LETTER

GC/GC/C/IRMS system for carbon isotope measurement of low level methane concentration

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A flow-through system, GC/GC/C/IRMS (gas chromatograph/gas chromatograph/combustion/isotope ratio mass spectrometer) was developed for carbon isotope analysis of methane in a sample of low level concentration. In this system, methane was roughly separated from a large amount of N₂ and O₂ in the first GC with packed column, then introduced into GC/C/IRMS and carbon isotopic composition was measured. The $\delta^{13}\text{C}$ of methane in a sample of 92 ml in volume with concentration of 11 ppm was successfully obtained with a standard deviation of $\pm 0.4\%$.

INTRODUCTION

A flow-through system for the measurement of natural abundance ratios of carbon isotopes, GC/C/IRMS (gas chromatograph/combustion/isotope ratio mass spectrometer) has been developed (Matthews and Hayes, 1978; Merritt *et al.*, 1994; Ricci *et al.*, 1994) and applied to wide scientific fields (Freeman *et al.*, 1990; Jasper and Hayes, 1990; Silfer *et al.*, 1991). Isotope analysis using GC/C/IRMS has an advantage that can simplify procedures for purification of gas mixtures and combustion of hydrocarbons. GC/C/IRMS system has also been applied to carbon isotopic measurement of methane (Sugimoto *et al.*, 1991; Zeng *et al.*, 1994; Merritt *et al.*, 1995), which has drawn scientific attention because of its efficiency as a greenhouse gas (Cicerone and Oremland, 1988). The carbon isotopic composition of CH₄ has been analyzed to know the origin (Whiticar *et al.*, 1986) or formation pathways of CH₄ (Sugimoto and Wada, 1995). However, GC/C/IRMS could be applied to methane only for samples with high methane concentration (usually higher than 1000 ppm), because the capillary column used in a GC/

C/IRMS restricts a gas volume which can be injected. The difficulty of complete separation of CH₄ from air is another problem. A system which can be applied to low methane concentration such as flux chamber air or atmospheric methane has been desired. Merritt *et al.* (1995) developed a system for atmospheric CH₄, in which CH₄ was concentrated by chilling the column to -118°C . It is not easy, however, to control the column temperature at -118°C . I developed a system with a gas chromatograph for rough, preliminary separation of methane from a large volume of air combined to a GC/C/IRMS.

EXPERIMENTAL PROCEDURES

The system developed in this study consists of two main components (Fig. 1). One is a gas chromatograph, GC(I), (Shimadzu GC-8A) with packed column of Molecular Sieves 5 A (MS-5A) (i.d. 5 mm, 5 m) and TCD (thermal conductivity detector). A gas sampler (MGC-5, Shimadzu) with MS-5A loop to trap sample gas is attached to GC(I). The other component is GC/C/IRMS (Finnigan MAT deltaS/GC) with a capillary col-

Fig. 1. Schematic diagram of GC/GC/C/IRMS system.

Fig. 2. Chromatographs of GC(I) and GC/C/IRMS. 10 ml of sample gas (200 ppm) was injected from the reservoir 1.

umn of Pora PLOT-Q (i.d. 0.32 mm, 25 m). A switching valve with MS-5A loop is placed between GC(I) and GC/C/IRMS to switch the carrier gas flow from GC(I).

A required sample volume depends on the sensitivity of IRMS. The system used in this study needs 0.5 to 2 μ l or more of CH₄ at room temperature and pressure (RTP) (21 to 83 nmol). Two standard gases containing CH₄, st-A and st-B, were used to test the system. The concentration of CH₄ was 1% for st-A and 2% for st-B, and nitrogen was balanced for both. Various methane concentrations were produced by mixing st-B and st-air (79% N₂ and 21% O₂ mixture).

A sample gas was introduced from reservoir 1 or 2, and collected in trap 1 (MS-5A, at liquid N₂ temperature). Before and during trapping sample gas, trap 1 was evacuated. It took about 5 min to collect sample gas to trap 1. Then, the sample gas was discharged from trap 1 to the GC(I) column, by changing He flow through a 6-way valve and heating trap 1 with hot water. In the GC(I) col-

umn CH₄ was separated from N₂ (Fig. 2). During CH₄ flowing out of TCD, the switching valve was turned to "collection" to trap CH₄ in a small MS-5A loop (trap 2) at liquid N₂ temperature. Other gases such as O₂, N₂ and CO₂ were vented out. The collected CH₄ in trap 2 was, then, discharged to GC/C/IRMS by heating trap 2 with a hair-drier. Required time was 16 min for the separation in GC(I) and another 7 min for IRMS.

The results of carbon isotopic composition are expressed with $\delta^{13}\text{C}$ values defined as follows:

$$\delta^{13}\text{C} = \left(\frac{R_{\text{sa}}}{R_{\text{st}}} - 1 \right) \times 1000 \text{ (‰)},$$

where R_{sa} and R_{st} are isotope ratios ($^{13}\text{C}/^{12}\text{C}$) for sample and standard (PDB), respectively. In the GC/C/IRMS, $\delta^{13}\text{C}$ values of samples were measured against a reference CO₂ (Ricci *et al.*, 1994). Since a shift of measured $\delta^{13}\text{C}$ values of sample CH₄ is sometimes observed, the $\delta^{13}\text{C}$ values of samples are usually corrected by normalizing to

the $\delta^{13}\text{C}$ of a standard CH_4 analyzed at the same condition as the samples (Sugimoto *et al.*, 1991). However, the $\delta^{13}\text{C}$ values before correction are considered in this paper, since the purpose of this study is to test the reproducibility of the system.

