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High-Precision Continuous-Flow Measurement of $\delta^{13}\text{C}$ and δD of Atmospheric CH_4

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We describe our development of a CH_4 preconcentration system for use with continuous-flow gas chromatograph combustion isotope ratio mass spectrometry (GC/C/IRMS). Precision of measurement of $\delta^{13}\text{C}\text{-CH}_4$ is 0.05‰ (1 σ) on multiple 60-mL aliquots of the same ambient air sample. The same front-end on-line CH_4 preconcentration system allows us to measure δD of CH_4 by gas chromatography IRMS when the combustion furnace is replaced with a pyrolysis oven (GC/P/IRMS). Precision of measurement for $\delta\text{D}\text{-CH}_4$ is 1.5‰ (1 σ) using 120 mL of ambient air based on multiple aliquots of the same air sample. These are the first reported measurements of atmospheric CH_4 using GC/P/IRMS methodology. Each isotope analysis can be made much more rapidly (30–40 min) than they could using off-line combustion of an air sample (1–6 h) followed by conventional dual-inlet IRMS measurements (12–20 min), while requiring much less total volume and retaining a comparable level of precision and accuracy. To illustrate the capabilities of our preconcentration GC/C/IRMS system, we compare the results of measurement of 24 background air samples made using both GC/C/IRMS and conventional vacuum line/dual-inlet IRMS methodology. The air samples were collected on a shipboard air sampling transect made across the Pacific Ocean in July 2000 and are part of an ongoing atmospheric CH_4 research program. The average difference between the two methods of IRMS analyses on these 24 samples is $0.01 \pm 0.03\text{‰}$ (95% confidence interval) for $\delta^{13}\text{C}\text{-CH}_4$. These are the first measurements to be reported of air samples directly intercompared for $\delta^{13}\text{C}\text{-CH}_4$ using both GC/C/IRMS and dual-inlet IRMS measurement methodology. Measurement of $\delta\text{D}\text{-CH}_4$ of these air samples is also presented as an illustration of the ability of this system to resolve small isotopic differences in remote air. High-precision measurement of $\delta^{13}\text{C}$ and δD of atmospheric CH_4 made using our coupled preconcentration GC/IRMS system will greatly improve our ability to utilize isotopic data in understanding spatial and temporal changes in atmospheric CH_4 and the biogeochemistry of its sources and sinks.

Understanding the CH_4 budget is important because CH_4 , a chemically reactive¹ and radiatively important² trace gas, is not

at steady state in the atmosphere.³ In recent years, stable isotopic information has provided major constraints on estimates of the sources and sink processes (i.e., CH_4 loss from reaction with OH, Cl, O(¹D), and soil bacteria) in the global CH_4 budget. Stevens and Rust⁴ first proposed that a mass-weighted stable carbon isotopic balance between CH_4 sources and sink processes and the $\delta^{13}\text{C}\text{-CH}_4$ value in the atmosphere would help constrain the CH_4 budget. Since then, additional measurements of atmospheric $\delta^{13}\text{C}\text{-CH}_4$ have further constrained the CH_4 budget, provided information on seasonal cycles in CH_4 sources and sink processes, and helped understanding of recent trends in CH_4 mixing ratio. In most instances, the additional measurements referred to have come from multiyear monitoring of specific widely spaced sites.^{5–10} Because spatial and temporal trends tend to be no larger than a few tenths of a mil, high precision and long-term stability of such measurement is necessary.

As a corollary, even fewer measurements of δD of atmospheric CH_4 exist using conventional IRMS, first because of increased problems with sample size (80–1500 L) and sampling logistics and second because of problems in using a vacuum line technique to recover combusted CH_4 as H_2O (eventually measured as H_2 gas) that are exacerbated when dealing with ambient CH_4 concentrations in air rather than elevated concentrations from CH_4 sources.^{11,12} Nonetheless, there are a few early measurements^{13,14}

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using conventional vacuum line techniques and recent work by Quay et al.⁶ that greatly expanded the data set. Bergamaschi et al.¹⁰ utilized tunable diode laser absorption spectroscopy to measure $\delta\text{D-CH}_4$ after its vacuum line preconcentration from 1000-L air samples. They obtained 1‰ precision, which was adequate to observe a seasonal cycle at their fixed clean air sample site. Additional such measurements would clearly be useful in studying changes in CH_4 and its growth rate, just as measurements of $^{13}\text{C}/^{12}\text{C}$ ratios in CH_4 are.

Despite the number of $\delta^{13}\text{C-CH}_4$ studies cited above, the lack of sufficient isotopic data to complement existing mixing ratio data of CH_4 has made it difficult to fully utilize in constructing a comprehensive CH_4 budget and in assessing spatial and temporal trends in CH_4 . This is primarily due to the requirements of sample collection and preparation for isotopic analysis of CH_4 in comparison to requirements for CH_4 mixing ratio determination. Atmospheric CH_4 sample preparation for analysis by dual-inlet IRMS requires anywhere from 20 to 300 L of whole air to be passed through a combustion vacuum train line depending on an individual laboratory's targeted precision.^{4,5,7,9,22} The sampling logistics and time spent in collecting such a large sample for eventual dual-inlet analyses also tended to make the overall isotopic measurement determination a lengthy process.

