In-situ CO measurements at Izaña global GAW station: GC-RGA system, data processing, and 2008-2011 time series

A.J. Gomez-Pelaez¹, R. Ramos¹, V. Gomez-Trueba¹,², Y. Gonzalez¹,³, R. Campo-Hernandez¹, and P. Novelli⁴

¹ Izaña Atmospheric Research Center, Meteorological State Agency of Spain (AEMET)
² Air Liquide Canarias
³ SIELTEC Canarias S.L.
⁴ NOAA-ERSL-GMD

16th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases, and Related Measurement Techniques (Wellington, New Zealand, October 25-28, 2011)
Scheme of this talk:

1) Izaña station
2) System configuration
3) Response function, calibrations, and processing
4) CO time series analysis
5) Estimation of standard uncertainty
6) Flasks-Continuous comparison, uncertainty, and weighted means

This work intended to be a peer review paper for the AMT GGMT special issue
Izaña Atmospheric Observatory:

- Global GAW Station,
- NDACC Station, ...
Measurement system scheme:

GC-RGA3 (Reduction Gas Analyzer)

Sampling/selection system scheme:
Modified internal configuration of the GC-RGA3:

- **Two-positions ten-ports injection valve** (positions: load/backflush, inject). Loop size: 1 ml
- **Two chromatographic columns** (pre-column (1): Unibeads 1S 60/80; main column (2): Molesieve 5A 60/80)
- **Carrier gas**: synthetic air (traps: Sofnocat and Molesieve)
- **Temperatures.** RGA: 265 ºC. Columns oven: 105 ºC

**Carrier flows:**

- **Load/Backflush position.** Backflush: 11.1 ml/min. Direct: 21.7 ml/min
- **Inject position:** 19.9 ml/min
Ambient air injection sequence:
20 minutes cycle with two 10 minutes subcycles.

- First: working gas
- Second: ambient air

*Sample loop flushing with ambient air has a larger flow rate than for the standards (working or Lab) and starts 5 minutes before.

Time sequence for the 10 minutes subcycle (valid calibrations and ambient air mode):

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Label</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>00:00</td>
<td>a</td>
<td>Start of sample loop flushing (100 ml/min)*. Electronic zero.</td>
</tr>
<tr>
<td>01:30</td>
<td>b</td>
<td>Start of chromatogram adquisition</td>
</tr>
<tr>
<td>01:55</td>
<td>c</td>
<td>End of sample loop flushing. Start of pressure equilibration.</td>
</tr>
<tr>
<td>02:00</td>
<td>d</td>
<td>Injection valve goes from “Load” to “Inject”</td>
</tr>
<tr>
<td>02:30</td>
<td>e</td>
<td>Injection valve goes from “Inject” to “Load”</td>
</tr>
</tbody>
</table>
Response function and calibrations:

Exponent \( b \) and working gas mixing ratio \( r_{wt} \) are obtained in the calibrations, which are carried out every 2 weeks, using between 3 and 5 WMO standard gases (5 levels since March 2009)

- **Lifetime of a work tank**: between 3 and 5 months
- **Calibration scheme** since March 2009. 5 cycles. Cycle: wt-s1-s2-wt-st3-st4-st5
- We have created a Fortran 90 code to process calibrations (with this and other types of cycles used in the past)
- \( h/h_{wt} \) is computed interpolating the heights of bracketing wt injections
- It is possible to discard single outlayer injections
- Mean \( h/h_{wt} \) and sample standard deviation are computed for each standard level
- **Coefficients. Least-squares fitting to the function** \( \ln r = \ln r_{wt} + b \ln \left( h/h_{wt} \right) \)
- The **Root Mean Square (RMS) of the residuals** is computed as:

\[
RMS = \sqrt{\frac{\sum_{i} \left( r_i - R(h_i / h_{wt}) \right)^2}{n-2}}
\]

where \( n \) is the number of standard levels, and \( R(h/h_{wt}) \) is the response function
The time dependent GC-RGA response function, for the working gas in use, is computed from the response functions determined in its calibrations:

- \( b \) is computed as the mean of the calibration values

- A linear drift in time is allowed for \( r_{\text{wt}} \) (Snedecor’s F tests are used, as described by Gomez-Pelaez & Ramos 2011).
Once the time dependent GC-RGA response function is known, ambient data processing can be done with a Fortran 90 code.

