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**A Widely Tunable Infrared Laser Spectrometer for
Measurements of Isotopic Ratios of Carbon Cycle Gases**

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ABSTRACT

We have developed a high precision infrared spectrometer for analysis of stable isotopologues of carbon cycle gases using a difference frequency generation (DFG) mid-infrared light source. The eventual instrument will be suitable for on-site field measurements of $^{13}\text{C}/^{12}\text{C}$ ratios in methane and carbon dioxide without returning samples to a laboratory facility for analysis. The DFG source is coupled to a dual-path length absorption cell which allows the major and minor isotopologues to be detected with the same precision while minimizing the temperature dependence of the measurements. The prototype instrument developed in this Phase II project has been demonstrated to detect $^{13}\text{CH}_4/^{12}\text{CH}_4$ ratios with a precision of 0.5 ‰ and an averaging time of 20 s using concentrated methane in air with a mixing ratio of 2700 ppm. Methods for concentrating ambient air for isotopic analysis using this technique have been evaluated. Extensions of this instrument to other species such as $^{13}\text{CO}_2$, C^{18}OO , and CH_3D are possible by substituting lasers at other wavelengths in the DFG source module. The real-time continuous measurement capabilities of this instrument will greatly enhance the applications of stable isotope analysis for greenhouse gas source assessment, ecological process studies, and oil and gas exploration.

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I. Problem Identification and Significance

Determining the factors which control the atmospheric abundance of carbon dioxide (CO₂) and methane (CH₄), the two most important directly emitted greenhouse forcing gases and the predominant atmospheric components of the carbon biogeochemical cycle, is a critical component of the U.S. Global Change Research Program's "vision and perspective for the decade ahead" [USGCRP, 1999]. That program cites understanding "Influences of Sources and Sinks for Carbon on the Earth's Surface" as one of seven critical issues whose importance "far outstrips any purely economic measurement" [USGCRP, 1999]. Similar calls to "Understand the changing global biogeochemical cycles of carbon and nitrogen," and to "Determine the fluxes of greenhouse gases into and out of the earth's systems" have been issued by the National Academies' Committee on Global Change Research [National Research Council, 1998]. Indeed, a much more complete understanding of the biogeochemical cycling of CO₂ and CH₄ is crucial if we are to devise efficient and cost effective means of reducing greenhouse gas emissions in order to meet our national goals expressed in the Kyoto Convention.

Both CO₂ and CH₄ have a wide range of sources and sinks with both natural and anthropogenic components [IPCC, 1995]. Since both gases are produced and consumed in biological activity, many of these sources and sinks are strongly tied to ecological processes and may represent significant feedback terms as climate changes. The great diversity of the biosphere has frustrated both accurate quantification and the acquisition of a predictive knowledge of many of these processes. Both gases also have large industrial sources driven by energy and transportation sector activities, and are also produced by biomass burning. Uptake by terrestrial plants and the ocean are large sinks for CO₂ that remain poorly quantified. Methane is lost by oxidation in the atmosphere and by soil uptake, both with persistent uncertainties.

The spatial and temporal variations in the isotopic concentrations of CO₂ and CH₄, coupled with knowledge of the degree of isotopic enrichment or depletion imposed by the chemical kinetics or biochemistry of source and sink processes can provide valuable constraints on the relative strengths of the fluxes controlling their atmospheric abundances [Trumbore, 1995]. For instance, measurements of the variation of ¹³C/¹²C in the atmosphere and oceans have provided important constraints on the fraction of fossil fuel combustion CO₂ being absorbed by the oceans [Quay et al., 1992; Tans et al., 1993; Francey et al., 1995]. Variations in the ¹³C/¹²C ratio of atmospheric CH₄ have also been used to clarify the dramatic and puzzling changes in atmospheric methane growth rates during the 1980s and 1990s (e.g. [Gupta et al., 1996]). The interest in this critical problem has led to extensive ongoing efforts to better characterize the ¹³C/¹²C signatures of various methane sources (e.g. [Bergamaschi et al., 1998; Sugawara et al., 1999; Chanton et al., 2000]). Furthermore, detailed mechanisms and rates for the various chemical and/or biological processes affecting CO₂ and CH₄ production and loss can often be determined by introducing isotopically labeled components and measuring the resulting changes in CO₂ and CH₄ composition [Schimel, 1993]. Stable isotopes, rather than rarer and more difficult to acquire and/or measure radioactive isotopes, appear to

offer the most promise for continuing studies of both trace gas source/sink fluxes and process mechanism/rate studies. While many of the studies performed to date have focused on $^{13}\text{C}/^{12}\text{C}$ values, there is promise of additional valuable information in $^{18}\text{O}/^{16}\text{O}$ data for CO_2 and D/H ratios for CH_4 , particularly if these data were easier to obtain [Bergamaschi et al., 1998](S. Tyler and R. Cicerone, private communication, 2000).

Stable isotope abundances are typically expressed in terms of δ units which are based on a comparison of the ratio of a rare to abundant isotope in a sample (e.g. $^{13}\text{C}/^{12}\text{C}$), R_x , to the same ratio in a standard sample, R_{std} ; they are defined as:
$$\delta_x = [(R_x - R_{\text{std}})/R_{\text{std}}] \times 1000.$$
 Thus, a measurement with a precision of one δ unit is equivalent to 0.1‰ or 1‰.

The standard method for determining trace gas stable isotope ratios is isotope ratio mass spectrometry (IRMS). IRMS is an extremely precise method, with $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values (analyzed as CO_2) typically obtained with precisions of 0.01-0.05‰ and 0.02-0.05‰, respectively. δD values (analyzed as H_2/HD) are not as precise, 1-3‰, and require samples enriched well above normal atmospheric CH_4 levels [Trumbore, 1995] (S. Tyler private communication, 2000). While its precision is very good the IRMS technique has a number of experimental drawbacks. Non- CO_2 carbon gas samples must be quantitatively separated from atmospheric CO_2 and completely oxidized before analysis. Hydrogen containing gases must be separated and quantitatively reduced to H_2 . For analyses based on CO_2 , atmospheric N_2O , which has the same molecular weight must be eliminated or the mass spectra suitably corrected. Gas chromatographic (GC) separation of CH_4 from air and water samples has been developed with $\delta^{13}\text{C}$ precisions of 0.2 to 0.9‰ reported [Merritt et al., 1995; Sansone et al., 1997]. Commercial IRMS and GC/IRMS units are available, but they are very expensive (typical units are ~\$250,000) and require permanent installation for reliable operation. Thus, field samples are normally returned to the laboratory and analyzed long after they are taken, prohibiting the guidance of sampling strategies by near realtime data. Furthermore, great care must be taken in preparing each sample for analysis making precise IRMS an extremely time consuming and taxing art and interface issues still trouble commercial GC/IRMS units making reliable measurements difficult (S. Tyler, private communication, 1999). Finally, all forms of IRMS inherently destroy the sample during the measurement. Given the importance of precise CO_2 and CH_4 stable isotope measurements to help understand greenhouse gas driven global climate change processes and to devise efficient and cost effective mitigation strategies plus the difficulty, excessive time and expense of performing IRMS isotopic abundance determinations, a clear opportunity for new technology exists.

II. Technical Approach

Our approach is to use high resolution tunable infrared laser differential absorption spectroscopy (TILDAS) to develop an isotope ratio spectrometer that could be used for both CO_2 and CH_4 isotopic variants. The instrument uses a widely tunable infrared laser light source based on difference frequency generation (DFG) techniques. The source is coupled to a novel dual-path length multiple pass absorption cell which allows simultaneous measurements of the major and minor isotopes using a single sample

volume and using absorption lines of similar temperature dependence. These innovations greatly improve the precision and applicability of the TILDAS method to isotopic measurements.

