

GAW Report No. 192

Guidelines for the Measurement of  
Atmospheric Carbon Monoxide

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# WORLD METEOROLOGICAL ORGANIZATION GLOBAL ATMOSPHERE WATCH



GAW No. 192

## GUIDELINES FOR THE MEASUREMENT OF ATMOSPHERIC CARBON MONOXIDE



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## 1. INTRODUCTION

The Global Atmosphere Watch (GAW) Programme of the World Meteorological Organization (WMO) aims at providing reliable long-term observations of the chemical composition and physical properties of the atmosphere that are relevant for understanding atmospheric chemistry and climate change. Reactive gases are one of the foci of the GAW programme. This group includes carbon monoxide (CO), which is present only in trace quantities in the atmosphere but plays an important role in atmospheric chemistry. Compatibility of data from different observational platforms and sites 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. Support of the long-term stability of the reference scales and its propagation to in-situ measurements are particular prerequisites to meet these demands.

In this document we focus on continuous in-situ and flask measurements of carbon monoxide performed from different platforms.

The quality assurance (QA) system developed within the GAW programme provides a unique framework to reach the required measurement compatibility and harmonization. The most recent QA framework is presented in the "WMO Global Atmosphere Watch (GAW) Strategic Plan: 2008-2015" [WMO, 2007].

The *primary objectives* of the GAW QA system are to ensure that measurement data are consistent, of known and adequate quality, supported by comprehensive metadata and sufficiently complete to describe global atmospheric states with respect to spatial and temporal distribution. The Quality Assurance system of GAW consists of a number of elements and requires for its implementation:

- The establishment and maintenance of a single reference scale (primary standard);
- The establishment of the procedures linking observations to the primary standard (including measurement guidelines and standard operating procedures, calibration procedures, guidelines for station audits and set up of comparison campaigns);
- Specification and rolling review of the Data Quality Objectives (DQO) and observational network by the designated Scientific Advisory Group (SAG);
- The use of harmonized terminology.

An overview of the terminology used in this document and recommended for use within the GAW programme is presented in Annex II.

Measurements of carbon monoxide have been made for over thirty years using a number of different techniques and calibration scales. At the moment the measurements are performed at a number of stations worldwide, however, large regions are still undersampled. This document was created by the WMO/GAW Scientific Advisory Group for Reactive Gases (SAG RG) with the objective to document the various sampling and measurement techniques in use and to contribute to a convergence of these techniques world-wide in the interest of promoting the principles and objectives of the GAW programme, in particular to establish a harmonized global data set of atmospheric carbon monoxide observations.

Thus, these Measurement Guidelines for CO are intended for use at stations and any other measurement platform where such measurements have recently been added to the programme or will be added in the foreseeable future as well as by institutions with experienced personnel and where pioneering work on CO has been performed for many years.

## 2. RATIONALE AND OBJECTIVES

Carbon monoxide (CO) is present only in trace quantities in the atmosphere but plays an important role in atmospheric chemistry. CO is part of a photo-chemically driven reaction sequence that links methane (CH<sub>4</sub>), formaldehyde, ozone (O<sub>3</sub>) and the hydroxyl radical (OH). In much of the background troposphere the reaction of CO and OH accounts for all of the chemical loss of CO and about 75% of the removal of OH. Reaction with OH is the primary removal pathway for some greenhouse gases such as CH<sub>4</sub>, therefore trends in atmospheric CO levels are expected to have an indirect effect on climate through their role in regulating OH. CO also plays an important role as a precursor of tropospheric ozone, an air pollutant and greenhouse gas. CO has a relatively long atmospheric lifetime, ranging from 10 days in summer in the tropics to more than a year over polar regions in winter [Seinfeld and Pandis, 1998].

Greatest CO mole fractions in the background troposphere at the surface are found in the high latitudes of the Northern Hemisphere (NH) and lowest CO occurs in the high latitudes of the Southern Hemisphere (SH). The annually averaged latitudinal gradient reflects the predominance of anthropogenic emissions in the Northern Hemisphere (Figure 1). CO exhibits a seasonal cycle driven by an imbalance of its source and sinks. In both hemispheres, reaction with OH leads to a minimum in summer. The NH winter maximum results largely from a build-up of anthropogenic emissions, while in the SH, biomass burning leads to a maximum in spring. The largest difference between the high northern and high southern hemispheres (~150 nmol mol<sup>-1</sup>†) occurs in February/March and the minimum (~10 nmol mol<sup>-1</sup>) in September/October.

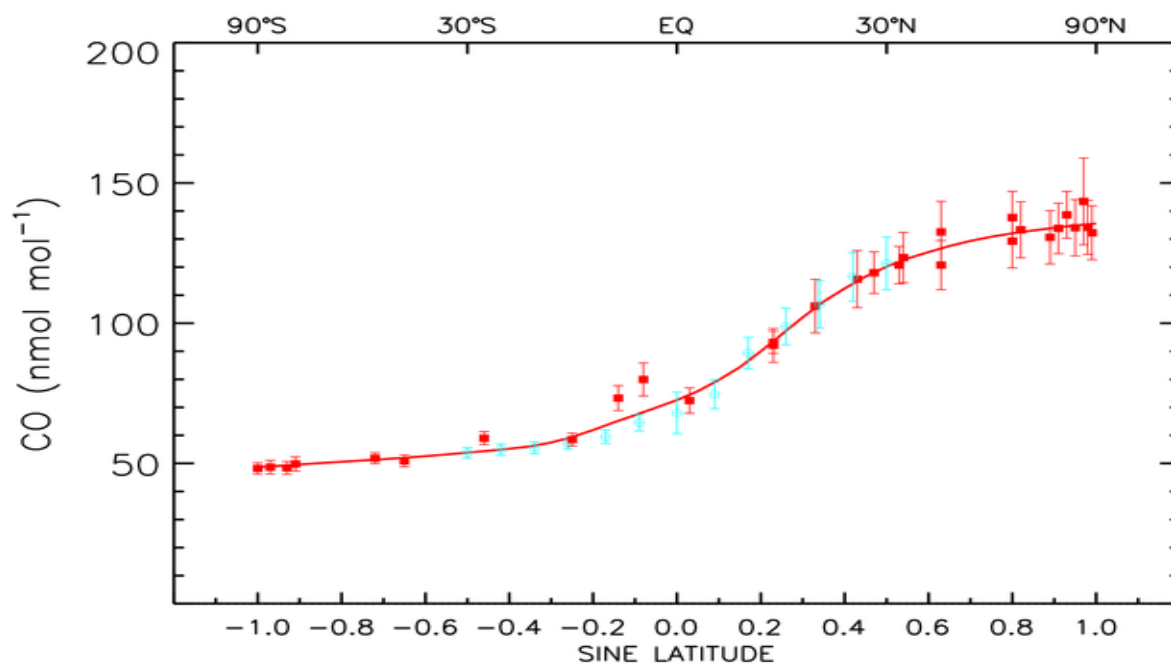


Figure 1 - Average annual CO latitudinal gradient (1994-2008) in the marine boundary layer from the NOAA global air sampling network (contributing network of the GAW programme). Squares (in red) present coastal and island sites, circles (in blue) are the results from trans-Pacific shipboard sampling. The error bars are one standard deviation and present the sum of both seasonal and inter-annual variability. More information is available at <http://www.esrl.noaa.gov/gmd/ccgg/flask.html>.

CO levels in urban locations and areas of regional-scale pollution are greater than those found in the background atmosphere, and can reach several parts per million (ppm =  $\mu\text{mol mol}^{-1}$ ) in urban areas. High levels of CO also contribute to local air pollution and ozone formation. Therefore, in industrialized countries emissions of CO are subject to regulations. Due to its

† 1 nmol mol<sup>-1</sup>  $\equiv$  1 ppb



prolonged lifetime, CO emissions can be transported far away from the original source regions. Measurements from space show that even in areas distant from CO sources, the CO levels may be twice as much as those observed in the marine background [Yurganov, et al., 2008].

Average CO in the northern hemisphere has decreased by as much as 15% since 1990, likely as a result of emission control laws [Novelli et al. 2003, Duncan et al. 2007]. Rates of change are sensitive to the period examined due to a high degree of inter-annual variability which is primarily caused by vegetation fire emissions. Trends in the tropics and the Southern Hemisphere have been small and so far difficult to quantify.

Most of the remaining uncertainties in our knowledge about the role of carbon monoxide in the troposphere can only be reduced if consistent observations from the ground, as well as from aircraft and satellites, are available on a global scale. The major objectives for a global CO measurement network are therefore to:

- Ensure that surface measurements made by different laboratories are compatible within the data quality objectives described below;
- More completely define the spatial and temporal distributions of CO;
- Validate satellite and ground based column measurements using ground-based measurements.

Such a globally harmonized data set can then be used to:

- Combine surface and remote measurements with numerical models of the atmosphere to better define the CO budget;
- Contribute to the assessment of the tropospheric oxidative capacity;
- Better understand CO trends, and to compare these with trends derived from emission inventory data;
- Better assess biomass burning emissions of CO and parameterize these in models (e.g. the use of fire count data from satellites).

### 3. DATA QUALITY OBJECTIVES FOR CO MEASUREMENTS

Data quality objectives (DQOs) define qualitatively and quantitatively the type, quality and quantity required of data and derived parameters to yield information that can be used to support decisions [WMO, 2007]. In particular, DQOs specify acceptable levels of uncertainty in the data, required completeness, compatibility and representativeness.

The inter laboratory compatibility objectives for CO are regularly updated during the biannual WMO/IAEA Meetings of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques [WMO, 2009a]. The DQOs, taking into considerations the expert meetings recommendations, for the GAW Programme are summarised as follows:

- Mole fractions of one and the same air sample determined by different laboratories and/or monitoring stations should be compatible to  $\pm 2 \text{ nmol mol}^{-1}$  (95% confidence level or coverage factor,  $k=2$ ), recommended averaging time for comparisons is 1 hour for continuous measurements;
- Standards should be compatible to  $\pm 1 \text{ nmol mol}^{-1}$  or 0.5% (whichever is greater,  $k=2$ );
- For the purpose of trend detection in the marine boundary layer, mole fractions between 40 and 250  $\text{nmol mol}^{-1}$  should be determined with a maximum uncertainty of  $\pm 2 \text{ nmol mol}^{-1}$  ( $k=2$ );
- For continental sites experiencing the influence of regional pollution and CO above 250  $\text{nmol mol}^{-1}$ , mole fractions should be determined with a maximum uncertainty of  $\pm 5 \text{ nmol mol}^{-1}$  ( $k=2$ );

- Data coverage (defined as the number of available values divided by the maximum possible number for an aggregation period) should exceed 66% for continuous measurements and be uniformly distributed in time. In all cases, the data coverage of an aggregated value must be specified.

Comparisons of CO measurements among laboratories (through round-robins, and other comparison sample exchanges) have shown differences in measurement results larger than these recommendations. The community as a whole is working towards reaching the above objectives.

The combined uncertainty of CO measurements should be comparable or smaller than DQOs. It can be estimated using a combination of specifications of the uncertainty of the calibration standards and experimental data. This assessment needs to be performed by each station or laboratory individually. The process is described in more detail in Chapter 8.4 of this document.

