WP4- NA4: Trace gases networking: Volatile organic carbon and nitrogen oxides Deliverable D4.2: Draft for standardized operating procedures (SOPs) for NOxy measurements

1 Introduction

ACTRIS (Aerosols, Clouds, and Trace gases Research InfraStructure Network) is a European Project aiming at integrating European ground-based stations equipped with advanced atmospheric probing instrumentation for aerosols, clouds, and short-lived gas-phase species. ACTRIS will have the essential role to support building of new knowledge as well as policy issues on climate change, air quality, and long-range transport of pollutants.

2 Rationale and Objectives

Several governmental institutions, mainly meteorological services and environmental protection agencies in Europe aim at providing reliable long-term observations of the chemical composition and physical properties of the atmosphere relevant for understanding atmospheric chemistry and climate change. Reactive gases are one of the foci; this group includes besides surface ozone (O_3), carbon monoxide (CO) and volatile organic compounds (VOC) also nitrogen oxides (nitric oxide (NO) and nitrogen dioxide (NO_2)), which are present only in trace quantities in the atmosphere but play an important role in atmospheric chemistry.

Measurements of nitrogen oxides have been made for decades using a number of different techniques and calibration scales (WMO 2011, Fuchs et al., 2010). However, in Europe there are only a couple of sites performing continuous, in situ measurements of nitrogen oxides. This document was created by the ACTRIS community with the objective to document the measurement techniques in use and to contribute to a convergence of these techniques in Europe to establish a harmonized European data set of atmospheric nitrogen oxides observations.

Compatibility of data from different observational platforms and sites is of crucial importance for the early detection of trends or slight variations in chemical composition of the atmosphere. In many cases, decades of time series are required to assess these changes with a certain degree of confidence. Support of the long-term stability of the reference scales and its propagation to in-situ measurements are particular prerequisites to meet these demands.

In this document we focus on continuous measurements of NO and NO_2 performed from surface stations.

Thus, these Measurement Guidelines for NO and NO_2 are intended for use at ACTRIS sites and any other measurement platform where such measurements have recently been added to the programme or will be added in the foreseeable.

3 Data Quality Objectives for NO and NO_2 Measurements

Data quality objectives (DQOs) define the type, quality and quantity required of primary data and derived parameters to yield information that can be used to support decisions. In particular, DQOs specify tolerable levels of uncertainty in the data, required completeness, comparability and representativeness based on the decisions to be made [WMO, 2007].

In case of NO and NO_2 the DQOs [WMO 2011] presented in Table 1 constitute a compromise between the scientific need, the physical and chemical properties of the studied compounds and the instrumental accessibility. The scientific needs are seen in either or a combination of (i) long-term monitoring to derive changes and trends in the atmospheric composition, (ii) monitoring to enable analyses of source-receptor relationships and transport processes, (iii) photochemical process-studies at the respective ACTRIS sites making use of all available data:

- For long term measurements, trends exceeding 1% per year should be discernable, hourly measurements with a minimum 66% coverage and appropriate accuracy (see Table 1) are required.
- Examination of source-receptor relationships and transport processes need a time resolution of at least one hour since air mass change occurs in this time frame.

- For chemical process studies a time resolution comparable to the lifetime of nitrogen oxides is required, which is in the range of 30 minutes to days.

It is assumed the measurements are undertaken on a continuous basis.

Taking into account the typical lifetime of nitrogen oxides, and the remoteness of the station with respect to distance from source areas, it is useful to set 3 different levels of DQOs according to the site characteristics, e.g. the typically encountered mixing ratios of NO_x.

