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Traceability of Long-Term Atmospheric Composition Observations across Global Monitoring Networks

Chemical Metrology Applied to the Measurements of Constituents in Air, Water, and Soil

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Abstract: High-quality and long-term comparable time series of the relevant atmospheric observations are the essential prerequisite to understand the dynamical, physical and chemical state of the atmosphere from seasonal to multi-decadal time scales. For relevant gaseous compounds such as ozone, methane (CH_4) and carbon monoxide (CO), the requirements are secured by tracing back these observations to common primary standards. Periodical audits of the system in operation and the performance of measurement sites provide additional information about data quality and comparability. The results of 48 audits conducted by the World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane (WCC-Empa) at global stations of the Global Atmosphere Watch programme (GAW) from 1996 to 2009 show that most of the audited sites meet the data quality objectives for ozone and methane whereas the situation is less uniform for carbon monoxide.

Keywords: Calibration · Monitoring networks · Quality assurance · Performance audit · Traceability

1. Introduction

The objective of global atmospheric monitoring networks such as the Global Atmosphere Watch (GAW) programme of WMO is to provide reliable long-term observations of the chemical composition and physical properties of the atmosphere that are relevant for atmospheric chemistry and climate change. Comparability of data from different stations is of crucial importance for the early detection of global trends or slight variations in chemical composition of the atmosphere. In many cases decades of time series are required to assess these changes with a certain degree of confidence. Thus long-term stability of the reference scales is a prerequisite to meet the demanding objectives of these observation networks. Within the GAW programme, which currently co-ordinates 26 ground-based atmospheric background monitoring stations with a global scope and several hundred stations of more regional scope, a dedicated quality assurance system ensures comparable data.[1] To achieve the required quality a traceability chain, as short as possible, links the primary standards from the Central Calibration Laboratories (CCL) to the station instruments (Fig.1, for terminology, see ref. [2]). World Calibration Centres (WCC), using transfer standards (TS), are assigned to conduct independent audits for quality control purposes, and also provide an essential link to the CCL in cases where the stations are unable to link directly.

An overview of GAW central facilities with definitions of responsibilities can be found in the GAW Strategic Plan.[1]

Within GAW primary standards (PS) are maintained at the Central Calibration Laboratories (CCLs). The CCLs for the parameters within the scope of WCC-Empa are the National Institute for Standards and Technology (NIST) for surface ozone and the National Oceanic and Atmospheric Administration-Earth System Research

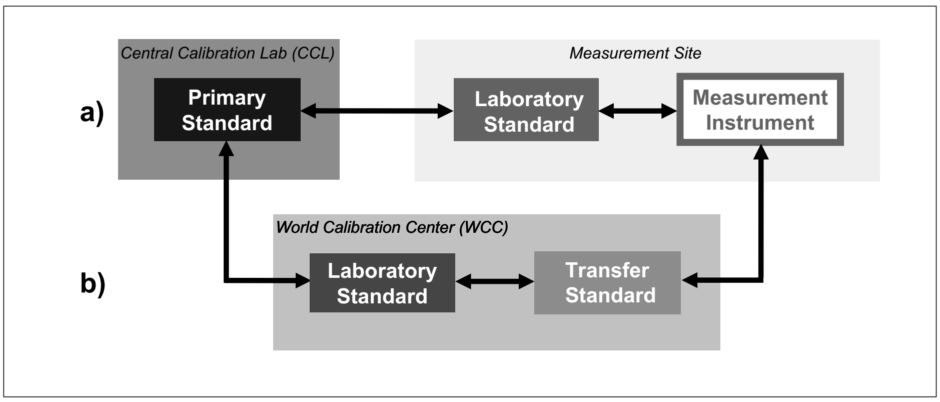

Fig 1. a) General traceability chain from the primary standards to atmospheric observations (measurements) at sites of a global network. b) Independent verification of traceability by system and performance audit carried out by the World Calibration Centres. Arrows indicate regular intercomparisons.

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Laboratory (NOAA-ESRL) for carbon monoxide and methane. Laboratory and Transfer standards (LS, TS) are used to ensure the propagation of the standards to the measurement sites and to perform regular on-site calibration (*e.g.* weekly) of the instrument to establish the relationship between values of quantities indicated by a measuring instrument and the corresponding values realized by standards.

