Document title : Water correction assessment test procedure

Document History:

Date	Version	Revision	Authors	Comments
28/01/2013	1	0	Benoit Wastine	Creation
23/10/2014	1	1	Ali Guemri	update
27/05/2015	1	2	Olivier Laurent	update
03/03/2016	1	3	Olivier Laurent	correction

Diffusion :

☐ ATC internal ☒ ICOS Community ☐ Public

Repository :

1. ATC Document Management System:

   Directory "\ramces\ramces_data\metro\DOCUMENTATION ICOS\ATC - Network Support (NS)/ ATC-NS-IN-PR-002 (Water Correction Assesment test procedure)_v1.2.docx"

2. ICOS Document Management System :

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Summary

1. Introduction

The GHG measurements are typically performed on dry samples. Indeed, GHG mole fractions are only meaningful when extrapolated back to dry-gas conditions. First, the high variability of water vapour in the atmosphere masks via the dilution effect the generally less variable concentrations of species of interest. Second, many traditional techniques suffer from significant uncorrected interference from water vapour.

In recent years, a new class of greenhouse gas analyzers capable of highly stable and precise measurements of GHG including water vapour has been commercialized. This precise water vapour measurement now allows post correction of the GHG mole fractions measured on wet gas streams based on formula precisely described elsewhere (Rella et al for Picarro analyzer). This document details a procedure to experimentally derive the water correction formula. The method described here, so called “water droplet method”, basically consists of humidifying a dry gas stream by adding a droplet of water in the sample line.

This procedure specifically relates to Picarro CO2/CH4/H2O instruments (G1301/G2301 series) but could be adapted to any other GHG instrument which measures precisely enough water vapour levels.

2. Recommendations

The procedure described here takes about 4-6 hours.

3. Material and Consumables

We recommend using the following parts to perform the water droplet experiment:

- 1 high pressure cylinder filled with dry air at the **site typical background mole fraction** of the different species measured (eg. Short term target gas used in ICOS)
- 1 pressure regulator which fits to the high pressure cylinder
- 1 syringe (<2 ml)
- Milli-Q filtered or deionized water. Avoid tap water.
- 1/16” Stainless Steel tubing or Synflex ¼”’ tubing
- Swagelok fittings
- Optional: 1 flow meter (eg. type ADM1000 from Agilent)

4. Procedure Description

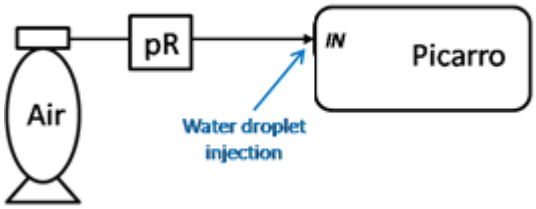


Figure 1: Schematic of the experimental setup (pR: pressure regulator)

4.1 Measure the high pressure cylinder without filter

We recommend a simple setup consisting in connecting the cylinder directly to Picarro inlet without any filter upstream the analyzer by using a 1/16" stainless steel tubing or Synflex ¼" tubing. Delivery pressure from the pressure regulator must be <0.2 bar to provide enough flow to the instrument (typically 200 ml/min). In case of a substantial pressure drop (eg. 1/16" tubing longer than 3m) the pressure delivered by the pressure regulator must be higher.
The cylinder must be measured first during at least 1 hour to 1 hour 30 minutes in order to ensure a proper flush and stabilization (typically raw data standard deviation of 0.02 ppm CO2 and 0.2 ppb CH4 over 5 minutes)

4.2 Injection of water droplet at the analyzer inlet

In order to inject a water droplet at the analyzer inlet, proceed as follow:

- Fill a syringe with **0.2 ml** of pure water filtered and deionized (*figure 2*). The easiest way to reach the targeted volume (ie. 0.2 ml) is to fill first a larger volume of water and then throw the excess out.
- Once, the syringe is filled with 0.2ml of water, draw air into the syringe as illustrated on *figure 3*. This will allow you a better injection into the instrument by spraying the droplet.

*Figure 2: Syringe filled with **0.2ml** of deionized water*

*Figure 3: Syringe filled with 0.2ml of deionized water **and air**. **Ready for injection***

- For a Picarro, disconnect the tubing (here Synflex) from the analyser inlet, inject the water inside the analyser inlet and reconnect the tubing to the inlet (figure 4). Act as quickly as possible.
  For other instrument, in case the GHG analyser is not equipped with an adequate internal filter to protect its measurement cell, the droplet injection must be done on an external filter installed at the instrument inlet. The filter might be heated (to 30-40°C) to allow higher water vapour content and faster evaporation.

