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Gas chromatography for measurement of hydrogen isotopes at tritium processing

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ABSTRACT

Analysis characteristics of the hydrogen isotopes H_2, HD, HT, D_2, DT and T_2 were experimentally studied using gas chromatography. A liquid nitrogen cooling column was employed for isotope separation, along with a thermal conductivity detector and a small-volume ionization chamber. The intensity ratio of the six hydrogen isotopes as measured by the thermal conductivity detection was H_2:HD:HT:D_2:DT:T_2 = 100:73:61:57:49:43. When the sampling volume was 1 cm^3, the estimated detection limits for H_2 and T_2 were, respectively, 20 and 50 Pa partial pressure and 200 and 500 ppm concentration. The 0.16-cm^3 ionization chamber could measure only the tritiated molecules, and the estimated detection limit for T_2 gas was 1 ppm. The retention time was reduced when the concentration was greater than 1%. In particular, when it was increased above 10%, identification of neighboring peaks tended to be difficult.

INTRODUCTION

To develop a fusion fuel gas-processing technology, various experimental studies have been performed in the Tritium Process Laboratory (TPL) [1] at the Japan Atomic Energy Research Institute (JAERI). To analyze experimental gases, including tritium, an analysis and measurement system (AMS) is installed in the TPL. Gas chromatography (GC) has conventionally been used as the gas analyzer, with the fundamental measurement method for isotopes of molecular hydrogen [2]. Primary studies have been performed by Moore and Ward [3] using non-radioactive hydrogen isotopes such as H_2, HD and D_2. They have separated not only hydrogen and deuterium but also their nuclear spin isomers on alumina at -196°C. While the separation of the p-H_2 and o-H_2 from o-D_2 and p-D_2 can be accomplished, the o-H_2 peak overlaps or is very close to the HD peak [4–6]. However, to analyze quantitatively only hydrogen isotope gases, the separation of isomers becomes rather a hindrance. Fujita and Kwan [6] reported that nuclear spin isomers can be separated only when catalysts causing their equilibration at the temperature used are absent. When a catalyst is present, both spin isomers are eluted as a single zone corresponding to the average of the two isomers. A suitable catalyst of column packing, activated alumina covered with ferric hydroxide or manganese chloride, and carrier gas, neon, have been identified [6,7].

Many experimental reports have described H_2, HD and D_2, but only a few have provided an analytical study of hydrogen isotopes including tritium [7–9]. Genty and Schott [7] reported quantitative analysis of hydrogen isotopes, H_2, D_2, T_2, HD, HT and DT, as a mixed gas.

Although the principal method for the analysis of hydrogen isotopes has been established, the following characteristics still require clarification: those to measure high-concentration tritium and other hydrogen isotopic mixed gases, which constitute fusion fuel gas; and those to identify all six hydrogen isotopes in various ratios. Therefore we experi-

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mentally measured the hydrogen isotopic mixed gases by GC and tried to identify and obtain their measurement characteristics.

EXPERIMENTAL

Tritium and tritiated isotopic gas analyses have been performed using GC in the analysis and measurement system (AMS) of the TPL. The AMS is made up of four gas-handling lines for: (1) preparation of isotopically equilibrated hydrogen isotopes; (2) the ionization chamber test; (3) isotopic hydrogen gas recovery by metal beds; and (4) analysis by GC [7]. Fig. 1 shows the AMS flow system, in which experimental gases were prepared. At first the vessel was filled with pure H_2, D_2 and T_2 gases. The purities of these isotopic hydrogen molecules were more than 99.9% for H_2, more than 99% for D_2 and about 99% for T_2. Then a fixed volume of the pure gas was sampled and analyzed by GC. Next, three gaseous mixtures of pure isotopic hydrogen, H_2–D_2, H_2–T_2 and D_2–T_2, each in a ratio of 1:1, were prepared. These gas mixtures were passed through an isotopic equilibrator packed with platinum black-coated alumina catalyst. The equilibrator temperature was about 295 K. Three hydrogen species, HD, HT and DT, were produced accordingly by the isotopic exchange reaction.

