The Value of On-site Comparisons During WCC Audits for Methane, Carbon Dioxide and Carbon Monoxide

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The Swiss Federal Laboratories for Materials Science and Technology (or Empa) operates the World Calibration Centre (WCC) for Surface Ozone, Carbon Monoxide, Methane and Carbon Dioxide (WCC-Empa) within the Global Atmosphere Watch (GAW) Program. It was recognized that parallel measurements in addition to the comparison of a limited number of compressed gases during on-site audits provide valuable information about data quality and data compatibility within a network. For this purpose, WCC-Empa is using a Picarro G2401 travelling instrument. During comparisons, the measurement set-up is made as independent as possible, and the WCC instrument is using its own calibration standards and inlet system (next to the existing inlet).

A first comparison was made in 2011 at the GAW station Cape Point, which resulted in valuable findings concerning the drying system for CH_4 and CO_2 . However, it was also recognized that the Picarro G2401 instrument was biased especially at low CO mole fractions due to imperfect compensation of the H_2O and CO_2 cross sensitivities (Figure 1, left panel). In the meantime, better correction functions were implemented (Figure 1, right panel), which should allow more accurate CO measurements over the entire mole fraction range.

This presentation will focus on technical advances in the water vapor correction, and first preliminary results of an on-site comparison at the GAW station Pallas (PAL) (starting in April 2012) will be presented. PAL is also operating a Picarro G2401 instrument, which is in contrast to the WCC-Empa analyzer drying the sample air by a Nafion dryer. In addition, CO_2 is also measured with an NDIR system (Licor-7000), and CO with a GC with mercuric oxide detector (Peak Performer 1 RCP).



Figure 1. Ratios of COreported/COdry mole fractions vs. the water vapor mixing ratios of a Picarro G2401 instrument for different CO levels. Left: before optimization of the water vapor correction function (individual 1-min measurement points and quadratic fits). Right: after optimization (linear fits).