



Development and field testing of a rapid and ultra-stable atmospheric carbon dioxide spectrometer

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Abstract. We present field test results for a new spectroscopic instrument to measure atmospheric carbon dioxide (CO₂) with high precision (0.02 μmol mol⁻¹, or ppm at 1 Hz) and demonstrate high stability (within 0.1 ppm over more than 8 months), without the need for hourly, daily, or even monthly calibration against high-pressure gas cylinders. The technical novelty of this instrument (ABsolute Carbon dioxide, ABC) is the spectral null method using an internal quartz reference cell with known CO₂ column density. Compared to a previously described prototype, the field instrument has better stability and benefits from more precise thermal control of the optics and more accurate pressure measurements in the sample cell (at the mTorr level). The instrument has been deployed at a long-term ecological research site (the Harvard Forest, USA), where it has measured for 8 months without on-site calibration and with minimal maintenance, showing drift bounds of less than 0.1 ppm. Field measurements agree well with those of a commercially available cavity ring-down CO₂ instrument (Picarro G2301) run with a standard calibration protocol. This field test demonstrates that ABC is capable of performing high-accuracy, unattended, continuous field measurements with minimal use of reference gas cylinders.

climate. To that end, various CO₂ instruments have been developed, using techniques such as tunable infrared laser direct absorption spectroscopy (TILDAS), non-dispersive infrared absorption (NDIR) spectroscopy, integrated cavity output spectroscopy (ICOS), cavity ring-down spectroscopy (CRDS), Fourier transform infrared spectroscopy (FTIR), and photoacoustic detection (Andersen et al., 2010; Baer et al., 2002; Engeln et al., 1998; Esler et al., 2000). Particular designs have targeted specific deployment purposes, such as long-term monitoring at remote sites, fast response eddy covariance measurement, mobile platform (i.e., car, ship, balloon, aircraft) in situ sampling, and atmospheric column concentration measurements. One limitation common to all the CO₂ instruments (and other stable gas instruments as well) is instrument response drift at various timescales (e.g., hours to days) and the associated need for use of calibration gases to maintain traceability to world standards. The logistics of tank operations – including filling, shipping, housing, pressure regulating, sampling, calibrating, and inter-comparing – are cost- and labor-intensive, especially so for instruments deployed in situ, and variations in the composition of gas delivered to the sensors may limit the accuracy of the measurement.

To address the problems presented by the need for periodic calibrations with gas standards, we developed an instrument called ABsolute Carbon dioxide, or ABC (Xiang et al., 2013). ABC relies on what we call the spectral null method, whereby the sample gas spectrum is divided by the spectrum in an internal, sealed quartz cell with a known CO₂ optical depth close to that of the sample. The null method

1 Introduction

Accurate and precise measurement of atmospheric carbon dioxide (CO₂) is key to monitoring and understanding anthropogenic impacts on atmospheric radiative forcing and

improves measurement precision and accuracy by reducing the influence of spectral variations associated with laser operating parameters (e.g., tuning rate, laser line width variation and mode purity), absorption line strength changes (e.g., with temperature), optics temperature variations, and spectral fitting. Previous tests showed the prototype instrument had a 1-second precision of $0.02 \mu\text{mol mol}^{-1}$ (ppm) and was stable to within 0.1 ppm over a month of unattended operation without calibration (Xiang et al., 2013).

Here we describe the field tests of a next-generation ABC instrument with improved performance demonstrated over many months of operation. The new instrument uses a different instrument platform equipped with better thermal and vibration control and integrated electronics. The instrument has been deployed to a research forest site to measure above-canopy CO₂ mixing ratios continuously for 8 months. Results from periodic surveillance tank measurements and from ambient sampling comparisons to a calibrated CO₂ instrument using CRDS (Picarro G2301) show stability within 0.1 ppm for the entire period. This performance puts the ABC instrument among the best CO₂ instruments currently available. It has great potential to be applied to long-term, remote monitoring networks for continuous unattended measurements, with a much simpler quality assurance process. The quartz reference cells could be calibrated at a central lab and delivered to remote sites to ensure consistent measurement standards. The new platform also has the potential to be adopted for other stable gas measurements and eddy covariance flux sampling.

