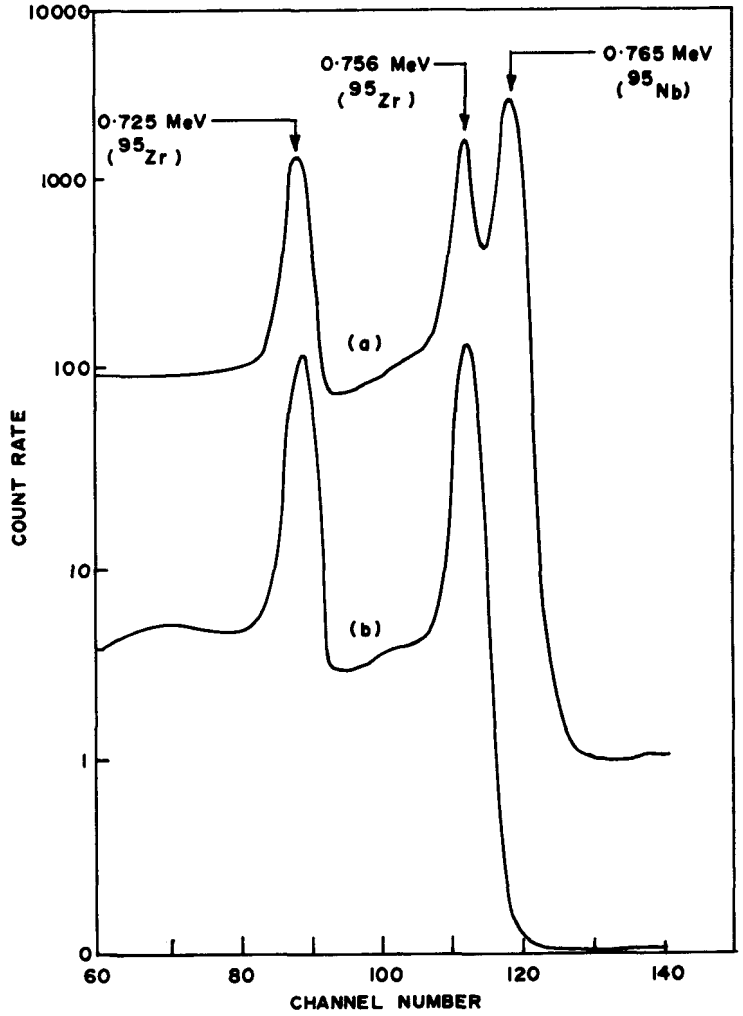

FIG. 2. Gamma-ray spectra of (a) ^{95}Zr–^{95}Nb tracer before being loaded onto the MnO_2 column, (b) ^{95}Zr separated from ^{95}Nb with 3 *M* HNO_3 + 0.05 *M* HF solution.

The degree of contamination of ^{95}Nb in the eluted ^{95}Zr fraction was determined immediately after its elution by carrying out the chemical separation of niobium. Here Nb was precipitated (carrier added before Zr separation) and the precipitate was counted in an end-window type

beta proportional counter for any activity. A lower limit of 1.5×10^5 was obtained for decontamination of Zr from Nb. This is the highest decontamination factor yet achieved for this separation. Experiments were also carried out to check if there was any contamination of the eluate due to Mn coming from the column, but no traces of Mn could be detected spectrophotometrically in the eluted Zr fraction.

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