

- (e) Amine und Aminhydrochloride: Methyl-, Dimethyl-, Äthyl-, Diäthyl-, Propyl-amin; Ephedrin, Norephedrin, Amphetamin, Pervitin
 (f) Phenolalkylamine: Adrenalin, Noradrenalin, Tyramin, Dopamin.

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- 1 R. W. FREEDMAN UND P. P. CROITORU, *Anal. Chem.*, 36 (1964) 1880;
 A. SATO UND E. V. RUDLOFF, *Can. J. Chem.*, 42 (1964) 635.
- 2 Z. HORII UND M. MAKITA, *Chem. Pharm. Bull. (Tokio)*, 13 (1965) 636; *C.A.*, 63 (1965) 7633.
- 3 Z. HORII, M. MAKITA UND Y. TAMURA, *Chem. Ind. (London)*, (1965) 1494.
- 4 C. C. SWEELEY, R. BENTLEY, M. MAKITA UND W. W. WELLS, *J. Am. Chem. Soc.*, 85 (1963) 2497.
- 5 E. D. SMITH UND H. SHEPPARD, *Nature*, 208 (1965) 878.
- 6 B. G. CREECH, *J. Gas Chromatog.*, 2 (1964) 194.
- 7 S. LINDSTEDT, *Clin. Chim. Acta*, 9 (1964) 309.
- 8 E. LARSSON UND B. SMITH, *Acta Chem. Scand.*, 3 (1949) 487.
- 9 J. F. KLEBE, *J. Am. Chem. Soc.*, 86 (1964) 3399.
- 10 L. BIRKOFER, A. RITTER UND F. BENTZ, *Chem. Ber.*, 97 (1964) 2196.
- 11 *U.S. Pat.*, 2876234, 3. März 1959; *C.A.*, 53 (1959) 12238.

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A column-switching technique for the analysis of mixtures of fluorocarbons labelled with a short lived isotope*

The technique of temperature-programmed gas chromatography is now well established as a means of separating mixtures of components with widely differing boiling points (see for example ref. 1). However, when performing repeated analyses on a series of samples there is inevitably some delay between runs while the column oven is being brought back to the starting temperature.

During work recently performed in these laboratories it was necessary to separate and assay a series of mixtures of CF_3^{18}F , CH_3^{18}F , $\text{C}_2\text{H}_3^{18}\text{F}$ and $\text{CF}_2^{18}\text{FI}$. The relatively short half-life (112 min) and the trace amounts of the samples involved demanded that these analyses be performed as speedily as possible.

The separation of CF_4 , $\text{C}_2\text{H}_3\text{F}$ and CF_3I presents no problem since the substances have widely differing retention volumes on an 8-m silicone oil column containing 40 g/100 g oil/firebrick run at 25°. However, under these conditions CH_3F and $\text{C}_2\text{H}_3\text{F}$ are only slightly resolved. Even a polar column such as de-activated alumina (25°) failed to provide a suitable separation.

A column combination which did prove to be successful was the 8-m silicone oil column (25°) coupled in series with a similar 5-m hexamethylphosphoramide (HMP)/firebrick column operating at 0°. Unfortunately it appeared that the trace quantities of CF_3I present in the mixture were irreversibly adsorbed on the latter column. The

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column-switching arrangement shown in Fig. 1 proved to be capable of avoiding this drawback.

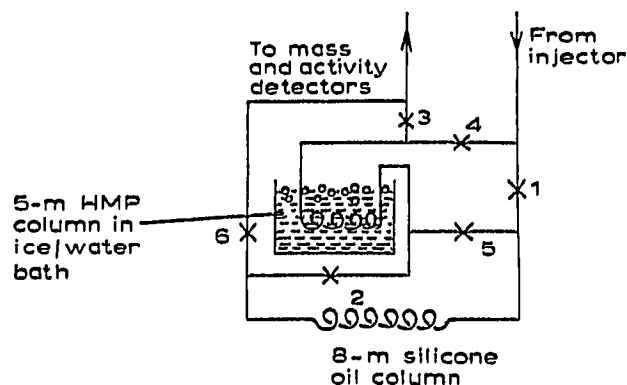


Fig. 1. Schematic diagram of the column-switching apparatus.

The on/off valves 1-6 were of the Hoke type (No. 465J) and the columns and interconnecting tubes made of $\frac{1}{4}$ in. O. D. copper or stainless steel. Connections and T joints were made with "Swagelok" fittings.

This somewhat complex arrangement was necessitated by the fact that the sensitivity of the proportional flow counters³ employed for the assay of ^{18}F is dependent upon the flow rate of the sample. In order that the flow rate should remain as nearly constant as possible whilst a sample was actually within the sensing chamber of the counter, the total length of column interposed between the injection port and the detectors was kept the same throughout the analysis.

