

Towards a stable and absolute atmospheric carbon dioxide instrument

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Towards a stable and absolute atmospheric carbon dioxide instrument using spectroscopic null method

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Abstract

We present a novel spectral method to measure atmospheric carbon dioxide (CO₂) with high precision and stability without resorting to calibration tanks during long-term operation. This spectral null method improves precision by reducing spectral proportional noise associated with laser emission instabilities. We employ sealed quartz cells with known CO₂ column densities to serve as the permanent internal references in the null method, which improve the instrument's stability and accuracy. A prototype instrument – *AB*solute Carbon dioxide (*ABC*) is developed using this new approach. The instrument has one-second precision of 0.02 ppm, which averages down to 0.007 ppm within one minute. Long-term stability of within 0.1 ppm is achieved without any calibrations for over a one-month period. These results have the potential for eliminating the need for calibration cylinders for high accuracy field measurements of carbon dioxide.

1 Introduction

Knowledge on the global budget and the transport of atmospheric carbon dioxide (CO₂) is essential to understanding the climate change effects introduced by this important greenhouse gas (GHG). Improvements in the measurement capabilities of CO₂ instruments can help to achieve this scientific goal. Among various instrument requirements, accuracy and precision are always the top priority and serve as the basis of meaningful scientific measurements and interpretations. Since most of the global CO₂ observation network monitoring stations are at remote measurement sites, the instrument's capabilities of in-field measurements, long-term unattended operation and stability are important concerns. In addition, regional flux studies involving tower or aircraft observations as well as eddy covariance flux measurements require real-time, fast response and automated operations.

In recent years, various CO₂ instruments have been developed in laboratories or made commercially available that are useful for advanced atmospheric science studies.

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Instrument techniques that have been used include tunable infrared laser differential absorption spectroscopy (TILDAS) (Tittel et al., 2003; Wofsy et al., 2011), non-dispersive infrared absorption (NDIR) spectroscopy (Komhyr et al., 1989; Stephens et al., 2011), integrated cavity output spectroscopy (ICOS) (Baer et al., 2002), cavity-enhanced absorption spectroscopy (CEAS) (Engeln et al., 1998; Rella et al., 2012), FT-IR spectroscopy (Esler et al., 2000), photoacoustic detection (Andersen et al., 2010) and so on. Based on these technologies, CO₂ instruments with high precision have been improved in terms of compactness, automation, low cost and survival under extreme environmental conditions. However, one common disadvantage in most previous instruments is that calibration tanks are employed and the majority of them cannot claim a good long-term (over months) stability without relying on these standards.

Calibration tanks are commonly employed in all stable atmospheric trace gas measurements in order to correct for instrument drifts and to assure measurement accuracies. The tedious and unregulated “tank science” adds another level of uncertainty to the measurements. Taking the case of CO₂ monitoring as an example, primary calibration tanks throughout the world are filled with compressed air and calibrated by the World Meteorology Organization (WMO) standards in order to have accurate and inter-comparable concentration information. Sources of filling air (e.g. natural or combustion) can have dramatic differences in isotopic compositions and further complicate the “CO₂ number” from tanks (this is further discussed in Sect. 3.3). Individual laboratories then use the primary tanks from WMO to calibrate their own secondary and even tertiary sets of tanks for field or lab measurements. The reported CO₂ mixing ratios from calibration tanks are significantly dependent on the individual tank conditions (e.g. fill gas source, impurities, usage, leakage, position, tank material, regulator characteristics) the environment conditions (e.g. temperature, humidity, pressure), as well as personal operation experiences and skills (Keeling et al., 2007). A blind inter-comparison test within WMO standard calibration tanks showed up to 0.2 ppm (parts per million dry air mole fraction) CO₂ mixing ratio difference within the 340 ppm and 380 ppm range (Daube et al., 2002). For ecosystem carbon flux estimation, this measurement bias at

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one site location can introduce an error estimation of $\sim 50 \text{ g C m}^{-2} \text{ yr}^{-1}$ at another site 500 km away, a number that is nearly half of the annual ecosystem flux maximum at this spatial scale (Stephens et al., 2011). To get rid of this labor intensive and unstable standard tank problem, we test the idea of employing a permanent and stable internal spectroscopic reference source, as an included feature of the spectroscopic null method, to replace the calibration tanks.

