Performance Evaluation of a New, Tunable-Diode Laser Trace-Gas Analyzer for Isotope Ratios of Carbon Dioxide

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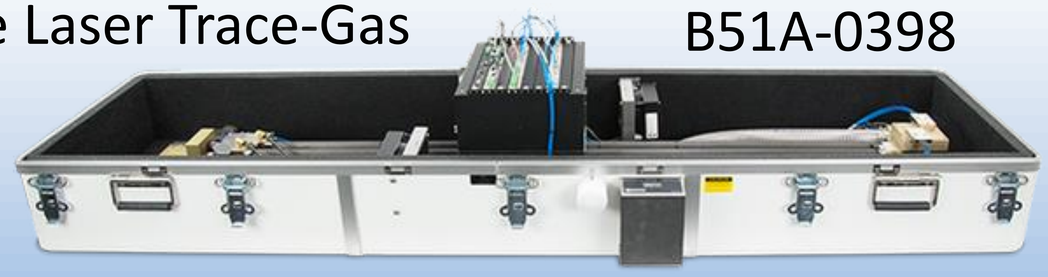


Introduction

Early field measurements of carbon dioxide isotope ratios using tunable diode laser spectrometry (TDLS) relied on cryogenically cooled lasers (Bowling, et al. 2003). Interband cascade lasers (ICLs) have enabled development of a family of tunable-diode laser trace-gas analyzers that do not require LN_2 to cool the laser. A recently released trace-gas analyzer for carbon dioxide isotopes, the TGA200A, Campbell Scientific, Inc., was evaluated for short- and long-term precision using Allan deviation analysis. Accuracy and linearity of CO_2 mixing ratio and isotope ratios were assessed with a set of 7 standard reference gases ranging from 298.35 to 971.48 ppm. Two analyzer variants were tested: one for CO_2, $\delta^{13}C$, and $\delta^{18}O$; and one for CO_2 and $\delta^{13}C$ at enhanced precision.

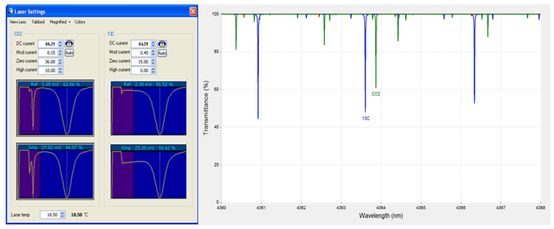
Materials and Methods

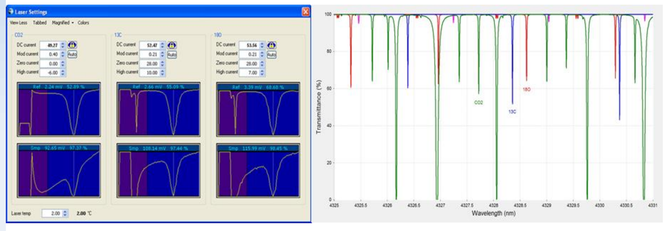
Lasers:

The TG200A was equipped with two lasers, "18O" and "13C". Tests were duplicated for each laser.

13C Laser
$^{12}C^{16}O^{16}O$ at 4363.9 nm
$^{13}C^{16}O^{16}O$ at 4363.6 nm

18O Laser
$^{12}C^{16}O^{16}O$ at 4327.7 nm
$^{13}C^{16}O^{16}O$ at 4328.4 nm
$^{12}C^{18}O^{16}O$ at 4328.6 nm



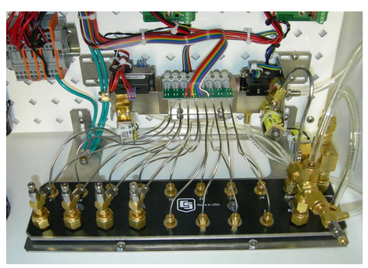


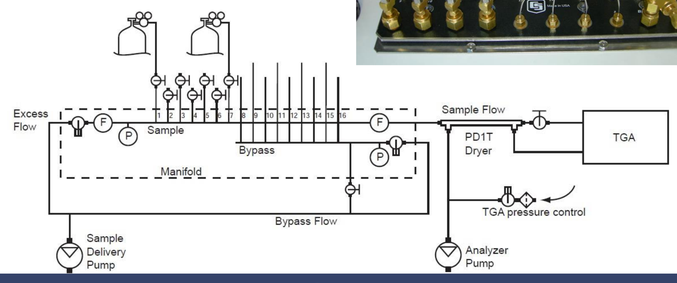
Sample System:

