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### Simple chromatographic separation of *para*- and *ortho*-hydrogen and -deuterium

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From time to time the need arises to analyse the relative *para* and *ortho* concentrations of hydrogen and deuterium. The most satisfactory method of analysis is by the chromatographic separation of the spin isomers, and numerous such spin separations have been reported since the original work of Moore and Ward<sup>1</sup>, and Van Hook and Emmett<sup>2</sup>. The best separations have been obtained with glass capillary columns operating at 77°K (ref. 3), or at lower temperatures<sup>4,5</sup>. However, glass capillary columns have a number of drawbacks. They require special etching before they are suited to this particular application, and they seem to turn into relatively expensive and complex systems.

An inherently simple technique involves the use of a copper column filled with activated alumina and operated in a bath of liquid nitrogen. Le Roy and co-workers<sup>6–8</sup> have used such a column with *n*-H<sub>2</sub> as the carrier. They have obtained partial separations of deuterium and were able to detect the excess *para*-hydrogen in a sample. A generally similar alumina system has been reported by Van Urk and Lindner<sup>9</sup> who used *n*-H<sub>2</sub> as the carrier gas for a partial separation of deuterium and a Ne–He mixture as the carrier gas for a complete separation of hydrogen. Quickert and Le Roy<sup>7</sup> have given a detailed analysis of the characteristics of their chromatographic separation system. A typical retention time for deuterium was approximately 7 min. and the separation factor for the partially resolved *p*-<sup>2</sup>H<sub>2</sub>/*o*-<sup>2</sup>H<sub>2</sub> peaks was about 1.1. Such alumina columns have a relatively high pressure drop (about 12 p.s.i.) at relatively low flow-rates (50 ml/min) and require a stable gas flow.

During the experiments reported here, an attempt was made to reproduce the previous results for alumina columns<sup>6,9</sup> using different mesh sizes of commercial chromatographic grade alumina. Only partial success was obtained and the separations (of *para*- and *ortho*-hydrogen, for example, using a He–Ne carrier) seemed to be dependent on individual samples of alumina as if random impurities were present in different batches of the alumina. The results were characterized by incomplete separations, shifting baselines, and long separation times. (A variety of other commercially available columns<sup>8</sup> packing was also tried, such as etched glass microspheres, with no success.)

A batch of 28–32 mesh alumina was prepared using as starting material irregular hunks (3–4 mesh) of commercial alumina. Particular care was taken to avoid the presence of ferromagnetic impurities which might act as a catalyst on the spin

isomers. The final alumina powder was poured into a new tube of soft copper, 4 m  $\times$  5/32 in. I.D. The copper tube was then wound into a column and baked for 48 h at 475°C with nitrogen (99.9% purity) flowing through the alumina.

Before an experiment on hydrogen or deuterium separation, the activated column was flushed at room temperature with the particular carrier gas to be employed and then immersed in a bath of liquid nitrogen. Signal detection was by a thermal conductivity detector (consisting of a bridge of four Gow-Mac tungsten filaments; bridge current 250 mA) which was also immersed in the liquid nitrogen bath.

Excellent separations of deuterium were obtained using hydrogen as a carrier, and of hydrogen using deuterium as a carrier; typical recorder traces are shown in Fig. 1a and b. The observed separation factors were 1.23 for  $o\text{-H}_2/p\text{-H}_2$  ( $n\text{-}^2\text{H}_2$  carrier) and 1.55 for  $p\text{-}^2\text{H}_2/o\text{-}^2\text{H}_2$  ( $n\text{-H}_2$  carrier). These separation factors compare favourably with those observed using glass capillary columns at lower temperatures<sup>3,4</sup>. In the present experiments the carrier gas flow-rate was set in the range of 12 to 14 ml/sec, which required a pressure drop of 4 to 5 p.s.i. across the column. The total time of analysis was about 150 sec, much faster than previously reported.

