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Precision Trace Gas Analysis by FT-IR Spectroscopy. 2. The $^{13}C/^{12}C$ Isotope Ratio of CO_2

M. B. Esler,*,† D. W. T. Griffith,† S. R. Wilson,† and L. P. Steele‡

Department of Chemistry, University of Wollongong, Wollongong NSW 2522, Australia, and CSIRO Atmospheric Research, Aspendale Vic 3195, Australia

We report the development of a method of carbon stable isotope ratio analysis based on 1-cm^{-1} resolution Fourier transform infrared (FT-IR) spectroscopy, deployable in both laboratory and field applications. We demonstrate the determination of the $^{13}C/^{12}C$ ratio of CO_2 (i.e., $\delta^{13}CO_2$) in air with an analytical precision of the order of ±0.1‰ (i.e., ±0.01%). The FT-IR method relies on calibration using synthetically calculated absorbance spectra and a multivariate calibration algorithm. The method requires no sample preparation other than optional drying of the sample and may be applied directly to ambient air samples containing ∼350 μmol mol^{-1} CO_2 (molar mixing ratio). It may also be applied to samples more concentrated in CO_2, such as human breath, ∼5% CO_2. We demonstrate the utility of the technique to the analysis of $\delta^{13}CO_2$ in air during an experimental field campaign and to the laboratory-based analysis of human breath. A similar method could also be used to determine the H/D ratio in atmospheric water vapor.

The two naturally occurring stable isotopes of carbon, ^{12}C and ^{13}C, have natural abundances of 98.89 and 1.11%, respectively (with the naturally occurring radioisotope ^{14}C $<10^{-10}$%). Since there are also three stable oxygen isotopes ^{16}O, ^{17}O, and ^{18}O, the single molecular species CO_2 exists in 12 stable isotopomeric forms, ranging in molecular weight from 44 to 49. However, more than 99.98% of CO_2 is accounted for by the four most abundant species $^{12}C^{16}O^{16}O$ (98.42%), $^{13}C^{16}O^{16}O$ (1.09%), $^{12}C^{16}O^{18}O$ (0.40%), and $^{12}C^{16}O^{17}O$ (0.075%).

Isotope ratios are usually expressed relative to some accepted standard in the "del" (δ) notation, for example

$$\delta^{13}C = [(R^{13}_{sample}/R^{13}_{standard}) - 1] \times 1000$$

where $R^{13} = {}^{13}C/{}^{12}C$ is the ratio of the abundances of ^{13}C and ^{12}C. δ values are expressed in units of ‰ (per mil). For $\delta^{13}C$ in CO_2, the usual reference standard is the V-PDB scale (Vienna Peedee Belemnite, maintained by the International Atomic Energy Agency; see ref 1). The $\delta^{13}C_{V\text{-}PDB}$ values of a material describe how far the isotope ratio in that material differs from the ratio in the standard. Material with a $\delta^{13}C_{V\text{-}PDB} < 0$ is said to be isotopically "light" relative to the V-PDB standard.

Analysis of the ratios of the isotopomeric forms of an individual atmospheric trace gas may provide information that is not accessible by analysis of the molecular species' mixing ratio alone. This is because various physical, chemical, and biological processes fractionate between the different isotopomers in distinct ways. Several recent publications use $\delta^{13}CO_2$ measurements to complement CO_2 mixing ratio measurements in attempting to constrain the global budget of atmospheric CO_2 (see, for example, refs 2 and 3).

The measurement of $\delta^{13}CO_2$ has also found many applications in plant and animal metabolism studies where $\delta^{13}C$ may be used as a tracer of a particular process, for example, photosynthesis.[4] A suite of diagnostic breath tests using $\delta^{13}CO_2$ analysis has been developed for human use (see, for example, refs 5−7). Typically a ^{13}C-labeled substrate is ingested and the changes in $\delta^{13}CO_2$ of respired CO_2 over subsequent minutes or hours is diagnostic of a particular disorder. For example, the recently discovered bacterium *Helicobacter pylori*,[8] now believed to be responsible for most stomach ulcers, is routinely diagnosed noninvasively by analysis of a subject's breath immediately after ingestion of a small amount of ^{13}C-labeled urea.[5,9] If the stomach lining has been colonized by the urease-secreting bacterium, it hydrolyses the [^{13}C]urea to $^{13}CO_2$ and ammonia. The $^{13}CO_2$ enters the blood stream and is subsequently exhaled.

