SEPARATION OF RARE EARTH ELEMENTS BY GAS CHROMATOGRAPHY OF THEIR CHLORIDES

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SUMMARY

Gas–solid chromatography separations of lanthanide chlorides were carried out on the glass capillary columns at $\leqslant 250°$ using aluminium trichloride vapours (40–170 mm Hg) as a component of the carrier gas. $AlCl_3$ forms volatile complexes with rare earth chlorides, and at the same time, modifies the surface of the column.

INTRODUCTION

Up to the present time, gas chromatographic separations of rare earth elements have only been carried out by using volatile chelates–trisdiketonates (including fluoroderivatives) with branched carbon chains. The general use of the GLC techniques[1,2] reported might not be possible owing to the complicated synthesis of the compound involved. Inorganic rare earth substances, as such, have not been employed in gas chromatography because of their low volatility.

Recently GRUEN AND ØYE[3] obtained spectroscopic evidence that heating neodymium trichloride in aluminium trichloride vapours (temperature range 200–800°) results in a much higher concentration of neodymium in the gas volume than that corresponding to the vapour pressure of neodymium chloride itself. They suggested that this might be due to the formation of volatile complexes of the general formula $Nd(AlCl_4)_nCl_{3-n}$. In the present work an attempt was made to utilize such species for the separation of rare earths by gas–solid chromatography. Preliminary experiments showed the formation of volatile complexes with aluminium chloride to be a common property of the chlorides of lanthanide elements. To prevent the dissociation of the complexes a mixture of an inert gas with the Al_2Cl_6 vapours was used as carrier gas. The latter served also for dynamic modification of the surface of the glass capillary column.

EXPERIMENTAL

Apparatus

Gas chromatography was performed in the apparatus shown in Fig. 1. Tube furnaces (1) (2) (3) and (4) maintained the required stepped temperature distribution

along a glass tube (5). This consisted of several welded sections; the spiral one (2.5 m × 1 mm I.D.) placed in a thermostat (1) served as the chromatographic column. Nitrogen (flow rate 12 ml/min), after passing through a flow meter (8), passed through a molecular sieve desiccant (9) and was saturated with aluminium chloride vapour in a tube (6). This was completely filled with the solid chloride and situated in furnace (4) where the temperature was 20–30° higher than in the thermostat (3), whose temperature corresponded to the required vapour pressure of Al_2Cl_6. The supersaturation arising was quickly destroyed by partial condensation of the vapours and thus a steady concentration was maintained. We used an Al_2Cl_6 partial vapour pressure between 40 and 170 mm Hg, the temperature of the furnace (3) being 138–155°.
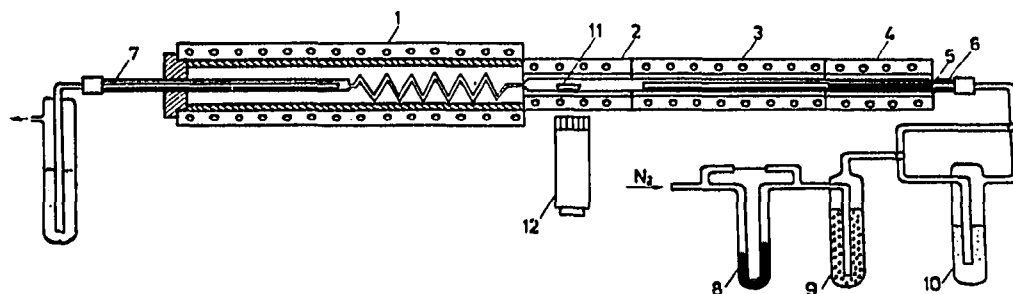

Fig. 1. The chromatographic apparatus (see text for description).

Sample introduction

The sample solution with radioactive tracers was evaporated in a glass boat and the residue was then evaporated to dryness first with concentrated nitric acid and then with concentrated hydrochloric acid. The boat was put into furnace (2) which is maintained at about 180°. Nitrogen, saturated with thionylchloride vapour in vessel (10) was passed over the sample for several minutes to dehydrate the rare earth chlorides. The tube (6) with solid aluminium chloride was then inserted and the carrier gas was passed through the system for 5 min. After stopping the flow the temperature of furnace (2) was raised rapidly to 500° after which the carrier gas was again supplied. The volatile compounds sublimed into the carrier gas, the rate of the process being followed by a chart recording the counting rate from a scintillation counter (12) with a Na(Tl)I crystal. The sample was introduced into the column in about 1 min.

The gaseous complexes of the rare earth elements condensed with aluminium chloride at the exit of the thermostat (1) in a tube (7) inserted into tube (5). One cm of tube (7) was extracted every 2 min from the thermostat and thus fractions of the condensate were collected. The chromatogram was observed by measuring the intensity of β and/or γ radiation along tube (7).

