# ICOS Atmosphere Station Specifications

Edited by O. Laurent

**Version 2.0**

September 2020

Please cite this document as:

ICOS RI (2020): ICOS Atmosphere Station Specifications V2.0 (editor: O. Laurent). ICOS ERIC. https://doi.org/10.18160/GK28-2188

Last revision: 22 September 2020

# Document History

| Version | Date | Actions |
|---|---|---|
| 1.0 | 2014-10-18 | Creation |
| 1.1 | 2015-10-21 | Add $N_2O$ section. Modify boundary layer section. Recommendation on sample drying. Met sensor list update. |
| 1.2 | 2016-08-09 | Modify Boundary layer section. Recommendation on the Short Term Working Standard for short term variability correction (especially for $N_2O$). Add table of the recommended air mixture for the gas tank. Met sensor list update. |
| 1.3 | 2017-11-15 | Include Picarro G5310 for CO and $N_2O$ measurement. Recommend the use of dryer for $N_2O$ measurement. Recommendation on the instrument inlet pressure. Met sensor list update. |
| 2.0 | 2020-06-06 | Include ARMON radon monitor for radon measurement (section 2.2.6.). Update on the flask sampling specifications (section 2.2.4.) and flask sampling strategy (section 3.1). Include radiocarbon sampling strategy (section 3.2). Include Ecotech Spectronus (FTIR) as a recommended instrument for $CO_2$/$CH_4$/CO/$N_20$ (sections 3.3 and 4.1). Modify recommendations for $H_2O$ management and buffer volumes (section 3.3). Update the recommended mole fraction for cylinders (Table 12). Recommendations for $O_2$ measurement (section 5). |

# Contents

# Introduction

ICOS (Integrated Carbon Observation System) has as its main mission to provide the long-term observations required to understand the present state and predict future behavior of the global carbon cycle and greenhouse gas emissions.

ICOS is a distributed research infrastructure comprising three coordinated, complementary operational observation networks: atmospheric observatories of concentrations of $CO_2$, $CH_4$, $N_2O$ and other greenhouse gases (GHG's), terrestrial flux tower sites to measure the ecosystem exchange of $CO_2$, water vapor and energy, and oceanographic observation platforms including volunteer ships monitoring air-sea fluxes.
Operational monitoring by these networks relies on several central facilities:

- an Atmosphere Thematic Center (ATC) for data processing, quality management and Research and Development (R&D),
- an Ecosystem Thematic Center (ETC)
- an Ocean Thematic Center (OTC),
- a Central Analytical Laboratory (CAL) for the preparation of calibration material and flask sample analysis,
- a data portal (Carbon portal) which will provide easy dissemination of and access to ICOS data and complementary products.

This document describes the ICOS specifications for atmosphere stations, which typically consist of a set of integrated analyzers that reside in a shelter with an air intake system that collects air on a mast. The document groups the main atmospheric specification into: measurement set up (chap. 2), measurement protocols (chap. 3), calibration and standards (chap. 4), data management (chap. 5) and quality management (chap. 6). The atmosphere Monitoring Station Assembly (MSA) meets regularly (at least once a year) to mainly review, among other things, the stations performance over the past year and discuss recent development and instrument evaluation.

Revisions and extensions of this document are expected on a yearly basis as the outcome of the annual ICOS atmospheric MSA meetings.
The latest version can always be obtained at the ATC website (*http://www.icos-atc.eu/*).
The writing of this document has been coordinated by Laurent Olivier (ICOS ATC) along with the contribution from many expert atmospheric scientists (see Chap. 9.4 for the list of contributors).

# 1. Rationale and Objectives

## 1.1. General objectives

Over the last decade, the ICOS community has evolved from a situation where GHG atmospheric measurements were done by more than fifteen laboratories over Europe with their own procedures, using scientific project funding, to a situation where procedures are harmonized and funding is better secured over the long term due to the establishment of a dedicated international legal structure: the ICOS ERIC whose members are committed member states within Europe. High precision, long term, compatibility and traceability are key aspects of the ICOS atmospheric measurement. This high precision is needed to correctly capture the atmospheric signal, which is smoothed out via atmospheric transport. This of course depends somewhat on the time and geographical extent of the study. But it remains that measurement can only be done once in time so that the best precision available, at a given time, is to be favored. This ensures that the best possible measurements are available for future reference. Maintaining high quality measurements over the long term is a challenge but a necessity for the global carbon cycle study where processes take place at various scales. These processes are especially important for long time scales for climate forcing. Data quality is critical to the success of ICOS. Monitoring stations are organized by national networks which must be standardized to produce data, which are compatible and of high quality over a long period of time. Principal investigators (PI) of the measurement sites are responsible to the first order quality control and assurance. This is complemented by a quality assurance plan put into place within the ATC.

## 1.2. Data quality objectives

### 1.2.1.Data quality

ICOS targets high quality data, which involves high precision measurement and stringent data quality management procedures (including data check/validation).

### 1.2.2.Data compatibility

In order to allow for a good interpretation of global or continental scale atmospheric data from different stations and networks, an essential component for atmospheric transport model inversion studies, the WMO sets the compatibility goal for measurement of the major greenhouse gases and related tracers in the GAW report n° 255 (WMO, 2020). These WMO recommendations, updated every two years by a panel of international experts, are summarized in the following table (cf. Table 1). ICOS targets the same compatibility goal within its own monitoring network as well as with other international networks, however over an extended concentration range (cf. 2.2.1.1).

| Component | Compatibility goal | Range in the unpolluted troposphere (2019) |
|---|---|---|
| $CO_2$ | ± 0.1 ppm (± 0.05 ppm in the southern hemisphere) | 380 to 450 ppm |
| $CH_4$ | ± 2 ppb | 1750 to 2100 ppb |
| CO | ± 2 ppb | 30 to 300 ppb |
| $N_2O$ | ± 0.1 ppb | 325 to 335 ppb |
| $SF_6$ | ± 0.02 ppt | 9 to 11 ppt |
| $H_2$ | ± 2 ppb | 400 to 600 ppb |
| $\delta^{13}C\text{-}CO_2$ | ± 0.01 ‰ | -9.5 to -7.5 ‰ vs. VPDB |
| $\delta^{18}O\text{-}CO_2$ | ± 0.05 ‰ | -2 to +2‰ vs. VPDB-$CO_2$ |
| $\Delta^{14}C\text{-}CO_2$ | ± 0.5 ‰ | -80 to 20‰ |
| $\Delta^{14}C\text{-}CH_4$ | ± 0.5 ‰ | 50 to 350‰ |
| $\Delta^{14}C\text{-}CO$ | ± 2 molecules $cm^{-3}$ | 0 - 25 molecules $cm^{-3}$ |
| $\delta^{13}C\text{-}CH_4$ | ± 0.02 ‰ | -51 to -46 ‰ vs. VPDB |
| $\delta D\text{-}CH_4$ | ± 1 ‰ | -120 to -63 ‰ vs. VSMOW |
| $O_2/N_2$ | ± 2 per meg | -900 to -400 per meg vs. SIO scale |

*Table 1: WMO recommendation for compatibility of measurements of greenhouse gases and related tracers (WMO, 2020).*

## 1.3. Network design

In order to achieve the main objective of the atmospheric network, i.e. providing maximum constraints to determine surface-atmosphere exchange fluxes, the ICOS atmospheric network needs to be carefully designed in terms of station locations. When atmospheric station data are used in inverse transport modelling (or data assimilation) to retrieve regional scale GHG budgets, the main aim is to reduce the uncertainty of the surface-atmosphere flux for targeted spatial and temporal scale, e.g. annually integrated fluxes at national scales. The resulting uncertainty is a combination of two terms, one of which depends on the *a priori* uncertainty in fluxes (prior knowledge), while the other depends on the uncertainty of the measurements (observational constraint), which also includes uncertainties associated with representing the observations in atmospheric transport models. These representation errors are associated with errors in advection (winds), errors in modelled vertical mixing (mixing height, parameterized convection), and unresolved or imperfectly modelled spatial patterns in fluxes. Overall these errors can be larger than the uncertainty of the measurement itself as targeted within ICOS and thus need to be considered. The prior uncertainty in fluxes is reduced when applying inversions, but the uncertainty reduction critically depends on (a) the sensitivity of the observations to the fluxes (footprints), and on (b) the spatial and temporal correlations of the prior uncertainty matrix. Very long correlation scales imply that a few observations are sufficient to constrain the fluxes, while short correlation scales result in uncertainty reduction only in regions directly “seen” by the network, i.e. the footprint region.

A network development task force has been formed within the ICOS preparatory phase to provide a network design recommendation for synergetic and optimal deployment of stations in Europe. Their interim report provides details on a network design assessment, which involved multi-transport model footprint simulations for hypothetical networks with a high station density. Without a complete propagation of the uncertainties mentioned above, a number of basic recommendations were given that are summarized in the following sections.
The recommendations on stations location, detailed in Section 2.1.1, are mainly based on the results of the network design study conducted within the ICOS-INWIRE project (http://www.icos-atc.eu/).

## 1.4. ICOS standardized network

In order to get a homogeneous dataset, ICOS aims to standardize the equipment, measurement protocol and the data processing. This is an important aspect for quality assurance but is however not sufficient. Indeed, in order to reduce the risk of a systematic bias within its standardized network, additional periodic measurements with different and independent techniques are performed. This includes a quality control travelling instrument (e.g. Fourier Transform Infrared (FTIR) analyzer as proposed by Hammer et al., 2012) and/or flask sampling, where flasks are analyzed in a central laboratory with independent technique (e.g. Gas Chromatography). Moreover, ICOS is involved in international intercomparison programs (ICP) to assure data compatibility with other international networks such as the WMO GAW. This includes the participation to the WMO round robin ICP and stations collocated with other networks so called super-sites. (e.g. AGAGE, NOAA).

# 2. Measurement setup

## 2.1. Station requirement

### 2.1.1. Station location

Based on the initial network design assessment provided by the network development task force, and following from the fact that footprints associated with atmospheric stations are relatively local (on the order of 100 km), the main recommendation is to ensure a homogeneous network that avoids large spatial gaps. In order to improve the estimate of GHG fluxes over land, which display much larger variation than over sea, the majority of the stations should be "continental stations" (see definitions below), while only a small number of stations should be located near the western coast ("coastal station") to quantify inflow, and a small number of stations should be placed on mountain tops ("mountain station") as they are more difficult to represent in transport models and in case of high mountains are less directly exposed to air-masses carrying strong surface flux signals from the European continent.

Definition of the 3 station types within the ICOS Network:

- <u>Continental station</u>: a station targeting predominantly continental air-masses.
  Example: Trainou (TRN, France) 47.965°N 2.112°E (tall tower)
- <u>Coastal station</u>: a station targeting predominantly marine air-masses.
  Example: Mace-Head (MHD, Ireland) 53.326°N 9.899°W
- <u>Mountain station</u>: a station targeting predominantly free tropospheric air (during night).
  Example: Jungfraujoch (JFJ, Switzerland) 46.547°N 7.985°E

It should be noted that urban stations, which may be deployed in the coming years are not part of the current ICOS network (neither Class 1 nor Class 2 ICOS atmospheric stations).

<u>Station location recommendations:</u>

- Nominal distance between stations: ≃ 300 km
- Minimum distance between stations: ≃ 50 km
- Avoid complex terrain where possible
- Avoid short distance (usually less than 40 km) from strong anthropogenic sources (e.g. city) especially if located upstream of the prevailing wind. This is to ensure that observations can be represented in atmospheric transport models with spatial resolution of around of 10-20 km. In case of proximity to strong anthropogenic sources, a footprint and representativeness analysis should be performed.
- No more than 10% of the total network as mountain stations (free troposphere) for the whole ICOS network

In addition to these recommendations, the ICOS Atmospheric station location should take into account the logistic and economic constraints by considering the existing infrastructure.
A list of existing tall towers (elaborated by the ICOS network design task force) in Europe is available on the ICOS ATC website (*http://www.icos-atc.eu/*). Moreover, the so called "historic stations" (those established prior to the ICOS preparatory phase) should be considered as an existing backbone for the network construction.

### 2.1.2. Station setup

ICOS defines two classes of atmospheric station (AS) according to the set of parameters measured. The Class 1 AS manages a large range of mandatory measurements, whereas Class 2 AS operates only a subset of these. The mandatory parameters for each category are given in Table 2.

Requirements for data quality and compatibility are the same for ICOS Class 1 and Class 2 stations.

| Category | Gases, continuous | Gases, periodical | Meteorology, continuous | Eddy Fluxes |
|---|---|---|---|---|
| **Class 1**<br>Mandatory parameters | • **$CO_2$, $CH_4$, CO** : at each sampling height | • **$CO_2$, $CH_4$, $N_2O$, $SF_6$, CO, $H_2$, $^{13}C$ and $^{18}O$ in $CO_2$**: weekly sampled at highest sampling height† <br>• **$^{14}C$** (radiocarbon integrated samples): at highest sampling height | • **Air temperature, relative humidity, wind direction, wind speed**: at highest and lowest sampling height*<br>• **Atmospheric Pressure**<br>• **Planetary Boundary Layer Height**** † | |
| **Class 2**<br>Mandatory parameters | • **$CO_2$, $CH_4$** : at each sampling height | | • **Air temperature, relative humidity, wind direction, wind speed**: at highest and lowest sampling height*<br>• **Atmospheric Pressure** | |
| Recommended parameters*** | • **$^{222}Rn$, $N_2O$, $O_2/N_2$ ratio**<br>• **CO** for Class 2 stations | • **$CH_4$ stable isotopes, $O_2/N_2$ ratio** for Class 1 stations: weekly sampled at highest sampling height | | • **$CO_2$** : at one sampling height |

* Atmospheric temperature and relative humidity recommended at all sampling heights
** Only required for continental stations.
*** Recommended for its scientific value but support from ATC in terms of protocols, data base, spare analyzer will not be ensured as long as the parameters are not mandatory.
† In needs of further specifications (see section 2.2.3 and 2.2.4).

*Table 2: ICOS AS parameter set.*

Regarding the sampling heights for the continuous gas analysis, ICOS specifies the following requirements for the three station types:

- Continental stations, targeting mixed layer air over land:
  - Top level of tall tower: >=100 m a.g.l. (exception: locations where a shorter tower can frequently, at least 30%, sample above nocturnal stable boundary layer)
  - Other mandatory levels: 10 m (recommended above vegetation), 50m (nominal; 40-70 m accepted), (100 m, 200 m, 300 m for taller towers)

  For instance, a tower with 300 m height should have sampling levels at about 10, 50, 100, 200, 300 m.
- Coastal stations, targeting marine air masses

- Top level: sufficiently high to avoid contamination e.g. by local sources
    - No other mandatory levels
- <u>Mountain stations</u>, targeting free troposphere
    - Top level: sufficiently high to avoid contamination e.g. by local sources
    - No other mandatory levels

## 2.2. Equipment requirements and selection

### 2.2.1. Continuous gas analyzer

#### 2.2.1.1. ICOS requirement

In order to meet the WMO compatibility goal (cf. 1.2.2) within the ICOS network, the continuous gas analyzers deployed must be compliant to the performance requirement specified in Table 3 below. As ICOS targets the best performance instrument suitable for a large operational network, these requirements may be updated regularly according to the user needs and by taking into account the overall improvement of performances expected for new analyzers emerging on the market. The requirements updates must be taken into account for buying new instrument.

| **Component** | **Guaranteed Specification Range** | **Precision**[1] *Std. dev. (1-σ); 1' / 60' average raw data* | **Repeatability**[2] *Std. dev. (1-σ);* 10' average raw data |
|---|---|---|---|
| $CO_2$ | 350 - 500 ppm | < 50 ppb / 25 ppb | < 50 ppb |
| $CH_4$ | 1700 - 2900 ppb | < 1 ppb / 0.5 ppb | < 0.5 ppb |
| $N_2O$ | 300 - 400 ppb | < 0.1 ppb / 0.05 ppb | < 0.1 ppb |
| CO | 30 - 1000 ppb | < 2 ppb / 1 ppb | < 1 ppb |
| $O_2/N_2$ | -1500 - 0 per meg | < 10 per meg[3]/ 5 per meg | < 7 per meg |

**Test conditions: dry air; room temperature: 20 °C ± 2°C; room pressure: atmospheric pressure with a natural variation.**

[1] Measuring a gas cylinder (filled with dry natural air) over 25 hours; first hour rejected (stabilization time).
[2] Measuring alternately a gas cylinder (filled with dry natural air) during 30 minutes and ambient air (not dried, except for $O_2$ measurement) during 270 minutes over 72 hours. Statistics based on the last 10 minute average data of each 30 minute cylinder gas injection (first 20 minutes rejected as stabilization time).
[3] Not all $O_2$ analyzers can report as high as 1 minute frequency. This should not preclude their acceptability as an ICOS analyzer, so for such analyzers, refer only to the 60 minute precision and 10 minute repeatability requirements.

*Table 3: Gas analyzer performance required by ICOS (as of June 2020).*

These performance requirements must be guaranteed by the manufacturer (analyzer's specifications) for the specified concentration range in dry air (cf. Table 3). The exception is for $O_2$ measurement, where it is accepted that currently no manufacturer sells $O_2$ analyzers to these specifications. Therefore, these performance requirements must be demonstrated by the ATC or associate laboratories.

For all gas species, the performance and robustness for long-term monitoring applications must be demonstrated during long-term (at least one year) field tests performed either by the ATC or associate laboratories with ATC coordination.
Moreover, any gas analyzer must be evaluated by the ATC Metrology Lab (or associated laboratories for $O_2/N_2$) prior to field deployment to establish the ICOS compliance certificate. The evaluation is carried out according to the ATC standard protocol. The test duration is estimated to be one month. When buying a new gas analyzer, the station PI must contact the ATC to schedule the evaluation date with a 3 month anticipation and manage the instrument delivery to ATC. If, for some reason, this evaluation has not been performed at the ATC before deployment (e.g. analyzer already installed before ATC was operational), the station PI must contact the ATC to schedule a convenient date. After repair (at the manufacturer) the operators must contact the ATC to determine if a repeated evaluation test at ATC is required.

The continuous gas analyzer must require low on-site maintenance and intervention, ideally limited to maintenance of pump (annual) and inlet filters. The instrument should not need any frequent (ideally less than every 5 years) maintenance at the manufacturer's premises. The after-sales service provided by the manufacturer must be reactive and efficient.

In order to limit the running cost and logistic, the requirement of any running consumable should be minimized. These instrument characteristics are also of high importance for the analyzer selection procedure. Relevant information published in the peer-reviewed literature will be also considered to make use of existing experience by ICOS-external experts.

#### 2.2.1.2. Analyzer selection meeting requirements

The ICOS ATC Metrology Lab is in charge of evaluation of the continuous gas analyzers available on the market and has made a list of instruments (cf. Table 4) compliant to ICOS requirements (cf. Section 2.2.1.1). This selection is based on the results of lab and field tests discussed during annual ICOS MSA. The update of this ICOS compliant analyzer list will be regularly discussed and validated during the MSA.
ICOS Atmosphere Stations must be equipped with instruments compliant with Section 2.2.1.1. Such suitable analyzers are listed in the Table 4, which measure the mandatory species required by their ICOS station Class (cf. Table 2).
The ICOS analyzer status lifetime has been fixed to a minimum of 5 years. Past this time, few services such as training and spare parts can be discontinued. However, the data will be still processed by the ATC.

| Brand | Model | Species | ICOS Compliance | | | Eligibility Conditions |
|---|---|---|---|---|---|---|
| | | | **$CO_2$** | **$CH_4$** | **CO** | |
| PICARRO | G1301 | $CO_2/CH_4/H_2O$ | • | • | - | |
| PICARRO | G2301 | $CO_2/CH_4/H_2O$ | • | • | - | |
| PICARRO | G2401 | $CO_2/CH_4/CO/H_2O$ | • | • | • | With ICOS specifications |
| PICARRO | G5310 | $CO/N_20/H_2O$ | - | - | • | |
| LGR | 907-0015 | $CO/N_20/H_2O$ | - | - | • | Precaution with Δ temperature |
| LGR | 913-0015 (EP) | $CO/N_20/H_2O$ | - | - | • | |
| ECOTECH | Spectronus | $CO_2/CH_4/CO/$ $N_20/H_2O/\delta^{13}C\text{-}CO_2$ | • | • | • | With ICOS recommendations (see Section 3.3 and 4.1.1) |

*• : ICOS Compliant   - : Not applicable*

*Table 4: list of continuous gas analyzers meeting the ICOS specifications (as of June 2020).*

ATC recommends that Station PIs who are not familiar with Ecotech Spectronus to take a specific training (by ATC or Ecotech) in order to handle properly the analyzer. It is also important to consider the consumable $N_2$ gas required by the Ecotech Spectronus. A 40 liter $N_2$ tank lasts about 6 to 7 weeks but lifetime might be slightly extended with a reduced flow rate (down to 80 ml/min) and fine flow control.

Refer to the ATC's Qualifying test reports for more detailed information (available on the ATC website, *http://www.icos-atc.eu/*).