The major technique employed in measurement of stable isotopes is isotope ratio mass spectrometry (IRMS), which distinguishes between distinct isotopomers of the one molecular species purely by mass. A mass spectrometer for CO_2 isotope analysis will usually have detectors for mass-to-charge (m/z) ratios of 44 ($^{12}C^{16}O_2$, but also traces of $^{14}N_2{}^{16}O$ in air samples), 45 ($^{13}C^{16}O_2$ and $^{12}C^{16}O^{17}O$), and 46 ($^{12}C^{16}O^{18}O$ and the much less abundant multiply substituted $^{13}C^{16}O^{17}O$ and $^{12}C^{17}O_2$). The existence of two

* Corresponding author: (e-mail) mesler@uow.edu.au; (fax) +61-2-4221-4287.
† University of Wollongong.
‡ CSIRO Atmospheric Research.

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CO_2 isotopomers of mass 45 Da, which cannot be resolved directly by IRMS, is potentially a limitation of the technique. Similarly, CO_2 samples derived from the atmosphere will usually have N_2O present as an impurity, the main isotopomer of which, $^{14}N_2{}^{16}O$, has mass 44 Da. A correction to the m/z 44 detector is required based on the amount of N_2O present and the efficiency with which it is ionized in the mass spectrometer. Protonated species may also cause problems in mass spectrometry, e.g., $^{12}C^{16}O_2H$ has mass 45 Da and may interfere with $^{13}C^{16}O_2$ determination. A high vacuum ($<10^{-5}$ Torr) and low impurity levels, especially of water vapor, must be scrupulously maintained.

The typical configuration for isotope analysis is dual-inlet IRMS, where there is rapid switching between two sources of CO_2, one being the sample CO_2, which has been cryogenically extracted from an air sample or gas mixture, the other being a well-characterized reference CO_2 gas. Dual-inlet IRMS can deliver precision levels of ±0.01‰ for $\delta^{13}C$.[10] Continuous-flow IRMS (CF-IRMS), an alternative configuration to dual-inlet IRMS, is capable of analyzing much smaller samples but offers lower precision, typically ±0.1‰ for $\delta^{13}C$.[11]

Several spectroscopic methods of $\delta^{13}C$ analysis have been proposed as alternatives to IRMS. These all exploit the fact that isotopic substitution will affect the distribution of vibrational and rotational energy states of a molecule. Thus, each distinct isotopomer of CO_2 has its own rotational−vibrational infrared spectrum, as illustrated in Figure 1. Analysis of carefully chosen features in the infrared spectrum of a sample containing a mixture of isotopomers can in principle be used to determine isotope ratios. Becker et al.[12] measured $\delta^{13}C$ in samples of CO_2 gas with a precision of ±4‰ using a tunable diode laser (TDL) to analyze a small spectral region around 2291 cm^{-1} that included two rotational lines, one each due to $^{12}C^{16}O_2$ and $^{13}C^{16}O_2$. Bergamaschi et al.[13] used a tunable diode laser to analyze $^{13}C/^{12}C$ and D/H ratios in methane, reporting precision levels of ±0.44 and ±5.1‰, respectively. Using another laser-based technique, laser optogalvanic spectroscopy, Murnick and Peer[14] determined $\delta^{13}CO_2$ in 5% CO_2 in N_2 samples to a precision of ±0.2‰.

