Ultrasonic Detector for High Precision Measurements of Carbon Dioxide[†]

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A new instrument for monitoring atmospheric CO_2 has been developed based on the measurement of the speed of sound in air. The instrument uses a selective scrubber to yield highly precise and accurate measurements of CO_2 mixing ratios at ambient concentrations. The instrument has a precision of 0.3 ppmv (1σ) with a signal that is independent of pressure and requires a flow rate of only 30 mL/min. Laboratory measurements of atmospheric CO_2 showed excellent agreement with values obtained by nondispersive infrared absorption. The instrument has the advantage of collecting continuous, high-precision data every 25 s and can be modified for vertical profiling studies using kites, balloons, or light aircraft for the purpose of measuring landscape-scale fluxes.

The release of carbon dioxide from fossil fuel burning results in an increase of ≈3 ppmv to the global atmosphere every year and is driving global climate change.[1] In order to model the global carbon cycle and make predictions of future climate change, measurements of landscape-scale fluxes are required that characterize areas on the scale of 100 km^2 or larger.[2] These measurements are needed to bridge the gap in scales between localized studies carried out near the surface and atmospheric modeling studies that attempt to assign sources and sinks on a global scale. The most viable approach to measuring of fluxes on such a large scale is vertical profiling of CO_2 with high-accuracy and high-precision instruments.

Because CO_2 has a long residence in the atmosphere, on the order of a few years, the spatial variability of its mixing ratio is very small. Variations of only a few ppmv need to be measured above an average background CO_2 concentration of 370 ppmv in order to derive information about CO_2 fluxes to and from the Earth's surface. It is generally considered that the minimal required precision for vertical profiling of CO_2 is about 0.3 ppmv.[3,4] A precision of 0.2 ppmv would be more than

adequate for most atmospheric applications and would be comparable to the precision and accuracy that can be obtained using presently available instrumentation and calibration techniques.

Many methods have been developed for the measurement of gaseous CO_2; however, only a few techniques are used to measure vertical profiles of atmospheric levels near 370 ppmv with a precision of ≤0.3 ppmv. Nondispersive infrared (NDIR) absorption is almost exclusively used for continuous monitoring, taking advantage of the fast response (10−20 Hz) and the high precision (0.1−0.2 ppmv) for field measurements. These detectors have been used for atmospheric CO_2 measurements on unmanned aerial vehicles in the troposphere and large balloons in the stratosphere.[5,6] However, NDIR instruments such as the Li-Cor Model 6252 are relatively large ($33.5 \times 24 \times 13$ cm), heavy (3.5 kg) and require 10−16 W of power. More importantly, these instruments are sensitive to pressure as a result of pressure broadening of the absorption lines and require bulky reference gases to continuously monitor drift, making them unsuitable for portable atmospheric monitoring using kites and small balloons. Recently, compact infrared absorption detectors, such as the Vaisala Carbocap, have become available that are lightweight and draw very little power, but these instruments are also pressure dependent and are designed for fixed site monitoring.[7]

A number of infrared laser techniques have been applied to atmospheric CO_2 measurements, including tunable diode laser absorption spectroscopy (TDLAS) and cavity ring-down spectroscopy (CRDS).[8−12] Laser based instruments perform well in atmospheric monitoring from fixed sites or aircraft, but are excessively large and heavy and consume too much power to use

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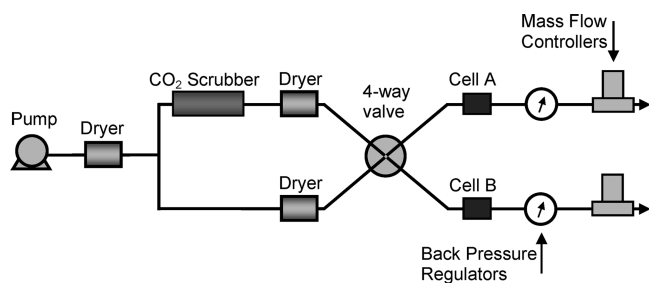
Figure 1. Schematic diagram of the ultrasonic CO_2 detector.

with kites and balloons. For example, a commercially available CRD spectrometer, the Picarro G1301, has sufficiently high precision (0.2 ppmv) for vertical profiling and requires infrequent calibration, but is large ($59 \times 43 \times 25$ cm), heavy (26 kg), and has a high power consumption (300 W).