#### 2.2.1.3. $N_2O$ analyzer

In ICOS, at this stage, $N_2O$ is not a required but a recommended parameter for continuous gas measurement (see Table 2). Several different $N_2O$ high precision analyzers were tested at the ATC (Lebegue et al., 2016). Based on the results discussed at the ICOS MSA in June 2015 in Dübendorf and in March 2017 in Lund, the following instrumentation recommendation can be made. This recommendation takes into account both absolute performance but also robustness, ease of operation etc.

The LGR-CO/$N_2O$ EP model from Los Gatos and the Picarro G5310 meet the specifications with an appropriate calibration strategy, especially considering the potential short-term variability in instrument sensitivity. To account for that, a dedicated short-term working standard must be measured at least every 10 hours to correct for instrument short-term variability. Unlike the target gas, which is used for data quality control purpose (cf. 4.1), the short-term working standard is used for data correction (specific post processing on the ICOS server). Such correction implies a dedicated tank (short-term working standard) in addition to the calibration and target tanks. This additional tank must fulfill the ICOS requirements for equipment (cf. 4.1.2). Like for the short-term target gas (cf. 4.1.1), the mole fraction of the short-term working standard should be close to the average value expected or measured on site (cf. Table 12). Particular attention has to be paid to the characterization of the temperature dependence and the drift of the instrument sensitivity. Moreover, given the accuracy of ATC determination of the $N_2O$ water vapor correction in regard to the demanding ICOS compatibility goal (0.1 ppb) and its variability over time, it is highly recommended to dry the air upstream both analyzers. As the LGR-CO/$N_2O$ EP and Picarro G5310 already qualify for CO, the ATC has already developed the corresponding data processing chain and is able to process $N_2O$ data from these analyzers.

Laboratory tests identified other $N_2O$ analyzers that meet the specifications but the proof of suitability for long-term operation in the field is still sparse for these instruments. ICOS operators are invited to perform long-term implementations and to share their experience during future MSAs.

### 2.2.2.Meteorological sensors

In order to characterize the weather conditions at ICOS atmosphere sites, ICOS requires monitoring of the following meteorological parameters: wind direction, wind speed, air temperature, relative humidity and barometric pressure. The corresponding ICOS meteorological sensor selection is based on the WMO recommendation specified in the WMO Guide N° 8 (Table 5) (WMO, 2008). However, as ICOS does not aspire to be part of a meteorological station network, the ICOS requirements on meteorological parameters is not as stringent as the WMO requirements. Indeed, the measurement uncertainty required by WMO is so stringent for certain meteorological variables (i.e. temperature), that adhering to WMO requirements would induce unnecessary investment for the ICOS Atmospheric Stations. Therefore, the ICOS measurement uncertainty (1σ on single data) requirements are based on the relaxed constraint of "*achievable uncertainty*" specified by the WMO.

| *Variable* | *Range* [1] | *Resolution*[2] | *Mode of measurement* [3] | *Required measurement uncertainty* [4] | *Sensor time constant* [5] | *Output average time* [6] | *Achievable uncertainty* [7] |
|---|---|---|---|---|---|---|---|
| Wind speed | 0 to 75m/s | 0.5m/s | Averaging | 0.5m/s [0m/s; 5m/s]<br>10% [5m/s; 75m/s] | Distance Constant | 2 and 10min | **0.5m/s [0m/s; 5m/s]**<br><br>**10% [5m/s; 75m/s]** |
| Wind direction | 0 to 360° | 1° | Averaging | 5° | 1s | 2 and 10min | **5°** |
| Temperature (Air) | -80 to +60°C | 0.1°C | Instantaneous | 0.3K [-80°C; -40°C]<br>0.1K ]-40°C; +40°C]<br>0.3K ]+40°C; +60°C] | 20s | 1min | **0.2 K** |
| Relative humidity | 0 to 100% | 1% | Instantaneous | 1% | 40s | 1min | **3%** |
| Barometric pressure | 500 to 1080hPa | 0.1hPa | Instantaneous | 0.1hPa | 20s | 1min | **0.3 hPa** |

1 Common range. Limits depend on local climatological conditions. It refers to the requirement established by the CBS Expert Team on Requirements for Data from Automatic Weather Stations in 2004.

2 Most stringent resolution as determined by the *Manual on Codes* (WMO-No. 306). It refers to the requirement established by the CBS Expert Team on Requirements for Data from Automatic Weather Stations in 2004.

3 Mode of measurement:
Instantaneous: in order to exclude the natural small-scale variability and the noise, an average value cover a period of 1 min is considered as a minimum and most suitable; averages over periods of up to 10 min are acceptable.
Averaging: average values over a fixed period, as specified by the coding requirements.
It refers to the requirement established by the CBS Expert Team on Requirements for Data from Automatic Weather Stations in 2004.

4 Recommended measurement uncertainty for general operational use, i.e. of level II data according to FM 12, 13, 14, 15 and its BUFR equivalents. They have been adopted by all eight technical commissions and are applicable for synoptic, aeronautical, agricultural and marine meteorology, hydrology, climatology, etc. These requirements are applicable for both manned and automatic weather stations as defined in the *Manual on the Global Observing System* (WMO-No. 544). Individual applications may have less stringent requirements. The stated value of required measurement uncertainty represents the uncertainty of the reported value with respect to the true value and indicates the interval in which the true value lies with a stated probability. The recommended probability level is 95 per cent (k=2), which corresponds to the 2 σ level for a normal (Gaussian) distribution of the variable. The assumption that all known corrections are taken into account implies that the errors in reported values will have a mean value (or bias) close to zero. Any residual bias should be small compared with the stated measurement uncertainty requirement. The true value is the value which, under operational conditions, perfectly characterizes the variable to be measured/observed over the representative time interval, area and/or volume required, taking into account sitting and exposure.
It refers to the requirement established by the CBS Expert Team on Requirements for Data from Automatic Weather Stations in 2004.

5 It refers to the typical operational performance established by the CIMO Expert Team on Surface Technology and Measurement Techniques in 2004.

6 It refers to the typical operational performance established by the CIMO Expert Team on Surface Technology and Measurement Techniques in 2004.

7 Achievable measurement uncertainty is based on sensor performance under nominal and recommended exposure that can be achieved in operational practice. It should be regarded as a practical aid to users in defining achievable and affordable requirements. It refers to the typical operational performance established by the CIMO Expert Team on Surface Technology and Measurement Techniques in 2004.

*Table 5: WMO operational measurement uncertainty requirements and instrument performance.*
(Annex 1.B of WMO-N. 8 -*Guide to Meteorological Instruments and Methods of Observation*, 2008*)*

The following sections provide the ICOS requirements and recommendations for each meteorological parameter. The ATC will maintain and update a list of sensors which meet those requirements. Station PIs are invited to contribute to update the list by requesting to ATC the evaluation of unlisted sensors.

The measurement uncertainties given in the following tables are sensor specifications provided by the manufacturer and will not be controlled by the ATC.

#### 2.2.2.1. Wind sensors

For maintenance reasons, ICOS recommends the use of 2D ultrasonic wind sensor instead of the conventional cup and vane or propeller wind sensors. Moreover, the sensor must be adapted to the weather conditions (operational temperature, icing). Thus, the sensor must be heated (with an appropriate power supply) if the station is prone to weather conditions including ice and snow.

ICOS requirements:

- Wind speed measurement uncertainty required by ICOS: **0.5m/s [0m/s; 5m/s]**<br>**10% [5m/s; 75m/s]**
- Wind direction measurement uncertainty required by ICOS: **5°**
- Wind speed range adapted to the site (i.e. mountain)
- Wind speed measurement resolution: **0.5 m/s**
- Wind direction measurement resolution: **1°**

| **Brand** | **Model** | **Wind speed measurement uncertainty** | **Wind direction measurement uncertainty** | **ICOS Status** |
|---|---|---|---|---|
| GILL | WindSonic | ±2% at 12 m/s | ±3º at 12 m/s | **ICOS Compliant** |
| GILL | WindSonic M | ±2% at 12 m/s | ±3º at 12 m/s | **ICOS Compliant** |
| GILL | WindObserver | ±2% at 12 m/s | ±3º at 12 m/s | **ICOS Compliant** |
| GILL | WindObserver 65/70/75 | ±2% at 12 m/s | ±2º at 12 m/s | **ICOS Compliant** |
| LUFT | Ventus | ± 2% RMSE(>2m/s) | ± 2° RMSE | **ICOS Compliant** |
| METEK | uSonic-3 Omni, uSonic-3 Scientific | ±0.1 m/s or 2% | ±2º at 5 m/s | **ICOS Compliant** |
| ROSEMOUNT | 1774W | ±0.4 m/s if ≤ 20m/s<br>±2% if > 20m/s | ±5° if ≤ 15.5m/s<br>±3° if > 15.5m/s | **ICOS Compliant** |
| THIES | Ultrasonic Compact | ± 2% RMS(>5m/s) | ± 2° | **ICOS Compliant** |
| THIES | Ultrasonic 2D | ± 2% RMS(>5m/s) | ± 1° | **ICOS Compliant** |
| THIES | 4.3121.32.000 | NA | ± 2.5° | **ICOS Compliant** |
| THIES | 4.3125.32.100 | NA | ± 2.5° | **ICOS Compliant** |
| THIES | 4.3303.10.XXX | ± 0,3 m/s resp. 2 % of reading | NA | **ICOS Compliant** |
| THIES | 4.3303.22.XXX | ± 0,5 m/s resp. 2 % of reading | NA | **ICOS Compliant** |
| VAISALA | WMT52 | ±0.3 m/s or ±3% [0m/s; 35m/s]<br>±5% [36m/s; 60m/s] | ±3° | **ICOS Compliant** |
| VAISALA | WS425 | ± 0.135 m/s or 3% of reading [0m/s; 65m/s] | ±2° (wind speed > 1 m/s) | **ICOS Compliant** |
| YOUNG | 85000 | ± 2% or 0.1 m/s (30 m/s)<br>± 3% (70 m/s) | ±2° | **ICOS Compliant** |

*Table 6: Wind sensors and their assessment for ICOS.*

#### 2.2.2.2. Temperature sensors

ICOS requirements:

- Temperature measurement uncertainty: **0.2K** on the temperature range adapted to the site.
- Temperature range adapted to the site (i.e. mountain)
- Measurement resolution: **0.1°C**

| Brand | Model | Temperature measurement uncertainty | ICOS Status |
|---|---|---|---|
| CAMPBELL | CS215 PWS | ±0.3°C at 25°C;<br>±0.4°C [+5; +40°C]<br>±0.9°C [-40°; +70°C] | **NOT ICOS Compliant** |
| LUFFT | WS3000 | ±0.1 °C [-40°C; +60°C] | **ICOS Compliant** |
| METEOLABOR | THYGAN VTP6 | ±0.15°C [-20°; +50°C] | **ICOS Compliant** |
| ROTRONIC | HC2-S3<br>HC2A-S3 | ±0.1 °C at 23°C ±5K | **ICOS Compliant** |
| ROTRONIC | MP102H<br>MP402H | ±0.1 °C at 23°C ±5K | **ICOS Compliant** |
| VAISALA | HMP45 | ±0.5 °C at -40°C<br>±0.2 °C at 20°C<br>±0.3 °C at +40°C | **NOT ICOS Compliant** |
| VAISALA | HMP60 | ±0.6 °C [-40°C; +60°C] | **NOT ICOS Compliant** |
| VAISALA | HMP110 | ±0.4 °C [-40°C; 0°C]<br>±0.2 °C [0°C; +40°C]<br>±0.4 °C [+40°C; +60°C] | **NOT ICOS Compliant** |
| VAISALA | HMP155 | ±0.12 °C at 20°C | **ICOS Compliant** |
| VAISALA | PTU300 | ±0.4 °C at -40°C<br>±0.2 °C at +20°C<br>±0.3 °C at +60°C | **NOT ICOS Compliant** |
| YOUNG | 41382 | ±0.3 °C at 0°C | **NOT ICOS Compliant** |

*Table 7: Temperature sensors and their assessment for ICOS.*

#### 2.2.2.3. Relative humidity sensors

ICOS requirements:

- Relative humidity measurement uncertainty: **3%** on the temperature and relative humidity range adapted to the site.
- Measurement resolution: **1%**

| **Brand** | **Model** | **Relative Humidity measurement uncertainty** | **ICOS Status** |
|---|---|---|---|
| CAMPBELL | CS215 PWS | ±2 %RH [0%; 90%] at 25°C<br>±4 %RH [90%; 100%] at 25°C | **NOT ICOS Compliant** |
| LUFFT | WS3000 | ±2 % [0%; 100%] | **ICOS Compliant** |
| ROTRONIC | HC2-S3<br>HC2A-S3 | ±0.8 % at 23°C ±5K | **ICOS Compliant** |
| ROTRONIC | MP102H<br>MP402H | ±0.8 % at 23°C ±5K | **ICOS Compliant** |
| VAISALA | HMP45 | ±3 %RH [0%; 90%]<br>±5 %RH [90%; 100%] | **NOT ICOS Compliant** |
| VAISALA | HMP60 | ±3 %RH [0%; 90%]<br>±5 %RH [90%; 100%] | **NOT ICOS Compliant** |
| VAISALA | HMP110 | ±1.7 %RH [0%; 90%]<br>±2.5 %RH [90%; 100%] | **ICOS Compliant** |
| VAISALA | HMP155 | ±1 %RH [0%; 90%]<br>±1.7 %RH [90%; 100%] | **ICOS Compliant** |
| VAISALA | PTU300 | ±1 %RH [0%; 90%]<br>±1.7 %RH [90%; 100%] | **ICOS Compliant** |
| YOUNG | 41382 | ±2 % at 20°C | **ICOS Compliant** |

*Table 8: Relative humidity sensors and their assessment for ICOS.*

#### 2.2.2.4. Barometric pressure sensors

ICOS requirements:

- Pressure measurement uncertainty: **0.3 hPa** on the pressure range adapted to the site.
- Barometric pressure range adapted to the site (i.e. mountain)
- Measurement resolution: **0.1 hPa**

| Brand | Model | Barometric pressure<br>Measurement uncertainty | ICOS Status |
|---|---|---|---|
| CAMPBELL<br>(SETRA) | CS100<br>(278) | ±0.5 hPa at 20°C<br>±2 hPa (-40 to +60°C) | **NOT ICOS Compliant** |
| DRUCK | RPT410V | ±0.5 hPa at 20°C<br>±2.5 hPa (-40 to +60°C) | **NOT ICOS Compliant** |
| LUFFT | WS3000 | ±0.1 hPa | **ICOS Compliant** |
| MICROSTEP-MIS | MSB181 | ±0.3 hPa (-40 to +60°C) | **ICOS Compliant** |
| VAISALA | PTB110 | ±0.3 hPa at 20°C | **NOT ICOS Compliant** |
| VAISALA | PTB210 | ± 0.15hPa at 20°C | **ICOS Compliant** |
| VAISALA | PTB210 | ± 0.15hPa at 20°C | **ICOS Compliant** |
| VAISALA | PTU300 | ±0.1 hPa at 20°C | **ICOS Compliant** |
| YOUNG | 61302 | ±0.2 hPa at 25°C<br>±0.3 hPa (-40 to +60°C) | **ICOS Compliant** |
| YOUNG | 61402 | ±0.2 hPa at 25°C<br>±0.3 hPa (-40 to +60°C) | **ICOS Compliant** |

*Table 9: Barometric pressure sensors and their assessment for ICOS.*

#### 2.2.2.5. Integrated weather station

ICOS requirements:

- Wind speed measurement uncertainty required by ICOS: **0.5m/s [0m/s; 5m/s]**
  **10% [5m/s; 75m/s]**
- Wind direction measurement uncertainty required by ICOS: **5°**
- Wind speed range adapted to the site (i.e. mountain)
- Wind speed measurement resolution: **0.5 m/s**
- wind direction measurement resolution: **1°**
- Temperature measurement uncertainty: **0.2K** on the temperature range adapted to the site.
- Temperature range adapted to the site (i.e. mountain)
- Temperature measurement resolution: **0.1°C**
- Relative humidity measurement uncertainty: **3%** on the temperature and relative humidity range adapted to the site.
- Relative humidity measurement resolution: **1%**
- Pressure measurement uncertainty: **0.3 hPa** on the pressure range adapted to the site.
- Barometric pressure range adapted to the site (i.e. mountain)
- Pressure measurement resolution: **0.1 hPa**

| Brand | Model | Wind speed meas. Uncertainty | Wind direction meas. uncertainty | Temperature meas. uncertainty | Relative Humidity meas. uncertainty | Barometric Pressure meas. uncertainty | ICOS Status |
|---|---|---|---|---|---|---|---|
| GILL | MetPak2 | ±2% at 12 m/s | ±3º<br>at 12 m/s | ±0.1°C | ±0.8 %RH<br>at 23°C | **±0.5 hPa** | **NOT ICOS Compliant** |
| VAISALA | WXT520 | ±0.3 m/s or ±3% [0m/s; 35m/s] | ±3° | ±0.2°C<br>[-52°C; -20°C] | ±3 %RH<br>[0%; 90%] | **±0.5 hPa<br>[0°C; +30 °C]** | **NOT ICOS Compliant** |
| | | | | **±0.4°C<br>[-20°C; +40°C]** | **±5 %RH<br>[90%; 100%]** | **±1 hPa<br>[-52°C; +60 °C]** | |
| | | ±5%<br>[36m/s; 60m/s] | | **±0.7°C<br>[40°C; +60°C]** | | | |

*Table 10: Integrated weather stations and their assessment for ICOS.*

### 2.2.3. Planetary boundary layer height retrieval instrument

The depth of the atmospheric vertical mixing by turbulence within the planetary boundary layer has a large effect on GHG concentrations; it is however not always well represented by atmospheric transport models. To reduce the adverse impact on inversion results, information on mixing heights can be used (Kretschmer et al., 2012).

Conclusions of the ICOS INWIRE project on the topic of BLH measurements were presented at the ICOS Atmosphere MSA in March 2016 in Brno, Czech Republic. Results from new versatile ceilometer/lidar BLH retrieval algorithms were shown. Good BLH detection score[11] and improved BLH selection were obtained. The improvement involved adapting the resolution to better suit edge detection, moving from a static to adaptive double thresholding to detect potential edge and using of a newer 2D Gaussian filter. The retrieved daytime PBL height differed from radiosonde data by less than 250m around 50%[1] of the time for the better instruments. These improved results still come with strong limitations like the one due to overlap issue for nighttime measurements.

On the other end, considering improvements made by atmospheric transport models, shown in projects like InGOS and Transcom-BLH, the ICOS Atmosphere MSA of March 2016 in Brno, agreed on the need to improve the BLH retrieval algorithm, assess the value of their implementation and validate the BLH measurements in the coming year before making any final recommendation on BLH measurements in this section. Collaboration was established with ICOS-external experts in the field and European automatic lidar and ceilometer networks to advance to a mature, operational level. It was agreed in the MSA that, in the meantime, this decision does not withhold the labeling process for ICOS atmospheric Class 1 stations. However, as soon as BLH measurement/retrieval recommendations are made, they should be implemented in class 1 stations without undue delay.

As far as ICOS atmosphere is concerned, it is therefore highly recommended at this point, to wait before buying any BLH instrument.

### 2.2.4. Flask sampling

Measurement of air periodically sampled in flasks at atmosphere stations allows additional parameter measurements ($SF_6$, $H_2$, $CO_2$ stable isotopes …), which are not performed by in-situ continuous analyzers and an independent quality control for continuous in-situ measurements (cf. 6.4). Moreover, a subset of the flasks can be analyzed for $^{14}C$ in $CO_2$ to allow determining the atmospheric fossil fuel $CO_2$ component ($ffCO_2$).

Within the ICOS atmosphere network, the air must be sampled by an automatic flask sampler, which will allow pre-defined sampling during suitable atmospheric conditions (cf. 3.1). Currently, the only accepted automatic flask sampler meeting the ICOS requirements is the automatic flask sampler designed and constructed at the Max Planck Institute for Biogeochemistry (MPI-BGC), available from the CAL FCL. Air sampling must be done every three days during mid-day with the approved ICOS 3 Liter flasks. The flasks to be used with the automatic flask sampler have been developed by ICOS CAL FCL with the company NORMAG (product code ICOS3000). Before delivery to the flask owner the flask manufacturer is compelled to test each ICOS flask with a setup provided by ICOS CAL FCL in a comprehensive final test. ICOS CAL FCL receives the successful test results. ICOS CAL FCL can provide information on the manufacturer of flasks and flask boxes that are used in the ICOS atmosphere station network. Before first use, flasks need to be sent to ICOS CAL FCL to pass a

[1] percentage in time (10 min bins) when a BLH candidate is detected.

standardized conditioning procedure of heating and pumping. Each Class 1 station is required to own approximately 100 flasks, in order to prevent logistical issues or CAL congestion. All ICOS flasks samples are analyzed by the CAL FCL in Jena, Germany. A subset of flasks is analyzed by the CAL CRL for $^{14}C$ in $CO_2$. The station PIs are invited to contact the CAL to get the latest information regarding flask specifications and automatic flask sampler availability. Station PIs agreed at the MSA meeting in Dübendorf 2015 that a possible delay in flask and sampler delivery does not impede the labeling process for ICOS atmospheric Class 1 stations.