The traceability of standards at different hierarchical levels can be achieved by regular performance audits (see below) or by round robins.[1]

2. Evaluation of Measurement Uncertainty

The ISO Guide to the Expression of Uncertainty in Measurement (GUM) provides a framework for determining the accuracy and precision of a measurement.[3–5] Even if all known sources of uncertainty, in particular a known calibration bias, were compensated for, the result of a measurement will still be uncertain to some degree. The GUM essentially advocates Gauss' method of error propagation for the combined standard uncertainty of an observation. Corresponding variances can be obtained from reliable sources of information such as instrument specifications, or they can be determined independently from experiments. The square root of the sum of the variances of all known independent sources of uncertainty represents the combined standard uncertainty. Typically, the distribution of variances is not well known and the GUM recommends applying a coverage factor k to arrive at expanded uncertainties that encompass confidence limits which likely cover the 'true' value. If the estimated variance originates from a normal distribution, a coverage factor $k = 2$ yields confidence limits of about 95%.

As an example, the combined expanded uncertainty of a carbon monoxide observation can be described as in Eqn (1)

$$U_X \approx 2\sqrt{u_{LS}^2 + u_{Analyzer,repeatability}^2 + u_{Analyzer,linearity}^2 + u_{Analyzer,drift}^2} \quad (1)$$

where u_{LS} is the standard uncertainty of a laboratory standard and $u_{Analyser}$ refers to the standard uncertainty of the analyser due to short-term variations (repeatability), non-linear response (linearity) and long-term drift (drift), respectively. As another example, the combined expanded standard uncertainty of an ozone mole fraction X measured with an ozone analyser based on UV absorption can be approximated by Eqn (2)

$$U_X \approx 2\sqrt{A^2 + B^2 \times X^2} \quad (2)$$

where A (typically in the range 0.6–1.8 nmol·mol^{-1}) and B (typically in the range 0.0025–0.01) are empirical parameters determined from the data.[6] They encompass information on the noise and drift characteristics of the ozone analyser and the transfer standard, as well as information on the uncertainty of the standard reference photometer (SRP, the primary standard). It is evident that a portion of the estimated uncertainty is independent of the ozone mole fraction, while another portion of it depends on the ozone mole fraction observed.

The GUM approach to the expression of uncertainty is widely accepted in the metrological world, although its approach to dealing with 'systematic errors' has been criticised.[7,8]

3. Primary Standard

In the GAW Programme the Central Calibration Laboratories (CCLs) provide and maintain the primary standards for given parameters. Primary standards have generally the highest metrological quality at a given location or in a given organization, from which measurements made there are derived.[1,2] For ozone the primary standard is the Standard Reference Photometer (SRP) built by NIST, which is based on ultraviolet absorption photometry of ozone at the 253.7 nm Hg line.[9–11] The primary standard of the two gases carbon monoxide and methane are provided as SI (International Systems of Units) traceable gravimetrically produced reference materials by NOAA-ESRL. The current primary standards within GAW are the WMO-2000 (CO) and the NOAA04 (CH_4) calibration scales.[12,13]

4. Audit Procedure

Empa – co-sponsored by MeteoSwiss – has operated the World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane (WCC-Empa) since 1996 as a Swiss contribution to the GAW programme. Under this mandate WCC-Empa is responsible for verifying the traceability of measurements to the designated reference within the GAW programme. This is implemented by system and performance audits, as illustrated in Fig. 2.[6] According to the GAW Strategic Plan, a *performance audit* is defined as a voluntary check of conformity of a measurement where the audit criteria are the data quality objectives (DQOs) for the parameter under review.[1] In the absence of formal DQOs, an audit will at least involve ensuring the traceability of measurements to the primary standard. A *system audit* is more generally defined as a check of the overall conformity of a station with the principles of the GAW quality assurance system.

The DQO for surface ozone as an example is illustrated in Fig. 3; whereas the DQOs for CO and CH_4 are ±2 nmol·mol^{-1} for both parameters.[6,14]

5. Results

To date WCC-Empa has performed 48 audits mainly at global GAW stations.[6]

