Notes

CHROM. 4371

The use of high-efficiency packed columns for gas–solid chromatography

I. The complete separation of $^{14}N_2$–$^{15}N_2$

In the last few years, several isotopic pairs were separated in our laboratory, either by means of partition or by adsorption gas chromatography[1,2]. All these studies were carried out with glass capillary columns. The good results obtained for some isotopic systems[3] encouraged us to try gas chromatographic separation of isotopes on a semipreparative scale. This paper reports the first results in this direction. The system investigated is $^{14}N_2$–$^{15}N_2$, a partial separation of which was already obtained using glass capillary adsorption columns[4].

It is well known that the isotope effect in systems other than deuterium-substituted compounds is appreciable only at very low temperature. Moreover, the capacity ratio of the substance eluted must have a value around 10 in order to use the column efficiency completely. These conditions were achieved by using Graphon, a partially graphitized carbon black kindly furnished by Cabot Corp., as adsorption medium and working at 77°K. In order to avoid peak tailing, a slight deactivation was necessary even at room temperature. This was accomplished by treating the adsorbent with a small amount of squalane (1‰ w/v), distributed on the surface in a very thin and uniform layer. Nitrogen was strongly retained at the temperature of liquid nitrogen so that a further deactivation was necessary. This was done by using a mixture of CO and H_2 as carrier gas. CO was more strongly adsorbed and acted as a mobile deactivator. Experiments were made to test oxygen, argon and methane as deactivators, but the results obtained were unsatisfactory.

A Carlo Erba Model AtC/f gas chromatograph equipped with a thermal conductivity cell was used. The apparatus was modified for low-temperature work by connecting the cell to the column, fitted in a large dewar container with two narrow copper tubings of negligible volume. The gas line was also modified to allow mixing of the

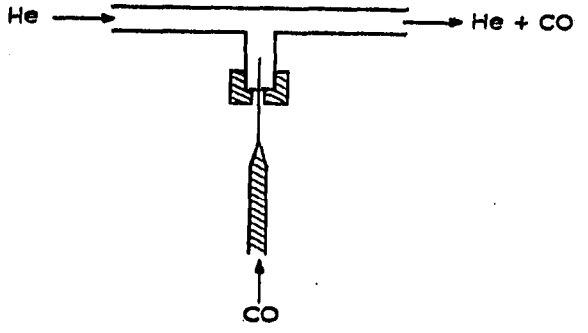

Fig. 1. Scheme of the mixing device.

carrier gas and the deactivating gas before entering the reference arm of the cell and the column. Mixing was effected by inserting in the carrier gas line a steel needle connected through a capillary to the cylinder of the deactivating gas. The scheme of the mixing device is shown in Fig. 1. The flow of the two gases was monitored by two rotameters before the mixing point, while the total flow rate was measured at the end of the column.

Columns were made of copper tubings each 15 m long. They were packed separately, tested and sealed together to the desired length of 60 m. The total number of theoretical plates, measured on the nitrogen peak was 45 000 with a linear gas velocity of 1.6 cm/sec where the minimum HETP was obtained. Such a low value of the linear gas velocity can be explained by the fact that at low temperature the diffusion is low so that the minimum of the Van Deemter curve is shifted towards the low velocities.

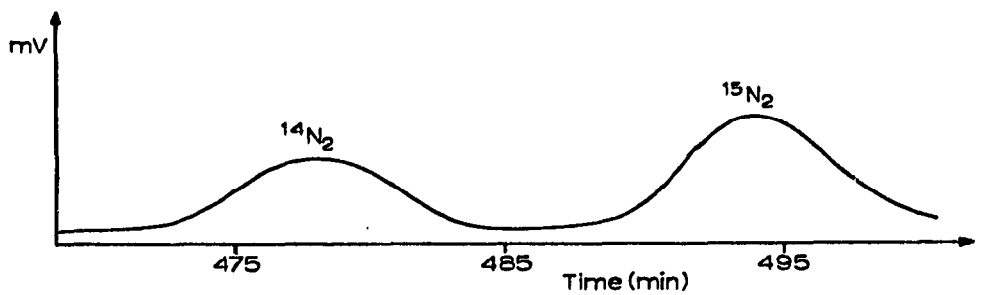

Fig. 2. Gas chromatographic separation of nitrogen isotopes. Column, 60 m × 4 mm I.D.; temp., 77°K; inlet pressure, 1.7 atm; flow rate, 75 ml/min.

Under these conditions the chromatogram shown in Fig. 2 was obtained. The sample injected was 0.2 cc. Resolution was 1.2 and the ratio of corrected retention volumes was 1.03, which shows that under our conditions an unusually large isotope effect takes place.

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