Recent initiatives to monitor and forecast atmospheric composition in near-real-time (e.g. the European MACC project (<http://www.gmes-atmosphere.eu/>)) have expressed a strong interest in rapid data delivery for model validation purposes. These applications require combined uncertainty of  $\pm 5 \text{ nmol mol}^{-1}$  ( $k=1$ ) for hourly values, but routine submission of preliminary data within 72 hours after sampling.

## **4. MEASUREMENT SETUP**

### **4.1 Location and siting requirements**

Choice of a sampling location for a chemical species should consider both the spatial distribution of its sources, its lifetime and its dispersion and transport. Carbon monoxide has a lifetime ranging from about two weeks in the tropics to over a year at the highest latitudes and therefore can be transported thousands of kilometres from its source location. Stations in the GAW network must be located such that the variables measured are regionally representative and normally free of the influence of significant local pollution sources. Determining the spatial and temporal representativeness of data is necessary to ensure it is used properly in scientific analysis.

A number of questions must be addressed to estimate what spatial and temporal scales the data represent. In particular this issue is important when comparing observations with models, where “model-data mismatch” (errors introduced because the spatial and temporal resolution of the model is different from that of the data) must be assessed to properly estimate uncertainties in calculated gas fluxes.

Hence, the representative quality of the measurements will be defined by the following factors:

- (a) How removed is the sampling site from anthropogenic and natural trace gas fluxes?
- (b) What is the impact of local meteorology on the measurements? This can manifest itself in many ways including upslope/downslope flow regimes at mountain sites, diurnal land-/sea breeze at coastal continental sites, and potential pollution sources in one wind sector but not in others.
- (c) What is the frequency of sampling? What is the goal of the measurements? What sampling frequency is needed to calculate time-averages (e.g., hourly, daily or monthly means).
- (d) For low-frequency sampling of discrete samples, is there a sampling strategy to be used (i.e., are samples collected only under specific meteorological conditions)?
- (e) Have the data been “selected” based on meteorological conditions or another species, or trajectories after the measurements were made?

Whether the sampling strategy is for background or regional air, it is important to avoid local contamination sources. The sample collection location on site should be set upwind of any buildings, garages, parking lots, generators, other emission sources – any nearby areas where fossil fuels or biomass may be combusted. Station personnel should also remain downwind of sample collection and refrain from smoking as necessary.

Measurement sites require electricity and access to the necessary supplies. Furthermore, temperature control and clean lab environment are required. Instrumentation should not be exposed to sunlight. No local pollution source should be in the vicinity of a measurement site. To avoid system contamination, components of stainless steel must be kept dry. Stainless steel or chemically resistant flexible tubing should be used.

#### **4.2 Air inlet design**

Carbon monoxide is stable under conditions normally encountered in inlet systems. Therefore a wide range of inlet materials is suitable for CO measurements. Considering that often more than one gas is measured at a given inlet, the materials should however be suitable for all of the measured parameters. Residence time is also not as critical for CO as for other compounds. Nevertheless, the residence time should be kept as short as possible mainly to assure an accurate time stamp. Under certain conditions where long residence times cannot be avoided, e.g. inlet systems on tall towers, a correction of the time difference between sampling and analysis should be made.

The whole inlet system should be kept clean, which is a requirement for all species. In addition, the inlet must be designed in a way avoiding condensation of water vapour. A trap for water vapour is in most cases required between the inlet and the instruments. Cryogenic systems or permeation dryers may be used.

### **5. SAMPLING TECHNIQUES**

#### **5.1 Measurements of flask air samples**

Collection of discrete air samples in flasks and their subsequent analysis at a central laboratory provides an economical approach for determining CO at multiple locations. The results can provide a comparable (for different locations) data set suitable for the analysis of monthly, seasonal and inter-annual variations. Air samples collected in flasks from aircraft measure both vertical and horizontal CO distributions. The main drawback to discrete sampling is its limited temporal frequency compared to continuous in-situ measurements. It is strongly recommended that new GAW sites also include co-located sampling with the NOAA/ESRL Carbon Cycle Group as part the station Quality Assurance/Quality Control (QA/QC) protocol.

(a) *Materials:* Air samples are easily contaminated for CO. Artefacts can result from the flask materials, sampling protocols and extended storage. These typically present themselves as elevated concentrations, but some materials are known to absorb CO. Metal and glass flasks are both used for CO measurements. Details of their production, age, valve type and cleaning procedures can affect the stability for CO.

The choice of flask material depends on the project. A key factor is the stability of the sample, which is effected by sample concentration, size and storage period. Small samples containing low CO levels and stored for longer periods are more susceptible to measurable artefacts than large, high CO samples stored for a short time. Titanium and stainless steel flasks with metal valves are frequently used during aircraft campaigns in which samples are measured soon after collection. Non electropolished flasks have been shown increasing CO concentrations in time, particularly at high ozone levels. Both NOAA and CSIRO use glass flasks with glass pistons and Teflon (PTFE or PFA) O-rings in their global sampling networks, programmes in which storage may last six months or more.

(b) *Operation and maintenance:* Procedures to collect air samples can be as simple as opening an evacuated flask to the atmosphere. More complex methods can involve computer-controlled, multi-flask packages. All procedures require consideration of local sources and wind direction when sampling for background conditions. Sample collectors must be trained to avoid accidentally contaminating samples. A record of each sampling event is necessary that includes sample site, sample taker, flask ID, equipment ID if applicable, date and time, wind direction, and any remarks that provide information on the condition of sampling. It is recommended that two flasks (a pair) be collected nearly simultaneously as part of the QA/QC procedures.

Maintenance requires that flask integrity be confirmed. Flasks should be leak tested and checked for liquid water and other deposits before each use. Glass flasks have been widely used for air sampling, but breakage can be high during transport and handling. The more complex flask systems can be prone to failures associated with hardware.

(c) *Time resolution:* Weekly sampling is suitable for long-term monitoring in the remote atmosphere. This frequency is sufficient for QA/QC and to define monthly and annual means and establish trends. Flask packages can be programmed for hourly or daily air collection. Aircraft programmes use flasks for hourly or daily sampling.

(d) *Known problems:* Contamination by materials during storage is often the greatest problem associated with flask sampling. Reports in the literature for metal canisters are sometimes contradictory. Porous rubbers can absorb/desorb CO. Glass flasks fitted with Teflon O-rings have proven reliable long storage periods. Laboratories should select their flasks based on the program and the stability required. Material tests, conducted over the anticipated time of sample storage, are recommended before starting a field programme.

## 5.2 Continuous observations

In-situ continuous observations provide information about CO variability on a time scale ranging from seconds to one hour depending on the measurement technique. In contrast to flask sampling, near-real-time data delivery can be realized using continuous measurements.

In-situ observations can be made using a broad variety of analytical techniques. Non-dispersive infrared radiometry (NDIR) is based on spectral absorption at 4.7  $\mu\text{m}$  [Parrish, *et al.*, 1994]. NDIR is frequently used for continuous measurements at remote locations; however instrument drift, limited precision and long averaging times are factors limiting the achievable data quality. Gas chromatography, when coupled with a number of different detectors (e.g. flame ionization (GC/FID) or hot mercuric oxide reduction/UV absorption (GC/HgO)) can provide high precision and adequate detection limits. The HgO-reduction detector tends to have a non-linear response over the range of atmospheric CO, and requires careful, repeated characterization of the detector response [Novelli *et al.*, 1991]. The GC/FID technique requires catalytic conversion of CO to CH<sub>4</sub> [van der Laan *et al.*, 2009]. For confidence in the results, the catalytic conversion efficiency must be determined on a regular basis. These type of issues complicate efforts to properly maintain instrument calibration and provide accurate measurements [Novelli, 1999]. GC measurements are quasi-continuous in nature and therefore may not detect fast changes of mole fractions that can be captured by high frequency measurements.

Several new measurement techniques have recently become available. The most established technique is based on resonance fluorescence of CO (induced by a high frequency discharge) in the vacuum ultraviolet (VURF). This method provides low detection limits with excellent precision in the range of atmospheric mixing ratios [Gerbig, *et al.*, 1999]. A commercially available instrument based on VURF is used in several laboratories, field sites and other platforms, e.g. in the CARIBIC ([www.caribic-atmospheric.com](http://www.caribic-atmospheric.com)) passenger aircraft project.

Recently spectroscopic techniques based on wavelength-scanned cavity ring down spectroscopy (WS-CRDS) and cavity-enhanced quantum cascade laser spectroscopy (QCL) have become available. The WS-CRDS technique operates using lasers in the near-infrared and is currently mainly used for measurements of carbon dioxide, methane, and ammonia. The QCL

technique measures in the mid-infrared and commercial instruments are available that can determine both CO and N<sub>2</sub>O with a single laser. Both WS-CRDS and QCL techniques provide CO measurements with low detection limits and excellent reproducibility.

Additional details for a number of in-situ measurement techniques are given in the following chapter, and QA/QC aspects are addressed in Chapter 8.

## **6. MEASUREMENT TECHNIQUES**

### **6.1 Non-Dispersive Infrared (NDIR) Detection**

#### **6.1.1 Instrumentation**

Several commercial non-dispersive infrared monitors (NDIR) are available for CO measurements. Most of these instruments use the gas filter correlation (GFC) technique to compensate for interferences, but instruments using catalytic removal of CO for the reference signal are also available. Some of these instruments underwent major improvements over the past years, which included the addition of permeation driers. Thus, large differences in instrumental performance are possible between different NDIR monitors. NDIR instruments are mainly used at sites with elevated CO concentrations, but can also be operated at remote locations with some precautions and sufficient integration time. In light of their high detection limit they are best used for measurements in the Northern Hemisphere, where the CO minimum reaches approximately 60 nmol mol<sup>-1</sup>. Reproducibility of the method is instrument dependant and ranges typically from ±4-10 nmol mol<sup>-1</sup> (2 standard deviations for hourly averages), minimum detection limit is 10-40 nmol mol<sup>-1</sup>.

#### **6.1.2 Operation, maintenance & QA/QC**

NDIR monitors are relatively simple and can be readily configured to operate unattended up to one month.

Frequent automatic zero checks are mandatory. Zero checks should be performed with CO-free air generated using a trap consisting of Schutze Reagent or hydrophobic noble metal catalyst (e.g. Sofnocat). Most NDIR CO analyzers show zero drift (a few to several dozen nmol mol<sup>-1</sup> per hour). Thus the appropriate interval for automatic zero checks must be evaluated at individual sites. The range for the frequency of automated zero checks usually is at least once per hour for instruments with a large drift and daily for instruments with a small drift. Frequent automatic span checks are also desirable but are less crucial compared to zero checks. The frequency should be between hourly and weekly checks.

Manual instrument calibrations should be performed at least monthly, or preferably every two weeks. It is recommended to use a calibration gas provided by CCL with the highest mole fraction in order to get a better signal to noise ratio. A zero calibration has to be made before each span calibration. The matrix of the calibration gas can either be air or nitrogen.

The instrument linearity should be checked at least up to the span gas concentration on a yearly basis.