We have developed a laboratory prototype *AB*solute CO_2 spectrometer (ABC) capable of measuring ambient air CO_2 mixing ratio with precision of 0.02 ppm at 1 Hz, and with long-term stability of 0.1 ppm on the time scale of a month, without resorting to any calibration tanks during long-term un-attended operation. These performances put the ABC instrument among the best quality CO_2 instruments currently available, and yet with the unique feature of not requiring calibration tanks. The technically novel features of this instrument are the spectroscopic null method and the use of a permanently sealed quartz cell as the internal standard. The null method improves the measurement precision by enabling the instrument to be much less sensitive to any spectral proportional noise, such as absorption line strength change (e.g. with temperature), laser tuning rate drift, laser multi-modes, optics temperature variation and spectral fitting routine uncertainty (Nelson et al., 2008). The sealed quartz cell improves the measurement accuracy and long-term stability by providing a known column density of CO_2 as an internal reference which is invariant over time or under environment condition changes. This work successfully demonstrates the spectroscopic null scheme and the use of a permanent internal reference for instrument stability improvements. The method also has the potential to be adopted on various spectrometers measuring stable atmospheric species without external calibrations. Following this successful laboratory demonstration, we are currently developing a field-deployable ABC instrument with many design improvements.

2 Experimental details

The fundamental technique we use for measuring ambient CO₂ mixing ratio is Tunable Infrared Laser Differential Absorption Spectrometry (TILDAS). Details of the instrument design as well as the data acquisition and analysis have been described before (McManus et al., 2006; Nelson et al., 2006). In general, we scan a tunable IR laser over the desired wavelength region and pass the laser light through a multi-pass sample cell at reduced pressure. The sample absorption is measured via non-linear least square fitting using simulated transition lines with known spectral parameters to obtain a quantitative mixing ratio. The experimental setup of ABC is distinct in the way that we aim to measure the nearly nulled ratio spectra between sample and reference paths. In this way the signal to noise ratio (SNR) and the long-term stability are greatly improved. The high performance of ABC also relies on a stable distributed feedback (DFB) diode laser, two sensitive and cryogen-free InAs detectors, an effective thermal control scheme for the optics and stable temperature and pressure measurements. In this section, we discuss in detail the special features of this instrument as compared to the other TILDAS spectrometers previously developed in our laboratory.

2.1 Null method

The null method has been employed by many spectroscopic instruments, such as NDIR analyzers and other quantum cascade laser spectrometers (QCLS) that we have developed. It helps reduce instrument noise associated with the finite depth of the absorption line, which we describe as “proportional noise” in the spectral analysis (i.e. noise that is proportional to the mixing ratio). Many kinds of instrument instabilities can affect the experimental spectrum and challenge the spectral fitting routine. Noise sources can be separated into two groups: baseline noise and proportional noise. Common sources of baseline noise are optical fringes, external beam absorption, spectral interferences from other species, laser power variation and electronic noise. Potential sources of proportional noise or drift include laser tuning rate, line width and mode purity variations,

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detector linearity variation, numerical noise in the spectral analysis algorithm, and errors in the measurement of the sample pressure, temperature and optical path length. Most spectroscopy instruments rely on frequent background and calibration gases to separately minimize these two types of noise.

For many of the spectroscopic instruments that we have developed, laser emission stability has been found to be a major instrument drift source. The laser instabilities come from electrical noise in the current controller or the modulation circuit, and from the temperature control of the laser. Both the baseline and absorption line shape are affected. In previous designs we have used laser power normalization and differential absorption methods to compensate for these drift sources. For single cell measurements, a secondary beam from the same laser may be employed to normalize (ratio) the sample beam and minimize the laser power variation effect on the baseline. The null method further advances this solution by matching the sample and reference absorptions from a single laser, which largely cancels the effects of laser output variations on the measurements.

The null method is a variant of the TILDAS approach. Based on the Beer-Lambert law and the ideal gas law, the sample CO₂ mixing ratio (MR_s) from differential measurements can be approximately expressed as:

$$MR_s = MR_r(T_s/T_r)(\sigma_{r,T}/\sigma_{s,T})(P_r/P_s)(L_r/L_s) + A_n(k_B T_s/\sigma_{s,T}P_s L_s) \quad (1)$$

where MR_r is the reference gas mixing ratio, P , T and L are pressure, temperature and optical path length, σ is the temperature dependent integrated absorption line cross section, A_n is the integrated absorbance of the normalized (ratio) spectrum, k_B is the Boltzman's constant, subscripts of "s" and "r" denote sample and reference parameters separately. Ideally, if temperature and pressure between the sample and the reference cell are carefully maintained to be the same, absorption line strength and line width are the same for both spectra. The first term of Eq. (1) is simplified to $MR_r \cdot L_r/L_s$, which is considered as the equivalent reference gas mixing ratio (MR_{r,eq}), as if the reference gas is measured in the sample cell. Equation (1) can then be transformed as:

$$MR_s = MR_{r,eq} + A_n(k_B T_s / \sigma_{s,T} P_s L_s) \quad (2)$$

We fill reference cells with a column density of CO₂ close to the equivalent for ambient CO₂ in the sample cell, so the absorption from the normalized spectrum is only a small fraction of that from the reference cell spectrum. The closer the sample and the reference absorption are to equal, the less proportional noise interference on the normalized spectrum is observed. An ideal case is a complete null (flat) spectrum where $A_n = 0$ and the second term in Eq. (1) is zero. As a result, knowledge of laser parameters such as tuning rate, mode purity and line width for spectral fitting are no longer needed. The sample mixing ratio is exactly the equivalent reference mixing ratio.

