



## CONTINUOUS FLOW IRMS APPLICATION TO CH<sub>4</sub>, NMHCS, AND N<sub>2</sub>O IN THE ATMOSPHERE AND THE OCEANS

N. YOSHIDA, U. TSUNOGAI, S. TOYODA  
Department of Environmental Science and Technology,  
Tokyo Institute of Technology,  
Yokohama, Japan

**Abstract.** The application of CF-IRMS to measurement of methane (CH<sub>4</sub>), non-methane hydrocarbons (NMHCS), and nitrous oxide (N<sub>2</sub>O) is outlined and preliminary information on isotopic variations in the atmosphere and oceans is presented. Labelling of these compounds is expected to provide a robust method for tracing sources, sinks and controlling processes in the environment.

### 1. INTRODUCTION

Methane and N<sub>2</sub>O are naturally occurring trace gases which have important roles in global warming and stratospheric ozone budget, while non-methane hydrocarbons (NMHCs) are controlling the atmospheric oxidation reactions which are major methane sinks as well. Isotope containing molecules (isotopomers) of these gases are considered to have information of their sources, sinks, and geochemical cycles. It was, however, difficult to determine their isotope ratios before the application of continuous flow IRMS, a most sensitive and precise analytical method at present.

Samples of 0.3 to 1 nmol are analyzed for several background atmosphere and for samples collected from terrestrial and marine environment along with latitudinal transect. Carbon 13 isotopic composition of methane and NMHCs has been found to have distinct information for the difference in their sources.

Information and data base for the global budget, sources and sinks strength are more limited for N<sub>2</sub>O than methane and carbon dioxide. Nitrogen and oxygen isotope ratios of atmospheric N<sub>2</sub>O are determined by tropospheric sources and stratospheric sinks, especially nitrification and denitrification in terrestrial and marine environments and UV photolysis. We have recently originated the isotopomer analysis of N<sub>2</sub>O.

Isotopic analysis of these naturally occurring gases have been found to have potential importance to provide quantitative constraints for reducing uncertainties with their budget, source and sink processes, and relative importance of the area or sphere to act as sources and/or sinks. Wider circulation and interlaboratory calibration of the standards for these gases in pure and the background levels becomes very important. Isotopomer standards should also be taken into account very soon.

### 2. CARBON ISOTOPIC COMPOSITIONS OF CH<sub>4</sub>, NMHCS AND METHYL CHLORIDE

Studies on the stable isotopic composition of atmospheric carbon species of greater than about ppmv mixing ratio, such as CO<sub>2</sub> and CH<sub>4</sub>, have provided valuable information for understanding the relative strengths of the production and removal processes involved in atmospheric cycling [1-3].

Samples of 0.3 to 1 nmol are analyzed for several background atmosphere and for samples collected from terrestrial and marine environment along with latitudinal transect using continuous-flow GC/C/IRMS. The samples collected from Indian Ocean are analyzed for their <sup>13</sup>C revealing the importance of the air-sea interactions and the oxidation of CH<sub>4</sub> in the deeper water columns.