Other preventative instrument maintenance includes inlet filter exchange and cleaning of optical parts. Intervals depend on pollution conditions, but are typically two weeks for filter changes and one year or more for cleaning. Some instruments require periodic replacement of consumables. Refer to instrument manuals for details.

Quality assurance includes regular calibrations, as well as flagging of zero/span values and data with known problems. The raw data, along with the flags and the calibrations, must be properly archived. On a regular basis, these data must be properly converted into final mole fractions, e.g. corrected for zero and span drift, and submitted to the data centre along with ancillary data.

### **6.1.3 Time resolution**

Precision of the NDIR improves with increasing averaging time. The time resolution of CO records from NDIR instruments should allow generation of hourly statistics, preferably from integrals taken over 1 to 10 minute periods. These should include arithmetic mean and standard deviation for each hour. A CO mole fraction with acceptable uncertainty usually cannot be determined in a measurement period shorter than one hour because of high frequency instrument noise.

### **6.1.4 Known problems**

Most NDIR instruments suffer from water vapour interference. Drying the sample air either through a permeation dryer or cold trap to a dew point of  $-30^{\circ}\text{C}$  or lower is required - especially at stations with low concentrations. Some instruments are already equipped with suitable dryers.

Zero drift is one of the most serious issues of NDIR analysers. Drift is often correlated with laboratory temperature; therefore good air conditioning helps to minimise these effects. Experience shows that GFC NDIR instruments are more prone to zero drift compared to cross flow modulation analyzers. However some of the currently available GFC instruments have built-in permeation driers and periodically monitor and correct for baseline by routing the sample stream through a heated CO scrubber.

## **6.2 Gas Chromatography with Mercuric Oxide Reduction Detection (GC/HgO)**

### **6.2.1 Instrumentation**

Gas chromatography (GC) combined with HgO reduction detector can be used for CO measurements. CO reacts with HgO, to produce mercury vapour which is detected by UV absorption. The chromatography typically requires dual columns: the first to separate  $\text{CO}_2$  from the sample and back-flushing to avoid contamination of the second, analytical, column. One of the advantages of this technique is that with appropriate columns simultaneous detection of hydrogen is possible with only one instrument. The commercially available GCs should be equipped with additional valves to select between ambient air and calibration gases or working standards. Furthermore the pressure in the sample loop should be equilibrated to ambient pressure before injection. Alternatively a constant pressure can be maintained in the sample loop. Reproducibility of the method is  $\pm 1-4 \text{ nmol mol}^{-1}$  (2 standard deviations of  $\sim 10$  analyses), minimum detection limit is about  $1 \text{ nmol mol}^{-1}$ .

### **6.2.2 Operation, maintenance & QA/QC**

The typically non-linear response of this technique makes careful calibrations necessary. A multipoint calibration covering the whole range of interest should be made using a suite of calibration standards or by dilution of a standard with carbon monoxide-free air. The calibration function tends to change over time and must be regularly checked, e.g. every two weeks. In addition, zero (blank) checks using CO free air are required. A full re-calibration of the instrument is necessary after any significant instrument maintenance, such as UV lamp or HgO replacement.

It is recommended to use a set of working standards during normal operation, preferably with a suitable range of mole fractions. Injection of three working standards covering the concentration range of interest at hourly intervals is optimal. One injection of a working standard per hour is regarded as the minimum. This is required to tie the daily calibration to the calibration function. Ambient data should be evaluated using the appropriate calibration function and the working standard results. Aging HgO reactant and UV lamps result in an increase in instrument noise requiring timely renewal.

### **6.2.3 Time resolution**

GC measurements have analysis times of typically 3 to 4 minutes. Injection frequency allows generation of hourly statistics and at least one injection of a working standard per hour.

### **6.2.4 Known problems**

The non-linear response, which may change with time, is the main difficulty. It requires a

set of high quality ambient CO levels standards at a station, or a system to perform accurate dilutions.

### **6.3 Gas Chromatography with Flame Ionization Detection (GC/FID)**

#### **6.3.1 Instrumentation**

Gas chromatography with a Flame Ionization Detector (FID) and a heated nickel catalyst (methanizer) can also be used for CO measurements. The catalyst converts CO in the presence of a flow of hydrogen gas to CH<sub>4</sub> which is then detected by the FID. The most critical part of the method is the nickel catalyst, because its conversion efficiency must be high and constant. Large sample volumes should be used to improve the signal-to-noise ratio. Reproducibility of the method is  $\pm 1-3$  nmol mol<sup>-1</sup> (2 standard deviations average of 10 analyses) and detection limit is 1-3 nmol mol<sup>-1</sup>. Additional technical details on such a system can be found in van der Laan et al. [2009].

An advantage of this technique can be the simultaneous detection of methane and carbon dioxide. If the GC is equipped with an additional electron capture detector, measurements of N<sub>2</sub>O and SF<sub>6</sub> can be made using one GC system.

#### **6.3.2 Operation, maintenance & QA/QC**

Typical operations and maintenance procedures of a GC method apply. These include regular checks of GC parameters such as retention times, peak width, sensitivity, and baseline noise. Furthermore, flow rates and pressures of carrier and detector gases should be checked regularly.

These systems require careful calibration. Linearity of response (for CO) is usually good, but should be confirmed using three or more standards or by dilution of a high concentration standard in regular intervals. In addition, zero checks using CO-free air are recommended. It is recommended to inject at least one working standard per hour. Ambient data should be evaluated using the appropriate calibration function and the working standard results. Conversion efficiency should be regularly calculated by comparing the CH<sub>4</sub>/CO ratio of the working standard with the corresponding GC responses. If the conversion efficiency drops below a certain level (e.g. 70%) or becomes unstable, the methanizer needs to be replaced. The maximum lifetime of a methanizer under optimal conditions is estimated to be five years. A heated methanizer loses efficiency irreversibly in absence of the hydrogen gas.

#### **6.3.3 Time resolution**

Injections with this technique are typically made every 6 to 10 minutes. Injection frequency allows generation of hourly statistics, and at least hourly injection of a working standard is recommended.

#### **6.3.4 Known problems**

Carbon dioxide is also converted to methane with high efficiency over the nickel catalyst therefore CO<sub>2</sub> and CO must be completely separated. Valve switching times and flow rates must be adjusted to avoid breakthrough of CO<sub>2</sub> from the pre-column to the main column. The most critical part of this technique is the nickel catalyst. Conversion efficiency must be high, sufficient and stable.

### **6.4 Resonance Fluorescence in the Vacuum Ultra-Violet (VURF)**

#### **6.4.1 Instrumentation**

The technique is based on a pulsed-discharge fluorescence of CO in the vacuum ultraviolet, followed by measurement of the emitted photons with a photomultiplier. The technique, which is very specific for CO, can provide excellent repeatability and reproducibility. Reproducibility of the method is  $\pm 0.4-2$  nmol mol<sup>-1</sup> (2 standard deviation for a 30 second average), minimum detection limit is less than 1 nmol mol<sup>-1</sup>.

#### **6.4.2 Operation, maintenance & QA/QC**

Frequent automatic calibrations are necessary because of decreasing sensitivity with time. To achieve the highest reproducibility typical calibration intervals are multiple times per day. VURF instruments require very high purity operating gases (99.999% or better) to prevent the system from degradation.

Further regular maintenance includes the exchange of inlet filters (e.g. every two weeks depending on pollution level), the regeneration of the moisture trap, operation and calibration gas replacement, check of the CO removing catalyst (to produce zero air) with an independent CO free zero air source, and cleaning of optical parts. The cleaning of optical parts requires trained personnel. The frequency of cleaning depends on the pollution level in the air being measured, as well as the purity of the operating gas. Cleaning of the optics is necessary whenever the sensitivity falls below 10 counts/ppb.

The oxygen content of calibration gases must be the same as in ambient air (20.90-21.00%) because the UV resonance fluorescence of carbon monoxide is quenched in the presence of oxygen. Natural variations in the oxygen content of ambient air are not large enough to introduce any significant bias into the measurements.

#### **6.4.3 Time resolution**

Depending on scientific needs a time resolution of the measurements of one second or better can be obtained.

#### **6.4.4 Known problems**

Degradation of windows and other optical parts is a concern. It is not recommended to use this technique on a continuous basis at highly polluted sites because organic compounds will contaminate the optics. Water interferes with the UV fluorescence of carbon monoxide. The analyser is equipped with a permeation drier to avoid interferences. It is recommended to monitor the operation of the pump, especially when regeneration intervals of the moisture trap become longer. In case of CO contamination of the purge air by the pump, the original pump must be replaced by a membrane pump. There is a need to make sure that both calibration and sample gas pass through the dryer. Alternatively, the permeation drier can be removed and replaced by a cryogenic water trap.

### **6.5 Wavelength-Scanned Cavity Ring Down Spectroscopy (WS-CRDS)**

#### **6.5.1 Instrumentation**

Wavelength-Scanned Cavity Ring Down Spectroscopy (WS-CRDS) is a relatively new analytical technique and its performance is expected to approach that of the VURF method. Reproducibility of the method is  $\pm 2 \text{ nmol mol}^{-1}$  (2 standard deviation for 5 minutes average), minimum detection limit is not determined.

#### **6.5.2 Operation, maintenance & QA/QC**

Stable long-term operation should be possible with minimal service or maintenance; however, due to the novelty of the technique no long-term experience has been gained so far (mid-2010).

The system requires calibration with at least one standard gas, and the linearity should be confirmed regularly using three or more standards or by dilution of a high mole fraction standard. In addition, zero checks using CO free air are recommended. The frequency of these maintenance checks need to be sufficient to account for instrument drift and will need to be determined empirically.

#### **6.5.3 Time resolution**

WS-CRDS is a high frequency measurement; however, current instruments show significant instrumental noise for short integration times. Typical  $2\sigma$  noise is approximately  $32 \text{ nmol mol}^{-1}$  for a time resolution of five seconds, and  $2 \text{ nmol mol}^{-1}$  for five minutes at ambient CO levels.



#### 6.5.4 **Known problems**

Due to the novelty of the technique no long-term experience has been gained yet (mid-2010).

### 6.6 **Cavity-Enhanced Quantum Cascade Laser (QCL) Instruments**

#### 6.6.1 **Instrumentation**

Cavity-Enhanced Quantum Cascade Laser (QCL) also is a relatively new monitoring technique for carbon monoxide, and its performance is expected to be comparable to, or even better than the VURF method. Reproducibility of the method is  $\pm 0.6$ - $1.2$  nmol mol<sup>-1</sup> (2 standard deviations for a 30 second average), minimum detection limit is less than 1 nmol mol<sup>-1</sup>.

#### 6.6.2 **Operation, maintenance & QA/QC**

No experience with this very recent method has been obtained so far (until mid-2010).

#### 6.6.3 **Time resolution**

QCL is a fast measurement technique, and data rates up to 20 Hz are possible.

#### 6.6.4 **Known problems**

Due to the novelty of the technique no long-term experience has been gained so far.

### 6.7 **Other techniques**

In-situ carbon monoxide measurements are also possible with other than the above measurement techniques. Because these other techniques are usually not used for routine measurements they are only briefly mentioned here. These techniques include Fourier Transform Infrared Spectroscopy (FTIR) [Esler, *et al.*, 2000] and Tunable Diode Laser Spectroscopy (TDLS) [Sachse *et al.*, 1987]. These techniques both provide multi-species analysis and can be implemented for in-situ continuous CO measurements.

