Performance test of a CRDS instrument for continuous CO_2/CH_4 measurement and its suitability for the ICOS atmospheric stations network

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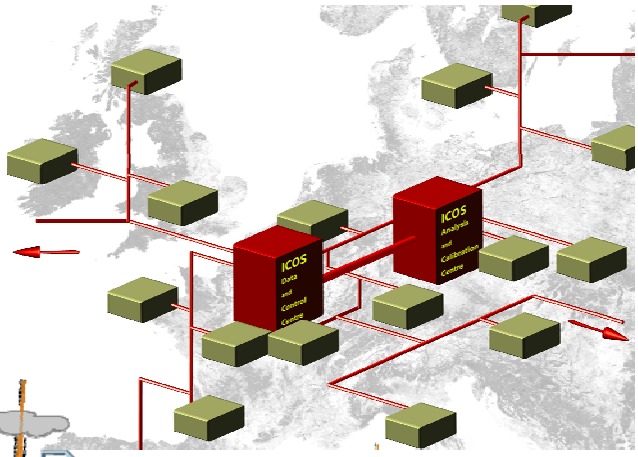
Introduction

ICOS (Integrated Carbon Observation System; http://www.icos-infrastructure.eu/) is a new European research infrastructure for quantifying and understanding the greenhouse balance of the European continent and adjacent regions. During its preparatory phase, the project will be developed to a fully operational level, but with a reduced number of observational sites. A part of the project is the construction of a network for atmospheric measurements. For this purpose, a prototype atmospheric station is under construction (Fig. 1).



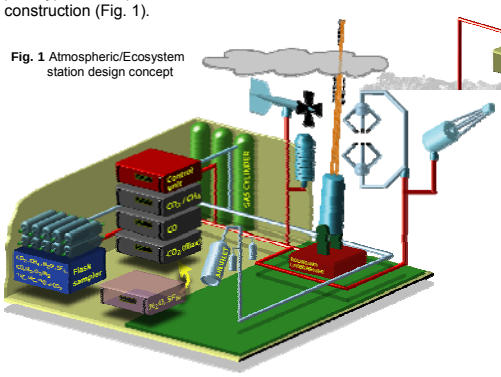


Fig. 1 Atmospheric/Ecosystem station design concept

ICOS stations are

- standardization of methods and equipment
- modularity
- automatic operation
- local and remote control
- dynamic technological updates (new techniques/gas species)
- less customization, calibration and maintenance
- lower cost
- continuous measurements + periodic "intelligent" sampling
- two level of sites (L1- full suite of parameters and L2 - subset)

Atmospheric stations
Core parameters - continuous (CO_2, CH_4, CO, PBLh, meteo)
Core parameters - periodic (flask samples - concentrations and isotopes)
Additional parameters (N_2O, SF_6, O_2/N_2, Rn-222, etc.)

Tests

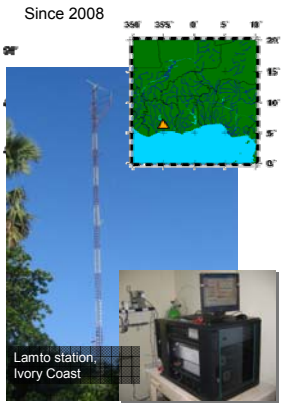
Amongst others, the Picarro G1301 $CO_2/CH_4/H_2O$ analyser is being tested at LSCE (Gif-sur-Yvette, France) and in the field (Lamto station, Ivory Coast) to evaluate its suitability for the ICOS atmospheric station prototype. We present a part of the tests, focusing on calibration routines, water vapour correction, and on preliminary results of a very low-maintenance drying system. Further test results can be found in Wastine et al. (2009).

Laboratory

Since 2007

Field

Since 2008



Calibration/drift

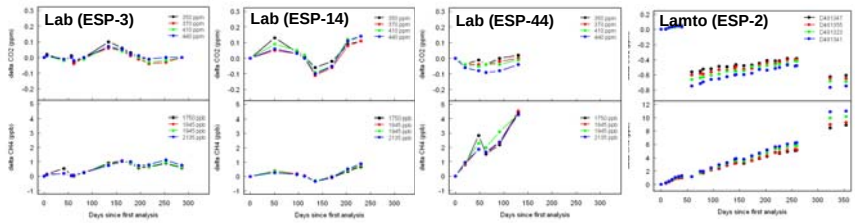
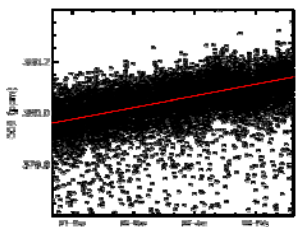
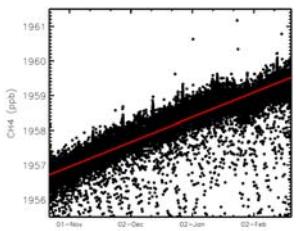


Fig.2 The analyzers were regularly (~ every two weeks) calibrated for CO_2 and CH_4 with four calibration gases. The observed drift for calibration gases is different between instruments.





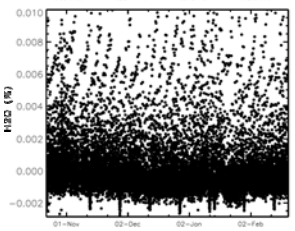


Fig.3 (above and right) Target gas measurements at Lamto station during Fall and Winter 2008/2009. The trend for CO_2 and CH_4 is in line with the trend for the calibration gases (see rightmost plot in Fig. 2) while the H_2O measurement remains stable.