The realization of the null method has raised some operational challenges. The first step is to balance the temperature and the pressure in the sample and the reference cell. Optical path lengths of the sample and the reference cell need to be accurately known in order to convert the absolute reference mixing ratio to the equivalent one in the sample cell. Although on a much smaller absorption level, the residual spectrum must still be measured accurately and the spectral fitting analysis should be able to simulate the relatively small absorption signal even in the presence of small pressure or temperature differences between the cells. Unequal ambient CO₂ absorption along the external paths of the sample and the reference line will cause baseline curvature in the normalized spectrum which is likely to change with time, if not purged or balanced by the path lengths. Thermally-driven optical fringes of a strength and free spectral range that can influence the measurement may be present in the optical system, so that careful thermal control of the optics is prudent. We targeted all the above issues in the development of ABC and demonstrate that the null method can be realized with good instrument performance.

2.2 Sealed quartz reference cell

The accuracy and the long-term stability performance of ABC are assured by permanently sealed quartz reference cells containing known column densities of CO₂ in dry

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“incomplete” reflection pattern (McManus, 2007; McManus et al., 2011). The extra absorption path between the cell front window and front mirror is included in the total path.

The quartz cell at the outer path in the setup picture serves as the major reference cell. The sample beam and the inner path quartz cell beam share the same detector. A shutter is installed to select between these two. The secondary quartz cell enables the instrument to check and characterize any system drifts in the sample detector and in the major quartz reference beam. External path lengths for these three beams are closely matched to minimize the effect of external-path CO_2 . Dry and CO_2 -free air is employed to purge the optical box at a slow flow rate to further reduce this potential interference. Purge gas is inconvenient in terms of remote operations and temperature disturbances. We plan to improve the hermetic sealing of the optical box and further balance the external beam paths in the next development step.

2.4 Spectral analysis

The spectral analysis of the normalized or nulled spectrum is complicated by the fact that there will inevitably be small pressure and temperature differences between the sample cell and the sealed reference cell. These will cause line shape differences between the sample and reference spectra and hence will induce a second derivative shape in the normalized spectrum near the null point. This effect will, of course, increase the residuals in the spectral fit if not included in the analysis. Hence, our spectral analysis software has been extended to do so. Rather than analyzing the null spectrum as a single Voigt line shape, it is analyzed as a ratio of Voigt lines whose shapes are determined by the sample pressure and temperature for one line and the reference pressure and temperature on the other.

An example of a null spectrum is shown in Fig. 2b. The sharp, low pressure absorption feature in the plot is the normalized sample spectrum with an absorbance of $\sim 2 \times 10^{-3}$ which is 100 times smaller than that from a single beam spectrum (Fig. 2a). The sample gas pressure was smaller than that of the quartz cell at the time of

measurement. Hence, the sharp feature shows a clear second derivative shape which is well described by the blue fit line from the spectral model.

The sharp spectral line is super-imposed on a much broader spectral feature. This is clearly the same CO₂ line but observed near atmospheric pressure. This feature was unexpected and appears to be due to CO₂ absorption within the sample detector sealed enclosure. It is not due to CO₂ in the external optical path since it was not reduced by purging the optical compartment with dry nitrogen. In addition, we tried switching the sample and the reference detectors and found that the broad absorption feature is associated with the sample detector. The reference detector doesn't show this feature so the feature does not get cancelled out in the null spectrum. This extra CO₂ in the sample detector is estimated to have much higher concentration than the ambient level and was relatively stable over the course of this study. We account for this broad absorption by fitting it separately with fixed concentration and pressure (one atmosphere). The latest version of the ABC instrument platform has two new detectors installed and is free of such interference.

2.5 Control and measurement of pressure and temperature

Long-term absolute CO₂ measurements require accurate pressure and temperature measurements. In order to achieve an accuracy of 0.1 ppm CO₂, the sample pressure reading should be stable within 1 part in 4000 of 5 Torr which is 1.25 mTorr. We use a 10 Torr capacitance manometer (MKS 122A) to monitor the sample cell pressure. The sensor is placed inside the temperature controlled optical box to reduce thermal drift and is connected to the sample cell through a short tube to reduce dead volume. In this work, all flowing measurements were made within 0.1 Torr of the 5 Torr set point and the calibration measurements were performed in cycles which required only a few hours relaxing the requirements on the pressure sensor. Hence, the results reported here are not subject to errors caused by inaccuracy or drift in the pressure sensor. However, long-term measurements using this approach would require a pressure sensor with long-term drift less than 1.25 mTorr at 5 Torr. Currently we are conducting long-term

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accuracy tests (zero- and span-drift) on three more pressure sensors: MKS 626B, MKS 627D and MKS 722A, all in the 10 Torr range.