### 6.8 **Summary of the available techniques and recommended applications**

Comparable CO measurements are possible using different analytical techniques. In Figure 2 it can be seen that four techniques described above (6.1- 6.4) were able to detect fast changes in the mole fractions [Zellweger, *et al.*, 2009]. The overall agreement was better than 2% for 1-hourly averages; the remaining bias between the techniques could be attributed to different temporal coverage (continuous vs. discrete methods) and measurement uncertainties.

#### **NDIR**

Advantages: Least expensive, common principle, little maintenance, robust  
Disadvantages: High detection limit depending on instrument, high instrument noise, drift, frequent zero and span checks and calibration are mandatory, requires careful calibration at least weekly  
*Recommended use:* Best suited for locations where CO concentrations are 3 or more times instrument detection limit, i.e. stations in the Northern Hemisphere or sites impacted by regional sources

#### **GC/HgO**

Advantages: Good repeatability, low detection limit, simultaneous detection of H<sub>2</sub>.  
Disadvantages: Non-linear response, labour intensive: requires regular determination of calibration function  
*Recommended use:* Remote sites, long-term monitoring at sites where measurements of H<sub>2</sub> are also of interest

#### **VURF**

Advantages: High frequency measurements, linear, low detection limit, good repeatability  
Disadvantages: Currently only one manufacturer, expensive, challenging cleaning procedures, two high-quality gases for operation needed  
*Recommended use:* For measurements requiring high temporal resolution and high reproducibility, e.g. for the calibration of standards

**GC/FID**

*Advantages:* Linear, low detection limit, good repeatability; simultaneous detection of CH<sub>4</sub>, CO<sub>2</sub> and N<sub>2</sub>O / SF<sub>6</sub> (using an ECD) possible.

*Disadvantages:* Labour intensive

*Recommended use:* Remote sites, long-term monitoring at sites where measurements of greenhouse gases (CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, SF<sub>6</sub>) are of interest.

**WS-CRDS**

*Advantages:* Linear, simultaneous detection of CO<sub>2</sub> and water vapour

*Disadvantages:* Currently only one manufacturer, expensive, only limited experience gained so far (mid-2010)

*Recommended use:* Moderately polluted or remote sites where long enough integration times are possible

**QCL**

*Advantages:* Linear, fast, low detection limits, simultaneous detection of N<sub>2</sub>O possible depending on the laser

*Disadvantages:* Currently only one manufacturer, limited knowledge due to short experience (mid-2010), expensive

*Recommended use:* For measurements requiring high temporal resolution and high reproducibility on small sample volumes, e.g. for the calibration of standards

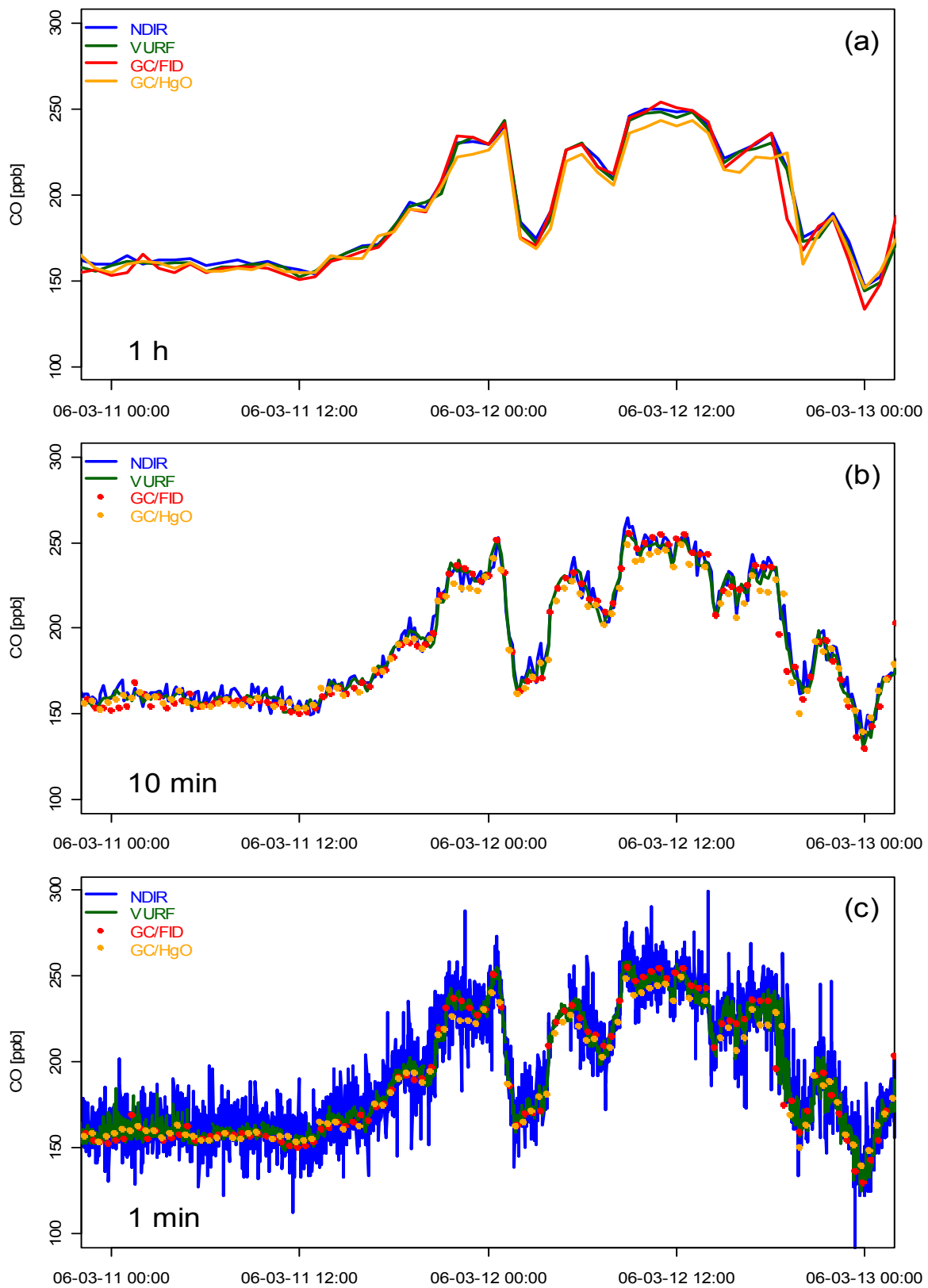


Figure 2 - CO time series obtained with four different measurement techniques for a selected period in March 2006 at Jungfraujoch (JFJ), for (a) one-hourly averages, (b) 10-minute averages (VURF, NDIR) / single injections (GC), (c) 1 minute averages (VURF, NDIR) / single injections (GC).

## 7. THE GAW CO SCALE

### 7.1 The NOAA and WMO reference scale

NOAA/ESRL is the Central Calibration Laboratory (CCL) for CO measurements in the GAW Programme. The NOAA/WMO reference scale for measurements of atmospheric CO (formerly cited as the NOAA/CMDL reference scale) is based upon several sets of CO-in-air mixtures prepared every 4-5 years by static gravimetric dilution ("primary standards") [Novelli, *et al.*, 1991]. The method requires a series of precise dilutions defined by the weights of a pure substance and a diluent gas (typically zero air). The first set was prepared during 1988-1989 and included seventeen gravimetric standards. These compared to within 1% to a 10  $\mu\text{mol mol}^{-1}$  NIST/SRM (National Institute of Standards and Technology, USA/Standard Reference Material) diluted to atmospheric levels using the gravimetric method. All measurements prior to 2001 were made using gas chromatography with hot mercuric oxide detection. The CCL maintains a suite of 12 secondary reference gases ranging from 20 to 500  $\text{nmol mol}^{-1}$  which display  $\sim 10$  year reproducibility of  $< 1 \text{ nmol mol}^{-1}$ . Mole fractions assigned to the secondary reference gases are compared to new sets of primary standards and adjusted if necessary. Laboratory and working standards are prepared with an uncertainty of  $\sim 2\%$  ( $k=2$ ).

Two scales are currently used as the WMO reference, namely WMO-2000 (1990-2003) and WMO-2004 (2004-present, i.e. year 2010). The 2000 scale is based upon measurements using GC-HgO with a correction for instrument non-linearity; the 2004 scale is based on measurements made by resonance fluorescence of CO in the vacuum ultraviolet (see section 6 for detailed descriptions of these measurement techniques). The two scales are consistent to better than 1  $\text{nmol mol}^{-1}$  at CO above  $\sim 110 \text{ nmol mol}^{-1}$  and 2-3  $\text{nmol mol}^{-1}$  between 40 and 110  $\text{nmol mol}^{-1}$  and agree well with different National Metrology Institute scales (NMI, all approx. 10  $\mu\text{mol mol}^{-1}$  in air, diluted to atmospheric levels). Since 2004 CCL calibrations have been made using VURF and are referenced to the 2004 scale. The 2004 scale is stable to within better than 2  $\text{nmol mol}^{-1}$  ( $k=2$ ). The VURF fluorescence technique allows a more precise and repeatable measurement than previous techniques thus providing improved calibration. The 2000 and 2004 scales will be revised to provide a single NOAA/WMO reference scale from 1990 onward.

Revisions to the WMO trace gas scales occur. These occur due to a variety of reasons, including reduction in the measurement uncertainty, correction for biases or other systematic errors, correction for drifting standards or re-evaluation of instrument response. All changes of the scale are documented and made public by CCL. Therefore it is necessary that the data management system used has the ability to reprocess mole fractions based on revised standard values.

### 7.2 Other reference scales

The Commonwealth Science and Industrial Research Organization (CSIRO) carbon monoxide calibration scale is sometimes referenced as Scripps Institution of Oceanography (SIO) scale (SIO-1998), especially for atmospheric CO measurements made within the Advanced Global Atmospheric Gases Experiment (AGAGE) programme. It is tied to the NOAA/WMO 1988 scale by a single standard with a CO mole fraction assigned of 195.7  $\text{nmol mol}^{-1}$  air. This standard is one of five synthetic mixtures of CO<sub>2</sub>, CH<sub>4</sub>, and CO in zero air (with CO mole fractions calibrated for CSIRO Atmospheric Research by NOAA/ESRL between 1992 and 1994). Only the standard with the highest CO mole fractions was used to link the CSIRO scale to the WMO-88 gravimetric CO scale because significant differences have been found between CSIRO's and NOAA's determination of relatively low CO-in-air mixtures exchanged since 1994 [Masarie, *et al.*, 2001].