Table 1 - Data Quality Objectives (DQOs) for NO and NO2 under differing conditions [WMO 2011]

Level	1 (basic)	2 (enhanced)	3 (high)
Site characteristics	Continental basic	Continental background	Pristine, marine background, free troposphere
Mean mixing ratio NOx	> 1 ppb	0.1 – 1 ppb	< 0.1 ppb
Scope (corresponding time resolution)	long term monitoring, trends (1 hour), source-receptor-relationship, transport processes (hour-minute), photochemical process studies (minute)		
Detection Limit (1 hour, 3-σ)	NO: 50 ppt NO$_2$:100 ppt	NO: 10 ppt NO$_2$:20 ppt	NO: 1 ppt NO$_2$:5 ppt
uncertainty (1 hour, 2- σ)[1]	NO: 40 ppt or 3% NO$_2$:80 ppt or 5%	NO: 8 ppt or 3% NO$_2$:15 ppt or 5%	NO: 1 ppt or 3% NO$_2$:3 ppt or 5%
uncertainty (1 month, 2- σ)[2]	NO: 2.5% NO$_2$: 3%	NO: 2.5% NO$_2$: 3%	NO: 1 ppt or 2.5% NO$_2$:3 ppt or 3%
data coverage	66%		
suggested method	CLD / PLC	CLD / PLC	CLD / PLC
alternative method (backup or QC reasons)	CRDS ; LIF ; DOAS ; TDLAS	CRDS ; LIF ; TDLAS	LIF

[1] whichever is the larger, e.g. for level 2 "enhanced" at NO$_2$ of 1 ppb an uncertainty of 50 ppt is required (5% of 1 ppb), at 0.2 ppb an uncertainty of 15 ppt would be required.

[2] assuming that the random uncertainties are negligible compared to the calibration uncertainty

Table 1 summarises the scientific goals, instrumental techniques, and sensitivity requirements for ACTRIS NO_x sites with different characteristics, including continental, continental background, and pristine marine locations. It should be recognized that Table 1 presents initial DQO requirements to be achieved in the NO_x network. These are expected to evolve in time for each site depending on the available technologies and the experience gained particularly in the early phase of ACTRIS NO and NO_2 monitoring.

Commercial instruments are available with the necessary characteristics to cover both basic (Level 1) and enhanced (Level 2) situations but only research instruments developed by skilled investigators are capable of providing real measurements in pristine conditions (Level 3). Since most of ACTRIS sites are equipped with the TE 42 TL analyser, DQO of Level 1 should be achievable.

In spite of a clear scientific need to establish the data quality objectives, the above formulated requirements will indeed present a difficult measurement challenge given the low levels of NO and NO_2 expected at many of the ACTRIS NO_x sites. Further, the need to quantify trends accurately over time at low ambient levels of NO and NO_2 places an additional burden on even the best measurement techniques, so that careful operation and thorough attention to detail will be required to achieve the DQOs necessary to make atmospherically relevant measurements of NO and NO_2.

4   Measurement Setup

4.1. Location and site requirements

Location and site requirements are closely related to the typical requirements for ACTRIS stations. As a primary requirement the station location should be chosen such that, for the variables measured, it is regionally representative (which means it should be typical in population, plantation, weather conditions and so on for the respective area) and is normally free of influence of significant local pollution sources.

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

Measurements sites should provide facilities which allow the operation of the instrumentation needed. This usually requires sufficient electrical power, a suitable data acquisition system and depending on the instrumentation other supplies. Additionally calibration gases, traceable back to the primary standard and a calibration unit with the possibility of gas phase titration (for calibration of NO2) are needed. Furthermore, a constant temperature (air-conditioning) is required for most measurements and instrumentation should not be exposed to sunlight. Finally, well trained personnel are essential.

4.2. Air inlet design

Typically nitrogen oxides are measured along with ground based ozone. Since the latter one is much more sensitive to inlet line material, the material used for collecting ozone (e.g. PFA Teflon^{TM}) is also suitable for nitrogen oxides. For measuring only nitrogen oxides also stainless steel can be used. However, due to possible interferences of NO_x measurements caused by O_3 (see section 7) simultaneously monitoring of O_3 mixing ratios is strongly recommended. OF course the NO and NO_2 analyser should be equipped with an inlet line filter like the ozone analyser is and it should be changed on a regular time basis (see 7.1).