2 Experimental details

We employ a variant of Tunable Infrared Laser Direct Absorption Spectroscopy (TILDAS) that incorporates a spectral null technique, comparing the sample spectra to spectra obtained from a permanently sealed quartz reference cell with known CO₂ column density. This facilitates high-accuracy, low-drift measurements of ambient CO₂ mixing ratios. Basic details of the instrument design, null method, sealed quartz reference cells, data acquisition, and spectral analysis are described by Xiang et al. (2013). Here we discuss in detail the major improvements of the next-generation ABC instrument, including a new instrument platform with improved thermal control, accurate sample cell pressure measurement, and better-integrated electronics.

2.1 Optics platform

ABC now uses an instrument platform originally developed for simultaneous detection of multiple species using dual lasers (McManus et al., 2010, 2011; Tuzson et al., 2013). A typical Aerodyne Dual (laser) system has dimensions of $53 \text{ cm} \times 66 \text{ cm} \times 71 \text{ cm}$ ($W \times D \times H$), weight of 72 kg, and draws electrical power of 500 W, 120/240 V, and 50/60 Hz.

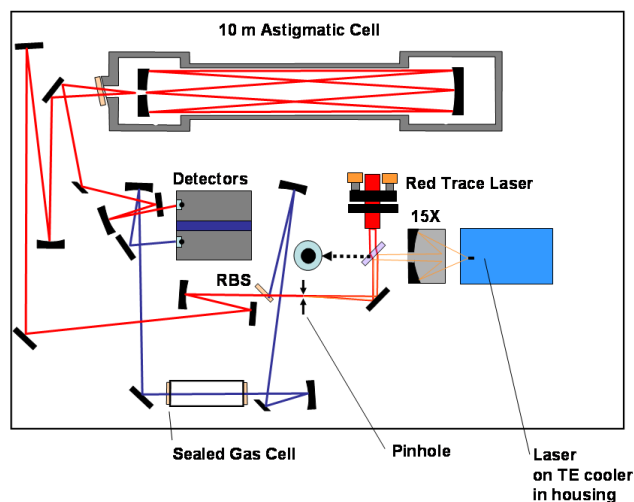


Figure 1. Diagram of the optical module for the ABC platform.

Figure 1 shows the optical module of the current ABC platform. The design is based on a $43 \text{ cm} \times 64 \text{ cm}$ breadboard.

Here we discuss in detail the special optical features of the current ABC instrument and contrast them with those of the prior ABC prototype. We used the same $2.7 \mu\text{m}$ distributed feedback (DFB) diode laser (Nanoplus, Germany), one quartz reference cell, and the AMAC-36 sample cell as in the first prototype instrument and installed two new 5-micron HgCdTe detectors. We selected a different $^{12}\text{C}^{16}\text{O}_2$ absorption line ($3733.4684 \text{ cm}^{-1}$) than the one used in the first prototype ($3735.8480 \text{ cm}^{-1}$). The new line is near another, weaker CO₂ absorption line that facilitates laser tuning rate characterization. The diode laser is positioned in a customized thermoelectric cooling (TEC) laser housing (blue in Fig. 1). Its output first gets collected and re-focused by a $15 \times$ reflecting objective mounted on a three-axis translation stage allowing for fine focus adjustments. A pinhole between the first reflecting mirror (black) and the wedged beam splitter (RBS, yellow) serves as a reference point for alignment, with the help from a visible trace laser. The main beam is separated by the RBS into two parts: the transmitted beam (red) goes into the sample multi-pass cell and gets detected by a 5-micron HgCdTe detector (Teledyne Judson Technologies, USA; J19TE4:5-3CN-R01M); the front reflected beam (blue) is directed into the quartz reference cell and collected by another detector of the same type as used in the sample beam. We adjusted the sample multi-pass cell absorption path length to $10.20 \pm 0.01 \text{ m}$ (19.4 cm mirror separation, 52 passes; McManus et al., 2011) to nearly match the column absorptions in the sample and the reference cells.