Using the single standard as the fixed reference point for linking to the WMO-88 gravimetric scale, dilution experiments at CSIRO showed differences between CSIRO and NOAA of up to 4  $\text{nmol mol}^{-1}$  at lower CO mole fractions. These differences are not constant over the time and are most pronounced at CO mole fractions less than 100  $\text{nmol mol}^{-1}$ , and are most likely due to different treatment of instrument non-linearity in each laboratory. The long-term stability of the CSIRO CO standards, and variations in instrument response over time, are monitored with  $\sim 20$  high-pressure cylinder standards maintained at CSIRO Marine and Atmospheric Research. These

standards have lifetimes of 4 – 10+ years, with CO mixing ratios spanning the range 20 – 400 nmol mol<sup>-1</sup> (additional information is provided at [http://cdiac.ornl.gov/ftp/ale\\_gage\\_Agage/AGAGE/gc-md/COcalibration.doc](http://cdiac.ornl.gov/ftp/ale_gage_Agage/AGAGE/gc-md/COcalibration.doc)).

Several NMIs such as the United States National Institute for Standards and Technology (NIST), the Netherlands Measuring Institute (NMI, in 2009 NMI was renamed as the Van Swinderen Laboratorium (VSL)) and the United Kingdom's National Physical Laboratory (NPL) produce and sell gravimetric carbon monoxide-in-nitrogen or carbon monoxide-in-air reference standards. In contrast to the above CO scales these standards cover only a concentration range starting at 10 µmol mol<sup>-1</sup> up to several percent CO in air or nitrogen. Such reference standards must be diluted when used for the characterization of instruments or calibration of standards.

*New stations must perform measurements on the official reference scale. For active stations submitted data are recommended to be converted to the WMO standard scale or a conversion factor(s), if known, must be reported as a part of meta data.*

### **7.3 Scale comparisons and harmonisation**

No systematic CO scale comparisons have been published since Novelli et al. [1998] although informal comparisons among various laboratories show differences well beyond those set out by the DQOs. It is therefore difficult to merge CO data sets from different labs. Comparisons of results from co-located sampling can be made using data available from the World Data Center for Greenhouse Gases (WDCGG, Tokyo, Japan); <http://gaw.kishou.go.jp/wdcgg/>). As noted previously, a primary objective of the GAW global CO network is to work towards bringing measurements to a compatibility of ±2 nmol mol<sup>-1</sup>.

## **8. QUALITY ASSURANCE AND QUALITY CONTROL**

The goal of GAW measurements is to produce long-term records of known quality that are adequate for their intended use. Hence it is imperative that the measurement activities be quality-assured and the data be quality controlled. The following general description of QA/QC principles is intended to serve individual stations as a basis from which their own guidelines for long-term QA/QC plans can be modified or adopted.

### **8.1 Calibration**

#### **8.1.1 Hierarchy of standards**

All methods used to measure atmospheric CO require reference gases. NOAA is the designated Central Calibration Laboratory for CO. The CCL maintains the scale with a set of the secondary standards. The secondary standards are used to calibrate CCL working standards (section 7.1). GAW stations should use either laboratory standards obtained from the CCL, or standards that are directly traceable to the NOAA/WMO scale.

Laboratory standards can be used to transfer the scale to working standards. Note that any analytical error in this transfer will be propagated into the working standards. The laboratory must then determine the combined standard uncertainty of the assigned value. Alternatively, the laboratory standards obtained from the CCL can be used directly as working standards. This provides the most direct link to the CCL.

Target cylinders (also referred to as target gases or target tanks) are well-calibrated CO mixtures in the range of ambient atmospheric concentrations. Target gases can be prepared on site and calibrated against laboratory or working standards. These cylinders are usually analyzed daily using the appropriate number of independent, successive measurements with the aim of monitoring the stability of the analytical system.

### **8.1.2 Calibration recommendations**

The quality of the measurement results can be no better than the quality of the calibration. Care should be given in choosing the correct calibration protocol for the measurements. Analytical methods which have a non-linear response need to be calibrated using multiple standards that span the CO range encountered onsite. Linearity of response is evaluated as the ratio of instrument response to standard assigned value. These response factors should be the lesser one of  $\pm 0.5\%$  of the mean and the reproducibility of the instrument over the range of CO to be considered linear.

Instruments with linear response can, in principle, be calibrated using a single standard; however, two standards spanning the range of CO are recommended. The relative change in two standards provides an indication of drift. The required frequency of calibration is instrument-dependent and should be determined empirically.

As noted previously, the CO mole fractions of standard gases may change over time. While the reasons for this are not well known, drift appears to be related to a number of cylinder characteristics, including material, pressure, and internal volume. Therefore, the stability of standards must be monitored through comparison of a family of cylinders, audits (Section 8.3) and by recalibration by the CCL at least every two years. Data processing system software must include the ability to reprocess raw data based on time-dependent changes in standard values.

## **8.2 Measurement protocol**

Each measurement site should have a field log book. This should preferably be electronic and remotely accessible. The field log should contain any information which may be important for the interpretation of the measurement data.

Each measurement instrument should further have its own (electronic) log book. The instrument log should contain all information on instrument maintenance, calibration, failures etc. Each measurement instrument should also have an (electronic) check list, which is completed regularly. Alternatively (or in addition) instrument status information may be collected on the data acquisition. Instrument check lists should contain relevant instrument information such as temperatures, flow rates, calibration factors, carrier and reference tank pressures, sensitivities etc. (depending on instrument type).

Instrument manuals should be available at the site.

Log book records can be used as a basis for corrective actions if needed. Log entries (site and instrument) should be available when data is reviewed. QC procedures should include regular visual time series inspection and comparison with other available data [WMO, 2003; 2009c]. Raw data should be flagged for further use and validated data may further be classified (Section 9.1). Data flags may vary depending on the analytical technique and the local environment, but should in general allow distinguishing between valid ambient data, data obtained during checks and calibrations, questionable data, and invalid data.

All data (including the raw data) must be properly archived and managed at the station.

## **8.3 Audit procedures**

The CCL has repeatedly conducted round-robin comparison experiments that are highly recommended to all flask analysis laboratories and that may also provide valuable QA information for continuous measurements.

The World Calibration Center (WCC) for carbon monoxide is hosted at Empa. WCC-Empa has endeavoured to improve the international comparability of continuous CO measurements by implementing an audit system at global sites of the GAW programme. These audits are conducted on site and are part of the QA system requested in the GAW Strategic Plan [WMO, 2007]. An audit involves representatives from WCC-Empa evaluating the overall conformity of a station with the principles of the GAW QA system, as well as performing an on-site comparison of reference

gases and instruments. These activities usually require about one week. Results of the audits are provided to the participants and made available at the official WCC web site (<http://gaw.empa.ch>) and GAWSIS. A more detailed description of the audit procedure can be found in the WMO Guidelines for the Measurement of Methane and Nitrous Oxide and their Quality Assurance (WMO/GAW Report No. 185, [WMO, 2009c]).

#### **8.4 Measurement uncertainties**

All measurement data must be associated with a corresponding uncertainty. The uncertainty largely depends on the measurement technique and the realisation of the measurement itself, including the design and operation of the complete analytical system. Due to the individuality and complexity of different analytical set-ups, each laboratory must assess the uncertainty of its own specific system. The following briefly discusses contributions to the overall combined standard uncertainty of the measurements. Depending on the realisation of a specific measurement, additional contributions to the uncertainty need to be considered. Uncertainty estimates should be derived and expressed according to international standards [GUM, 2008].

In essence, the *combined uncertainty* of a measurement contains contributions due to the sampling, the calibration scale, the transfer of the calibration scale to the instrument, the repeatability (short term variability) of the instrument, the reproducibility (longer term variability, including drift) of the instrument, and uncertainty introduced during data processing. Not all of these components can be clearly separated, e.g., uncertainty due to the transfer of the scale is linked to the limited repeatability and reproducibility of analytical equipment, and the distinction is somewhat arbitrary. In general, these contributions are independent, and therefore, the combined uncertainty is the square-root of the sum of the squared individual contributions. When the input quantities contain dependencies, terms containing covariances should account for this, which may increase or decrease the combined uncertainty. Uncertainties of measurements should always be reported with a statement of the *confidence level* or *coverage factor*.

##### **8.4.1 Uncertainty of the calibration scale**

The uncertainty of the calibration scale has a direct influence on the uncertainty of CO measurements. The accuracy in the CCL CO scale is less relevant than the ability of the CCL to propagate the scale to participating GAW laboratories/stations. The difference between the 2000 and 2004 CO scales is a negative bias of the 2000 scale compared to the 2004 scale of 2-3 nmol mol<sup>-1</sup> below ~110 nmol mol<sup>-1</sup>. Above ~110 nmol mol<sup>-1</sup>, two scales are compatible to better than 1 nmol mol<sup>-1</sup>. After 2004, using the 2004 scale, the uncertainty is estimated to be better than 2 nmol mol<sup>-1</sup> (k=2) over 40 to 300 nmol mol<sup>-1</sup>. The change resulted from lower errors associated with the analysis and the calibration functions.

##### **8.4.2 Uncertainty of the instrument calibration**

All analytical techniques for carbon monoxide measurements require calibration using standard gases. Each calibration results in setting new instrument calibration factor(s) (zero and span for linear instruments) or in a new calibration function (for non-linear detectors). Because only a limited number of calibrations are carried out, each single calibration may result in a bias to the true but unknown calibration of the instrument. The contribution of the calibration process to the combined uncertainty of the measurement is dependent on the measurement technique. It is expected that this contribution is smaller for the GC/FID, the UV Fluorescence and QCL techniques in comparison to the NDIR technique, because of good repeatability, linearity and frequent calibrations. For the NDIR technique, considerably larger instrument repeatability and drift add to the uncertainty of each calibration. For the GC/HgO technique, a potentially large contribution due to non-linearity must be expected, possibly resulting in an insufficient characterisation of the calibration function if only few standards are used.

If laboratory standards obtained from the CCL are used for to calibrate working standards, the additional uncertainty introduced by the calibration has to be considered.

The contribution of the calibration uncertainty to the overall uncertainty can be estimated using the reproducibility of repeated calibrations.

### **8.4.3 Uncertainty of the instrument**

All analytical techniques exhibit limited repeatability and reproducibility.

*Repeatability* - refers to the random fluctuations of repeated measurements. The uncertainty of a value due to repeatability can be reduced by averaging successive observations. There is no point in increasing the number of measurements once the uncertainty reaches its minimum. This point must be determined empirically.

A useful measure in this context is the minimum variance obtained from an Allan plot (e.g., [http://en.wikipedia.org/wiki/Allan\\_variance](http://en.wikipedia.org/wiki/Allan_variance)) that basically indicates after what integration time (or number of repetitions) the instrument drift becomes the factor limiting the quality of an observation. In the assessment of measurement uncertainty, it is critical to report the averaging time or the number of repetitions. If averaging times are long enough, a bias due to different analytical technique should not be observed in well-calibrated equipment. It has been shown [Zellweger, *et al.*, 2009] that instrument-specific uncertainties can be neglected for one hourly averages with four different CO measurement techniques (NDIR, VURF, GC/FID, GC/HgO as presented in Figure 2).

*Reproducibility* - Frequent calibration of the instruments, or frequent application of calibration gases with known mole fractions help characterise the instrument drift and are needed in post-processing of observations. The frequency of such checks and calibrations depends on the nature of the instrument, the availability and consumption of calibration gases, and the trade-off between time spent for calibration and time spent for measurement.

### **8.4.4 Uncertainty of data processing**

Some measurement techniques require post-analytical data treatment, e.g. for the compensation of zero or span drift, or nonlinear response of the detector. Such corrections are associated with uncertainties, which need to be considered in the uncertainty budget.