Temperature influences the instrument's stability through a variety of mechanisms including phase motion of optical fringes. Fringes are frequently a problem in laser spectrometers. Their free spectral range (FSR) can be large, depending on the source resonator separations in the optical system. There may exist several fringes of different FSR and the combined effects further complicate the baseline structure on the spectrum (Werle, 2011). Fringes with FSR comparable to the sample absorption line width can bias the spectral fitting results and their movements with time can affect the instrument's short-term and long-term stability. We made several efforts to suppress fringe effects. They include careful optical design and alignment, fixing every component tightly, using mirrors with high reflectivity, using the astigmatic multi-pass cell, tilting quartz cell windows, wiggling some optical components, temperature and current stabilizing the laser, locking the laser emission line stringently, averaging high frequency fringe features on the baseline. We also tried fitting the interfering fringe with a sine wave and following its movement. The fringe effects were greatly suppressed after all the above efforts.

We improved the temperature stability of the optics by adopting a re-circulating liquid coolant scheme instead of the electronic heating scheme originally used. The old control scheme involves active heating of the optical box several degrees above the environment temperature, with a slightly higher set point for the box cover than for the bottom plate in order to generate a vertical temperature gradient to suppress convection. The heat dissipation from the laser and detectors inside the enclosure complicates the thermal distribution. We have tested and demonstrated that the liquid cooling scheme results in better thermal control of the optical box. The liquid output from a chiller, ThermoCube 300 (Solid State Cooling Inc, USA), first goes to the laser peltier, then to several cooling plates attached beneath the bottom of the optical table. Due to the large thermal capacity of the coolant and the tight connection of all optics to the table, the dissipated heat from the internal heat sources is removed quickly and effectively. The

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chiller output temperature is set at room temperature (296 K) to minimize thermal gradients. We thermally isolated the optical box with 5 cm polystyrene foam (thermal resistance of $2 \text{ K m}^2 \text{ W}^{-1}$). This control scheme reduces optical table temperature variation to 1 part in 100 of the room temperature variation. The sample gas gets temperature stabilized by first going through a long copper coil inside the optical box. The sample and the quartz cells were designed to be strongly thermally coupled to the optical table and were therefore assumed to be at the same temperature. Any temperature differences were certainly small and their impact was minimized by the small temperature dependence of the absorption line strength ($0.08 \% \text{ K}^{-1}$ at 296 K).

3 Instrument performance

3.1 Null effect

The null method and the improved temperature stability greatly improve the instrument precision and short-term stability. One example of this improvement is a 3-h temperature experiment. In this test we chose to measure the spectral ratio of the two sealed quartz cells. Since both the sample and the reference quartz cells were filled at the same time through an Ultra-Torr Tee connector (Swagelok), the CO_2 mixing ratios in these two cells are almost the same, giving rise to a nearly nulled ratio spectrum. During the 3-h measurement period, we challenged the instrument with rapid room temperature variations up to 5 K. The room temperature profile is shown in the bottom panel of Fig. 4 with its scale on the left. Optics temperature was measured at the same time and its profile is shown also in the bottom panel of Fig. 4 with a much smaller scale on the right. Room temperature variation caused the laser frequency to drift subtly, demonstrated by the absorption peak position change (in cm^{-1}) shown in the middle panel of Fig. 4. The measured equivalent CO_2 mixing ratio from the sample quartz cell is shown at the top panel of Fig. 4. All measurements were at 1 Hz.

around 10 K and the overall temperature change during the measurement month was ~ 20 K.

Figure 6 shows long-term measurement result of CO₂ mixing ratio at 1 Hz between 16 April and 22 May 2011 without any calibration or operational intervention. We ran a daily median filter through the whole dataset to reveal the long-term trend. The results show essentially no drift within one-month period and less than 0.1 ppm day-to-day CO₂ variations, indicating that the null method effectively reduces long-term measurement drift. This quartz cell comparison demonstrates the instrument's potential capability to achieve measurement accuracy which meets the WMO standards (± 0.1 ppm) without the use of field calibration.

3.3 Potential accuracy

Direct calibration of the ABC instrument with primary standards is the ideal approach to instrument calibration. It should be more accurate than calibration with secondary standards and would have the added benefit that the primary standards are typically supplied with a well known isotopic composition. Hence, it would be the preferred approach for one-time calibration of the commercial instrument at the time of production. However, the calibration approach tested in this work was comparison to secondary standards which are tied to primaries by a NDIR measurement. We adopted this approach because we wanted to be able to monitor and verify the instrument frequently and for an extended time period. Moreover, this indirect approach is the method that most end users would be likely to choose to verify instrument performance. In this section we show an example of how to compare the measurements between a Licor instrument (broad band absorption) and ABC (single peak absorption).