Drying system

A low-maintenance drying system based on nafion dryers and a high pressure dryer (for the purge gas) is being developed at LSCE. The objective is a system that does not need consumables for drying the nafion purge gas (e.g. $Mg(ClO_4)_2$) and that dries efficiently the sample air without modifying its trace gas composition. The preliminary results are encouraging. Such a system would be particularly useful on high-humidity sites (e.g. Lamto station) as high humidity of the sample increases the uncertainty of the measurement (see section "H_2O correction").

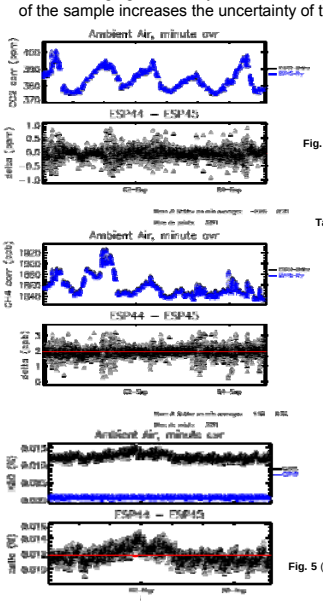


Fig. 5 (left) Comparison of ambient air measurement using our nafion system (ESP44) and a cryocooler (-65°C; ESP45). CO_2 is corrected using the Picarro analyzer internal correction and CH_4 using the LSCE in-house empirical correction.

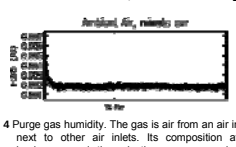


Fig. 4 Purge gas humidity. The gas is air from an air inlet next to other air inlets. Its composition after having passed through the purge gas drying system is close to concurrent sample air (ΔCO_2 = 0.41 +/- 0.28 ppm, ΔCH_4 = 0.74 +/- 1.16 ppb).

Table 1 Summary of the drying efficiency of the different drying systems tested at LSCE.

	ΔCO_2 (ppm)[1]	ΔCH_4 (ppb)[1]	H_2O (%v)[2]
Peltier (-30°C)	0.17	1.80	0.035
Peltier + Nafion	0.11	1.12	0.023
Peltier + $Mg(ClO_4)_2$	0.004	1.26	0.0008
Nafion	≈ 0.05	≈ 1	≈ 0.012

[1] difference anayzer raw value - corrected value
[2] residual water vapour concentration in the sample

Table 2 Measurement of a gas from a calibrated cylinder (CO_2=393.45 ppm; CH_4=1895.57 ppb) using the same pathway through the drying setup as for the sample.

Nafion dryer purge gas	CO_2 (ppm)	CH_4 (ppb)
= sample air	393.42	1895.41
lab air	393.42	1895.36
N_2	393.41	1895.42

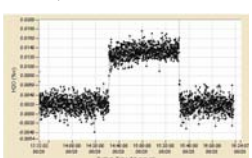


Fig. 6 Water vapour concentration during alternate measurement of cryocooler and nafion-dried sample air (G1301 acquisition software screenshot).

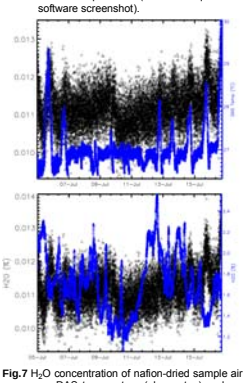


Fig.7 H_2O concentration of nafion-dried sample air vs. DAS temperature (above, top) and vs. ambient air H_2O concentration (above, bottom).

H_2O correction

All our analyzers have the same built-in CO_2 correction (below):

$$CO_{2corr} = \frac{CO_{2raw}}{1.0 - 0.01244 \times H_2O}$$

We found indications that the correction parameter 0.01244 may change through time/between analyzers, which could (e.g. at high ambient humidity; at Lamto the average is 3.0 to 3.5 %v.H_2O with peaks of up to 4 %v.H_2O) cause a measurement error of more than 0.1 ppm CO_2 (Fig. 8).

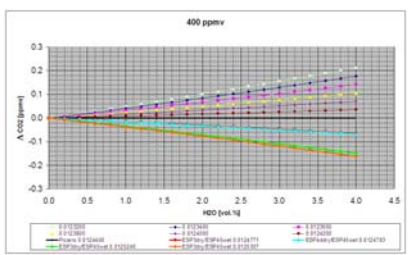


Fig.8 Difference between the Picarro-corrected CO_2 value and the value obtained by a correction function determined empirically by measuring the same sample with two Picarro analyzers - one equipped with a cryocooler ("dry") and the other without sample drying ("wet"). The above example is for sample air that has 400ppm CO_{2raw} and varying H_2O concentrations.

Although the H_2O measurement appears stable (Fig. 3), the absolute value was observed to change (although not significantly) after restarting the analyzer. The absence of a reliable H_2O calibration and longer transition/purge times due to surface effects etc., speak for the continuation of sample drying for long-term high-precision measurements. In this context, we also suggest that the H_2O correction function for very low concentrations should be validated.

Table 3 Error (in ppm) induced by the water vapour content on the CO_2 measurement

CO_2	Water vapour content (%v)			
	2 %	1 %	0.1 %	0.01 %
350 ppm	- 8.7	- 4.4	- 0.4	- 0.04
450 ppm	- 11	- 5.5	- 0.6	- 0.06

(from Wastine et al. 2009)

REFERENCES
Wastine et al. (2009) Evaluation of the EnviroSense 3000i analysers for continuous CO_2/CH_4 measurements by CRDS. *ICOS Report No. 1.*

LAMTO station (Ivory Coast), panoramic view from the tower - © M. Ramonet 2008