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Gas-Chromatographic Analysis of Mixtures of Hydrogen Isotopes Using Different Samples Loops

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In this paper, the analysis of different mixtures of hydrogen isotopes using capillary molecular sieve 5 Å column and different sample loops are reported. It is realized a comparative study to develop or improve existing methods for the qualitative and quantitative determination of the composition of gas mixtures of hydrogen isotopes. The results are presented in chromatograms for different H_2, HD, D_2 mixtures and different operated parameters.

Key Words: Gas chromatography, Pulsed discharge helium ionization detector, 5 Å molecular sieve, Sample loops.

INTRODUCTION

Chromatography is unique in the history of analytical methodology and is probably the most and versatile technique available to the modern analyst. In a single procedure it can separate a mixture into its individual components and simultaneously determine quantitatively the amount of each component[1]. The samples may be gaseous, liquid or solid in nature and may range in complexity from a single substance to a multicomponent mixture containing widely differing chemical species.

All chromatographic separations are carried out using a mobile and a stationary phase. As a result of this prerequisite, the primary classification of chromatography is based on a physical nature of the mobile phase. Thus, all separation processes that utilize a gas as the mobile phase are classed as gas chromatography.

Gas chromatography separation of hydrogen isotopes have been reported in the literature dating[2] from the late 1950's. Basically, three approaches have been employed to effect separations on an analytical scale and these approaches may be distinguished on the basis of the column packing material used.

The species isotopic of hydrogen are: H_2, D_2, T_2, HD, HT, DT. Molecular hydrogen can occur as H_2, D_2, T_2, HD, HT, DT, ortho-H_2, para-H_2, ortho-D_2 or para-D_2, where

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D stands for ^2H and T for ^3H. The separation of hydrogen isotopes is generally easy, for their physical properties differ considerably. In all the cases the order of elution is the order of volatility, with H_2 first and D_2 last. Molecular hydrogen occurs in two isomeric forms, namely with its two proton spins aligned either parallel (ortho-hydrogen) or antiparallel (para-hydrogen). In the state of thermal equilibrium at room temperature dihydrogen contains 25 % of para-hydrogen (nuclear singlet state) and 75 % of ortho-hydrogen (nuclear triplet state). Ortho- and para-hydrogen may easily be separated on column of molecular sieve. In all cases, the para-form appears before the ortho-form. Ortho- and para-deuterium are not so easily separated[3]. Normal deuterium contains 66 % ortho-deuterium and 33 % para-deuterium.

EXPERIMENTAL

The gas chromatograph employed in this work was a type 3800 from Varian Analytical Instrument. The Varian 3800 gas-chromatograph is equipped with a capillary molecular sieve 5 Å column with following characteristics: The length of the GC column is: 75 m; The inside diameter of the GC column is: 0.32 mm; The film thickness of the GC column is: 30 mm.

A Pulsed Discharge Helium Ionization Detector (PDHID) is used as detector. The temperature of the filament of detector was fixed at 200 ºC. The carrier gas used was: Helium (99,999 % purity). It is recommended that a quality grade of helium 5.0 (99,999 % pure or better) be used at all times. The sample loops used for these analysis was: 5, 50 µL. The operating temperature of the GC column for these experiments was -99 and -75 ºC. The temperature of the oven of the GC column was maintained in the range of 0 °C to -99 °C, by spraying liquid nitrogen into the oven. A temperature controller to control the liquid nitrogen flow and the heater was used[4].

RESULTS AND DISCUSSION

For the analysis of gas mixtures containing hydrogen isotopes, the analysis of two sample of mixtures of hydrogen isotopes with different concentration, using temperature of the oven column at -99 and -75 ºC and different sample loops: 5 and 50 µL are presented.

The first sample has 5 % concentration of deuterium in the hydrogen isotopes mixture and the second sample has 50 % concentration of deuterium in the hydrogen isotopes mixture. The method used was calibrated with standard gas of protium and deuterium by external standard calibration type.