Continuous-flow gas chromatograph combustion isotope ratio mass spectrometry (GC/C/IRMS), or isotope ratio monitoring GC/MS, was introduced by Matthews and Hayes¹⁵ in 1978 for $\delta^{13}\text{C}$. Samples to be analyzed are introduced directly into the source of the isotope ratio mass spectrometer, rather than using the inlet, by way of a continuous viscous flow stream of inert carrier gas. Individual species in the sample gas are both separated and prepared individually prior to their measurement by using an in-line capillary gas chromatograph and a microcombustion furnace placed along the carrier stream (see *Org. Geochem.* **1994**, 21 (6/7), a special issue devoted to applications of continuous-flow GC/C/IRMS). This method became commercially available and widely utilized by the late 1980s because it required less total sample and preparation time. Tobias and Brenna¹⁶ illustrated that high-precision D/H ratios of organic compounds could be similarly determined using on-line pyrolysis (P), the spontaneous thermal decomposition of organics to products carbon and H_2 . Burgoyne and Hayes¹⁷ shortly thereafter developed a system for quantitative pyrolysis at temperatures above 1430 °C for *n*-alkanes. A commercial system became available in 1999 that showed conversion efficiency of 99.7% for CH_4 at 1440 °C and a precision of 1.3‰.¹⁸ However, application to atmospheric trace gas study using continuous-flow IRMS is limited due to the low concentrations of atmospheric trace gas species and the relatively high precision necessary for their study. Pioneering work was done by Merritt et al.,¹⁹ who measured $\delta^{13}\text{C-CH}_4$ at levels down to ambient CH_4 concentrations. Although a reported precision of measurement of $\delta^{13}\text{C-CH}_4$ of 0.2‰ (1 σ) looked encouraging, an intercomparison with the conventional vacuum line technique was not performed

at that time. More recent work by others obtains the precision necessary to observe seasonal and temporal changes in modern $\delta^{13}\text{C-CH}_4$ ²⁰ and in ice core $\delta^{13}\text{C-CH}_4$.²¹

Here we report the design and development of a front-end on-line atmospheric CH_4 preconcentration system for use with a continuous-flow GC/IRMS system. We began by obtaining a commercially available CH_4 front-end preconcentration unit designed by Finnigan MAT (Bremen, Germany). This unit was tested for several months in both off-the-shelf mode and with a minor change to the design (i.e., adding I_2O_5 on silica gel to the ascarite/MgClO₄ chemical trap to remove CO) but was found to be unsatisfactory for the purpose of measuring $\delta^{13}\text{C}$ of atmospheric background CH_4 with the specifications we require for precision and accuracy of measurement. Much like the traditional off-line vacuum line approach, the commercial preconcentration unit oxidized sample CH_4 and preconcentrated resultant CO_2 prior to chromatographic separation. However, the system falls short of separating CH_4 from contaminant species that are ultimately trapped with and measured as signal CO_2 . These contaminants include the following: (1) ambient CO_2 not quantitatively removed with a chemical trap and subsequent liquid nitrogen trap, (2) bleed of CO_2 and/or hydrocarbon contaminants from the chemical trap, and (3) CO not removed that is oxidized along with CH_4 .

Our design and development of a CH_4 preconcentrator is based on the design philosophy of Merritt et al.¹⁹ and our own innovations. It improves on precision of measurement of $\delta^{13}\text{C-CH}_4$ and allows for measurement of $\delta\text{D-CH}_4$. In our system, only the sample inlet with its two three-way valves and six-port switching valve remains in place from the original Finnigan preconcentrator while the ISODAT (custom Finnigan software) process control of the aforementioned valves and two adjustable lever arms for raising and lowering cryotrap remain as valued features. All other operations are manual in its present state. We report on measurements of both $\delta^{13}\text{C}$ and δD of atmospheric CH_4 made with our system from background air samples used in a study of CH_4 in the equatorial Pacific Ocean. The $\delta^{13}\text{C}$ values are intercompared to our own measurements of the same samples made using established dual-inlet IRMS methodology (which are themselves intercompared with other international research groups to ascertain their accuracy and precision). The δD values are the first to be measured using continuous-flow IRMS methodology that we are aware of.

EXPERIMENTAL SECTION

Sample Collection. Air samples were collected from a container ship of P & O Nedlloyd during a Pacific Ocean transect between Los Angeles, CA, and Auckland, New Zealand. Depending on wind direction, the air is sampled through Dekabon type 1300 tubing (12.7-mm o.d., Furon Dekoron, Aurora, OH) mounted on either port or starboard side of the ship's bridge with the inlet well forward of the exhaust funnels. Samples were collected into high-pressure aluminum cylinders made by Scott-Marin, Co. (Riverside, CA) which have been treated internally to minimize wall effects. A RIX compressor type SA-3 (RIX industries, Oakland, CA) was used to pressurize the cylinders. Air was filtered and