Other methods have been developed for CO_2 field measurements based on conductometric detection and pH-sensitive dyes. Several conductometric sensors have been developed based on the hydrolysis of CO_2 in water,[13−15] but only one has been reported with a precision as low as 0.36 ppmv.[16] The principal limitation of this conductometric method is that it is not easily miniaturized. Also, it is necessary to use a bicarbonate scrubber to remove potential interferences from strongly acidic gases. Several methods use optical monitoring of pH-sensitive dyes that change in response to the formation of carbonic acid from gaseous CO_2.[17−22] These methods are limited by the consumption of reagents and long response times have been reported for methods using dyes immobilized on a solid support.

We have developed a new method based on ultrasonic detection for measuring carbon dioxide with high precision and accuracy. Ultrasonic detection has been used successfully for many years in a variety of applications, including highly accurate flask sample measurements of CO_2 using gas chromatography.[23] Rather than chromatographic separation, our instrument avoids interference from other atmospheric constituents using a scrubber to selectively remove CO_2. This approach allows measurements to be made in real time, at a fast rate, and without the large size, weight and power requirements of a GC. In addition, it is based on a purely physical property rather than a chemical reaction and has a response that is virtually independent of ambient pressure, unlike NDIR instruments.

EXPERIMENTAL SECTION

Instrument. A schematic diagram of the ultrasonic CO_2 detector is shown in Figure 1. A diaphragm air pump

(Sensidyne, model 60) is used to pressurize the sample. Next, Drierite (anhydrous calcium sulfate, Fisher Scientific) is used to remove the bulk of the moisture in the gas. The sample flow is then split, and half of it is scrubbed by Ascarite II (sodium hydroxide coated on non fibrous silica, Fisher Scientific) to remove CO_2 from the sample. Both gas flows are then scrubbed with Drierite followed by phosphorus pentoxide (Fisher Scientific, ACS grade) to reduce moisture to trace levels. The gas flows are directed to either cell A or cell B of the detector using two solenoid valves (Pneutronics, 25−10−5-NV) that are configured in a 4-way, crossover configuration. The detector is a Tremetrics Ultrasonic Detector (USD) that was originally designed to be used for gas chromatography applications with a small dead volume (180 μL), inherently fast electronic response time, and very low required flow rates (10−60 mL/min).[24,25] A phase meter (Tracor, 704) was used to measure the response of the Tremetrics USD. After the detector, back pressure regulators (Porter Instruments, 9000AMBF100) are used to maintain constant pressure in the detection cell, and miniature mass flow controllers (Pneucleus, 21B-00050N-01) are used to maintain constant flow.

RESULTS AND DISCUSSION

Theory. The ultrasonic detector measures the phase difference between two signals, such as the waveform driving an ultrasound transmitter (source) and the waveform detected by an ultrasound receiver (detector). Changes in the gas composition between the transmitter and receiver will produce a phase shift between the two signals. Phase shifts can also be measured between a receiver in a reference cell and a receiver in a sample cell. The measured phase difference is proportional to the velocity of the sonic wave, which in this case is proportional to the concentration of CO_2 in air.

The velocity of sound in an ideal gas is given by

$$v = \left(\frac{\gamma RT}{M}\right)^{1/2} \tag{1}$$

where M is the molecular weight of the gas, γ is the ratio of molar heat capacities (C_p/C_v), R is the gas constant and T is the absolute temperature.[26] The time for a sound wave to travel a distance s from its source is s/v, and the phase delay in degrees is given by

$$\phi = \frac{360 f s}{v} = \frac{360 f s \left(\frac{M}{\gamma}\right)^{1/2}}{(RT)^{1/2}} \tag{2}$$

where f is the frequency of the wave.[26] This equation shows that a change in phase delay, which can be measured as a phase shift, is a function only of the molecular weight, heat capacity and temperature of the gas.

