SEPARATION OF RARE-EARTH FISSION PRODUCT ELEMENTS FROM $^{106}$Ru AND $^{137}$Cs BY CHLORIDE SUBLIMATION

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The possibility has been investigated of separating rare-earth fission fragment elements from $^{106}$Ru and $^{137}$Cs by high-temperature sublimation (950 °C) of chlorides, with their subsequent gas adsorption separation in a quartz tube under a temperature gradient in a flow of the carrier-gas $Ar + SOCl_2$. The temperatures corresponding to the maxima of the element precipitation zones are: 630-660 °C ($^{144}$Ce), 770-780 °C (0.7-6 µg $^{140}$La+La), 920 °C (1.5 mg Ce or La), 420-450 °C ($^{106}$Ru), 280-300 °C ($^{137}$Cs). The coefficients of element separation have been calculated.

For the separation of indicator amounts of rare-earth elements and $^{106}$Ru and $^{137}$Cs, fractional sublimation of the chlorides of the latter at 650 °C has been used. Rate constants and effective activation energies of the overall processes of chlorination-sublimation of the elements have been determined.

During isolation and determination of rare-earth fission fragment elements in irradiated materials using extraction and ion-exchange methods, certain difficulties are caused by the separation of ruthenium, which is characterized by the complicated behaviour of its ions in solution.1, 2 The literature method of ruthenium separation by distillation in the form of ruthenium tetroxide from acid solutions2 is not sufficiently effective.

In this connection the present paper reports the possibility of rare earth element separation from $^{106}$Ru and $^{137}$Cs (a long-lived separation product) by anhydrous chloride sublimation in a quartz tube under a temperature gradient in a flow of carrier-gas. The principles of the method and the equipment were described previously.3-5

Experimental

A quartz tube with an internal diameter of ~ 4 mm and 600-1000 mm length was placed into a tube furnace, along which a temperature drop was created in the direction of gas flow. The temperature gradient was determined in a number of experiments.
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by the thermal conduction of an insulated copper tube, one end of which was heated in the furnace. In other cases the gradient was created with the aid of a special furnace with a non-uniform winding. Argon saturated with thionylchloride was used as carrier-gas. The flow rate of the carrier-gas was about 1.2 l/h. The isotope solution was placed in a graphite boat and evaporated under an IR-tube. The activity of the samples was 0.08-02 mCurie. The boat was placed into the quartz tube in a fixed position. Argon was blown through the system for 1 min, then an Ar+SOCl₂ mixture was passed through it, and after 2 min the furnace heating was switched on. Control of the sublimation process in the start zone was realized with the aid of a scintillation counter with a NaI crystal, placed in front of the furnace, as well as by measuring the gamma-activity of the boat before and after the experiment.

When the experiment was finished, the gamma-activity in the tube length was determined by stretching the latter near the scintillation counter with a diaphragm, the readings being taken with an intensimeter and a recording potentiometer.

Results and discussion

The behaviour of rare-earth elements in the processes of chlorination-sublimation and chloride transfer in the quartz tube under a temperature gradient is exemplified by ⁴⁴Ce and ¹⁴⁰La. It was previously established⁵ that during chlorination of the sample on a graphite substrate at 900-960 °C for 2 hrs more than 96% of the ⁴⁴Ce is sublimed and the maximum of the adsorption zone (activity peak) of the chloride formed is at 630-660 °C. A preliminary treatment of the sample with liquid thionyl chloride directly on the substrate favours the more rapid course of the chlorination process and a more complete chloride sublimation. In the case of larger amounts (1.5 mg Ce) sublimation from the substrate under the above conditions is about 90% and the chloride formed condenses in the zone with maximum at 920 °C.

Lanthanum behaves identically to cerium in processes of chlorination and sublimation. In the process of lanthanum chloride transfer the maxima of the isolation zones for samples of 0.7-6 μg and 1 mg La labelled with ¹⁴⁰La are at 770-780 and 920 °C respectively.

¹⁰⁶Ru behaviour has been studied in a wide temperature range from 460 to 960 °C. As follows from Fig. 1, the rate of ruthenium chlorination-sublimation increases with temperature increase. At > 600 °C ruthenium is practically quantitatively sublimed from the substrate during 2-3 hrs. As it is known that ruthenium forms di-, tri- and tetrachlorides with different stabilities at different temperatures, ² it is of interest to investigate ruthenium transfer in the quartz tube in an Ar+SOCl₂ flow as a function of the starting temperature, in the 460-960 °C range, at which chlorination-sublimation was carried out. It was established that under the given conditions ruthenium is isolated in the zone with maximum at 420-450 °C, apparently in the form of trichloride, which is stable up to 450 °C. ²