Recently isotope-selective nondispersive infrared (NDIR) spectrometers have been reported.[15−17] One such instrument has been designed primarily for analysis of CO_2 in exhaled breath for diagnostic purposes. For 500-mL breath samples, typically containing ∼4% CO_2, $\delta^{13}CO_2$ is determined with a precision of ±0.4‰. This level of precision is typical for the various NDIR instruments surveyed. There are a few recent accounts of measurements of $\delta^{13}CO_2$ using FT-IR spectroscopy, the first two by Kindness and Marr.[18,19] Their first technique employs 0.25-cm^{-1} resolution spectroscopy to analyze pure CO_2 samples at subambient pressures. The areas of several $^{12}C^{16}O_2$ and $^{13}C^{16}O_2$ rotational lines around the ν_3 transition (∼2350 cm^{-1}) are measured to perform the isotopic analysis. The level of precision reported for analysis of pure CO_2 samples was ±12‰. Their later method employed 1-cm^{-1} resolution spectroscopy and elevated sample pressures, ∼10 bar, to provide a $\delta^{13}CO_2$ precision of ±8‰. Söderholm et al.,[20] briefly described a method using quite low resolution (8 cm^{-1}) FT-IR spectroscopy of air samples combined with a multicomponent analysis algorithm to achieve a much higher precision level for $\delta^{13}CO_2$, of ±0.7‰. Our own approach was previewed briefly for both high- (0.004 cm^{-1}) and low-resolution (1 cm^{-1}) FT-IR spectroscopic determination of CO_2 isotope ratios in Griffith et al.[21]

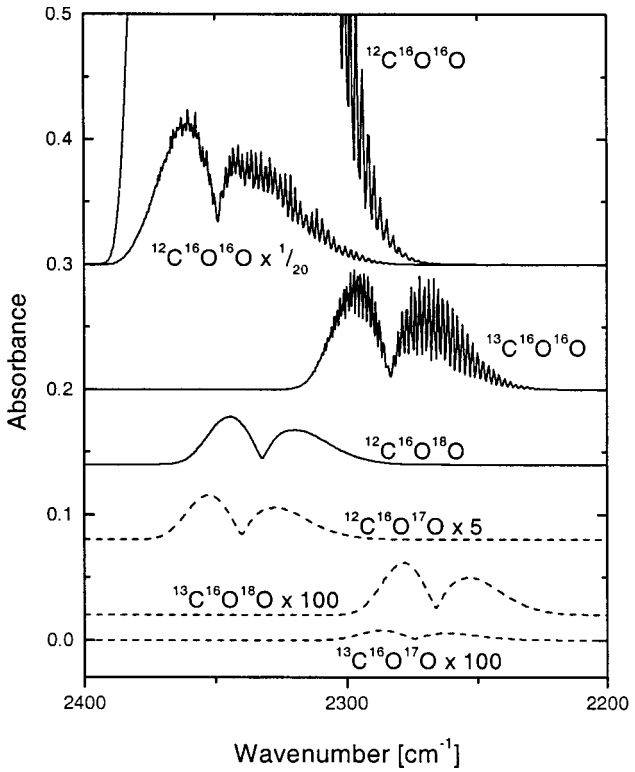

Figure 1. FT-IR spectra at 1-cm^{-1} resolution of the first six most abundant isotopomers of CO_2.

We describe fully here a new FT-IR spectroscopic method of $\delta^{13}CO_2$ analysis, which offers significantly improved precision and flexibility over the existing infrared spectroscopic methods.

EXPERIMENTAL SECTION

The configuration of the instrument used is essentially the same as that given in the companion paper to this work,[22] which describes the precise measurement of atmospheric trace gas

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mixing ratios (see also ref 23). Specifically, a commercially available Bomem MB100 FT-IR spectrometer, with 1-cm^{-1} maximum resolution, globar source, KBr beam splitter, and liquid nitrogen-cooled InSb infrared detector, was used to analyze air or breath samples introduced to a gas cell. In addition, some of the breath analysis results reported here were obtained on a Bio-Rad FTS175C spectrometer. For a full discussion of experimental considerations, see ref 22. Here we will summarize them, elaborating only where specifically appropriate for $\delta^{13}CO_2$ analysis.