### 2.2.5.Radiocarbon ($^{14}C$) sampler

The atmospheric fraction of the $CO_2$ radioactive isotopologue, $^{14}CO_2$, is used as a fossil fuel tracer in order to identify the anthropogenic pollution sources (fossil fuel combustion). Since the carbon in fossil fuels is totally depleted in $^{14}C$, its emission and mixing in the atmosphere causes a depletion of the observed $^{14}C$ fraction in atmospheric $CO_2$.

The currently recommended ICOS sampling method for two weekly integrated samples is chemical absorption of atmospheric $CO_2$ in NaOH solution.

The $^{14}CO_2$ sampler consists in pumping continuously ambient air over two weeks through a $CO_2$ absorbing sodium hydroxide (NaOH) solution. In order to enlarge the NaOH reaction surface, the solution is held in a rotating glass tube filled with a packed bed of glass Raschig rings. Using this method, the atmospheric $CO_2$ is absorbed nearly quantitatively in the NaOH solution. The sample is then sent to the ICOS CAL CRL in Heidelberg, Germany for analysis. The station PIs requiring an appropriated integrated $^{14}CO_2$ sampler (at least all the Class 1 ICOS AS) must contact the ICOS CAL CRL. Currently, only the integral $^{14}CO_2$ sampler produced by ICOS-CRL is eligible for the ICOS network. For a potential certification of another integrated $^{14}CO_2$ sampler please contact the CRL and the ATC.

The air pumped for analysis should be taken from the highest sampling level on tall tower.

In addition to the integrated sampling described above, event-based flask sampling is regularly conducted at Class 1 stations with the standard flask sampler (cf. 2.2.4) using 3 liter Normag flask (reference ICOS3000, see section 2.2.4)

### 2.2.6. Radon monitor

At the present stage, Radon-222 measurements are not mandatory but recommended in ICOS (see Table 2). Radon-222 is recognized as a very valuable measurement, in particular for trace gas flux estimates.
There are three different radon measurement principles in use at European and global atmospheric stations: (1) Measurement of Radon-222 ($^{222}Rn$) with a two filter system (e.g. ANSTO system (e.g. Williams and Chambers, 2016)), (2) measurement of $^{222}Rn$ daughters attached to aerosols and accumulated on one filter, and determination of $^{222}Rn$ from its daughter activity assuming a height-dependent disequilibrium factor (e.g. Heidelberg system, Levin et al., 2002) and (3) direct measurements of $^{222}Rn$ and $^{220}Rn$ (thoron) concentrations based on the α spectrometry of $^{218}Po$ and $^{216}Po$, respectively, on a implanted planar silicon detector surface and using a high electrostatic field (e.g. Grossi et al., 2020). The positive ions of polonium that are moved to the detector by the electrostatic field result exclusively from the α-decay of $^{222}Rn$ and $^{220}Rn$ within the spherical detection volume. [e.g. Atmospheric Radon MONitor (ARMON) system). Method (1) is advantageous

at tall towers to avoid loss of radon daughters in long tubing, however the measurement system is large and it may be difficult to host it at remote stations where space is limited. A radon monitor using method (2) has been developed at UHEI-IUP and improved within the ICOS-Preparatory Phase. Extensive tests have also been carried out to quantify the loss of radon daughters in ½ inch OD 1300 Synflex tubing of up to 200m length, in order to develop respective correction functions and use it at ICOS stations. Furthermore, extensive inter-comparison campaigns between the ANSTO and the UHEI system have been performed (e.g. in the frame of the InGOS (Integrated non-CO2 Greenhouse gas Observing System) project, Schmithüsen et al., 2017). A radon monitor based on the method (3) has been developed at the Institut de Tècniques Energètiques of the Universitat Politècnica de Catalunya (INTE-UPC) and calibrated at the INTE-UPC reference radon chamber, which allows the control of environmental parameters (i.e. temperature and relative humidity). The ARMON has been tested during laboratory experiments under extreme environmental conditions and it has been compared during intercomparison field campaigns with monitors based on methods (1) and (2) (Grossi et al., 2020).

As announced at the ICOS Atmosphere MSA of June 2015 in Dübendorf, the ATC is able to process Radon data recorded with ANSTO analyzers (including automatic quality control). Pre-processed data from the Heidelberg Radon Monitor (HRM) can be processed by the ATC as "black box" data.

<u>ATC recommendation</u>:

As currently only the ANSTO monitors have been fully characterized, were long-term and widely deployed world-wide, and are inter-compared with other systems, ATC recommends this monitor to be installed at ICOS stations for direct high-precision atmospheric $^{222}$Radon observations. The monitor is commercially available from the Australian Nuclear Science and Technology Organization (ANSTO). Data processing has been fully established at the ATC so that its measurements can be directly integrated in the ICOS data processing chain. Other systems, such as the ARMON or the one-filter HRM system are accepted if e.g. required correction functions for disequilibrium and aerosol loss in tubing are applied, and their full characterization has been finalized. This will be pursued in the framework of the European Metrology Program for Innovation and Research (EMPIR), with the project "Implementation of radon metrology for the analysis for the atmospheric budget of greenhouse gases and radiation protection in the environment" started in June 2020 and involving ICOS-external and ICOS-internal partners. The outcome of this project will guide the ICOS community in the future concerning improved atmospheric radon instrumentation and standardization.

#### 2.2.7.Eddy flux measurement

The equipment requirements and corresponding protocols for eddy flux measurement are available on the ICOS ETC website (*http://www.icos-etc.eu/icos/documents/instructions*). These protocols have been published in a special issue of the International Agrophysics (*http://www.international-agrophysics.org/Issue-4-2018,7048, 2018*).

### 2.3. Equipment integration

#### 2.3.1. Continuous gas analyzer

In order to limit the temperature variation around the instruments, it is highly recommended to install them inside a temperature controlled (ideally +/-2°C) room (e.g. air conditioning). The room temperature should be adapted to the site setup and meteorological conditions, neither too low to avoid possible condensation in the tubing in summertime (inside/outside temperature gradient must be limited) nor too high to avoid overheating instrument (reducing Hardware lifetime and instrument temperature regulation performance). A typical room temperature is around 23°C. Moreover, as instruments are mostly sensitive to rapid temperature variation, it should be ideally installed in an enclosed mounting rack to buffer temperature change potentially induced by the air conditioning air flow. This setup additionally limits the amount of dust particles around this instrument.

The gas analyzer must be associated with an air sampling and distribution system (cf. 2.4.1). This system allows sampling the air at different heights on a tall tower and measuring different gas cylinders. Thus, a single instrument can automatically and sequentially analyze the air at different tower heights and be calibrated according to a specific sequence. It is important that the analyzers and the sequencer (also called scheduler) which manages the distribution system (valves) are well synchronized with a time server (e.g. GPS or internet NTP server). This secures the identification of the origin of the gas analyzed (which cylinder or which sampling height) with the appropriate time stamp.

### 2.3.2. Meteorological sensors

The sensor installation should be as compliant as possible to the WMO recommendation resumed in the WMO Guide to Instruments and Methods of Observation N°8 (WMO, 2018).
The temperature and relative humidity sensor must be installed in a radiation shield (e.g. a Campbell MET 21 or a Vaisala DTR13) in order to provide a protection from the scattered as well as direct solar radiation and rain. The radiation shield must be well ventilated. However, in order to avoid failure and maintenance, ICOS recommends using a naturally ventilated large radiation shield which offers sufficient performance for ICOS purposes, instead of a forced ventilated radiation shield.
Concerning the air pressure measurement, the wind can induce dynamic pressure fluctuations on static pressure (Liu, 1989). In order to minimize this issue, ICOS recommends using the barometer with an appropriate pressure port (e.g. Young 61002).
The wind sensor must be kept away from local obstructions (e.g. building, tree, interface box) as much as possible. The WMO recommends installing the wind sensor at a minimum distance of 10 times the obstacle height.

<u>Sensor sitting (height above the ground level):</u>

For Atmosphere Stations with a single air sampling height, the wind sensor must be collocated with an air inlet for continuous gas analysis if the location is suitable as pertains to WMO recommendations. If the air inlet location is in the vicinity of a substantial obstruction, the wind sensor must be installed on an independent mast 10m above the ground level located in a more suitable environment. The temperature and relative humidity sensors must be installed in an appropriate shield at least 2m from any important surface (e.g. ground, shelter). Moreover, the temperature and humidity sensor shield as well as the barometer pressure port must be freely exposed to the wind.

In the specific case of sites with several sampling heights (tall tower), the Atmospheric Station must be equipped at least with a set of a wind sensors (speed and direction), a temperature and relative humidity sensor at the highest and lowest sampling heights on the tower. Moreover, ICOS recommends installation of temperature and relative humidity sensors at the intermediate sampling height(s) as applicable. ICOS requires the use of a single barometer which can be equally installed at any height. However, for maintenance, ICOS recommends setting up the barometer in an easy access location (e.g. lowest sampling height or ground level).

In order to minimize the wind shadow effect induced by the tower structure, the wind sensor must be installed facing the prevailing wind at a significant distance from the tower by using a dedicated arm. The arm length depends on the type of tower construction. For instance, for a light framework steel tower, the wind sensor should be at least at 3 meters away from the tower structure. For a massive concrete tower, the arm should be longer, as long as possible (best effort). An alternative option consists in duplicating the wind sensors (on opposite sides of the tower) at each sampling heights.
These wind shadow considerations do not concern the top of the tower.

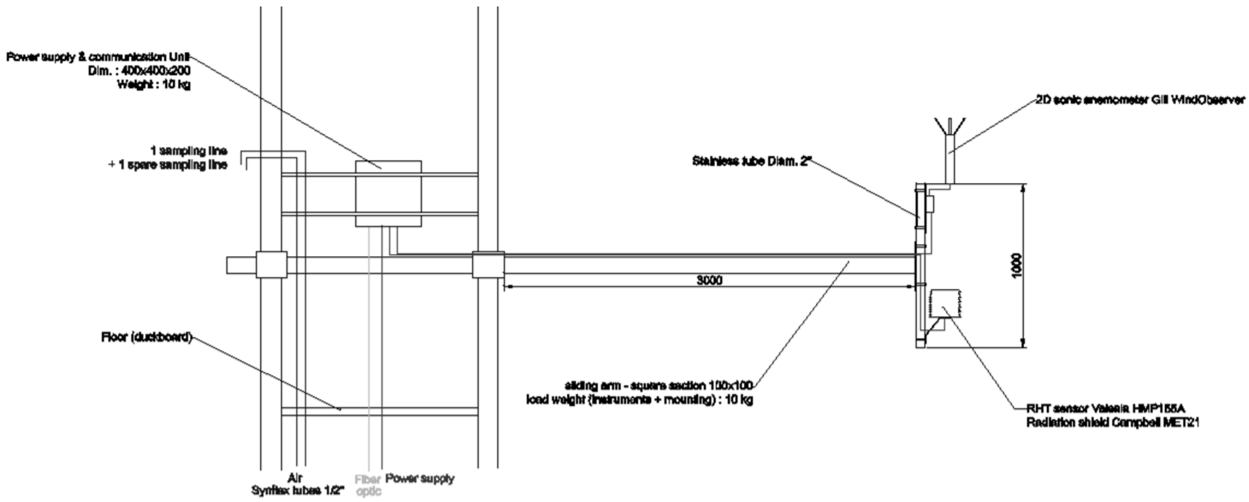



*Figure 1: Example of sensor installation on tower (at OPE station).*

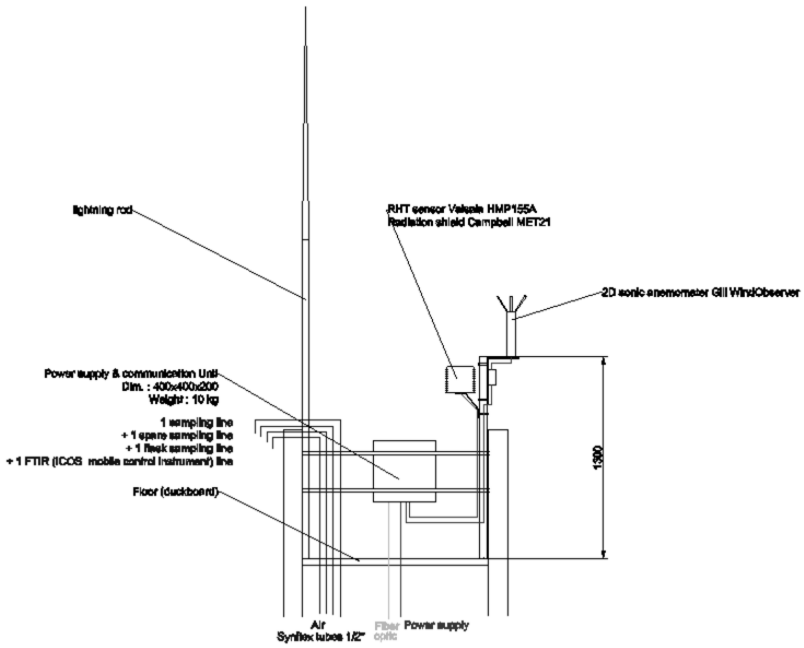



*Figure 2: Example of sensor installation at the tower top (at OPE station).*

### 2.3.3. Planetary boundary layer height retrieval instrument

The ceilometer or lidar must be collocated with the tall tower to provide suitable data to use and integrate for atmospheric modelling. However, in certain cases, the BLH can be retrieved from an external and dense ceilometers/lidar network if the network setup (instrument specs, instrument location beside ICOS AS) and its raw data management are ICOS compliant (ATC requirement in terms of data format, transfer...). The precise criteria for such a network acceptance is still to be defined.

### 2.3.4. Flask sampling

The flask sampler must have its own dedicated, independent sampling line. The sampling line must consist of 1300 Synflex tubing. The air must be sampled from the same location as the highest sampling height used for the continuous gas analysis. If $O_2$ analysis will be carried out on any flask samples, then an aspirated radiation shield should be incorporated at the air inlet (Blaine *et al.*, 2006; and see also section 5.2 for more details).

### 2.3.5. Radiocarbon sampler

The Radiocarbon sampler must have its own dedicated sampling line. The sampling line must consist of 1300 Synflex tubing. The air must be sampled from the same location of the highest sampling height of the continuous gas analysis and the flask sampler.

### 2.3.6. Radon monitor

A dedicated intake line for radon is mandatory.

If the ANSTO method is used (see 2.2.6), air sampling should be from the highest sampling height of continuous gas sampling. The intake line specifications must fulfil ANSTO recommendations (e.g. high flow rate, tubing diameter).

If the HRM method is used, sampling height should be ≤ 100m at a height with continuous gas sampling. A dedicated 1300 Synflex tubing should be used. The detector head must be installed at the bottom of the tower. The tubing from the air inlet to the detector must be as straight as possible (especially avoiding angles with small radii of curvature) in order to limit aerosol loss. For this same reason, any kind of filter is proscribed upstream of the detector. Thus, the air inlet consists of a simple rain guard.

With the ARMON method (see section 2.2.6.), air can be sampled at any height of the tall tower without any restriction on the length and/or form of the sampling line as it is not based on aerosol measurement. However, the sampled air has to be dried to around 2000 ppm (e.g. by using a Nafion dryer).

### 2.3.7. Shelter and tower setup requirement/recommendation

Special attention should be paid to the sampling line installation in order to avoid the risk of stagnant water (rain, condensation) in the line. This can induce artifacts regarding the $CO_2$

measurement. It is additionally recommended to avoid any "low point" (cf. Figure 3) along the sampling line. The sampling should always follow a negative slope.

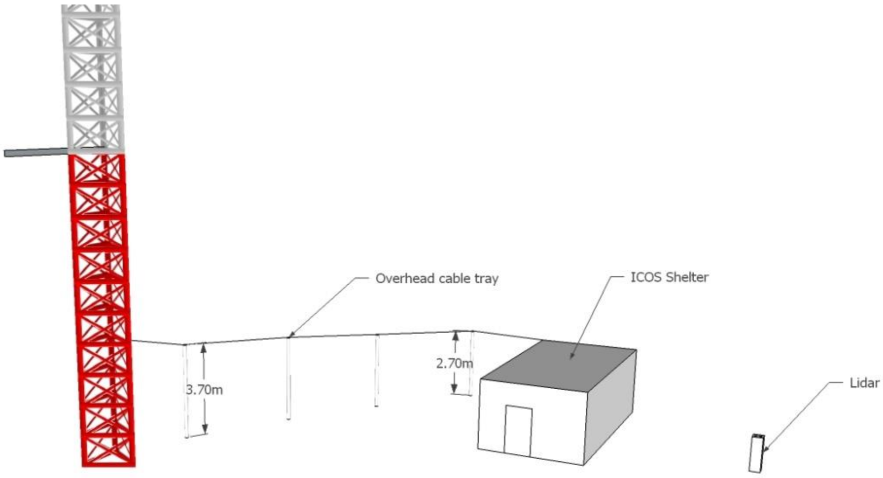



Figure 3: Example of sampling line installation.

## 2.4. Air Sampling design

### 2.4.1. Continuous measurement

#### 2.4.1.1. Plumbing design

ICOS does not impose any standardized architecture but it is recommended that station PIs contact ATC for guidance. A suggested Class 1 and 2 station design can be provided (Figure 4 and 5) by the ATC to assist station design if requested. Any part (filter, dryer, pressure regulator, pressure transducer, etc) installed on the sampling line must be approved by ATC or tested (with support of ATC) to prove it does not induce any artifact on the measurement.

#### 2.4.1.2. Ambient air sampling

Tubing to use for sampling:

- Recommended tubing: Synflex 1300 manufactured by EATON. If possible, in one single piece (without connector).
- Alternative to the Synflex tubing: stainless steel tubing by paying special attention to the risk of water condensing (especially with the outdoor/indoor temperature difference).

It is required to continuously flush the sampling line by using a dedicated pump for each sampling line or a shared pump or blower.
The tubing diameter and the flushing flow rate should be selected to limit the residence time (ideally under 1 minute; except for $O_2$ measurement – see section 5.2). Moreover, the tubing and other sampling parts must be chosen taking into account the leak and water vapor condensation

issue. For instance, a significant pressure drop in the sampling line helps to prevent condensation but require a special care regarding the leak issue.

In terms of practicality, an ICOS AS which is not equipped with a tall tower can use a ¼" Synflex tubing (<40 m length) with a flushing flow rate around 5-10 SLPM.

The sampling line should be made of a minimum number of parts, especially connectors, which should be used sparsely due to the possible inherent leakage. Thus, it is highly recommended that the Synflex tubing be a single piece.

In order to protect the sampling line from water, the air inlet must be equipped with a rain guard. Using a proper filter on the inlet is currently under consideration. Laboratory and field tests for filter assessment under specific weather conditions (ice, snow, fog) are currently in progress.

Aside from the dedicated sampling lines required in section 2.3 (flask sampling, radon, radiocarbon) and the one(s) required for the continuous gas analyzers, ICOS requires at least the following additional sampling lines:

- One dedicated sampling line at the highest sampling height for the travelling instrument (see section 6).
- A spare sampling line at each sampling height for quality control purpose (cf. 6.4). These spare lines allow swapping lines when one is obstructed.

It is recommended to install a dryer (e.g. conventional fridge, Peltier cooler) in the sampling line when there is a risk of water condensation (e.g. dew point onsite is often above the air conditioned room temperature). This system should be installed as close as possible to the sampling line's entry point in the room to avoid condensing upstream from the water trap.
The use of a liquid alarm sensor (e.g. from M&C products) might be beneficial in the case of using drying system to prevent any liquids from entering the gas analyzers.
It is highly recommended to follow the ATC guidance especially regarding the pressure at the instrument inlet: avoid significant pressure change (pressure during ambient air sampling and gas tank sampling should be close), respect the pressure range defined by ATC for your instrument during its initial test at ATC Metrology Lab (see your instrument ATC report).

#### 2.4.1.3. Gas distribution equipment

The required equipment is a rotary valve from Valco (model EMT2SD). The number of ports must be adapted to the station setup (number of tower sampling heights and gas cylinders).
Alternative options may be accepted after proving its suitability (dead volume, material compatibility, absence of leakages) with ATC support.

#### 2.4.1.4. Monitoring of station ancillary data

In order to assist the stations' PIs for the data control and validation, ICOS requires the automated monitoring of the following mandatory Station Ancillary Data (also called "diagnostic parameters" in ATC software tools):

- Flushing flow rate of each tubing
- Instrument flow rate
- Room temperature

These mandatory parameters can be completed by other parameters specific to the station sampling design (temperature of the cryogenic water trap, flushing flow rate of buffer volume, ...).