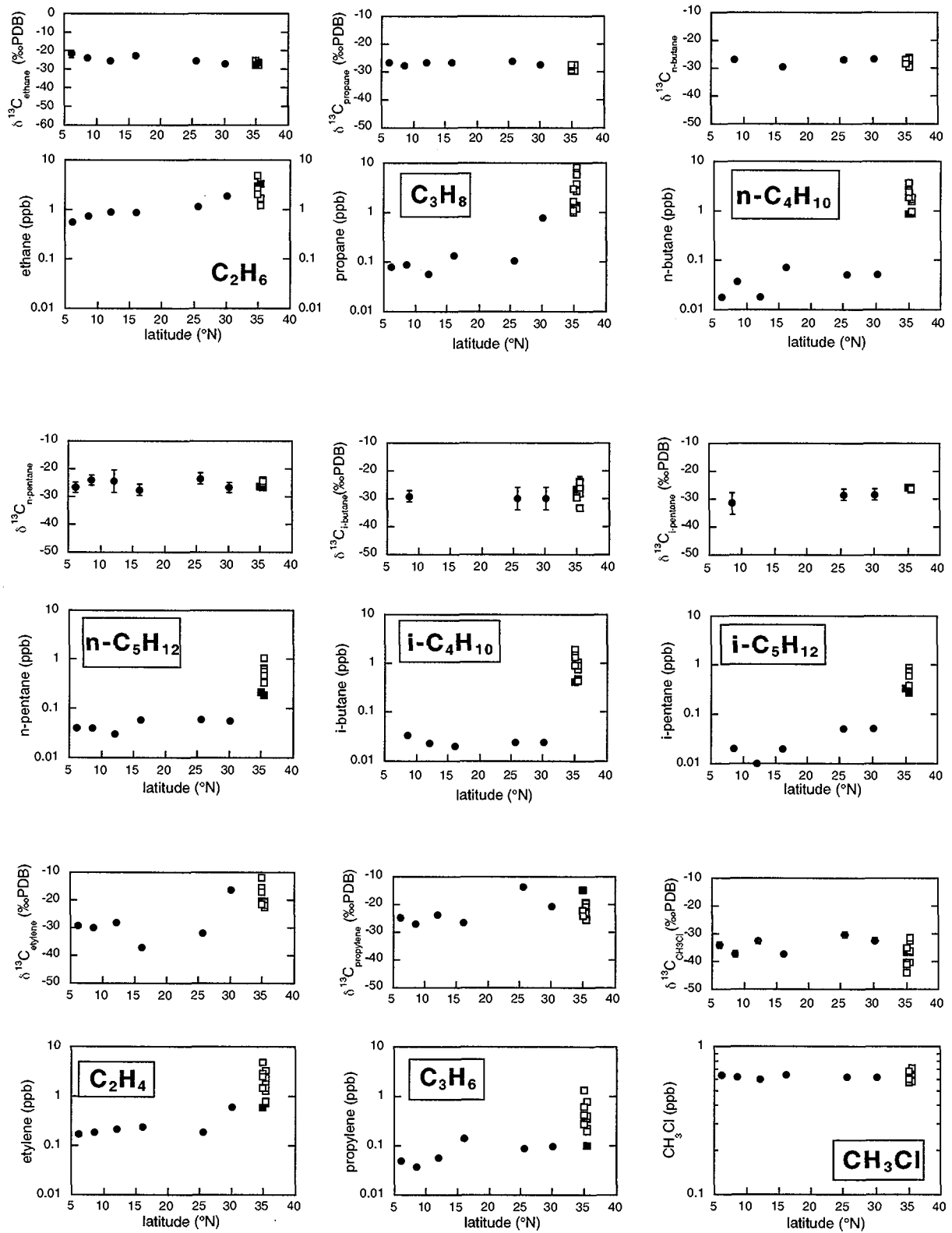


Fig. 1. Latitudinal variations of the measured mixing ratios and the carbon isotopic compositions of NMHCs and CH<sub>3</sub>Cl in maritime (solid circles), coastal (solid squares), and urban atmospheres (open squares).

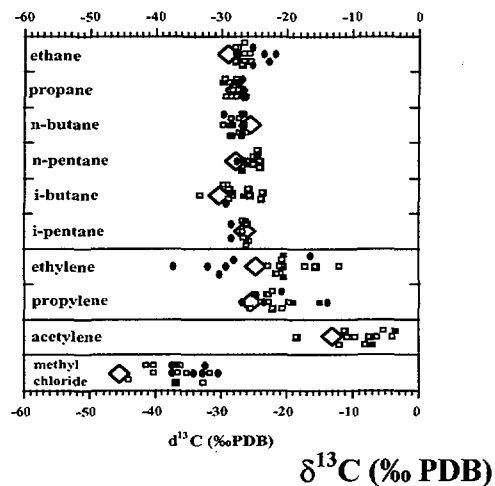


Fig. 2. Isotopic compositions of each component in samples (see Fig. 1 for the symbols), together with that of biomass burning plume (C-3 plant [5]) (large open diamonds). Isotopic data with more than 2 per mil error are excluded.

In the case of trace components such as light NMHCs and methyl chloride, however, data describing their isotopic compositions are scarce [4, 5], especially regarding those in maritime atmosphere.  $C_2$ – $C_5$  non-methane hydrocarbons (NMHCs) and methyl chloride in the remote maritime atmosphere are analyzed in regard to their variation of mixing ratio and  $^{13}C/^{12}C$  ratio ( $\delta^{13}C$ ), together with those in polluted urban and coastal atmospheres in Japan [6]. NMHCs show large atmospheric mixing ratio differences between urban (coastal) and maritime atmospheres probably due to emission from urban areas and degradation within the maritime atmosphere as shown in Fig. 1. Reflecting isotopic fractionation during the degradation within the maritime atmosphere, ethane shows large and systematic  $\delta^{13}C$  variation between urban (around  $-27\text{‰}$  Peedee belemnite(PDB)) and maritime atmospheres (up to  $-22\text{‰}$  PDB). Except for ethane, however, alkanes show small isotopic variation around  $\delta^{13}C = -27 \pm 2\text{‰}$  PDB ( $1\sigma$ ) without systematic isotopic differences between urban and maritime atmospheres, suggesting both small  $\delta^{13}C$  variation within major emission sources and also little isotopic fractionation during atmospheric degradation for alkanes other than ethane.