A 9.8-m path length White cell provides sufficient path length for ambient air measurements, while a 10-cm single-pass cell is sufficient for breath. For CO_2 and $\delta^{13}CO_2$ analysis alone, ~2 min of scanning (64 coadded scans) was sufficient. In the case of air where it was desirable to simultaneously analyze for CH_4, N_2O, and CO in addition to CO_2 and $\delta^{13}CO_2$, a spectrum averaging time of ~8 min (256 coadded scans) was used. A liquid nitrogen-cooled InSb detector was used, which had a specific peak detectivity (D^*) of 1.9×10^{11} cm $Hz^{1/2}$ W^{-1}. A band-pass filter was used to select only the region containing the main CO_2, CH_4, N_2O, and CO absorption features between 2000 and 3200 cm^{-1}. Alternatively, when it was not required to analyze for CH_4, such as in breath samples, a narrower band-pass filter was used, to select only the region containing CO_2, CO, and N_2O, i.e., 2000−2400 cm^{-1}. Sample pressure and temperature were measured using a capacitance manometer and platinum resistance detectors (RTDs), respectively, and logged using a 16-bit data acquisition and control card. The spectrometer and cell were enclosed in a box thermostated to better than ±0.1 °C and purged with dried high-purity N_2 at a rate of 500−1000 mL min^{-1}. Sample processing was automated using a program in the GRAMS-Array Basic language (Galactic Industries Inc.), which activated solenoid valves in the sampling manifold, controlled spectrum collection, and logged temperature and pressure. Typically, all samples were analyzed at close to ambient temperature and pressure. Air samples were normally dried by passing over anhydrous magnesium perchlorate. Drying was not essential when only $\delta^{13}CO_2$ was the object of the analysis, as H_2O spectral absorption features do not significantly overlap with those of the CO_2 features used in the analysis. However, the absence or presence of H_2O in the sample will have a volumetric effect on mixing ratio determinations.

Quantitative Analysis. The quantitative analysis of the spectra is essentially the same as that described in the companion paper,[22] with one significant addition, the treatment of the various isotopomers as individual species. Briefly, the program MALT is first run to generate a set of synthetic absorbance spectra calculated from the infrared line parameters of the HITRAN database, and from the experimental conditions being modeled, e.g., temperature, pressure, path length, instrument resolution, and species concentrations. This set of calculated spectra closely models the behavior of a real FT-IR spectrometer and serves as the training set for a calibration based on the linear least-squares chemometric algorithm classical least squares (CLS).[24] Using this CLS calibration, a real gas mixture spectrum collected on the modeled FT-IR instrument is fitted, by a linear least-squares criterion, with pure component spectra derived from the CLS calibration step. The parameters of the least-squares fit directly provide a measure

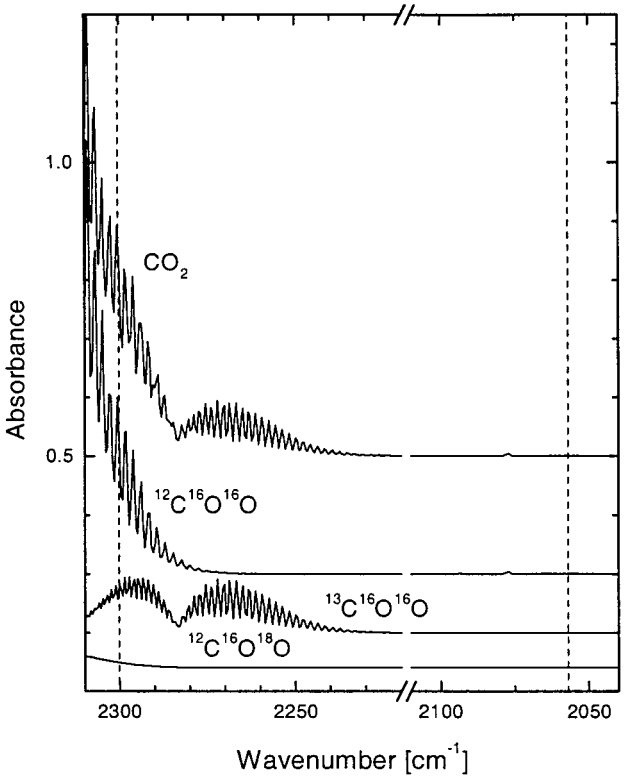

Figure 2. Optimal spectral window (bounded by dashed lines) for $^{12}CO_2$, $^{13}CO_2$, and hence $\delta^{13}CO_2$ analysis, 2300−2060 cm^{-1}.

of the concentrations of the components in the real sample. For isotope analysis, individual isotopomers are treated as independent species in the MALT calculation and the CLS quantitative analysis. Since $\delta^{13}CO_2$ is a ratio, the precision of its determination is expected to be improved over that of either $^{12}CO_2$ or $^{13}CO_2$ alone, from the cancellation of some sources of error.