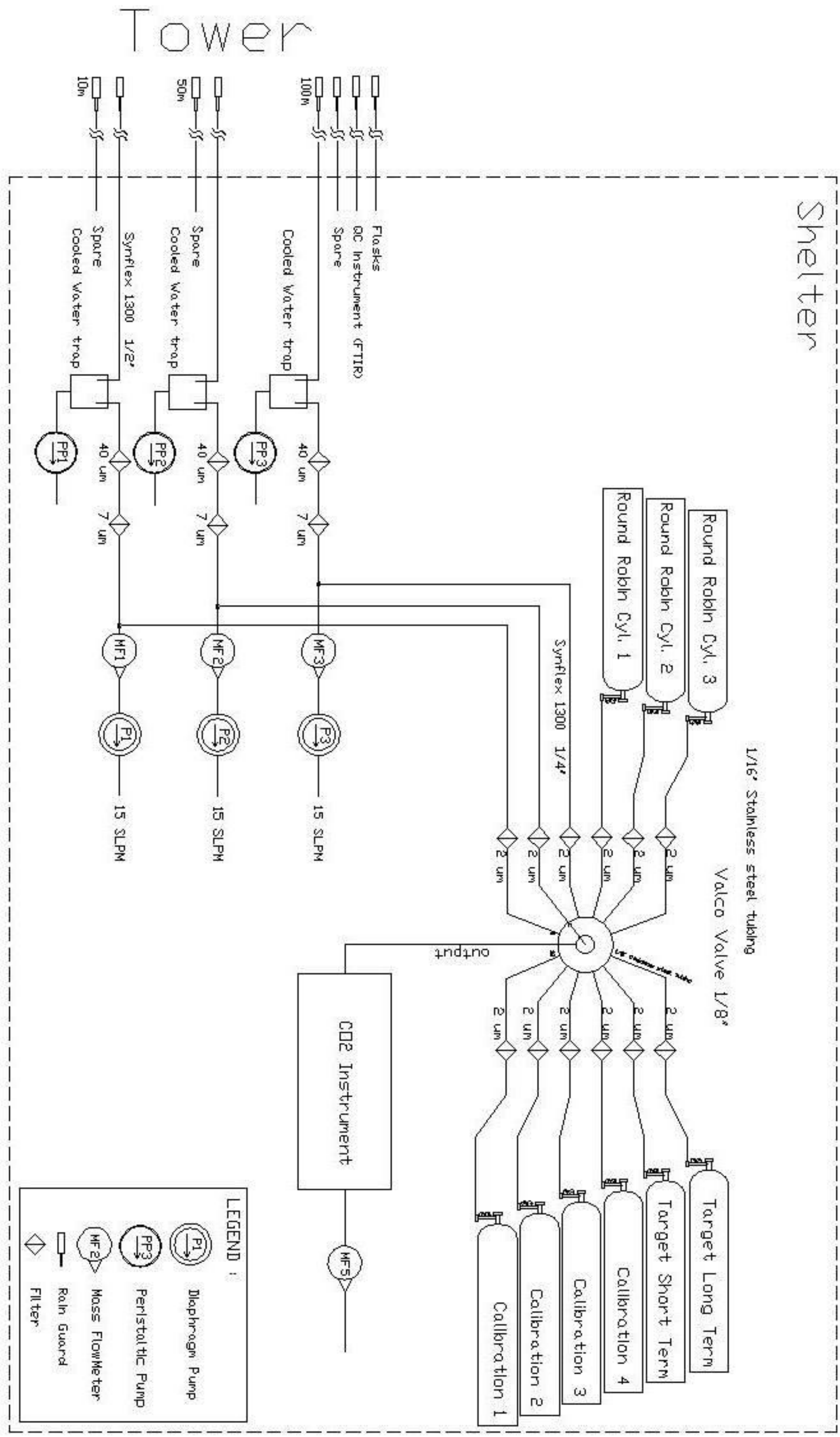



*Figure 4: ICOS AS plumbing design suggestion (multi sampling height tower).*

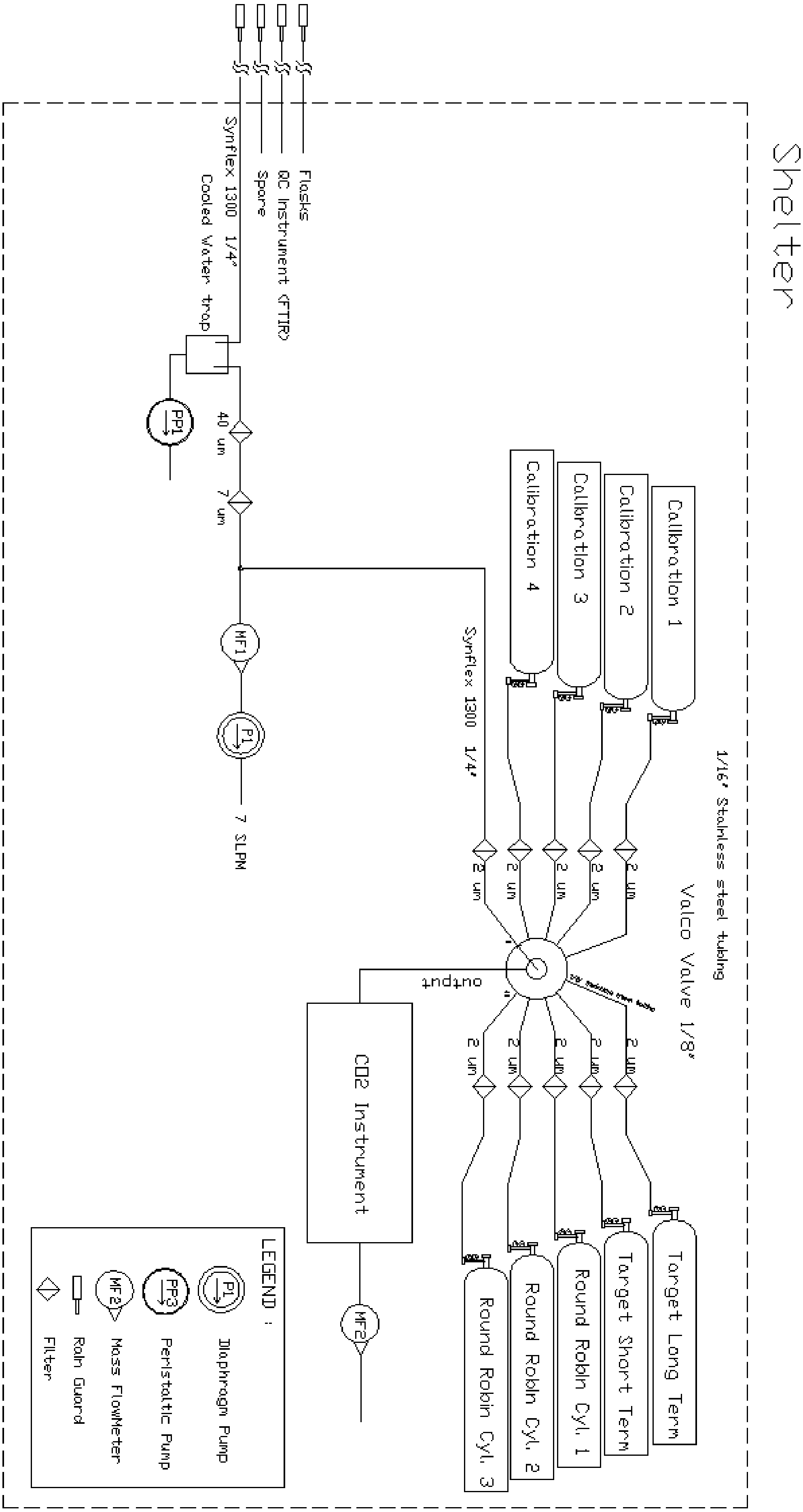



*Figure 5: ICOS AS plumbing design suggestion (single sampling height).*

### 2.4.2. Periodical sampling

For flask and radiocarbon sampling (integrated sample), the recommended tubing, Synflex 1300 tubing manufactured by EATON, should be, if possible, one single piece (without connector) in order to limit the risk of leakage along the sampling line.

## 2.5. Maintenance

In order to reach the 80% data coverage objective (agreed upon as an objective made at the 5th ICOS AS workshop in Arona, October 8th-9th 2012) targeted by ICOS, it is important to perform a regular and appropriate preventive maintenance to the different instruments, sensors and part of the atmospheric stations.

- Gas analyzer:
  The maintenance is instrument specific. See the manufacturer recommendations or the ATC specific note on the corresponding instrument. It is recommended to regularly schedule the instrument pump maintenance. Monitoring the flow rate (mandatory diagnostic parameter) or internal parameters such as the "outlet valve value" on Picarro analyzer, helps the operator to schedule the maintenance.
- sampling system (cf. the annex)
- Meteorological sensors:
  The meteorological sensors' maintenance procedure and periodicity recommended by the manufacturer must be respected. At a minimum, ICOS recommends an annual basic maintenance. This operation consists in the cleaning of the different sensors and the corresponding integration parts (e.g. radiation shield, pressure port), the control of sensor fastening, especially the wind sensor orientation, and visual check of the installation (cable condition …). According to WMO recommendations, the radiation shield may have to be repainted every 2 years depending on atmospheric pollution.
- PBLH sensor: depending on the instrument.
- Radon Monitor:
  For the HRM radon monitor, the aerosol filter must be changed at least once a month (or more frequently for sites with high concentrations of aerosols).

# 3. Measurement protocol

## 3.1. Flask sampling strategy

The ICOS flask sampling strategy has been described in a dedicated peer-reviewed paper (Levin et al., 2020).

Flasks should be sampled during 1 hour integrated with 1/t decreasing flow rate (to compensate the buffering effect), i.e. the collected sample should represent a real mean of ambient air, in order to be representative and better comparable to current model resolution. Also, synchronizing in situ continuous observations and integrated flask sampling is important for the quality control aim. This latter requirement is easier to achieve with longer integration times in flask sampling. This means, however, that for comparison reasons, the continuous in situ observations must be kept at the flask sampling height during the entire flask sampling period (i.e. no calibration gas measurement, no switching of in situ intake heights during flask sampling, no profile information available). This also means that flow rates, delay volumes and residence times in the tubing as well as timing of both, flask and in-situ sampling systems must be properly managed to be taken into account for the quality control inter-comparison. Before starting the 1hour flask sampling, the flask and sampling line must be flushed during 30 minutes.

The ICOS sampling scheme for continuous in-situ measurement quality control and large scale monitoring of additional compounds ($SF_6$, $H_2$, $CO_2$ stable isotope…) for continental flux estimate purpose, is to sample one single 3 liter flask every third day, independent of ambient $CO_2$ variability. Indeed, thanks to this sampling scheme, those flasks with low within-hour variability (on average one flask per week) could be used for the quality control aim, while all flask samples would deliver as much as possible representative data for all additional trace components analyzed in the FCL solely on flasks. This sampling scheme must be done with 12 flasks of the overall 24 flask managed by the automatic flask sampler. The remaining 12 flasks in the sampler would be reserved for $ffCO_2$ event sampling. In order to have a realistic chance to catch all possible events at a station, the sampler would be set to fill one of these flasks on each day between the regular every third day sampling. As continuous trace gas measurement data are transferred from the station to the ATC every night, level-1 CO data are available on the next morning after flask sampling the day before. These data will then be automatically evaluated at the ATC for potentially elevated CO to decide if the flask that had been collected on the day before has potentially an elevated $ffCO_2$ concentration and should be retained for $^{14}CO_2$ analysis. If yes, the flask sampler will obtain a respective message from the ATC. If not, the flask can be re-sampled.

- <u>For continental station (equipped with a multi sampling height tall tower):</u>

In order that all flask sample results are useful for flux estimates with current regional inversion models, flasks should be collected during mid-day or early afternoon. Ideally, flask must be sampled between 11h and 15h (local time) but not always at the same time. During this period of the day, atmospheric mixing is strong and model transport errors are smaller than during night. For all samplings, wind speeds should be larger than about 2 $ms^{-1}$, so that the sampled footprint is well defined. This strategy has been developed for tall tower sites that are located not directly at the coast, i.e. that are of predominantly continental character.

As modelers are mostly interested by data from the highest level of the tower (largest footprint, most representative, etc), all flasks must be sampled from that highest level on a dedicated sampling line (see section 2.3.4).

- For coastal and mountain station:

Flask sampling strategy has not been defined yet for coastal and mountain stations. Station PI should consider their site specific feature in order to get flask sample results useful for flux inversion modelling. Depending from the altitude and the geographical locations, mountain station could sample flask early morning or during daytime (in the case the measurement site is more exposed to regional emissions by diurnal PBL growth or thermal wind regime) while coastal station may sample flask from "clean air" sector alternatively to "continental" sector.

## 3.2. Radiocarbon sampling strategy

Two-week integrated radiocarbon sampling should be made at Class 1 stations using CO2 absorption in the NaOH radiocarbon sampler. The purpose of these integrated samples is to monitor long-term changes in the atmospheric $^{14}CO_2$ levels.

This long-term sampling strategy is complemented by additional dedicated $^{14}CO_2$ event flask sampling as described in Levin et al. (2020). In between the three daily quality control sampling (described in 3.1), potential $^{14}CO_2$ event flask is sampled during afternoon hours. During these $^{14}CO_2$ event flask samplings, the in-situ instruments shall NOT measure at the flask sampling intake height only but shall perform the standard vertical profiling between all available inlet height.
A flask sample shall be retained for $^{14}CO_2$ analysis if the CO level during the sampling exceeds a threshold which has to be individually defined by the station PI. One day after sampling, the ICOS flask sampler communicates automatically with the ATC and receive information if the in-situ CO level during the sampling exceeded the PI-defined threshold. In this case, the sample is retained for $^{14}CO_2$ analysis otherwise the flask will be resampled. The Carbon Portal provides special Jupyter notebooks, to allow the station PIs to investigate observed and modelled time series of CO, $CO_2$, $ffCO_2$ and $bioCO_2$. These Jupyter notebooks are developed to assist the station PIs in defining the station-specific CO threshold, used as criteria to select the flask samples which will be retained for $^{14}CO_2$ analysis. The PI-defined CO threshold could be season dependent, depending on a potential seasonal change in the fossil fuel fix in the catchment area of the station.
To get familiar with the Jupyter notebooks please go to: *https://exploredata.icos-cp.eu*. No registration is required, just provide a unique username and the generic password: msa. Please navigate to: /project_jupyter_notebooks/RINGO_T1.3/RINGO_T1.3_flasksampling_v5.ipynb. Here you find the commented example of the notebook used for the ICOS flask sampling paper. This example serves as a template can be edited by the station PI to explore its own station, however as non-registered user you cannot save your changes. Thus, we advise you to register via sending an email to: *jupyter-info@icos-cp.eu* to get the full access and to personalize your notebook.
The FCL together with the Carbon Portal is developing an additional $^{14}CO_2$ event flask sampling method which is based on forecasted back-trajectories. Therewith, event sampling of predefined "areas of interest" can be accomplished. The station PI defines specific catchment areas of interest and the flask sampler is triggered to perform a $^{14}CO_2$ event flask sampling once the forecast system predicts that the catchment area of interest will be sampled by the air mass. This event sampling pattern was developed during the RINGO project and is currently being operationalized for all ICOS stations by the FCL.

### 3.3. Continuous measurement sampling strategy

Ambient air sampling sequence on tall tower:

All sampling heights should be sampled sequentially within an hour in order to get hourly representative data for each sampling height. Among all the sampling heights, the highest is the most important (for background signals suitable for modeling purposes). Therefore, if one sampling height is to be favored, it should be the uppermost position.

Sample drying:

The following recommendations were presented and discussed during the Atmosphere MSA of June 2015 in Dübendorf and completed during the following MSAs.

The presence of water vapor in the sample can induce important errors in measurements if it is not properly dealt with (for example by drying the sample or applying water vapor corrections). If there is a risk of water condensation at the site (especially in southern of Europe for example, depending mostly on atmospheric dew point and the shelter temperature), it is recommended to use a dryer installed close to the sampling tubing entrance point in the room. Two drying options are proposed:

1. Via a cryogenic water trap (at least -50°C). This option offers the best performance but is demanding in terms of maintenance and the risk of leakage might be an issue. Risk of leakage can be significantly reduced by using Swagelok QF-series quick connects at those points in the line where the traps need to be disconnected for removing ice.
2. Via Nafion (model MD from Perma Pure). The performance is lower compared to cryogenic water trap but brings nevertheless satisfactory[2] results. The residual water level downstream of the Nafion is too high to avoid water vapor correction. Nafion dryer induces artifacts on $CO_2$ and $N_2O$ measurement (Laurent et al., 2019) but it can be mostly corrected by passing the calibration gases through the Nafion as well.

Without any risk of water condensation (most of the European sites), either instrument specific $H_2O$ correction determined by ATC can be implemented or a dryer listed above (Nafion or cryogenic water trap) can be installed upstream the GHG analyzer. For GHG analyzers not equipped with a dryer, the instrument-specific water corrections determined by ATC Metrology Lab must be implemented and must be checked on a regular basis, at least once a year (ideally every 6 months) with the ATC water vapor assessment test: ATC “water droplet test” or Mobile lab audit with humidifying bench.

As the regular on site ATC “water droplet test” might be demanding for station technical staff and for ATC (support, configuration change…) and water vapor sensitivity might change erratically, ATC highly recommends to install a Nafion dryer at the GHG analyzer inlet which provides good performance without any maintenance.

The recommended Nafion dryer set up consists of a Perma Pure MD-070-144-S-4 used in the “reflux mode” as shown on the figure 6. Perma Pure PD series should be avoided as it induces more significant artifact on $CO_2$ and $N_2O$ measurement than MD series. Even if these artifacts should be mostly corrected by passing calibration gases through the Nafion dryer, the risk of a significant remaining artifact on calibrated data is a bit higher compared to Perma Pure MD series which induce lower intrinsic artifacts.

[2] It is to be noted nevertheless that the Nafion behavior is known on only relatively short periods. The long term (several years) behavior still needs to be assessed properly.

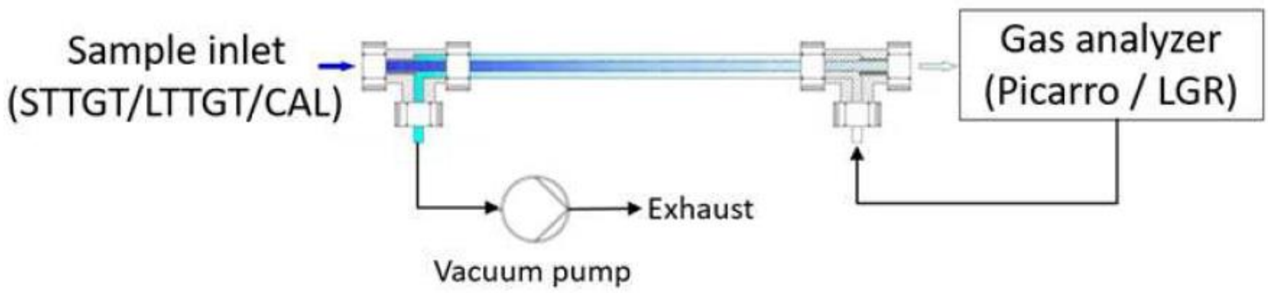



*Figure 6: Nafion dryer installation setup ("Reflux" mode).*

This drying setup does not require an additional pump for a Picarro as the external Picarro pump ("vacuum pump" on the diagram above) can be used for sampling through the Nafion and for the purge counter flow.

For LGR analyzer, the internal pump (if equipped) must be bypassed with the software interface ("fast mode") or by applying the external pump on the LGR vacuum port.

It is important to pass all the different kinds of gas (ambient air, calibration gases, target gases, short term working standard) through the Nafion.

Any option choice/change must be traced by ATC for proper data processing.

The Ecotech Spectronus integrates a build-in drying system made of a Nafion membrane and an additional magnesium perchlorate. Even if the Nafion membrane use to induce significant artifacts on $CO_2$ and $N_2O$, as the Calibration gases are also passing through the Nafion, these artifacts are mostly corrected by the calibration. However, the Nafion can be bypassed and replaced by an external dryer (cryogenic water trap or Peltier dryer). Such modification must be validated with dedicated tests.

Buffer volume use:

The interest in using a buffer volume for the continuous in-situ gas analysis has been studied and presented during MSA 2015 in Dübendorf, MSA 2017 in Lund and MSA 2018 in Jena. The last study focus in particular on the interest in having high frequency data (otherwise smoothed out if buffer volume is used) for precise QC and data validation, and the "representativeness error" otherwise made on the hourly data when multi sampling heights are used without buffer (incomplete hour data set due to the multiplexing). Based on these studies, ATC cannot neither reject nor generalize the buffer volume use within the ICOS atmosphere network as it may depend on the specific setup at the site. Sites which are facing regular and significant local contamination should not use buffer volume as the spike detection (only suitable without buffer) impact must be higher than the representativeness error related to the data discretization (multi sampling height sampling without buffer). The Buffer volume can still be used depending to site specification and Station PI expertise on buffer volume. The buffer time constant must be adjusted (depending to buffer volume and flow rate) according to the multi sampling height sequence in order to take into account the data gap (while sampling other levels). The interest regarding the deconvolution of a data set from a buffer volume should be studied. The implementation of buffer volumes does not apply to stations with a single sampling height which should not be using a buffer volume.