RESULTS AND DISCUSSION

Separation of CH_4 from air

When the sample gas volume was greater than 20 ml, CH_4 peak in GC(I) was on the tail of N_2 peak. Consequently, the mixture of CH_4 and N_2 was introduced into GC/C/IRMS. If the separation of CH_4 from N_2 in the GC/C/IRMS capillary column was not perfect, the $\delta^{13}\text{C}$ of CH_4 was interfered with the noise signal of 45/44 caused by N_2 (Fig. 3). However, it is possible to separate CH_4 from N_2 by cooling the column. To analyze CO_2 at the same time, Sugimoto *et al.* (1991) kept the column temperature at 0°C , because the retention

time of CO_2 became much longer at lower temperatures. In the current system, since CO_2 dose not enter into the GC/C/IRMS, small loop of the capillary column in GC/C/IRMS (about 60 cm long) was put into an ethanol/liquid N_2 slush kept at about -60 to -80°C to separate CH_4 from N_2 .

Combustion efficiency

When combustion of CH_4 is not complete, remaining CH_4 causes a deviation of $\delta^{13}\text{C}$ depending on the pressure in IRMS due to the isotope fractionation during the combustion and the reaction among ionized molecules derived from CO_2 and CH_4 in the ionization chamber (Sugimoto *et al.*, 1991; Zeng *et al.*, 1994). Using the current system, CH_4 was completely combusted at furnace temperatures higher than 830°C . The combustion was, therefore, done at 850°C .

Sensitivity

The $\delta^{13}\text{C}$ of st-A (1% CH_4) was measured for CH_4 with the absolute amount of 0.5 to 3 μl at RTP (50 to 300 μl of injection volume). When the amount of CH_4 was 3 μl , the standard deviation of $\delta^{13}\text{C}$ was less than $\pm 0.3\text{‰}$ (Fig. 4). The reproducibility was low with small sample volumes due to the sensitivity of IRMS. When the amount of CH_4 was less than 1 μl , a shift of $\delta^{13}\text{C}$ and increasing standard deviation were sometimes observed with decreasing the amount of CH_4 . The direction of $\delta^{13}\text{C}$ shift varied case by case. In many cases, however, $\delta^{13}\text{C}$ of CH_4 decreased with decreasing the amount of CH_4 , whereas, the $\delta^{13}\text{C}$ of CO_2 increased with decrease of the amount of CO_2 . Such a shift of $\delta^{13}\text{C}$ with decrease of the sample amount may be caused by the reaction with H_2O in the ion source of IRMS, since the $\delta^{13}\text{C}$ shift was eliminated by baking the capillary column. The GC/GC/C/IRMS for low level concentration of CH_4 was, therefore, tested using 1 and 2 μl of CH_4 .

Test for low level concentration of CH_4

The samples of the mixture of st-B and N_2/O_2 with the concentration of 200 to 11 ppm CH_4 (10 to 92 ml in the volume) were tested. The gas

Fig. 3. 45/44 signal caused by N_2 . When the sample volume is greater than 20 ml, N_2 entered into GC/C/IRMS with CH_4 produces signals of 45/44 and 46/44, and interferes with the $\delta^{13}\text{C}$ measurement for CH_4 (a). The perfect separation of CH_4 from N_2 is achieved by keeping the small loop of the capillary column at about -70°C (b).

volume less than 50 ml can be introduced into the GC(I) column at once. Accordingly, when a sample volume was greater than 50 ml, the sample was divided into some fractions at the sampler. The CH₄ from each fraction was then collected in trap 2 and introduced into GC/C/IRMS at once. The $\delta^{13}\text{C}$ of CH₄ was successfully measured for the concentration down to 11 ppm with a standard deviation of $\pm 0.4\text{‰}$ (Table 1). The procedure with trap 2 is essential for samples with low CH₄

concentration. In the case of high CH₄ concentration, it is possible to analyze $\delta^{13}\text{C}$ without trap 2, because the peak of CH₄ flowed out of GC(I) is not broad. While, for samples with low CH₄ concentration, in other words large sample volume, the peak width of CH₄ from GC(I) was broader than 1 min (Fig. 2), and CH₄ needs to be concentrated at trap 2.

The sensitivity of GC/C/IRMS used in this study is not high enough for the analyses of the

Fig. 4. $\delta^{13}\text{C}$ values and standard deviations for CH₄ with the absolute amount of 0.5 to 3 μl at RTP. 50 to 300 μl of st-A was injected.

Table 1. $\delta^{13}\text{C}$ of CH₄ for st-B obtained in the experiment with low level CH₄ concentration

CH ₄ (μl)*	$\delta^{13}\text{C}$ (‰)	Concentration (ppm)	Volume (ml)
2	-66.3	200	10
2	-66.0	100	20
1	-66.4	100	10
1	-65.3	50	20
2	-65.9	200	10
1	-65.6	100	10
1	-65.5	11	92
1	-65.4	11	92
Ave.	-65.8		
st.dev.	± 0.4		

*The absolute amount of CH₄ in a sample gas at RTP.

atmospheric CH₄ with concentration of 2 ppm. It is possible, however, to analyze atmospheric CH₄, if the sample gas is divided into several fractions before introducing into GC(I), or if a GC/C/IRMS with more sensitive IRMS is used. The concentration of CH₄ handled in this study (>10 ppm) is equivalent to that observed in a flux chamber air or incubation experiments for various CH₄ sources. Accordingly, GC/GC/C/IRMS developed in this study can be applied to $\delta^{13}\text{C}$ measurement of CH₄ in various fields.

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