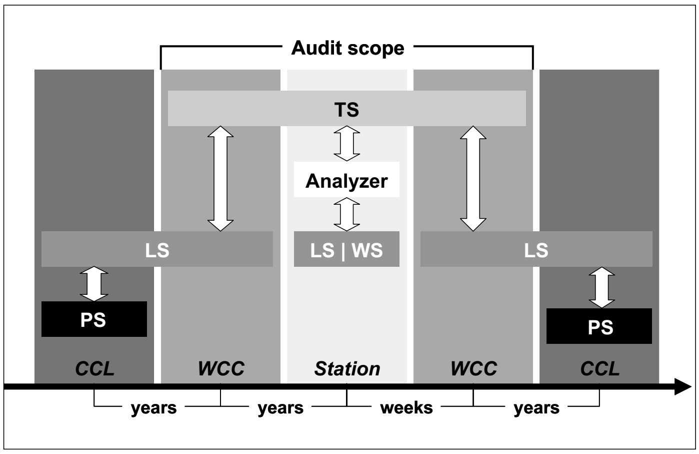

Fig. 2. Schematic diagram of the traceability of standards and the scope of a performance audit. Regular inter-comparisons and re-calibration (arrows) of the laboratory standards (LS) against the primary standard (PS) maintained by the Central Calibration Laboratory (CCL) ensure traceability. The purpose of an audit is to verify this traceability by conducting inter-comparison experiments with a travelling or transfer standard (TS) that is carried by the World Calibration Centre (WCC). At the station, LS should be used for calibration of instrumentation, and working standards (WS) are used for quality assurance purposes.

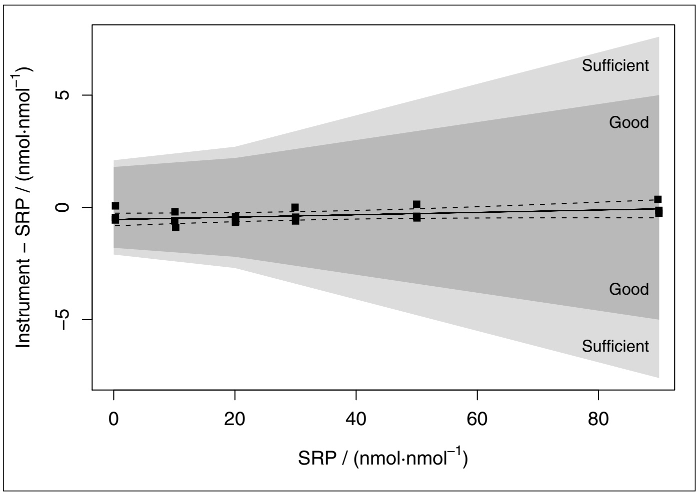

Fig. 3. Bias of an ozone analyser (TEI 49i) with respect to the SRP as a function of concentration. Each point represents the average of the last 10 one-minute values at a given level. Areas defining 'good' and 'sufficient' agreement according to GAW assessment criteria are delimited by gray colours.[6] The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands.

In this paper we discuss results for surface ozone and carbon monoxide inter-comparisons. Audits focussing on methane measurements usually show that results are in agreement within DQOs and are therefore not discussed in this article.

5.1 *Surface Ozone*

Audit results for surface ozone are summarised in Fig. 4 as intercept vs. slope of the linear regression analysis. The bias was calculated with respect to the WCC-Empa reference (NIST Standard Reference Photometer #15). Most of the audited sites meet the DQOs for surface ozone, but differences between various instrument types were observed. Audits conducted during the early years of WCC-Empa were often related to Dasibi 1008 Series and Monitor Labs 8810 instruments. Both models showed larger biases compared to more recently used instrument types such as TEI instruments. These latter instruments show improved intercept / slope combinations which were well centred around 0/1 (intercept/slope). However, the overall variation of the older TEI 49 models is larger compared to the newer TEI 49C- and 49i-series instruments.

5.2 *Carbon Monoxide*

The audit results for carbon monoxide are shown in Fig. 5 as intercept vs. slope of the linear regression analysis. In contrast to ozone, the DQOs were not met in most cases, and significant differences were found between different measurement principles. Basically, measurements traceable to a common reference are expected to be homogeneously distributed around the origin (0/1; intercept/slope). This result was indeed observed for NDIR instruments but due to relatively high instrumental noise, and consequently poor repeatability of this technique, large variations were found. In contrast, vacuum UV resonance fluorescence and GC/FID instruments showed only small intercepts because both techniques have linear response functions and better repeatability compared to NDIR. In most cases the slope was also close to one for these techniques. A clearly different pattern was observed for GCs with an HgO detector. These instruments showed a tendency for negative intercept – positive slope combinations. A possible reason for this might be that some of these instruments were calibrated using standards that were not traceable to the common reference. However, if the calibration function is properly accounted for the non-linearity of the detector, only a shift in the slope would result. For the investigated cases this was often not attained, either due to inadequate calibration functions and/or a set