We evaluated the instrument accuracy using three certified tanks with CO₂ mixing ratio ranging from 338 ppm to 403 ppm, a span of 65 ppm around the typical ambient level. These three tanks were prepared separately by Scott-Marrin and Scott Specialty gas companies, and were calibrated by a NDIR analyzer (Licor 6251) using primary

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standards at Harvard University traceable to the WMO Central Calibration Lab (CCL) CO₂ standards.

We used one of these tanks to calibrate the quartz reference cell, and measured the other two using the ABC instrument. We sampled these tanks alternately to test the instrument's response at different CO₂ levels. Measurements were made for at least 5 min and were repeated 5–10 times for each tank. The calibration and measurement results for the tanks are listed in Tables 1 and 2 and the detailed explanation follows.

CO₂ mixing ratios from the ABC measurements and from the Licor calibrations cannot necessarily be directly compared at the 0.1 ppm accuracy level because of potential variation in the isotopic compositions of the calibration gases. ABC probes a single absorption line of the major isotopologue ¹²C¹⁶O₂ (hereafter referred to as 626), and hence directly measures the 626 concentrations. ABC can report the *total* CO₂ mixing ratio by assuming that the sample gas has a known isotopic composition. This is completely acceptable for atmospheric composition measurements where the isotopic composition of background air does not vary enough to be significant. However, calibration gases can have significantly different isotopic compositions which could prevent the ABC instrument from reporting the *total* CO₂ concentration with 0.1 ppm accuracy when measuring a calibration tank with unknown isotopic composition.

The response of the Licor instrument is more complex. The Licor uses an optical band-pass filter designed to transmit primarily the absorption band of 626. However, absorption bands from the other CO₂ isotopologues shift to lower wavenumbers and are partially included in the transmission region. The effect of the isotopic composition on the Licor response is dependent on the filter position, which can vary from instrument to instrument even within the same Licor model. Tohjima et al. (2009) quantified the theoretical relative molar response (RMR) of three Licor analyzers (Li-6252, Li-6252, and Li-6262) to each isotopologue based on the infrared absorbance by the individual isotopologues. In order to compare the measurements made by Licor and ABC, we use the RMRs provided by Tohjima et al. to correct the Licor measurements for isotopic variation and to express the results as measurements of the primary (626)

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quartz cell CO₂ while the other one was treated as the sample tank. Three separate analyses of the same data were performed, with each analysis using a different tank as the basis for the calibration. ABC error estimations shown in Table 2 are the 1 standard deviation from repeated measurements. The differences between ABC measurements and the corrected Licor values for 626 mixing ratio are generally within 0.2 ppm.

4 Summary and future development

An ABC prototype instrument measuring ambient dry air CO₂ mixing ratio is developed in this study. The special features of this instrument are the use of the spectroscopic null method and the use of stable internal reference cells to replace the labor-intensive and uncertain calibration tanks. These features have been demonstrated to improve the instrument's real-time performance: one-second precision of 0.02 ppm CO₂, long-term stability within 0.1 ppm over one month and the potential accuracy of less than 0.2 ppm without calibration while in use. The fast time-response, low drift and high precision of the ABC instrument are exceptional.

This work also implies the potential for spectroscopic measurements of other chemically inert atmospheric species without calibration tanks, but with equivalent or better measurement performances.

In future work, we plan to include water vapor in the measurement. The current instrument requires drying the sample which is a disadvantage for unattended remote monitoring. Spectral regions with co-existing CO₂ and water absorption lines with appropriate line separations and line strengths are available. The additional spectral line broadening from the presence of water can be accounted for within the existing spectral analysis model. Successfully implementing this would eliminate the need to dry the sample gas stream.

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Table 1. Calibration tank CO₂ information. Errors are 1 standard deviation from repeated measurements.

| Tank ID | Raw CO ₂ ^a (ppm) | δ ¹³ C ^b (‰) | δ ¹⁸ O ^b (‰) | Corrected total CO ₂ ^c (ppm) | 626 ^d (ppm) |
|---------|--|------------------------------------|------------------------------------|--|------------------------|
| #1 | 338.072 ± 0.006 | −39.9 ± 0.46 | 1.98 ± 0.2 | 338.0150 | 332.8332 |
| #2 | 346.728 ± 0.011 | −49.4 ± 0.3 | 35.2 ± 0.2 | 346.6295 | 341.3062 |
| #3 | 402.937 ± 0.006 | −36.7 ± 0.35 | 4.26 ± 0.17 | 402.8773 | 396.6835 |

^a The raw values of CO₂ mole fractions in tanks were measured by modified Licor 6251 (Daube et al., 2002) and calibrated against tanks (filled with natural air) traceable to the NOAA total CO₂ standards. Measurements were repeated twice for each tank.