Fig. 2 show the experimental flow line for GC. Four sampling tube volumes were possible: 1, 5, 10 or 20 cm^3. The volume chosen depended on the gas concentration. In this study, the 1-cm^3 sampling tube was selected, because it was expected to give less radioactive waste gas. Neon was used as the carrier gas.

Sampled gas was carried to the chromatography column packed with manganese chloride-coated alumina particles (Yanako Hydroisopack, made by Yanagimoto Kogyo). The column was kept cold using liquid nitrogen. At the same time only the carrier gas was passed to the reference column, which was heated up to 120°C. After passing through the column, the gas was detected with the thermal conductivity detector (TCD), and then the tritium concentration was measured using an ionization chamber. There were two ionization chambers having volumes of about 0.16 and 21.6 cm^3. The characteristics of these ionization chamber are reported elsewhere [10]. We used the smaller ionization chamber, because the holding time of the detecting gas was short and sharp peaks could be obtained. The analyzed gas was carried to the effluent tritium gas removal system (ERS) at the TPL. Most of the remaining experimental gas was recovered by a metal bed, in which isotopic hydrogen gas getter was packed. Experimental conditions are summarized in Table I.

RESULTS AND DISCUSSION

Gas chromatograms of hydrogen isotopes

Fig. 3 shows gas chromatograms measured with

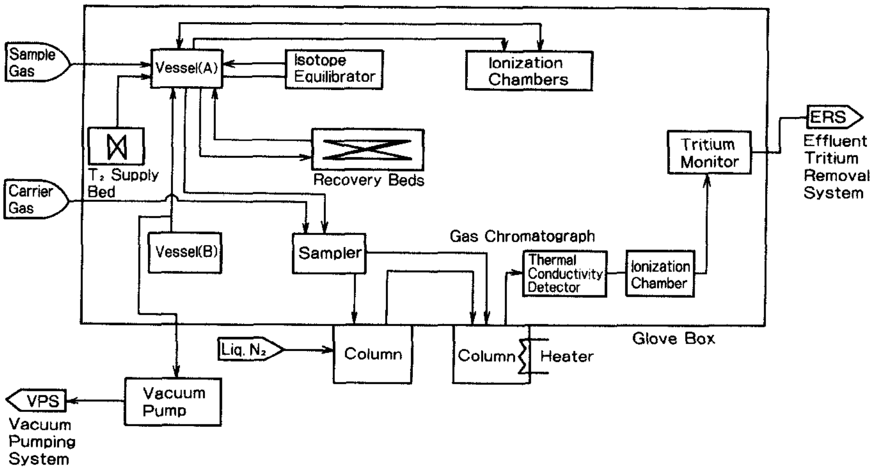

Fig. 1. Flow diagram of experimental gas preparation line. This loop is the AMS installed at the TPL.

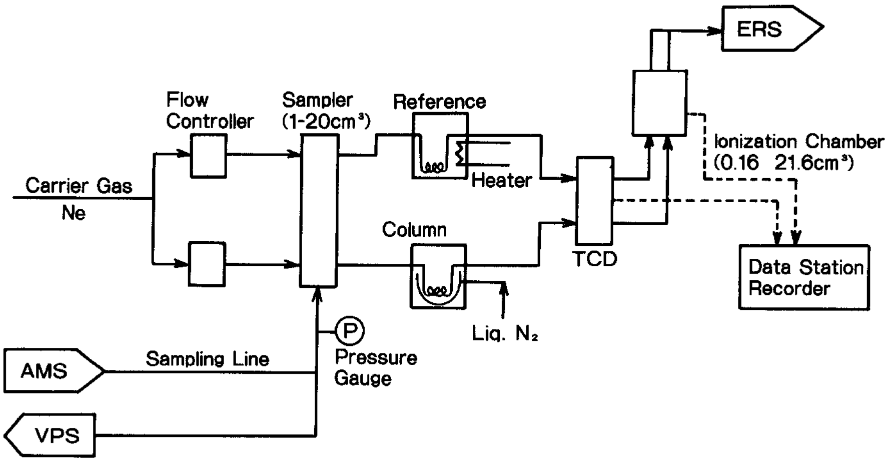

Fig. 2. Flow diagram of gas chromatography for hydrogen isotopes analysis.

