Short Communication

CHROM. 4763

Separation of transuranium elements by gas chromatography of their chlorides

Recently we have shown[1] the possibility of separation of chlorides of lanthanide elements by gas chromatography at relatively low temperature when using the vapours of aluminium trichloride as a component of the carrier gas. The starting point was the work of GRUEN AND ØYE[2,3] who have found that Al_2Cl_6 vapours interact with solid $NdCl_3$ to form gaseous complexes containing neodymium. We have verified[1] that this is the common property of lanthanide elements. By adding Al_2Cl_6 vapours into the carrier gas in the chromatographic experiments we were able to synthesise the complexes at the moment of introduction of the sample of lanthanide chlorides into the column. The excess of Al_2Cl_6 also suppresses the dissociation of the unstable complex molecules. The experiments were carried out in glass capillary columns (2.5 m × 1 mm I.D.) at 250° by the method of gas–solid chromatography. In this case the vapours of aluminium trichloride also serve to modify dynamically the surface of the glass[4,5].

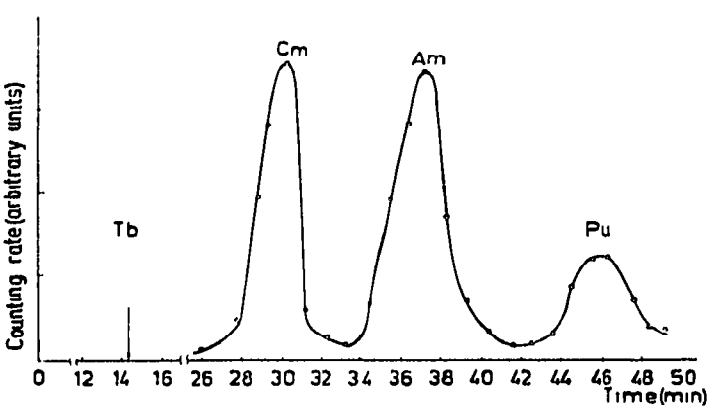
Here we report experiments on the separation of the transuranium elements by an analogous technique. We also investigated the behaviour of protactinium and uranium. Use was made of isotopes ^{231}Pa, ^{233}U, ^{237}Np, ^{239}Pu, ^{241}Am and ^{244}Cm in amounts not in excess of 1 μg.

The details of the experimental procedure were described in the previous report[1]. In the present work we used a longer column (10 m × 1 mm I.D.). It should be noted that the chromatogram was measured by collecting fractions of the Al_2Cl_6 condensate at the exit of the column and by measuring their radioactivity. For the identification of the alpha active elements a fraction was dissolved in hydrochloric acid, about 100 μg of lanthanum carrier were added and then precipitated by an excess of the sodium hydroxide to dissolve aluminium hydroxide. The precipitate was painted onto a metallic disc and the alpha spectrum measured with a surface-barrier detector and multichannel pulse-height analyser.

Some examples of the separation of various mixtures are shown in Figs. 1–3. Beta active ^{160}Tb was added to all samples as a monitor.

It can be seen from Fig. 1 that curium and americium are eluted from the column in the order of decreasing atomic number and are found on the chromatogram at the position of lighter lanthanide elements. The same situation arises when separating tervalent ions of Am and Cm by ion-exchange chromatography[6]. This provides the first experimental evidence that trichlorides of transuranium elements form with Al_2Cl_6 complexes of the same type as trichlorides of lanthanide elements.

The elution of plutonium just after the peaks of americium and curium (Fig. 1) with similar separation factors of the adjacent elements indicates without any doubt that under the conditions of our experiments plutonium exists in the tervalent state. This is in agreement with the fact that the only higher plutonium chloride known, $PuCl_4$, is very unstable and may exist only in the gas phase in an excess of chlorine[7].



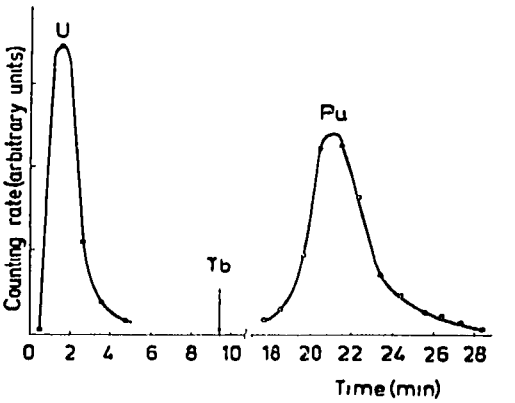


Fig. 1. Separation of a plutonium–americium–curium mixture. Column temperature, 250°; Al_2Cl_6 partial vapour pressure, ~ 100 mm Hg, helium flow rate, 8 ml/min.

Fig. 2. Separation of a uranium–plutonium mixture. Column temperature, 255°, Al_2Cl_6 partial vapour pressure, ~ 100 mm Hg; helium flow rate, 8 ml/min

The elution of plutonium in such a position relative to Am and Cm as that shown in Fig. 1 is uncommon in chromatography of transuranium elements as, for example, in ion-exchange and extraction chromatography separations plutonium as a rule is found in solution in a higher oxidation state than 3 +.

It can be seen from Figs. 2 and 3 that the retention times of chlorides of protactinium, uranium and neptunium are very small. One of the possible explanations is that these elements are chlorinated, under the conditions of the experiment, to their higher chlorides, which themselves are rather volatile. However, on the basis of the available data one would expect that at 500°, which is the temperature at introduction of the sample, these higher chlorides will dissociate to form tetrachlorides. So it seems more probable that the short retention time, in any case for Np and U, is due to the high effective volatility of complexes of aluminium trichloride with

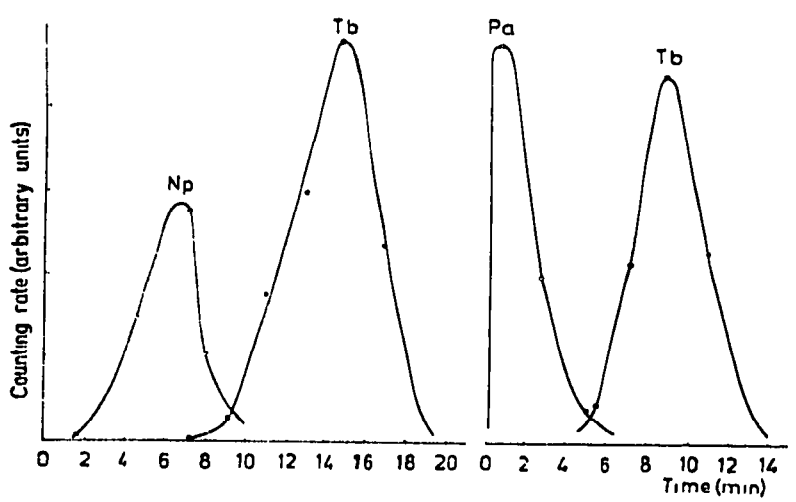


Fig. 3. Chromatograms of chlorides of protactinium and neptunium. Column temperature, 250°; Al_2Cl_6 partial vapour pressure, ~ 100 mm Hg; helium flow rate, 8 ml/min

tetrachlorides of the above elements. GRUEN AND MCBETH[8] proved the existence of such complexes of UCl_4.

It should be noted that at the effectiveness of 100–150 theoretical plates the column provides quite a good separation of the pair americium–curium. The peaks are almost symmetrical, thus providing evidence that Al_2Cl_6 vapours are very efficient in modifying the surface of the glass.

The suggested method of separation of transuranium elements can be used for solving various problems of radiochemical analysis.

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