Alkenes show large  $\delta^{13}C$  variation from  $-37$  to  $-12\text{‰}$  PDB for ethylene and from  $-27$  to  $-14\text{‰}$  PDB for propylene as shown in Fig. 2. Combination of both large  $\delta^{13}C$  differences between major sources (especially between land and maritime sources) and large isotopic fractionation effect during atmospheric degradation can be suggested for alkenes. Methyl chloride also shows large isotopic variation from  $-44$  to  $-30\text{‰}$  PDB in spite of their similar atmospheric mixing ratios from 580 to 710 parts per trillion by volume (pptv), probably due to the contribution of highly  $^{13}C$ -depleted, anthropogenic methyl chloride especially to urban atmospheres.

The general  $\delta^{13}C$  pattern of NMHCs and methyl chloride in polluted urban city air agrees strongly with those of biomass (C-3 plant) burning plumes, suggesting that thermal breakdown of C-3 plant (or related organic matter) is one of the representative sources of these hydrocarbons in urban atmospheres. Further investigations of the isotopic signature of source materials as well as laboratory studies of isotopic fractionation processes resulting from atmospheric degradation will improve our understanding of the sources, sinks, and atmospheric distributions of NMHCs and methyl chloride.

### 3. DETERMINATION OF NITROGEN ISOTOPOMERS OF NITROUS OXIDE

Nitrous oxide ( $N_2O$ ) is a trace gas in the atmosphere that plays an important role in the tropospheric greenhouse effect and stratospheric chemistry, which regulates the ozone layer. Although its tropospheric concentration is increasing by 0.2–0.3% per year [7], the global budget and/or cycle of  $N_2O$  has not been well understood because it has a variety of sources (both natural and anthropogenic)

and sinks. Nitrogen and oxygen isotope ratios of  $N_2O$  for several environments have been reported and they are considered to be useful parameters for examining the source–sink relationship.

Previous studies of isotopic characterization of  $N_2O$  have been based on the elements contained in the molecule, i.e. nitrogen and/or oxygen [6–19]. Additional information, however, would be obtained if the intra-molecular distribution of nitrogen isotopes could be determined, since the  $N_2O$  molecule has an asymmetric linear structure (N–N–O) and thus site preference of nitrogen isotopes in naturally occurring fractionation processes is expected. For example, Yung and Miller [20] estimated that  $^{15}N^{14}N^{16}O$  and  $^{14}N^{15}N^{16}O$  have different fractionation factors in the stratospheric photodissociation based on a theoretical calculation. Hence, determination of isotopomers of  $N_2O$  in the environment and those incorporated in processes simulated in the laboratory has the potential to reveal the contribution of sources and sinks of  $N_2O$ , either recognized or proposed ones.

A new method [21] for the determination of the nitrogen isotopomers (intra-molecular distribution of the nitrogen isotopes) of nitrous oxide has been developed in the present study as illustrated in Fig. 3. The precision of isotope ratio measurements at each specific site relative to the reference gas is better than 0.1‰ for pure  $N_2O$  samples introduced through a conventional dual-inlet system on a mass spectrometer equipped with a special ion collector system.

Although it is found that the observed isotope ratio is affected by rearrangement reactions in the ion source, a correction can be applied using an experimentally determined rearrangement fraction. Calibration of the standard  $N_2O$  for isotopomer measurements is performed by two procedures: (1) preparation of an  $N_2O$  standard by thermal decomposition of  $NH_4NO_3$ , (2) relative measurements with pure NO.

This new technique is expected to become a useful tool for studying mechanisms of production and consumption, and the global budget of  $N_2O$ . Applications of this technique to various environmental samples are now under investigation.