Specific recommendation for Ecotech Spectronus (FTIR):
The Spectronus must be continuously flushed (at least at 80 ml/min) with $N_2$ gas. A careful background measurement and calibration must be performed after changing the $N_2$ gas tank. The Spectronus can be used in flow mode (the measurement cell is continuously sampling) or in static mode (the measurement cell is prepared with several vacuums - settling time - and then fill with the sample at a given pressure) in order to save gas. In static mode, ATC highly recommend to use at least 6 minute (ideally 10 minutes) settling time for ambient air measurement and 10 minute settling time for calibration and gas tank measurement.

For a station with a single sampling height (mountain and coastal station), both measurement modes can be used:

- Flow mode for ambient air (with 10 minutes settling time at the beginning of ambient air measurement)
- Static mode for calibration (with 10 minutes settling time at each tank measurement)

For a station with several sampling heights (continental station…), ATC recommends to use only the static mode with a possible shorter settling time (to be tested in each individual set-up). Taking into account this minimum settling time and the static measurement time itself, it seems difficult to spend less than 10 minutes in total for one sampling level.

## 3.4. Planetary boundary layer height profile strategy

The Ceilometers/Lidars will be continuously operated to provide backscatter profiles throughout the day and night.

# 4. Calibration, standards

## 4.1. Continuous gas analyzer

### 4.1.1. Calibration protocol

An appropriate calibration strategy depends on the instrumentation in use and on ambient conditions of the respective station.

Calibration requirement:

- Gas tank required:
  - 3 or 4 Calibration Standards: During the Demonstration Experiment no significant difference has been detected using 3 or 4 Calibration Standard tanks. However, the fourth tank maybe useful if a problem occurs with one tank. As a result, 4 tanks are highly recommended for remote sites.
  - 2 Target Gases:
    - A performance Target Gas (also called short-term target gas) used for daily Quality Control (QC) and uncertainty estimation.
    - An archive Target Gas (also called long-term target gas) used also for QC purposes but over the station lifelong to interlink different calibration sets.
  - Depending on the Quality management strategy, additional QC gases may be required or recommended (dedicated gas for intake system test…).

  In Addition to these gases, a Short Term Working Standard (STWS) to correct short term variability is highly recommended for $N_2O$ measurement with the LGR $CO/N_2O$ or Picarro G5310 analyzers (also, an STWS is a requirement for $O_2$ measurement – see section 5.5). The use of such an additional gas for measurements of other species is under study.
  All calibration, STWS and target gases have to be prepared (e.g. tank filling) and calibration and target gases have to be calibrated by the ICOS CAL (cf. 4.1.3). All cylinders are owned by the stations.

- During the step 2 of the ICOS labelling process, an initial test period is conducted in order to define the best calibration strategy adapted to the station setup: stabilization time, injection duration (depending on the stabilization time in relation with the flow rate and the dead volumes), calibration frequency and number of calibration cycles. This test period must last at least 3 months in order to get a sufficient amount of data for a detailed analysis. The initial test consists in using a stringent calibration strategy.

  For CRDS (Cavity Ring-Down Spectroscopy) instrumentation, the initial test calibration setup should be as follows:
  - Gas injection duration: 30 minutes
  - Number of cycles (tank analysis) during a calibration: 4
  - Calibration frequency: every 15 days
  - Performance target frequency: every 7 hours

  Depending on the initial test results, the calibration strategy must be then adjusted (with ATC support). However, the calibration must respect the minimum ICOS calibration requirement (cf. Table 11).

| | Min. number | Min. frequency | Min. gas injection duration | Min. calibration cycle number | Range | Expected lifetime (*40L tanks*) |
|---|---|---|---|---|---|---|
| **Calibration Standard** | **3** | 1 month* | 15 minutes or site specific* | 2* | Span the unpolluted atmospheric range | > 4 years |
| **Performance Target gas** | **1** | 24 hr* | 15 minutes or site specific* | - | Low concentration | > 6 months |
| **Archive Target gas** | **1** | 1 month | 15 minutes or site specific* | - | High concentration | > 20 years |

**can be higher depending to the initial site test results*

*Table 11: Minimum ICOS requirements for the calibration and QC of an ICOS CRDS analyzer.*

In order to assist station PIs in the calibration optimization, the ATC provides:

- systematic comparison of linear/quadratic fits should be implemented
- data products for calibration optimization

It should be noted the ICOS processing chain applies a linear interpolation to the data in-between two calibrations in order to refine the calibration coefficients.

For quality control and performance estimate purposes, the continuous gas analyzers regularly measure 2 types of target gases: A performance target gas and an archive target gas. See the corresponding sections 6.4 and 6.5 for detailed information.

In addition to measuring the short term target at least once a day, ideally twice a day at a frequency allowing the tank measurement at different time of the day over several weeks (e.g. every 10 hours), it is required to measure the short term target just after a calibration to measure it in “super dry” conditions allowing a better assessment of the overall H2O related uncertainty.

Specific recommendation for Ecotech Spectronus (FTIR):
It is recommended to measure calibration and target gas tank in static mode in order to save gas. A calibration should consist of measuring 2 cycles of at least 3 calibration tanks in static mode (with 10 minute settling time). A calibration should be performed twice a month and after each $N_2$ tank change. With such a calibration strategy, the calibration gas tanks should last more than 10 years.

For fine quality control, ATC recommends to measure a short term target in static mode every 10 hours. Thereby, the short term target should last about a year.

A long term target should be measured at the calibration frequency (at least once a month).

#### 4.1.2.Calibration equipment

The CAL is in charge of tank filling and analysis (calibration and target gases). Gas containers (tanks) are not provided by the CAL and must be bought by station owners according to the CAL/ATC's requirements.

The ICOS tank setup (tank + valve) meeting the aforementioned CAL/ATC requirements include:

- Cylinder: 6061 Aluminum cylinder manufactured by Luxfer UK (π-certified)
- Cylinder valve: Rotarex membrane valve (D200 type with PCTFE seat). Body material: brass or stainless steel
- Pressure regulator fitting: DIN 14 by preference, CGA 590 also possible (CGA 580 less favored)
- Cylinder volume: 40L or 50L recommended (other volumes accepted if argued)

The CAL has the capability to install the cylinder head valves. Thus, station owners are encouraged to send their cylinders without having the head valves installed which would allow the CAL to visually inspect the inside of the cylinders before filling.

European suppliers selling the above mentioned material e.g. are MATAR (Italy) and Deuste Gas Solutions (Germany).

Required pressure regulator: two models are accepted

- SCOTT Specialty Gases MODEL 14 M-14C (or -14B) Nickel-plated brass.
- TESCOM Serie 64-3400 Stainless steel electropolish with PCTFE valve seat and the use of Stainless steel High purity gas pressure gauge (e.g. Bourdon Haenni UPG2).

Any other setup/part must be approved by ATC along with the appropriate compliance test. Test criteria are to be defined.

At the station, it is highly recommended that cylinders and associated pressure regulators are installed in an air temperature controlled room in order to avoid potential bias induced by temperature variation. Moreover, it is recommended that tanks and pressure regulators are installed within a dedicated enclosed rack to buffer temperature changes potentially induced by the air conditioning air flow. The ideal cylinder position within the rack is horizontal in order to limit stratification and fractionation effects.
The cylinder pressure regulator must be adjusted in order to keep the difference of pressure at the instrument inlet during cylinder measurement and ambient air measurement below 0.5 bar. Moreover, in order to limit the artefact of a possible leakage, it is recommended to adjust the

pressure regulator in order to get a pressure at the instrument inlet slightly above atmospheric pressure (100 - 200 mbar). Avoid higher pressure to limit the gas consumption (usually proportional to the gas pressure applied at the instrument inlet).
Pressure regulator and tubing must be appropriately flushed. For GHG measurement, this flushing period (so called "stabilization period") is determined during the station initial test period (step 2 of the labelling process; see above section 4.1.1).

### 4.1.3.Standard production and calibration

The Flask and Calibration Laboratory (FCL) entity of the Central Analytical Laboratory (CAL) prepares standard air mixtures for the set of ICOS parameters for continuous monitoring. The air mixture produced is made of real natural air. For calibration of field instruments, the air mixture has to cover the full range of atmospheric mixing ratios that can be expected at a monitoring site considering diurnal, seasonal, inter-annual variability and the currently observed long-term trends (see below for the recommended air mixture of the different tanks).

The recommended mole fraction for the different gas cylinders are represented in the table 12. These values must be re-evaluated every year at the MSA taking into account the current mean value, range of atmospheric variations and the trend in the atmosphere. The values given in table 12 are standard recommendations, which can be adapted by station PIs based on the range of observed concentrations at their sites, especially for peri-urban sites. The CAL FCL will use the table 12 to prepare the standards if no specific values have been expressed by station PIs. The CAL FCL will prepare the Short Term Target (STT) and Short Term Working Standard (STWS) with slightly different mole fractions.

| *2020* | | **$CO_2$** | | **$CH_4$** | | **CO** | | **$N_2O$** | | **$O_2$** | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Trend | | *≈ +2.5 ppm/yr* | | *≈ +5 ppb/yr* | | *≈ 0 ppb/yr* | | *≈ +1 ppb/yr* | | ≈ -25 per meg/yr | |
| Site | | *Bckgnd* | *Peri-urban* | *Bckgnd* | *Peri-urban* | *Bckgnd* | *Peri-urban* | *Bckgnd* | *Peri-urban* | *Bckgnd* | *Peri-urban* |
| **3 CAL set** | **CAL 3** | 460 | 480 | 2150 | 2300 | 250 | 400 | 345 | 350 | -970 | -1080 |
| | **CAL 2** | 425 | 430 | 1950 | 1970 | 150 | 200 | 335 | 335 | -775 | -830 |
| | **CAL 1** | 390 | 390 | 1850 | 1850 | 60 | 60 | 325 | 325 | -580 | -580 |
| **4 CAL set** | **CAL 4** | 460 | 480 | 2150 | 2250 | 250 | 400 | 345 | 350 | -970 | -1080 |
| | **CAL 3** | 430 | 440 | 2000 | 2100 | 175 | 200 | 338 | 340 | -810 | -860 |
| | **CAL 2** | 410 | 415 | 1900 | 1950 | 100 | 100 | 333 | 333 | -690 | -690 |
| | **CAL 1** | 390 | 390 | 1850 | 1850 | 60 | 60 | 325 | 325 | -580 | -580 |
| **LTT** | | 460 | 480 | 2150 | 2300 | 250 | 400 | 340 | 345 | -970 | -1080 |
| **STT** | | 410 | | 1950 | | 100 | | 335 | | -690 | |
| **STWS** | | 410 | | 1950 | | 100 | | 335 | | -690 | |

*Table 12: Values of the mole fractions recommended for the gas cylinders.*

The CAL FCL manages the high-pressure cylinder preparation, which consists in testing and conditioning of high-pressure cylinders before the filling and a dew-point control. High pressure cylinders so prepared are then calibrated by the FCL prior to shipment to the atmospheric stations.

The atmospheric stations must provide their own high pressure cylinders equipped with the accepted valve and connector types (see 4.1.2) along with the valid pressure test certificate.

According to WMO recommendations, a recalibration schedule for the ICOS monitoring stations of every third year is assumed. It is intended to provide stations with a replacement set of standards for this period of recalibration to be returned by the station immediately after receipt of their proper calibration standard suite. The respective additional high pressure cylinders are owned by the CAL FCL.

Part of the QC strategy will also be a re-analysis of the long-term target gas at the stations (again every third year, with an 18 month time lag to the re-calibration of the calibration standards).

The cylinders should be replaced once the cylinder pressure has decreased to 30 bar in order to allow the CAL performing a last cylinder calibration before their pressure reaches the critical value estimated at 20 bar by the WMO (cf. GAW report N°255). The exception to this protocol is STWS cylinders, which do not need to be reanalyzed by the CAL, and thus the pressure can be depleted further to ~20 bar. Cylinder replacement must be initiated by the station PI who must contact the CAL within a 3 month anticipation. Given this anticipated need and the frequent use of the short-term target, it is highly recommended to have a spare cylinder on-site. Regarding the calibration scale replacement, the entire set of cylinders cannot be replaced at once for logistic limitation (e.g. required replacement cylinders from the CAL to overcome the temporary absence of the station cylinders). The calibration cylinders can be replaced by a maximum of 2 at once. Therefore, this limitation requires a longer anticipation (ideally 6 months). Contact the CAL for up-to-date information.

## 4.2. Other instruments

### 4.2.1. Meteorological sensors

The sensors should be calibrated according to the periodicity specified in Table 13 or the manufacturer recommendation if more stringent and justified. The traceable calibration must be carried out by the manufacturer or a certified laboratory.

| **Sensor** | **Calibration periodicity (month)** |
|---|---|
| Wind sensor | |
| *Ultrasonic* | none |
| *w/ moving parts (propeller or cup)* | 24 |
| Temperature sensor | 12 |
| Relative humidity sensor | 12 |
| Barometric pressure sensor | 24 |

*Table 13: Recommended meteorological sensor calibration periodicity.*

### 4.2.2. Radon monitor

The HRM monitor detector shall be checked every 6 months with a $^{241}Am$ α-source.
The ANSTO Radon monitor is automatically calibrated with a provided and dedicated unit (Rn source must be purchased separately).
The calibration of the ARMON monitor should be checked every 2 years. A mobile reference radon monitor, calibrated at a reference radon chamber, could be used.
The calibration and quality control protocols for each method will be studied within the EMPIR project started in June 2020 and will be described in a further version of this document.

### 4.2.3. Eddy flux instrument

The calibration and protocols for eddy flux measurement are available on the ICOS ETC website (*http://www.icos-etc.eu/icos/documents/instructions*). These protocols have been published in a special issue of the International Agrophysics (*http://www.international-agrophysics.org/Issue-4-2018,7048, 2018*).

## 4.3. Central Analytical Laboratory services

The Central Analytical Laboratory (CAL) is divided in 2 entities, the Flask and Calibration Laboratory (FCL)(cf. 4.1.3) and the Central Radiocarbon Laboratory (CRL). It provides the following services to the atmospheric network:

- provision of calibrated standard gases in high-pressure cylinders (FCL)
- analysis of ICOS parameters (cf. Table 2) from periodical sampling (FCL and CRL)
- supply of samplers for integrated $^{14}CO_2$ analysis (CRL)

<u>Flask air sample analysis at the FCL</u>

The FCL analyzes air samples in flasks collected by the ICOS network for additional periodical analysis of the species (cf. Table 2) and for Quality Control purposes. The flasks are owned by each station. Once analyzed, The FCL checks each flask before sending them back to the stations to avoid sample loss. Potential error sources include leaking valves and humidity in the flask. Defective valve seals will be replaced; broken flasks will be disposed of after notification to the flask owners. At each station, a sufficient number of flasks (100) are needed to assure a constant supply for the sampling program.

Sampling details for flask air samples have to be transmitted to an FTP server by the stations at the latest when a complete batch of flasks is shipped to the FCL. Such shipments should be announced by the station PIs through a web front-end of the CAL database. This database will document all steps of the flask handling including sample collection, the individual measurement steps within the CAL, flask checks and shipments. This will allow for tracking the processing status of any and each flask.

The flask sample analysis results are sent to the ATC server to be processed (QC task) and stored in the ATC database.

Radiocarbon sample analysis at the CRL

The CRL analyzes the radiocarbon samples collected by the class one stations in the ICOS network. Two different sampling strategies are foreseen: integrated sampling (two-weekly) and event based sampling of individual grab samples.

Integrated samples:
The CRL will build the samplers for the integrated radiocarbon sampling and provide them to Class1 stations at cost price. The standard sampler is the robust and field proofed chemical absorption sampler using NaOH solution (cf. 2.2.5).

Individual samples:
Event based radiocarbon flask sampling is performed using the ICOS flask sampler (c.f. 2.2.4). Using the 3L glass flasks (c.f. 2.2.5) is required. All event-based radiocarbon samples are first analyzed at the FCL for trace gases and stable isotopes. After analysis at the CRL the flasks are returned to the FCL to be conditioned and leak tested before they are shipped back to the station. The flask sampler software allows the station operator selecting the flask usage (quality control and 14C analysis); depending on the choice, flask will be forwarded to CRL or not.

The radiocarbon sample analysis results are sent to the ATC server via the CAL database to be stored in the ATC database.

# 5. Specifications unique to $O_2$ measurement

$O_2$ is a recommended ICOS parameter which requires specifics sampling setup and special handling considerations compared to the mandatory ICOS parameters for continuous gas measurement. The purpose of this dedicated $O_2$ section is to avoid confusion and useless consideration for station PI focusing only mandatory parameters specifications. This section provides all specifications to upgrade an ICOS atmosphere station with $O_2$ measurement.

## 5.1. $O_2$ analyzer options

As for $N_2O$, in ICOS at this stage, $O_2$ is not a mandatory parameter but a recommended parameter for continuous gas measurement (see Table 2). No $O_2$ analyzers have yet been tested by the ATC, however, some ICOS members have many decades of experience operating such analyzers, including in demanding field applications such as at very remote locations and on board ships and aircraft. Based on these experiences, the following analyzer recommendations can be made. All of these analyzers have the potential to exceed the performance requirements listed in Table 3. However, it is very important to be aware that rigorous gas handling protocols and procedures are essential in order to meet these performance requirements. High-precision $O_2$ measurement is much more sensitive to gas handling procedures than is the case for most trace gas measurement. To illustrate this, all four atmospheric *in situ* $O_2$ analyzers currently in routine use that are mentioned below require pre-treatment drying of the sample air and calibration gases, to a dew point of at most -75°C. Other $O_2$-specific gas handling requirements are discussed in other sections of this document.

The *Sable Systems International* FC-2 "Oxzilla" differential oxygen analyzer is the $O_2$ analyzer currently most widely used for *in situ* measurement. A number of homemade modifications are necessary in order to meet the performance requirements (Stephens *et al.*, 2007). In addition, it is necessary to employ a mass spectrometer-like "changeover valve" to switch sample air and reference gas (referred to as a short term working standard, STWS, in section 4.1 above) between the two internal fuel cell sensors, to mitigate the effects of baseline drift in the fuel cells. The typical switching frequency is once per minute (Stephens *et al.*, 2007), although recently, once per 30 seconds has been shown to improve performance for some measurement system designs (Pickers *et al.*, 2017).

The *Qubit Systems* S104 "DOX" differential $O_2$ analyzer is based on the same fuel cell technology as the Oxzilla and appears to be a very similar analyzer, albeit with some key differences. As with the Oxzilla, a few customizations need to be made, and a changeover valve needs to be employed. As yet, there are no publications by the high-precision atmospheric $O_2$ community using this analyzer, but preliminary laboratory results show similar precision and repeatability as the Oxzilla (P. Pickers, UEA, personal communication).

The *Servomex* PM1155 paramagnetic oxygen sensor module is also able to meet the ICOS performance requirements (see, for example, Manning *et al.*, 1999). This sensor has either been used integrated into the *Columbus Instruments International* "Paramax 101" analyzer (no longer manufactured) or stand-alone, with homemade customized electronics and temperature control built around it (Bonne *et al.*, 2012). At *Servomex*, the PM1155 has been superseded by the PM1158. In the mid-2000s, it was discovered that, for our application, the PM1158 was a significantly inferior sensor, exhibiting short-term noise that was three times worse than the PM1155 (Kozlova and Manning, 2009). Around that time, *Servomex* agreed to a one-off bulk order of the obsolete PM1155s for our community. It is unclear whether such an order could be repeated, or if the PM1158 has been upgraded or improved since the mid-2000s. As with the fuel cell analyzers, to meet ICOS performance requirements, a changeover valve must be employed, alternating between sample air and reference gas, with a switching frequency of the order of once every 5 to 10 minutes. Unlike the fuel cell analyzers, however, the *Servomex* is a single-cell analyzer. This means that one cannot measure sample air continuously, as periodically one must pass reference gas through the cell. A typical sampling scheme might be 10 mins of sample air analysis, followed by 5 mins of reference gas analysis.

The most precise atmospheric $O_2$ analyzer currently in routine use is the vacuum ultraviolet (VUV) analyzer (±0.5 per meg precision on a 1-min mean; Stephens *et al.*, in prep. 2020), and it is also ideally suited to all field applications (Stephens *et al.*, 2003). This analyzer is significantly more precise than any commercial analyzer on the market, even when taking into account homemade customizations. However, no commercial supplier exists for this analyzer. Interested ICOS scientists should contact Dr. Britt Stephens, National Center for Atmospheric Research (NCAR), Boulder, Colorado, USA. As with the other $O_2$ analyzers, a changeover valve is needed, typically switching between sample air and a reference gas every 2 seconds. As with the paramagnetic analyzers, the VUV is a single-cell analyzer.

The four analyzers mentioned above have proven performance. In addition, two new commercial analyzers still under development may have promising potential to ICOS, manufactured by *Aerodyne Research Inc.* and *Picarro Inc*. Prototypes of both analyzers have been shared with ICOS members. At this stage, it is not possible to say whether these two analyzers are able to meet the ICOS performance requirements (Table 3) without further laboratory testing. Two key attractions of these two analyzers is that they may not need pre-treatment drying of the sample air (or partial drying may be sufficient) and they may be closer to "off-the-shelf" analyzers compared to the $O_2$ analyzers currently in use, which all require significant homemade modifications. Having said that, as mentioned at the beginning of this section, much of the challenge in high-precision $O_2$ measurement is with respect to the gas handling upstream of the analyzer, and not so much with respect to the analytical technique or analyzer employed.