The traceable accuracy and the long-term measurement stability performance of ABC are assured by the permanently sealed quartz reference cell containing known column density of CO₂ in dry air. Column density is the product of the CO₂ number density and the optical path length of the quartz

cell (10 cm). Detailed quartz cell descriptions can be found in Xiang et al. (2013). We fill the quartz cell with 4 % CO₂ (in volume, from a pure CO₂ tank source) in a total of 5 Torr (0.7 kPa) dry, CO₂-free air, in order to obtain the equivalent CO₂ mixing ratio in the quartz cell close to the ambient level (the ABC sample cell has an optical path length about 100 times that of the quartz cell). The cell has been pumped before the filling to avoid internal water desorption and sealed by a glass-blower after the filling. The equivalent CO₂ mixing ratio in the sealed quartz cell (or the “null point”), at the fixed position inside the current ABC platform, has been calibrated to be 385.20 ± 0.02 ppm using reference gas cylinders traceable to the WMO standards (Tans et al., 2009) in the laboratory. Repeated quartz cell reposition tests under laboratory and field transport conditions were performed, and no CO₂ measurement shift outside 0.1 ppm range was observed.

2.2 Pressure measurement

For ABC to obtain 0.1 ppm long-term measurement stability, the pressure sensor measurement must be stable to within 1 part in 4000 (0.25 ‰), which is about 1 mTorr (~ 0.1 Pa) at the sample cell pressure of about 5 Torr (~ 660 Pa). We tested the long-term zero- and span- drift of three commercial sensors: MKS 626B, MKS 627D and MKS 722A (MKS Instruments Inc., USA). These sensors all operate up to 10 Torr with similar specified accuracies (0.15, 0.12, and 0.5 % of the reading, respectively), but they differ in size, settings, and price. During the test, all three sensors were connected to the ABC sample cell with switch valve controls. The MKS 627D is temperature self-controlled (the temperature dependence of its zero reading after control is 20 ppm full span (F.S.) K⁻¹ according to the specification) and was therefore placed outside the temperature-controlled ABC optics box. The other two sensors have greater zero-reading temperature dependencies (50 ppm F.S. K⁻¹ for the 626B and 80 ppm F.S. K⁻¹ for the 722A according to the specification) and so were placed inside the optics box. The ABC sample cell was also connected to a HOVAC DRI-2 pump system with valve control to serve as the “true” zero pressure. This system combined a molecular drag pump and a diaphragm pump and was capable of pumping the system down to 10^{-5} Torr (10^{-3} Pa), which is 2 orders of magnitude smaller than our pressure accuracy requirement. The sample cell was switched to HOVAC pumping periodically for the pressure sensor zero test.

We examined the pressure sensor zero drift periodically over 3 months (Fig. 2). Intensive zero pressure measurements (hourly) were made in the beginning, and the frequency was gradually reduced (from every 3 h to twice every day) towards the end of the test period. Data gaps in Fig. 2 are due to other ABC stability tests, but the vacuum system setup was not changed during those periods. Results show that the MKS 626B had the least zero-reading drift, less than 1 mTorr over the 3-month period (excluding the initial sensor stabilizing and vacuum system out-gassing period). The MKS 722A

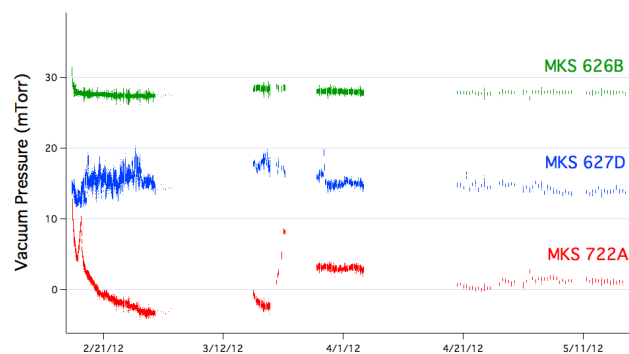


Figure 2. Measurements of the zero drift for three commercial pressure sensors over 3 months. Measurement frequency changes from hourly in the beginning to 3 hourly and twice daily at later times. Data gaps are due to other stability tests and the vacuum connection remains the same throughout this period.

had the worst performance, with drifts and sporadic changes up to 10 mTorr. These big changes did not appear in the measurements of the other two sensors and were likely associated with the turning on of the 722A sensor. This test was repeated on the MKS 626B later for an even longer time (6 months) and again its zero-drift was no more than 1 mTorr.

