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Note

Quantitative gas chromatographic analysis of hydrogen isotopes, H_2, H^2H and $^2H_2$, with a reduction gas detector

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Standard mass chromatographic instruments cannot accurately analyze a gas sample for the stable gaseous isotopes of hydrogen [H_2, deuterium ($^2H_2$) and H^2H]. A few papers have described gas chromatographic (GC) techniques which can separate and detect these isotope[1–7]. However, for the most part these techniques can measure only high concentrations of these compounds[4–7] and often require pre-concentration or pre-purification of the sample prior to analysis. In this paper, we present a simple, sensitive and accurate GC method for the assay of trace amount of H_2, H^2H and $^2H_2$ which eliminates the need for pre-treatment of the sample.

EXPERIMENTAL

Reagents and chemicals

Deuterium was obtained from Union Carbide (New York, NY, U.S.A.) and hydrogen from Matheson (East Rutherford, NJ, U.S.A.). H^2H was prepared as described below.

Instrumentation

A Beckman Model GC-55 gas chromatograph equipped with a Model RG D-2 reduction gas detector (Trace Analytical, Menlo Park, CA, U.S.A.), a gas sampling loop (capacity 0.18 cm^3), a cryogenic unit and an HP 7100B recorder (Hewlett Packard, Avondale, PA, U.S.A.) was used. Separation was obtained via a 12 ft. × 3/16 in. copper column (I.D. 2 mm) containing molecular sieve 4A (60–80 mesh) (Alltech Assoc., Deerfield, IL, U.S.A.). The cryogenic unit consisted of an inner cylinder within a large Dewar flask which was filled with liquid nitrogen. The column was placed in the inner cylinder. The temperature of the column was maintained at -180 ± 2°C by varying the flow of air and/or nitrogen into the inner chamber. The column was pre-conditioned overnight at 250°C with helium as the carrier gas. Helium was used as the carrier gas and the column flow-rate was 24 ml/min; the helium was pre-purified by passage through a silica gel–molecular sieve 5A trap (Analabs, North Haven, CT, U.S.A.) and a catalytic combustion filter (Trace Analytical).

Quantitation

H_2 and $^2H_2$ were diluted with either nitrogen or helium to appropriate con-

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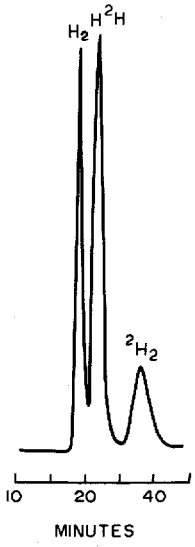

Fig. 1. GC Separation of H_2, H^2H and $^2H_2$ on a molecular sieve 4A column. Flow-rate: 24 ml/min.

centrations and applied directly to the GC column. H^2H was prepared by equilibration of a known mixture of H_2 and $^2H_2$ by means of a tungsten filament heated to red heat for 5 min[5]. This was accomplished by installing a port-hole in a 40-W electric light bulb. The port-hole was sealed with a rubber stopper and the bulb flushed with nitrogen. A mixture of H_2 and $^2H_2$ was then introduced into the bulb via a large syringe and ignited as above. Aliquots of the equilibrium mixture were removed from the bulb with a syringe and injected into the GC column. Quantitation of H_2, H^2H and $^2H_2$ was obtained by triangulation of the respective peak areas. Calibration of H^2H was accomplished with the equilibration mixture equation of the isotopes according to Genty and Schott[5].

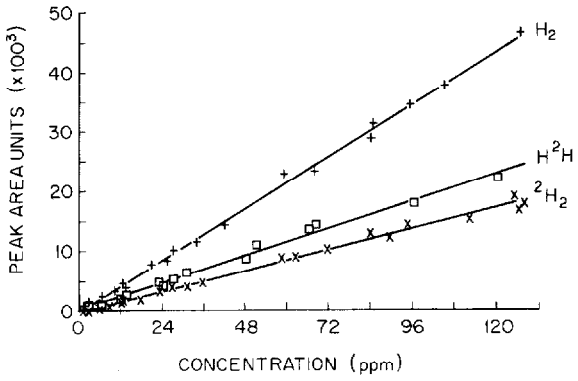

Fig. 2. Calibration curves for H_2, H^2H and $^2H_2$.