The isotopes [144]Ce, [143]Pr, [147]Pm, [155]Eu, [148,150]Gd, [160]Tb, [159]Dy, [165,167]Tm, [166]Yb and [170]Lu without or with several micrograms of a carrier were used.

Volatile complexes

Runs with separate elements showed that at an Al_2Cl_6 vapour pressure of ≈ 100 mm Hg the chlorides of Ce, Pr, Pm, Gd, Tb, Dy, Tm, Yb and Lu rapidly form volatile complexes, which can be transported by the carrier gas in the broad range of temperature (150–500°) investigated. The retention time was found to decrease

with increasing atomic number. Peculiar behaviour was observed in the case of europium which sublimed very slowly from the boat and was found to be distributed all along the gas conduit.

We suppose that the volatility of lanthanide chlorides in the presence of aluminium chloride can be accounted for by the formation of compounds of the general formula $LnAlCl_6$ (where Ln is the lanthanide element). This composition is suggested by analogy with the stoichiometry of vapour complexes such as $NaAlCl_4$[4], $BeAlCl_5$[5], $FeAlCl_6$[6] and $KLnCl_4$[7] reported earlier. These last compounds are rather strong bonded, their stability increasing from Lu to La. NOVIKOV AND GAVRYUCHENKOV[7] have pointed out that, as a general rule, complex compounds are formed in the vapour phase by those chlorides which themselves incline to dimerization, and that the double compounds are often more stable towards dissociation than any of the related dimeric species. Dimers of rare earth trichlorides were reported to be reasonably stable, the heat of dimerization being from 32 to 48 kcal/mole[7,8]. These data give additional support to the suggested existence of $LnAlCl_6$ complexes.

Thus the peculiar behaviour of europium, as compared with other lanthanides, can evidently be accounted for by the instability of europium trichloride. This decomposes upon heating to yield $EuCl_2$[9] which does not form dimeric molecules in vapour state[8]. Ytterbium is also capable of forming a dichloride, however, it showed 'normal' behaviour. This is explained by the big difference between the enthalpies of decomposition from the trichloride to dichloride: these are reported[10] as 12 kcal/mole and 24 kcal/mole for liquid $EuCl_3$ and $YbCl_3$, respectively. The value for $SmCl_3$ is 27 kcal/mole and so samarium would be expected to behave like other lanthanides.

Retention time vs. temperature and Al_2Cl_6pressure

Generally speaking, one may expect the retention time of the complex to depend on the column temperature in a complicated way. With an increase of temperature two factors producing opposite effects are operative. Firstly, the desorption step is accelerated, making the retention time of the complex shorter. On the other hand and for the same reason, the modifying action of the Al_2Cl_6 vapour becomes weaker, which can result in an increase of the effective heat of adsorption of the complex.

The temperature dependence of the position and shape of the emerging peak is shown in Fig. 2 for ^{160}Tb with Al_2Cl_6 partial vapour pressure of 115 mm Hg. The
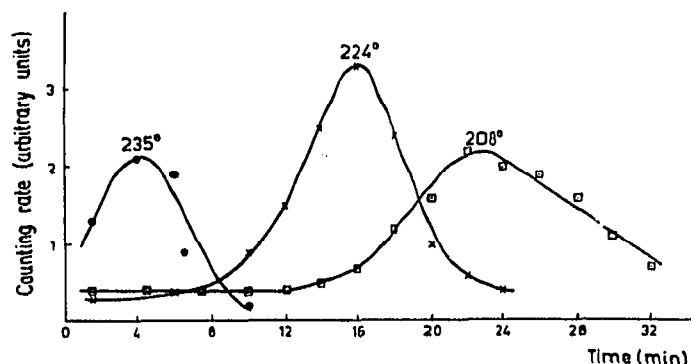

Fig. 2. Temperature dependence of terbium chromatogram (4 μg of carrier). Al_2Cl_6 partial vapour pressure 115 mm Hg, nitrogen flow rate 12 ml/min.

heat of adsoption for the terbium complex was calculated from the retention time data using a molecular kinetics equation[11]. The values obtained, *viz.* 30.4 kcal/mole at 208°, 31.0 kcal/mole at 224° and 30.3 kcal/mole at 235° are within the limits of experimental error and hence the peak shift is mainly due to the accelerated desorption of the complex molecules.

