A high accuracy analyzer for airborne measurements of greenhouse gases (CO_2 and CH_4)

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1. Introduction

Measurements on board aircraft complement those made on towers and satellites, and are essential for observations in the free troposphere and lower stratosphere covering regional to continental scales. In-flight calibrations and careful air drying techniques were employed in all previous in situ airborne measurements of CO_2 and CH_4 within the troposphere in order to guarantee their accuracy, which demands considerable maintenance in the field. We present a high accuracy analyzer using the CRDS technique for continuous measurements of CO_2, CH_4 and H_2O with minimum maintenance in the field during the Balanço Atmosférico Regional de Carbono na Amazônia (BARCA) phase B campaign in Brazil in May 2009. Unlike any previously deployed instrument for high accuracy airborne measurements of tropospheric CO_2, this analyzer (Picarro Inc., CA, USA, model G1301-m) was flown without a drying system and without any in-flight calibration gases.

2. Water correction functions

we assess 1) if the water measurements are adequate for correcting the dilution and pressure-broadening effects 2) if the water correction functions are stable over time.

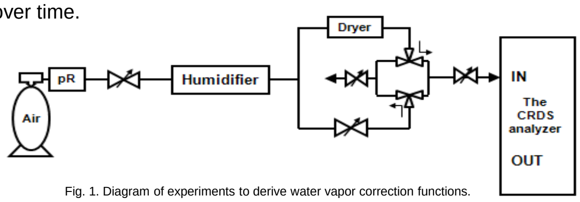

Fig. 1. Diagram of experiments to derive water vapor correction functions.

A series of experiments has been carried out (see Fig. 1) The humidifier was sequentially set to dew points 0°C, 5°C, 10°C, 15°C, 20°C, 25°C, 30°C and 35°C corresponding to measured water vapor mixing ratios from 0.6 % to 6 %. Results in Fig 2 show the water correction functions can be represented by quadratic fits; good transferability between CFADS15 and CFADS37 proves the corrections are not likely to change over time.

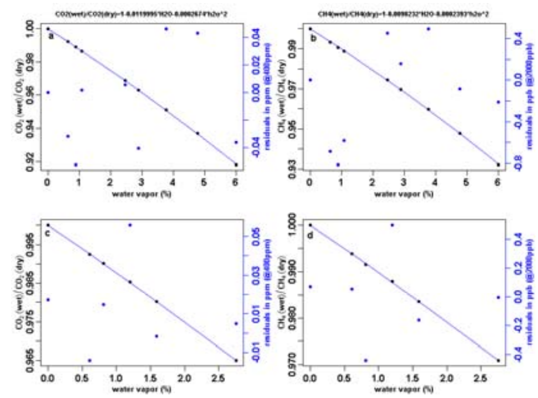

Fig. 2. a-b. Quadratic fits of CO_{2wet}/CO_{2dry} and CH_{4wet}/CH_{4dry} vs. H_2O mixing ratios; c-d. Results from similar experiments done with CFADS15, with the curve showing the fits from experiments using CFADS37

3. Calibration of the CRDS analyzer using synthetic air

Calibration of the CRDS analyzer with synthetic air CO_2 standards requires corrections for pressure-broadening effect due to variations of the main components N_2, O_2 and Ar and for isotopic effect due to differing isotopic signatures in synthetic vs. ambient air.

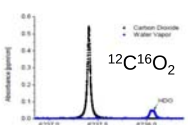

Fig. 3 Scanned pectral profile of $^{12}C^{16}O_2$ (courtesy of E. Crosson)