^b Isotopic compositions of CO₂ in the tanks were calibrated by the Aerodyne QCLS_CO₂ isotope instrument, referencing to a standard tank characterized by IRMS at the Stable Isotope Ratio Facility for Environmental Research at the University of Utah. δ¹³C values are on the VPDB scale (R13.VPDB = 0.0111797), δ¹⁸O values are on the VSMOW scale (R18.VSMOW = 0.0020052).

^c The total CO₂ were calculated by correcting the tank CO₂ isotopic compositions for those in natural air (−10‰ for δ¹³C and 40‰ for δ¹⁸O), and by correcting the Licor responses using mean RMR values (1.00565, 0.33 and 1.345 for 626, 636 and 628) from the two Li-6252 instruments studied in Tohjima et al. (2009).

^d The fraction of total CO₂ that is 626 (F626) was calculated as

$$F_{626} = F_{16} \cdot F_{12} \cdot F_{16} \approx [1/(1 + R_{18} + R_{17})] \cdot [1/(1 + R_{13})] \cdot [1/(1 + R_{18} + R_{17})]$$

F₁₆ is the fraction of total oxygen that is ¹⁶O; F₁₂ is the fraction of total carbon that is ¹²C.

$$R_{18} = (\delta^{18}\text{O} + 1) \cdot R_{18.\text{VSMOW}}$$

$$R_{13} = (\delta^{13}\text{C} + 1) \cdot R_{13.\text{VPDB}}$$

We assume the R₁₇ value from VSMOW (0.0003799) for all three tanks since we did not measure them.

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Table 2. ABC-prototype accuracy performance. All reported values are for the major CO₂ isotopologue 626, in units of ppm. Errors are 1 standard deviation from repeated measurements.

| | Cal Tank (Licor) | Sample Tank (ABC) | | | Bias (ABC – Licor) | | |
|----|------------------|-------------------|----------------|----------------|--------------------|--------------|-------------|
| | | #1 | #2 | #3 | #1 | #2 | #3 |
| #1 | 332.833 ± 0.006 | NA | 341.214 ± 0.06 | 396.906 ± 0.02 | NA | -0.09 ± 0.06 | 0.22 ± 0.02 |
| #2 | 341.306 ± 0.011 | 332.926 ± 0.06 | NA | 396.844 ± 0.09 | 0.09 ± 0.06 | NA | 0.16 ± 0.09 |
| #3 | 396.684 ± 0.006 | 332.611 ± 0.02 | 341.146 ± 0.09 | NA | -0.22 ± 0.02 | -0.16 ± 0.09 | NA |

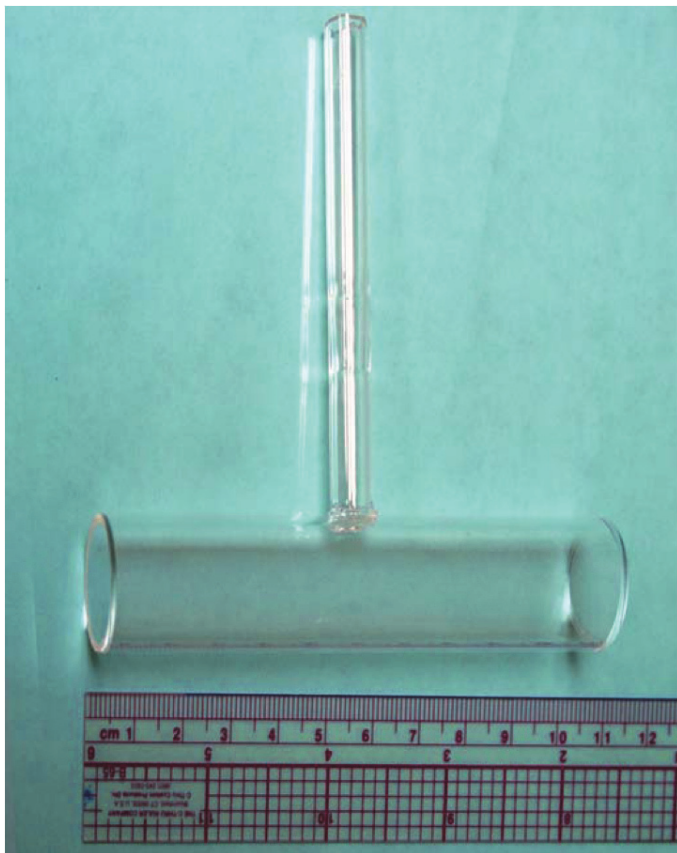


Fig. 1. Unsealed quartz reference cell. The seal tube has graded transitions from quartz to pyrex, where the cell is sealed.