To maximize the precision of $\delta^{13}CO_2$ analyses by FT-IR, we used the same method of choosing the optimal spectral region as was described in Esler et al.[22] While the $^{12}CO_2$ and $^{13}CO_2$ windows may be optimized independently rather than using a single CO_2 window we have found that for the analysis of air with 9.8-m path length the region 2300−2060 cm^{-1}, illustrated in Figure 2, is suitable for both isotopomers. A similar region was used for breath analysis. As illustrated in Figure 2, $^{12}C^{18}O^{16}O$, the third most abundant CO_2 isotopomer, has significant absorbance at the upper edge of this spectral window, indicating that it should be included as an additional independent species in the calibration. None of the less abundant isotopomers ($^{12}C^{17}O^{16}O$ or the doubly substituted species) have significant absorbance in the $^{12}CO_2$ or $^{13}CO_2$ optimal windows so have been left out of the calibration. Since $^{12}C^{18}O^{16}O$ is included in the calibration, in principle it is possible to derive a value for $\delta^{18}CO_2$ (i.e., the ratio $^{18}O/^{16}O$ in CO_2). However, in practice, using 1-cm^{-1} FT-IR spectroscopy, the $^{12}C^{18}O^{16}O$ mixing ratio and hence $\delta^{18}CO_2$ is determined with a degree of precision too poor to be useful for the determination of small variations in natural abundance. $\delta^{18}CO_2$ analyses may be viable using 1-cm^{-1} spectroscopy where there are very large enrichments, such as in metabolic tracer studies using ^{18}O-labeled substrates, or by using higher resolution FT-IR spectroscopy.[21,25]

It is expected that the raw $\delta^{13}CO_2$ value produced by applying the MALT/CLS process to the spectrum of a sample will have a

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systematic error associated with it. Therefore, an independent means of absolute calibration is required, ideally by reference to accepted calibration standards. For air analyses we have used air standards provided by GASLAB (Global Atmospheric Sampling LABoratory, CSIRO Atmospheric Research, Australia), which have been assigned CO_2 mixing ratios values relative to the NOAA/CMDL (U.S. National Oceanic and Atmospheric Administration, Climate Monitoring and Diagnostics Laboratory) maintained scale and $\delta^{13}CO_2$ values relative to the $\delta^{13}C_{V\text{-}PDB}$ scale. For calibration of breath analyses, we have used a set of three 5% CO_2 in air standards with $\delta^{13}CO_2 = -23.5$, -17.0, and -7.4‰ on the V-PDB scale (Cambridge Isotope Laboratories).

VERIFICATION OF METHOD AND APPLICATIONS

A series of experiments has been performed to determine the analytical precision of the approach described above and to demonstrate its utility in different research applications. Details of the analytical precision for $\delta^{13}CO_2$ analysis in air as well as the retrieval of vertical profiles of CO_2 and $\delta^{13}CO_2$ during an atmospheric field campaign are presented below. For the analysis of human breath, the precision has also been determined and the application to the diagnosis of *H. pylori* infection is outlined.

Air Analysis. Precision for air analysis was determined by replicate measurements of single air samples. Every 6-min for 72 min (12 cycles) a sample of air was introduced to the 9.8-m path length White cell from a single calibration tank, under computer control. The calibration tank air was known from independent gas chromatographic and IRMS analysis by GASLAB to have a CO_2 mixing ratio of 358.14 μmol mol^{-1} and a $\delta^{13}CO_2$ of -7.8‰, typical of unpolluted air. Two minutes of each 6-min cycle was taken up with collecting a 64-coadded scan single-beam spectrum of the sample. The other 4 min was for pumping the sample away and refilling the cell with a fresh sample. A single-beam spectrum of the evacuated cell was used as the reference spectrum in generating a set of 12 absorbance spectra. These spectra were analyzed using the CLS prediction procedure. After accounting for a slow instrument drift due to a change in the laboratory temperature, the standard deviation of the $\delta^{13}CO_2$ analyses (around the mean) was ±0.12‰. The experiment was repeated with 20 cycles of 15 min (total 5 h), where a 256-coadded scan spectrum was collected each cycle. For this experiment, the $\delta^{13}CO_2$ analytical precision achieved was ±0.15‰.

