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Improvements in the Carbon Dioxide and Methane Continuous Measurement Programs at Izaña Global GAW Station (Spain) during 2007-2009

A.J. Gomez-Pelaez, R. Ramos,
Izaña Atmospheric Research Center, Meteorological State Agency of Spain (AEMET)

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Abstract

Continuous in-situ measurements of atmospheric CO_2 and CH_4 have been carried out at Izaña Global GAW station (Tenerife, Spain) since 1984. In the present report, we briefly summarize some improvements done in those programs during 2007-2009. Firstly, we deal with the CO_2 program. In January 2007, we installed a new NDIR analyzer (Li-7000), which became our main CO_2 analyzer. The instrumental system is briefly described, additionally to the acquisition/control software and raw data processing numerical code, which have been developed by us. Some details are provided about the processes used to transfer the WMO scale to the atmospheric CO_2 measurements, together with the instrumental response function used, its determination and uncertainty. We perform an uncertainty propagation analysis, *obtaining a standard uncertainty of 0.035 ppm for the consistency of our atmospheric CO_2 measurements with the WMO-X2005 CO_2 scale*. Secondly, the CH_4 program is considered. The new numerical codes developed by us to integrate peak area and to process calibrations are very briefly described. Finally, our intercomparison activities are mentioned.

Instrumental system and acquisition/control software for CO_2 measurements

In January 2007, we installed a new CO_2 measurement system based on a Li-Cor 7000 NDIR analyzer, to substitute our old Siemens Ultramat-3, which had been working from 1984 to 2006 (see Gomez-Pelaez et all, 2006, and references therein) and broke down in January 2007. In April 2008, we installed an additional NDIR analyzer (Li-Cor 6252) working in series with the main NDIR analyzer, in order to have duplicated measurements (we plan for the future to separate them in two fully independent measurement systems).