A comparative study is presented between gas chromatograms obtained using different sample loops and different temperature of the oven column. The gas chromatograph column was conditioned before use for the separate of the hydrogen isotopes mixtures. Next 2 chromatograms presented the analysis of the sample number 1 and 2 using 5 µL sample loop.

The method described in this was based on using a capillary molecular sieve 5 Å column which has been operated at -99 ºC. In Figs. 1. and 2, a good separation of the mixture of the isotopes species of the hydrogen for the sample number 1 and sample number 2 can be observed.

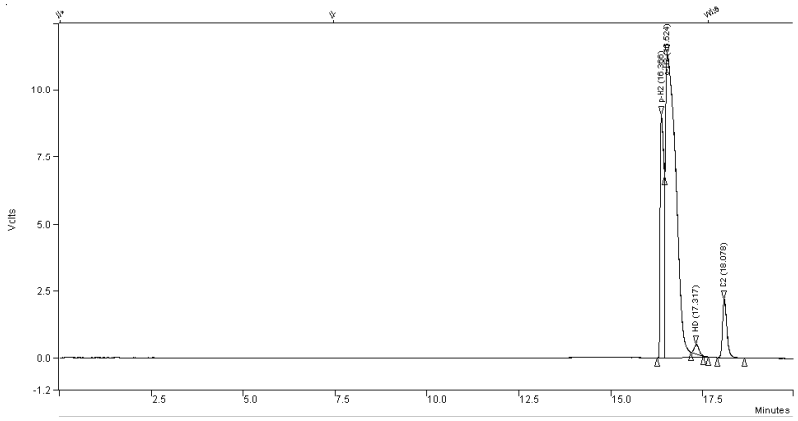

Fig. 1. Chromatogram of sample 1 at -99 ºC temperature of column and 5 µL sample loop

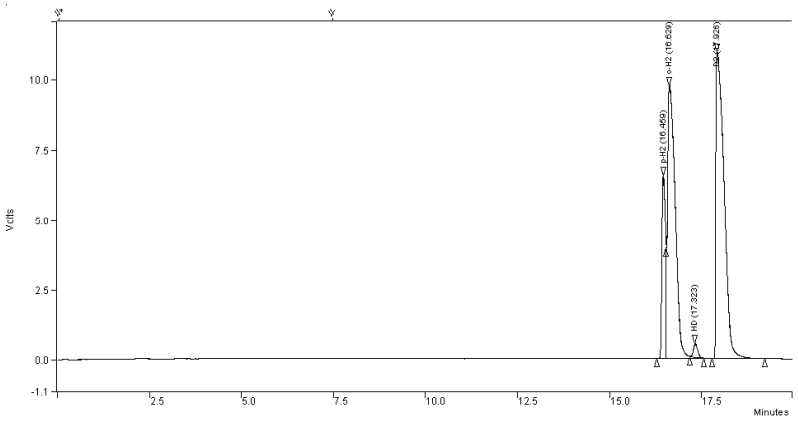

Fig. 2. Chromatogram of sample 2 at -99 ºC temperature of column and 5 µL sample loop

It is also a good separation of the two isomeric forms of hydrogen, ortho-hydrogen and parahydrogen. In both cases, the carrier flow rate was 4.1 mL/min, the linear velocity was 31.9 cm/s and the pressure was 15 psi. The retention times were about 17-19 min.

In Figs. 3 and 4, a bad separation is also observed using the 50 µL sample loop. In these analysis, the same temperature of the oven column is operated but another sample loop is used. In Fig. 3, a separation for the next species of hydrogen: HD and ortho-hydrogen and para-hydrogen can not be observed but in Fig. 4, a bad separation of these species are observed.