With the temperature held constant, the phase shift will change in a predictable way with the molecular weight of the

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gas. If an analyte of molecular weight M_2 is added to matrix gas of molecular weight M_1, the change in phase is given by

$$\Delta\phi = 180 s f n \left[\frac{M_1}{RT\gamma_1}\right]^{1/2} \left\{\left(\frac{M_2 - M_1}{M_1}\right) + \frac{C_{p2}}{C_{p1}}\left(\frac{\gamma_1}{\gamma_2} - 1\right)\right\}$$

(3)

where n is the mole fraction of the analyte, and the subscripts 1 and 2 refer to the matrix gas and analyte, respectively.[26] Equation 3 shows that the phase shift is directly proportional to the mole fraction of the analyte.

Considering the composition of air, there are four constituents that could potentially interfere at the 0.05 ppmv level or higher. In order of ambient mixing ratio these are oxygen, water (up to a few % mole ratio), methane (up to a few ppmv), and hydrogen (typically 0.5 ppmv). Nitrogen and argon have extremely long lifetimes and are very well mixed in the atmosphere. Water is present at large mixing ratios in the atmosphere and has a high tendency to adsorb to surfaces. As a result, complete cancellation of the water signal is impossible when switching between H_2O-scrubbed and H_2O-unscrubbed air. In principle, the instrument design would cancel contributions from any potential interference. Desiccants and cryogenic drying were evaluated as means to remove water from the air flow. Selectivity against variations in O_2, CH_4 and H_2 was achieved by use of a CO_2 scrubber that selectively modulates CO_2 in the presence of these potential interferences.

The response of the USD is highly sensitive to temperature since the speed of sound increases as the square root of temperature. Equation 3 can be simplified so that the phase shift for a given analyte and carrier gas can be approximated as

$$\phi = c\left(\frac{n}{T^{1/2}}\right)$$

(4)

where c is a collection of constants, n is the mole fraction of the analyte gas, and T is the absolute temperature. We can determine the relative sensitivities to mole fraction of analyte and to temperature by taking the derivatives of the phase shift with respect to each of these variables, then taking the ratio of the derivatives to give the result

$$\frac{d\phi}{dn} = \frac{-2T}{n}\frac{d\phi}{dT}$$

(5)

From eq 5, the temperature change producing the same phase shift as a 0.1 ppmv increase in mole fraction of analyte at a mixing ratio of 370 ppmv and a cell temperature of 363 K is −0.2 K. Given that the required precision for vertical profiling of CO_2 is about 0.3 ppmv, the temperature needs to be held constant to ±0.6 °C. Since our instrument measures the difference between CO_2-scrubbed and unscrubbed air, the temperature only needs to be this stable over the valve cycle time, which is typically <1 min.

Evaluation of Ultrasonic Detection for CO_2 Measurements. The Tremetrics Ultrasonic Detector operates in one of two detection modes, outputting data from one or the other cell,

or from the difference between the two cells. Use of the difference mode tends to stabilize the baseline by canceling effects from variations in flow rate and pressure. However, our experiments showed no significant improvement in precision or drift when operating the instrument in difference mode.

Several plumbing configurations were evaluated, and the setup in Figure 1 was found to work best. In this configuration, a 4-way valve is switched periodically so that the air flow and CO_2-scrubbed air flow are directed alternately to cells A and B, and the signal is measured as A minus B. In this way, the signal is always measured relative to CO_2-scrubbed air and the amplitude of the square wave is doubled. Chemical interferences may also be reduced since each cell sees the same amount of scrubbed and unscrubbed air on average so that any contaminants appear at equal concentrations in both cells.