The TG200A was connected to a sampling system that selected the inlet with solenoid valves, dried the sample, and controlled the pressure in the dryer and in the TGA200A sample cell. A CR3000 datalogger (Campbell Scientific, Inc.) measured and controlled sample and excess flow, pressures in the non-selected intake tubes, the dryer, and the TGA sample cell. Data were recorded at 10 Hz.

A three-stage diaphragm pump (Edwards XDD1) pulled the sample through the TGA and a small double-head diaphragm pump (Parker BTC-IIS) pulled the excess and bypass flows to allow pressure control. A PD1T dryer (Campbell Scientific, Inc.) equipped with a 1.8 meter length of Nafion® tubing was purged in reflux mode using the TGA vacuum outlet. All samples measured in this study were dry compressed gases, making the dryer not strictly necessary. It was included because it is the normal configuration for low-flow air sample measurements.

The flow rate was 200 ml·min^{-1} subsampled to the TGA200A and controlled to 30 mb. Excess flow was approximately 50 ml·min^{-1} for Allan variance analysis, and 200 to 300 ml·min^{-1} for the accuracy/linearity test. The pictures and schematic below, illustrate the TGA200A sampling system.





References

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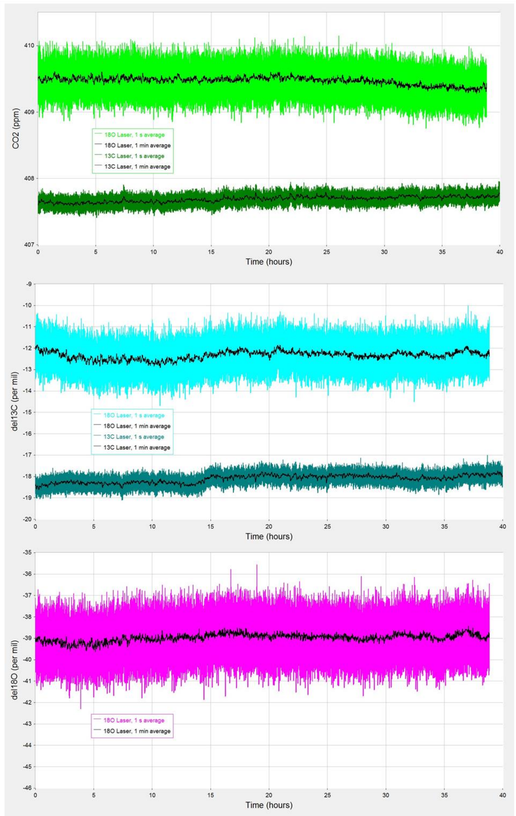
Long-Term Precision



The TGA200A sampled air from a compressed air cylinder over approximately 40 hours to assess long-term precision. Individual isotopolog concentrations measured by the TGA200A were converted to the total CO_2 and isotope ratios:

$$C_T = \frac{(C_{12C} + C_{13C} + C_{18O})}{1 - (N_{12C} + N_{13C} + N_{18O})}$$

- C_T is total CO_2 mixing ratio
- C_{12C}, C_{13C}, and C_{18O} are mixing ratios for individual isotopologs
- N_{12C}, N_{13C}, and N_{18O} are natural abundances for individual isotopologs (from hitran.iao.ru, 5/22/2015)
- C_{18O} and N_{18O} were set to zero when the 13C laser was used

Isotope ratios were calculated using standard delta notation:

$$\delta^{13}C = \left(\frac{{}^{C_{13C}}/_{C_{12C}}}{R_{13C}} - 1\right) * 1000‰$$

$$\delta^{18}O = \left(\frac{{}^{C_{18O}}/_{C_{12C}}}{R_{18O}} - 1\right) * 1000‰$$

- R_{13C} is the standard ratio for δ13C, 0.0111797 (Griffis, et al. 2004)
- R_{18O} is the standard ratio for δ18O, 0.004176698 (from Allison et al., 1995, doubled to account for two atoms of oxygen)

The data were block averaged to 1 second and to 1 minute, and the resulting time series were overplotted (left). The standard deviation of the 1-minute averages over the entire approximately 40 hours is a measure of the long-term drift (below).