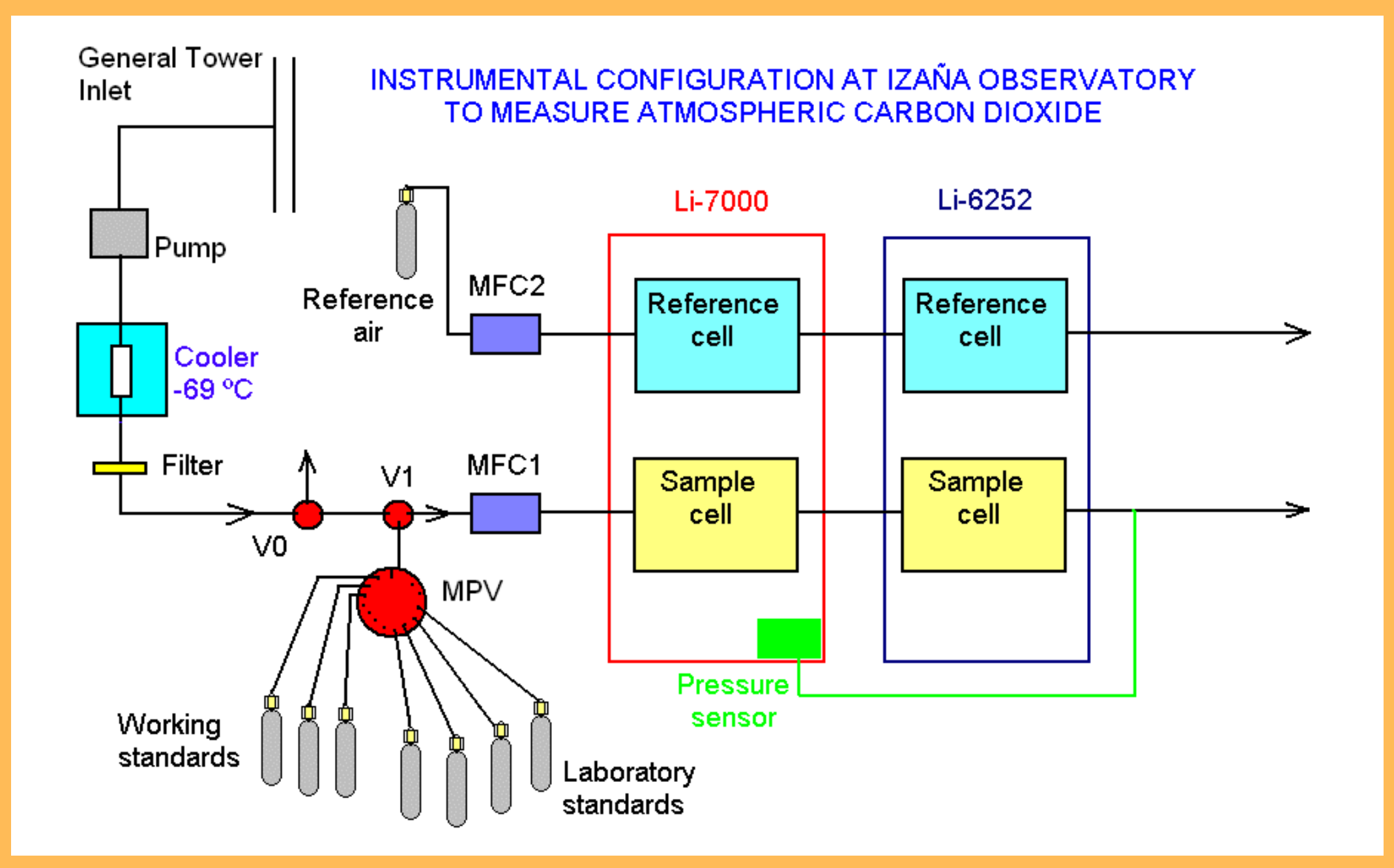

Figure 1. Instrumental configuration at Izaña Observatory to measure atmospheric CO2 with two NDIR analyzers working in series.

Figure 1 shows the instrumental configuration. The general ambient air inlet, which is situated on top of the building tower (30 m height) and provides ambient air for all instruments that analyze it, is an 8 cm I.D. stainless steel pipe and has a high flow rate. A tube branches from the general air pipe toward a pump that provides dried ambient air (frost point of -69ºC) to the NDIR analyzers. MPV is a Valco multiposition valve with 1 outlet and 16 inlets connected to the working and laboratory standards. Valves V0 and V1 are 3-port-2-position valves. Both are commuted simultaneously, in such a way that, in the first position ambient air flows through both valves and MFC1, whereas in the second position gas coming from the MPV flows through MFC1 while ambient air is vented to the laboratory. MFC1 and MFC2 are mass flow controllers, which are regulated to 7.4% of 3.000 mln/min and 25% of 30 mln/min, respectively (n denotes normal conditions: 0ºC and 1 atm). There are 3 m of PTFE tube at the outlets of the Li-6252 cells to prevent any diffusion from the laboratory. The pressure sensor of the Li-7000 measures pressure inside the tube located downstream of the Li-6252 sample cell.

We do not rely on the internally processed signal of the NDIR analysers, but only on the raw data measured by the IR detectors (number of counts). Before using those analyzers for operative ambient air measurements, we carried out some tests to set the best configuration for our purposes. We discovered the following two important facts. We set for Li-7000 the “Reference Estimation Mode” (REM), because in this mode AGC (Automatic Gain Control) is kept constant, and noise is much smaller. We set for Li-7000 and Li-6252 an internal signal averaging of 1 second for data output. We verified that raw channels are averaged (in apparent contradiction with the Li-7000 instruction manual, which seems to indicate that only derived channels are averaged).

Using software developed at our center, raw data are acquired at 1 Hz rate using RS-232 ports and stored in daily files. Also one time per day, the acquisition software sends configuration instructions to the analyzer, and stores the replies of the analyzer in another file. For the Li-7000, the following channels are acquired: raw data from the 4 IR detectors (2 detectors per cell, centred in CO_2 and H_20 absorption bands), cells temperature, pressure (detailed in a previous paragraph), diagnostic variable, relative humidity inside the detectors housing, and an external channel (laboratory temperature was acquired during 2007). For the Li-6252, only two channels are acquired: difference between the signals generated by the detector when it sees the sample and reference cells, and cells temperature. The control software (developed at our center) makes the valves V0, V1, and MPV follow a given time sequence.