### **8.4.5 Other sources of uncertainty**

In addition to the above factors, interferences and/or changing environmental conditions may further influence the measurements and consequently have an influence on the associated uncertainties. These influences are often difficult to assess, but should not be neglected for the uncertainty budget. In particular, the inlet and sampling system must be checked regularly for leaks and degradation.

## **9. DATA MANAGEMENT**

### **9.1 Data evaluation, flagging and control**

Here data processing and evaluation is described. Data processing may include both automatic quality control and manual review.

The purpose of data evaluation, flagging and control is to arrive at a time series of mole fractions that represents ambient conditions and to clearly identify artefacts as such. No entries should ever be removed from a data set. Samples designated as not representing atmospheric composition should be identified by a character in the data string (flagged). The periods of automatic and/or manual calibration or maintenance as well as instrument problems should be clearly flagged. Instrumental problems are sometimes not obvious and identifying them in the time series may require significant experience. A well-maintained logbook is indispensable to aid this process.

Additionally plotting the mole fractions preferably in conjunction with some other variables that are expected to correlate with ambient carbon monoxide is recommended. The purpose of this



is to identify data points that are clearly outliers<sup>‡</sup>. More sophisticated data analysis (e.g. curve fitting) is also a useful tool for identifying outliers. Outliers should be flagged as such.

The calibrated and evaluated CO data of high temporal resolution will be aggregated to hourly, daily, weekly, monthly and yearly averages. Each time aggregate should be accompanied by an appropriate uncertainty estimate (Section 8.4).

Validated data can be further classified according to the origin of air masses. Such flags should then be explained in metadata (section 9.2), which should be submitted to the data centre along with data and ancillary data (in particular, meteorological data) of relevance for data interpretation.

For rapid delivery of data, automatic processing and data quality control (including simplified flagging) is required. These preliminary data are not required to conform with the DQOs.

## 9.2 Metadata

Metadata is information about the data (in this document the data is CO mole fraction) that is necessary to make use of data. Mole fractions without metadata are incomplete, and by themselves of limited value. Metadata states what a dataset is all about, where and when the data were collected, the reference scale, method, measurement unit, operator, and other critical information needed to understand the data.

The World Data Centre for Greenhouse Gases (WDCGG), which is responsible for archiving carbon monoxide data for GAW, has published a data submission and dissemination guide [WMO, 2009b] that explains the requirements and procedures to be followed.

## 9.3 Ancillary data

The distinction between ancillary data and metadata is largely a matter of perspective. Unlike metadata, ancillary data are not indispensable for using the data but serve as additional information valuable for interpreting it. The most relevant ancillary data in this context are the meteorological variables: temperature, pressure, relative humidity, wind direction and wind speed.

## 9.4 Data archiving at the station or laboratory

The data producer is responsible for design and maintenance of an appropriate data archive (see e.g., [Masarie and Tans, 2003]). It is recognized that different laboratories may choose to implement the guidelines and examples therein in different ways. The following general guidelines apply:

1. Data and corresponding metadata should be recorded and archived with reference to Universal Time Coordinated (UTC).
2. Date/Time stamps should be expressed in ISO standard format<sup>§</sup> and must be clearly indicated whether they mark the beginning or end of the sampling period covered for continuous measurements<sup>\*\*</sup>, and the start time of sampling for discrete measurements<sup>††</sup>.

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<sup>‡</sup> Considering a measurement result to be a random variable, 'outliers' are confined to values that are not sampled from the same distribution as the regular measurements. Examples include abnormal readings due to a power surge, defective sensors, contamination, or operator interference. Values that remain unexplained even after scrutiny and within a reasonable distance from the median should be regarded as 'extreme' values. Whereas 'outliers' can be removed from the analysis of a set of experimental results, 'extreme' values cannot. All data should remain in the data set, appropriately flagged.

<sup>§</sup> The ISO 8601 notation for date and time is yyyy-mm-dd HH:MM:SS or: yyyymmddHHMMSS. This notation does neither specify the time zone nor any deviation from it (such as day light savings time). This information must be given in the context. If the date and time refer to Universal Time Coordinated (UTC) and this is not obvious from the context, a 'Z' may be added to the date and time string.

<sup>\*\*</sup> Measurements are called 'continuous' if air is continuously sampled and the analytical result is an integral with a specified temporal resolution. These analyses are usually averaged internally by the instrument to obtain aggregates. A typical example is an

3. All raw data must be kept in electronic form in at least two physically different and safe locations and must not be altered in any way.
4. Provisions must be in place to guarantee readability of the raw data files for the indefinite future. This may require reformatting the raw data which is not considered an alteration.
5. Raw data and the relevant logbook(s) must be readily available.
6. Data products (such as aggregates) should be calculated from the highest frequency data available. All procedures must be unambiguously documented.

### **9.5 Data submission**

The global data archive for carbon monoxide measurements is the World Data Centre for Greenhouse Gases (WDCGG) maintained by the Japan Meteorological Agency (JMA, <http://gaw.kishou.go.jp/wdcgg>). All CO data obtained as part of the GAW programme should be submitted within one year to the WDCGG. Continuous and quasi-continuous data may be reported as hourly averages (preferred) or higher aggregates. The data must be accompanied with appropriate metadata. The WDCGG also accepts flask and campaign data. Submittal of ancillary data is encouraged. Data submitters should consult the WDCGG data submission guidelines [WMO, 2009c] or contact the WDCGG for instructions.

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*NDIR analyzer: Air is passed continuously through the sample cell, readings are taken every few seconds and aggregates of 1 minute or more are reported.*

*†† Measurements are called 'discrete' if air is sampled and analyzed at discrete points in time (grab samples). Typical examples include flask sampling programmes or GC systems that fill a sample loop prior to each injection.*

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## Abbreviations and Acronyms

AGAGE	Advanced Global Atmospheric Gases Experiment
CCL	Central Calibration Laboratory
CMDL	Climate Monitoring and Diagnostics Laboratory, NOAA (now Global Monitoring Division of the Earth System Research Laboratory, NOAA ESRL)
CSIRO	Commonwealth Scientific & Industrial Research Organisation
DQO	Data Quality Objectives
ECD	Electron Capture Detector
Empa	Swiss Federal Laboratories for Materials Testing and Research
ESRL	Earth System Research Laboratory, NOAA
FID	Flame Ionisation Detector
GAW	Global Atmosphere Watch (WMO Programme)
GC	Gas Chromatography
GG or GHG	Greenhouse Gases
GMD	Global Monitoring Division (as part of NOAA ESRL)
ICP	InterComParison experiment
ISO	International Organization for Standardization
MG	Measurement Guidelines
NDIR	Non Dispersive Infrared
NIST	National Institute of Standards and Technology
NMI	National Metrology Institute, National Measurement Institute
NOAA	National Oceanic and Atmospheric Administration (USA)
QA	Quality Assurance
QA/SAC	Quality Assurance/Science Activity Centre
QC	Quality Control
QCL	Quantum Cascade Laser Spectroscopy
SAG	Scientific Advisory Group
SIO	Scripps Institution of Oceanography
SOP	Standard Operating Procedure
SRM	Standard Reference Material
VURF	Vacuum-UV Resonance Fluorescence
WCC	World Calibration Centre
WDCGG	World Data Center for Greenhouse Gases
WMO	World Meteorological Organization
WS-CRDS	Wavelength-Scanned Cavity Ring Down Spectroscopy

## Terms and Definitions

For convenience, the main QA/QC-related terms and definitions used in this document are given in this section. A more comprehensive glossary is available through the internet: <http://gaw.empa.ch/glossary.html>

### Adjustment of a measuring system (adjustment)

Set of operations carried out on a measuring system so that it provides prescribed indications corresponding to given values of a quantity to be measured [1].

#### NOTES

- 1) *Types of adjustment of a measuring system include zero adjustment of a measuring system, offset adjustment, and span adjustment (sometimes called gain adjustment).*
- 2) *Adjustment of a measuring system should not be confused with calibration, which is a prerequisite for adjustment.*
- 3) *After an adjustment of a measuring system, the measuring system must usually be recalibrated.*

### Assigned value (of a quantity)

Synonym for conventional true value [2].

#### NOTE

*The term 'conventional true value' is no longer defined in the VIM [1], which distinguishes between conventional value and true value.*

### Audit

- 1) Performance audit: Voluntary check for conformity of a measurement where the audit criteria are the data quality objectives (DQOs) for the specific parameter. In the absence of formal DQOs, an audit will at least involve ensuring the traceability of measurements to the Reference Standard. [7]
- 2) System audit: More generally defined as a check of the overall conformity of a station with the principles of the GAW system [7].

### Calibration

Operation that, under specified conditions, in a first step, establishes a relation between the quantity values with measurement uncertainties provided by measurement standards and corresponding indications with associated measurement uncertainties and, in a second step, uses this information to establish a relation for obtaining a measurement result from an indication [1].

#### NOTES

- 1) *A calibration may be expressed by a statement, calibration function, calibration diagram, calibration curve, or calibration table. In some cases, it may consist of an additive or multiplicative correction of the indication with associated measurement uncertainty. [1]*
- 2) *Calibration should not be confused with adjustment of a measuring system, often mistakenly called "self-calibration", nor with verification of calibration.*
- 3) *Often, the first step alone in the above definition is perceived as being calibration.*

### Central Calibration Laboratory (CCL)

Within the WMO/GAW network, the laboratory responsible for maintaining the standard scale for the species under consideration.

### Combined standard measurement uncertainty

Standard measurement uncertainty that is obtained using the individual standard measurement uncertainties associated with the input quantities in a measurement model.

#### NOTE

1) In case of correlations of input quantities in a measurement model, covariances must also be taken into account when calculating the combined standard measurement uncertainty; see also ISO/IEC Guide 98-3:2008, 2.3.4

#### Conventional reference scale

Quantity-value scale defined by formal agreement [1].

#### NOTES

1) The scale is based upon a number of primary measurement standards and a measurement procedure to interpolate other values.

2) Within WMO/GAW, the conventional reference scale refers in particular to the calibration scale used within the GAW network. In the case of CO this scale is implemented as a family of gas cylinders maintained at the CCL (NOAA).

#### Correction

Compensation for an estimated systematic effect [1].

#### NOTES

1) See ISO/IEC Guide 98-3:2008, 3.2.3, for an explanation of 'systematic effect'

2) The compensation can take different forms, such as an addend or a factor, or can be deduced from a table.

#### Coverage factor

Number larger than one by which a combined standard measurement uncertainty is multiplied to obtain an expanded measurement uncertainty [1]

#### NOTES

1) A coverage factor is usually symbolized  $k$  (see also ISO/IEC Guide 98-3:2008, 2.3.6).

2) Coverage factors are typically in the range 2 to 3.

#### Coverage interval

Interval containing the set of true quantity values of a measurand with a stated probability, based on the information available [1].

#### NOTES

1) A coverage interval does not need to be centred on the chosen measured quantity value (see ISO/IEC Guide 98-3:2008/Suppl.1).

2) A coverage interval should not be termed "confidence interval" to avoid confusion with the statistical concept (see ISO/IEC Guide 98-3:2008, 6.2.2).