Principally there are some problems concerning the inlet line:

- Changes in traces gas concentrations in the inlet line may be caused by heterogeneous processes, namely by interactions between gas phase and wall of the inlet line: adsorption, absorption, diffusion and chemical reactions at the wall.
  $\Rightarrow$ The material of inlet line must have a smooth surface (otherwise adsorption), non-porous (otherwise absorption & diffusion) and inert (otherwise reaction). An approved material is PFA-Teflon™, a perfluoralkoxy-Teflon^{TM} with totally fluoridated propylene side chains:

$$-\left[CF_2 - CF_2\right]_m -\left[CF\left(-O - C_3F_7\right) - CF_2\right]_n$$
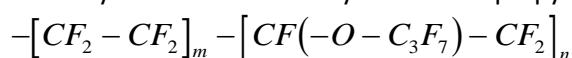
  For measuring ozone never use stainless steel tubes or fittings anywhere in the system since they remove ozone very effectively

- After time of inlet use the surface changes due to condensation of vapours (organic / inorganic) and aerosol deposition.
  $\Rightarrow$ The solution for this problem is cleaning and heating of the inlet line. The cleaning interval has to be chosen such that no trace substance loss occurs but measurement interruption is short. This strongly depends on site conditions. A suggestion is: one per year at remote, twice per year at clean rural and up to monthly at urban sites, respectively. The temperature of the inlet line has to be chosen high enough that no condensation occurs but not too high that thermal decomposition of other trace gases (e.g. PAN) will become an artefact. Controlled heating a few degrees (3-4°) above ambient temperature is best.

- Gas phase processes also may lead to changes in trace gas concentration, because of different conditions in the inlet line compared to ambient. For example the reaction: $NO_2 + h\nu \rightarrow NO + O$ is stopped due to the lack of sunlight in the inlet line, but the back reaction: $NO + O_3 \rightarrow NO_2 + O_2$ continues, leading to an enhanced NO_2/NO ratio.

$\Rightarrow$ The residence time (tube length x diameter / flow velocity) in the inlet line must be as short as possible. Recommended is a residence time of smaller than 5 seconds, better smaller than 2s. However, length is mostly defined by actual facts. With a small diameter the surface/volume ratio gets worse and surface artefacts are enhanced. Along with an enhancement of flow velocity, a pressure decrease could occur and this again could cause problems like converting some substances from particulate into gas phase e.g. $HNO_3(aq) \rightarrow HNO_3(g)$; PAN depletion or depletion of $N_2O_5 \rightarrow NO_2 + NO_3$ could occur. When designing a new inlet line, the above mentioned problems must be taken into account. A very good way to test the inlet line is by feeding a small tube (e.g. 1/16" or 1/8" tube into the existing ¼" or larger inlet line) with constant calibration gas flow into the inlet line such that the mixing ratios of NO and NO_2 are measured at various positions of this "standard addition tube" along the inlet line between inlet and instrument and changes in the concentrations of NO or NO_2 can be detected.
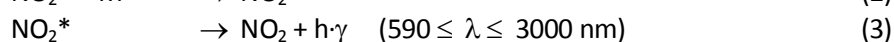
Additionally the signals for NO and NO_2 should be corrected for ozone and H_2O artifacts as described in chapter 7.3.

5   Measurement Techniques

5.1. Techniques for NO
5.1.1. Chemiluminescence

GAW recommends the gas-phase reaction of nitric oxide (NO) in a low-pressure ozone-induced chemiluminescence detector (CLD) for measurement of ambient NO. This technique (Fontijn et al., 1970) follows the reactions:

$$NO + O_3 \qquad \rightarrow NO_2^* + O_2 \qquad\qquad\qquad (1)$$
$$NO_2^* + M \qquad \rightarrow NO_2 \qquad\qquad\qquad\qquad (2)$$
$$NO_2^* \qquad\qquad \rightarrow NO_2 + h\cdot\gamma \quad (590 \leq \lambda \leq 3000\ nm) \qquad (3)$$

This provides a sensitive and selective measurement of NO once detector response is determined according to equation 4:

Ambient NO = (ambient signal – background signal – artefact signal) / sensitivity   (4)