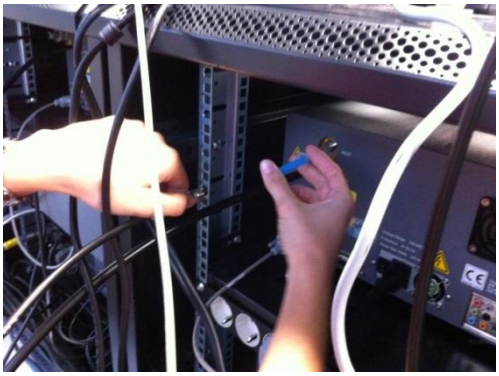
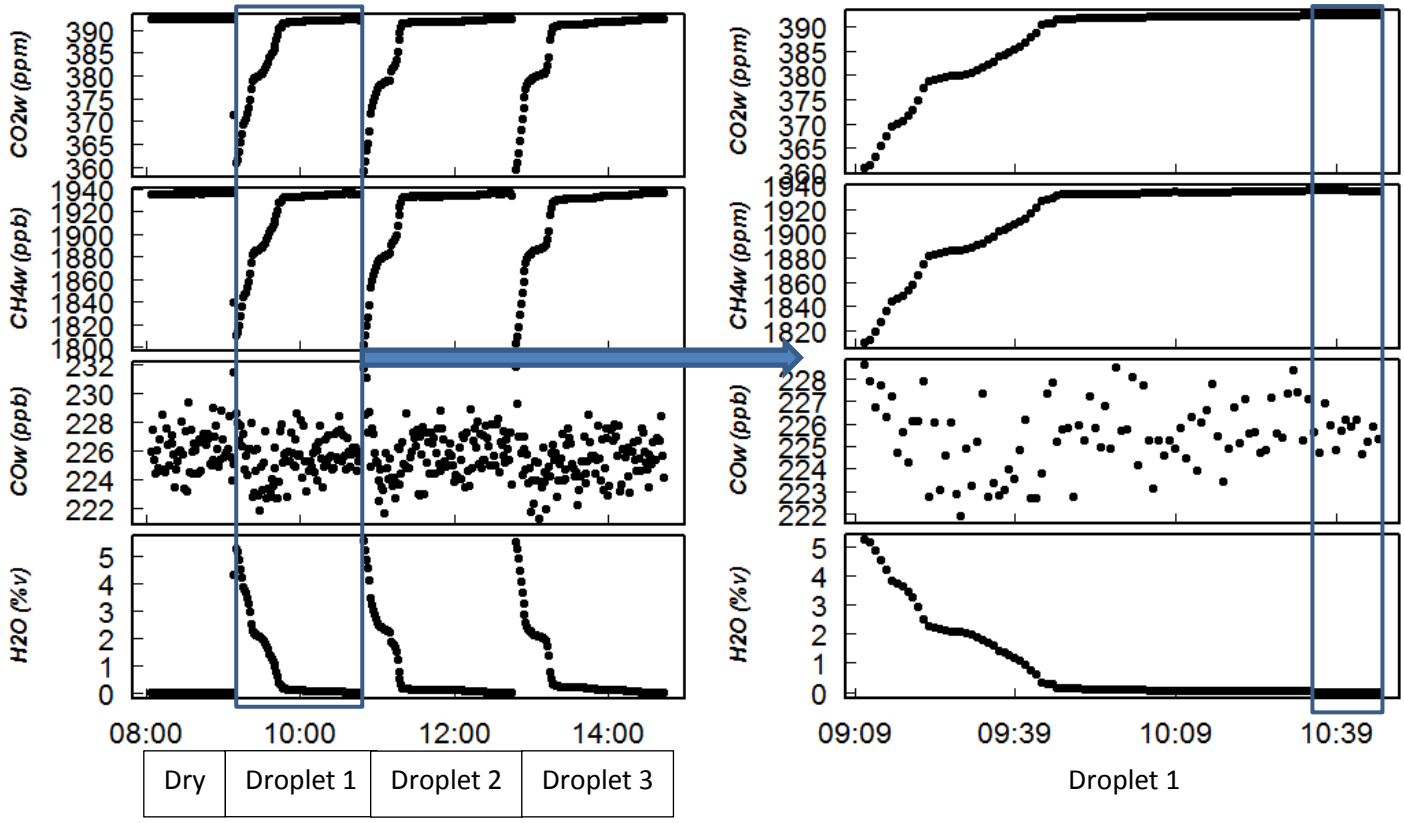
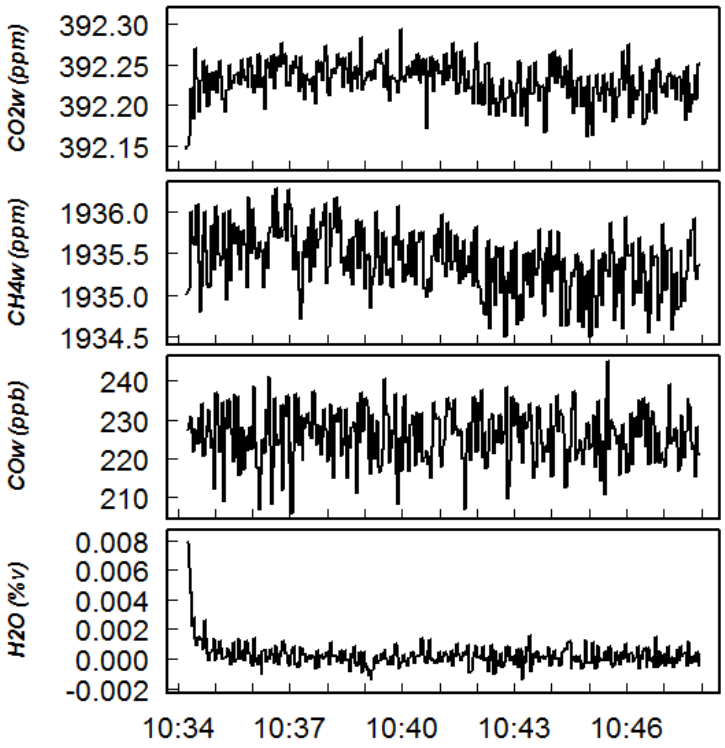