the TCD for pure H_2, D_2 and T_2 gases. The gas chromatogram of H_2 does not show peaks of other molecular hydrogen isotopes. In the D_2 gas chromatogram, a small HD peak was detected as an impurity. The D_2:HD peak-area ratio was 99.54:0.46. On the other hand, pure T_2 gas includes HT, as well as a little helium and a trace of H_2. The T_2:HT peak-area ratio obtained was 98.6:1.4. The source of hydrogen is considered to be residual gas in the process line or at the metal bed, because pure H_2 gas was used previously to activate the metal.

Fig. 4 shows a gas chromatogram of pure T_2 gas at 1.8 kPa. The upper chromatogram was measured with the 0.16-cm³ ionization chamber and the lower with the TCD. When the partial pressure of T_2 gas sample is low and its peak height is small, a peak for the impurity DT is observed. When the T_2 gas pressure is high, the DT peak might be hidden by the T_2 peak. Fig. 5 shows gas chromatograms of the mixture of H_2, D_2 and T_2 gases after passing through the equilibrator. The six isotopes of molecular hydrogen can be detected individually with the TCD. On the other hand, only the three tritium-bonding hydrogen molecules, T_2, HT and DT, are detected with the ionization chamber.

TABLE I

EXPERIMENTAL CONDITIONS OF GAS CHROMATOGRAPHY FOR HYDROGEN ISOTOPES ANALYSIS

Specification of analyzer	Measurement conditions
Column diameter, 1/8 in.	Carrier gas, neon
Length, 3 m	Carrier gas flow-rate, 50 cm³/min
Absorber, manganese chloride-coated alumina (Yanako Hydroisopack)	Sampling gas volume, 1 cm³
	Column temperature, 77 K
Detector, TCD, ionization chamber (effective volume 0.16 cm³)	TCD temperature, 393 K
	Filament current, 70 mA
	Ionization chamber, applied voltage, 40 V; electric field strength, 200 V/cm

Calibration

Fig. 6 shows calibration curves for H_2, HD, HT, D_2, DT and T_2 as plots of partial pressure *versus* TCD intensity. Linearity is confirmed for each isotope of molecular hydrogen. The intensity order is obtained as $H_2 > HD > HT > D_2 > DT > T_2$. Detection limits as measured with the TCD are between 20 and 50 Pa, *i.e.*, between 200 and 500 ppm. Fig. 7 shows linear calibration of the six isotopes of molecular hydrogen obtained with the TCD. The slopes of the lines are the proportional coefficients of TCD sensitivity to partial pressures of isotopic hydrogen gas. Using the individual proportional coefficients the sensitivity ratio obtained is H_2:HD:HT:D_2:DT:T_2 = 100:73:61:57:49:43. This sensitivity ratio should be proportional to the thermal conductivity balance of each hydrogen isotope and neon gas. The thermal conductivities of pure H_2, D_2, T_2 and neon gases are presented in Table II [11–13]. Although the theoretical sensitivity ratio