CH_4 program novelties

Our main system to measure CH_4 is based on a DANI 3800 GC-FID in operation since 1984, whose description can be seen in Gomez-Pelaez et all 2006. Since 2005, some minor changes have been introduced in the system:

- the time for sample loop pressure equilibration before injection has been increased to 15 seconds;
- a system of pump, 3-port-2-position valve with vent to laboratory, cooler, and Valco multiposition valve, similar to that described in Figure 1 of Gomez-Pelaez&Ramos 2009 has been implemented;
- the air drier for the DANI GC-FID and for the Varian GC-ECD has been replaced by another one working at -70ºC;
- an additional acquisition system was installed in January 2006, based on a Varian 16 bits ADC board, working at 40 Hz in the range 0-1 V, in combination with Varian Star software, having two different acquisition systems working simultaneously since then;
- calibrations (alternative injections of working standard and laboratory standard) are performed with 12 cycles (at least), instead of 7 cycles.

We have developed new software in FORTRAN 90 to process calibrations. The main conceptual novelty concerns the discarding of outlier injections. Since sample loop temperature and pressure are not kept constant, there is a small drift in the instrumental response. To identify outliers, we fit to the sequence of working standard (laboratory standard) CH_4 peak areas a quadratic polynomial in time, being the residuals the parameter used to identify and discard clear outliers.

We have developed in FORTRAN 90 a numerical code to integrate the area of the CH_4 chromatographic peak. The chromatograms obtained with the new acquisition system are transformed to ASCII format (40 points per second). A Savitzky-Golay filter of order 2 and width 199 is used to smooth noise without changing peak shape (e.g. see Dyson, and/or Press et all). Then, the start and end of the CH_4 peak are identify, baseline is placed, and area integration is performed (it is out of the scope of the present report to describe in detail the numerical schemes used). Processing the calibrations of the last three years using the peak areas obtained with both integrators (the old and new ones), we get a smaller standard deviation and a better time consistency for working standards with the new integrator.

Intercomparison activities

- We have collected flask samples for NOAA-ESRL-GMD-CCGG since November 1991. Therefore, we can intercompare our CO_2, CH_4, N_2O, SF_6, and CO continuous in-situ measurements with collocated NOAA flask measurements. In particular, we participate in the Carbon Cycle Measurement Community InterComParison (ICP) experiment lead by NOAA-ESRL, however, we are still not able to process and interchange data automatically.

- Additionally, as Global GAW station, periodic scientific audits are performed at Izaña Observatory by WMO World Calibration Centres (e.g. WCC for Surface O_3, CO and CH_4 ; and WCC for N_2O), and in particular “blind” measurements of travelling standards are performed.

- Izaña is participating in the WMO2009 Intercomparison. Unfortunately, we have not participated in all the previous CO_2 round-robins.

Transfer of CO_2 WMO scale, instrumental response function, data processing, and uncertainty

Our laboratory standards have been purchased from WMO GAW CO_2 CCL (NOAA), and they maintain the link with the WMO CO2 scale through intercomparisons with newly purchased laboratory standards (till present) or through periodic recalibration of them by the CO_2 CCL (in the future). Currently, we are using the WMO-X2005 CO_2 scale. Working standards and the reference tank are filled at Izaña Observatory with dried natural air (3 ppm of H_2O typically) using a filling system similar to NOAA-ESRL-GMD-CCGG´s system (see Kitzis & Zhao). Along their lifetime, working standards are calibrated every 2 weeks against a set of 4 laboratory standards. Measuring with the analyzers 3 working standards from minute 30 to minute 39 (during 3 minutes each one) every hour, we get the information necessary to determine accurately the response function of each analyzer. Since our main instrument is Li-7000, all what follows in this section concerns the analyzer Li-7000.

The processing (described in the following paragraphs) from raw data to obtain CO_2 mixing ratios taking into account the hierarchy of calibrations is done using FORTRAN 90 numerical codes programmed by us.

Firstly, we pre-process raw data, which means computing 30 (or 45) seconds means and standard deviations of the 9 channels (acquired at 1 Hz) and of previously computed 1 Hz raw data $\Delta cw = crw - csw$, where *crw* and *csw* are counts of the CO_2 band IR detector of the reference and the sample cells, respectively. To denote such means for Δcw we will use ***V***.