Infrared techniques are frequently used when precise, high temporal or spatial resolution measurements of CO₂, CH₄ and related trace gases are required. For small molecules like CO₂ and CH₄ TILDAS techniques are generally more sensitive, and usually more precise, than competing non-dispersive infrared (NDIR) or Fourier transform infrared (FTIR) techniques [Kolb et al., 1995]. For isotopic measurements, the high spectral resolution of tunable infrared laser techniques is particularly attractive since they are more capable of isolating spectral features attributable to each isomer of interest. For instance, while Griffith and co-workers [Esler et al., 2000b; Esler et al., 2000a] have recently demonstrated an FTIR system capable of making $\delta^{13}\text{C}$ measurement of CO₂ in whole air with a precision of 0.1 ‰ it is clear that due to band overlaps this instrument cannot provide precise $\delta^{18}\text{O}$ measurements for CO₂ or δD for CH₄ without going to an order of magnitude higher spectral resolution (0.1 cm⁻¹) and a much more expensive spectrometer. Even then $\delta^{13}\text{C}$ measurements for CH₄ may not be feasible.

TILDAS techniques, usually employing either tunable lead salt diode or Zeeman tuned rare gas lasers, have been widely deployed to make CO₂, CH₄ and related atmospheric trace gas (CO, N₂O, NO, NO₂, H₂CO, HOOH, HNO₃, etc.) measurements for both mapping atmospheric concentration distributions and for micrometeorological or tracer ratio measurements of surface fluxes (e.g. [Poldowski and Lowenstein, 1993; Webster et al., 1994; Weinhold et al., 1994; Lamb et al., 1995; Zahniser et al., 1995; Güllük et al., 1997; Nelson, 1998; Weinhold et al., 1998; Mosher et al., 1999]). In our laboratory at Aerodyne Research, Inc. (ARI), we have extensive experience in fielding both tunable lead salt diode laser systems (e.g. [Zahniser et al., 1995; Nelson, 1998]) and Zeeman tuned rare gas laser instruments (e.g. [Lamb et al., 1995; Mosher et al., 1999]).

The use of TILDAS techniques to make trace gas stable isotope measurements has also been previously addressed. Lee and Majkowski [Lee and Majkowski, 1986] used lead salt diode lasers to measure $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ in CO. Recently, Kerstel et al. [Kerstel et al., 1999] have described an optically pumped color center laser system for determining δD , $\delta^{17}\text{O}$, and $\delta^{18}\text{O}$ in water vapor. For the target gases of primary interest here, Becker et al. [Becker et al., 1992b] described a lead salt laser system for $\delta^{13}\text{C}$ measurements of CO₂ in the 2291 cm⁻¹ region with a reported precision of 4‰, while Bergamaschi et al. [Bergamaschi et al., 1994] have developed a lead salt diode laser system to measure $\delta^{13}\text{C}$ and δD for CH₄ in the 3007 cm⁻¹ and 3042-3044 cm⁻¹ regions with a standard deviation for IRMS measurements of 0.44 ‰ and 5.1‰, respectively. Bergamaschi et al. [Bergamaschi et al., 1998] have reported using this latter system to determine δD for an extensive set of field samples. In addition, in our laboratory at ARI, Keabian et al. [Keabian, 1996] have developed the concept of using a Zeeman tuned HeNe laser system to make both $\delta^{13}\text{C}$ and δD for CH₄ near 2999 cm⁻¹, with a calculated precision of 0.5‰ for each isotopic abundance using a sample size of 62 μmole of pure methane. We have also demonstrated detection of ¹³CO₂/¹²CO₂ ratios with a precision of 0.2 ‰ using liquid nitrogen cooled lead-salt TDL system [McManus et al., 2002].

Finally, using a newly developed quantum cascade laser in the 1241 cm^{-1} region, Kosterev et al. [Kosterev et al., 1999] have just demonstrated $\delta^{13}\text{C}$ and δD measurements of uncertain precision for samples of CH_4 enriched to 15.6 ppmv.

The major barrier to the more general use of TILDAS technology to isotopic measurements has been the lack of reliable, high spectral purity, widely tunable, continuous wave (cw), mid-infrared laser sources. The two laser types most widely used for field measurements both have drawbacks. Tunable lead salt diode lasers are currently available from only two commercial sources, require cryogenic cooling for cw operation, have limited tuning ranges for each diode, and are not always available in the wavelength regions best suited for isotopic measurements (lately $\sim 3000\text{ cm}^{-1}$ lasers for CH_4 are scarce.) Zeeman tuned rare gas lasers are not commercially available (we make our own at ARI), cover only a few wavelength regions and have very limited tuning ranges. Quantum cascade lasers are very promising, with higher power and potential wider tuning ranges than lead salt diodes, but they are currently only commercially available for research use, noncryogenic cw QCLs are not yet commercially available, and QCLs in general are not available in the $\sim 3000\text{ cm}^{-1}$ range best suited for CH_4 isotopic measurements or the $\sim 2300\text{ cm}^{-1}$ region for optimal CO_2 isotopic measurements at this time.

However, an exciting new broadly tunable, high power non-cryogenic mid-infrared source has recently become available. This source employs difference frequency generation (DFG) in the nonlinear optical material periodically poled lithium niobate (PPLN). The most impressive published exploitation of this material for mid-infrared spectrometry has come from a Rice University/Naval Research Laboratory collaboration headed by Frank Tittel and Lew Goldberg. This collaboration has recently reported on one PPLN DFG system pumped by a combination of a near infrared distributed Bragg reflector near infrared diode laser at 1083 nm and an extended cavity widely tunable (814-870 nm) near infrared diode which produced over a half a μW of continuously tunable cw output between 3058 and 2273 cm^{-1} [Tittel et al., 1999]. This same collaboration has also reported on a high power, high spectral purity system pumped with diode laser seeded fiber amplifiers that tunes continuously in the 3000 cm^{-1} spectral region required for CH_4 isotopic measurements [Lancaster et al., 1999a; Lancaster et al., 1999b].

DFG laser sources utilizing PPLN with near infrared diode laser inputs represent an attractive and feasible widely tunable, non-cryogenic mid-infrared technology for carbon cycle trace gas isotopic abundance measurements. In fact, while the effort in this program concentrated on $\delta^{13}\text{C}$ and δD in CH_4 and $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in CO_2 , extension of the DFG/PPLN system to slightly longer wavelengths will allow its use for determinations of $\delta^{13}\text{C}$ and $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in CO as well as $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ in N_2O , whose sources and sinks are both also of considerable interest to the global change research community [Bergamaschi et al., 1998; IPCC, 2001].

III. Project Objective

The overall objective of the Phase II project was to design and construct a field deployable instrument for precise spectroscopic measurements of isotope ratios for methane and carbon dioxide. The performance goal for the instrument is to measure $\delta^{13}\text{C}$ with a precision of 0.3 to 0.5 ‰ and a δD in the range of 0.5 to 3.0 ‰ for methane samples that have been preconcentrated to $\sim 3000\text{ }\mu\text{mol/mol}$ using simple activated charcoal sorption/desorption techniques. This same instrument was to be designed to measure $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of CO_2 in whole air samples with a precision in the range of 0.3 to 0.5‰. The analysis of the isotopic ratios needs to be automatic and require measurement times of 10 minutes or less.