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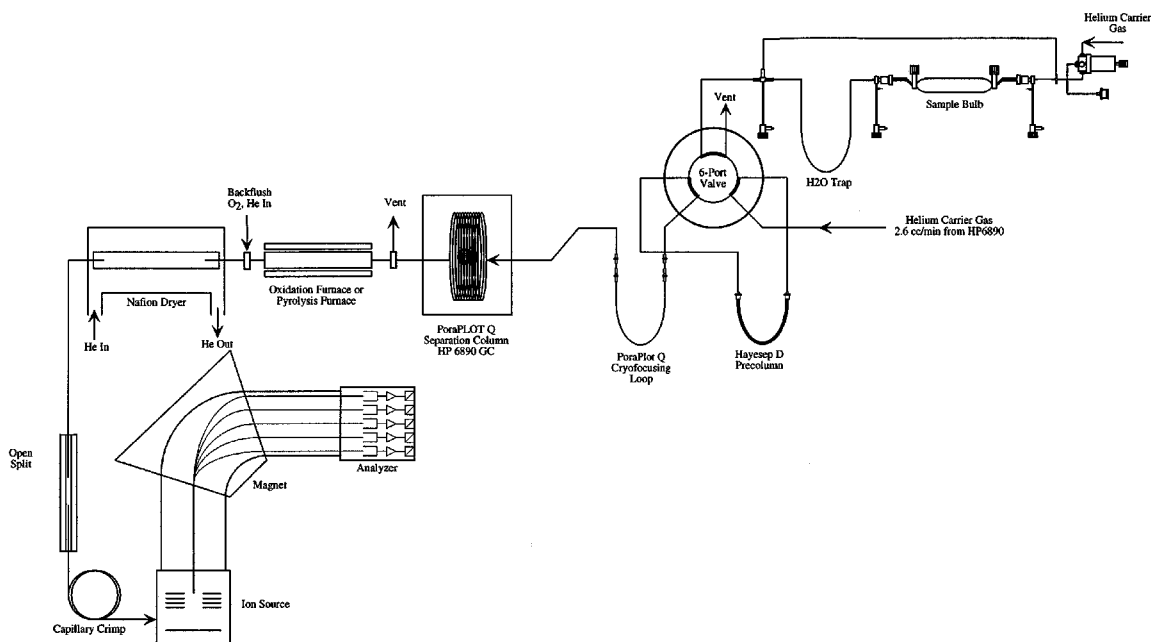


Figure 1. Schematic view of continuous-flow preconcentration gas chromatograph isotope ratio mass spectrometer system for measurement of $\delta^{13}\text{C}$ and δD of atmospheric CH_4 .

dried by a series of stainless steel traps filled with molecular sieve 4A or magnesium perchlorate before passing through the compressor. The compressor had been specially cleaned prior to its use following the methods described in Lowe et al.²² in order to avoid any contamination of the CH_4 or CO trace gases being studied from the air samples.

Air Sample Analysis via Continuous-Flow IRMS. The preconcentration GC/IRMS system is shown in Figure 1. A clean dry air sample is introduced from a pressurized canister or cylinder into an evacuated (10^{-3} mbar) 60- or 120-mL (for carbon and hydrogen isotopic measurements, respectively) sample bulb through a purged gas transfer line to a pressure of 1 atm. This typically yields $0.107\ \mu\text{L}$ of CH_4 (32.8 nmol) for carbon analysis and $0.217\ \mu\text{L}$ of CH_4 (65.5 nmol) for hydrogen analysis at background ambient CH_4 concentrations. The sample is swept by UHP helium (Oxygen Services Co., Costa Mesa, CA) through the first two traps at 55 mL/min. The first trap, 1.59-mm (o.d.) stainless steel tubing (Alltech Chromatography Supplies, Deerfield, IL) placed in liquid nitrogen (LN_2) at $-196\ ^\circ\text{C}$, is designed to trap out residual H_2O from the sample not removed during sampling (also trapping some CO_2). The precolumn, 20 cm \times 3.18 mm (o.d.) stainless steel tubing packed with 100/120 mesh Haysep D (Alltech), is placed in a LN_2/n -pentane bath maintained at $-130 \pm 2\ ^\circ\text{C}$. It is designed to preferentially and quantitatively adsorb CH_4 .²³ The bulb is flushed with a volume of He equivalent to at least 8 times the sample volume so that $>99.999\%$ of the CH_4 has been removed from the sample bulb and quantitatively trapped on the precolumn. This step (which takes 900 s) purges of $>99.99\%$ of the N_2 and O_2 entrained in the sample flow while allowing absorption of CH_4 onto the precolumn. Limiting the amount of N_2 and O_2 in the system dramatically lowers the IRMS

signal background, improving overall precision of measurement. To cryofocus, the precolumn is warmed and CH_4 is transferred by He carrier at 2.6 mL/min to a 70-cm loop of 0.32-mm (i.d.) PoraPLOT Q capillary column (Chrompack, Raritan, NJ) jacketed by 1.59-mm (o.d.) stainless steel tubing, ~ 20 cm of which is maintained in the LN_2 /pentane bath at $-130\ ^\circ\text{C}$. This step furthers the removal of N_2 and O_2 from the air sample. To release the CH_4 , the cryofocusing loop is brought out of the low-temperature bath and warmed to room temperature, thereby transferring the sample CH_4 onto the GC separation column.