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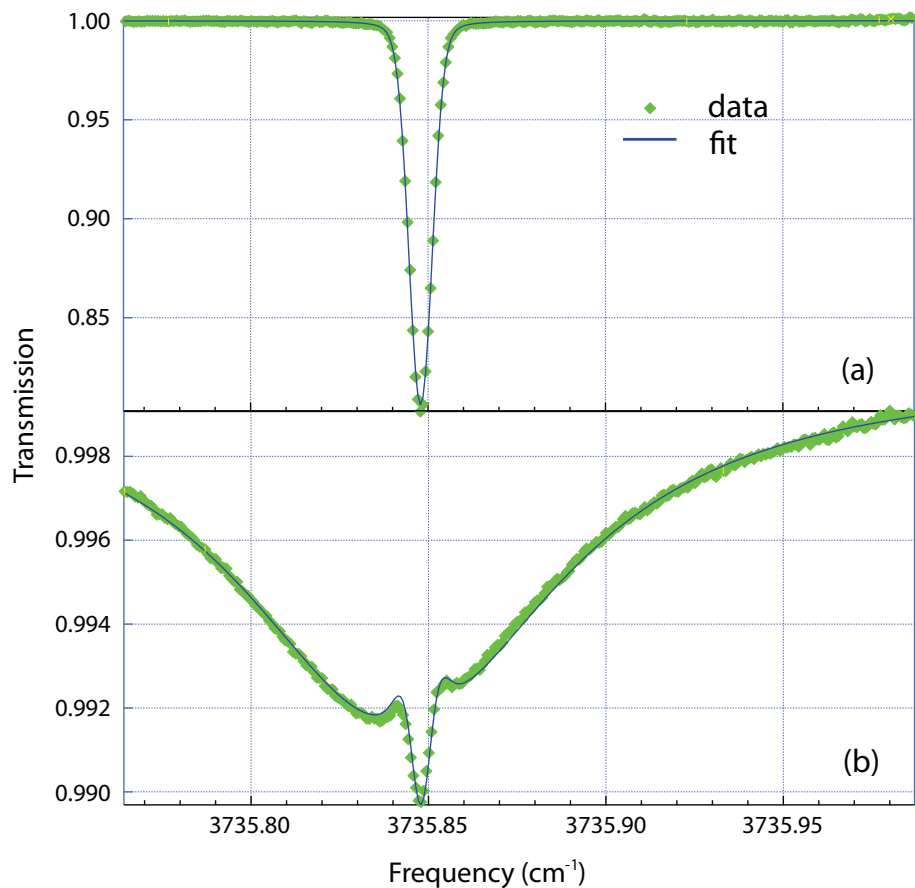


Fig. 2. Transmission spectra of **(a)** single reference beam and **(b)** normalized (ratio) sample beam.

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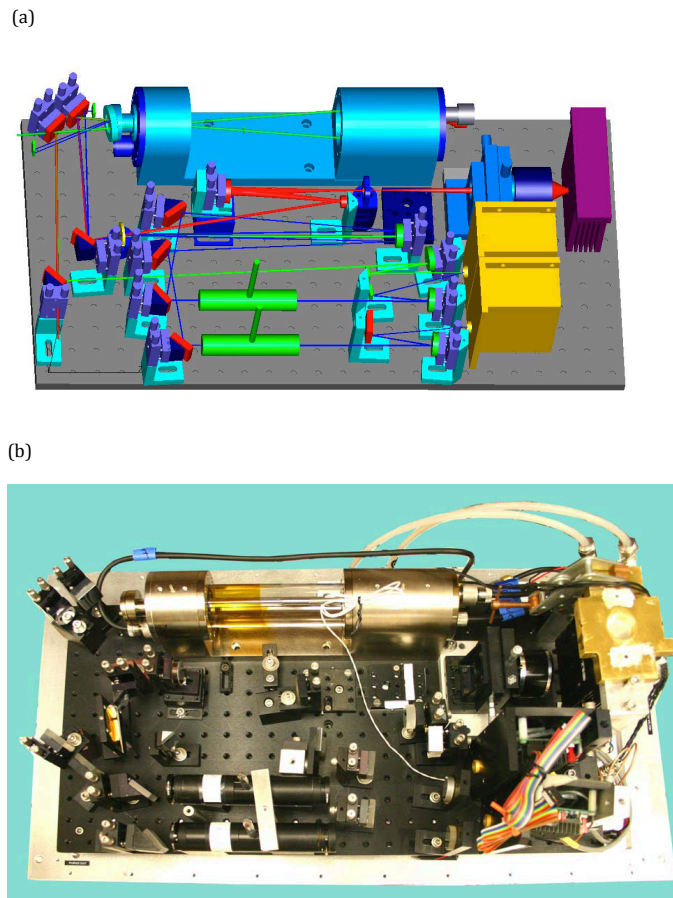


Fig. 3. ABC-prototype optical layout: **(a)** design and **(b)** photograph.