The instrument was constructed and tested for methane isotopes using the approach outlined earlier. A widely tunable infrared source based on laser difference frequency generation is tuned to spectral absorption lines of methane. The source is rapidly swept across lines from both the major and minor isotopic components which are closely spaced in frequency, and which have similar transition ground state energies (for insensitivity to temperature). Light from the IR source is split to follow both short (0.4m) and long (36 m) absorption paths through the same sample cell. Spectra measured in the short path for the major isotopic component and spectra in the long path for the minor isotopic component have similar (and nearly optimal) absorption depths. The spectra are automatically analyzed using Aerodyne proprietary, high precision TILDAS signal processing techniques (TDLWintel program). Specific technical objectives are listed below:

- Task 1: DFG Laser Source Design and Construction
- Task 2: Isotope Spectrometer Design and Construction
- Task 3: Data Acquisition and Processing System Development
- Task 4: Instrument Testing and Validation with Isotopic Standards

IV. Project Team

The Phase II work was a collaboration between Aerodyne Research, Inc., Sandia National Laboratory and the University of California at Irvine. Sandia was responsible for the design and construction of the DFG infrared source (Task 1). Aerodyne Research was responsible for the remainder of the instrument, including the optical and electronic modules (Tasks 2 and 3). Aerodyne also was responsible for overall instrument integration and testing, as well as project management. The University of California at Irvine assisted in testing and validation with isotopic standards (Task 4)

V. Phase II Results: DFG Laser System for $^{13}\text{CH}_4/^{12}\text{CH}_4$ Measurements

DFG Laser Source Design and Construction

There are a variety of near-IR tunable and fixed-frequency lasers that can serve as DFG pump and signal sources. The most capable tunable lasers are the Littman extended-cavity diode lasers (ECDLs). They are typically able to coarsely scan over 10's of nm with continuous mode-hop-free tuning ranges that vary from 1-2 cm^{-1} (e.g. lasers manufactured by Sacher Laser Corporation) to the full 10's of nm coarse-tuning bandwidth of the diode (e.g. lasers manufactured by New Focus, Inc). Ramping is

possible at rates of up to 2 kHz depending on the scan range. The specified spectral linewidths of the ECDLs are ≤ 300 kHz, with a time-averaged linewidth when ramping for 1 second of 1 MHz. Other tunable diodes are the distributed feedback (DFB) sources, which have a more limited tuning range (~ 10 cm⁻¹ via temperature; 1-2 cm⁻¹ mode-hop-free). Unfortunately, those lasers are presently only available at wavelengths close to the telecommunications bands at 1550 nm and 1310 nm. Fixed frequency lasers include miniature solid-state devices (Nd:YAG, Nd:YLF, and Nd:YVO₄) and Fabry-Perot laser diodes. The latter were excluded from consideration due to concern over the lower frequency stability associated with that type of cavity.

In Phase I several options for the design of the DFG laser source were studied. The option chosen offers the least risk at the expense of a compromised tuning range. In this strategy for generating tunable mid-IR radiation for use in the isotope spectrometer, there are two ECDLs, each mixed with a single common fixed-frequency solid-state laser at 1053 nm. The fixed-frequency laser is resonated. In this design the power-product exceeds that which is necessary for achieving the isotope spectrometer specification by a wide margin. The 1053 nm laser and the 1550 nm ECDL are widely-used devices that have well-established performance and multiple vendors. The 1053 nm laser is available in very narrow linewidth (≤ 1 MHz). The 847 nm ECDL is a less widely-used wavelength, but still available from two sources.

The general design for the optical arrangement for generation of the 3.3 μm light is given in Figure 1. A compact arrangement was built and delivered by Sandia to ARI for incorporation into a measurement instrument[Lehmann, 2003]. A detailed description of the DFG laser is given in the Thesis by Uwe Lehmann [Lehmann, 2003]. The design strategy for the dual laser system is shown in the schematic in Figure 2. The single laser (single ECD) form of this design was delivered to ARI in Phase II for $^{13}\text{CH}_4/^{12}\text{CH}_4$ measurements.

Selection of Specific Spectroscopic Region for Methane Isotope Analysis

The isotope analysis method measures the absorption of lines of the major and minor isotopes and compares the absorption ratio for the sample to that of a reference gas. Ideally, we would like to monitor the major and the next two most abundant minor isotopes simultaneously. A set of lines must meet the following requirements:

- 1) Lines from the major and each of the two next most abundant minor isotopes need to be close enough together that the scanning range of the laser system (roughly 2 cm^{-1}) can cover all three isotopes.
- 2) The lines should have similar absorbances at natural abundance in order to minimize the dynamic range required of the detection system.
- 3) The lines need to be non-overlapping and free of interference from other atmospheric species. The primary source of interfering lines is H_2O vapor.
- 4) The lines need to have similar lower state energy levels so that the variation of line strength with temperature is closely matched. In other studies [Becker et al., 1992a; Bergamaschi et al., 1994; Kerstel et al., 1999], this has presented a problem because the much larger abundance of the major isotope meant that sets of lines that met requirement (2) came from very different lower energy levels. However, the unique cavity configuration demonstrated in this Phase I project allows detection at two discrete pathlengths, 0.4 m for the major isotope and 36 m for the minor isotopes. This in turn allows detection of lines from similar lower state energy levels. If we control the temperature to within 0.1 K between the sample and reference measurements (easily achievable), the lower state energy levels can be separated by 100 to 300 cm^{-1} and still maintain a precision of 0.2‰ to 0.5‰ [Bergamaschi et al., 1994].

Suitable sets of lines were identified by generating spectra and looking for lines that met the above requirements. Line positions and line strengths for the isotopes of CO₂ and CH₄ were taken from the HITRAN (High-resolution TRANsmission) data base [Rothman et al., 2003]. A set of methane lines shown in Figure 3 were studied in Phase II with the Sandia DFG source. The transmission in the upper panel would result from

multipass (36 m) detection and the lower panel from the short path length detection (0.4 m). The mixing ratio for the simulation was 3000 ppm. The minor isotopic species is measured with the longer pathlength while the major species is measured with the double pass detection scheme. The lower state energy levels, given beneath the lines in the figure in units of cm⁻¹, are approximately equal for the ¹²CH₄ and ¹³CH₄ isotopic lines in this region (105 vs. 157 cm⁻¹)

Spectrometer Design

The Aerodyne optical module was designed to collect and condition the infrared light from the DFG source, transport the light to the multipass cell, and then transport light from the cell to a pair of infrared detectors. The transport and focusing optics were entirely reflective, thus avoiding possible interference fringes from transmissive components. The various elements of the design are described below.

The DFG source produces light at 3.3 μm. Light is collected with an objective and then directed into the optical train. A visible trace laser beam is coaligned with the infrared

path to ease alignment. The IR beam and the trace beam come to a first focus at a pinhole, which serves as an input aperture. Past the first focus, the beam is transported and refocused into the cell. The beam into the cell are narrow (with $F\# > \sim 100$) and approximately match the beam focal properties to the cell. A matched beam reproduces the focal properties of a stable recirculating mode in the cell, which minimizes the beam size on the mirrors.

Just in front of the cell, the beam is split into two parts, which separately follow short and long paths through the cell. That arrangement allows generation and separation of the on-axis 2-pass beam with a single element. It maintains nearly equal distances for the two paths on the input side, so that optical matching to the cell is accomplished with a single set of optics. It also produces an appropriate power balance between the two paths.