The separation column is a 0.32 mm (i.d.) \times 25 m PoraPLOT Q column (Chrompack) and is temperature, pressure, and flow regulated by a Hewlett-Packard 6890 GC maintained at a constant flow of 2.6 mL/min. The chromatography allows separation of CH_4 from residual gas components in the air, namely, N_2 , O_2 , Ar, CO_2 , CO, nonmethane hydrocarbons, etc., not fully trapped or purged in preconcentration that may otherwise interfere with isotopic measurement. For carbon isotopic analysis, the GC (equipped with a cryogenic unit) is temperature programmed to $-50\ ^\circ\text{C}$ and ramped to $30\ ^\circ\text{C}$ just prior to CH_4 elution to resolve an unknown contaminant peak that otherwise interferes with masses 45 and 46 eluting just after the main CH_4 peak. In the case of hydrogen analysis, this peak does not interfere with masses 2 and 3 and the column is run isothermally at $30\ ^\circ\text{C}$. As CH_4 elutes from the separation column, it is either quantitatively oxidized to CO_2 and H_2O for carbon isotopic analysis or pyrolyzed to H_2 and C for hydrogen isotopic analysis. In the former case, column effluent passes through a 1.59 mm (o.d.) \times 30 cm alumina tube packed with CuO, NiO, and Pt wires maintained at a constant temperature of $960\ ^\circ\text{C}$ by a ThermoQuest/Finnigan combustion furnace. To maintain its oxidative capacity, the NiO and CuO catalysts are regularly reoxidized with UHP O_2 for several hours at $560\ ^\circ\text{C}$. For hydrogen analysis, pyrolysis occurs in a 1.59 mm (o.d.) \times 30 cm hollow alumina tube maintained at a constant temperature of

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1450 °C by a ThermoQuest/Finnigan TC unit. Upon exiting the furnace, the sample is routed through a 0.6 mm (i.d.) \times 20 cm Nafion dryer (Permapure Inc., Toms River, NJ) with a counter current of 50 mL/min UHP He to strip the effluent of H₂O resulting from combustion or column bleed. The Nafion dryer, coupled with regular column baking and extensive drying of air samples prior to column injection, keeps the H₂O signal (¹⁸i) from column effluent at <3 pA at all times during analysis measured by monitoring mass 18 at all times throughout several test runs. This is equivalent to a dew point of <−85 °C based on derivations from Leckrone and Hayes,²⁴ measured ionization efficiency of CO₂ in the Delta Plus XL, and relative ionization efficiencies of CO₂ and H₂O from Straub et al.^{25,26} Background H₂O has a notable impact on precision of measurement of $\delta^{13}\text{C}$ via an interfering mass 45 signal from HCO₂⁺ ions generated in the ion source. For measurement of $\delta\text{D-CH}_4$, H₂O similarly interferes with mass 3 ion currents by creating excess H₃⁺ in the ion source, contributing to measurement nonlinearity.²⁷ Given the stickiness of H₂O in the ion source region, we divert flow from column effluent at all times during the processing of a sample except for 400 s when reference and sample peaks are measured. We find background levels of ¹⁸i of <3 pA to be sufficiently low to allow for high precision, accuracy, and linearity of $\delta^{13}\text{C}$ and δD of CH₄ measurement at our signal-to-noise ratio.

Samples are introduced into the IRMS via an open split design of ThermoQuest/Finnigan (Combustion III interface), maintaining a split ratio of roughly 6.5:1, a 0.05-mm (i.d.) capillary allowing ~0.4 mL/min helium carrier into the ion source (i.e., 0.016 μL of CO₂ (5 nmol) and 0.066 μL of H₂ (20 nmol) for carbon and hydrogen analyses, respectively). Chromatograms and peak shapes for $\delta^{13}\text{C-CH}_4$ and $\delta\text{D-CH}_4$ are shown in Figure 2a and b for typical air samples. The column flow rate relative to flow entering the IRMS allows for a balance between well-defined peak shape, successful chromatographic separation, oxidation or pyrolysis efficiency, and sensitivity. Peak widths are 20 s (depending only slightly on concentration) with a full width at half-maximum of 8.5 s. CH₄ peak intensities (heights) are ~12 nA (3.5 V mass 44) for $\delta^{13}\text{C}$ and ~5.5 nA (5.5 V mass 2) for δD on 60- and 120-mL aliquots of ambient air, respectively. Importantly for peak integration, peak shapes are consistent between isotopomers (i.e., masses 44, 45, and 46 or 2 and 3) and the slight delay of the lighter isotopomers as a result of increased column molecule interactions is adjusted for as described in Ricci et al.²⁸

Isotope ratio measurements are made on a 3-kV ThermoQuest/Finnigan Delta Plus XL system as either CO₂ (masses 44, 45, and 46) or H₂ (masses 2 and 3) relative to working reference gases of UHP CO₂ and H₂ (Oxygen Services Co.). Note in the chromatograms that each sample is bracketed by standards (square peaks admitted directly to the ion source in a balance of helium carrier gas via a second open split) on either side of the sample peak (Gaussian peaks) to adjust for machine drift, which can result from changes in carrier gas, column bleed, or electronic drift