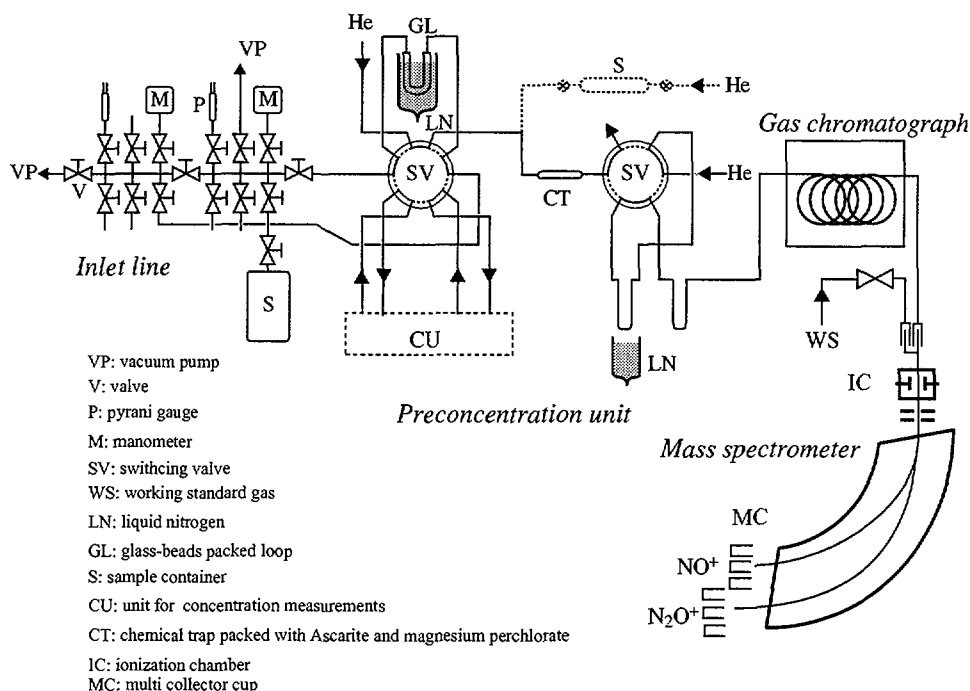


Fig. 3. Schematic diagram of the measurement of  $N_2O$  isotopomers on a mass spectrometer.

## REFERENCES

- [1] MOOK, W.G., KOOPMANS, M., CARTER, A.F., KEELING, C.D., *J. Geophys. Res.* **88**, (1983)10915–10933.
- [2] LOWE, D.C., BRENNINKMEIJER, C.A.M., BRAILSFORD, G.W., LASSEY, K.R., GOMEZ, A.J., NISBET, E.G., *J. Geophys. Res.* **99** (1994) 16913–16925.
- [3] SAUERESSIG, G., BERGAMASCHI, P., CROWLEY, J.N., FISCHER, H., HARRIS, G.W., *Geophys. Res. Lett.* **22** (1995) 1225–1228.
- [4] CONNY, J.M., CURRIE, L.A., *Atmos. Environ.* **30** (1996) 621–638.
- [5] RUDOLPH, J., LOWE, D.C., MARTIN, R.J., CLARKSON, T.S., *Geophys. Res. Lett.* **24** (1997) 659–662.
- [6] TSUNOGAI, U., YOSHIDA, N., GAMO, T., *J. Geophys. Res.* **104** (1999) 16033–16039.
- [7] INTERGOVERNMENTAL PANEL ON CLIMATE CHANGE (IPCC), In *Climate Change 1995: The Science of Climate Change*; HOUGHTON, J.T., MEIRA FILHO, L.G., CALLANDER, B.A., HARRIS, N., KATTENBERG, A., MASKELL, K., Eds., Cambridge University Press: Cambridge, UK (1995).
- [8] YOSHIDA, N., MATSUO, S., *Geochemical Journal* **17** (1983) 231–239.
- [9] YOSHIDA, N., HATTORI, A., SAINO, T., MATSUO, S., WADA, E., *Nature* **307** (1984) 442–444.
- [10] WAHLEN, M., YOSHINARI, T., *Nature* **313** (1985) 780–782.
- [11] YOSHIDA, N., MORIMOTO, H., HIRANO, M., KOIKE, I., MATSUO, S., WADA, E., SAINO, T., HATTORI, A., *Nature*, **342** (1989) 895–897.
- [12] KIM, K.R., CRAIG, H., *Nature* **347** (1990) 58–61.
- [13] THIEMENS, M.H., TROGLER, W.C., *Science* **251** (1991) 932–934.
- [14] UEDA, S., OGURA, N., WADA, E., *Geophys. Res. Lett.* **18** (1991) 1449–1452.
- [15] KIM, K.R., CRAIG, H., *Science* **262** (1993) 1855–1857.
- [16] CLIFF, S.S., THIEMENS, M.H., *Science* **278** (1997) 1774–1776.
- [17] RAHN, T., WAHLEN, M., *Science* **278** (1997) 1776–1778.
- [18] YOSHINARI, T., ALTABET, M.A., NAQVI, S.W.A., CODISPOTI, L., JAYAKUMAR, A., KUHLAND, M., DEVOL, A., *Mar. Chem.* **56** (1997) 253–264.
- [19] DORE, J.E., POPP, B.N., KARL, D.M., SANSONE, F.J., *Nature* **396** (1998) 63–66.
- [20] YUNG, Y.L., MILLER, C.E., *Science* **278** (1997) 1778–1780.
- [21] TOYODA, S., YOSHIDA, N., *Anal. Chem.* **71** (1999) 4711–4718.