tion procedures, as cited in the reviews by GREEN[4] and by COLEMAN[6]. Our data show, moreover, that (i) many qualitative separations are easily carried out using the inexpensive amine Amberlite LA-1: some examples are given in Fig. 2; (ii) the rapidity of the separation method outlined above makes it superior to most other methods of qualitative analysis so that detailed investigation would certainly be of interest, together with its possible quantitative application (*cf.* ref. 2).

The use of the rapid thin-layer technique described here is, moreover, important in view of the reliable predictions that can sometimes be made about the results of ion-exchange or extraction procedures under comparable circumstances.

Investigations are now in progress on the use of other supports, amines and complexing agents. Attention has already been given to the use of paper-chromatographic procedures analogous to those outlined by CERRAI AND TESTA[1,3]. It was found that good results are obtained when using 0.15 *M* Amberlite LA-1·HCl solutions in chloroform or benzene; Whatman No. 1 paper was used throughout. Schleicher and Schüll paper No. 2043a gave comparable results, while Schleicher and Schüll 2040a and 2045a were somewhat less satisfactory. In general, the results are comparable to those given above for the thin-layer experiments. Excellent separations can be accomplished in 3–4 h.

Chemical Laboratory, Free University,
Amsterdam (The Netherlands)

U. A. TH. BRINKMAN
G. DE VRIES

1 C. TESTA, *J. Chromatog.*, 5 (1961) 236.
2 E. CERRAI AND C. TESTA, *J. Chromatog.*, 5 (1961) 442; 6 (1961) 443.
3 E. CERRAI, *Chromatographic Reviews*, Vol. 6, Elsevier, Amsterdam, 1964, p. 129.
4 H. GREEN, *Talanta*, 11 (1964) 1561.
5 K. A. KRAUS AND F. NELSON, *Proc. 1st Intern. Conf. Peaceful Uses At. Energy, Geneva, 1955*, Vol. 7, p. 113.
6 C. F. COLEMAN, *Nucl. Sci. Eng.*, 17 (1963) 274.

Received January 25th, 1965

J. Chromatog., 18 (1965) 142–144

Notes

Thin-layer chromatographic method for the separation of rare earths

Although thin-layer chromatography (TLC) has proved to be an excellent and rapid separation technique in organic and biochemical analysis, it has found little use in inorganic separations. The technique offers many unique advantages, the most important being its rapidity and the possibility to use corrosive reagents and impregnations. The separation of some adjacent rare earths (R.E.) with a rapid chromatographic technique is interesting in view of radiochemical studies. The use of TLC

was not put forward yet, until an article from PIERCE[1] appeared during the course of our work.

It appears from the literature that the best separation factors between adjacent R.E.'s are obtained with di-(2-ethylhexyl) phosphoric acid (HDEHP). This acid, originally used as an extracting agent[2], has already been applied in chromatography column- and paper partition).

All these techniques used reversed phase chromatography[3–6]. This is also the case with the above mentioned TLC separation. The only attempt to use HDEHP as a mobile phase is due to WINCHESTER (personal communication). We have tried the normal phase method by impregnating silica gel with buffers or acids and eluting with HDEHP.

Preparation of thin layers

Silica gel H was used, to avoid the presence of calcium sulphate, which can possibly give rise to difficulties, as its solubility in an aqueous phase is far from negligible.

Plates prepared without a binding agent offered, however, low mechanical resistance. Better results were obtained by adding 6 % soluble starch as a binder. The starch was sieved before mixing with the silica gel, purified according to SEILER[7]. The mixture was then sieved again through a 350 mesh sieve. To obtain 20 plates of 5 × 20 cm, 30 g of this mixture were slurried with 57 ml water and shaken vigorously for 3 min. The layers were then prepared with the Shandon applicator (thickness of layer 250 μ) and air-dried at room temperature overnight.

To adjust the pH of the stationary phase, the silica gel was slurried with an adequate buffer. Impregnation by acids was achieved by developing the plates first with the acid in question ($HClO_4$ was preferable to HCl since it gave more reproducible results) and again drying overnight.

Development

Development was achieved by the ascending method in Shandon development chambers lined with filter paper. The mobile phase (HDEHP, with a controlled purity better than 99.5 %) was preequilibrated with the stationary phase and separated from it by centrifugation. A solution in carbon tetrachloride was used.