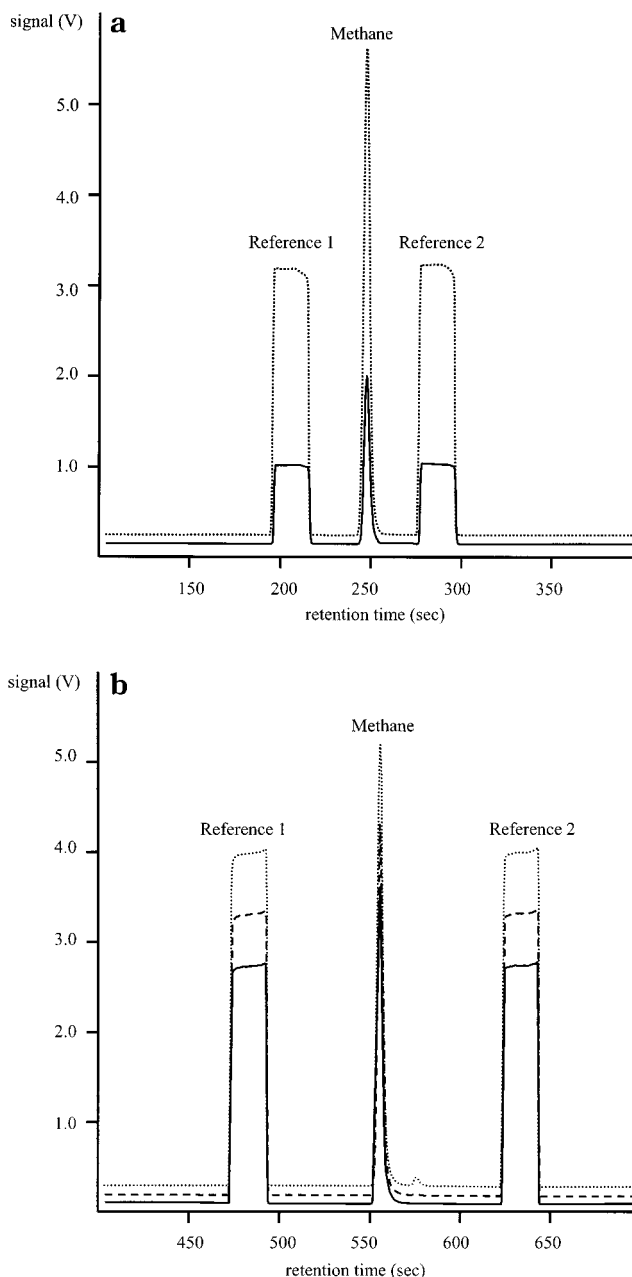


Figure 2. Chromatograms and peak shapes for CH₄ in a typical air sample. Gaussian sample chromatographic CH₄ peaks are bracketed with square reference gas peaks admitted directly to the ion source in a balance of carrier gas. (a) shows peak intensities for masses 44 (solid line), 45 (dashed line), and 46 (dotted line) from sample and reference CO₂ for measurement of $\delta^{13}\text{C-CH}_4$. (b) shows peak intensities for masses 2 (dotted line) and 3 (solid line) from sample and reference H₂ for measurement of $\delta\text{D-CH}_4$.

intrinsic to continuous-flow systems. Extensive laboratory tests indicate that machine drift can result in errors of up to 0.3‰ ($\delta^{13}\text{C}$) over the course of 1 h if not corrected for. Precon-GC/C/IRMS samples take ~40 min to run while precon-GC/P/IRMS samples take ~30 min.

For isotopic CH₄ work in elevated concentrations, only minor modifications are made to the system to adapt for a considerable range of concentrations, i.e., 10–1000 ppm.¹¹ Although linearity of measurement of the Delta Plus XL is excellent within a factor of 2 or 3 when working in the optimum signal intensity, the linear

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range is poor relative to other detectors. In our system, the dual-valved bulb is replaced with an 11-mL Pyrex vessel fitted with a gastight rubber septa to allow for a range of syringe injection volumes to account for variations in concentration among different samples (known from prior measurement on a separate GC flame ionization detector (FID) system). Run times were shortened to 20 min as the necessity for purging air from the preconcentration traps is considerably dissipated with higher concentrations. In doing so, and in using syringe-type injections into the carrier stream, precision is sacrificed somewhat. Typical precision for 10–1000 ppm CH₄ samples is 0.1–0.2‰ for $\delta^{13}\text{C}$. However, in a majority of CH₄ source studies, natural variability far exceeds this precision of measurement. Previous studies using conventional vacuum line techniques normally require several hours of work for one isotopic measurement require sample sizes necessarily much larger.¹¹