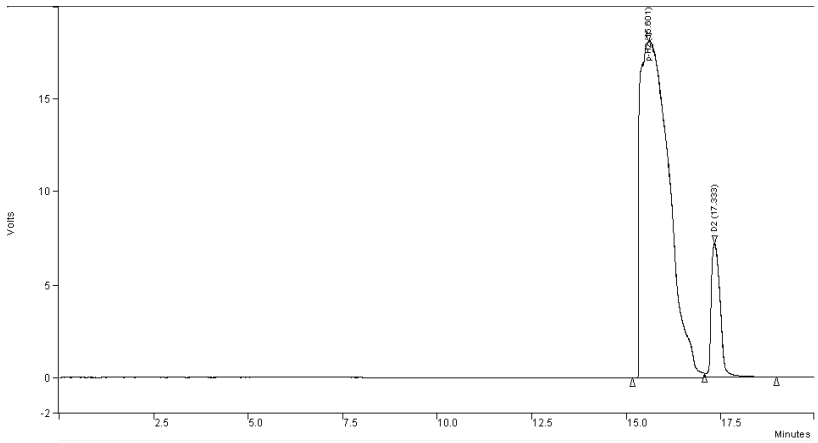

Fig. 3. Chromatogram of sample 1 at -99 ºC temperature of column and 50 µL sample loop

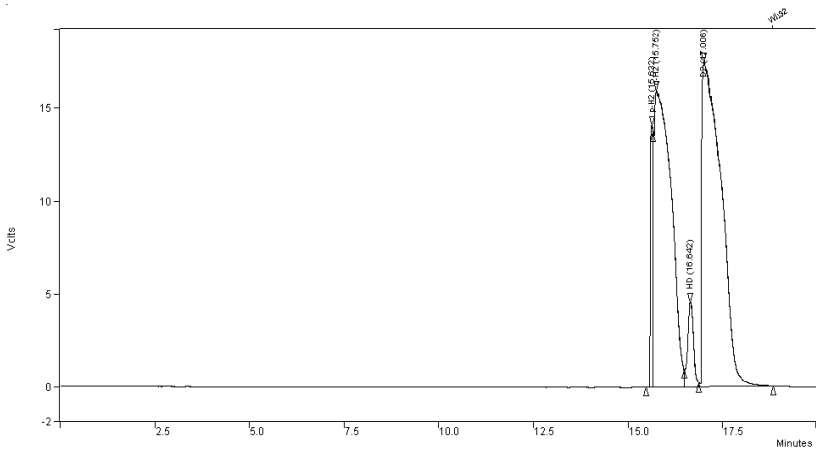

Fig. 4. Chromatogram of sample 2 at -99 ºC temperature of column and 50 µL sample loop

In all cases, the carrier flow rate was 4.1 mL/min, the linear velocity was 31.9 cm/s and the pressure was 15 psi. The retention times were about 17-19 min.

Figs. 5 and 6 presented the analysis of the samples number 1 and 2 using 5 µL sample loop and at -75 ºC temperature of oven column.

Figs. 7 and 8 presented the analysis of samples number 1 and number 2 using 50 µL sample loop and at -75 ºC temperature of oven column.

The method described in this was based on using a capillary molecular sieve 5 Å column which has been operated at -75 ºC.

In all cases, one can observed a bad separation of the mixture of hydrogen isotopes at this temperature of oven column. At -75 ºC temperature of column, the carrier flow rate was 3.4 mL/min, the linear velocity was 29.7 cm/s and the pressure was 15 psi.

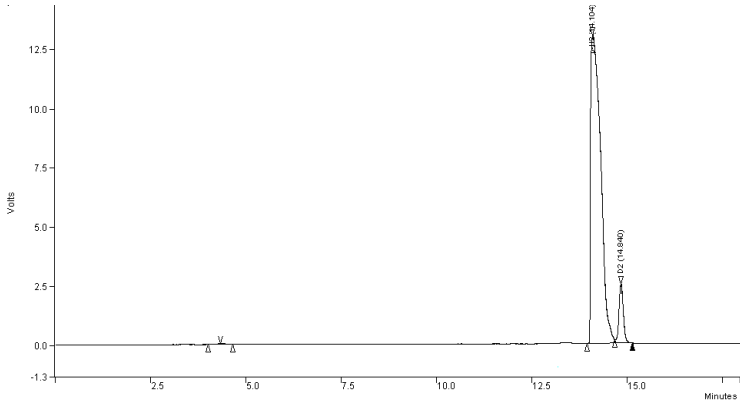

Fig. 5. Chromatogram of sample 1 at -75 ºC temperature of column and 5 µL sample loop