The following sketches give a schematic overview of operating mode:
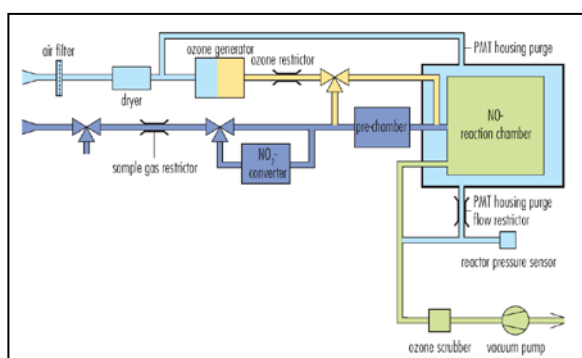
Fig. 1a: Flow scheme of NO chemiluminescence

detector   (courtesy of ECO Physics)!!
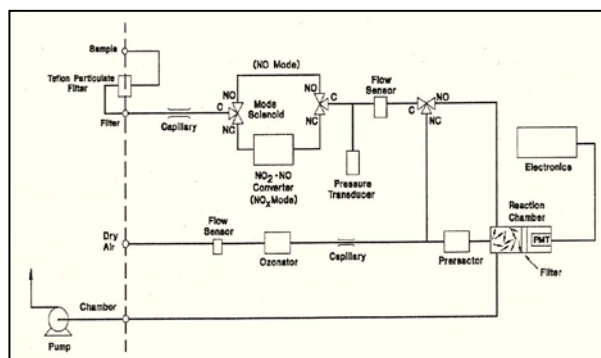
Fig. 1b: Flow scheme of Thermo Instruments 42 TL

NO chemiluminescence detector

In the reaction chamber ambient air is mixed with O_3 and reactions (1)-(3) take place. The light released from reaction (3) passes a window, equipped with a red/infrared filter (according to the wavelengths of emission) and enters the photomultiplier tube (PMT) connected to the reaction chamber. Since the reactions are very fast the geometry of the reaction chamber has an influence on the sensitivity: The reactions should take place directly in front of the PMT window. For a better signal/noise ratio the PMT is cooled, e.g. by a Peltier cooling device. Due to potentially sub-ambient temperature gradient the PMT window is purged by dry air to avoid condensation.

In most instruments, the ozone generator provides high ozone levels (in ppm range) by silent electrical discharges which are necessary for a fast reaction sequence. To speed up the reaction velocity it is recommended to use pure oxygen instead of dry air for generating ozone. Using pure oxygen enhances the sensitivity roughly by a factor of 2. Experience showed that the long term stability of the ozone generator could be enhanced by the use of a short length of silicone tubing in the line supplying oxygen to the generator to provide a very small but significant amount of humidity which diffuses through the silicon from lab air. A reduction in background signal could be achieved by humidifying the oxygen/ozone flow before its entrance into the low pressure region of the instrument with help of a water bubbler or an inverse Nafion^{TM} dryer. This precaution reduces an unspecific chemiluminescence of ozone generated inside the reaction cell or on its walls. However the latter described improvement could also cause some problems if set up isn't done properly. For that this procedure is recommended only for users which are very familiar with that item.

According to reaction (2), a huge part of excited NO_2* molecules is deactivated radiationless by collision with N_2, O_2 or water molecules. To minimize this, low pressure and therefore a strong pump is recommended. However a too small pressure and therefore a short residence time impedes quantitative reaction of NO with O_3, leading to lower signal. (Hint: Experiments with an ECO Physics CLD 770 AL ppt showed lowering pressure down to 20 mbar still led to an increasing signal. Same experiments with a TE 42 CTL do not lead to definite results up to February 2012. There will be a clear recommendation after successfully completing the experiments.)