Air Sample Preparation for Dual-Inlet IRMS. Preparation of the samples for isotopic analysis by dual-inlet IRMS was done using a combustion vacuum line designed to separate CH₄ from other air sample constituents and to convert it to CO₂ and H₂O. After first separating and trapping CO₂ and H₂O from the air stream using a LN₂ cold trap at –196 °C, I₂O₅ on silica gel (Schütze reagent, Leco Corp., St. Joseph, MI) was used to convert CO to CO₂. This CO₂ was then trapped at –196 °C using LN₂. Product CO₂ from CH₄ combustion was then separated from potential contaminants of less volatility by using an ethanol/dry ice bath at approximately –78 °C. The CH₄ was quantitatively converted to CO₂ in a furnace packed with platinum catalyst (1% loading) supported on 3-mm alumina pellets at 745 °C. Details regarding the vacuum line design and procedure have been reported previously.^{7,9} A subsequent manometric measurement was used to determine the volume of CO₂ recovered for comparison to that expected from the known CH₄ concentration and volume of air sample processed. CH₄ mixing ratios from samples were measured using a Hewlett-Packard 5880A GC fitted with a FID.⁹ Our mixing ratio working standard is based on the NOAA/CMDL reference scale.²⁹ Our level of precision of measurement of CH₄ is ± 5 –10 ppb.

Determination of $\delta\text{D-CH}_4$ in a Calibration Gas. Since there exists no widely accepted method for determining $\delta\text{D-CH}_4$ in air (as there is in the case of $\delta^{13}\text{C-CH}_4$) at ambient atmospheric CH₄ concentrations (~ 1.78 ppm), we used a lecture bottle of Research Grade CH₄ (99.99% Linde Division Union Carbide, Danbury, CT) as a calibration gas. This calibration gas was diluted to 8850 ppm with ultrapure air (scrubbed of hydrocarbons, CO₂, and water vapor, Scott Marin, Inc.) into a 6-L canister to a total pressure of 1500 Torr. To determine $\delta\text{D-CH}_4$, small volumes of this sample were processed on a vacuum line designed to quantitatively oxidize CH₄ to CO₂ and H₂O trapping the constituents in LN-cooled Pyrex trap. Briefly, the dilute gas is passed at 8 mL/min through a Pyrex H₂O/CO₂ trap at –196 °C followed by a 25 mm \times 150 mm quartz furnace packed with platinized quartz wool (Shimadzu, Tokyo, Japan) held at 750 °C. The resulting H₂O and CO₂ are collected in a Pyrex trap at –196 °C and separated via distillation with an ethanol/dry ice bath at –78 °C. H₂O from combustion is then transferred to a Pyrex tube containing 0.250

g of zinc shot, following which the H₂O is reduced to H₂ in an offline reduction reaction at 500 °C.³⁰

Dual-Inlet IRMS Isotope Measurements. Dual-inlet IRMS measurements are made on a 10-kV Finnigan MAT model 252 relative to working gas standards. Our working CO₂ reference gas on the dual-inlet IRMS instrument is pure CO₂ with a value of –47.61‰ ($^{13}\text{C}/^{12}\text{C}$) versus V-PDB (designated NZME, obtained from NIWA in Wellington, New Zealand). Another working gas purchased from Oztech Gas Co. (Dallas, TX) with assigned value of –39.78‰ versus V-PDB is routinely compared to it. Both gases have been intercompared to two internationally recognized CO₂ standards, NBS-19 (CaCO₃) and IAEA-CO-9 (BaCO₃), which have established values of 1.95 and –47.12‰ versus V-PDB, respectively.³¹ Versus our NZME reference, clean dry CO₂ gas standards made from these carbonates had measured values of 1.92 and –47.18‰ for NBS-19 and IAEA-CO-9, respectively. Our precision of measurement on the clean dry CO₂ gas standards above is ± 0.01 ‰. Reproducibility of measurement of $\delta^{13}\text{C-CH}_4$ in whole air samples collected to provide ~ 200 -L volume of gas or higher is ± 0.05 ‰ when all errors associated with sample collection, processing, and analysis have been taken into account.

Our working H₂ reference gases are a suite of three H₂ cylinders which were purchased from Oztech Gas Co. These have been assigned calibrated isotope ratio values with respect to V-SMOW by Oztech (–108.0, 165.3, and –306.8‰) and are intercompared regularly in our laboratory with measurement precision of ± 1.0 ‰ to ensure consistency in our measurements over time. One gas (–306.8‰) was selected to be our working H₂ reference gas for the MAT 252.

On the continuous-flow GC/IRMS, working reference gases of UHP CO₂ and H₂ from Oxygen Services Co. were assigned values by comparison to our NZME CO₂ reference gas and from H₂ reference gases described above. They have assigned values of -34.28 ± 0.01 ‰ (1σ , $n = 5$) $\delta^{13}\text{C-CO}_2$ versus V-PDB and -169.4 ± 0.5 ‰ $\delta\text{D-H}_2$ (1σ , $n = 5$) versus V-SMOW based on nine standard/sample determinations per aliquot for five aliquots of the same gas.