Raw data obtained for a 349.2 ppmv CO_2 standard in air at a pressure of 60 psig (pounds per square inch gauge, 414 kPa), flow rate of 65 mL/min and detection cell temperature of 90 °C are shown in Figure 2. By modulating the valves, step changes are generated in the USD signal, and the amplitude of the square wave produced is proportional to CO_2 concentration. The noise on the initial rise and fall of the step changes result from large pressure pulses that occur during valve switching. The average precision for 1 s measurements on the top of each square wave corresponds to 0.10 ppmv.

The precision was measured using a 397.5 ppmv standard of CO_2 in air at a pressure of 60 psig and using Ascarite II as the CO_2 scrubber. The average precision for six CO_2 measurements, each 1 min in duration, is 0.17 ppmv. The average precision for the baseline over the 6.5-min period between 50 and 440 s is 0.38 ppmv, indicating low frequency drift contributions to noise on the time scale of a few minutes. Baseline correcting the data with a third order polynomial fit improved the precision over this period to 0.30 ppmv. The observed baseline drift is likely due to minute temperature fluctuations.

Effect of Pressure. The pressure was varied over the range 10−60 psig (69−414 kPa) while sampling a 397.5 ppmv CO_2 standard in air at a flow rate of 65 mL/min using Ascarite II as the CO_2 scrubber. The effect of pressure on the CO_2 signal is shown in Figure 3. Signals were converted to equivalent CO_2 mixing ratios based on the average signal for samples in the range 20−60 psig. No signal could be detected above the noise at ambient pressure (0.8 atm). Above 20 psig, the signal was found to be independent of pressure. The signal is quite sensitive to pressure below 20 psig, but applying a linear regression to points in the range 20−60 psig gave a statistically insignificant slope of −0.05 ppmv/psig. The reason for a reduced sensitivity measured at 10 psig is likely due to the high level of noise in the measured signal at low pressures, resulting in errors measuring the edges of the raw step function. The pressure independent response is a highly desirable property of the USD for vertical profiling and also for measurements at ground level since the barometric pressure varies with weather conditions.