Discarding of outliers is done in a similar way as in Gomez-Pelaez et al. (2006) for CH4:

- firstly for the $h_{wt}/r_{wt}$ time series (with thresholds $5\sigma, 4\sigma, 3.5\sigma$ from the running means of 7, 2, and 0.19 days, respectively)

- then for the ambient air mole fraction series (with thresholds $4.5\sigma, 4\sigma, 3.5\sigma$ from the running means of 30, 3, and 0.26 days, respectively)
CO time series analysis:

Daily night mean CO fitting:
Interannual trend (2\textsuperscript{nd} order polynomium) + Annual cycle (4 Fourier harmonics)

- 3.5 years of data: harmonics are not needed for the interannual trend
- Assumption: the same annual cycle for all the years
Estimating "internal" standard uncertainty:

Response function: \( r = r_{wt} \left( \frac{h}{h_{wt}} \right)^b \), internal standard uncertainty:

\[
\sqrt{(RMS)^2 + \left( \frac{r}{r_{wt}} \sigma_{r_{wt}} \right)^2 + \left( b \cdot r \frac{h_{wt}}{h} \frac{\sigma_{h/h_{wt}}}{\sqrt{3}} \right)^2 + \left( r \ln \frac{h}{h_{wt}} \sigma_b \right)^2}
\]

(1) Consistency between the laboratory standards and the response function (\( RMS \))
(2) Consistency of the work gas mole fraction along its lifetime (\( \text{ConsisWT} \))
(3) Repeatability of relative height for hourly means (\( \text{Repeat}_h\text{rel} \))
(4) Uncertainty in the exponent (\( \text{UncerExp} \))
Typical values of the uncertainty components and combined uncertainty:

<table>
<thead>
<tr>
<th></th>
<th>RMS</th>
<th>ConsisWT</th>
<th>Repeat_hrel</th>
<th>UncerExp</th>
<th>Combined</th>
</tr>
</thead>
<tbody>
<tr>
<td>2008</td>
<td>0.8</td>
<td>0.92</td>
<td>0.27</td>
<td>0.53</td>
<td>1.41</td>
</tr>
<tr>
<td>2009-2011</td>
<td>1.1</td>
<td>0.56</td>
<td>0.25</td>
<td>0.09</td>
<td>1.27</td>
</tr>
</tbody>
</table>

These are estimated typical values. Indeed, the combined uncertainty and its components can be estimated for each ambient air injection, so having a time series for each uncertainty component.
Continuous in-situ hourly means versus NOAA weekly flasks:

Fortran90 code to compare in-situ continuous hourly means with NOAA flasks. The comparison has the following novel characteristics:

1. Flasks only are accepted if have flags “...” or “..P”, and both members of the pair are present. 

\[ r_{f1}, r_{f2} \Rightarrow r_f, \sigma_f = \left| r_{f2} - r_{f1} \right| / \sqrt{2} \]

2. Each pair is compared with the hourly mean \((r_c)\) simultaneous in time (the hourly mean time interval must contain the time of the pair sampling).

\[ \text{dif} = r_f - r_c, \quad \sigma_{\text{dif}} = \sqrt{\sigma_f^2 + \sigma_c^2} \]

“internal” standard uncertainty of the difference
3. Global and annual difference means and standard deviations are computed using 3 types of means (and standard deviations):

- **Mean** is the conventional mean.

- **FWMean** is a “full” weighted mean computed following the minimum variance method (maximum likelihood for Gaussian distributions).

\[
\langle \text{dif} \rangle_{FW} = \left( \frac{\sigma_{\text{inv}}^2}{n} \right) \sum_{i=1}^{n} \frac{\text{dif}_i}{\sigma_{\text{dif}_i}^2} \quad \text{with} \quad n/\sigma_{\text{inv}}^2 = \sum_{i=1}^{n} 1/\sigma_{\text{dif}_i}^2
\]

- **WMean** is an “intermediate” weighted mean. The same equations apply but \(\sigma_{\text{dif}_i}\) is replaced by the median of \(\sigma_{\text{dif}}\) for those \(\sigma_{\text{dif}_i}\) smaller that the median of \(\sigma_{\text{dif}}\)

The basic idea: differences with a larger uncertainty provide information of a lower quality to compute de mean.

Means and their standard deviations have the following values:

<table>
<thead>
<tr>
<th></th>
<th>Est. dev.</th>
<th></th>
<th>Est. dev.</th>
<th></th>
<th>Est. dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>0.82</td>
<td>WMean</td>
<td>0.65</td>
<td>2.81</td>
<td>0.64</td>
</tr>
<tr>
<td></td>
<td>5.36</td>
<td></td>
<td></td>
<td></td>
<td>2.46</td>
</tr>
</tbody>
</table>
CO comparison results for 2009-2011 are much better than those for 2008.
Which are the differences with NOAA’s software for flasks-continuous comparison:

- More accurate time correspondence (so, do not rely on time persistence)

Flasks within this period are compared by NOAA with the hm hh:30

Flasks within this period are compared by us with the hm hh:30

Time period of the hourly mean (hm) hh:30

- Rejection of flasks with flags: “.X.” and “.XP”. Non-background conditions means larger internal variability and larger uncertainty.

- For CO2 at Izaña, we get smaller departures from zero of the annual conventional means (because the differences have smaller random and systematic “noise”)

- The uncertainty of the differences is computed

- Weighted means based on uncertainty are used
Thank you for your attention!