RESULTS AND DISCUSSION

Comparison of $\delta^{13}\text{C-CH}_4$ Continuous-Flow GC/C/IRMS versus Vacuum Line Dual-Inlet IRMS. We intercompared the $\delta^{13}\text{C-CH}_4$ measurements made on our continuous-flow precon-GC/C/IRMS system with measurements made with our established vacuum line dual-inlet IRMS methodology. We used 24 whole air samples collected on a recent shipboard transect in July 2000 from Los Angeles, CA, to Auckland, NZ. The measurements from the shipboard transect are shown in Figure 3a. Samples were processed once each on the platinum catalyst vacuum line and the resultant CO₂ was measured against the NZME working $\delta^{13}\text{C-CO}_2$ standard. Yields were $100.5 \pm 0.2\%$ based on CH₄ mixing ratio measurement via GC-FID and manometric volume determination of resultant CO₂. Isotope measurements were made on the MAT 252 and are reported relative to V-PDB. Two of these air samples were replicated after the entire set was measured. These agreed within 0.02‰ of the original determination.

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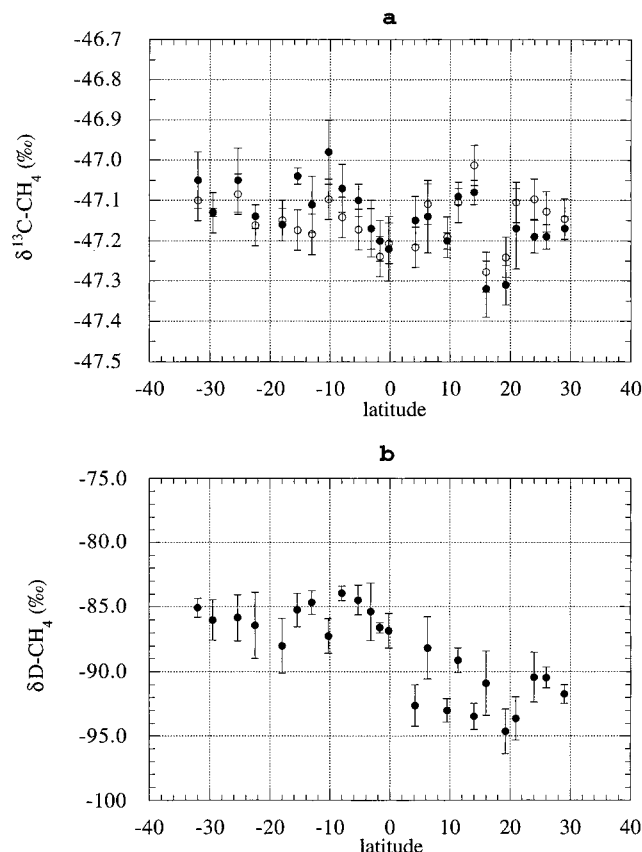


Figure 3. Results from continuous-flow measurement of (a) $\delta^{13}\text{C}-\text{CH}_4$ (closed circles) compared with vacuum line dual-inlet IRMS (open circles) and (b) $\delta\text{D}-\text{CH}_4$ of 24 whole air samples collected on a July 2000 Pacific Ocean transect.

All continuous-flow precon-GC/C/IRMS $\delta^{13}\text{C}-\text{CH}_4$ measurements were replicated three times from three separate aliquots of a given sample cylinder. Averages and standard deviations (1σ) of measurements for the 24 samples are shown in Figure 3a. The average precision of measurement on the continuous-flow $\delta^{13}\text{C}-\text{CH}_4$ system is 0.05‰ (1σ) (range $0.01\text{--}0.10\text{‰}$) and is within a factor of 3 of the shot noise limit.³² This level of precision approaches that obtained via conventional vacuum line and dual-inlet IRMS $\delta^{13}\text{C}-\text{CH}_4$ measurement.^{9,22} Sample blank was determined by running 60 mL of UHP helium carrier gas through the entire process. Several tests determined the CH_4 blank to have less than a 1-mV signal (3.3 pA), corresponding to an upper limit of 8 pmol of CH_4 . The CH_4 blank may be from carrier gas impurity or from the Haysep-D precolumn blank.

Figure 3a shows excellent agreement between the two methods of determination. Except for one case, agreement between sample pairs is within one standard deviation. Although these air samples were collected in a month that typically exhibits little or no interhemispheric gradient in $\delta^{13}\text{C}-\text{CH}_4$,^{22,23} even small changes in $\delta^{13}\text{C}-\text{CH}_4$ on the order of $0.1\text{--}0.2\text{‰}$ are detected by either system of measurement. A comparison of paired measurements averaged $0.01 \pm 0.03\text{‰}$ (95% confidence interval), indicating that any difference between the two methods can be explained by error associated with precision of measurement rather than systematic error. On the basis of this evidence, the continuous-flow system

presented here obtains adequate precision and accuracy with which to measure $\delta^{13}\text{C}-\text{CH}_4$ on background CH_4 concentrations while spatial and seasonal changes tend to be on the order of $0.1\text{--}0.3\text{‰}$ and long-term temporal changes even smaller. However, with its time-tested reliability, the conventional vacuum line dual-inlet IRMS system is still very valuable. In particular, with the vacuum line there is a validation of CO_2 yield from CH_4 after a sample is processed. Such validation does not occur with continuous-flow measurements. Typically, calculations of yield based on peak area or height do not meet the level of precision necessary to indicate small changes in overall system performance. Furthermore, the nine sample/standard (the number is operator selectable) determinations of $\delta^{13}\text{C}-\text{CO}_2$ made via dual-inlet IRMS on each sample provides for precision of measurement of 0.01‰ . As a result, for sample calibrations we find the conventional IRMS system to be ultimately more reliable and accurate. However, for ease of sample collection and speed of sample processing, the continuous-flow system is unequaled and can provide a high level of precision so long as careful intercalibration with whole air standards is maintained.