In addition to zero drift, we examined the span drift of all three commercial pressure sensors around the working pressure of the sample cell. The cell pressure was controlled by a flow controller (500 sccm range, MKS 0248A-00500SV) and varied within 0.1 Torr around 5 Torr during normal operation. Due to the lack of absolute pressure references in this range, we chose to check for span drift by comparing these three MKS sensors in pairs. Over a 1-month test period (15 February–17 March 2013), the most stable pressure reading comparison was between the MKS 627D and the MKS 626B. The ratio of their pressure readings (P_{627D}/P_{626B} , zero-drift corrected) was 1.0023 ± 0.0001 (1 standard deviation), suggesting very small span drift (0.01 percent) between the two sensors around the cell pressure. Based on these zero- and span-drift tests, we choose to install the MKS 626B in the ABC system, to measure the sample cell pressure with mTorr (0.25 ‰) accuracy.

2.3 Temperature control

Temperature influences the instrument’s stability through a variety of mechanisms including the phase motion of optical fringes, changes in laser tuning, and temperature dependence of the CO₂ absorption line strength combined with temperature measurement errors. In developing the first ABC prototype, we improved the temperature stability of the optics by adopting a re-circulating liquid coolant scheme (Xiang et al., 2013). A commercial thermoelectric chiller, ThermoCube 300 (Solid State Cooling Inc, USA), was used in that setup. More recently a new chiller permitting remote control of its set point with mK resolution was developed

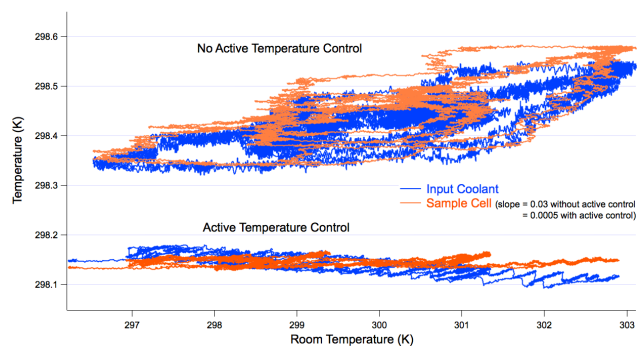


Figure 3. Temperature control effects on the ABC optics with and without a newly developed active control loop.

(Oasis 3, Solid State Cooling Inc, USA). We have been able to couple ABC and the Oasis 3 to realize active temperature control of a selected point in the optics enclosure, further improving instrument stability.

Usually, re-circulating chillers regulate temperature by attempting to maintain the fluid in the chiller at a fixed, manually selected set point. There are two problems with this approach: (1) some thermal loss/gain from/to the fluid en route to/from ABC is inevitable, so that if the fluid temperature in the chiller is stable, then the fluid temperature inside ABC will vary with the room temperature, and (2) the temperature of the fluid output by the chiller is potentially dependent on the room temperature as well. To help relieve these problems, we built a temperature control feedback loop between ABC and the Oasis 3 whereby the Oasis 3 set point is adjusted (via USB with 1 mK resolution) in order to maintain a stable temperature at a fixed location inside the optics box.

The benefit of the water temperature feedback control loop is illustrated in Fig. 3. Without the active control loop (top panel), the measured temperatures of the sample cell inside the optics box (orange) and of the coolant input to the optics box (blue) have a 1-part-in-30 dependence on the ambient temperature variation. With the active control loop using the sample cell as the sensing point (bottom panel), the coolant temperature is continuously adjusted by TDLWin-tel (the ABC control software), via the Oasis 3, such that the sample cell temperature stayed constant to within about 30 mK around 298.15 over 7 K changes in the ambient temperature (i.e., temperature of the control point varies by less than 1 part in 200 of the ambient temperature changes). We also improved the thermal stability of the separate electronics box through insulation and closed-loop ventilation with a heat exchanger and a separate chiller.

3 Instrument field performance

3.1 Harvard Forest deployment

We field-tested the ABC instrument at the Harvard Forest Environmental Measurements Site (HF-EMS) from June 2013 until February 2014 – a test period of 8 months. HF-EMS is a long-term ecological research site located in Petersham, Massachusetts, USA. The site is heavily forested, dominated by red oak and red maple. It has been described in detail elsewhere (Wofsy et al., 1993; Goulden et al., 1996; Urbanski et al., 2007). ABC measures from the eddy flux tower (30 m tall), along with two other CO₂ instruments: an Aerodyne CO₂-isotope spectrometer (Wehr et al., 2013) and a Picarro G2301 (Picarro Inc., USA).