Thus with valves 1, 2 and 3 open and 4, 5 and 6 closed the sample enters the

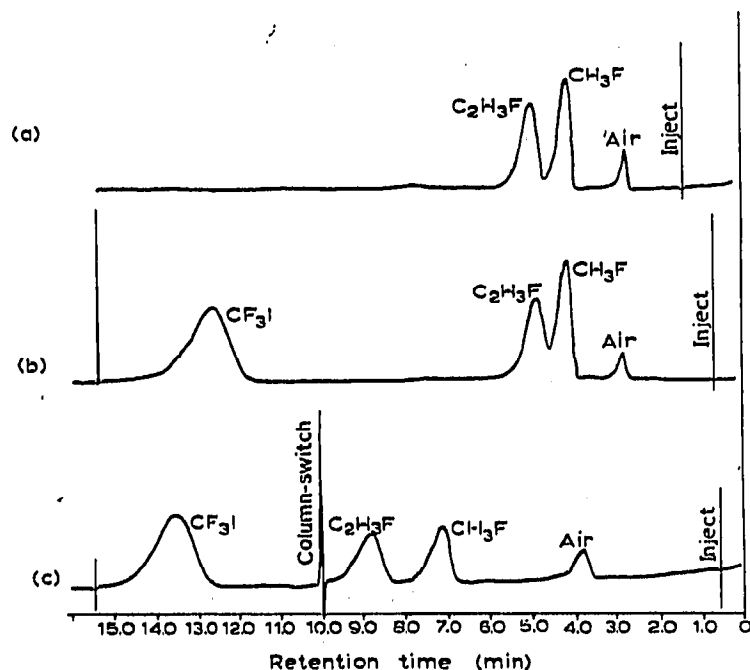


Fig. 2. Chromatograms of air- CH_3F - $\text{C}_2\text{H}_3\text{F}$ - CF_3I mixtures on (a) the hexamethylphosphoramide (HMP) column (0° , flow rate 105.6 ml/min); (b) silicone oil column (25° , flow rate 97.4 ml/min); (c) HMP-silicone combination column in the switching apparatus (0° (HMP) and 25° (silicone), flow rate 104.2 ml/min).

silicone column and the more rapidly moving CF_4 , CH_3F and $\text{C}_2\text{H}_3\text{F}$ components pass on into the HMP column and thence to the detectors.

If now, following elution of $\text{C}_2\text{H}_3\text{F}$, valves 1, 2 and 3 are closed and 4, 5 and 6 opened the direction of gas flow within the HMP column is reversed whilst the flow within the silicone column continues in the same direction. Thus, apart from a short period of flow instability following the column-switch the flow rate remains constant within 1-2% and the CF_3I is eluted with only slightly greater retention volume compared with an analysis using the silicone column alone.

Fig. 2 shows a comparison between chromatograms of mixtures of air, CH_3F , $\text{C}_2\text{H}_3\text{F}$ and CF_3I obtained using the HMP (a) and silicone columns (b) separately and in the column-switching apparatus (c). These analyses were performed using macro-quantities of material and a Gow-Mac thermistor detector.

The degree of separation of CH_3F and $\text{C}_2\text{H}_3\text{F}$ is approximately the same on the separate HMP and silicone columns, and in each case is considerably worse than the separation observed with the series arrangement of these columns.

The CF_3I peak has substantially the same shape on both the silicone and the complex column arrangement whilst the retention volume for this compound appears to have been increased from 1,150 ml to 1,350 ml due to the switching process. This presumably arises because of the time taken to stabilise the flow as the direction of the gas stream in the HMP column is reversed.

In applying this technique generally there appear to be only a few limitations. For example the retention volume of species X (e.g. CF_3I) on the first column A should be great enough to allow the other components of the mixture to elute from column B before X actually enters B. On the other hand if a component is weakly retained on A and strongly (but not irreversibly) retained on B then switching the columns before Y is eluted from B simply causes Y to re-pass through B in the reverse direction and thence through A once more. Provided the correct columns are chosen Y can be made to elute after X.

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1 A. B. LITTLEWOOD, *Gas Chromatography*, Academic Press, New York, London, 1962, p. 219.

2 N. COLEBOURNE, J. F. J. TODD AND R. WOLFGANG, *Chemical Effects of Nuclear Transformations*, Vol I, Intern. At. Energy Agency, Vienna, 1965, p. 149.

3 R. WOLFGANG AND C. F. MACKAY, *Nucleonics*, 16, No. 10 (1958) 69.

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