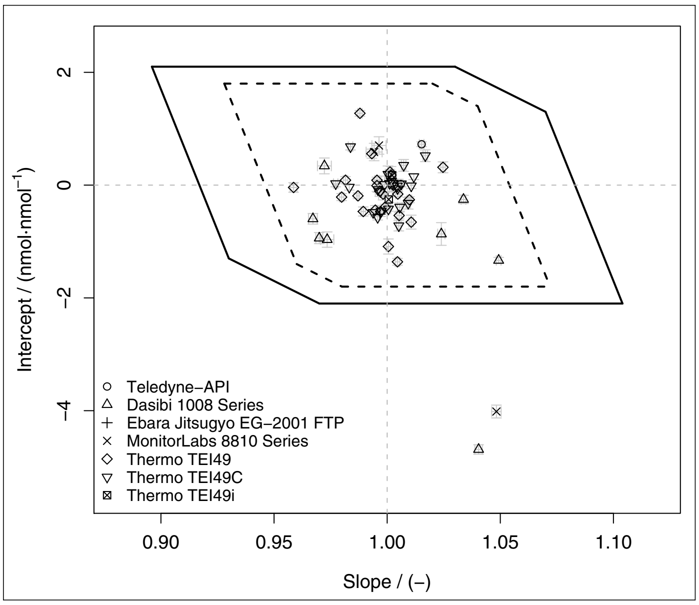

Fig. 4. Intercept vs. slope for ozone audits conducted by WCC-Empa between 1996 and 2009. The limits displayed cover the range of slope-intercept combinations for sufficient (solid line) and good agreement (dotted line) for the range 0–100 nmol·mol^{-1}.[6]

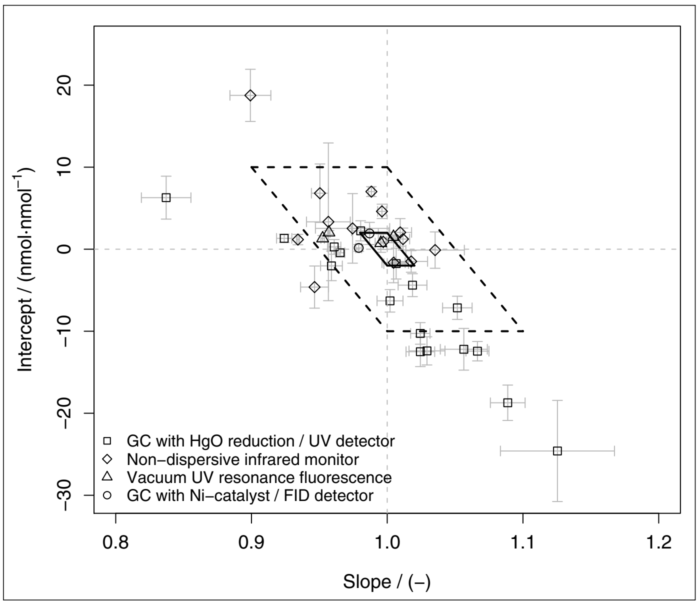

Fig. 5. Intercept vs. slope for CO audits conducted by WCC-Empa between 1997 and 2008 for different measurement techniques. The intercept/slope pairs are referenced against the WMO-2000 CO scale. The rhomboids displayed cover the range of slope-intercept combinations for a maximum of 2 nmol·mol^{-1} (solid line, corresponding to the DQO) and 10 nmol·mol^{-1} (dotted line) bias for the concentration range 0–200 nmol·mol^{-1} CO.

of reference gases with internal inconsistency. In addition, drift of reference standards may have further affected the calibration of these instruments.[12]

Despite the large deviations observed during WCC-Empa audits, accurate and precise CO measurements using different analytical techniques are feasible, provided that instruments are calibrated carefully and appropriate averaging times are used.[15]

6. Conclusion

WCC-Empa audit results for surface ozone, carbon monoxide and methane from 1996 to 2009 showed good results for ozone and methane inter-comparisons. The DQO of ±2 nmol·mol^{-1} for CO is often not attained. The worldwide comparability of CO measurements is still a matter of concern, although audit results demonstrate that the DQO of ± 2 nmol · mol^{-1} for CO can be achieved. The noncompliance of the DQOs originated in an inhomogeneity of the calibration scale over time and issues inherent to the analytical techniques empolyed. The good results for ozone intercomparisons demonstrated that the current DQO for surface ozone could be tightened. In general, the agreement between the audited stations and WCC-Empa improved over time for all parameters because of better analytical techniques and analysers and/or the impact of WCC-Empa audits.

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