3) A coverage interval can be derived from an expanded measurement uncertainty (see ISO/IEC Guide 98-3:2008, 2.3.5).

#### Coverage probability

Probability that the set of true quantity values of a measurand is contained within a specified coverage interval [1].

#### NOTES

1) This definition pertains to the Uncertainty Approach as presented in the GUM [4].

2) The coverage probability is also termed "level of confidence" in the GUM [4].

#### Data Quality Objectives (DQOs)

Qualitative and quantitative statements that clarify the objectives of observations, define the appropriate type of data, and specify tolerable levels of uncertainty. DQOs will be used as the basis for establishing the quality and quantity of data needed to support decisions.

#### NOTE

1) *Decisions in this context include scientific decisions (e.g. significance testing of trends) as well as decisions of political or societal dimension.*

#### Expanded measurement uncertainty)

Product of a combined standard measurement uncertainty and a factor larger than the number one [1] quantity defining an interval about the result of a measurement that may be expected to encompass a large fraction of the distribution of values that could reasonably be attributed to the measurand [4].

#### NOTES

- 1) *The factor depends upon the type of probability distribution of the output quantity in a measurement model and on the selected coverage probability [1].*
- 2) *The term "factor" in this definition refers to a coverage factor [1].*
- 3) *Expanded measurement uncertainty is termed "overall uncertainty" in paragraph 5 of Recommendation INC-1 (1980) (see the GUM) and simply "uncertainty" in IEC documents [1].*

#### Indication

Quantity value provided by a measuring instrument or a measuring system [1].

#### NOTES

- 1) *An indication may be presented in visual or acoustic form or may be transferred to another device. An indication is often given by the position of a pointer on the display for analog outputs, a displayed or printed number for digital outputs, a code pattern for code outputs, or an assigned quantity value for material measures.*
- 2) *An indication and a corresponding value of the quantity being measured are not necessarily values of quantities of the same kind.*

#### Instrumental bias

Average of replicate indications minus a reference quantity value [1].

#### Laboratory standard

Standard of highest rank at an individual laboratory or station traceable to the WMO/GAW standard scale.

#### Measurand

Quantity intended to be measured [1].

#### Measured quantity value

Measured value of a quantity measured value quantity value representing a measurement result.

#### NOTES

- 1) *For a measurement involving replicate indications, each indication can be used to provide a corresponding measured quantity value. This set of individual measured quantity values can be used to calculate a resulting measured quantity value, such as an average or median, usually with a decreased associated measurement uncertainty.*
- 2) *When the range of the true quantity values believed to represent the measurand is small compared with the measurement uncertainty, a measured quantity value can be considered to be an estimate of an essentially unique true quantity value and is often an average or median of individual measured quantity values obtained through replicate measurements.*
- 3) *In the case where the range of the true quantity values believed to represent the measurand is not small compared with the measurement uncertainty, a measured value is often an estimate of an average or median of the set of true quantity values.*
- 4) *In the GUM [3], the terms "result of measurement" and "estimate of the value of the measurand" or just "estimate of the measurand" are used for 'measured quantity value'.*



## Measurement

Process of experimentally obtaining one or more **quantity values** that can reasonably be attributed to a **quantity** [1].

### NOTES

- 1) *Measurement does not apply to **nominal properties**.*
- 2) *Measurement implies comparison of quantities and includes counting of entities.*
- 3) *Measurement presupposes a description of the quantity commensurate with the intended use of a **measurement result**, a **measurement procedure**, and a calibrated **measuring system** operating according to the specified measurement procedure, including the measurement conditions.*

## Measurement accuracy (accuracy of measurement, accuracy)

Closeness of agreement between a measured quantity value and a true quantity value of a measurand [1].

## Measurement bias

Estimate of a systematic measurement error [1].

## Measurement Guideline (MG)

Written instruction that provides basic information on various issues related to the measurement of a specific quantity. It usually covers major aspects ranging from instrumental set-up to obtaining final data and metadata of known quality.

### NOTE

*MGs permit more flexibility for the way the measurements are conducted than SOPs. Therefore MGs are used in the case of complex systems that can be differently set up and operated in practice. For each instrument type and set-up, SOPs should be developed and available to the operators of a system, see 'measurement procedure'.*

## Measurement error (error of measurement, error)

Measured quantity value minus a reference quantity value [1].

### NOTES

- 1) *The concept of 'measurement error' can be used both a) when there is a single reference quantity value to refer to, which occurs if a calibration is made by means of a measurement standard with a measured quantity value having a negligible measurement uncertainty or if a conventional quantity value is given, in which case the measurement error is known, and b) if a measurand is supposed to be represented by a unique true quantity value or a set of true quantity values of negligible range, in which case the measurement error is not known.*
- 2) *Measurement error should not be confused with production error or mistake.*

## Measurement precision (precision)

Closeness of agreement between indications or measured quantity values obtained by replicate measurements on the same or similar objects under specified conditions [1].

### NOTES

- 1) *Measurement precision is usually expressed numerically by measures of imprecision, such as standard deviation, variance, or coefficient of variation under the specified conditions of measurement.*
- 2) *The 'specified conditions' can be, for example, repeatability conditions of measurement, intermediate precision conditions of measurement, or reproducibility conditions of measurement (see ISO 5725-3:1994).*
- 3) *Measurement precision is used to define measurement repeatability, intermediate measurement precision, and measurement reproducibility.*
- 4) *Sometimes "measurement precision" is erroneously used to mean accuracy.*
- 5) *Measurement precision is a measure of the dispersion of values.*

### **Measurement procedure**

Detailed description of a measurement according to one or more measurement principles and to a given measurement method, based on a measurement model and including any calculation to obtain a measurement result [1].

#### **NOTES**

- 1) A measurement procedure is usually documented in sufficient detail to enable an operator to perform a measurement. [1].
- 2) A measurement procedure can include a statement concerning a target measurement uncertainty.
- 3) A measurement procedure is sometimes called a standard operating procedure (SOP).
- 4) Within WMO/GAW, a measurement procedure can be replaced by a measurement guideline (MG) if a measurement can be realized in too many different ways.

### **Measurement repeatability (repeatability)**

Measurement precision under a set of repeatability conditions of measurement [1].

### **Measurement reproducibility (reproducibility)**

Measurement precision under reproducibility conditions of measurement [1].

#### **NOTES**

- 1) Relevant statistical terms are given in ISO 5725-1:1994 and ISO 5725-2:1994.
- 2) see NOTES under reproducibility condition of measurement.

### **Measurement result (result of a measurement)**

Set of quantity values being attributed to a measurand together with any other available relevant information [1].

#### **NOTES**

- 1) A measurement result generally contains "relevant information" about the set of quantity values, such that some may be more representative of the measurand than others. This may be expressed in the form of a probability density function (PDF).
- 2) A measurement result is generally expressed as a single measured quantity value and a measurement uncertainty. If the measurement uncertainty is considered to be negligible for some purpose, the measurement result may be expressed as a single measured quantity value. In many fields, this is the common way of expressing a measurement result.
- 3) In the traditional literature and in the previous edition of the VIM [2], measurement result was defined as a value attributed to a measurand and explained to mean an indication, or an uncorrected result, or a corrected result, according to the context.

### **Measurement standard (etalon)**

Realization of the definition of a given quantity, with stated quantity value and associated measurement uncertainty, used as a reference [1]. See standard for a related definition.

#### **EXAMPLES**

- 1) 1 kg mass measurement standard with an associated standard measurement uncertainty of 3  $\mu\text{g}$ .
- 2) 100 Ohm measurement standard resistor with an associated standard measurement uncertainty of 1  $\mu\text{Ohm}$ .

### **Measurement trueness (trueness of measurement, trueness)**

Closeness of agreement between the average of an infinite number of replicate measured quantity values and a reference quantity value.

#### **NOTES**

- 1) Measurement trueness is not a quantity and thus cannot be expressed numerically, but measures for closeness of agreement are given in ISO 5725.

- 2) *Measurement trueness is inversely related to systematic measurement error, but is not related to random measurement error.*
- 3) *Measurement accuracy should not be used for 'measurement trueness' and vice versa.*
- 4) *Measurement trueness is an important concept for comparisons, e.g. to determine if measurements at different sites are on the same scale.*

### **Measurement uncertainty (uncertainty of measurement, uncertainty)**

Non-negative parameter characterising the dispersion of the quantity values being attributed to a measurand, based on the information used [1].

#### **NOTES**

- 1) *Measurement uncertainty includes components arising from systematic effects, such as components associated with corrections and the assigned quantity values of measurement standards, as well as the definitional uncertainty. Sometimes estimated systematic effects are not corrected for but, instead, associated measurement uncertainty components are incorporated.*
- 2) *The parameter may be, for example, a standard deviation called →standard measurement uncertainty (or a specified multiple of it), or the half-width of an interval, having a stated coverage probability.*
- 3) *Measurement uncertainty comprises, in general, many components. Some of these may be evaluated by Type A evaluation of measurement uncertainty from the statistical distribution of the quantity values from series of →measurements and can be characterized by standard deviations. The other components, which may be evaluated by Type B evaluation of measurement uncertainty, can also be characterized by standard deviations, evaluated from probability density functions based on experience or other information.*
- 4) *In general, for a given set of information, it is understood that the measurement uncertainty is associated with a stated quantity value attributed to the measurand. A modification of this value results in a modification of the associated uncertainty.*
- 5) *The concept of "uncertainty" is explained in detail in GUM [4]. In practice the term "error" (measurement error) seems to be often used when actually "uncertainty" is meant. An error is viewed as having two components, a random and a systematic component [4]. As further stated in this reference, "error" is an idealised concept and errors cannot be known exactly. "Error" and "uncertainty" are not synonyms, but represent completely different concepts.*

### **Measuring instrument**

Device used for making measurements, alone or in conjunction with one or more supplementary devices [1].

#### **NOTE**

- 1) *A measuring instrument that can be used alone is a measuring system.*

### **Measuring system**

Set of one or more measuring instruments and often other devices, including any reagent and supply, assembled and adapted to give information used to generate measured quantity values within specified intervals for quantities of specified kinds [1].

#### **NOTE**

- 1) *A measuring system may consist of only one measuring instrument.*

### **Metrological comparability of measurement results (comparability)**

Comparability of measurement results, for quantities of a given kind, that are metrologically traceable to the same reference [1].

#### **NOTES**

- 1) *For this definition, a 'reference' can be a definition of a measurement unit through its practical realization, or a measurement procedure including the measurement unit for a non-ordinal quantity, or a measurement standard.*
- 2) *Metrological comparability of measurement results does not*

necessitate that the measured quantity values and associated measurement uncertainties compared be of the same order of magnitude.

### **Metrological compatibility of measurement results (compatibility)**

Property of a set of measurement results for a specified measurand, such that the absolute value of the difference of any pair of measured quantity values from two different measurement results is smaller than some chosen multiple of the standard measurement uncertainty of that difference [1].