## 5.2. Special gas handling considerations for $O_2$ measurement

If the specifications listed in this section are incompatible with specifications given in previous or subsequent sections, then those written in this section should be followed, for all $O_2$ measurement. Improved gas handling designs continue to be developed for $O_2$ measurement, with the aim to eventually achieve the WMO compatibility goal (±2 per meg). Some examples are evident in this section (e.g. new 'tee' junction design). For any changes or upgrades to these ICOS $O_2$ gas handling protocols, it is essential that it is demonstrated that the proposed change does not create any artifacts, imprecision or bias. This must be demonstrated to significantly better than the precision and repeatability goals listed in Table 3 above.

The GHG sampling design shown on Figures 4 and 5 are not suitable for O2 measurement. Indeed, no tees can be used that divide an air stream into two paths, because $O_2$ will fractionate with respect to $N_2$ at such tee junctions. Therefore, sampling lines on the tower can only be flushed at the flow rate required by the analyzer (typically 100-200 mL/min). To compensate for this, 1/2" OD tubing should not be used, but rather 1/4" OD tubing, to prevent unacceptably long residence times of the sample air in the tubing. For a 300 m tower, the pressure drop will only be of the order of 20 mbar for 1/4" tubing, which is quite acceptable (for a flow rate of 200 mL/min). This arrangement does, however, still result in reasonably long residence times: 22 mins in the scenario given here.

The one exception to the $O_2/N_2$ tee fractionation problem is the tee created by the peristaltic pumps (see PP1, PP2 and PP3 in Figures 4 and 5). To ensure that these tees do not create problems, however, as low a flow rate as possible should be used for the peristaltic drain.

Note that there have been non-comprehensive investigations into designing a tee junction that does not fractionate $O_2$ with respect to $N_2$, as discussed in Stephens *et al.* (2007) and Kozlova and Manning (2009). These two studies were not fully compatible however, demonstrating the need for further research. More recently, UEA have continued these investigations with promising results, suggesting that a satisfactory tee design could be developed for ICOS (P. Pickers, UEA, personal communication). This would mean significantly less gas handling changes needed to ICOS towers to add $O_2$ measurement.

Additional modification to the gas handling design shown in Figures 4 and 5 is needed for $O_2$ measurement as a consequence of avoiding tee junctions. First, flushing pumps P1, P2 and P3 cannot be used; MF1, MF2 and MF3 are not needed, and the tees immediately in front of these sensors must be removed. The tower tubing lines, however, must be continuously flushed when they are not being sampled. To achieve this, either a different model Valco valve can be used (e.g. “SF flow-through”), instead of the “SD dead-ended” model shown in Figures 4 and 5, or an additional 3-way solenoid valve can be added, with a flushing pump, where the solenoid valve is only triggered to employ the flushing pump when the line is not being sampled. As a consequence of these requirements, it is highly recommended that a station is equipped with a dedicated $O_2$ sampling system (sampling line, air sample distribution and drying), in addition to the GHG sampling system. An example of a typical system for $O_2$ is given in Figure 7.

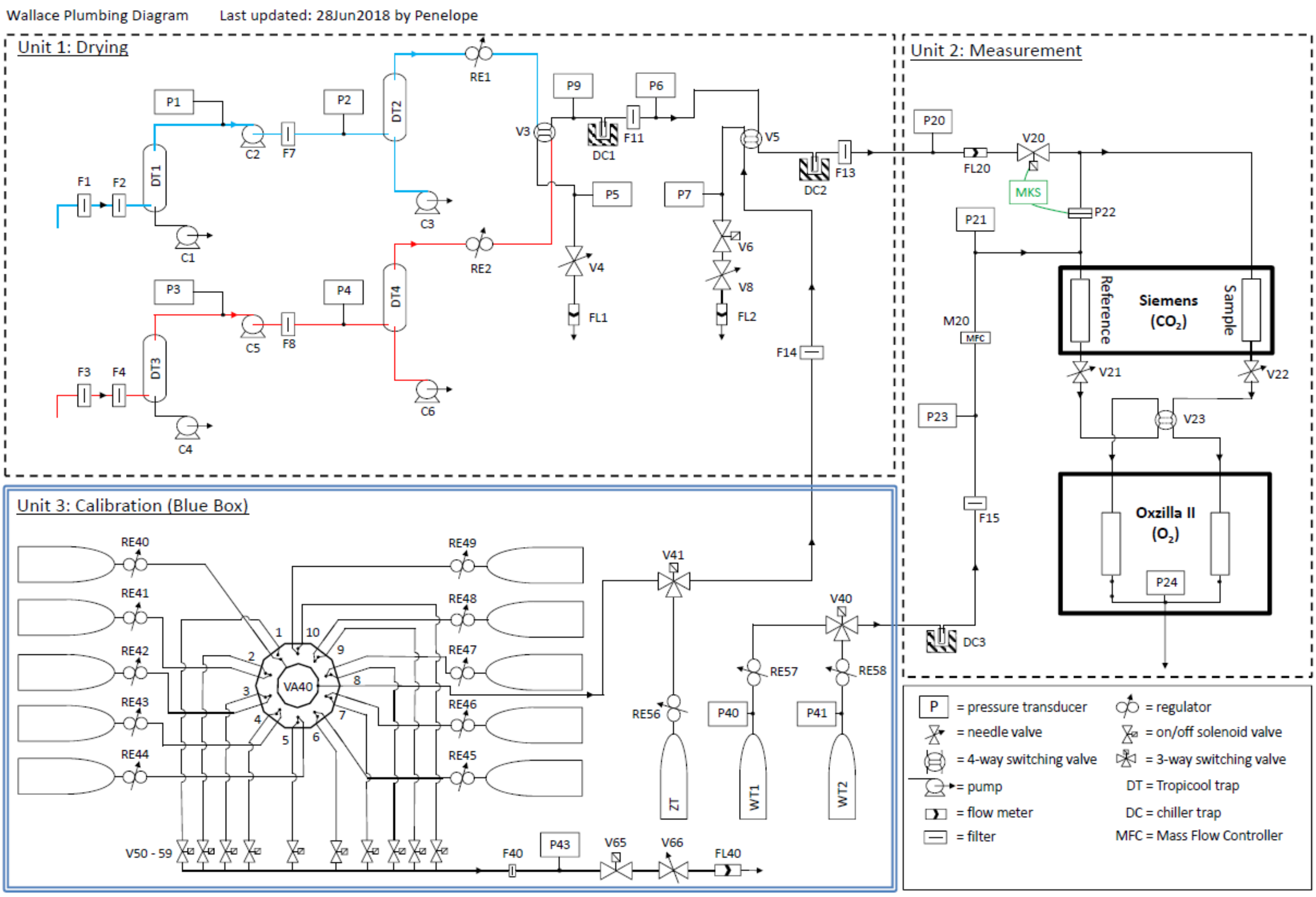



*Figure 7: Example of sampling design for $O_2$ measurement.*

Instead of a rain guard (section 2.4.1.2.), an aspirated air inlet must be used (Blaine et al., 2006). We recommend the R. M. Young, model 43502 "aspirated radiation shield". Note that this requirement results in an additional logistical demand on the station, since the blower inside the radiation shield requires 12 VDC power, thus a DC power cable is required on the tower. It is also a requirement that the diagnostic software monitors the current supplied to the blower, to ensure that the blower is operating correctly (wind gusts can sometimes disable the blower).

The four $O_2$ analyzers currently in routine use that are discussed in section 5.1. above require positive pressure in their sensor cells and thus require a sample pump to be incorporated into the sample lines. We strongly recommend a special order of the *KNF Neuberger Ltd.* PM86 model, with an aluminum head, PTFE valve plate and PTFE coated CR diaphragm. If any other pump is used, it must first be verified (preferably by the ATC or suitable associate laboratory) that it does not create any artifacts in $O_2$ or $N_2$, to a level significantly better than the precision values given in Table 3.

Drying of the sample air is currently a requirement for $O_2$ measurement, to a dew point of at least -75°C, corresponding to a water vapor content of 1.2 ppm (at atmospheric pressure). At this level of drying, the dilution effect from the remaining water vapor on the $O_2$ mole fraction causes a bias of 1.6 per meg in the $\delta(O_2/N_2)$ ratio of the sample air (see section 9.2. for an explanation of "per meg" units and use of $\delta(O_2/N_2)$ ratios). As a cautionary example, drying to a slightly warmer dew point of -70°C, corresponding to a water vapor content of 2.6 ppm, would result in an unacceptable bias in $\delta(O_2/N_2)$ ratio of the sample air of 3.4 per meg. As mentioned in section 5.1. above, for the new $O_2$ analyzers under development by *Picarro Inc.* and *Aerodyne Research Inc.*, partial drying or no drying may be possible, but this requires further research and investigation. Particularly relevant to such research is the imprecision in the water vapor measurement. As indicated in this paragraph, an imprecision in water vapor measurement of ±1.2 ppm would impose an additional ±1.6 per meg imprecision in the $O_2$ measurement (in addition to the imprecision in the $O_2$ measurement itself; how the imprecisions from the two measurements are added depends on several factors such as whether the uncertainties are correlated or uncorrelated).

To achieve such drying typically requires a two-stage drying system, with the first stage condensing water vapor to liquid form via a refrigerator or Peltier element cooler, then removing the liquid via a peristaltic pump. The second stage typically involves a cryogenic cooler unit that freezes most remaining water vapor. MD Series Nafion dryers have been tested (as first stage drying), but with inconsistent results by different operators. In consequence, Nafion is not recommended. Magnesium perchlorate can be used at the second stage, so long as the pressure and temperature are kept constant. Also acceptable is to use a magnesium perchlorate trap as a third stage, after a second stage cryogenic cooler that is warmer than -75°C.

To reduce the frequency of station visits to clean out ice-filled cryogenic cooler traps, the first stage drying typically includes a trap placed both upstream and downstream of the sample pump. With a trap placed downstream of the sample pump, the increased pressure delivered by the pump will result in additional water vapor condensing and being carried away by the peristaltic pump, thus reducing ice build-up in the cryogenic cooler. A well-designed drying system needs cryogenic cooler trap replacement only once every two months (for flow rates of ~100 mL/min), minimizing operator visits to the station.

Calibration standards and Target gases are almost always dried to better than -75°C when prepared by the CAL or associate laboratory. Nevertheless, as an additional quality control measure, and to prevent possible water dilution biases (see above), it is good practice to pass both sample air and calibration/target gas through a second trap installed in the cryogenic cooler. Similarly, a third cryogenic trap should be employed to dry the STWS gas before it passes through the $O_2$ analyzer. This is even more pertinent, since the STWSes are typically not prepared by the CAL.

Similar to the water dilution influence discussed above, variations in $CO_2$ mole fraction cause significant variations in $O_2$ mole fraction. This means that to report $O_2/N_2$ ratios in sample air, the $CO_2$ mole fraction must also be known for the exact same air parcel. The most straightforward way to achieve this requirement, with the lowest potential for additional measurement uncertainty, is to incorporate a $CO_2$ analyzer in series with the $O_2$ analyzer. To date, this has never been attempted with a Picarro, Los Gatos or Spectronus $CO_2$ analyzer. Given the disparate pressure and flow requirements for these analyzers, such integration would be difficult (but not impossible). Instead, a low-cost NDIR $CO_2$ analyzer can be used. Although such analyzers require frequent calibration, this is anyway a requirement of all current $O_2$ analyzers, thus such a strategy does not impact significantly on the consumption of calibration gases.

The alternative technique is to correct for the $CO_2$ dilution effect via post-processing of the data, using $CO_2$ data from an independent sampling system at the same station. If this strategy is employed, great care must be taken that the correction is applicable to the same air parcel, by considering the volume of air in the sensor cells ($O_2$ vs $CO_2$) and the residence times of the sample (and calibration) air in the tubing, which is likely to be different for the $O_2$ and $CO_2$ sensors, and different between sample air and calibration gas. A second issue with this approach is that typically the $O_2$ and $CO_2$ analyzers will undergo calibration routines and target gas analyses at different times, and so the procedures for $CO_2$ dilution correction on the $O_2$ data will require some data extrapolation (or additional gaps in the data), which will result in additional analytical uncertainty.

Regarding wetted materials, plastics must be avoided. If rubber is used as a wetted material (e.g. for o-rings), only Viton should be used (Buna-N must be avoided, for example), and the amount of Viton in contact with the air stream should be minimized. This means that Viton o-rings are acceptable (e.g. in *Swagelok* quick connectors), but for example, a Viton valve plate on a sampling pump is not acceptable. Teflon can be used as a wetted material, but it must not be used for any components that create seals, because $O_2$ and $N_2$ diffuse through Teflon. Moreover, Nafion dryers should not be used for $O_2$ measurement.

Oxygen measurement can be much more sensitive to small leaks compared to trace gas measurement (Keeling *et al.*, 2007). This is because $O_2$ may fractionate preferentially to $N_2$ through an orifice that is leaking, whereas for trace gases, the primary concern at the location of a leak is contamination from room air getting into the sample air stream (and, of course, loss of gas). For this reason, operators must be far more thorough and diligent in ensuring that there are no leaks at any point in the $O_2$ measurement system. This frequently requires what is called "pressure leak checking", since leak checking with Snoop™ is often not sensitive enough. A pressure leak check is where a section of tubing and fittings are sealed at above-ambient pressure with a pressure transducer included in the section. The volume of the closed-off section is estimated, and thus by monitoring any decrease in pressure recorded by the transducer over time, the leak rate can be estimated. As one typical example, for tubing between a calibration cylinder and its associated regulator (a region that is particularly sensitive to the possibility of $O_2/N_2$ fractionation through an orifice because of being at very high pressure), an acceptable leak rate is considered to be 5 µL/min or less.

## 5.3. $O_2$ Specific diagnostic data

For $O_2$ measurement, the following additional ancillary data should be monitored:

- Current supplied to aspirated radiation shields;
- Temperatures of both stage 1 and stage 2 drying units;
- Line pressures at strategic points, for example, downstream of the sample pump and downstream of the cryogenic cooler trap;

Temperatures inside the thermally insulated calibration gas enclosure; temperatures at a minimum of two points (front and back) should be monitored. See section 5.5. for more details.

## 5.4. $O_2$-specific considerations in sampling strategy

In the case of $O_2$ measurement, for a tall tower with alternate sampling from different heights, switching between heights every 20 mins might be problematic. Small flow and pressure disturbances caused by switching between sample lines will disturb the dynamic equilibrium whereby $O_2$ and $N_2$ are absorbed and desorbed from all wetted materials, depending on the flow and pressure regime. Thus, immediately after switching to a new sample line, the first several minutes of data will need to be discarded as a new equilibrium is reached. This length of time could be longer than 20 minutes, which would require a slower switching sequence between sampling lines. This equilibrium time can be significantly reduced by minimizing the volume of the cryogenic cooler traps (achieved by filling with Pyrex glass beads), and by ensuring that the flushing flow rates of the sample lines is as close as possible to the analyzer sample flow rate (which can be achieved by employing mass flow controllers, for example). The equilibrium time is also dependent on the length of Synflex tubing on the tower, so for a sampling line at the top of a 300 m tower, and with the utmost care taken to return to equilibrium as fast as possible as described here, of the order of 5-10 minutes of data would need to be discarded, which would still allow hourly sampling at all heights in the case of a tower with sampling from three heights.

## 5.5. Calibration

The following protocols and requirements are in addition to those given in section 4 above.

At present, the CAL-FCL is unable to prepare calibration and target gases.

For $O_2$ measurement, consumption of calibration standards is likely to be much more rapid than for CRDS analyzers, since the $O_2$ analyzers currently in use all require calibration every 24-48 hours. For this reason (as well as the current situation with the CAL-FCL not being able to prepare $O_2$ calibration standards), it may be desirable to prepare an independent set of $O_2$ calibration standards. There is no analytical reason for doing so, but it may improve practicalities and efficiencies at the station. Frequency of Target gas analysis can be the same on $O_2$ analyzers as for CRDS analyzers.

All $O_2$ analyzers require a Short Term Working Standard (STWS) (see section 5.1 above for details). Note that air bought from commercial high pressure gas providers (e.g. Air Liquide) is not acceptable, so such STWS cylinders must be prepared in-house or by an ICOS associated laboratory.

The calibration equipment (tank, pressure regulator) can be mostly similar to the GHG specifications (see section 4.1.2). However, the $O_2$ community has no experience with stainless steel cylinder head valves, so brass should be used. Also, CGA cylinder connectors are preferred to avoid the o-ring present in DIN 14 connectors (although Viton was mentioned as being an acceptable wetted material, in moderation, for $O_2$ measurement in section 5.2 above, this is not true at high pressure).

Calibration and target cylinder regulators need to be flushed before analysis of that cylinder begins. Typical values are 10 minutes of “fast flushing” at 500 mL/min, followed by 5 minutes of “slow flushing” at 100 mL/min (more specifically, slow flushing must be done at the analyzer flow rate). The degree of flushing needed is a combination of a certain minimum volume of air that needs to pass through the regulator and a certain minimum flushing time needed. In other words, one cannot simply do very fast flushing to reduce overall calibration times, as then the minimum flushing time criteria would not be met. In addition, the amount of flushing required has been found to depend on how long it has been since the cylinder and regulator were last analyzed. This means, for example. that the LTT cylinder regulator will require more flushing than the STT cylinder regulator. One can shorten total calibration times by employing an “SF” flow-through model Valco valve. This valve allows one to analyze one calibration cylinder regulator while simultaneously flushing another regulator. The slow flushing time is specific to $O_2$ measurement and is needed to re-establish $O_2/N_2$ equilibrium in the regulator and all fittings, which is dependent on the flow and pressure regime. Regarding the on-site cylinder installation, horizontal orientation is a mandatory requirement (Keeling *et al.*, 2007). In addition, unless room temperature short-term (minutes to hours) and diurnal variations are significantly less than 1°C, then all calibration and target cylinders must be installed in a thermally insulated enclosure. Typically, the enclosure is constructed with walls containing 100-150 mm thick insulation. Within this enclosure passive temperature control is preferred to active control, as active control has greater potential to create temperature gradients within the enclosure. The enclosure should be raised off the ground and must not be flush with any walls of the building. No heating or cooling sources should be placed near the enclosure. It is essential to monitor temperatures inside the enclosure, particularly at the front and back, as it is temperature gradients along the length of the calibration cylinders that would be most problematic. As an example, although the relevant thermal diffusion coefficients are unknown at high pressures, at 1 atm (1.013 bar) a temperature gradient of 0.3°C could lead to 18 per meg differences in $\delta(O_2/N_2)$ due to thermal diffusion (Keeling *et al.*, 1998). Thus, a minimum of two high precision temperature sensors should be installed, with four to six sensors preferred. In the case of very stable room temperature where an insulated enclosure is not employed, it is still necessary to monitor temperatures as described here.

After a cylinder has been installed horizontally, a minimum of 72 hours must pass before the cylinder can be used. This is to allow any pre-existing gradients in the $O_2/N_2$ ratio inside the cylinder when it was in a vertical position to be eliminated.

# 6. Data management

## 6.1. Overview

Daily datasets sent to the ATC will be automatically processed and stored in the ATC database. The processing can be simple or multi-step depending on the type of instrument (e.g. the Picarro data get corrected whereas there is no correction currently applied on meteorological data).

In all cases, the processing is flexible and all processing steps are traced and the maximum of metadata is associated to the data. To ensure this performance, the system needs two types of information: metadata and processing parameterization which must be provided by the station PIs.

It is absolutely necessary to keep the information up to date. This is the responsibility of station PI's to keep the ATC database updated with all the modifications/interventions occurred at the station. For instance, if an instrument breaks down and is replaced by another one of the same model, or when an instrument is moved around, the database must be updated. Similarly target or calibration tank changes must be registered as well as any change in the air intake system or the measurement protocol.

The details of the information to provide, the data format and transfer procedure in order to send data to the ATC are described in detail in the document "ProvidingDataToATC" available on the ATC website (*http://www.icos-atc.eu/*).

Prior to starting to send the data once a day, the station PI must:

- Open a SFTP account (associated to the station) on the ATC server in order to allow the data transfer to ATC. Require to fill and sign a form available on the ATC website.
- Open an SSH account (associated to a person) to access to the ATC tools for data mining, data flagging and configuration modification. Same requirements as for SFTP (unique form).
- Register the station and its instrument with the appropriate form available on the ATC website.

## 6.2. Metadata

Here we define metadata as the "information related data content". This information will allow the end users to know from where the data are coming from and how they have been obtained.

Metadata must be fed by the station PI into the system through the ATC configuration application called ATCConfig (application available on the ICOS server; required a ssh account for station PI; application handbook available online).