ABC was plumbed in parallel with the Aerodyne CO₂ isotope spectrometer. Both instruments received gas from the same valve manifold, with ABC taking about 400 sccm of the total 3500 sccm flow via a tee inserted immediately before the isotopic spectrometer. The manifold sampled the air at the top of the canopy for most of the time, with intermittent sampling of vertical canopy profiles and of the secondary reference gas cylinders for the CO₂-isotope spectrometer (also called the working tank pairs: low span between 350 and 360 ppm and high span between 450 and 455 ppm). We stress that these working tanks were never used to calibrate ABC; indeed, ABC has not been calibrated once since its movement to the Harvard Forest in June 2013. It has been measuring continuously at 1 Hz without any maintenance, except for occasional site power, purge gas (i.e., CO₂- and H₂O-free gas), and pump failures. The restored performance of ABC was not affected by power or pump failure. The instrument automatically restarts itself and continues requiring data after power failures. After a pump replacement, the sample flow rate should be checked and maintained the same as before to ensure measurement stability. All of the ABC CO₂ values reported here, including the working tank gas values, come directly from the instrument's real-time measurements.

3.2 Field performance – stability

The daily performance and long-term stability of ABC in the field were evaluated by using the working tank pairs (hourly) as well as five reference tanks (occasionally) as surveillance tanks. Each working tank pair (aluminum cylinders; Airgas Inc., USA) was measured every 1.5 h and was replaced once the internal pressure dropped below about 500 psi. There are a total of five pairs of working tanks measured over the 8 months. Another five reference tanks (aluminum cylinders; Scott Specialty Gases and Scott-Marrin Inc., USA) were measured three times on site with 5 months apart (dates and values in Table 1). Figure 4a shows ABC's daily mean working tank measurements with error bars indicating the sub-daily measurement variation (1 standard deviation). Measurements of five reference tanks are also plotted with longer

Table 1. Surveillance tank CO₂ information and repeated ABC measurements at Harvard Forest in between June 2013 and February 2014. Errors are 1 standard deviation from repeated measurements.

	Licor CO ₂ ^a (ppm)	δ ¹³ C ^b (‰)	δ ¹⁸ O ^b (‰)	Corrected CO ₂ (ppm) ^c	ABC CO ₂ (ppm)	Measurement date
Aluminum gas cylinders						
#1	346.728 ± 0.011	−48.94 ± 0.26	+35.57 ± 0.23	346.6306	346.18 ± 0.03	9 Sep 2013
					346.33 ± 0.01	30 Jan 2014
					346.38 ± 0.01	20 Feb 2014
#2	377.651 ± 0.016	−37.12 ± 0.19	+6.27 ± 0.13	377.5929	377.54 ± 0.03	9 Sep 2013
					377.55 ± 0.01	30 Jan 2014
					377.56 ± 0.02	20 Feb 2014
#3	402.937 ± 0.006	−37.38 ± 0.15	+6.10 ± 0.09	402.8743	402.82 ± 0.03	9 Sep 2013
					402.79 ± 0.02	30 Jan 2014
					402.78 ± 0.02	20 Feb 2014
#4	422.128 ± 0.027	−37.52 ± 0.17	+5.52 ± 0.12	422.0622	422.01 ± 0.03	9 Sep 2013
					421.69 ± 0.02	30 Jan 2014
					421.66 ± 0.01	20 Feb 2014
#5	457.196 ± 0.004	−38.04 ± 0.20	+4.97 ± 0.13	457.1233	456.66 ± 0.03	9 Sep 2013
					456.45 ± 0.04	30 Jan 2014
					456.41 ± 0.02	20 Feb 2014
Steel gas cylinders ^d						
#1	332.693 ± 0.016	−10.34	+34.31	332.6947	332.91 ± 0.04	19 Jun 2013
					332.91 ± 0.04	11 Sep 2013
					332.89 ± 0.03	22 Oct 2013
					332.87 ± 0.05	20 Dec 2013
					332.78 ± 0.09	30 Jan 2014
332.91 ± 0.02	20 Feb 2014					
#2	431.150 ± 0.051	−15.10	+30.80	431.1392	430.65 ± 0.03	19 Jun 2013
					430.55 ± 0.03	11 Sept 2013
					430.51 ± 0.03	22 Oct 2013
					430.29 ± 0.04	20 Dec 2013
					430.21 ± 0.04	30 Jan 2014
430.35 ± 0.02	20 Feb 2014					
#3	496.444 ± 0.060	−15.13	+30.93	496.4314	495.06 ± 0.04	19 Jun 2013
					495.07 ± 0.07	11 Sep 2013
					494.70 ± 0.05	22 Oct 2013
					494.17 ± 0.07	20 Dec 2013
					493.97 ± 0.02	30 Jan 2014
494.10 ± 0.04	20 Feb 2014					