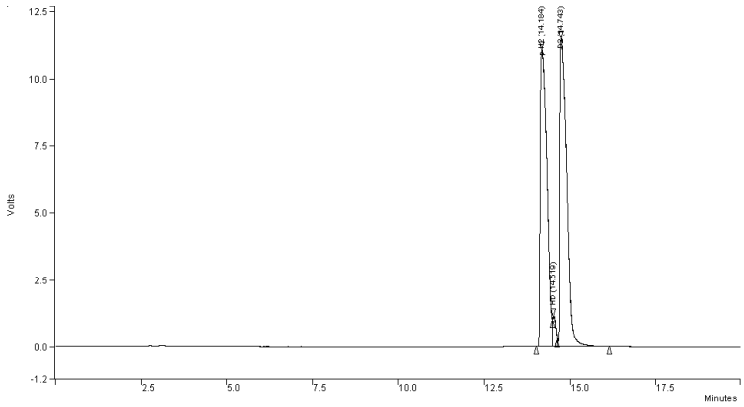

Fig. 6. Chromatogram of sample 2 at -75 ºC temperature of column and 5 µL sample loop

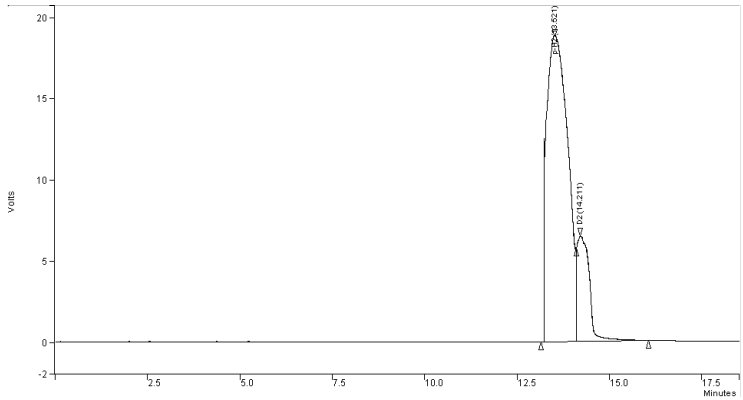

Fig. 7. Chromatogram of sample 1 at -75 ºC temperature of column and 50 µL sample loop

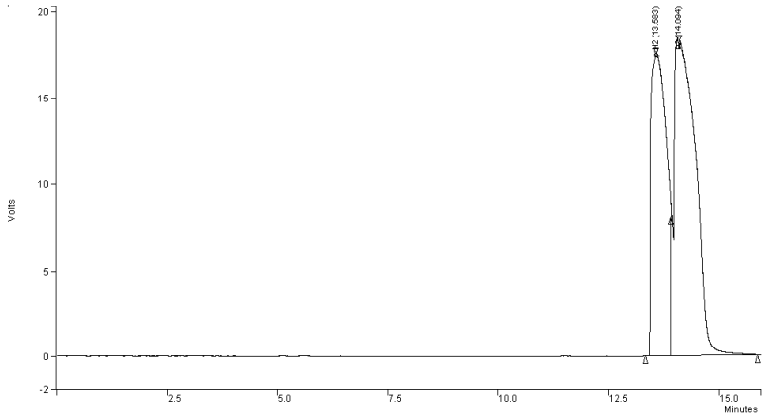

Fig. 8. Chromatogram of sample 2 at -75 ºC temperature of column and 50 µL sample loop

Conclusion

In this paper, one can observed an unsatisfying separation of isotopic species of hydrogen at -75 ºC temperature of column and a good separation of isotopic species of hydrogen at -99 ºC temperature of column. Also, a good separation of the two isomeric forms of hydrogen, ortho-hydrogen and para-hydrogen are observed at -99 ºC and 5 µL sample loop.

Between these two sample loops used, a good separation was obtained using 5 µL sample loop. Conclusively, the good method is based on using a capillary molecular sieve 5 Å column which has operated at -99 ºC and using 5 µL sample loop.

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