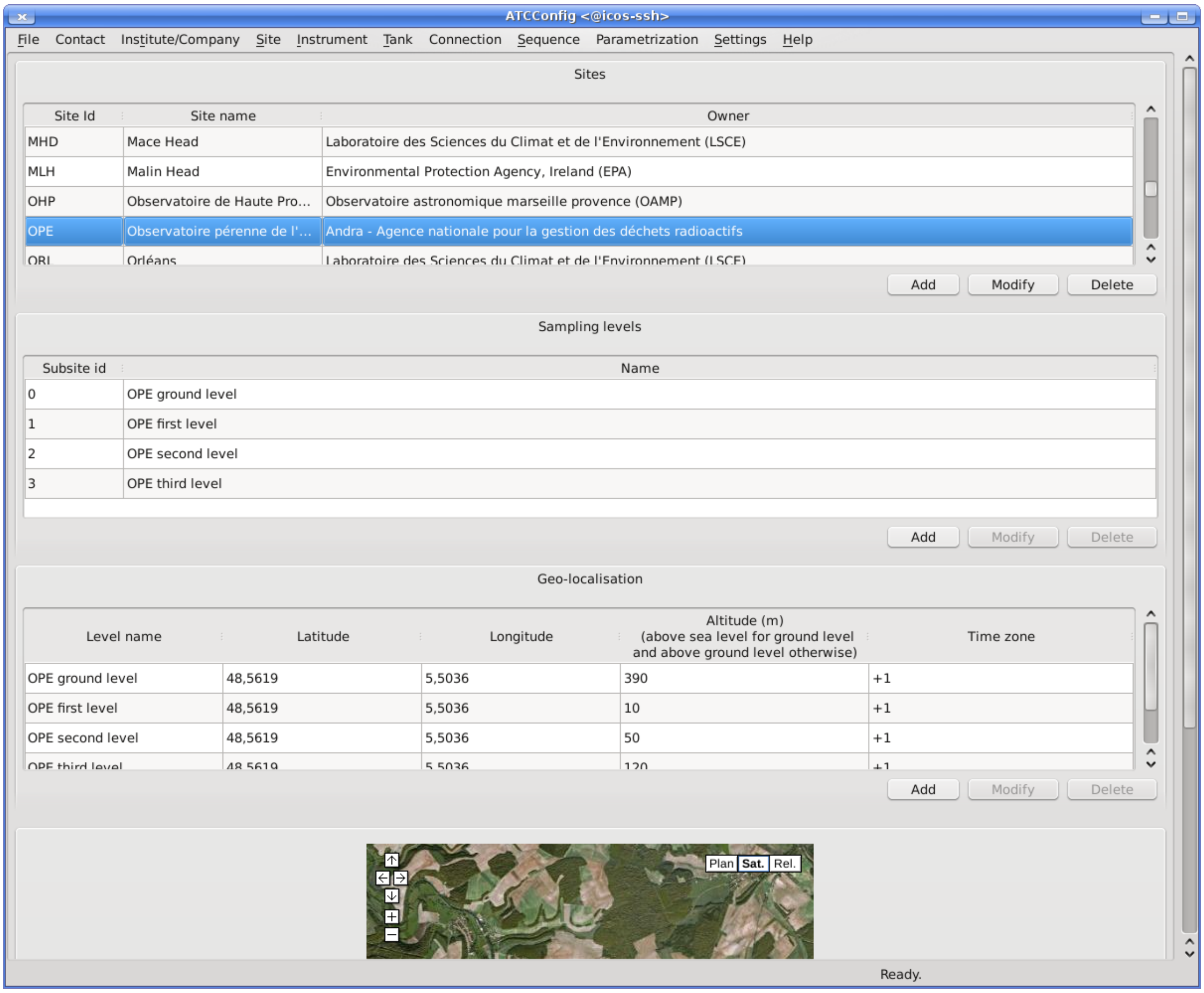



*Figure 8: ATCConfig software (screen capture).*

The categories of metadata to provide are:

- institute/laboratory
- station general information
- instrument
- tank
- flask

## 6.3. Data processing and archiving

The processing chains are flexible and need to be configured. Configuration is specified for each instrument and site as an instrument can be moved from one station to another. Most of the information is managed by the ATCConfig application.

All the data timestamps (beginning of the time interval if averaging) must be given in UTC since the ATC database assumes so and does not perform checks on this. Moreover, all configuration information must also be given in UTC.

There is a processing chain per instrument type, which implies that the requested information, parameterization and file format are also defined by instrument type.

All the data files sent to the ATC are archived. For some instruments, like the Cavity Ring Down Spectrometer from Picarro Inc., only a subset of the data is processed by the ATC (the complete list of variables or the spectrum files are not processed). Archiving the complete data set including the raw spectrum files has been considered but not implemented yet.

## 6.4. Additional station metadata and station ancillary data

It has been suggested that some additional ancillary data and metadata from the station would be helpful to better understand and qualify the measured trace gas data.

Discussions about information to provide and its frequency are still ongoing.

Mandatory Station Ancillary Data:

- Flushing flow rate for each sampling line used for continuous gas analysis
- Instrument flow rate
- Room temperature

Mandatory Station Metadata:

- Sampling, conditioning and distribution system diagram with part reference
- Buffer volume use (Yes/No)
- Drying system use (Yes/No)
- Type of drying system
- Sample pressurization pump use (Yes/No)
- Tank pressure (monthly manually monitored value)

## 6.5. Data quality control

The ATC provides an application called ATCQc (application available on the ICOS server; required a ssh account; application handbook available online) to allow PIs to manually qualify/flag their data. This is an important and mandatory step in ICOS. Data can be qualified/flagged at 2 aggregation level (raw and hour/injection). Data qualification/flagging applies to gas analyzers data (ambient or tank data), radon and meteorological data.

Using a secured encrypted connection to ATC data server, PIs have direct access through ATCQc to their data and can manually reject invalid/contaminated/outlier measurements.

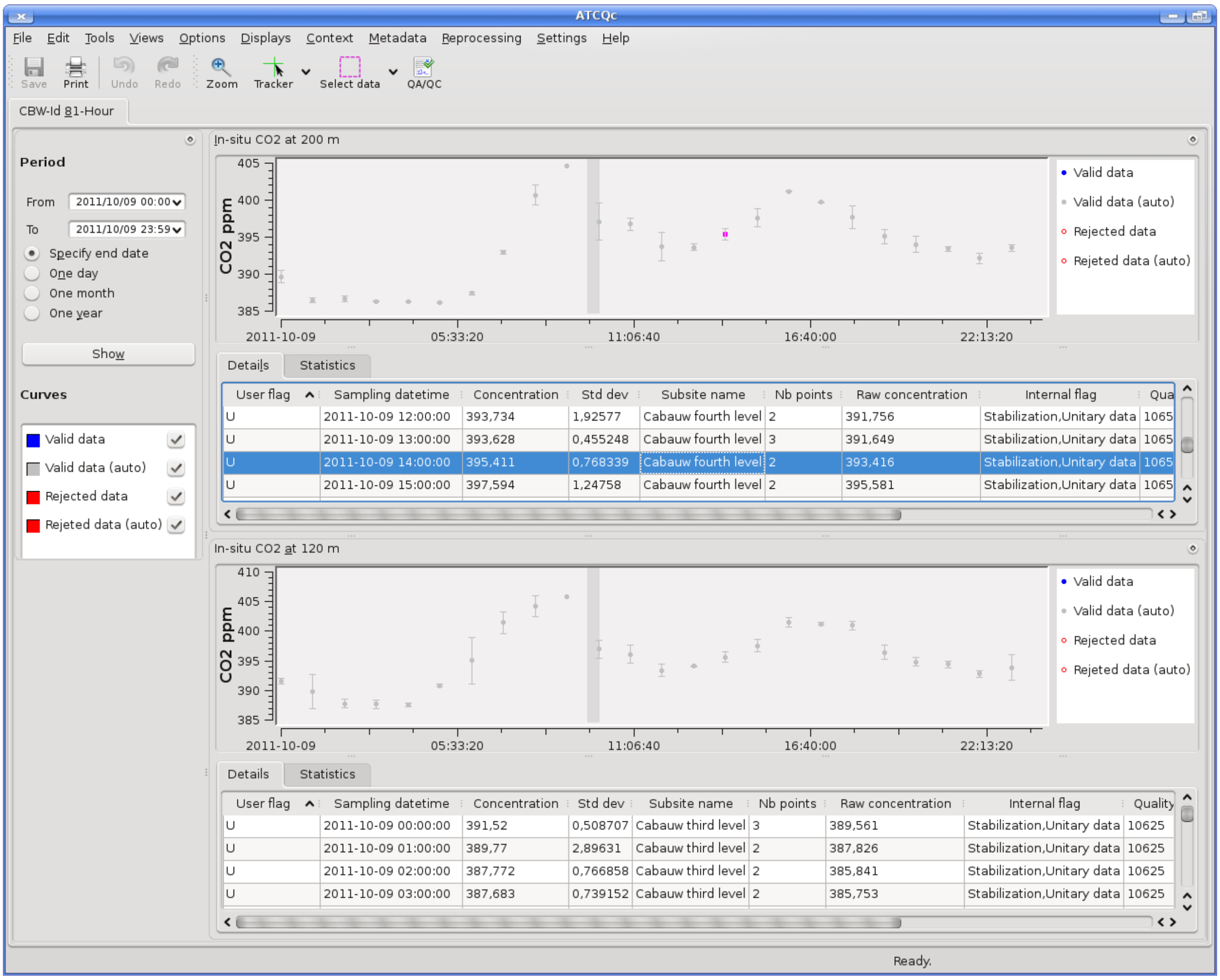
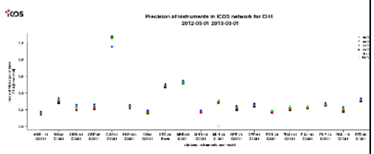
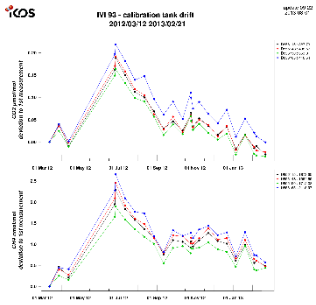
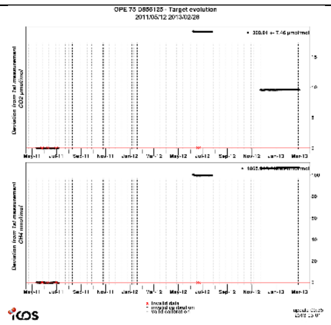
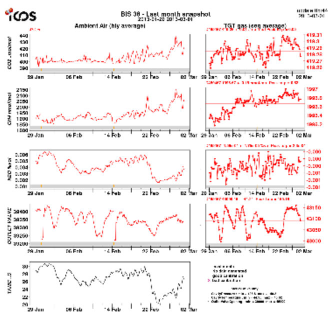


*Figure 9: ATCQc software (screen capture).*

As an additional assistance to PIs, available instrument ancillary data and station ancillary data can be displayed.

In addition to ATCQc, ATC offers a bundle of graphical data products freely available online to allow PIs to qualify and monitor their instrument. Those plots are daily generated, for each station.

A web application developed by ATC allows to discover all these ICOS instrumental products online (*http://www.icos-atc.eu/dp*).

| #id | Family | Description | Product Example |
|---|---|---|---|
| 0000 | Metadata | P0000.1 Instrument installed on the network<br><br>P0000.2 Calibration gas concentration | AMS;43;AAB1A;p,rh,rain,t,ws,wd<br>AMS;47;machi;rn<br>AMS;111;G2301;co2,ch4,h2o<br>AMS;112;Analy;co2<br>BIS;19;Carib;co2<br>BIS;24;Envir;co2,ch4,h2o<br>BIS;38;G1301;co2,ch4,h2o<br>BIS;114;senso;unknown<br>CBW;53;m3;rn<br>CBW;81;G2301;co2,ch4,h2o<br>CBW;110;m3;rn<br>CRP;42;G1301;co2,ch4,h2o<br>GIF;15;HP689;co2,ch4,sf6,co,h2,n2o<br>GIF;32;machi;rn<br>GIF;44;AAB1A;p,rh,rain,t,ws,wd |
| 0001 | Tracking accuracy of an instrument | P0001.1 Precision instrument in ICOS Network<br><br>P0001.2 Time series of minute SD<br><br>P0001.3 Table of instrument precision<br><br>P0001.4 Time series of minute SD |  |
| 0002 | Calibration monitoring | P0002.1 Result of calibration per calibration cycle<br><br>P0002.2 Calibration tank drift<br><br>P0002.3 Residue evolution<br><br>P0002.6 Evolution of the calibration equation<br><br>P0002.7 Linear and default fit residual comparison |  |
| 0003 | Target gas monitoring | P0003.1 target gas evolution in time<br><br>P0003.2 Instrumental drift |  |
| 0004 | Air monitoring | P0004.1 Last year snapshot<br><br>P0004.2 last month snapshot<br><br>P0004.3 last week snapshot<br><br>P0004.4 last 3 days snapshot<br><br>P0004.5 valid data snapshot<br><br>P0004.6 Data validation advancement |  |

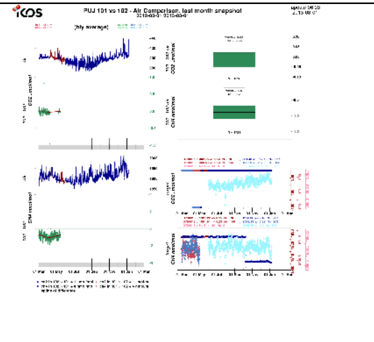
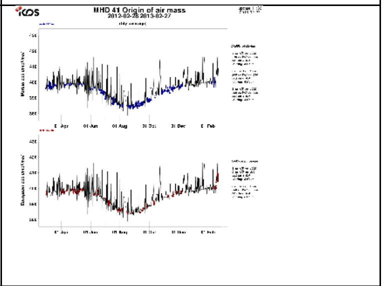
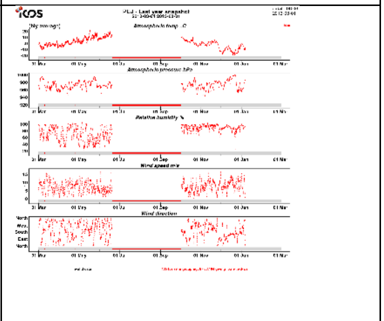
| | | | |
|---|---|---|---|
| 0006 | Comparisons instruments/in struments | P0006.1 comparison of instruments on the same site over a year<br><br>P0006.2 comparison of instruments on the same site over a month |  |
| 0008 | Value-added products | P0008.1 Data selection sector (Ocean or continent) |  |
| 0009 | Meteo | P0009.1 Last year meteorological data<br><br>P0009.2 Last month meteorological data<br><br>P0009.3 Last week meteorological data<br><br>P0009.4 Last 3 days meteorological data |  |

*Table 14: Examples of Data products provided by ATC (non-exhaustive).*

Synthetic information is summarized and can quickly be accessed through a "panel board", specific to each station (see *http://www.icos-atc.eu/stations*, and click a station). All data products are regularly (daily to weekly depending to the type) refreshed to take into consideration some possible recent modifications made by PIs on measurement, through ATCQc, for example.

## 6.6. Data revision

The data revision is ensured by the ATC when a primary calibration scale is changed or a drift in the composition of a calibration gas was identified.

# 7. Quality management

High, proven quality is a requirement in order for the ICOS data to be useful. ICOS has adopted compatibility targets of the Global Atmosphere Watch (GAW) program of the World Meteorological Organization (WMO). To achieve these targets ICOS implements a quality management plan, which defines quality assurance and quality control measures. Credibility of the ICOS data depends critically on the performance of transparent quality control. In this chapter, we first give an overview of quality management and then list quality control actions.

## 7.1. Quality management overview

The definitions of quality assurance (QA) and quality control (QC) as given in the GAW report No. 185 are quite general:

- Quality Control: Operational techniques and activities that are used to maintain and verify given requirements for quality.
- Quality Assurance: all planned and systematic actions necessary to provide adequate confidence that a product, process or service will satisfy given requirements for quality.

From these definitions the major differences between QC and QA are summarized in Table 15 along with some examples for their applicants for trace gas measurements.

| | **QC** | **QA** |
|---|---|---|
| **Orientation** | Product | Process |
| **Time horizon** | Reactive | Pro active |
| **Usage** | find problems | prevent problem |
| **Focus** | Data accuracy | How to properly design and perform a measurement process |
| **Examples for an atmospheric ICOS station** | | |
| | Target measurements | Measurement guidelines |
| | Co-located flask measurement | Staff training |
| | Use flows, cooler temperatures and pressures for initial data flagging. | Monitoring flows, cryocooler temperature, changing valves, etc. |
| | Inter-comparison activities, travelling instrument | Regular calibration, leak detection |

*Table 15: Summary of QC and QA differences along with examples for GHG measurements.*

In addition to QC and QA, the quality audit is another quality management term defined as "the process of systematic examination of a quality system (QA and QC) carried out by an internal or external quality auditor or an audit team. Quality audits are typically performed at predefined time intervals and ensure that the institution has clearly defined internal system monitoring procedures linked to effective action. This can help determine if the organization complies with the defined quality system processes and can involve procedural or results-based assessment criteria".

## 7.2. Quality management system targeted for the ICOS atmospheric network

### 7.2.1. Quality assurance

In ICOS, the initial validation of the station, the use of common, pre-tested instruments, standardized measurement systems, trained personnel, centralized production of calibration and target gases together with common data processing including on-line quality checking and warnings creates a good foundation for data quality assurance and high compatibility of the measurements.

Quality assurance is directly linked to good laboratory praxis and the ICOS measurement guidelines mentioned in the present document. It is mandatory for each station to have a printed version of the measurement guidelines at the station, which will serve as a reference book for bench work. At those stations where the personnel is not very fluent in English, the Station PI should prepare a translated version of these guidelines.  The measurement guidelines should also cover a detailed maintenance schedule for the wearing parts of the station and for performing leak tests. The ATC is encouraged to include a detailed maintenance section in the electronic station logbook and send reminders to the station PIs.

Another aspect of the QA deals with the training of personnel. The ATC will offer training for ICOS station personnel. We recommend one mandatory training session for all ICOS station personnel, even if the respective personnel is already experienced in trace gas measurement. This will help in unifying the measurement and quality control process within the ICOS network. The scope of the ATC training session will be adapted to the prior experience of the participants.

### 7.2.2. Quality control

Quality control is the verification of the fulfilling of the data quality objectives for each ICOS atmospheric station. It thus provides important information on the performance of the station as well as on the network compatibility internally together with other sources of observations. The ICOS atmospheric station network QC is split into three different hierarchies: station internal QC, ICOS internal QC and ICOS external QC. These different levels of QC assure compatibility and credibility of the data.

**Station internal QC:** All QC actions/measurements performed at a station, *without referencing* to any station external body (e.g. repeatability checks, target measurements, line tests, etc.).
*Aims:* Assuring that the station performance meets the data quality objectives (DQOs)

**ICOS internal QC:** All QC actions/measurements performed at a station, *referencing* to an ICOS central facility that supervises data quality objectives (e.g. flask vs. continuous comparison, Round/Star-Robins, travelling instrument, etc. with the ICOS CAL).
*Aims:* External verification of station performance including (parts of the) data processing, assuring network compatibility.

**ICOS external QC:** All QC action/measurements performed at a station, referencing to an ICOS external body. (e.g. WMO-Round Robins).
*Aims:* Generate credibility for the ICOS data, by having a completely independent validation outside the ICOS framework.

### 7.2.3. Quality audit

ICOS targets two different hierarchies of quality audits: Internal and external quality audits.
The **internal quality audits** will be carried out by auditors from an ICOS central facility. Internal audits shall check and verify the stations compliance to the ICOS measurement guidelines and the quality control procedures.
The **external quality audits** have to be performed by an external body and will focus on the validation of the entire ICOS quality management system and its implementation. We propose a frequency of every 5 years for the external quality audits, ideally performed by an audit team from a non-European organization with distinguished experience in atmospheric trace gas monitoring networks.

## 7.3. Requirements for a comprehensive quality control strategy

The requirements for a comprehensive quality control system of an atmospheric GHG network are complex. Thus, multiple tools will be needed to cover the various aspects. In the following, the key points which have to be addressed by such a comprehensive quality control system are listed:

- **Precision:** The precision of the applied quality control measure defines the needed statistics to detect differences on the order of the data quality objectives (DQOs). Preferably the precision of an applied QC measure should be at least twice the requested DQOs precision.
- **Frequency:** Comparison frequency must allow for the rapid detection of potential problems.
- **Comprehensiveness:** It must describe which parts of the analytical set-up are tested and should preferably test all parts of the measurement system.
- **Concentration range coverage:** It should be suitable for the considered station and slightly exceed the stations ambient concentration range.
- **External station validation:** This quality control item is mandatory to create credibility of the network data.