Besides NO, some other hydrocarbons (alkenes) and other trace substances react with O_3 followed by chemiluminescence in the red/infrared region. Since most of the other reactions are slow compared to $NO+O_3$ the use of a prechamber can solve this problem: During "prechamber mode" the $NO+O_3$ reaction takes place inside the prechamber so that only the slower reactions of O_3 with interfering agents are counted. This interference signal together with the dark current of the PMT and unspecific chemiluminescence of ozone generated in the reaction cell or on the walls is called the "detector background signal (bkgrd)". The prechamber volume must effectively mix the reagent and sample streams and allow sufficient reaction time to destroy ambient NO before the sample enters the reaction chamber. In case the ozone concentration is too low or the residence time in the prechamber is too small the background signal of the instrument is enhanced and the detection limit is worsened. In case the residence time in the prechamber is too large, the interference signal is already reduced in the reaction chamber giving rise to too small interference correction with the consequence that part of the interference signal might be counted as NO signal. A good compromise is a residence time in the prechamber on the order of 2 reaction time scales of $NO+O_3$. However, design and dimensions are chosen by the manufacturer. A high-conductance Teflon three-way solenoid valve is typically used to switch reagent O_3 between sample mode (O_3 added directly to CLD chamber) and background mode (O_3 added upstream to the prechamber). Detector background levels must be determined routinely, approximately at least once per hour, or best, at every measurement cycle to account for potential instrumental drifts over time.

A detector "artefact", or unwanted differences (positive or negative) in signal relative to the measured detector background, can often be observed in CLDs even when sampling NO-free air. Artefact levels can be determined by overflowing the sample inlet with an excess of ultrapure cylinder air, and alternating between sample and background (prechamber) modes. Artefact signals can arise from spurious CLD pressure differences between these two modes, or from real, non-zero amounts of NO in even ultrapure cylinder air. Detector artefact levels must be determined routinely, approximately once every two days to make an accurate determination of ambient NO in the low picomole/mole (pptv) range. For measurement sites remote from NO sources – including potential biogenic/soil sources of NO within a few meters of the inlet – ambient night time NO concentrations are expected to be identical to zero due to reaction with ambient O_3. If this condition is satisfied, a comparison of the detector background signal to the ambient signal measured after dark should give a measure of the detector artefact signal. Having a detector signal close to zero during night but significant different from zero during zero air measurement one should inspect the zero gas for possible leaks or exausted cleaning cartridges. Having substantial and similar counts during zero air and night-time ambient air measurement is a strong hint for a detector artefact signal (It is very unlikely to have similar counts originating from NO residuals in zero air AND from sources in ambient air during night-time.).

By calculating the difference between "measurement mode", "prechamber mode" and "artefact signal" according to equation (4), a highly selective signal for the ambient NO mixing ratio is achieved.
Principally this technique is only able to measure NO, all other nitrogen oxides must be converted.

5.1.2. Other techniques for NO

Other techniques like chemiluminescence reaction with Luminol[TM] after conversion of NO to NO_2 by Cr_2O_7 are not recommended by GAW.

5.2. Techniques for NO_2
5.2.1. NO_2 Photolysis and detection as NO

GAW recommends the photolytic conversion (PLC) of ambient nitrogen dioxide (NO_2) using an adequate light source like Xenon high pressure or metal halide lamps or ultraviolet light-emitting diodes (UV-LEDs) (then called "blue light converter" (BLC)) followed by CLD for measurement of the formed NO (Winer et al., 1974). Following photolysis, the CLD signal is due to ambient NO, plus the fraction of NO_2 converted to NO. Ambient NO_2 can be calculated by difference (Kley and McFarland, 1980) providing a sensitive and selective measurement of NO_2 once the photolysis efficiency "S_c" is determined.

The residence time in the photolysis chamber should be about one second. Ambient air is irradiated with appropriate wavelengths and NO_2 is photolysed to NO and oxygen. Subsequently ambient air enters the CLD and the converted fraction of NO_2 along with ambient NO is measured and described as NO.c.

Since the measurement of NO /NO_2 is sequential, the NO_2 mixing ratio in ambient air has to be calculated in the following way:

background measurement $\Rightarrow$ pre chamber $\Rightarrow$ bkgrd
NO measurement $\quad\quad\quad \Rightarrow$ reaction chamber $\Rightarrow$ NO
NO.c measurement $\quad\quad \Rightarrow$ converter + reaction chamber $\Rightarrow$ NO.c

calculation NO_2:
$$NO_2 = \frac{[NO.c - bkgrd] - [NO - bkgrd]}{S_C}$$

calculation NO_x:
$$NO_x = \frac{[NO.c - bkgrd] - [NO - bkgrd]}{S_C} + [NO - bkgrd]$$

Taking into account loss of NO and enhancement of NO_2 due to ozone reaction in inlet line and quenching effects caused by water vapor formulae as given in section 7.3 should be used for calculating most accurate NO and NO_2 ambient air mixing ratios.