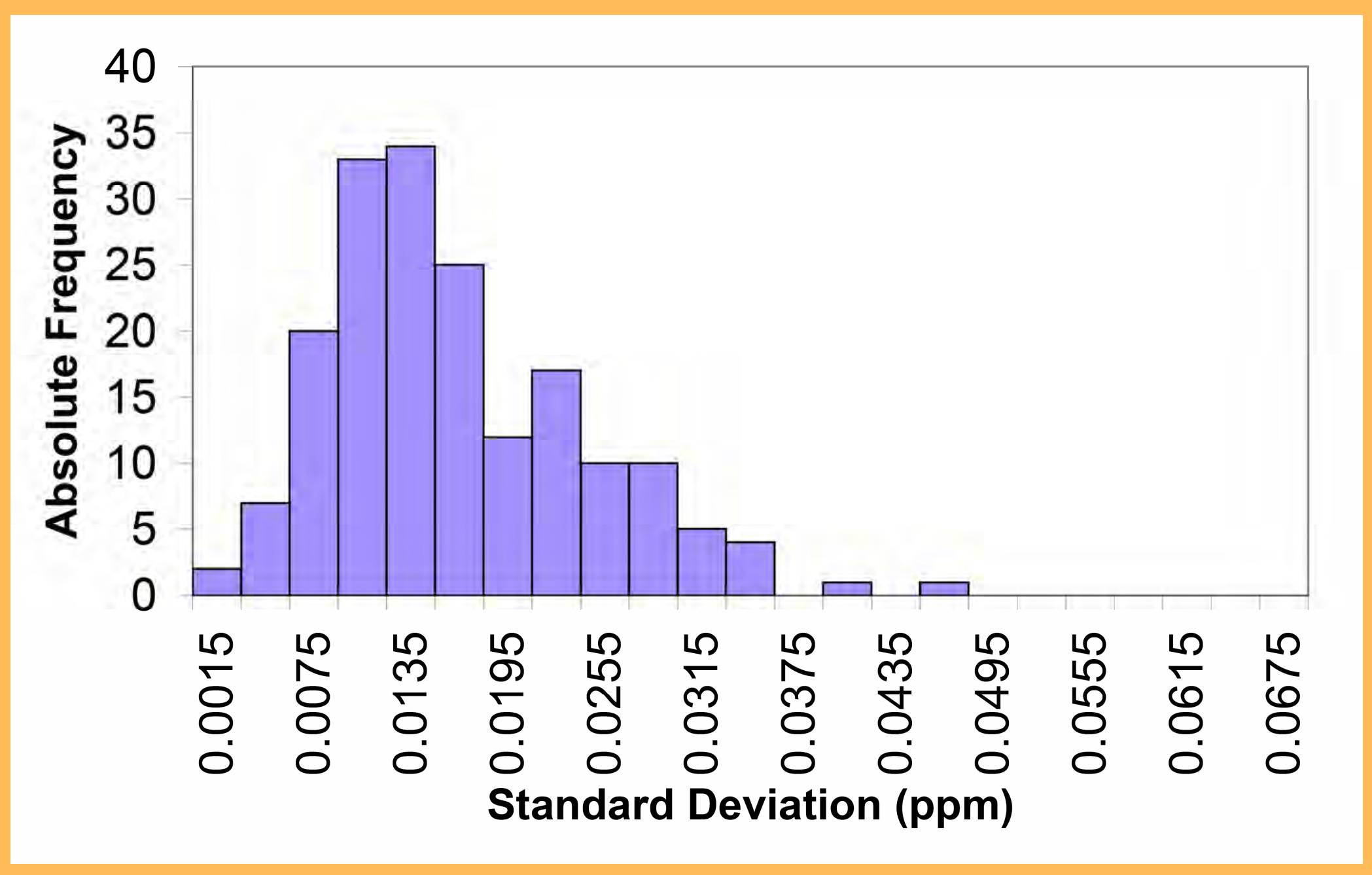

Figure 2. Histogram with the empirical standard deviations of the working standards, obtained during the calibrations of them against the laboratory standards, for the period February 2007 – April 2009. **Median: 0.015 ppm; 68th percentile: 0.019 ppm**

We are grateful to V. Garcia-Ayala for developing the acquisition/control software, and to C. Lopez for helping with the electronic of the CO_2 instrumental system. AJG is grateful to Duane Kitzis for pointing out the convenience of disconnecting the pipe of the pressure sensor from the Li-7000 sample cell and then closing its connection hole in the cell wall.