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

^b Isotopic compositions of CO₂ in the aluminum surveillance 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 (SIRFER) 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). Isotopic compositions of CO₂ in the steel surveillance tanks were measured directly by IRMS at SIRFER, University of Utah.

^c The corrected CO₂ values 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 Repeated ABC measurements of steel surveillance tanks show large variations associated with environment temperature. See discussion in Sect. 3.4 for details.

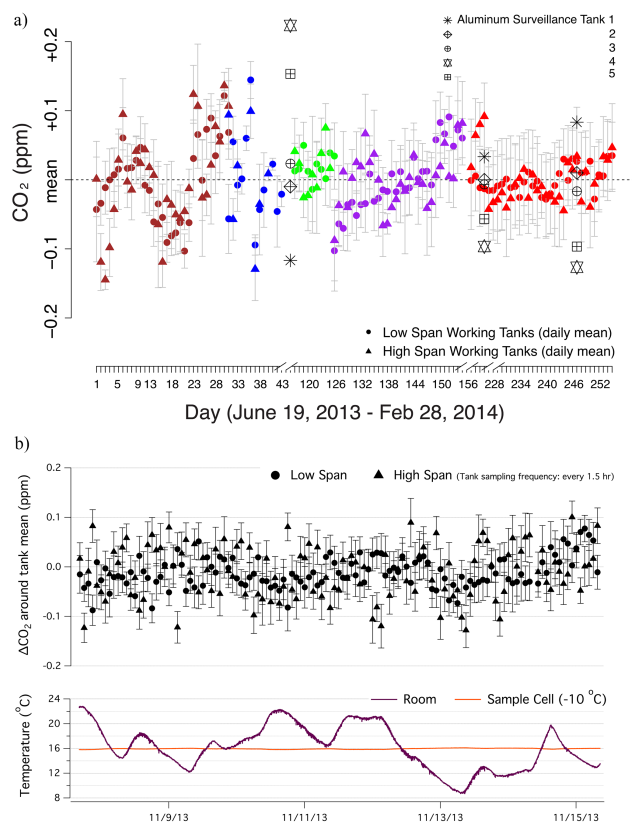


Figure 4. (a) Daily average of working tank pairs and individual surveillance tanks measured by ABC at Harvard Forest between 19 June 2013 and 14 February 2014. Working tank pair (low span in square, and high span in triangle) was measured twice every 3 h for 2 min each. Each pair (in different colors) lasts for about 1 month. Data are plotted around the mean of all measurements for each tank. Error bars show the 1 standard deviation of all working tank measurements on each day. Data gaps are due to power, purge gas or pump failure. (b) Week-long ABC working tank measurements at Harvard Forest, during which the room temperature varied 14 K. Each symbol represents one-time tank measurement (not the daily average as shown in a). Data points and error bars show the mean and the standard deviation in the last 30 s of each 2 min measurement period (sampling rate at 1 Hz). Concurrent temperature profiles of the instrument room and the sample cell are also shown for reference (lower panel).

time coverage from the same individual tank. In general, ABC showed no systematic drifts and the day-to-day CO₂ variation was below about ± 0.1 ppm, which meets the World Meteorological Organization Data Quality Objectives for the Northern Hemisphere (WMO, 1993).

Figure 4b shows ABC's working tank measurements over a 1-week period which was chosen because the room temperature varied by 14 K. Despite this very large temperature swing, all individual tank measurements (not merely the daily average) were stable within ± 0.1 ppm CO₂, showing

no measurable temperature dependency even at this very high level of measurement precision.