The retention time depends on the partial vapour pressure of the aluminium chloride in the carrier gas. At a fixed column temperature the elution can be made faster and the peak narrower by increasing Al_2Cl_6 vapour pressure. The data obtained for [160]Tb chloride at a column temperature of 220° are shown in Fig. 3. The Al_2Cl_6 vapour pressure equation used was that given in ref. 12. The strong dependence of the retention time on the quantitative composition of the carrier gas seems to support the suggestion about the dynamic modification of the glass surface by adsorption of aluminium chloride vapours[13, 14].
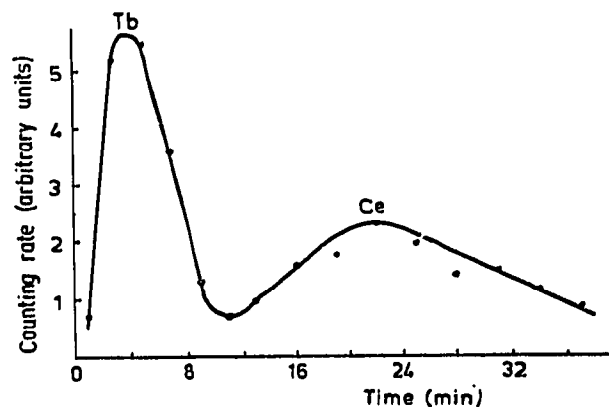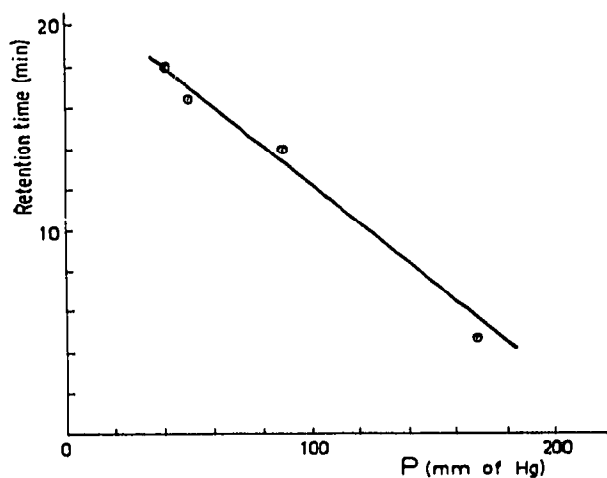
Fig. 3. Retention time of terbium at 220° as a function of Al_2Cl_6 partial vapour pressure. Nitrogen flow rate 12 ml/min.

Fig. 4. Separation of a terbium–cerium mixture. Column temperature 250°, Al_2Cl_6 partial vapour pressure 40 mm Hg, nitrogen flow rate 12 ml/min.
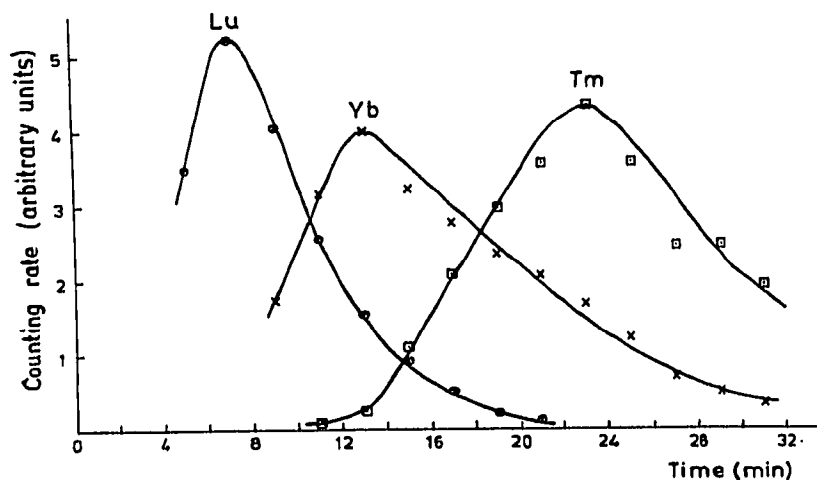
Fig. 5. Separation of a thulium–ytterbium–lutecium mixture. Column temperature 168°, Al_2Cl_6 partial vapour pressure 40 mm Hg, nitrogen flow rate 12 ml/min.

Separations

Satisfactory separations of some rare earth mixtures were achieved in spite of using a very short capillary column. The chromatogram of a ^{144}Ce–^{160}Tb mixture is given in Fig. 4. Fig. 5 shows the result of an experiment with the neighbouring heavy lanthanides—Tm, Yb and Lu. In this case the fractions of condensate were analysed for the isotope content by measuring the most characteristic and abundant γ-rays of the above elements in the < 0.5 MeV region with a Ge(Li) spectrometer. The separation factors obtained, $\alpha_{Lu/Yb} = 1.8$ and $\alpha_{Yb/Tm} = 1.7$, are considerably better than those for the same elements in ion-exchange chromatography[15,16] and in GLC of chelates[1,2,17]. Still higher separation factors were achieved with reversed phase partition chromatography[18] but with an inverted sequence of elution.

CONCLUSION

The evident advantages of the technique described are the very simple synthesis of the volatile compounds in the course of sample introduction and the possibility of working with both trace and macroquantities of elements.

High separation factors make the method promising and allow one to hope that good separations can be achieved. Work is in progress to determine the optimum conditions for separation of mixtures of the lanthanide and transuranium elements.

ACKNOWLEDGEMENTS

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