To calibrate the working standards against a set of 4 laboratory standards, we use a pyramidal sequence repeated 5 times, similar to that described in sect. 3.1 of Zhao&Tans. In every pyramidal sequence, each tank is measured 2 times. Each tank measurement lasts 3 minutes, but only the last 45 seconds are pre-processed (because the previous time is considered as cell flushing). A typical calibration lasts 3 hours. We use two different methods to process the calibrations (the difference between the resulting mixing ratios assigned to the working standards with both methods is typically smaller than 0.005 ppm). The first method is similar to that described in sect. 3.1 of Zhao&Tans. The second method consists in fitting by least squares the set of (typically) 40 measurements for the laboratory standards (r_i , T_i , t_i-t_1 , V_i) with the **response function**

$$V = a_1 + a_2 r + a_3 r^2 + a_4 T + a_5 (t - t_1) , \qquad (1)$$

where *r* is CO_2 mixing ratio, *T* is cells temperature, *t* is time, t_1 is the time of the first measurement in the calibration, a_1 , a_2 , a_3 , a_4 , and a_5 are the coefficients to determine, and *i* runs from 1 to 40 (typically). We have chosen this response function, after carrying out many tests with different types of response functions. Note that there are 4 levels (laboratory standards) of mixing ratio and the response function is quadratic in such quantity. After determining the coefficients, mixing ratio can be assigned to each working standard measurement (being the solution with positive root for the quadratic algebraic equation, the appropriate one), and afterwards, mean and standard deviation for each working standard. Figure 2 shows such standard deviations (obtained using one mean value per pyramidal sequence, so using typically 5 values to compute each standard deviation, for getting a quantity comparable with the first method). Operatively, we use the second method to process calibrations, because for ambient air measurements we use that shape for the response function, too.

To determine mixing ratio drifts in time for the working standards along their lifetimes (several months) Snedecor´s F tests have been used (see e.g. Martin), being the null hypothesis “mixing ratio is constant”, and its alternative “linear (or quadratic) drift in time”. We require a confidence level of at least 99% to reject the null hypothesis. Usually, the null hypothesis is accepted.

To determine accurately the (time dependent) response function of the system, every hour we use 3 levels of mixing ratio (working standards) bracketing atmospheric level, with around 20 ppm of separation between the highest and the lowest level. So, to obtain the response function for the time interval (50 minutes) between two successive entering of working standards, we fit by least squares 12 working standard measurements (4 working standard sets of measurements: the 2 immediately before and the 2 immediately after the considered time interval) with the response function

$$V = a_1 + a_2 (r + < a_3 / a_2 > r^2) + < a_4 > T + a_5 (t - t_r) , \qquad (2)$$

where t_r is the centre of the time interval, $<a_3/a_2>$, and $<a_4>$ are mean values obtained from the global set of working standards-laboratory standards calibrations; a_1 , a_2 , and a_5 are the coefficients to determine. Figure 3 shows RMS residuals of the working standards from these fittings (taking into account the degrees of freedom: 9, because there are 12 “points” to fit and 3 parameters to determine), and some statistics for which we have used the mean value of $\partial V / \partial r$ at *r*=385 ppm (2075 counts/ppm) to transform from counts to ppm. Several statistical tests are applied to the working standard measurements and the obtained response functions, to identify and discard periods in which the system is not working appropriately.