The cell is our 36 meter design, with 182 passes (for the long path) in a base length of 20 cm, and with a volume of 0.3 l. The short path length is two passes, based on a single reflection from the back mirror of the cell. Two separate beams emerge from the cell, which are directed toward two focusing mirrors and two cooled detectors.

The DFG-based instrument used for measurement of methane isotopes is shown in Figure 4. This test system included the DFG laser system (1), the multipass/double pass cell (2), optics for separating the laser into 2 paths, and also providing a normalization path (3), and infrared detectors (4). Infrared detectors (InSb) that were mounted in a large lead salt tdl dewar were used in this system, as these were available for use. But more compact detectors would be incorporated into other systems.

Figure 4. Photo of DFG Isotope system in Lab. 1: DFG laser. 2: Multipass cell 3: optics 4: infrared detectors

A key feature of the instrument is the dual path length absorption cell [McManus et al., 2002]. Our approach is to use the same measurement volume with two different path lengths for the two species, that have a ratio of path lengths similar to the difference in mixing ratios. In this approach, the absorption depths will be similar for the more abundant species in the short path and the less abundant species in the long path. Thus, the measurements on the two paths are simultaneously optimized to have the absorption depth providing the highest precision. Since the two measurement paths share the same volume, the gas concentrations, temperatures and pressures are precisely the same. Thus, error effects which depend on these variables are largely canceled.

For this project we designed an optical arrangement to efficiently couple light into an astigmatic Herriott cell with two different path lengths. The setup uses one of our standard low-volume astigmatic Herriott cells. The cell is normally adjusted to provide 182 passes in a 20 cm base length, which gives a path length of 36 meters. With 3.8 cm diameter mirrors, the enclosed volume is 0.3 liters. The mirrors have a reflectivity of 99.1% from 3 to 10 μm resulting in a 20% transmission of light through the cell.

A diagram of the cell coupling arrangement is shown in Figure 5. The two path lengths are defined by the number of cell passes, either 2 (0.4 m pathlength) or 182 (36 m pathlength). The beam for the 2 pass leg is injected nearly straight on the cell center axis,

Figure 5 Dual Path Length Absorption Cell

and it returns nearly on the same axis after reflecting from the back mirror. The beam for the 182 pass pattern is injected at an angle to the center axis (~ 5 degrees) and it exits on the opposite side of the axis, i.e. separated from the input beam by 10 degrees. The method of injecting the light into both paths is to place a beamsplitter on the cell center axis. Light from the laser reflects from the front face of the beamsplitter into the 2 pass path. Light transmitted by the beamsplitter is injected off-axis, to follow the 182 pass path. The beamsplitter is composed of low-index material (BaF_2) which reflects $\sim 8\%$ (S-polarization, 45 degrees) and transmits 92%. This creates an appropriate balance between the powers in the different paths. There should be more initial power in the 182 pass path because light will be lost in the multiple reflections. A secondary reflection from the back face of the BS will slightly weaken the 182 pass input beam (to $\sim 85\%$ of the initial

laser power). The 2 pass light is collected after transmission through the beamsplitter, which introduces only a small additional loss. The secondary unwanted reflections from the beamsplitter produce weak beams which are spatially offset and thus are easily blocked, reducing the chance of interference fringes.

This optical arrangement solves several problems at once. It allows generation and separation of the on-axis 2-pass beam with a single element. It maintains nearly equal distances for the two paths on the input side, so that optical matching to the cell is accomplished with a single set of optics. It produces an appropriate power balance between the two paths. The efficient use of light in the setup is important for achieving the maximum precision.

The method of signal normalization was employed with the DFG system to improve dramatically the precision of the measurements. This differs from our experience with cw TDL lasers with which we have not used this technique as it was never deemed to be necessary due to lower source noise. In Figure 6 is methane data collected at 10 Hz without normalization is compared to normalized data. The rms in this data stream dropped from 110 ppb Hz^{-1/2} to 4 ppb Hz^{-1/2}.

Laboratory Measurements of Methane Isotopes

A series of laboratory measurements were conducted with the prototype DFG laser at 3.3 μ m incorporated into the ARI Isotope Spectrometer. Concentrated methane samples were made using pure methane diluted with room air to obtain a mixing ratio of approximately 2700 ppm in the sample. In Figure 7 approximately 15 minutes of continuous 1 second measurements is shown. The absorption cell pressure was 20 torr during these measurements to maintain spectral separation of the lines, which is possible with the narrow linewidth of the cw laser.

The 1 sec source noise was reduced in the ratio of the isotopes. The 1sec RMS was 7‰ and 8‰ for the double pass $^{12}\text{CH}_4$ and multipass $^{13}\text{CH}_4$, respectively. Because the source of some of the noise in each is the same, the ratio of the data streams ($^{13}\text{CH}_4/^{12}\text{CH}_4$) has reduced noise. The 1 sec rms of the ratio is 2‰.

Figure 7 $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ measurement with ARI isotope spectrometer and 3.3 μm DFG laser. Top panel: Blue: $^{12}\text{CH}_4$ mixing ratios; Red: $^{13}\text{CH}_4$ mixing ratios. Bottom panel: The isotope ratio ($^{13}\text{CH}_4/^{12}\text{CH}_4$) versus time.

The long term stability of the measurement is evaluated using the Allan variance technique [Allan, 1966; Werle et al., 1993] which distinguishes high frequency random variations in the measurement from systematic variations at longer time scales. The contributions of random noise will decrease with $t^{-1/2}$, so that a plot of variance (σ^2) with increasing integration time would be expected to have a slope of -1 until other systematic drifts due to temperature, optical instability, or laser instability dominate. An Allan plot of the ratio of the minor and major isotopologues is shown in Figure 8. The variance of $^{13}\text{CH}_4/^{12}\text{CH}_4$ decreases approximately with t^{-1} as would be expected for random noise. The observation that the decrease in the variance does not follow exactly the t^{-1} line (solid grey line in Figure 8), indicates the presence of noise sources in the 1 to 10 s time scale. The variance has a minimum at 20 seconds corresponding to a minimum of σ_{Allan} 0.5‰. The limiting factor in the noise appears to be due to excess noise in the fiber amplifier. Design improvements are expected to eliminate this source of noise and extend the precision to 0.1‰.

The ARI-Sandia DFG isotope spectrometer has been demonstrated for the analysis of methane isotopologues. The incorporation of the DFG laser into the TILDAS system has the advantages of a widely tunable laser with narrow linewidth ($<0.001\text{ cm}^{-1}$) and excellent beam quality. These features are very important for monitoring multiple lines in a limited spectral region, and for maximizing the optical depth of the features. The disadvantage of the laser system, however, is its relative complexity as compared to TDL and QCL systems. For the case of methane detection by mid-infrared absorption, isotope ratio measurements require sample concentration for ambient measurements. This applies also to mid-ir absorption systems with QCL or TDL lasers and the similar pathlengths.

Instrument Testing and Validation using Isotope Standards

We are continuing to test the DFG system and validate isotope samples/standards received from UC Irvine. Eight cylinders containing a range of methane mixing ratios and isotope mixtures were prepared and analyzed by S. Tyler's group at UC Irvine and delivered to ARI for testing. The characteristics of the samples are given in Table 1. The methods used to prepare these samples are outlined in general below, and described in more detail in a report from UC Irvine in the Appendix. Three of the standards were made from the dilution of pure CH_4 ; the remaining are concentrated ambient laboratory samples. The concentration process to enhance the mixing ratio of methane in air is extremely difficult to accomplish without affecting the isotopic abundance in the sample.