The effect of pressure on precision is shown in Figure 3. The precision was strongly dependent on pressure, with the best precision being obtained at the highest pressure tested, 60 psig. Pressure increases the intensity of the acoustic wave generated
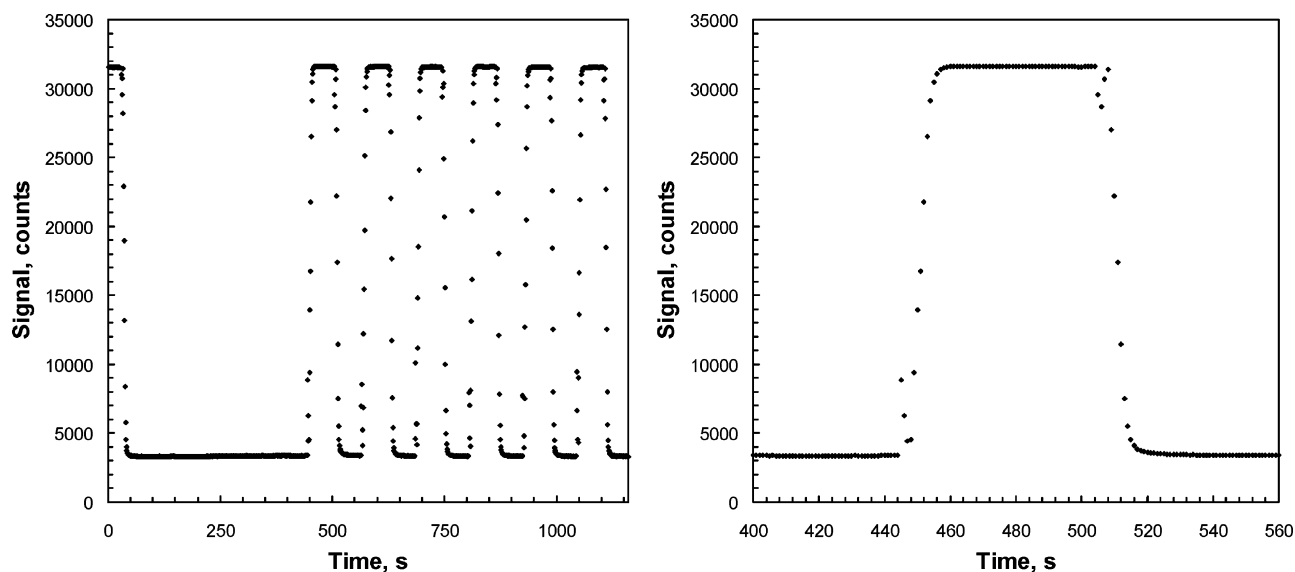
Figure 2. Measurement of a 349.2 ppmv CO_2 standard (60 psig, 65 mL/min, 90 °C) using the ultrasonic detector: Raw data for six measurement cycles (left); expanded view of the first measurement cycle (right).
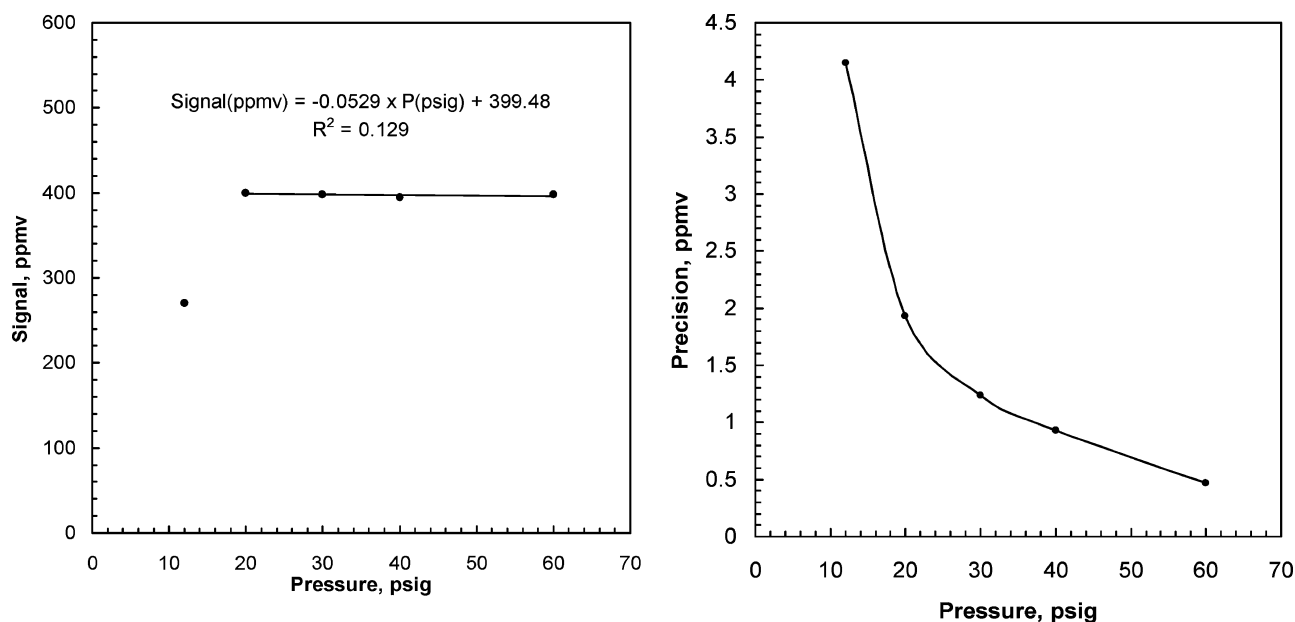

Figure 3. Effect of pressure on the USD signal and precision.

by increasing the mechanical transfer of energy to the gas. Therefore, as pressure increases, the increased intensity of the acoustic wave is measured with a higher signal-to-noise ratio.

