

Evaluation of the Picarro G1301 and deployment at three Irish sites

B. Wastine^{1,2}, C. Kaiser¹, C. Vuillemin¹, J. V. Lavrič¹, M. Schmidt¹, M. Ramonet¹, F. McGovern², P. O'Brien^{2,4}, D. Dodd², S. O'Doherty³, G. Spain⁴

¹: LSCE/IPSL, CEA-CNRS-UVSQ, Gif sur Yvette, France
²: Environmental Protection Agency, Clonskeagh Road, Dublin 14, Ireland
³: School of Chemistry, University of Bristol, Bristol, UK
⁴: National University Galway, Ireland

1. Introduction

ICOS (Integrated Carbon Observing System) aims to create a European network of standardized measurement stations for greenhouse gases. Several characteristics of the cavity ring-down spectroscopy (CRDS) make it attractive for a deployment in such a monitoring network: combined measurements of several trace gases, high sensitivity and good linearity, field deployable and low maintenance. In 2008, the ICOS Instrumentation group, within the LSCE RAMCES team, tested the EnviroSense CRDS analyser (now called G1301), marketed by PICARRO Inc. and designed for continuous measurement of CO₂, CH₄ and H₂O. In the frame of its participation in ICOS, the Irish Environmental Protection Agency (EPA) is on the way to develop the Irish greenhouse gas monitoring network. Following the RAMCES group's recommendations, EPA decided to install three PICARRO G1301 analysers in Mace Head (West coast), Carnsore Point (South-East coast) and in Malin Head (North coast).

2. Evaluation at LSCE

> **Precision:** 0.02 ppm CO₂ and 0.1 ppb CH₄ for one minute averaged measurements (measurement of one calibration gas during 19 hours)

> **Repeatability** (fig. 1): estimated to 0.01 ppm for CO₂ and 0.04 ppb for CH₄ (measurement of a calibration gas every 7 hours for 40 minutes over a three day period).

> **No significant drift** observed in a two month period when measuring regularly a set of four calibration gases over a 350-450 ppm range in CO₂ and a 1750-2150 ppb range in CH₄. One calibration per month seems to be a reasonable recommendation for high-quality atmospheric measurements.

> **No significant effect of varying flow rate** on the measurements. However, a sufficient flow rate (at least 100 ml/min) is required when using a multi-position valve to ensure a reasonable stabilisation time after valve switching (less than 10 minutes).

> **Low sensitivity of the analysis to the ambient temperature** (fig. 2).

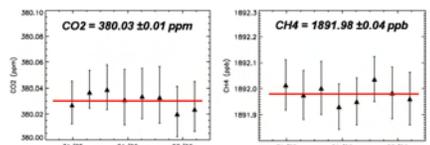


Fig. 1: CO₂ and CH₄ averaged concentrations (30 minutes) measured for one calibration cylinder.

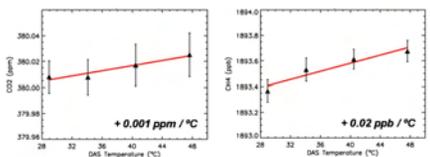


Fig. 2: CO₂ and CH₄ concentrations measured for one calibration gas at different temperatures.

> **Water vapour correction:**

The presence of water vapour in the sample generates an underestimation of the CO₂ and CH₄ concentrations due to dilution and spectral line broadening effects. To take into account this influence, PICARRO has established an empirical correction for the CO₂ measurement. By comparing wet and dry ambient air measurements with two EnviroSense analysers (ESP2 and ESP3), we showed that this correction was efficient (mean difference of 0.04 ± 0.23 ppm between the wet and dry measurements). PICARRO has not developed a water correction for CH₄. However, we showed that the CH₄ measurements can be water corrected in a similar way than the CO₂ measurements (fig. 3 and 4a,b).

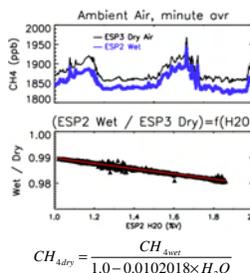
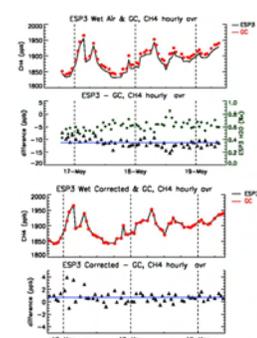


Fig. 3 (left): water correction function established for the CH₄ measurements by measuring the same ambient air with two EnviroSense analysers (ESP2 and ESP3). For one instrument (ESP3) the air was previously dried using a cryocooler.

Fig. 4a,b (right): atmospheric CH₄ concentrations measured by the EnviroSense (ESP3) and the GC (HP 6890) at LSCE. Measurements on the ESP3 instrument were performed with non-dried air whereas the GC system used a cryocooler. Without applying the water correction to the ESP3 (4a), the mean difference between the Picarro and the GC was about -1.1 ± 1.8 ppb. By applying our empirical correction function (4b), the mean difference is reduced to 0.8 ± 0.9 ppb.