	18O laser	13C laser
CO_2 (ppm)	0.06	0.04
$\delta^{13}C$ (‰)	0.19	0.18
$\delta^{18}O$ (‰)	0.18	NA

Accuracy and Linearity

The accuracy and linearity of the TGA200A was evaluated by measuring a set of standard tanks, fitting a curve to the results, and plotting the residual errors.

The standard tanks span mixing ratios from 298 to 971 ppm (see table below left). These tanks were obtained from NOAA ESRL GMD in either 2007 or 2010, for CO_2 mixing ratio calibrations. The isotope ratios given for the tanks obtained in 2010 are intended for correcting the CO_2 mixing ratio, not as isotopic standards. The 2007 tanks were obtained from GMD in 2007 before isotope ratios were routinely measured. Isotope ratios for these tanks were measured with the TGA200A.

A tank of ultra-zero air was also measured. The CO_2 mixing ratio for this tank was confirmed to be zero by comparing it to room air pulled through a bottle of molecular sieve (data not shown).

Tank Serial Number	CO_2 Mixing Ratio (ppm)	$\delta^{13}C$ (‰)	$\delta^{18}O$ (‰)	Year Obtained
CC310080	298.35	– 8.6	– 1.6	2010
CA07548	391.77	– 8.86	– 8.61	2007
CC325114	593.32	– 16.5	– 14.8	2010
CC324472	697.03	– 18.8	– 18.75	2010
CA07594	794.81	– 21.66	– 21.94	2007
CC325116	892.30	– 21.7	– 23.2	2010
CC325129	971.48	– 22.5	– 24.95	2010

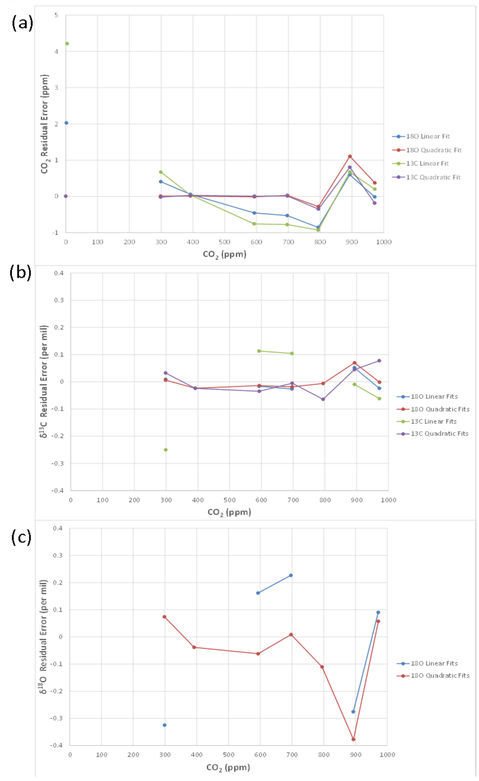
The data were processed two ways: with a linear fit to the 5 tanks for which isotope ratios were measured by GMD, and a quadratic fit excluding the 3 highest-concentration tanks. This quadratic fit included the zero air, and it also included the 392 ppm tank, using isotope ratios determined by the TGA200A.

Total CO_2 residuals of the linear fits (a) are all within ± 1 ppm, and are consistent between the two lasers. It is apparent from the figure that the TGA200A has a slight nonlinearity, especially considering the zero air data. The residuals for the 3 highest-concentration tanks suggests there may be an error in one or more of these tanks.