Effect of Flow Rate. Figure 4 is a plot of the ultrasonic detector precision versus flow rate for a 397.5 ppmv CO_2 standard in air, a pressure of 60 psig, and Ascarite II as the CO_2 scrubber. The signal has been converted to equivalent CO_2 concentration by normalizing the average signal to 397.5 ppmv. From the slope of the linear regression line, it is seen that a change in the flow rate of 2 mL/min is required to cause a 0.1 ppmv change in the signal. Considering that the flow rate can be regulated to much better than 1%, the effect of flow rate on the signal is negligible. It is shown in Figure 4 that the USD response is flow dependent at flow rates less than 30 mL/min. Inspection of the raw signal shows that below that flow rate the signal does not completely level off between valve half cycles.

Therefore, the reduced sensitivity observed with flow rate probably results from inadequate flushing of the dead volume in the plumbing rather than an inherent property of the USD.

The effect of flow rate on the precision of the measurement is shown in Figure 4. The precision improves dramatically with decreased flow rate, which is advantageous considering that low flow rates reduce the consumption of scrubber materials. A precision of 0.3 ppmv, corresponding to a relative standard deviation of 0.08%, was obtained at a flow rate 5 mL/min and an inlet pressure of 60 psig. Lower flow rates may improve the precision further; however, the dead volumes in the tubing and connections prevent accurate CO_2 measurements at lower flows with a valve half cycle of 25 s.

Effect of Temperature. For gas chromatography, the detection cells are temperature regulated at typically 150 °C; however, temperatures this high are not required for atmospheric measure-
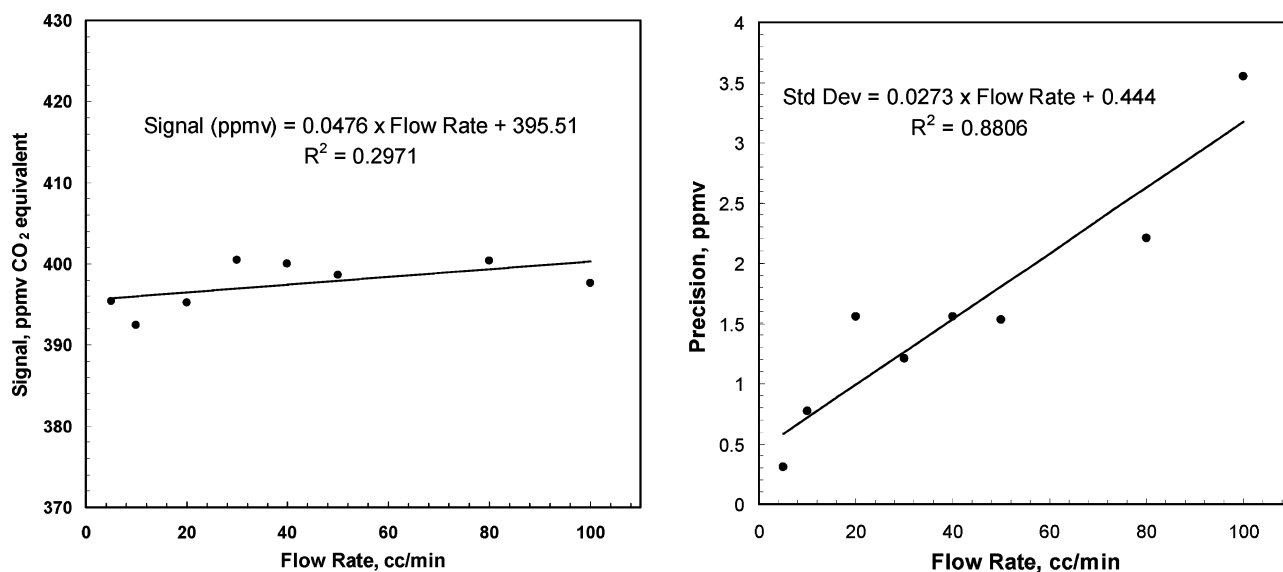
Figure 4. Measured effect of flow rate on the USD signal and precision.

ments of CO_2. Because the speed of sound increases as the square root of temperature, the sensitivity of the instrument decreases as the square root of temperature; making a lower operating temperature desirable. When operated at ambient temperature, distorted signal step functions were obtained, probably due to adsorption/desorption of air constituents to surfaces in the instrument. We chose to operate the instrument at an intermediate temperature of 90 °C where distorted step functions were not observed.