These results demonstrate that ABC is capable of measuring at remote sites for almost a year (and probably longer) without maintenance or calibration. Its stability of < 0.3 ppm peak to peak over 8 months surpasses or competes with that of any major brand CO₂ spectrometer (Andrews et al., 2014; Richardson et al., 2012; Picarro G2301 Analyzer Data Sheet, http://www.picarro.com/products_solutions/trace_gas_analyzers/co_co2_ch4_h2o).

3.3 Field performance – ambient sampling

We compared ABC's ambient air measurements to those of a Cavity Ring-Down Spectrometer (Picarro G2301) sampling at the same height through a different inlet on the same flux tower, and the results show relatively good agreement between the two.

The Picarro instrument has been measuring at the HF-EMS since the summer of 2012. It was set up to measure CO₂, CH₄, and H₂O at eight heights on the tower (0.3, 0.8, 4.5, 7.5, 12.7, 18.3, 24.1 and 29.0 m). The reported CO₂ from the Picarro G2301 has been corrected for water interference (lab characterization following Rella et al., 2013, and Chen et al., 2010) and for the CO₂ response curve (on-site calibration). One reference tank is measured by Picarro every 6 h to monitor instrument drift. Both the Picarro calibration tanks and the ABC reference tanks were calibrated against WMO standards at Harvard University, but using different instruments (Picarro and Licor, respectively).

Figure 5 compares CO₂ time series from ABC and the Picarro G2301, for the same height on the tower (29.0 m, through different inlets) during a week in between 2 and 8 January 2014. The two instruments tracked each other very well. The signals display relatively small daily CO₂ variations above the canopy due to low biological activity in winter. The Picarro G2301 measurements have a ~ 3 s output interval while ABC measures at 1 Hz and can be set even faster (10 Hz with 0.09 ppm precision, compared to 0.15 ppm precision at every 5 s for Picarro G2301). The mean CO₂ difference of the two measurements (ABC – Picarro G2301) is -0.04 ± 0.22 ppm during this 1-week period. ABC currently measures Nafion (Perma Pure PD-200T-48) dried air samples but does have the potential for water measurement and correction. Spectral regions with co-existing CO₂ and water absorption lines with appropriate line separations and line strengths are available (Xiang, 2013).

3.4 Field performance – accuracy

We used two sets of surveillance gas cylinders to test the accuracy of ABC and characterize its response to the CO₂ mixing ratio. One set has five aluminum tanks (Scott Specialty Gases and Scott-Marrin Inc., USA; same as those used for stability test in Sect. 3.2); the other set has three steel tanks

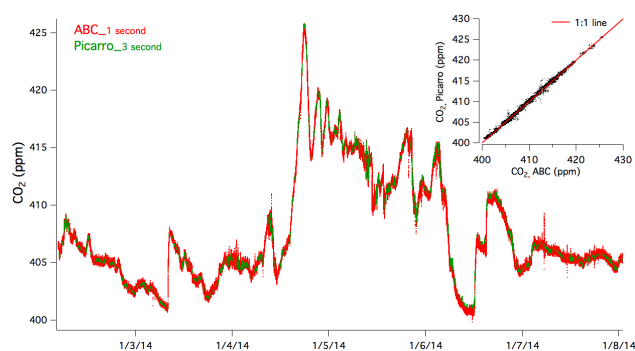


Figure 5. Ambient air measurements from ABC and Picarro above the canopy in Harvard Forest between 2 and 8 January 2014.

(Airgas Inc., USA) primarily serving as the reference gas cylinders for the CO₂-isotope spectrometer. All surveillance tanks were calibrated by a NDIR analyzer (a modified Licor 6251) at Harvard University and were traceable to the WMO Central Calibration Lab (CCL) CO₂ standards. We corrected the Licor measured CO₂ values for all cylinders according to their isotopic compositions and the Licor relative molar response (Tohjima et al., 2009; Xiang et al., 2013). The mixing ratio and isotopic composition of CO₂ in each cylinder are summarized in Table 1.