An evaluation of the concentration feasibility is given in the UC Irvine Report in the Appendix.

As given in the table, different concentration media were utilized to make the samples (e.g. Porapak Q, Silica Lite, HayeSep D). The media were able to concentrate air samples with various levels of success. We plan to measure isotope ratios of these standards. This may be difficult for the samples at the lower range of mixing ratio, e.g. the Silica Lite samples with mixing ratios of ~9 ppm.

Table 1: Methane Isotope Standards from UC Irvine

List of UC Irvine Samples Sent to Aerodyne				
Canister #	Description	CH₄ conc. in ppm	δ¹³C-CH₄ in per mil	δD-CH₄ in per mil
RC-9	CH ₄ in Air STD diluted from pure	175	-48.3	-165.0
RC 13	CH ₄ in Air STD diluted from pure	806	-48.3	-165.0
ST-7	CH ₄ in Air STD diluted from pure	7460	-48.3	-165.0
ST-11	Silica Lite -80 C/ -120 C	8.8	approx. -46.7	-113.4
ST-10	Silica Lite -80 C/ -120 C	8.9	approx. -46.7	-115.4
RC-15	Silica Lite -80 C/ -120 C	9.3	approx. -46.7	-112.1
RC-12	HayeSep D -120 C/ -120 C	27.5	approx. -46.7	-112.0
RC-19	Porapak Q -196 C/ -120 C	21.7	approx. -46.7	-92.9
All canisters pressurized to approx. 5 psig				

Isotope Ratio Analytical Procedures at UC Irvine. Two methods are used to prepare and analyze air samples for stable isotope ratio analyses. One method uses conventional dual inlet isotope ratio mass spectrometry (IRMS). In this method, air samples are processed using a combustion vacuum line -- a necessary step to separate CH₄, CO and CO₂ from other constituents of the air sample and to convert CH₄ and CO to CO₂. These samples are then measured on the UC Irvine Finnigan Mat model 252 dual inlet IRMS instrument. The reproducibility of $\delta^{13}\text{C}$ measurements from 200 liters or more of replicate air samples, when all possible errors associated with differences in sample canisters, sample pumping, vacuum line processing, and isotope measurement are taken into account, is $\pm 0.05\text{‰}$ for $\delta^{13}\text{C}$ of CH₄ and $\pm 0.02\text{‰}$ for $\delta^{13}\text{C}$ of CO₂.

The second method of obtaining stable isotope data uses our continuous flow gas chromatograph/combustion IRMS instrument (Finnigan Delta XL+). It is necessary to preconcentrate background levels of either CH₄ or CO₂ before they enter the cf-GC/C/IRMS using this system. UC Irvine has designed and developed a CH₄ concentrator based on the framework of the commercially available preconcentrator made by Finnigan Mat for rapid, precise analyses of atmospheric CH₄, but not for atmospheric CO₂ [Rice et al., 2000]. The results for CH₄ can be compared to measurements made using an older conventional IRMS instrument. With the new cf-IRMS system we have a precision of $\pm 0.05\text{‰}$ in measuring $\delta^{13}\text{C}$ -CH₄ (from ~50 ml of whole air) and $\pm 1.5\text{‰}$ in measuring δD (from ~100 ml of whole air).

Dual Inlet IRMS Isotope Gas Standards. The working CO₂ reference gas on the dual inlet IRMS instrument is pure CO₂ with values of -47.61‰ ($^{13}\text{C}/^{12}\text{C}$) and -16.72‰ ($^{18}\text{O}/^{16}\text{O}$) versus v-PDB and v-PDB-CO₂ respectively (designated NZME, obtained from NIWA in Wellington, New Zealand). Another working gas purchased from Oztech Gas Co. (Dallas, TX) with assigned values of -39.78‰ and -25.78‰ versus v-PDB and v-PDB-CO₂ respectively is routinely compared to it. Both gases have been inter-compared 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 PDB and v-PDB-CO₂, respectively, and -2.20‰ and -15.28‰ versus v-PDB and v-PDB-CO₂, respectively [Stichler, 1995]. Versus our NZME reference, clean dry CO₂ gas standards made from these carbonates had measured values of 1.92‰ and -2.11‰ for NBS-19 and -47.18‰ and -15.45‰ for IAEA-CO-9. Our precision of measurement on the clean dry CO₂ gas standards above is $\pm 0.01\text{‰}$. Reproducibility of CH₄ in whole air samples collected to provide ~200 liters volume of gas or higher is $\pm 0.05\text{‰}$ when all errors associated with sample collection, processing, and analysis have been taken into account.

VI. Summary and Conclusions

We have developed a high precision infrared spectrometer for analysis of stable isotopologues of carbon cycle gases using a difference frequency generation (DFG) mid-infrared light source. The eventual instrument will be suitable for on-site field measurements of $^{13}\text{C}/^{12}\text{C}$ ratios in methane and carbon dioxide without returning samples to a laboratory facility for analysis. The DFG source is coupled to a dual-path length absorption cell which allows the major and minor isotopologues to be detected with the same precision while minimizing the temperature dependence of the measurements. The prototype instrument developed in this Phase II project has been demonstrated to detect $^{13}\text{CH}_4/^{12}\text{CH}_4$ ratios with a precision of 0.5 ‰ and an averaging time of 20 s using concentrated methane in air with a mixing ratio of 2700 ppm. Extensions of this instrument to other species such as $^{13}\text{CO}_2$, C^{18}OO , and CH_3D are possible by substituting lasers at other wavelengths in the DFG source module. The real-time continuous measurement capabilities of this instrument will greatly enhance the applications of stable isotope analysis for greenhouse gas source assessment, ecological process studies, and oil and gas exploration.

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APPENDIX

Evaluation of Feasibility for Concentrating Methane Samples from Ambient Air

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Final Report for Aerodyne Research, Inc.

Regarding Subcontract No. ARI 10148-1

**“Widely Tunable Infrared Laser Spectrometer for Measurement of
Isotopic Ratios of Carbon Cycle Gases”**

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Abstract

Mid-IR laser technology has advanced to the point where it is now possible to do a laser spectroscopic measurement for stable isotopes (^{13}C and ^{18}O) of carbon dioxide at atmospheric concentrations [McManus et al., 2002]. Although the laser technique is not as precise or accurate as continuous flow mass spectrometry (cf-IRMS) [Rice et al., 2001], one advantage of the laser system is that it is portable and may be used to measure isotopic ratios *in situ* while the cf-IRMS system is stationary and requires a laboratory setting. However, using the laser system it is much more difficult to measure isotopic methane (CH_4) than it is to make similar isotopic measurements of carbon dioxide (CO_2) owing to its lesser abundance. Methane (at ~ 1.8 ppm, parts per million) exists at approximately 200 times less concentration in background air than CO_2 (~ 360 ppm). Therefore, the laser system must have a way to look at concentrated CH_4 before it is deemed useful as a portable device to measure CH_4 in ambient air at or near background levels. We report on the development of a method to pre-concentrate CH_4 in air to a concentration detectable by the laser system in order to measure isotope ratios with a suitable precision and accuracy for use in field studies.