The effect of sample temperature also was investigated. A 381.2 ppmv gas standard was sampled through the $^1/_8$ in. stainless steel tubing of a cryogenic trap without coolant. The sample was delivered by an air pump at a pressure of 22 psig and flow rate of 60 mL/min. Next, coolant (dry ice/methanol) was added to the trap and the signal was measured again. The measured CO_2 concentration increased by only 0.33 ppmv for this 100 °C decrease in inlet air temperature. The effect is small since the air must still pass through about 50 cm of 1/16 in. stainless steel tubing, the CO_2 scrubber, a moisture scrubber, and a solenoid valve before reaching the detection cell.

Water Vapor Scrubber. Atmospheric samples are dried before analysis because water vapor varies drastically in the troposphere and can significantly affect the CO_2 mixing ratio.[4−6] In addition, water vapor is detected in the USD with a sensitivity of ≈73% of that of CO_2, therefore, it is necessary to remove water vapor to levels well below 1 ppmv to not interfere with CO_2 measurements. Both Anhydrone (magnesium perchlorate) and Drierite have been used as drying agents in measuring atmospheric CO_2, however, Drierite has been shown to partially adsorb CO_2 when exposed to high concentrations.[27] For our experiments, Drierite was selected for drying the sample because it is inexpensive, readily available, easy to use with a color indicator and able to reduce water vapor in air to 5.7 ppmv. Experiments using Drierite as the only desiccant produced spurious results, as would be expected because it has a low water scrubbing efficiency. However, Drierite

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followed by P_2O_5, which reacts with water to form phosphoric acid, did produce highly reproducible results.

The instrument was evaluated for water vapor interference using Drierite/P_2O_5 as the drying agent. First, the signal was obtained from a 381.6 ppmv CO_2/air standard, sampled from an overflow by an air pump and passed through the instrument at a pressure of 22 psig and flow rate of 60 mL/min. Next, a Nafion moisture exchange tube was installed in-line and immersed in water, increasing the relative humidity of the air standard from 0% to 82% relative humidity (RH) without otherwise changing the composition of the air. The humidity was measured using a thermohygrometer (Cole Parmer, 37951−00). The water vapor had no effect on the response of the USD, indicating that the Drierite/P_2O_5 desiccant trap is efficient at water removal.

CO_2 Scrubber. Ascarite II (sodium hydroxide coated on non fibrous silica) and soda lime were evaluated as CO_2 scrubbers. Flow through a cylinder (2.5 cm diameter × 5 cm) filled with Ascarite II was found to be highly efficient at CO_2 removal. The signal was found to be independent of flow rate (Figure 4), indicating that the size of the scrubber is adequate for completely scrubbing CO_2.

Soda lime is used for generating CO_2-free air used as the reference gas in NDIR CO_2 monitors. However, the use of soda lime with the USD resulted in a much smaller signal from CO_2 that was much noisier than measurements using Ascarite II. Similar results were observed with the soda lime scrubber positioned before the dryer. The cause of the increased noise and reduced signal was not determined, but may be due to desorption of some volatile compound produced when air contacts soda lime. Based on these results, it was concluded that Ascarite II is the material of choice for CO_2 measurements using the USD.