The instrument was used in the month-long experimental field campaign, OASIS '95,[26] to analyze air samples retrieved from several different heights from 0.5 to 22 m on a stationary tower located in a field of rapidly growing spring pasture. Figure 3 illustrates, as an example, the simultaneous vertical profiles obtained by FT-IR of CO_2 and $\delta^{13}CO_2$ at 10:30 p.m. one night within the nocturnal boundary layer (NBL). (For these types of data, the convention is to plot height on the *y*-axis). The data can be understood in terms of boundary layer dynamics and plant and soil activity. At night, plant respiration constitutes a source of CO_2 within the NBL which is established under a temperature inversion some tens of meters above the ground. The gases

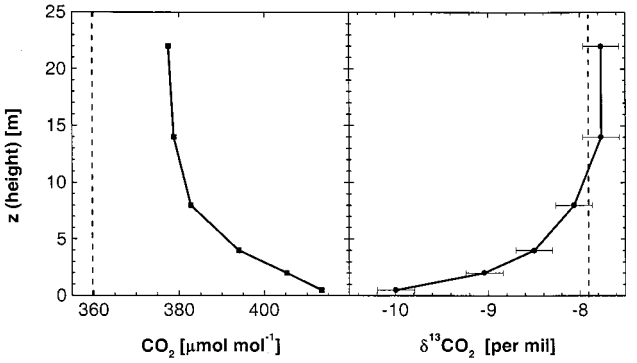

Figure 3. Simultaneous CO_2 and $\delta^{13}CO_2$ vertical profiles at a 22-m tower located in pasture, 10:30 p.m. during nocturnal boundary layer conditions. Error bars are ±0.2 μmol mol^{-1} CO_2 and ±0.2‰ $\delta^{13}CO_2$, (±1 std dev). Dashed lines indicate typical background tropospheric CO_2 mixing ratio and isotope ratio $\delta^{13}CO_2$.

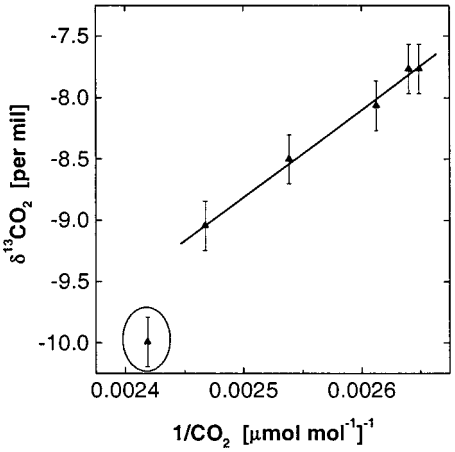

Figure 4. $\delta^{13}CO_2$ vs inverse CO_2 concentration for the nocturnal profile of Figure 3. Regression line illustrated is for the case excluding the outlier (circled).

respired by the plants and soil are trapped in the shallow NBL and a very strong negative $d[CO_2]/dz$ gradient is seen, where z is distance above ground. In addition, the CO_2 respired by the plants in the NBL is expected to have the characteristic $\delta^{13}CO_2$ signature of plant tissue, i.e., ~-28‰. The atmospheric CO_2 into which this isotopically light respired air is being mixed will typically have $\delta^{13}CO_2$ of ~-8‰. Thus, within the NBL, a characteristic positive $d\delta^{13}CO_2/dz$ gradient accompanies the negative $d[CO_2]/dz$ gradient, as shown in Figure 3. (Conversely, during the day while photosynthesis was occurring, the plants were drawing down CO_2 from the atmosphere. The vertical profile of CO_2 mixing ratio showed the positive $d[CO_2]/dz$ gradient characteristic of photosynthetic drawdown.) Following the method of Keeling,[27] the isotopic signature of the plant-respired CO_2 may be determined from the *y*-intercept of the plot of $\delta^{13}CO_2$ vs $[CO_2]^{-1}$, illustrated in Figure 4. If the apparent outlier is included in the analysis of the FT-IR data, the retrieved source term for respired CO_2 is -30.4 ± 2.5‰. Excluding the apparent outlier returns a source term of -25.7 ± 0.8‰. Similar measurements were made in an adjacent paddock, during the same campaign, by conventional IRMS methods. The resulting estimate for the respiration source term was -26.8 ± 0.14‰.[28] Within the limits of precision