Introduction

Atmospheric CH_4 has been increasing steadily in concentration for at least the last 200 years and exhibits a dramatic although variable higher increase overall in the last 25 years or so. Increasing atmospheric CH_4 is of concern because it is a strong absorber of infrared radiation, which involve CH_4 in the greenhouse effect and enhanced global warming, and because it is the most abundant hydrocarbon in the atmosphere, taking part in many important stratospheric and tropospheric chemical reactions. Therefore, a concern of the scientific community is to identify sources of atmospheric CH_4 and to quantify their fluxes to provide an accurate CH_4 budget.

One way to quantify CH_4 is to study its stable isotopes. Several elements of biological and geological importance occur naturally with two or more stable isotopes. For example, there are two stable isotopes of carbon with atomic mass numbers twelve and thirteen, and two stable isotopes of hydrogen with atomic mass numbers of one and two (deuterium). The relative amounts of any two stable isotopes of the same element vary because of the natural differences in stable isotope composition of biogeochemical compounds. This results from processes of formation and destruction, which fractionate the isotopic pools representing substrate and product.

Studies of CH_4 using isotopes focus on differentiating between different sources of CH_4 , each with characteristic isotopic ratios of carbon and hydrogen resulting from the process forming the CH_4 , studies of atmospheric CH_4 transport and mixing between different air masses, and chemical loss processes of CH_4 which are differentiated by the way they fractionate remaining CH_4 . The measurement results are nearly always expressed in δ notation, using the following equation where, using carbon as an example, $^{13}\text{C}/^{12}\text{C}(\text{sam})$ is the carbon isotope ratio in a sample and $^{13}\text{C}/^{12}\text{C}(\text{std})$ is the carbon isotope ratio of Pee Dee Belemnite carbon, a conventional standard.

$$\delta^{13}\text{C} = [^{13}\text{C}/^{12}\text{C}(\text{sam}) / ^{13}\text{C}/^{12}\text{C}(\text{std}) - 1] \times 1000$$

Objective

The laser spectroscopy system currently has a sensitivity such that it requires the equivalent to approximately 360 ppm of CO₂ (background concentration) at a total air pressure of 15 torr in a 0.3 L cell in order to differentiate between ¹³C and ¹²C carbon [McManus et al., 2002]. For similar differentiation between ¹³C and ¹²C or D and H in CH₄, one requires the amount of background CH₄ (~1.8 ppm) normally observed in about 100 times as much air volume as for CO₂ but in a total air pressure of 30 torr. (This requirement can be relaxed somewhat for air in CH₄ source regions assuming elevated ambient CH₄ concentrations of several ppm are present.) Therefore, all the CH₄ in 67 liters (100 x 2 x 0.3 L = 67 L) would need to be concentrated in a similar cell at 30 torr.

In practice, it will be very difficult to transfer only ~30 torr of air from one volume (CH₄ trap) to another (laser cell) in the field without a vacuum system and strict control because CH₄ is normally a non-condensable gas. However, because the maximum cell pressure for optimum results can be as high as ~0.5 atm (~380 torr), one could attempt to trap CH₄ in air from as much as 12.5 times as much air volume. It is much more practical to have a system which transfers the CH₄ by flushing through the trap and bringing the cell total pressure up to as much as ~0.5 atm in the process. Furthermore, as the laser system sensitivity is improved, less total CH₄ will be needed in the cell, as the sensitivity for absorption spectroscopy is based on concentration rather than total molecules of CH₄. For instance, if the laser system detect were to be improved by a factor of 10, only a tenth as much air volume, or 6.7 L, actually needs have its CH₄ extracted and ready for delivery to the cell whether it is delivered in a total pressure of 30 torr, 360 torr, or something in between. Allowing for the possibility of improvements in the system conditions overall, our goal has been to quantitatively extract all the CH₄ from quantities of about 100 to 10 L of air and test the feasibility of delivering it to the laser system.

Experimental Methodology

Requirements of Preconcentrator. The CH₄ preconcentrator must be able to process approximately 10 L of air in a short time so that *in situ* laser isotope measurements can be made with enough frequency to study local variations in CH₄ isotope ratios spatially and temporally. Processing in this sense means cryogenically trapping CH₄ onto an absorbent and then releasing it when a large enough amount has been captured.

Methane in air is extremely difficult to trap cryogenically and requires the use of solid absorbent traps in addition to cryo-temperatures. Some success has been reported in the past on large volumes (e.g. CH₄ trapped from 1.5 m³ of whole air for measurements of ¹⁴CH₄) using RIX type sweet air compressors and large traps (>500 g. molecular sieve and/or activated charcoal) held at liquid nitrogen (LN₂) temperature (T = -196°C) [Lowe et al., 1988; Wahlen et al., 1989]. Subsequent isotope analysis of captured CH₄ has been made in the lab after releasing the CH₄ into a vacuum line in the lab for further purification and combusting it to CO₂ for dual inlet IRMS analysis. Extreme caution has always been exercised in releasing trapped CH₄, which is done slowly at room temperature or higher, because other gases such as N₂, O₂, and Ar are invariably trapped along with CH₄ at high partial pressures. These gases need to be purged from the trap without losing CH₄ and without a volatile pressure release (i.e. explosion).

In our case, where only about 10 L of whole air is processed and the captured CH₄ is to be released directly into a measurement device, the laser photocell has the advantage of not needing pure CH₄ sample gas as other gases (such as CO₂ and water vapor) do not interfere with

the IR-type measurement of CH_4 . However, the requirements for non-trapping of high partial pressures of N_2 , O_2 , and Ar is still important and the sample CH_4 must be released into the laser's glass photocell in a controlled fashion. With all this in mind we require a preconcentration system that has suitable trapping material and trap design, practical low and high temperature cyro-control over the trap, and a compact design that is portable for field use. The final configuration of the preconcentrator must have a sample delivery that is compatible with both our cf-IRMS instrument in the lab and with the laser isotope measurement system of Aerodyne. This last requirement is necessary so that captured CH_4 can be analyzed in our lab to calculate trapping efficiency and isotope ratio integrity (i.e. no isotope fractionation during trapping or release of CH_4) of the preconcentrator.

Figure 1. Methane Trapping Line

Design of Preconcentrator. The preconcentration system consists of a small gas manifold which includes a water vapor U-shaped trap (necessary to avoid overloading the solid absorbent), a packed solid absorbent U-shaped trap, pressure release valve, pressure and vacuum gauges, and a bypassable purge line for reconditioning the traps with zero air (see Figure 1). Sample gas enters via a small diaphragm pump/compressor (KNF Neuberger, Inc., model N022) with sampling rate controlled by a mass flow controller (MKS Instruments, Inc.) with flow integrator. Although AC current in the lab powered our system, the power requirements are small and capable of being fulfilled using portable power generation. In our tests, once the desired volume of whole air had been processed, sample CH_4 from the solid absorbent trap was released into a ~0.5 L stainless steel round canister connected to the manifold. This 0.5 L canister serves two purposes, 1) it allows us to measure CH_4 in it using either our gas chromatograph (for concentration) or IRMS instruments (for isotope ratios), and 2) it approximates the 0.3 L photocell of the Aerodyne laser isotope spectroscopy instrument.

Test Configurations. Three absorbing materials were used to trap methane. They are as described as follows. SilicaLite (Hisiv 300) [UOP LLC] with 1/16" (1.5 mm) particle diameter

is a molecular sieve developed from high silica zeolites. It has a pore structure for adsorbing molecules with up to 0.6 nm diameter. Porapak Q [Alltech Associate Inc.] is a 50-80 mesh size (surface area 500-600 m²/gram) cross-linked porous divinylbenzene/ethylvinylbenzene polymer. Porapak Q is slightly polar. Hayesep D [Alltech Associates, Inc.] is a 60-80 mesh size (surface area 795 m²/gram). Hayesep D is a high purity divinylbenzene polymer with high surface area. It is non-polar.