Intercomparison with NDIR Detection. The accuracy of the USD method was evaluated by an intercomparison with the standard nondispersive infrared absorption method. Outdoor air was sampled simultaneously using the ultrasonic detector and a

Table 1. Intercomparison of the USD and NDIR Instruments for Measuring Outside Air[a]

date	time	temperature (°C)	humidity (%RH)	NDIR CO_2 (ppmv)	USD CO_2 (ppmv)	error (ppmv)
4/09	12:30	20.7	18.0	401.2	400.0	−1.2
4/09	16:02	20.7	11.6	469.0	469.2	+0.2
4/11	13:30	22.0	16.3	391.5	392.9	+1.4
4/11	13:50	22.3	15.7	396.2	395.5	−0.7
4/11	14:15	20.4	18.6	411.8	410.9	−0.9
4/11	14:40	21.2	17.8	393.3	393.7	+0.4
4/11	15:09	20.5	18.3	391.0	391.5	+0.5
4/11	15:33	22.0	18.9	390.8	392.2	+1.4
4/11	16:00	21.3	17.4	383.8	384.6	+0.8
4/11	16:30	21.9	16.8	389.1	390.2	+1.1

[a] Average Error: +0.30 ppmv. Standard deviation:0.95 ppmv. Standard error of mean:0.32 ppmv.

NDIR CO_2 monitor (Li-Cor, 6252). Because the CO_2 mixing ratio in urban air is high variable, outside air samples were collected using a diaphragm pump (Sensidyne, AA120CVVF30VC1) to simultaneously fill two 3-L Tedlar bags (SKC, 232−03). The ultrasonic detector, NDIR monitor, and two CO_2 standards (certified by the National Oceanic and Atmospheric Administration (NOAA) Climate Monitoring and Diagnostics Laboratory (CMDL), 342.66 and 392.82 ppmv CO_2) were connected to a Teflon manifold with a vent to atmosphere to maintain the gases at ambient pressure. The contents of the Tedlar bags were sampled simultaneously by both instruments. The NDIR monitor was operated in differential mode using a flow of a CO_2 (397.5 ppmv in air) through the reference cell, which has been demonstrated to have an accuracy of 0.14 ppmv.[4] Results of the outdoor air measurements are shown in Table 1. The average error is 0.30 ± 0.32 ppmv CO_2, where the uncertainty is expressed as the standard error of the mean, indicating no significant difference from the USD and NDIR measurements.

Miniaturization for Field Measurements. The USD was originally designed for use with benchtop gas chromatographs and will require miniaturization for field work. The detector assembly has dimensions 10 × 10 × 9 cm and weighs 4.5 kg, and the phase meter is built in a rack mount enclosure with dimensions 43 × 40 × 13 cm and weighs 8.2 kg. By fabricating the cells from aluminum and reducing the oven size while adding thermal insulation, the detector can be reduced to 2 kg. The electronics can be redesigned into a compact circuit board powered by 12 V DC to permit use of a battery, alleviating the need for large power transformers and greatly reduce the size and weight. The mass flow controllers can be replaced with a combination of needle valves, flow meters, and pulse-width modulation of the pump to allow control of the flow rate. Other components of the instrument such as the pump, dryers, CO_2 scrubber and back pressure regulators have been miniaturized in commercially available portable instruments. Redesigning the ultrasonic detector can yield a complete instrument with a small size (25 × 15 × 15 cm), low weight (<4 kg) and reduced power consumption (<20 W), which is comparable to instruments used on vertical profiling balloons and powered parachutes.[4,16,28]

CONCLUSIONS

A new ultrasonic instrument for atmospheric carbon dioxide measurements has been constructed and evaluated. The instrument is selective for CO_2, capable of measuring mixing ratios at ambient concentrations with high precision (0.3 ppmv), and has a response that is independent of pressure. The instrument requires a flow rate of only 30 mL/min, greatly increasing the lifetime of calibration standards and scrubber material compared to NDIR instruments. Atmospheric measurements were made simultaneously with a nondispersive infrared spectrophotometer showing excellent agreement. Miniaturization of the present design will make the instrument suitable for evaluating landscape-scale CO_2 fluxes using kites, balloons, and light aircraft.

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