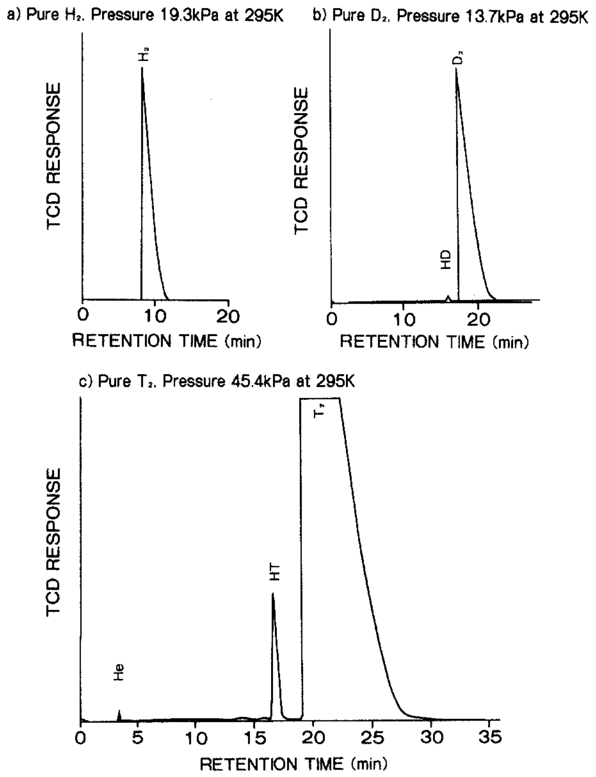

Fig. 3. Gas chromatograms of pure hydrogen isotopes, H_2, D_2 and T_2, obtained with the TCD.

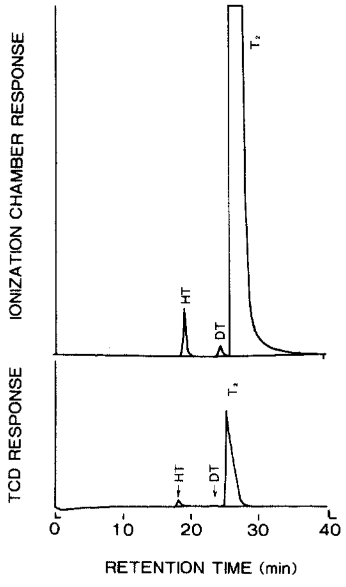

Fig. 4. Gas chromatograms of pure T_2 gas (pressure, 1.8 kPa at 295 K) detected by the 0.16-cm^3 ionization chamber and TCD.

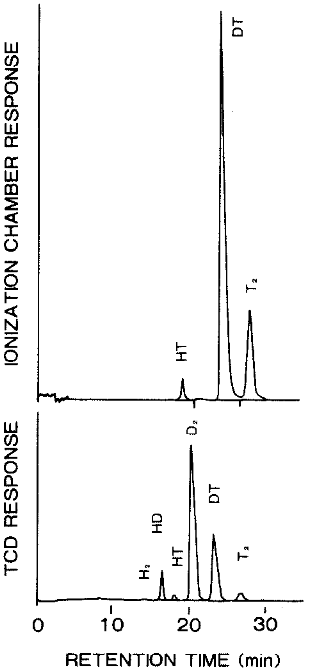

Fig. 5. Gas chromatograms of a mixture of gaseous hydrogen isotopes (pressure, 2.1 kPa at 295 K) detected by the 0.16-cm^3 ionization chamber and TCD. Mixing ratio is H_2:HD:HT:D_2:DT:T_2 = 0.1:4.7:1.4:58.6:30.9:4.4.

is H_2:D_2:T_2 = 100:69:41, the measured ratio is 100:57:43, representing a difference of about 20%. The reason for this is unclear, but it is thought that thermal conduction to the gas layer from the sensor wire is affected by radiation or circulation of flow gas. However, this ratio might be constant for this detector. So this ratio can be used for quantitative analysis of hydrogen isotopes as proportional coefficients. Using this calibration coefficient, the purity of T_2 is estimated to be 99.05% and that of D_2 is 99.6%.

Fig. 8 shows the calibration curves for tritium and tritiated hydrogens in the 0.16-cm^3 ionization chamber. There is a linear relation between partial pressure and ionization current. The detection limit depends on the sensitivity of the ionization chamber and chamber volume, for example when using the 21.6-cm^3 chamber sensitivity might increase, and the retention time would be longer and the peak width would be broadened. For radio-GC, a smaller volume seems to be a better choice. The detection limit for T_2 gas is about 0.1 Pa (1.0 ppm concentra-

