Abstract

Continuous in-situ measurements of atmospheric CO₂ and CH₄ have been carried out at Izaña Global Station (Tenerife, Spain) since 1984. In the present report, we briefly summarize some improvements done in those programs during 2007-2009. Firstly, we describe the CO₂ program. In January 2007, we installed a new NDIR analyzer (LI-7000), which became our main CO₂ analyzer. The instrumental system is briefly described, additionally to the acquisition/control software and new data processing numerical code, which have been developed by us. Some details are provided about the processes used to transfer the VAMO scale to the atmosphere. We report on the instrumental response function used, its determination and uncertainty. We perform an uncertainty analysis of the CO₂ working standards used to set the instrument's zero point. As an example, the method to determine, and for CO₂ measurements.

We have developed new software in FORTAN 90 to process calibrations. The main conceptual novelty consists in the discarding of outlier rejection. 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 sequential working standard (standard laboratory) CH₄ peak areas a quadratic polynomial in time, being the residuals the parameter used to identify and discard clear outliers.

We have developed in FORTAN 90 a numerical code to integrate the area of the CH₄ chromatographic peak. The chromatograms obtained with the new acquisition system are transferred 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 al.). Then, the start and end of the CH₄ peak are identified, 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), a small standard deviation and a better time consistency for working standards with the new integrator are obtained.

Intercomparison activities

We have collected flash samples for NOAA-EEL-ND-GMD-CO₂ since November 1991. Therefore, we can intercompare our CO₂, CH₄, N₂O, SF₆, and CO while monitoring the background concentrations by using NOAA-EEL-ND-CO₂, however, we are still not able to process and intercalibrate data automatically.

Additionally, as Global GAW station, periodic scientific audits are performed at Izaña by NOAA-ESRL, but no technical intercomparisons have been done.

Ch₄ program novelties

Our main system to measure CH₄ is based on a DANI 310 GC-FID in operation since 1984, whose description can be seen in Gomez-Pelaez et al. at 2006. Since 2005, some minor changes have been introduced in the system:

• for the sample loop pressure equilibration before injection has been increased by 15 seconds;
• a system of pump, 3-port-2-position valve with vent to laboratory, cooler, and VAMO multiposition valve, similar to that described in Figure 1 of Gomez-Pelaez & Ramos 2009 has been implemented;
• the all new acquisition system was installed in January 2008, based on a Vaisala 16 bits AOA, working at 40 Hz in the range 0-1 V, in combination with a Vaisala star software, having two different electronic systems working simultaneously since then.

To determine accurately the (time dependent) response function of the system, we have developed in FORTRAN 90 a numerical code to integrate the area of the CH₄ chromatographic peak. The chromatograms obtained with the new acquisition system are transferred 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 al.). Then, the start and end of the CH₄ peak are identified, 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), a small standard deviation and a better time consistency for working standards with the new integrator are obtained.

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