Each of the absorbing materials was weighed out and placed inside one of several U-shaped stainless steel tubes with varying diameters and lengths which served as traps for CH₄. Weights ranged from ~4 to ~11 g of material. U-trap sizes that were tested include 6.3 mm, 9.5 mm and 12.7 mm dia. doubled-valved traps of lengths up to ~25 cm foot. Trapping flow rates tested ranged from 0.25 to 5 liters per minute (LPM). Several cryo and warming temperatures were tested. U-trap cryotemperatures were reached using dewars of LN₂ (-196°C), dry ice/ethanol slush (~-80°C), and n-pentane/ethanol slush (~-120°C), while warming temperatures were applied using boiling water (~100°C), room temperature water (~23°C), and a hand-held heat gun (Fisher Scientific).

Protocol for Preconcentrator Tests. In all of our tests, laboratory air was used as the air to be sampled for CH₄. Optimum flow rate was tested using the variable settings on the MKS flow controller. Although flow rates (sampling rates) of up to 5 LPM were tested., in practice these tended to overload the traps with the major gases in air (i.e. N₂, O₂, Ar) regardless of the absorbent material used. Most testing was done at 1 LPM.

Each air stream sampled was subjected to drying using the moisture trap. Moisture trap temperatures tested included -196 C, -120 C, -80, and -15 C (ice with rock salt). Similarly, each CH₄ absorbing material and trap size was tested one at a time. Absorbent traps were tested in tandem with one of the cold bath temperatures described above. The lab air stream was passed through the trapping system and out into the lab through vent 2. After a suitable test volume of air had been processed through the system, the absorption trap was quickly closed at both ends and the compressor stopped. Vent 1 was then opened and the zero air stream flowed through the moisture trap to purge the trap and re-condition it for the next sampling. Meanwhile, the absorbent trap was warmed using one of the tested warming temperatures. The heat gun was used to release even more gas during many of the trials.

Upon warming, CH₄ (and other trapped gases) was quickly released into an evacuated 0.5 L stainless steel canister using the outlet valve of the trap. This step led to varying total gas pressures being released which were monitored by the pressure gauge. This step was designed to approximate similar conditions in the field where the outlet trap valve would be opened such that gases would be released directly into the laser photocell. In practice, either too little total pressure or pressure much greater than 1 atm was often the result.

In our tests, the total pressure depended on trapping times, CH₄ absorbent amount and type, and especially cryo temperature used. In cases where the pressure released was low, the trap was flushed (once the moisture trap had been reconditioned) with the zero air stream to bring the total pressure up to ~1 atm. In cases with too much pressure, the experiment had to be modified. In those cases the identical test conditions were re-tried up to the point where the CH₄ was trapped -- then the trap was vented through vent 2 while still under the cryo temperature used to trap CH₄. The desired result would be to purge gases such as O₂ while still holding the CH₄ for later release.

Results

A range of flow rates was tested while varying both trap size and trapping temperature. Some tests were repeated under identical parameters as previous tests to establish reproducibility. In practice it was hard to control the amount of CH₄ potentially loss while purging higher partial pressures of fixed gases from the traps while retaining CH₄. It was also difficult to release all CH₄ actually trapped after purging the higher concentrated O₂, N₂, and Ar. Many tests were attempted to trap CH₄ from ~100 L of lab air. The results shown in each case are the best attempts to obtain high yields of trapped and released CH₄.

The first series of tests were made using SilicaLite as the CH₄ absorbent. From data in Table 1 we learned several things. At higher flow rates and relatively higher trapping temperatures, SilicaLite was unable to trap a high percentage of available CH₄. Part of the problem, however, might have been that in trapping 100 L of air, such a large volume of O₂, N₂, and Ar were also trapped that it was very difficult to purge the fixed gases without also releasing some of the trapped CH₄.

Table 1. SilicaLite CH₄ Preconcentration Tests with CH₄ Trap at -120°C on 100 L of Lab Air

Amount of CH Absorbent and Trap Size	Flow Rate in LPM	H ₂ O Trap Temp. in °C	Conc. of Recovered CH ₄ in ppm	Expected Conc. of CH ₄ in ppm	% Yield of CH ₄ Recovery
11.91 g / 3/8" dia.	1	-80	28.9	387.2	7
11.66 g / 3/8" dia.	3.7	-80	17.2	387.2	4
11.66 g / 3/8" dia.	5	-80	0	380	0

As shown in Table 2, by processing lower volumes of air, recovery of CH₄ improved somewhat but not to an extent great enough to make a good measurement of isotopic CH₄ likely. However, the moisture trap (which being hollow, is unlikely to trap O₂, N₂, or Ar at any temperature) may have operated better at -120°C than at -80°C in keeping H₂O and possibly CO₂ from taking up active sites on the CH₄ absorbent trap, thereby improving CH₄ yield.

Table 2. SilicaLite CH₄ Preconcentration Tests with CH₄ and H₂O Traps at -120°C on Lab Air

Amount of CH Absorbent and Trap Size	Flow Rate in LPM	Total Air Processed in L	Conc. of Recovered CH ₄ in ppm	Expected Conc. of CH ₄ in ppm	% Yield of CH ₄ Recovery
14.55 g / 3/8" dia.	2.5	55	19.15	209.0	9
11.66 g / 3/8" dia.	2.5	10	10.28	38.38	27
11.66 g / 3/8" dia.	1	10	4.54	38.0	11
11.66 g / 3/8" dia.	1	1.2	1.43	4.57	31
4.16 g / 1/4" dia.	1	10	1.09	38.0	3

Table 3 shows the results of testing SilicaLite traps at varying temperatures while holding the flow rate, and the moisture trap parameters constant. None of these results are outstanding but we were surprised to find that the CH₄ trap worked best in these comparisons at -80°C. This could have been due to a combination of less O₂, N₂, and Ar being trapped at that temperature and having found an optimum cold temperature for the CH₄ trap.

Table 3. SilicaLite CH₄ Preconcentration Tests at 1 LPM Flow Rate on ~10 L of Lab Air

Amount of CH ₄ Absorbent and Trap Size	CH ₄ Trap Temp. in °C	H ₂ O Trap Temp. in °C	Conc. of Recovered CH ₄ in ppm	Expected Conc. of CH ₄ in ppm	% Yield of CH ₄ Recovery
11.66 g / 3/8" dia.	-80	-120	10.13	38.15	26
11.66 g / 3/8" dia.	-120	-120	4.54	38.0	11
11.66 g / 3/8" dia.	-196	-120	3.85	38.0	10

In Table 4, data for different amounts of air being processed by SilicaLite at -80°C are shown. The yield of recovered CH₄ falls off with increasing total air volume as expected.

Table 4. SilicaLite CH₄ Preconcentration Tests at 1 LPM and H₂O Traps at -120°C on Lab Air

Amount of CH ₄ Absorbent and Trap Size	CH ₄ Trap Temp. in °C	Total Air Processed in L	Conc. of Recovered CH ₄ in ppm	Expected Conc. of CH ₄ in ppm	% Yield of CH ₄ Recovery
11.66 g / 3/8" dia.	-80	10	10.13	38.15	26
11.66 g / 3/8" dia.	-80	25	8.78	95.0	9
11.66 g / 3/8" dia.	-80	50	9.30	190	5

Data from a series of tests made using HayeSep D as the CH₄ absorbent are shown in Table 5. Unlike the results for SilicaLite material, the best results were obtained when both the CH₄ trap and moisture trap were at -120°C. The CH₄ recovery of 58% on 10 L of air was the best obtained.