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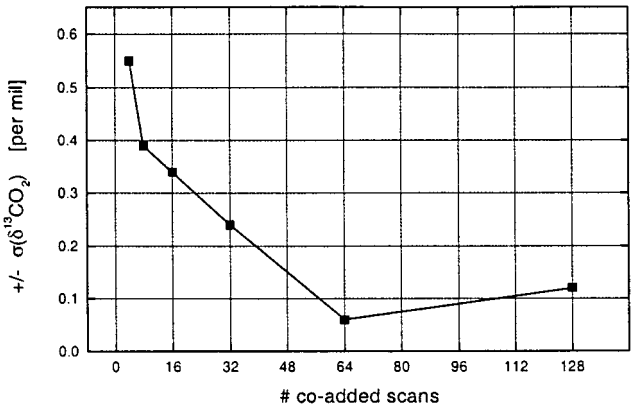

Figure 5. Analytical precision of $\delta^{13}CO_2$ determination vs number of coadded scans determined from replicate analyses of human breath.

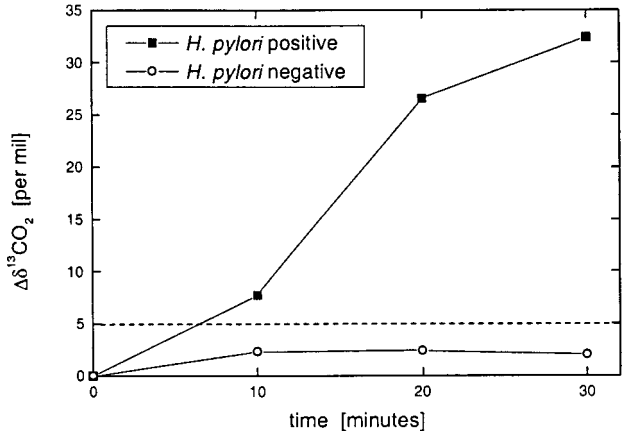

Figure 6. $\delta^{13}CO_2$ in exhaled breath at time 0, 10, 20, and 30 min after ingestion of 100 mg of [^{13}C]urea, for two patients for the purpose of noninvasive diagnosis of *H. pylori* infection status.

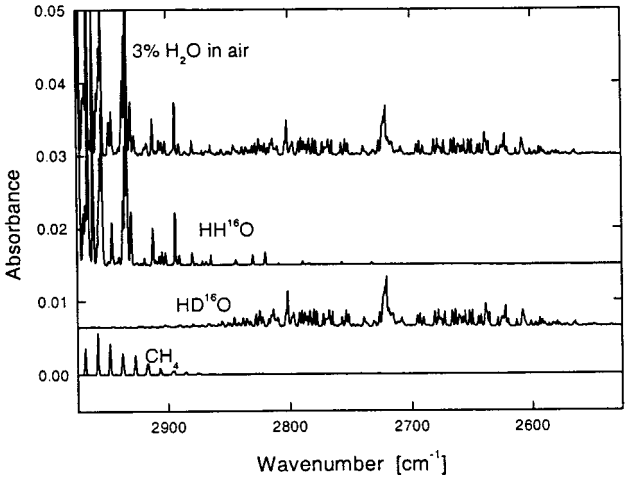

Figure 7. FT-IR spectrum of moist air showing that the deuterated water isotopomer $HD^{16}O$ is resolved from the parent species $HH^{16}O$ at low (1-cm^{-1}) spectral resolution.

of the FT-IR in situ analysis, and considering natural variation (temporal and spatial) in the respiration source term, it is in good agreement with the independent IRMS analysis. To our knowledge, this is the first report of any method of stable isotope ratio analysis being accomplished in situ, in the field.