The quadratic fits cause the residuals below 700 ppm (including zero air) to virtually disappear (± 0.03 ppm). The quadratic residuals above 700 ppm are unreasonably large. This discrepancy will be investigated in 2016 when the tanks can be returned to GMD for recalibration.

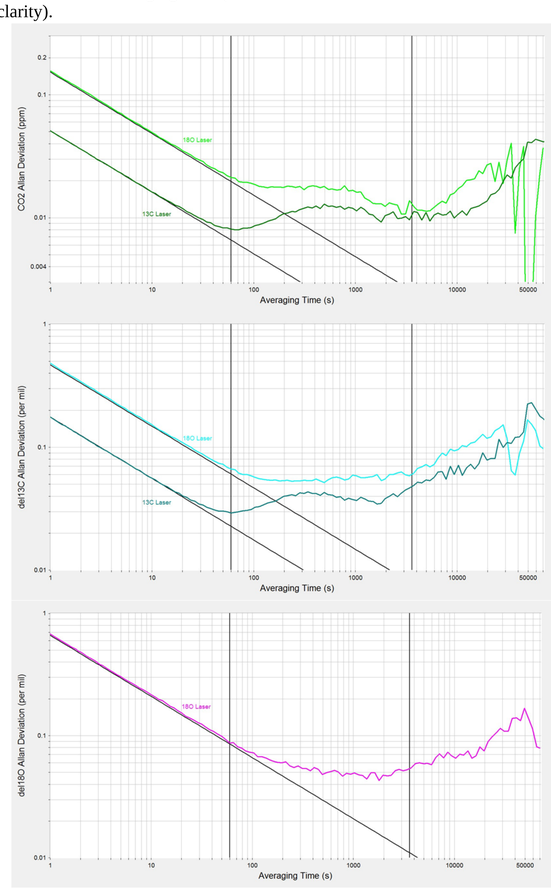
Residual $\delta^{13}C$ errors are shown in (b). The quadratic fits give residuals within ± 0.03 ‰ for the tanks below 700 ppm. Residuals are generally larger for the higher-concentration tanks, similar to the CO_2 residuals.

The residual $\delta^{18}O$ errors are larger than those for $\delta^{13}C$, as shown in (c). The quadratic fit to the lower-concentration tanks provides all residuals within ± 0.1 ‰. The 892 ppm tank has an especially large residual error.



Allan Deviation

The Allan deviations (Allan, 1996) are based on the original (10 Hz) data with no block averaging. The X axis is the averaging time, shown from 1 second to 20 hours. Vertical bars mark averaging times of 1 minute and 1 hour. The ideal Allan deviation is shown below for each curve. These are based on the Allan deviation at 0.1 second divided by the square root of the averaging time (Allan deviations from 0.1 to 1 second are not shown for clarity).



Conclusions

The TGA200A is very accurate. Residuals of quadratic fits from 0 to 700 ppm:

- CO_2: ± 0.03 ppm
- $\delta^{13}C$: ± 0.03 ‰ (300 to 700 ppm CO_2)
- $\delta^{18}O$: ± 0.1 ‰ (300 to 700 ppm CO_2)

The TGA200A is very stable. Standard deviation of 1-minute block average over ~ 40 hours:

- CO_2: < 0.1 ppm
- $\delta^{13}C$: < 0.2 ‰
- $\delta^{18}O$: < 0.2 ‰

Allan deviation analysis shows the TGA200A has excellent precision for practical averaging times and calibration intervals:

- CO_2: < 0.02 ppm from 1 minute to 3.5 hours (18O laser) and from 7 seconds to 8 hours (13C laser)
- $\delta^{13}C$: < 0.1 ‰ from 30 seconds to 3 hours (18O laser) and < 0.05 ‰ from 15 seconds to 1 hour (13C laser)
- $\delta^{18}O$: < 0.1 ‰ from 50 seconds to 6 hours (18O laser)

Future Work

This study will be repeated once the set of standard gases is retested and extended:

- The existing standard gases will be returned to GMD for calibration
- New standard gases have been ordered to extend the range of CO_2 up to 2500 ppm and to provide high-accuracy isotope ratios

Acknowledgments

Karen Wolfe for technical editing, layout, and design support.