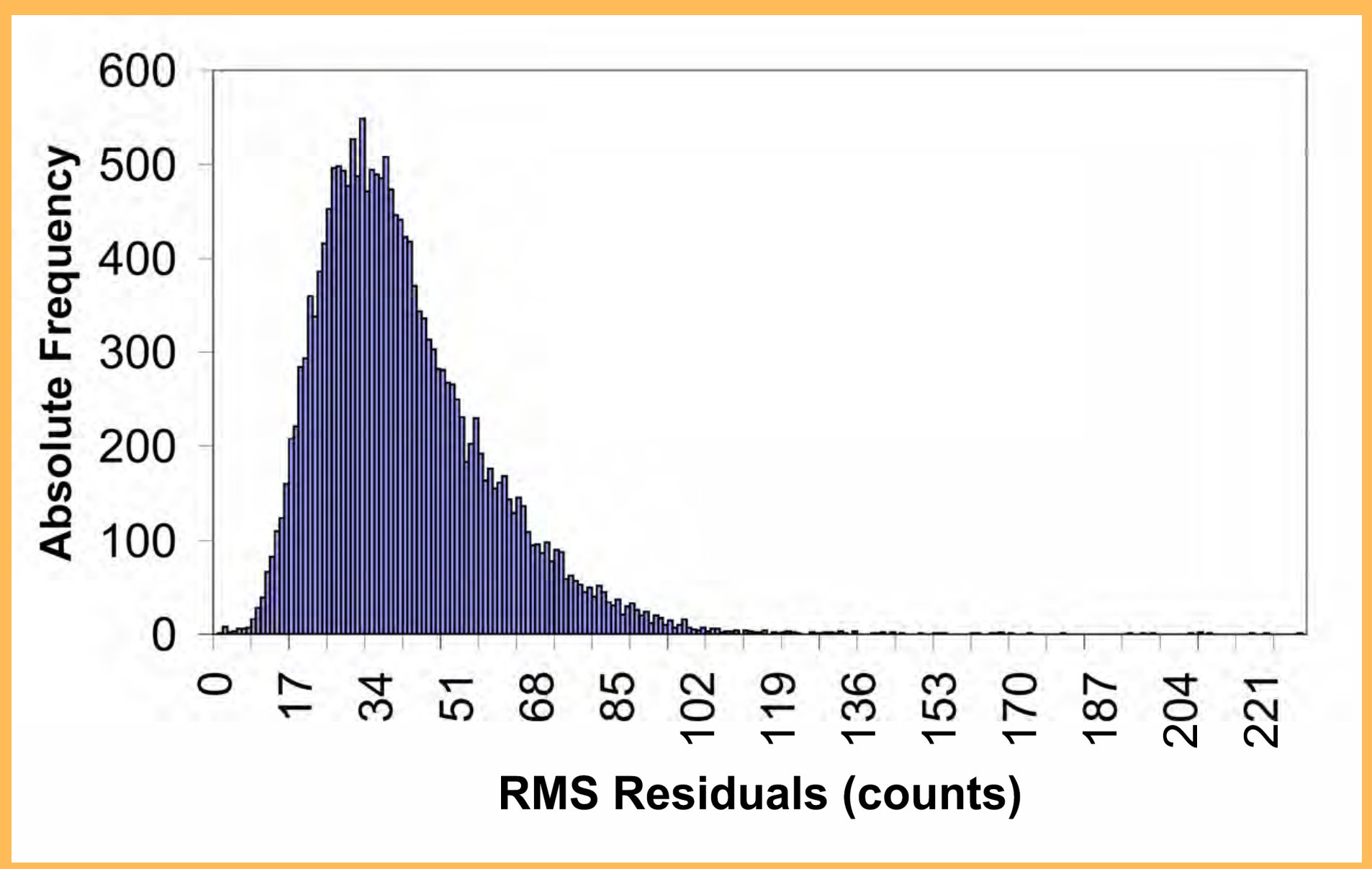

Figure 3. Histogram with the Root Mean Square (RMS) residuals of the working standards from the (time dependent) response function fittings, during the period February 2007 – April 2009. **Median:** 35.7 counts vs. **0.017 ppm**; **68th percentile:** 44.0 counts vs. **0.021 ppm.**

After pre-processing atmospheric air raw measurements (30 seconds means), mixing ratio is assigned using the computed response functions. Then, 10 minutes, hourly, daily, and monthly means and standard deviations are computed, and submitted to WCDGG.

To estimate the consistency of our atmospheric CO_2 measurements with the WMO-X2005 CO_2 scale we proceed as follows. Following Zhao&Tans partially, the standard uncertainty of a standard level n, U_n , that represents its consistency with the WMO scale, can be computed as

$$U_n = \left[U_{\mathrm{ndir}}^2 + \left(\gamma U_{n-1}^2 \right) \right]^{1/2} , \qquad (3)$$

where U_n is the random standard uncertainty of the NDIR instrument used, $\gamma = 1$ (maximum propagation coefficient), and U_{n-1} is the standard uncertainty of the previous standard level. According to Zhao&Tans, for WMO tertiary standards U_3=0.02 ppm. Taking into account that our laboratory standards are WMO tertiaries, and our instrument has U_{ndir}=0.019 ppm (see Figure 2, we use 68th percentile), then our working standards have U_4=0.028 ppm. Performing a final iteration, our atmospheric CO_2 measurements have U_5=0.035 ppm, where in this case we have used U_{ndir}=0.021 ppm (see Figure 3, we use 68th percentile), which in this case represents the standard uncertainty in the internal consistency of the response function. In conclusion, we obtain a standard uncertainty of 0.035 ppm for the consistency of our atmospheric CO_2 measurements with the WMO-X2005 CO_2 scale.

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