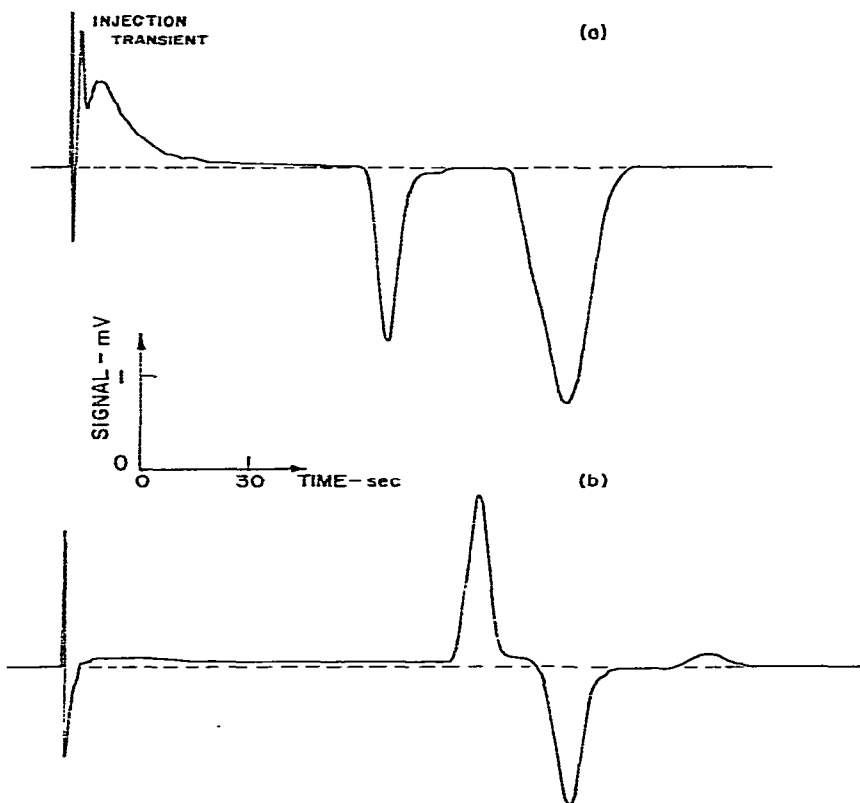


Fig. 1. (a). Separation at 77°K of  $n\text{-}^2\text{H}_2$  in an alumina column using  $n\text{-H}_2$  as the carrier gas. (b). Separation at 77°K of  $n\text{-H}_2$  in the same column as for (a), using  $n\text{-}^2\text{H}_2$  as the carrier gas. In both cases the thermal conductivity detector was at 77°K.

Separations were also attempted using He and a Ne-He mixture as carrier gases. The helium carrier provided a separation for hydrogen (but not for deuterium), but with highly distorted hydrogen peaks. The Ne-He carrier gas gave a clear separation for hydrogen, with some tailing of the peaks, but none for deuterium. Both of these carrier gases required a much higher pressure drop across the column, even at lower flow-rates, and it seemed to be the relatively high pressures which obviated the deuterium separation.

There did not seem to be any obvious characteristic of the various aluminas which made them suitable for this application. However, successful columns were easily identified by the large amount of hydrogen (or deuterium) carrier adsorbed during cooldown, as noticed previously by Quickert and Le Roy<sup>7</sup>. The cooldown adsorption was characteristic of a good column whatever the grain size of the alumina; the best overall results, however, were obtained when the column was able to operate at high carrier flow-rates and with small pressure drops.

It may seem surprising to use deuterium gas as the carrier in a chromatographic experiment, but the net expense was about the same as that for the Ne-He carrier. The column reported here was also suited for the detection of excess  $p$ -H<sub>2</sub>, using  $n$ -H<sub>2</sub> as the carrier (after Schultz and Le Roy<sup>6</sup>), but the sensitivity was reduced and there seemed to be no particular advantage to the technique. The immersion of the detector in the bath of liquid nitrogen gives an important improvement in sensitivity. The column response becomes non-linear with respect to relative spin isomer concentration, and calibration is required. Immersion in a bath of ethanol and dry ice also gives excellent sensitivity, but an undesirable baseline drift which arises apparently from gradual changes in the temperature of the bath. The column was also tested in an external magnetic field of about 1 kG, with no noticeable change in its performance.

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