3. Deployment in Ireland



Malin Head:
55°22' N, 07°20' W, 22m asl
Start: Oct. 09



Carnsore Point:
52°11' N, 06°22' W, 9m asl
Start: Oct. 09



Fig. 5: location of the three CO₂ and CH₄ monitoring sites.

EPA is funding a greenhouse measurement network in Ireland following the ICOS recommendations in terms of instrumentation, metrology and data management. Three sites have been chosen: Malin Head, Mace Head and Carnsore Point. These sites were previously established as EMEP (European Monitoring and Evaluation Programme) monitoring stations and are equipped for remote access. They are located in coastal areas with limited local influence. The sites have been chosen to optimize the GHG flux's calculation over Ireland by inversion modelling.

Set-up at Mace Head:

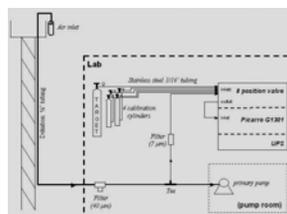


Fig. 6: schematic analytical set up at Mace Head.

The first instrument package was installed at Mace Head in May 2009. The air inlet is located at the top of a 25 meter mast. A KNF N86KT.18 primary pump flushes the Dekabon 1/2" inlet tubing at 2-3 L/min. The main flow is split using a tee allowing the internal pump of the G1301 to suck the air into the optical cavity. A combination of Swagelok filters are used to prevent dust and particles. The G1301 is coupled to a 8 position Valco valve. In addition to the ambient air line, four calibration cylinders (10L) and one Target cylinder (40L) are connected to the valve. They have been filled by Steininger (Germany) and calibrated for CO₂ and CH₄ at LSCE against the WMO x2002 scale. We use Scott Specialty Gases 14M-14C pressure regulators with the high pressure cylinders.

4. First results at Mace Head

Calibration strategy and Quality Control:

We calibrate the analyser every 10 days and measure the TARGET cylinder every 7 hours for 30 minutes. Our calibration scale ranges from 340 to 460 ppm CO₂ and from 1700 to 2150 ppb CH₄. A calibration sequence consists of repeated measurement (5 times) of each standard for 30 minutes. The results obtained in a three month period (Fig. 7) show that the measured CO₂ concentrations are drifting randomly with time whereas the measured CH₄ concentrations are increasing. This was not observed during the tests done at LSCE. The corrected measurements of the TARGET cylinder indicate a good repeatability in CO₂ and CH₄ (Fig. 8).

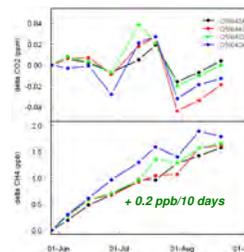


Fig. 7 (left): drift in CO₂ and CH₄ concentrations as measured for the four calibration cylinders since late May 2009.

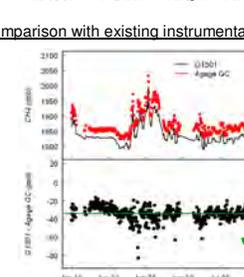


Fig. 8 (right): corrected mean CO₂ and CH₄ concentrations (final 10 minutes of 30-minute analysis periods) and associated error bar (1 σ) for the TARGET cylinder.

Comparison with existing instrumentation:

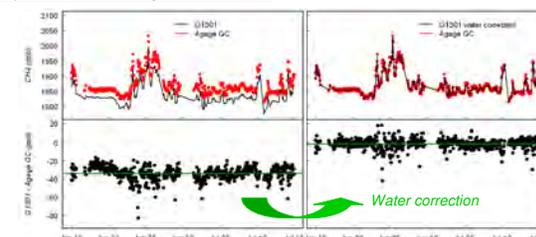


Fig. 9a,b: atmospheric CH₄ concentrations measured by the AGAGE GC and by the G1301, without (9a) and with water correction applied (9b). By applying the water correction established at LSCE in 2008 to the G1301 measurements, the mean difference between the 2 instruments is reduced from -34 ± 7 ppb to -2 ± 6 ppb.

The Advanced Global Atmospheric Gases Experiment (AGAGE) has been conducted at Mace Head since 1987 in collaboration with the School of Chemistry, University of Bristol. AGAGE monitors the important gases in the Montreal Protocol (CFCs and HCFCs) and the significant non-CO₂ gases in the Kyoto Protocol, including methane. The AGAGE methane measurement is made in dried air using a Carle AGX-211 gas chromatograph equipped with a FID. The CH₄ concentrations are referenced to a gravimetrically prepared, CH₄-in-air, calibration scale developed at Tohoku University, Sendai, Japan, in collaboration with the Nippon Sanso company. We measured the calibration cylinders of the G1301 on the AGAGE GC and we converted the CH₄ concentrations measured by the G1301 into the AGAGE scale. Then, we compared the 2 instruments over a 1 month period (Fig. 9a,b).