5.2.2. Chemical NO_2 reduction & detection as NO

Chemical reduction of NO_2 at a hot metal surface (mostly molybdenum) is widely used. The efficiency is larger than 98% with a strong decay at the end of lifetime. The big disadvantage of this set up is that not only NO_2, but also other nitrogen oxides are reduced (e.g. PAN, HNO_3). This could lead to an analytical error of 100% or more in rural/remote areas. For this reason it is clearly recommended NOT to use chemical converters but instead PLC / BLC converters in networks like ACTRIS or GAW.

5.2.3. Other techniques for NO_2 detection

Currently, instruments using Cavity Enhanced Absorption Spectroscopy (CEAS), Cavity Ring Down Spectroscopy (CRDS), Cavity Attenuated Phase Shift (CAPS) and other related techniques are developed and first commercial instruments become available. However, these instruments first have to prove their suitability for long-term monitoring within the DQO specified in this Guideline. ACTRIS will take part in such studies and contribute to the evaluation of new instruments.

6 Primary standards and calibration centre for NO and NO_2

6.1. Central calibration laboratory (CCL) and primary standard (PS)

The role of the Central Calibration Laboratory (CCL) is to maintain and disseminate primary standards to which measurement results within the GAW- and ACTRIS-network can be made traceable [WMO, 2008] thus underpinning the long-term accuracy of data.

Probably NPL is going to take over the role as CCL in collaboration with BIPM. The calibration gas for round robins will originate from NPL.

At present only NO in nitrogen is foreseen as primary standard, usable also for NO_2 by gas phase titration (GPT). NO in N_2 ($\geq$ 5.0) is stable in the range of 450 ppb $\leq$ m.r.$\leq$10 ‰ in specifically passivated cylinders. Drift at 50 ppm standard is about -0.2% - -0.02% year^{-1}. Maybe in the future there will be an additional NO_2 standard. First tests showed a robust standard of 10 ppm NO_2 in the presence of 1000 ppm O_2. Depending on the material of the cylinder HNO_3 is formed in the range of 10 - 200 ppb. Intercomparison of NMI's yielded deviations < 0.5%.

6.2. World Calibration Centre (WCC)

One main task of WCC is to assist the GAW stations to link in-situ observations to the primary standard. This should be done through regular calibrations, round robins, side-by-side measurements and audits.

The research Centre Juelich (Germany) has volunteered to operate the WCC for NO_x in GAW. In ACTRIS this institution is a subcontractor and works a calibration centre, too.

7 Quality Assurance and Quality Control

7.1. Measurement and measurement protocol

Typically the chemiluminescence analyzers measure NO and NO_2 mixing ratios sequentially, but quasi continuously (see chapter 5). In order to archive the best data possible, quality checks on a regular basis are required. The following actions are suggestions which have to be adapted for the special requirements at the individual sites.

All actions taken on the instrument or related to the instrument (inlet, pump, data aquisition, ...) must be written down in a station logbook with the respective time. The time zone of the logbook entries should also be clearly documented.

On regulary time intervals the following items should be checked (check lists help):

1.) Routinely checks (e.g. every time the operator is on site):
Connections to the instrument:
- Electrical power: Is the cord really fixed?
- Data aquisition: Are all cables fixed
- Inlet line: is the inlet line leak-proof? Is no room air pulled in? (Unusual spikes in data corresponding to presence of personal in lab are hints towards a leaky inlet line.) Are there any signs of condensaion in the inlet line. Are the flow and temperature(s) of the inlet line in the allowed range (control unit of inlet line)?
- Dry air supply for flushing the PMT window: Is the dry air correctly connected? Is the drying unit working well, or has the silica gel cartridge to be regenerated? It is very important to feed dry air into the CLD which is used for rinsing the PMT window. Humidity leads to condensation at the PMT window follwod by significant loss of sensitivity and too much humidity can lead to a demolition of the PMT or connected electronics.
- Oxygen supply: Is the oyxgen supply correctly connected and is the pressure of the oxygen cylinder sufficient? Check for time to order a new oxygen cylinder (consider delivery time). **(Hint: To improve the sensitivity of CLD the ozone source should be operated with pure oxygen.)**
- Is the clock of the data acquisition system ok?