Detection of rare earths and determination of R_F values

To detect the R.E.'s, radioactive tracers were used. Most of these were prepared by irradiation of silica ampoules containing about 200 μl of a solution of the nitrates in water (5 mg element/10 ml) in the BR-1 reactor. Some isotopes were obtained from "The Radiochemical Centre", Amersham (^{91}Y) or the S.C.K., Mol (^{144}Ce, ^{153}Gd). The tracers were detected on the plates with a self built Geiger-Müller scanner coupled to a recorder. The R_F's were determined from the resulting graph. In some cases an autoradiographic technique was applied using Structurix Röntgenfilm D7, Gevaert. In this last case the R_F values were obtained by densitometry.

Results

Since HDEHP is itself strongly adsorbed on the silica gel layers a second front s formed, the first front being due to carbon tetrachloride. All the R_F values were

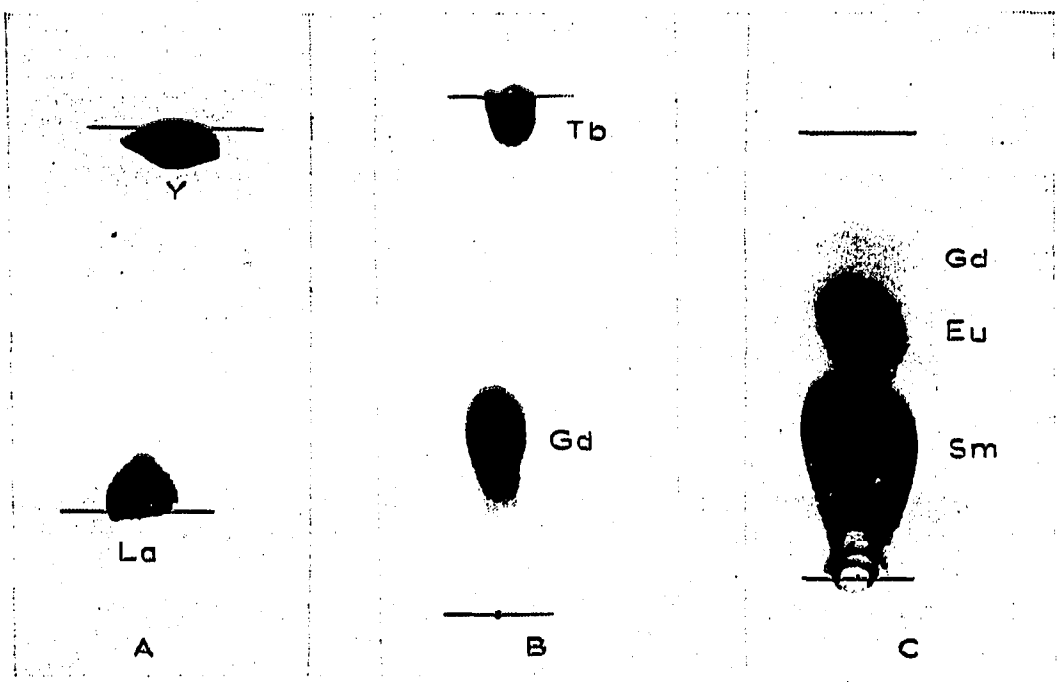

Fig. 1. Autoradiography of rare earth separations. (A) La–Y; stationary phase: buffer of pH 1.08. (B) Gd–Tb; stationary phase: 0.4 *M* $HClO_4$. (C) Sm–Eu–Gd; stationary phase: 0.3 *M* $HClO_4$.

determined with the HDEHP as the reference front. It was necessary to use 1 *M* HDEHP since in the case of a 0.1 *M* solution, the second front lies 9 cm under the first front when this has moved 12 cm. For 1 *M* HDEHP under the same conditions the second front lies only 1 cm behind the first.