3.1 Corrections for the pressure-broadening effect

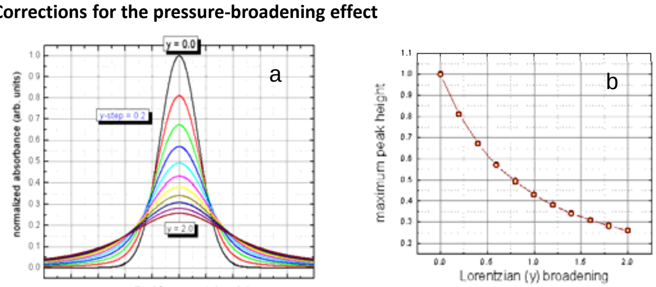

Fig. 4 a. For constant mixing ratios of CO_2 in air, profiles vary according to widths (parameterized by y); b. Correlation between the peak height and the width of the spectral profiles (courtesy of Chris Rella)

3.2 Corrections for variations in carbon isotopologues

The $\delta^{13}C$ and $\delta^{18}O$ values of ambient CO_2 are -8.2 ‰ and +41.9‰. A good estimate for the $\delta^{13}C$ and $\delta^{18}O$ values of the our synthetic air standards is -37 ± 11 ‰ and 24 ± 10 ‰, respectively. The corrections can be achieved by the following equation:

$$CO_{2syn} = CO_{2meas} \times \left[\frac{1 + {}^{13}R_{ref} \times (1 + \delta^{13}C_{syn}) + 2 \times {}^{18}R_{ref} \times (1 + \delta^{18}C_{syn})}{1 + {}^{13}R_{ref} \times (1 + \delta^{13}C_{atm}) + 2 \times {}^{18}R_{ref} \times (1 + \delta^{18}C_{atm})} \right]$$

Table1. Calibration of the CRDS using ambient and synthetic air standards

Tanks	MPI Cal. (ppm)	CRDS Meas. (ppm)	CRDS Meas. – MPI Cal. (ppm)	CRDS Meas. With corrections (ppm)	CRDS Meas. With corrections – MPI Cal. (ppm)	O2 [%]
Amb1	391.22	391.29	0.07	391.29	0.07	20.95
Amb2	379.82	379.77	-0.05	379.77	-0.05	20.95
Amb3	324.22	324.25	0.03	324.25	0.03	20.95
Syn1	407.78	406.95	**-0.83**	407.66± 0.17	**-0.12± 0.17**	**20.17**
Syn2	392.83	392.45	**-0.38**	392.94± 0.17	**0.11± 0.17**	**20.63**
Syn3	372.97	372.35	**-0.62**	373.01± 0.17	**0.04± 0.17**	**20.25**

4. Comparison during BARCA

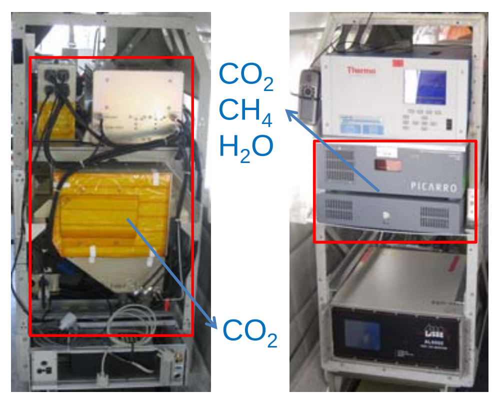

Table 2. Comparisons of the CRDS (right) with an NDIR analyzer (left) on board the same aircraft

Flight No.	Date (mmdd)	Difference (ppm)	Difference 1σ (ppm)	Difference after cross-calibration (ppm)	Difference after cross-calibration 1σ (ppm)
000	0511	1.39	0.87	—	—
001	0515	0.28	0.20	—	—
002	0517	0.20	0.23	-0.02	0.25
003	0517	0.22	0.20	-0.02	0.20
004	0519	0.34	0.32	0.11	0.32
005	0519	0.21	0.28	-0.04	0.28
006	0521	0.12	0.22	-0.11	0.26
007	0521	0.11	0.26	-0.13	0.25
008	0522	—	—	—	—
009	0523	—	—	—	—
010	0523	—	—	—	—
011	0526	0.20	0.18	-0.05	0.19
012	0526	0.18	0.15	-0.06	0.16
013	0527	0.38	0.23	0.15	0.23
014	0527	—	—	—	—
015	0528	0.21	0.22	-0.04	0.22

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