Table 5. HayeSep D CH₄ Preconcentration Tests at 1 LPM Flow Rate on ~10 L of Lab Air

Amount of CH Absorbent and Trap Size	CH ₄ Trap Temp. in °C	H ₂ O Trap Temp. in °C	Conc. of Recovered CH ₄ in ppm	Expected Conc. of CH ₄ in ppm	% Yield of CH ₄ Recovery
7.02 g / 3/8" dia.	-80	-120	4.32	38.76	11
7.02 g / 3/8" dia.	-120	-120	22.04	38.22	58
7.02 g / 3/8" dia.	-196	-120	10.37	39.48	26

More tests of HayeSep D material are shown in Table 6 using the optimum combination of temperatures found for the CH₄ and moisture traps. Methane recovery was not improved by going to a larger trap, nor did it approach 58% when a smaller trap was used. The 1/2" dia. trap was tested partly to attempt to process a larger volume of air.

Table 6. HayeSep D CH₄ Preconcentration Tests at 1 LPM Flow Rate on ~10 L of Lab Air

Amount of CH Absorbent and Trap Size	CH ₄ Trap Temp. in °C	H ₂ O Trap Temp. in °C	Conc. of Recovered CH ₄ in ppm	Expected Conc. of CH ₄ in ppm	% Yield of CH ₄ Recovery
0.99 g / 1/4" dia.	-120	-120	2.13	38.3	6
2.39 g / 1/4" dia.	-120	-120	8.42	42.56	20
7.02 g / 3/8" dia.	-120	-120	22.04	38.22	58
19.48 g / 1/2" dia.	-120	-120	13.0*	95.0*	14*

* -- total volume of air processed was ~25 L

Results for the third CH₄ trapping material tested, Porapak Q, are shown in Tables 7 and 8. The main points to be made are that the best CH₄ yields were made on relatively small volumes of air, i.e. 5.5 and 10 L volumes, and that Porapak Q appeared to work best at a temperature of -196°C. The highest CH₄ yield obtained in any of the tests (71%) was for 10 L of lab air processed with the CH₄ trap at -196°C and the moisture trap at -120°C.

Table 7. Porapak Q CH₄ Preconcentration Tests at 1 LPM Flow Rate on ~10 L of Lab Air

Amount of CH Absorbent and Trap Size	CH ₄ Trap Temp. in °C	H ₂ O Trap Temp. in °C	Conc. of Recovered CH ₄ in ppm	Expected Conc. of CH ₄ in ppm	% Yield of CH ₄ Recovery
10.08 g / 3/8" dia.	-80	-120	3.50	38.53	9
10.08 g / 3/8" dia.	-120	-120	20.00	38.76	52
10.08 g / 3/8" dia.	-196	-120	27.16	38.0	71

Table 8. Porapak Q CH₄ Preconcentration Tests at 1 LPM and H₂O Traps at -120°C

Amount of CH Absorbent and Trap Size	CH ₄ Trap Temp. in °C	Total Air Processed in L	Conc. of Recovered CH ₄ in ppm	Expected Conc. of CH ₄ in ppm	% Yield of CH ₄ Recovery
10.08 g / 3/8" dia.	-120	5.5	13.76	20.75	66
10.08 g / 3/8" dia.	-120	10	20.00	38.76	52
10.08 g / 3/8" dia.	-120	25	17.23	95.0	18
10.08 g / 3/8" dia.	-120	50	17.91	190.0	9
3.11 g / 1/4" dia.	-120	11	5.68	42.6	13

Isotope Measurements

Thus far, little mention of isotope values of CH₄ has been made. The laboratory air, which was tested a few times during the course of our experiments from whole air samples introduced into our cf-IRMS instrument, was consistently found to have $\delta^{13}\text{C}$ and δD values of CH₄ -46.5 to -46.9‰ and -95 to -99‰, respectively. These values are similar to tests of our lab air made at other times. Therefore lab air, although it was not measured in each test of the CH₄ preconcentration system, was taken to be approximately those values noted above.

Most of the tests of the CH₄ preconcentration system did not include testing the isotope ratio of the recovered CH₄ because the CH₄ yields were deemed too poor to be of value to the laser isotopic measurement instrument. However, in several of the higher yielding tests recovered CH₄ was measured isotopically by our cf-IRMS instrument for δD to determine whether the process was isotopically fractionating appreciably. The results are shown in Table 9.

Table 9. CH₄ Preconcentration Tests with CH₄ Absorbent and H₂O Traps at -120°C on Lab Air

Amount of CH ₄ Absorbent and Trap Size	CH ₄ Trap Material	Total Air Processed in L	Conc. of Recovered CH ₄ in ppm	% Yield of CH ₄ Recovery	δD of Recovered CH ₄
11.66 g / 3/8" dia.	SilicaLite	10**	8.87	23	-115.4
11.66 g / 3/8" dia.	SilicaLite	25**	8.78	9	-113.4
11.66 g / 3/8" dia.	SilicaLite	50**	9.30	5	-112.1
7.02 g / 3/8" dia.	HayeSep D	25	19.34	20	-107.2
7.02 g / 3/8" dia.	HayeSep D	50	27.48	14	-112.0
7.02 g / 3/8" dia.	HayeSep D	52	22.51	12	-111.3
19.48 g / 1/2" dia.	HayeSep D	25	13.0	14	-115.3
10.08 g / 3/8" dia.	Porapak Q	25	17.23	18	-106.5
10.08 g / 3/8" dia.	Porapak Q	50***	21.69	11	-92.9
10.08 g / 3/8" dia.	Porapak Q	50	17.91	9	-115.4
10.08 g / 3/8" dia.	Porapak Q	10***	27.16	71	-137.5

** -- CH₄ Absorbent Trap at -80°C

*** -- CH₄ Absorbent Trap at -196°C

Even though CH₄ yields are well below 100% and have a wide range of values, the δD value is fairly consistent around -110‰. Two outliers from this value are both cases where Porapak Q material was held at -196°C. In general then, the incomplete recovery of CH₄ appears to result in a shift in δD of recovered CH₄ toward isotopically lighter values. The two outliers are likely a result of the difficulty of purging appreciably more unwanted O₂, N₂, and Ar originally trapped at -196°C than at higher temperatures without losing some CH₄ and isotopically fractionating it in the process.

Conclusion

The recovered CH₄ from 5 of the tests listed in Table 9 has been saved and is being stored in 0.5 L canisters for testing by the laser instrument. In addition, three CH₄ isotopic reference gases each with values of $\delta^{13}C = -48.3\text{‰}$ and $\delta D = -165\text{‰}$ have been made in the following CH₄ concentrations: 7460 ppm, 806 ppm, 175 ppm. We plan to test these with the laser system later this year when the Aerodyne project scientists are ready to make the measurements.

In summary, the design of a portable field-ready CH₄ preconcentrator from whole air which can quickly deliver a CH₄ sample aliquot to a laser photocell for rapid analysis is not feasible under the current set of requirements. However, if the sensitivity of the laser system toward CH₄ can be increased, it might be possible. Results for trapping and recovery of CH₄ from ~10 L of air showed some promise and further tests might reveal a sampling protocol under a given set of parameters and conditions for the preconcentrator that would yield consistent and accurate results.

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