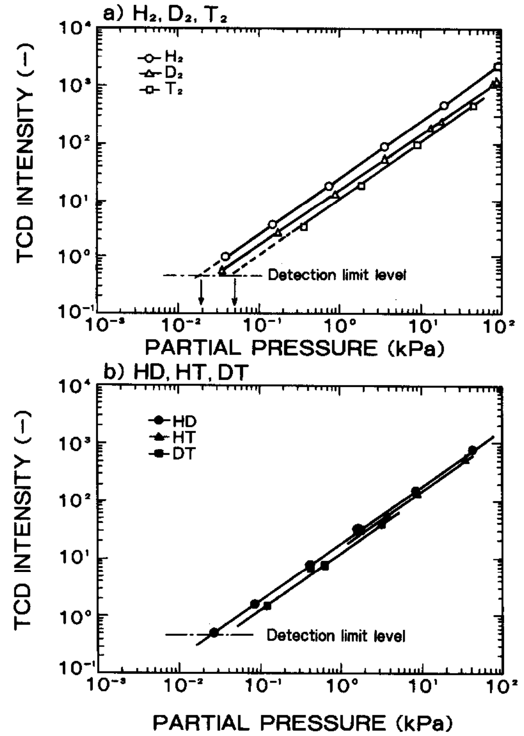

Fig. 6. Relationships between partial pressures of hydrogen isotopes and TCD intensity.

tion and 4.0 · 10^{-10} mol mass). The ionization chamber shows a response to lower concentrations of tritium gas, and the limit can be expected to be lowered by decreasing the noise level. But it is difficult to obtain a higher signal-to-noise ratio because of the memory effect due to contamination inside the chamber.

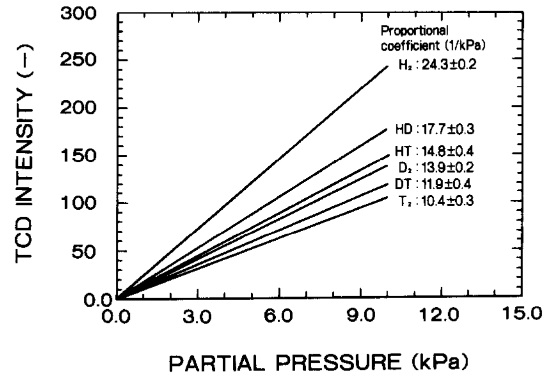

Fig. 7. Proportional coefficients of hydrogen isotopes measured for TCD intensity per unit partial pressure.

TABLE II

THERMAL CONDUCTIVITIES (TC) OF ISOTOPIC HYDROGEN AND CARRIER GASES AT 300 K

Molecular gas	TC (10^{-4} J/s·mK)
H_2	1815
D_2	1406
T_2	1036
Helium	1499
Neon	493

Concentration effect

Generally peak separation ability depends on the retention time interval and peak width. When column conditions are constant, retention time, t_R, is expressed as [14]:

$$t_R = \frac{k \cdot K_A \cdot z}{v} \tag{1}$$

where k is a coefficient, K_A is the adsorption equilibrium coefficient [concentration in adsorption phase (mol/g)/concentration in carrier gas (mol/cm^3)], z is the length of the column bed (cm) and v is the flow-rate of carrier gas (cm/s).

Of course, a long retention time gives a good separation, so it is useful to activate the column packing, *i.e.*, to increase adsorption ability, and to employ a longer column and decreased flow-rate of the carrier gas. In our experiments the same column was used and the flow-rate of carrier gas was fixed. The relationships between partial pressures of hydrogen isotopes and retention times are shown in Fig. 9. On increasing the partial pressure, the retention time is shortened. On the other hand, when the partial pressure is decreased, the retention time gradually becomes longer, and finally it becomes constant at extremely low partial pressure. This means that the adsorption equilibrium coefficient is dependent on partial pressure, *i.e.*, on concentration. It is considered that the ratio of the hydrogen isotopic concentration in the adsorption layer and in the carrier gas layer must be constant at low concentrations. But the ratio might decrease on increasing the objective gas concentration.

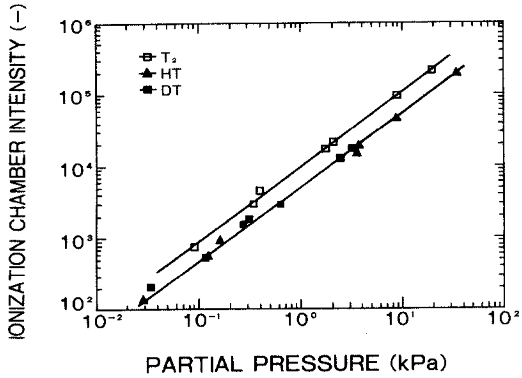

Fig. 8. Relationships between partial pressures of tritiated hydrogen isotopes and the 0.16-cm^3 ionization chamber intensity.