Comparison of $\delta\text{D}-\text{CH}_4$ Continuous-Flow GC/P/IRMS versus Vacuum Line Dual-Inlet IRMS. Measurements of $\delta\text{D}-\text{CH}_4$ of the research grade CH_4 Linde calibration gas standard were made by processing nine different $\sim 100\text{-mL}$ aliquots on the platinumized quartz wool vacuum line. Isotopic measurements were made on the dual-inlet MAT 252 IRMS instrument against the -306.8‰ working H_2 reference gas. H_2O "blank", contaminant H_2O from sources other than CH_4 , was determined by processing identical volumes of ultrapure air. It was determined to be less than $60\text{ }\mu\text{L}$ on sample sizes of $\sim 1.7\text{ mL}$ of sample H_2O from CH_4 . The isotope value of the research grade Linde calibration gas was determined to be $-55.5 \pm 3.5\text{‰}$ (1σ , $n = 9$) $\delta\text{D}-\text{CH}_4$ versus V-SMOW.

To run this standard on the continuous-flow precon GC/P/IRMS system (designed to run background levels of CH_4), the 8850 ppm standard was diluted to $1.765 \pm 0.008\text{ ppm}$ with ultrapure air into a 6-L canister pressurized to 1500 Torr. Measurements were made on 120-mL aliquots in a manner identical to that of an air sample as detailed above. On this system, the average isotope value was determined to be $-55.8 \pm 1.3\text{‰}$ (1σ , $n = 7$). Average offset between these two methods of determination is 0.3 ± 3.0 (95% confidence interval). The results show no statistical difference between these two methods and indicate that quantitative determination of $\delta\text{D}-\text{CH}_4$ is internally consistent and can be measured using this continuous-flow system.

Measurements of the 24 ambient air samples from the latitudinal transect were made three times each from three 120-mL aliquots of air from the cylinder. Analogous to measurement of $\delta^{13}\text{C}$, isotope determinations are made based on two bracketing reference gas peaks as shown in Figure 2b, correcting for small drifts in instrumental performance. Averages and standard deviations (1σ) for the 24 transect samples are shown in Figure 3b. Average precision of measurement was $\pm 1.5\text{‰}$ (1σ) (range $0.7\text{--}2.5\text{‰}$) and continues to improve as the system is further refined. The 24 air samples were measured three times each with average values of -85.8 ± 1.2 and $-91.7 \pm 2.0\text{‰}$ for the southern and northern hemispheres, respectively. Our δD data compare well to the recent data of Quay et al.,⁶ who reported measurements (n

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= 95) of $\delta\text{D-CH}_4$ from several cruises between 55° N and 65° S in the Pacific Ocean between 1989 and 1995. Average values were -81 ± 3 and $-91 \pm 5\text{‰}$ for the southern and northern hemispheres, respectively.

CONCLUSION

We have proven our system design and methodology for $\delta^{13}\text{C-CH}_4$ measurements by subjecting it to identical standards and intercalibration criteria as that demanded by researchers using dual-inlet IRMS to measure atmospheric CH_4 .^{8,9} Much faster isotopic analyses of atmospheric CH_4 without a loss in precision of measurement are made possible by using our CH_4 preconcentrator with continuous-flow IRMS method. Data reported here are the first data to be measured using both dual-inlet IRMS and continuous-flow IRMS for $\delta^{13}\text{C}$ measurement of atmospheric CH_4 and are the first to be reported using continuous-flow precon-GC/P/IRMS to measure δD of atmospheric CH_4 . Precision of measurement of 0.05‰ for $\delta^{13}\text{C-CH}_4$ and 1.5‰ for $\delta\text{D-CH}_4$ using continuous-flow IRMS proves adequate to determine spatial and temporal trends necessary to characterize atmospheric CH_4 .

Aside from the high level of precision obtainable, it is now possible to collect many more samples in a given time period because of the smaller air sample volume needed for analysis. The faster analysis time of continuous-flow GC/IRMS also allows

one to better keep up with the heavy workload generated by numerous sample collections. As an example, the CH_4 isotopic data presented in Figure 3 form a subset of our ongoing study of CH_4 and CO in air over the equatorial Pacific Ocean.³³ In this research, we collaborate with scientists at the National Institute of Water and Atmospheric Research (NIWA) in New Zealand who initiated the program in June 1996.²² The two laboratories have intercalibrated data sets through a sample exchange program and alternate sampling trips through a transect between Auckland, NZ (35° S) and Los Angeles, CA (35° N). Data such as these currently provide detail on the spatial and seasonal variation of mixing ratio and $\delta^{13}\text{C}$ of CH_4 over the Pacific equatorial region, including the intertropical convergence zone and both northern and southern temperate zones. Increased sampling frequency and measurement throughput made possible by continuous-flow GC/IRMS would be ideal for this type of study.

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