RESULTS

A typical separation of H_2, H^2H and $^2H_2$ is depicted in Fig. 1. The identities of H_2 and $^2H_2$ were confirmed by comparison with the results of prior injections of pure H_2 or $^2H_2$. Separation of these isotopes was dependent on the maintenance of the column at near liquid nitrogen temperatures. At higher temperatures (-165 to -170°C), H_2 was adequately separated from $^2H_2$ but H^2H was not separated from H_2. A similar separation could not be obtained when nitrogen or argon was used as the carrier gas.

Fig. 2 shows the excellent sensitivity and linear response of the reduction detector to varying concentrations of the isotopes. The correlation coefficients of H_2, H^2H and $^2H_2$ were 0.998, 0.994, and 0.996, respectively, for concentration ranges from 0 to 120 ppm.

DISCUSSION

Most previous GC techniques for assaying hydrogen isotopes have utilized columns packed with alumina treated with iron(III) hydroxide[2,3,5] or etched glass beads[6,7]; however, the preparation of these supports requires special attention in order to achieve efficient separation[5]. In contrast, molecular sieve 4A requires little preparation and achieves good separation of the hydrogen isotopes. A similar good separation of hydrogen isotopes on molecular sieve has been reported previously by Conti and Lesimple[4].

The separation requires temperatures of about -180°C, because at higher temperatures H_2 is not distinguished from H^2H. The necessity for maintaining the column temperature at approximately -180°C requires that helium rather than nitrogen or argon be used as the carrier gas, as attempts to employ the latter at lower temperatures failed to yield adequate separations.

The detector commonly employed in the GC analysis of hydrogen is the thermal conductivity detector. Unfortunately, the similar thermal conductivities of hydrogen and helium render this detector very insensitive to hydrogen when helium is used as the carrier gas. Although the sensitivity is much greater when argon or nitrogen is used as the carrier gas, these gases cannot be employed at the temperatures required for the separation of the isotopes of hydrogen. For this reason, pre-concentration of samples containing low concentrations of hydrogen isotopes has been utilized in previous work[4,5,7] employing a thermal conductivity detector.

The reduction detector employed in this work has several advantages over the thermal conductivity detector. The sensitivity of the reduction detector is not influenced by the carrier gas, thus permitting the use of helium. This detector also is more sensitive to H_2, $^2H_2$ and H^2H than is the standard thermal conductivity detector (even under optimal conditions) and therefore no pre-concentration of samples is required. Lastly, hydrogen and carbon monoxide are the only gases commonly found in biological systems which are detected by the reduction detector. Thus gases such as methane which may elute with the hydrogen isotopes at -180°C are not detected by the reduction detector. In contrast, initial purification procedures may be required in order to eliminate methane and other gases that elute with the hydrogen isotopes when the thermal conductivity detector is employed.

The method described utilizes relatively inexpensive and simple GC equipment to measure the stable isotopes of hydrogen. The technique provides accurate, reproducible results with greater sensitivity than that obtained in previous work.

REFERENCES

1 C. O. Thomas and H. A. Smith, *J. Phys. Chem.*, 63 (1959) 427.
2 W. R. Moore and H. R. Ward, *J. Phys. Chem.*, 64 (1960) 832.
3 J. King, *J. Phys. Chem.*, 67 (1963) 1397.
4 M. L. Conti and M. Lesimple, *J. Chromatogr.*, 29 (1967) 32.
5 C. Genty and R. Schott, *Anal. Chem.*, 42 (1970) 7.
6 T. Gaumann, O. Piringer and A. Weber, *Chimia*, 24 (1970) 112.
7 M. Neumann-Spallart, *Anal. Chem.*, 54 (1982) 826.