ABC responds very linearly to CO₂ between 330 and 500 ppm, though there is detectable nonlinearity less than 0.2 ppm. Figure 6 shows the repeated ABC measurements of all surveillance tanks between June 2013 and February 2014 without any calibration or correction applied. Linear regression of all aluminum tank measurements (340–460 ppm) has a slope of 0.997, 3‰ different from unity. The average fit residual for each tank is less than 0.2 ppm different from Licor calibrated values. At this 0.2 ppm CO₂ level, it is difficult to accurately attribute the bias sources to instrument uncertainties of ABC or Licor (e.g., instability, linear response, isotope effects, interferences) and tank drifts (e.g., due to fill gas sources, impurities, usage, leakage, position, tank material, regulator characteristics, ambient temperature, humidity, pressure, and personal operation; Keeling et al., 2007). However, we do observe nonlinearity based on the fit residuals for aluminum tank measurements. According to the null spectral scheme, ABC's accuracy and the stability both deteriorate as the sample CO₂ value deviates away from its null point (i.e., the effective CO₂ mixing ratio of ABC's quartz reference cell) of 385.20 ± 0.02 ppm. This can partly explain the observed nonlinearity.

We did not include steel surveillance tanks in the above discussion because of their observed instabilities with ambient temperature. In a short-term temperature test, clear contrast was observed as we alternately measured a steel (Airgas Inc., USA) and an aluminum CO₂ tank (Scott-Marrin Inc., USA). Both experienced a rapid temperature increase from about 4 °C to room temperature in an hour. During this hour,

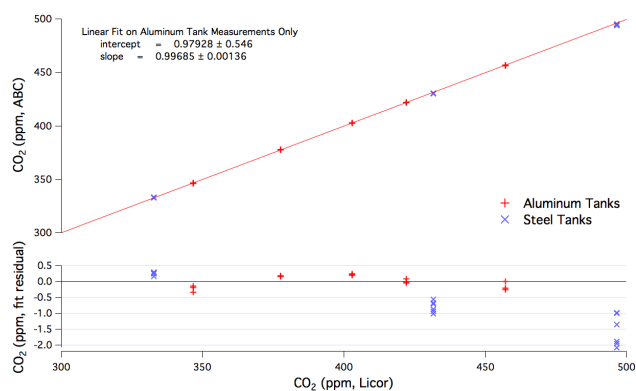


Figure 6. Repeated surveillance tank measurements at Harvard Forest field site between June 2013 and February 2014, showing the general linear response of ABC to CO₂ mixing ratios between 330 and 500 ppm. No calibration was performed during this 8-month period.

ABC measurements from the steel tank went up by 0.7 ppm; meanwhile those for the aluminum tank stayed constant. Over the 8-month field test, repeated ABC measurements of steel tanks (housed without temperature conditioning) also show tight and positive correlations with ambient temperature: up to 0.13 ppm CO₂ variation (Δ) and the temperature correlation coefficient (R) is 0.73 for the 332.7 ppm tank; $\Delta = 0.44$ ppm, $R = 0.91$ for the 431.2 ppm tank; and $\Delta = 1.10$ ppm, $R = 0.96$ for the 496.4 ppm tank. On the other hand, we did not observe this temperature correlation for the aluminum surveillance tanks (housed in the same room with steel tanks). Surface reactions and gas impurities are likely the causes for this temperature effect on steel tanks. Our results reinforce the recommendation from NOAA ESRL/CCGG (US National Oceanic and Atmospheric Administration Earth System Research Laboratory/Carbon Cycle Greenhouse Gases Group) for the use of aluminum rather than steel gas cylinders as references for high-precision CO₂ measurements (Kitzis, 2009).

4 Summary

We have developed a spectrometer for measuring absolute CO₂ mixing ratios in ambient air and demonstrated its long-term field deployment in this study. The major improvements compared to the lab-based prototype are improved temperature stabilization, and mTorr-level sample cell pressure measurement accuracy. Field measurements showed exceptional instrument stability and accuracy: repeatability to within 0.1 ppm over 8 months without any on-site calibration, and accuracy to within 0.2 ppm compared to Licor calibrated values traceable to the WMO standards. Field comparison with a Picarro CO₂ instrument showed good agreement.

The ABC instrument is designed for long-term continuous monitoring of atmospheric CO₂ at remote sites. Its stability

and accuracy without calibration gas consumption allow for simpler and less expensive operation without loss of reliability. The ABC instrument could also facilitate a global monitoring network with a central calibration lab for characterizing the quartz reference cells, which could be easily shipped to sites for inter-comparison or to serve as long-term stable references. This development work has moreover confirmed the potential of spectroscopic measurements for accurate, long-term, remote monitoring of other stable atmospheric species (and their isotopologues) with minimal reference gas consumption.

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