Figure 4: View of the experimental setup- The water droplet is injected at the instrument inlet using a syringe.

- Wait for the **total evaporation** of the droplet (around 1h30). The humidification of the gas stream typically goes up 6 %v depending to the analyser internal temperature (reported as DAS temperature on a Picarro). Allow a minimum of **10 minutes** flushing once the droplet has completely evaporated (**H2O value < 0.005 %v**) to get stable "dry" measurement periods between each injection.

Repeat the procedure at least 3 times.





End of droplet evaporation:

H2O < 0.002% during at least 10 minutes

Figure 5: CO2, CH4 and H2O concentrations as reported by the instrument while the water droplet is being evaporated.

4.3 Data processing

To derive the water correction coefficients, we look at the ratio $\frac{C_{wet}}{C_{dry}}$ over the H2O covered range. We call C_{wet}, the CO2 or CH4 concentrations reported by the instrument during the evaporation of the droplet and without any water correction applied. We call C_{dry}, the CO2 or CH4 concentration reported by the instrument without humidification of the dry gas stream, and without any water correction applied.

Figure 6 illustrates the CO2, CH4 and H2O reported values during an experiment where 3 droplets were injected. We can observe CO2 and CH4 spikes that correspond to the time when the sample line was disconnected at the filter inlet in order to inject the droplet. We usually discard the 1 to 2 minute period following the droplet injection the data points for stabilization time.