Breath Analysis. A Bio-Rad FTS175C spectrometer, with InSb detector, operating at 1-cm^{-1} resolution, was configured with a 10-cm single-pass gas cell for the purpose of $\delta^{13}CO_2$ breath analysis. To assess precision, the gas cell was filled to atmospheric pressure with N_2 and a single-beam spectrum of four coadded scans was collected to serve as a reference spectrum. The cell was then filled to atmospheric pressure with exhaled breath. A set of consecutive replicate single-beam spectra of this sample was collected, each replicate spectrum also the result of four coadded scans, taking 8 s to collect. The ratios of the members of this set to the reference spectrum were calculated to provide a set of consecutive replicate absorbance spectra of the breath sample. Each absorbance spectrum in this set was analyzed for $^{12}CO_2$ and $^{13}CO_2$. The short-term analytical precision of $^{12}CO_2/^{13}CO_2$ measurement was determined as the standard deviation in the $^{12}CO_2/^{13}CO_2$ ratio after the longer term drift was removed from the data. The small degree of drift can be attributed to the instrument being incompletely purged at the time of the experiments. This experiment was repeated for reference and sample spectra consisting of 8, 16, 32, 64, and 128 coadded scans. In each case, there were at least 15 consecutive replicates, more often 20−40. The results, illustrated in Figure 5, show a $^{13}CO_2/^{12}CO_2$ best measurement precision of the order of ±0.06‰ for 64 coadded scans (2-min scanning time). As was seen with air analysis as well (see Esler et al.[22] this issue), collecting more than ~64 coadded scans does not result in improved precision, due to instrument drift becoming the limiting factor for longer scanning times.

The [^{13}C]urea breath test was administered to two subjects, one known by independent diagnostic methods to be infected with the *H. pylori* bacterium, the other not infected. Samples of their breath were collected before ingestion (baseline) and at 10, 20, and 30 min after ingestion of 100 mg of [^{13}C]urea and were subsequently analyzed for $\delta^{13}CO_2$ using the FT-IR method. The change in $\delta^{13}CO_2$ (i.e., $\Delta\delta^{13}CO_2$) over the baseline value is plotted against time in Figure 6. Typically, a $\Delta\delta^{13}CO_2$ of > +5‰ at $t = 30$ min is a positive diagnosis of *H. pylori* infection.[5] A clear difference can be seen in the *H. pylori* positive and negative cases.

DISCUSSION

While the FT-IR method of isotope ratio analysis has been verified and applied specifically here to CO_2, the method is applicable, at least in principle, to other molecules and isotopes of interest, even using a low-resolution benchtop instrument. For example, Figure 7 illustrates the MALT-calculated absorbance spectrum of moist air (3% H_2O by volume) in the region 2525−2975 cm^{-1}. There are only three species that have significant absorption features in this region, $HH^{16}O$, $HD^{16}O$, and CH_4, and they are well resolved at 1-cm^{-1} resolution. MALT/CLS modeling predicts that FT-IR will have a δD in H_2O analytical precision of the order of ±1‰. Considering the very large D/H fractionations observed in nature, this would be more than adequate to resolve natural D/H variations. FT-IR δD analysis, unlike IRMS, would not require conversion to pure H_2 before analysis. On the other hand, there would need to be careful attention paid to the "stickiness" of water during any sample handling and analysis, lest this introduce spurious D/H fractionation.

(28) Lloyd, J., Australian National University, 1996 (personal communication).

Extending the method developed here for 1 cm^{-1}, to 0.1-cm^{-1} resolution analyses (the current limit of benchtop FT-IR instrument resolution), $\delta^{13}C$, $\delta^{18}O$, and $\delta^{17}O$ in CO may be resolved, and also δD in CH_4. At high resolution (<0.01 cm^{-1}), all isotopomers of the low-molecular-weight gas-phase species may be resolved using FT-IR spectroscopy. This is described by Griffith et al.[25] in which high-resolution FT-IR isotope ratio methods are developed and applied, for example, to simultaneous determination of $\delta^{13}C$, $\delta^{18}O$, and $\delta^{17}O$ in CO_2, as well as to the resolution of symmetry isotopomers such as $^{16}O^{16}O^{18}O$ and $^{16}O^{18}O^{16}O$, or $^{14}N^{15}N^{16}O$ and $^{15}N^{14}N^{16}O$.

CONCLUSION

We have described a novel method of precise and accurate stable isotope analysis using FT-IR spectroscopy. The method may be applied to whole air or breath samples for the determination of $\delta^{13}C$ in CO_2. Simultaneous analysis of $\delta^{13}CO_2$ and CO_2, CH_4, CO, and N_2O mixing ratios in air is achieved. For both air and breath samples, the precision of $\delta^{13}CO_2$ retrieval is of the order of ±0.1‰. The analysis is carried out on a benchtop, 1-cm^{-1} resolution instrument and can be used for in situ measurements and in field studies. The method is in principle applicable to other stable isotope ratio analyses; however, these may require the use of higher resolution FT-IR spectroscopy.

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