#### **NOTES**

1) *Metrological compatibility of measurement results replaces the traditional concept of 'staying within the error', as it represents the criterion for deciding whether two measurement results refer to the same measurand or not. If in a set of measurements of a measurand, thought to be constant, a measurement result is not compatible with the others, either the measurement was not correct (e.g. its measurement uncertainty was assessed as being too small) or the measured quantity changed between measurements.*

2) *Correlation between the measurements influences metrological compatibility of measurement results. If the measurements are completely uncorrelated, the standard measurement uncertainty of their difference is equal to the root mean square sum of their standard measurement uncertainties, while it is lower for positive covariance or higher for negative covariance.*

### **Metrological traceability**

Property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty [1].

#### **NOTES**

1) *For this definition, a 'reference' can be a definition of a measurement unit through its practical realization, or a measurement procedure including the measurement unit for a non-ordinal quantity, or a measurement standard.*

2) *Metrological traceability requires an established calibration hierarchy.*

3) *Specification of the reference must include the time at which this reference was used in establishing the calibration hierarchy, along with any other relevant metrological information about the reference, such as when the first calibration in the calibration hierarchy was performed.*

4) *For measurements with more than one input quantity in the measurement model, each of the input quantity values should itself be metrologically traceable and the calibration hierarchy involved may form a branched structure or a network. The effort involved in establishing metrological traceability for each input quantity value should be commensurate with its relative contribution to the measurement result.*

5) *Metrological traceability of a measurement result does not ensure that the measurement uncertainty is adequate for a given purpose or that there is an absence of mistakes.*

6) *A comparison between two measurement standards may be viewed as a calibration if the comparison is used to check and, if necessary, correct the quantity value and measurement uncertainty attributed to one of the measurement standards.*

7) *The ILAC considers the elements for confirming metrological traceability to be an unbroken metrological traceability chain to an international measurement standard or a national measurement standard, a documented measurement uncertainty, a documented measurement procedure, accredited technical competence, metrological traceability to the SI, and calibration intervals (see ILAC P-10:2002).*

8) *The abbreviated term "traceability" is sometimes used to mean 'metrological traceability' as well as other concepts, such as 'sample traceability' or 'document traceability' or 'instrument traceability' or 'material traceability, where the history ("trace") of an item is meant. Therefore, the full term of "metrological traceability" is preferred if there is any risk of confusion.*

9) *To minimize the accumulation of measurement uncertainty, institutes should maintain as direct a path as possible between their laboratory standards and the CCL.*

### **Primary measurement standard (primary standard)**

Measurement standard established using a primary reference measurement procedure, or created as an artifact, chosen by convention [1].

## EXAMPLES

- 1) Primary measurement standard of amount of substance concentration prepared by dissolving a known amount of substance of a chemical component to a known volume of solution.
- 2) Primary measurement standard for pressure based on separate measurements of force and area.
- 3) Primary measurement standard for isotope amount-of-substance ratio measurements, prepared by mixing known amount-of-substances of specified isotopes.

## Quality assurance

All planned and systematic actions necessary to provide adequate confidence that a product, process or service will satisfy given requirements for quality [5].

## Quality control

Operational techniques and activities that are used to fulfill given requirements for quality [5].

## Quantity

Property of a phenomenon, body, or substance, where the property has a magnitude that can be expressed as a number and a reference [1].

## NOTE

*The generic concept 'quantity' can be divided into several levels of specific concepts, e.g., 'length' can be specified as 'radius', or even more specifically, as 'radius of a circle'. The VIM [1] gives more detail and examples.*

## Random measurement error (random error of measurement, random error)

Component of measurement error that in replicate measurements varies in an unpredictable manner [1].

## NOTES

- 1) A reference quantity value for a random measurement error is the average that would ensue from an infinite number of replicate measurements of the same measurand.
- 2) Random measurement errors of a set of replicate measurements form a distribution that can be summarized by its expectation, which is generally assumed to be zero, and its variance.
- 3) Random measurement error equals measurement error minus systematic measurement error.
- 4) Because only a finite number of measurements can be made, it is only possible to determine an estimate of random error.

## Reference-value scale

Synonym for conventional reference scale

## Reference measurement standard (reference standard)

Measurement standard designated for the calibration of other measurement standards for quantities of a given kind in a given organization or at a given location [1].

## NOTE

*1) The term 'reference standard' was used in the WMO/GAW Reports 142 [6] and 156 to indicate the WMO/GAW primary standards or the organisation that maintains them. Since then, the term 'primary standard' has been preferred, in keeping with the ISO definition.*

## Repeatability condition of measurement (repeatability condition)

Condition of measurement, out of a set of conditions that includes the same measurement procedure, same operators, same measuring system, same operating conditions and same location, and replicate measurements on the same or similar objects over a short period of time [1]

## NOTES

1) A condition of measurement is a repeatability condition only with respect to a specified set of repeatability conditions.

2) In chemistry, the term "intra-serial precision condition of measurement" is sometimes used to designate this concept.

### **Reproducibility condition of measurement (reproducibility condition)**

Condition of measurement, out of a set of conditions that includes different locations, operators, measuring systems, and replicate measurements on the same or similar objects [1].

#### NOTES

1) The different measuring systems may use different → measurement procedures.

2) A specification should give the conditions changed and unchanged, to the extent practical.

### **Secondary measurement standard (secondary standard)**

Measurement standard established through calibration with respect to a primary measurement standard for a quantity of the same kind [1].

#### NOTES

1) Calibration may be obtained directly between a primary measurement standard and a secondary measurement standard, or involve an intermediate measuring system calibrated by the primary measurement standard and assigning a measurement result to the secondary measurement standard.

2) A measurement standard having its quantity value assigned by a ratio primary reference measurement procedure is a secondary measurement standard.

3) For trace gas measurements within WMO/GAW, this refers to a standard (natural air or synthetic gas mixture) with mole fractions for target species that are obtained from comparisons made by the Central Calibration Laboratory with primary standards kept at its laboratory.

### **Standard**

Material measure, measuring instrument, reference material or measuring system intended to define, realize, conserve, or reproduce a unit of one or more values of a quantity to serve as a reference [2].

#### NOTES

1) See measurement standard for current definition.

2) In the case of trace gas measurements, generally any gas (natural air or synthetic gas mixture) with assigned mole fractions traceable to an accepted standard scale.

3) Within WMO/GAW, the standard scales for CO is maintained by NOAA.

### **Standard Operating Procedure (SOP)**

A written document that details the method for a programme, operation, analysis, or action with thoroughly prescribed techniques and steps, and that is officially approved as the method for performing certain routine or repetitive tasks [5].

#### NOTE

*In WMO/GAW, the term is understood to refer to a document that describes the measurement and quality assurance processes involved in obtaining the value of a quantity in as much detail as necessary to be able to achieve stated data quality objectives. For a similar term, see 'measurement procedure'.*

### **Standard measurement uncertainty (standard uncertainty of measurement, standard uncertainty)**

Measurement uncertainty expressed as a standard deviation [1].

### **Systematic measurement error (systematic error of measurement, systematic error)**

Component of measurement error that in replicate measurements remains constant or varies in a predictable manner [1].

## NOTES

1) A reference quantity value for a systematic measurement error is a true quantity value, or a measured quantity value of a measurement standard of negligible measurement uncertainty, or a conventional quantity value.

2) Systematic measurement error, and its causes, can be known or unknown. A correction can be applied for a known systematic measurement error. [1]

3) Systematic measurement error equals measurement error minus random measurement error [1].

4) Systematic error may be constant or may depend on the value of the measurand.

5) For a measuring instrument, see also bias.

### Target cylinder (target gas)

Cylinder containing natural air or a synthetic gas mixture with assigned trace gas mole fractions that is treated as an (unknown) sample in a sequence of analyses.

#### NOTE

The target cylinder, or target gas, is used for quality control measures. In the hierarchy of standards the target gas is usually on the same level as a working standard.

### Tertiary standard

Standard calibrated at the CCL by comparison with secondary standards

#### NOTE

For trace gases, it is the CCL (NOAA) tertiary standards that are used as laboratory standards by the World Calibration Centres (WCC), GAW stations and participating laboratories.

### Transfer measurement device (transfer device)

Device used as an intermediary to compare measurement standards [1].

## NOTES

1) Sometimes, measurement standards are used as transfer devices.

2) For trace gas measurements within WMO/GAW, this refers in particular to compressed gas cylinders (natural air or synthetic gas mixture) for use at different locations with an assigned mole fraction of one or more trace species resulting from comparisons with laboratory standards by an approved laboratory, such as the WCC. In the case of short lived species an instrument from WCC can be transferred to the measurement location (e.g. for audit purpose).

3) The term transfer standard is often used in the same sense as travelling measurement standard. Here, 'transfer standard' is reserved for purposes when the standard scale is actually transferred.

### Travelling measurement standard (travelling standard)

Measurement standard, sometimes of special construction, intended for transport between different locations [1].

#### NOTES

1) For trace gas measurements within WMO/GAW, this refers in particular to compressed gas cylinders (natural air or synthetic gas mixture) for use at different locations with an assigned mole fraction of one or more trace species resulting from comparisons with laboratory standards by an approved laboratory, such as the WCC.

2) For stable gases, this is usually a high-pressure cylinder calibrated at the CCL or WCC for the purpose of audits or round-robin experiments.

### True quantity value (true value of a quantity, true value)

Quantity value consistent with the definition of a quantity [1].

#### NOTES

1) In the Error Approach to describing measurement, a true quantity value is considered unique and, in practice, unknowable. The Uncertainty Approach is to recognize that, owing to the

*inherently incomplete amount of detail in the definition of a quantity, there is not a single true quantity value but rather a set of true quantity values consistent with the definition. However, this set of values is, in principle and in practice, unknowable. Other approaches dispense altogether with the concept of true quantity value and rely on the concept of metrological compatibility of measurement results for assessing their validity.*

*2) In the special case of a fundamental constant, the quantity is considered to have a single true quantity value.*

*3) When the definitional uncertainty associated with the measurand is considered to be negligible compared to the other components of the measurement uncertainty, the measurand may be considered to have an "essentially unique" true quantity value. This is the approach taken by the GUM and associated documents, where the word "true" is considered to be redundant.*

### **World Calibration Centre (WCC)**

Part of the GAW network, responsible for quality assurance measures for one or more components, by way of audits and intercomparisons.

#### **NOTE**

*For each component under consideration, the WCC refers to the calibration scale maintained by the CCL designated by GAW.*

### **Working measurement standard (working standard)**

Measurement standard that is used routinely to calibrate or verify measuring instruments or measuring systems [1].

#### **NOTES**

*1) A working measurement standard is usually calibrated with respect to a reference measurement standard. [1]*

*2) In relation to verification, the terms "check standard" or "control standard" are also sometimes used. [1]*

*3) For stable gases, any gas (natural air or synthetic gas mixture) with assigned mole fractions of one or more trace species obtained from comparisons with the laboratory standard(s) of an individual laboratory or station, or from comparisons with transfer standards provided by another laboratory, such as the WCC.*

*4) For measurement of stable trace gases, usually gas cylinders denoted as working standards are employed as calibration cylinders for routine measurements.*

## **References for ANNEX II**

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This document has been reviewed by the SAG for Reactive Gases  
(see <http://www.wmo.int/pages/prog/arep/gaw/ScientificAdvisoryGroups.html>).

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