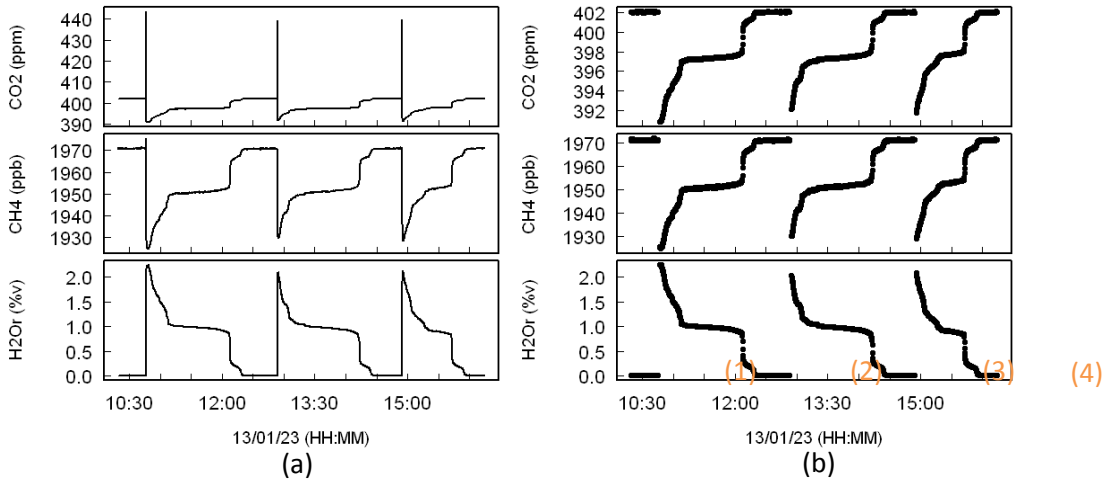
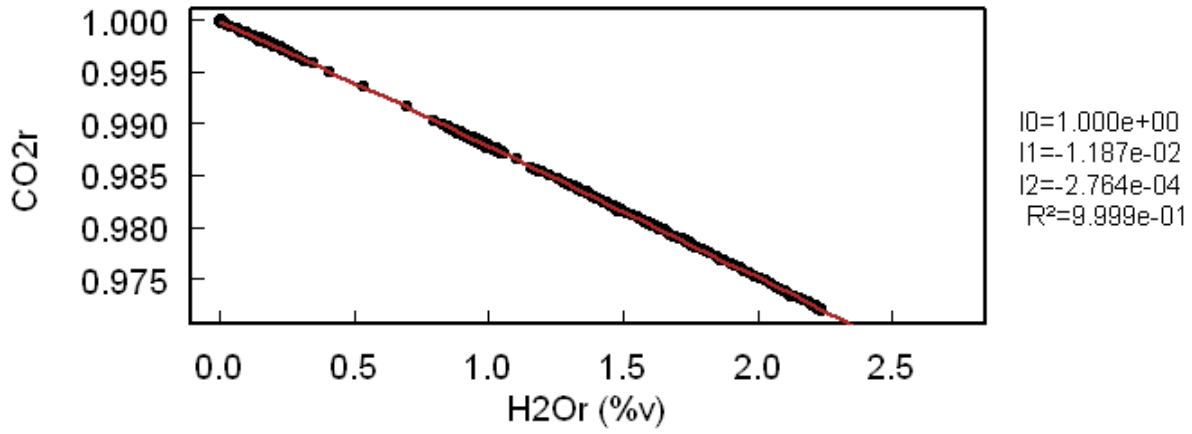


Figure 6 : a) CO2, CH4 and H2O concentrations as reported by the instrument during the whole experiment when 3 droplets have been injected. b) with the transient points removed

The Cdry value considering the first measurement period where target after reaching stability (from 45 minutes to 1 hour when the H2O level is below 0.004% by volume).

Three injections of water droplets are collected in a single data set, and we plot the ratio $\frac{C_{wet}}{C_{dry}}$ depending on the water vapor level and we get the water correction coefficients from a quadratic form, as shown in Figure 6:

$$\frac{Cwet}{Cdry} = 1 + I1 \times H2Or + I2 \times H2Or^2$$



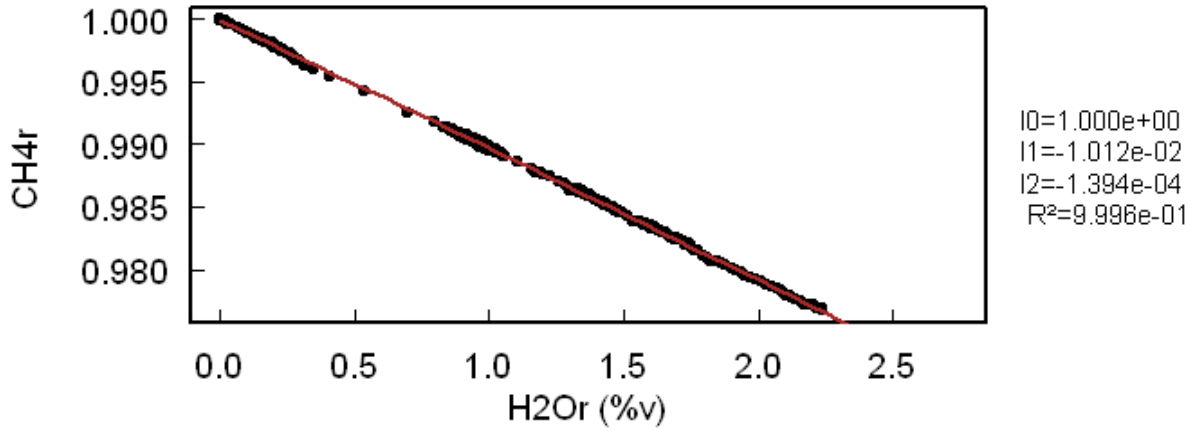


Figure 2a,b: $\frac{C_{wet}}{C_{dry}}$ ratios plotted as function of water vapour level for CO2 (a) and CH4 (b) corresponding to one water droplet injection experiment

5. References

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