Table 16 summarizes the quality control approach that could be applied at field stations and classifies them according to the previously defined quality characteristics. Each QC technique mentioned has its own strengths and weaknesses.

| | Precision | Frequency | Comprehensiveness | Conc. Range | External validation |
|---|---|---|---|---|---|
| **Target gases** | High | Sub-daily | No | Limited | Limited |
| **Flask vs. in-situ** | Low | Weekly | Full | Entire | Yes |
| **Cylinder RR*** | High | 1-2 per year | No | Limited | Yes |
| **Travelling instrument** | High | occasional | Full (ability to pinpoint individual problems) | Entire | Yes |

*Table 16: Classification of existing quality control approaches according to the pre-defined quality characteristics. Cylinder RR* (Round Robin) is a circulating gas cylinder whose concentration is not known by AS personnel. Analysis result at each station is used for testing the performance of the station.*

## 7.4. Quality control strategy for the ICOS atmospheric network

The QM strategy as proposed does fulfill all needs in terms of precision, frequency, concentration range coverage, external validation as well as comprehensiveness. The diversity of the applied QC measures complements one another and offers sufficient redundancies to act as a defensible QM system.

For Quality Control of ICOS atmospheric measurements, the targeted duties are:

1) Entire check of proper functioning of the instrumentation (including instrumental validation and qualification phase at ATC Metrological Lab) and the intake system before a station becomes operational. The AS PI must prepare a full description of the measurement system and protocols, which will be checked by ATC (check list provided by the ATC). This is checked while the MobileLab is performing an intercomparison/audit on site.

2) High frequency instrument target gas (also called "Performance target gas") measurements at the station to be able to quickly detect malfunctioning of the instrument, insertion point: Selection valve. Concentration ranges for all species at the expected low end of the concentration range (background conditions) for the particular station.

3) Low frequency instrument target gas (also called "Archive target gas") measurements to be able to quantify system stability over decades, insertion point: Selection valve. Concentration ranges for all species above the expected high end of the concentration range for the particular station.

4) Measurement systems, which have devices such as filter, sampling pump, drier, buffer volumes, in the inlet line upstream of the analyzer, have to be tested by a target gas measurement, which has an insertion point upstream of these devices. The test conditions (e.g. sample flow rate and pressure) have to be comparable to the conditions for the ambient sampling. The same target gas has to be measured at the selection valve insertion point as well. This test has to be done during maintenance visits at least twice per year. The concentrations of this target should be close to background conditions for the respective station. See the last version of the ATC procedure available on the ATC website and ICOS document platform (Alfresco).

5) Regular (at least on weekly basis is highly recommended) data inspection (including calibration and target gas measurements) by stations PIs using ATC Data Products and the ATCQc tool and participation in the Monitoring Station Assembly.

6) Yearly intake system test, testing the entire sample intake line (all heights). Intake system tests may be done by inserting a gas of a known concentration to the inlet, or comparing ambient air concentrations swapping between the sample inlet and the spare line (ideally simultaneously with 2 instruments or in very stable ambient conditions if only one instrument available) or as a leak test. See the last version of the ATC procedure available on the ATC website and ICOS document platform (Alfresco).

7) Regular flask – in-situ measurement comparison for Class 1 stations on a weekly basis from the highest sampling height.

8) Yearly check of laboratory-air. For Class 1 stations it is mandatory to fill a 3 L flask with room air when the installation of the station is finished. This test must be repeated at least once a year if the station is equipped with instruments that use $^{14}C$ sources as beta emitters. $^{14}C$ is often used for neutralization in aerosol particle counters. An example of this is the “Sharp 5030i” model from Thermo Scientific. For the test, disconnect the sample intake line from the flask sampler and fill a flask with room air. This sample must be specially marked and sent to the CRL for $\Delta^{14}CO_2$ analysis.

9) Mobile Lab, ATC Metrology Lab, CAL FCL should be involved in the WMO Inter Comparison Program (ICP) as well as a subset of ICOS stations.

9) The ATC Mobile Lab serving as a diagnostic tool particularly for stations where systematic biases in the flask vs. in-situ comparison occur. During a Mobile Lab visit, a system and performance audit will be conducted.

An additional QC task (not mandatory) is to measure blank (e.g. synthetic air or $N_2$ grade: 5.0) and laboratory air on a weekly basis.

## 7.5. Measurement uncertainties

The measurement uncertainties are currently estimated by ATC using performance target gas measurement. This first uncertainty estimate will be completed with other error estimate studies (e.g. error on water vapor correction, on representativeness of the hourly average data for multi sampling height sites). The detailed computation of this global uncertainty estimate is still to be implemented.

# 8. Outlook

The present document describes the current state of the ICOS requirements and recommendations for the atmospheric stations. Few topics such as PBLH measurement require additional work to define the corresponding requirements and recommendations.
The next release of this document will present the results of the ongoing work and the update of the actual specifications described here.

# 9. References

## 9.1. Abbreviations and acronyms

**ACTRIS -** Aerosols, Clouds, and Trace gases Research InfraStructure Network

**AGAGE** - Advanced Global Atmospheric Gases Experiment

**ANSTO -** Australian Nuclear Science and Technology Organisation

**AS** - Atmosphere Station

**ATC** - Atmosphere Thematic Center

**BLH** - Boundary Layer Height

**CAL** - Central Analytical Laboratory

**CRDS** – Cavity Ring Down Spectrometer

**CRL** – Central Radiocarbon Laboratory

**EMPA** - Swiss Federal Laboratories for Materials Science and Technology

**ETC** - Ecosystem Thematic Center

**ERIC** - European Research Infrastructure Consortium

**FCL** – Flask and Calibration Laboratory

**FTIR** – Fourier Transform Infrared

**GAW** - Global Atmosphere Watch (WMO programme)

**HRM -** Heidelberg Radon Monitor

**ICOS** - Integrated Carbon Observation System

**ICOS-INWIRE** - ICOS Improved sensors, NetWork and Interoperability for GMES

**ICP** - Intercomparison Program

**InGOS** - Integrated non-$CO_2$ Greenhouse gas Observing System

**LTT** - Long-Term Target

**MPI** - Max Planck Institute (Germany)

**MSA** - Monitoring Station Assembly

**NDIR** - Non-Dispersive Infrared

**NOAA -** National Oceanic and Atmospheric Administration (USA)

**OD -** Outside Diameter

**OTC** - Oceanic Thematic Center

**PBLH** - Planetary Boundary Layer Height

**PI** - Principal Investigator

**PPB** - Parts Per Billion (see definition chap 8.2)

**PPM** - Parts Per Million (see definition chap 8.2)

**PPT** - Parts Per Trillion (see definition chap 8.2)

**PTFE** - Polytetrafluoroethylene

**QA** - Quality Assurance

**QC** - Quality Control

**Scripps** - Scripps Institution of Oceanography (USA)

**SFTP** - SSH File Transfer Protocol

**SIO** - Scripps Institution of Oceanography (USA)

**STT** - Short-Term Target

**STWS** - Short-Term Working Standard

**UHEI** - University of Heidelberg (Germany)

**VIM** - International Vocabulary of Metrology

**VPDB** - Vienna Pee Dee Belemnite (Isotope Standard)

**VSMOW** - Vienna Standard Mean Ocean Water (Isotope Standard)

**VUV** - vacuum ultraviolet $O_2$ analyzer

**WMO** - World Meteorological Organization

## 9.2. Terms and definitions

**Calibration cylinder (also referred to as calibration gas or calibration standard):**
Cylinder containing natural dry air or a synthetic gas mixture with assigned trace gas mole fractions that is used routinely to calibrate the gas analyzer on site. In ICOS, the calibration cylinders are prepared with natural dry air and calibrated (mole fraction assignment) against a WMO scale by the ICOS CAL, or the Scripps scale in the case of $O_2$.

**Gas concentration unit** (used in this document):
Mole fractions of substances in dry air (dry air includes all gaseous species except water)

ppm = µmol/mol =$10^{-6}$ mole of trace substance per mole of dry air
ppb = nmol/mol =$10^{-9}$ mole of trace substance per mole of dry air
ppt = pmol/mol =$10^{-12}$ mole of trace substance per mole of dry air

In the case of $O_2$ measurement, the analyzers mentioned above (section 5.1.) all measure $O_2$ mole fraction (in dry air). Because $O_2$ is not a trace gas, however, its mole fraction can be significantly influenced by variation in other species such as $CO_2$, therefore the convention is to report all data as $O_2/N_2$ ratios on the so-called "per meg" scale, defined as (Keeling and Shertz, 1992):

$$\delta\left(\frac{\mathrm{O_2}}{\mathrm{N_2}}\right)\ (per\ meg) = \left(\frac{(\mathrm{O_2/N_2})_{\mathrm{sample}} - (\mathrm{O_2/N_2})_{\mathrm{reference}}}{(\mathrm{O_2/N_2})_{\mathrm{reference}}}\right) \times 10^6$$

The relationship between $O_2/N_2$ ratios, expressed as $\delta(O_2/N_2)$ and $O_2$ mole fraction, expressed as $\delta X_{O_2}$, is given by (Kozlova *et al.*, 2008):

$$\delta\left(\frac{O_2}{N_2}\right)\ (per\ meg) = \frac{\delta X_{O_2}\ (ppm) + \left(X_{CO_2} - 363.29\right) \times S_{O_2}}{S_{O_2} \times (1 - S_{O_2})}$$

where $X_{CO_2}$ is the $CO_2$ mole fraction (in ppm), 363.29 is an arbitrary $CO_2$ reference value implicit in the definition of the Scripps $O_2/N_2$ scale and $S_{O_2}$ is the standard mole fraction of $O_2$ in air, taken as 0.209392 (Tohjima *et al.*, 2005).

**Quality assurance:**
All planned and systematic actions necessary to provide adequate confidence that a product, process or service will satisfy given requirements for quality.

**Quality control:**
Operational techniques and activities that are used to maintain and verify given requirements for quality.

**Measurement repeatability**:
According to the VIM, the measurement repeatability is the measurement precision under a set of measurement 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.
In order to evaluate the instrument performance, ICOS assess the measurement repeatability (cf. Table 3) by measuring alternately a gas cylinder (filled with dry natural air) during 30 minutes and ambient air (not dried) during 270 minutes over 72 hours, and calculating the standard deviation (1σ) of the last 10 minute average data of each 30 minute cylinder gas injection (first 20 minutes rejected as stabilization time).

**Target cylinder (also referred to as target gas)**:
Cylinder containing natural dry air or a synthetic gas mixture with assigned trace gas mole fractions that is routinely treated as an (unknown) sample in a sequence of analyses. In ICOS, the target cylinders are prepared with natural dry air by the CAL. They are used for quality control measures.

## 9.3. Bibliography

List of the documents referenced in the present document:

Blaine, T. W., Keeling, R. F., and Paplawsky, W. J.: *An improved inlet for precisely measuring the atmospheric Ar/$N_2$ ratio*, Atmospheric Chemistry and Physics, 6, 1181-1184, 2006.

Bonne, J.-L., Delmotte, M., Lavrič, J. V., Manning, A. C., Bopp, L., Brand, W., Kazan, V., Stohl, A., and Cloué, O.: *Four years of atmospheric oxygen and carbon dioxide record at Ivittuut, southern Greenland*, EGU General Assembly, Vienna, 2012,

Grossi, C., Chambers, S. D., Llido, O., Vogel, F. R., Kazan, V., Capuana, A., Werczynski, S., Curcoll, R., Delmotte, M., Vargas, A., Morguí, J.-A., Levin, I., and Ramonet, M.: *Intercomparison study of atmospheric $^{222}Rn$ and $^{222}Rn$ progeny monitors*, Atmos. Meas. Tech., 13, 2241–2255, https://doi.org/10.5194/amt-13-2241-2020, 2020.

Haeffelin, M., Angelini, F., Morille, Y., Martucci, G., Frey, S., Gian Paolo Gobbi, Lolli, S., O'Dowd, C.D., Sauvage, L., Xueref-Rémy, I., Wastine, B. and Feist, D.G. : *Evaluation of Mixing-Height Retrievals from Automatic Profiling Lidars and Ceilometers in View of Future Integrated Networks in Europe*. Boundary-Layer Meteorology, pp. 1–27, 2011

Hammer, S., Konrad, G., Vermeulen, A. T., Laurent, O., Delmotte, M., Jordan, A., Hazan, L., Conil, S. and Levin, I.: *Feasibility study of using a "travelling" $CO_2$ and $CH_4$ instrument to validate continuous in situ measurement stations*. Atmos. Meas. Tech., 6, 1201–1216, 2013

Keeling, R. F., Manning, A. C., McEvoy, E. M., and Shertz, S. R.: *Methods for measuring changes in atmospheric $O_2$ concentration and their applications in southern hemisphere air*, J. Geophys. Res.-Atmos., 103, 3381-3397, 10.1029/97JD02537, 1998.

Keeling, R. F., Manning, A. C., Paplawsky, W. J., and Cox, A. C.: *On the long-term stability of reference gases for atmospheric $O_2$/$N_2$ and $CO_2$ measurements*, Tellus Series B-Chemical and Physical Meteorology, 59, 3-14, 10.1111/j.1600-0889.2006.00228.x, 2007.

Keeling, R. F., and Shertz, S. R.: *Seasonal and interannual variations in atmospheric oxygen and implications for the global carbon cycle*, Nature, 358, 723-727, 10.1038/358723a0, 1992.

Milroy, C., Martucci, G., Lolli, S., Loaec, S., Sauvage, L., Xueref-Remy, I., Lavrič, J. V., Ciais, P. and O'Dowd, C. D.: *On the ability of pseudo-operational ground-based light detection and ranging (LIDAR) sensors to determine boundary-layer structure: intercomparison and comparison with in-situ radiosounding*, Atmos. Meas. Tech. Discuss., 4, 563-597, 2011.

Kozlova, E. A., and Manning, A. C.: *Methodology and calibration for continuous measurements of biogeochemical trace gas and $O_2$ concentrations from a 300-m tall tower in central Siberia*, Atmospheric Measurement Techniques, 2, 205-220, 10.5194/amt-2-205-2009, 2009.

Kozlova, E. A., Manning, A. C., Kisilyakhov, Y., Seifert, T., and Heimann, M.: *Seasonal, synoptic, and diurnal scale variability of biogeochemical trace gases and $O_2$ from a 300 m tall tower in central Siberia*, Glob. Biogeochem. Cycles, 22, 10.1029/2008GB003209, 2008.

Kretschmer, R., Gerbig, C., Karstens, U., and Koc F.-T. : *Error characterization of CO2vertical mixing in the atmospherictransport model WRF-VPRM*, Atmos. Chem. Phys., 12, 2441–2458, 2012**.**

Laurent, O., Philippon, C., Yver Kwok, C., Rivier, L., Ramonet, M.: *How to deal with water vapor for Greenhouse gas dry mole fraction measurement with Cavity Enhanced Spectrometer: water vapor correction vs Nafion dryer*, Poster (P12) at the 20th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases, and Related Measurement Techniques (GGMT-2019), https://community.wmo.int/meetings/ggmt-2019, 2019.

Lebegue, B., Schmidt, M., Ramonet, M., Wastine, B., Yver Kwok, C., Laurent, O., Belviso, S., Guemri, A., Philippon, C., Smith, J. and Conil, S.: *Comparison of nitrous oxide ($N_2O$) analyzers for high-precision measurements of atmospheric mole fractions.* Atmos. Meas. Tech., 9, 1221-1238, doi:10.5194/amt-9-1221-2016, 2016.

Levin, I., Karstens, U., Eritt, M., Maier, F., Arnold, S., Rzesanke, D., Hammer, S., Ramonet, M., Vítková, G., Conil, S., Heliasz, M., Kubistin, D. and Lindauer, M.: *A dedicated flask sampling strategy developed for ICOS stations based on CO2 and CO measurements and STILT footprint modelling*. Atmospheric Chemistry and Physics, https://doi.org/10.5194/acp-2020-185, 2020.

Levin, I., Born, M., Cuntz, M., Langendörfer, U., Mantsch, S., Naegler, T., Schmidt, M., Varlagin, A., Verclas, S., and Wagenbach, D.: *Observations of atmospheric variability and soil exhalation rate of Radon-222 at a Russian forest site: Technical approach and deployment for boundary layer studies*, Tellus B, 54, 462–475, 2002.

Manning, A. C., Keeling, R. F., and Severinghaus, J. P.: *Precise atmospheric oxygen measurements with a paramagnetic oxygen analyzer*, Glob. Biogeochem. Cycles, 13, 1107-1115, 10.1029/1999GB900054, 1999.

Pickers, P. A., Manning, A. C., Sturges, W. T., Le Quéré, C., Mikaloff Fletcher, S. E., Wilson, P. A., and Etchells, A. J.: *In situ measurements of atmospheric $O_2$ and $CO_2$ reveal an unexpected $O_2$ signal over the tropical Atlantic Ocean*, Glob. Biogeochem. Cycles, 10.1002/2017GB005631, 2017.

Schmithüsen, D., Chambers, S., Fischer, B., Gilge, S., Hatakka, J., Kazan, V., Neubert, R., Paatero, J., Ramonet, M., Schlosser, C., Schmid, S., Vermeulen, A., and Levin, I.: *A European wide 222radon and 222radon progeny comparison study*, Atmos. Meas. Tech., 10, 1299–1312, https://doi.org/10.5194/amt-10-1299-2017, 2017.

Stephens, B. B., Bakwin, P. S., Tans, P. P., Teclaw, R. M., and Baumann, D. D.: *Application of a differential fuel-cell analyzer for measuring atmospheric oxygen variations*, Journal of Atmospheric and Oceanic Technology, 24, 82-94, 10.1175/JTECH1959.1, 2007.

Stephens, B. B., Keeling, R. F., and Paplawsky, W. J.: *Shipboard measurements of atmospheric oxygen using a vacuum-ultraviolet absorption technique*, Tellus Series B-Chemical and Physical Meteorology, 55, 857-878, 10.1046/j.1435-6935.2003.00075.x, 2003.

Tohjima, Y., Machida, T., Watai, T., Akama, I., Amari, T., and Moriwaki, Y.: *Preparation of gravimetric standards for measurements of atmospheric oxygen and reevaluation of atmospheric oxygen concentration*, Journal of Geophysical Research D: Atmospheres, 110, 1-11, 2005.

VIM, International vocabulary of metrology – *Basic and general concepts and associated terms (VIM)*. 3rd edition, Joint Committee for Guides in Metrology (JCGM), JCGM 200:2012Williams, A. G. and Chambers, S. D.: *A history of radon measurements at Cape Grim*, Baseline Atmospheric Program (Australia) History and Recollections, 40th Anniversary Special edn., 131–146, 2016.

World Meteorological Organization, *20th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Measurement Techniques (GGMT-2019).* Crotwell, A.; Lee, H.; Steinbacher M., World Meteorological Organization. GAW report N° 255, 2020

World Meteorological Organization, *Guide to meteorological instruments and methods of observation*. WMO N°8, 7th edition, 2008.

World Meteorological Organization, *Guide to meteorological instruments and methods of observation*. WMO N°8, 2018.

World Meteorological Organization, *Guidelines for the Measurement of Methane and Nitrous Oxide and their Quality Assurance*. GAW report N° 185, WMO/TD-No. 1478, 2009.

World Meteorological Organization, *Guidelines for the Measurement of Atmospheric Carbon Monoxide*. GAW report N° 192, WMO/TD-N° 1551, 2010

World Meteorological Organization, *Strategy for the Implementation of the Global Atmosphere Watch Programme (2001 - 2007),* GAW Report N° 142, 2001

## 9.4. List of contributors

The persons listed below have actively contributed to the writing and reviewing process of the present document and/or the previous versions:


Aaltonen, H. (FMI, Finland)

Baum, S. (MPI, Germany)

Cristofanelli, P. (CNR-ISAC, Italy)

Delmotte, M. (LSCE, France)

Dvorska, A. (CzechGlobe, Czech. Rep.)

Gerbig, C. (MPI, Germany)

Gomez-Pelaez, A. (AEMET, Spain)

Grossi C. (INTE-UPC, Spain)

Grant, A. (University of Bristol, England)

Hammer, S. (UHEI, Germany)

Hanus, V. (CzechGlobe, Czech. Rep.)

Hazan, L. (LSCE, France)

Jordan, A. (MPI, Germany)

Laurent, O. (LSCE, France)

Laurila, T. (FMI, Finland)

Lavric, J. (MPI, Germany)

Levin, I. (UHEI, Germany)

Lindroth, A. (Lund University, Sweden)

Manning, A. C. (UEA, England)

Morgui, J. A. (IC3, Spain)

O'Doherty, S. (University of Bristol, England)

Paris, J. D. (LSCE, France)

Pavelka, M. (CzechGlobe, Czech. Rep.)

Pilegaard, K. (DTU, Denmark)

Plass-Duelmer, C. (DWD, Germany)

Ramonet, M. (LSCE, France)

Reiter, I. (OAMP, France)

Rivier, L. (LSCE, France)

Schmidt, M. (LSCE, France)

Steinbacher, M. (Empa, Switzerland)

Tarniewicz, J. (LSCE, France)

Vermeulen, A. (ECN, Netherlands)

Wastine, B. (LSCE, France)



Acknowledgments:

ICOS atmosphere MSA and first ICOS workshop attendees and especially those involved in the ICOS working groups are gratefully acknowledged for their contributions.