The application of buffers as stationary phase is very limited since at high pH (2.23) all the R.E.'s have large distribution constants and thus migrate with the

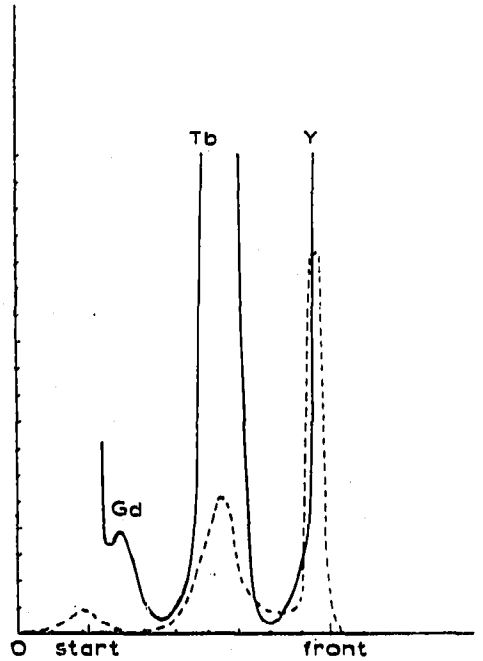

Fig. 2. Separation of Gd–Tb–Y. ——— densitometric analysis. – – – – – – Geiger-Müller scanning.

front. Only La has an R_F of 0.30 and can be easily separated from the rest. With a KCl–HCl buffer (pH 1.08) La has an R_F of 0.05, Ce 0.55, whereas Nd and the others migrate with the front. The separation of Y and La is shown in Fig. 1A. To separate the heavier R.E.'s lower pH's in the stationary phase are required which is obtained by impregnation with acids. In this way Eu and Sm can be separated completely with 0.2 M $HClO_4$. The separation Y–Tb–Gd (Y front, Tb 0.57, Gd 0.16) was achieved with 0.4 M $HClO_4$ as the stationary phase and is shown in Fig. 2. All these separations, however, suffer from the fact that a residual activity of nearly 5% is irreversibly fixed on the spotting place. Since spotting of the R.E.'s was done in an aqueous solution, it was assumed that this technique disturbed the pH of the stationary phase. The R.E.'s were therefore first extracted into HDEHP and then spotted in the organic phase. This technique allowed good separations of Tb–Gd (Fig. 1B), Eu–Gd and Eu–Gd–Sm (Fig. 1C) within at most 70 min.

Although as yet only the group Tb, Gd, Eu and Sm has been examined thoroughly and at most three R.E.'s have been separated, it is reasonable to expect that this method should be valuable to separate any combination of three adjacent R.E.'s and, in favourable circumstances, even five on one plate. This can be concluded from the fact that for example Eu, Sm and Gd (Fig. 1C) have R_F's of 0.29, 0.54 and 0.73, respectively. Tb should have an R_F of approx. 1 while the R_F of Nd would be approx. 0.

Work is now in progress to examine other R.E. separations with this technique.

Institute for Analytical Chemistry, State University of Ghent (Belgium)

A. DANEELS
D. L. MASSART*
J. HOSTE

1 T. B. PIERCE AND R. F. FLINT, *Anal. Chim. Acta*, 31 (1964) 595.
2 D. F. PEPPARD, G. W. MASON, L. MOIER AND W. J. DRISCOLL, *J. Inorg. Nucl. Chem.*, 4 (1957) 344.
3 E. CERRAI AND C. TESTA, *J. Chromatog.*, 8 (1962) 232.
4 E. CERRAI AND C. TESTA, *J. Inorg. Nucl. Chem.*, 25 (1963) 1045.
5 T. B. PIERCE AND P. F. PECK, *Nature*, 195 (1962) 597.
6 J. W. WINCHESTER, *J. Chromatog.*, 10 (1963) 502.
7 H. SEILER, in E. STAHL (Editor), *Dünnschichtchromatographie*, Springer Verlag, Berlin, 1962.

Received February 1st, 1965

* Research fellow of I.I.K.W. (Belgium).

Gas chromatography of inositols as their trimethylsilyl derivatives

Gas chromatography is now a standard technique in carbohydrate structure determination. Owing to their non-volatile nature, however, carbohydrates must be first converted into suitable derivatives. Methoxy and acetoxy derivatives of mono- and oligosaccharides have been analyzed successfully by gas chromatography. More recently, a trimethylsilylation technique[1] was introduced for the same purpose, and the range of applicability of gas chromatography of carbohydrates was expanded greatly. Compounds as large as a tetrasaccharide have been analyzed by gas chro