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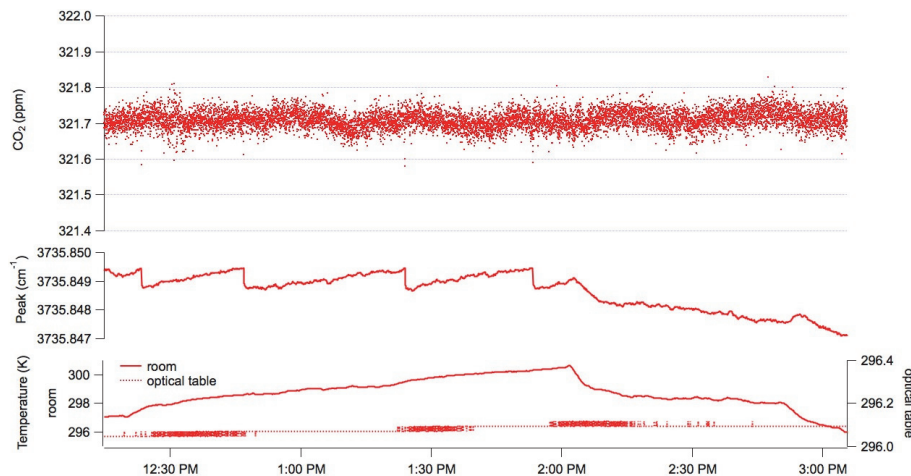


Fig. 4. Short-term stability test of ABC. 1 Hz time series plots of: temperature profiles (bottom), CO₂ absorption line peak position (middle) and equivalent CO₂ mixing ratio from a second sealed quartz cell (top).

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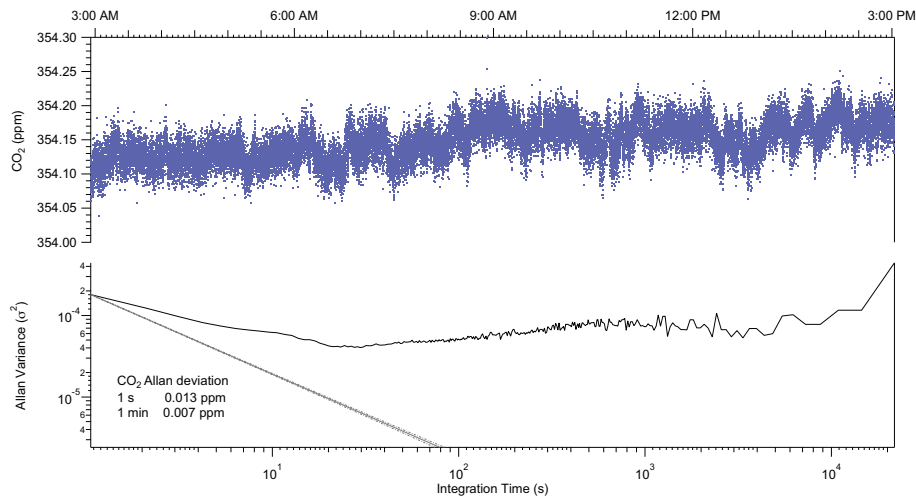


Fig. 5. Instrument performance of measuring a tank source for 12 h continuously. Top panel shows the real-time 1 Hz data; bottom panel is the Allan variance plot showing the instrument's one-second precision of 0.013 ppm and 0.007 ppm with one minute averaging.

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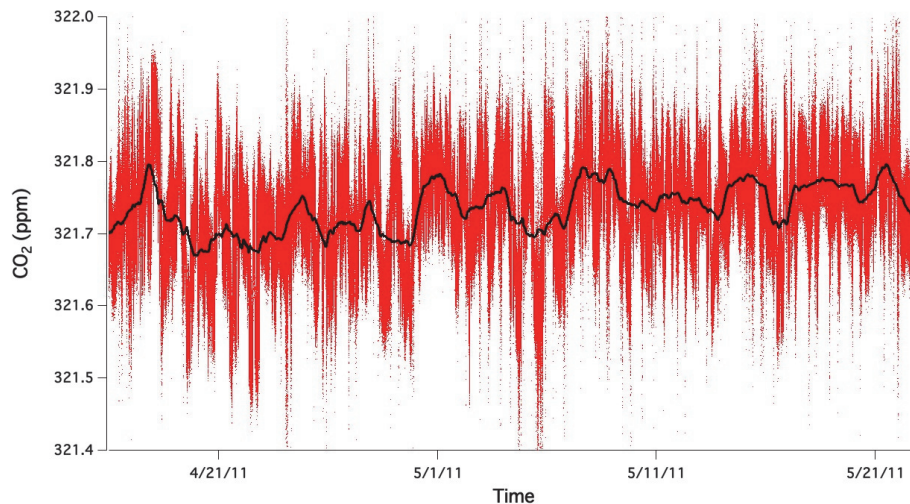


Fig. 6. One month continuous monitor of the CO₂ mixing ratio from a second sealed quartz cell without any calibration. Sample rate is 1 Hz. Real-time data are shown in red without any averaging. The black line is the smoothing results from daily running median.

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