When analyzing a mixed gas of low and high concentrations of hydrogen isotopes, the retention times of both isotopes of hydrogen might overlap. A remarkable shift of retention time occurs at partial pressures above 1 kPa. To avoid peak overlapping, longer retention time would be effective, and the following two methods may be considered. One is to increase the activity of the absorber by aging at high temperature for a long time, and the other is to decrease the carrier gas flow-rate. However, too much aging shortens the life of the column packing and a lower gas flow-rate needs a much longer analysis time, so that more than half an hour would be needed to separate all the isotopes of hydrogen. It then becomes difficult to measure a small amount of one isotopic gas mixed with a large amount of another.

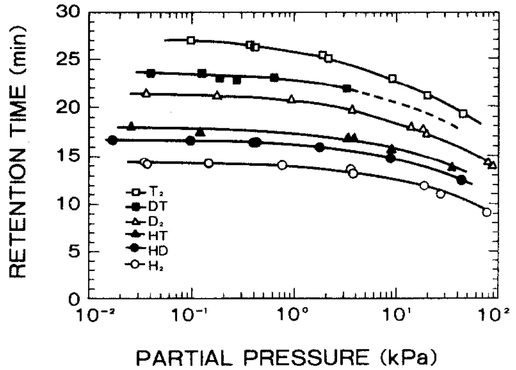

Fig. 9. Effect of hydrogen isotopic gases partial pressures on retention times.

Improvement of detection limits

To apply GC to the tritium gas-processing system, higher sensitivity is required. Generally, GC output *versus* unit concentration gas is expressed as [15]:

$$S = \frac{A \cdot \mathrm{FR}}{\mathrm{RS} \cdot \mathrm{CS} \cdot W} \tag{2}$$

where S is the intensity of a peak (V cm^3/g), A is the peak area on the recorder chart (cm^2), FR is the flow-rate of carrier gas (cm^3/s), RS is the sensitivity of the recorder (V/cm), CS is the chart speed (cm/s) and W is the quantity of sample gas (g).

As shown in Fig. 5, a gas mixture of the six hydrogen isotopes can be detected by GC using the TCD. The detection limit with the TCD is 20 Pa for H_2 and 50 kPa for T_2. To improve these limits it might be useful to increase the sampling volume or to decrease the carrier gas flow-rate, as indicated by eqn. 2. However, increasing the sampling volume increases the amount of radioactive waste gas effluent. On the other hand, as pointed out in the previous section, decreasing the carrier gas flow-rate means a longer analysis time. Another important way of improving the sensitivity is to have an extremely high signal-to-noise ratio. However, with the present commercially available measurement equipment, it does not seem to be easy to achieve a higher ratio.

Future study must look at ways of avoiding these shortcomings of GC and developing an improved gas measurement system for the fusion fuel gas process.

CONCLUSIONS

The characteristics of GC when applied to isotopic hydrogen analyses were experimentally obtained using a liquid nitrogen cooling column, with a TCD and an ionization chamber. The following results were obtained.

(1) The intensity ratio for hydrogen isotopes measured with the TCD was H_2:HD:HT:D_2:DT:T_2 = 100:73:61:57:49:43.

(2) When the sampling volume was 1 cm^3, the detection limits for H_2 and T_2 were estimated to be, respectively, 20 and 50 Pa partial pressure and 200 and 500 ppm concentration.

(3) Using the 0.16-cm^3 ionization chamber, the intensity ratio obtained for T_2:HT:DT was 2:1:1

according to the atomic fraction in the isotopic molecules. The detection limit for T_2 gas was estimated to be 1 ppm concentration and $4 \cdot 10^{-10}$ mol mass.

(4) On increasing the hydrogen isotope concentration above 1%, the retention time tended to drop. Furthermore, when the concentration was increased to more than 10%, neighboring peak identification became difficult.

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