Check of (meta)data:
   All metadata should be stored, the use of a data aquisition systems is recommended.

- Is the inlet flow and the chamber pressure in the expected range? Is there a drift in chamber pressure? Since chamber pressure directly affects the sensitivity of the instrument (quenching) it has to be constant. Otherwise recalibration is needed. Drift in chamber pressure or inlet flow might be a hint for a blockage of the inlet line or a weakening of the pump.
- Are the temperatures (PMT, reaction chamber, photolysis cell, CLD) in the allowed ranges? Especially the PMT temperature is important since it directly affects the noise of measurement.
- Are the NO and NO_2 data in a typical range? NO_2 data are typically some 2-5 times higher than NO during day time. If they are more or less equal, this is a strong hint of defective conversion.
- Is the background signal in the prechamber mode in the expected range? Problems might be a hint for a weakening of the ozone generator.
- Are there "artifact signals" during night and measurement with zero air (see 5.1. and 7.3.)?
- Do the data displayed at the instrument match with the respective data in the data file of the aquisition system? This is a simple and effective test whether the data flow from instument to data storage is o.k..

2.) Routinely maintenance
- every 2nd day (depending on aspired precision of measurement): calibration (span check) and determination of conversion efficiency
- every 2nd week (depending on pollution level): change of inlet line filter
- every 3rd month (depending on pollution level and capacity of drying cartridge): change of filters at dry air and oxygen inlet; regeneration of drying cartridge. First the CLD is shifted to stand by mode. Then the filters and cartridges are exchanged. (Hint: It is convenient to use a silica gel and a drierite ($CaSO_4$) cartridge in serial connection. The silica gel absorbs most of humidity, subsequently the dew point is further lowered by the drierite. The silica gel can be easily regenerated by means of a microwave during some minutes. During that time the system can continue operation with the drierite cartrige alone (in this case the CLD needn't put to stand by mode). With this setup the drierite cartridge has to be regenerated ony every third month in a cabinet dryer.)
- every 6th month (depending on pollution level): cleaning of reaction chamber, cleaning of photolysis chamber; (durable loss in counting rate is a hint toward a dirty cell, loss in conversion efficiency even when using a new lamp is a hint towarts a dirty photolysis chamber). Refer to instrument manual for dissassembling reaction and photolysis chamber. Warning: The PMT, as long as under electrical power, will be destroyed by incident light. Once dissambled the cleansing is like the following: First rinse with deionised water. For more persistent deposits use a lint-free cloth. Don't scratch the walls or any glass part. Don't use organic solvents or acids!
- every 6th month: multi-point calibration with primary station standard.
- on demand: At NO_2 conversion efficiency below 40% or unsteadiness of lamp: Change of Xe-photolysis lamp, (other conditions and limits for other types of converters e.g. Blue Light Converter).
- Some instruments require periodic replacement of consumables, e.g. valves. Refer to instrument manuals for details.

7.2. Calibration procedure

Since the chemiluminescence technique is not an absolute measuring method and sensitivity depends on parameters like cell temperature or pressure, which can change with time, frequent zero and span checks are mandatory.

Depending on data quality objectives, recalibrations have to be performed on regular basis and in such intervals that the expected deviation between consecutive calibrations is lower than the uncertainty of the measurement. Zero checks are not as important as span checks for the more sensitive instruments which are equipped with a prechamber. However, to ensure that zero air contains only traces of nitrogen oxides causing a signal well below the detection limit, zero checks should always be performed together with span checks. According to the DQOs, recalibration should be performed at least once per

week, every second day, twice a day for level 1, 2, and 3 sites, respectively. It is recommended to calibrate the CLD at typical ambient air concentration. The instrument linearity should be checked up to the span gas concentration at least once a year.
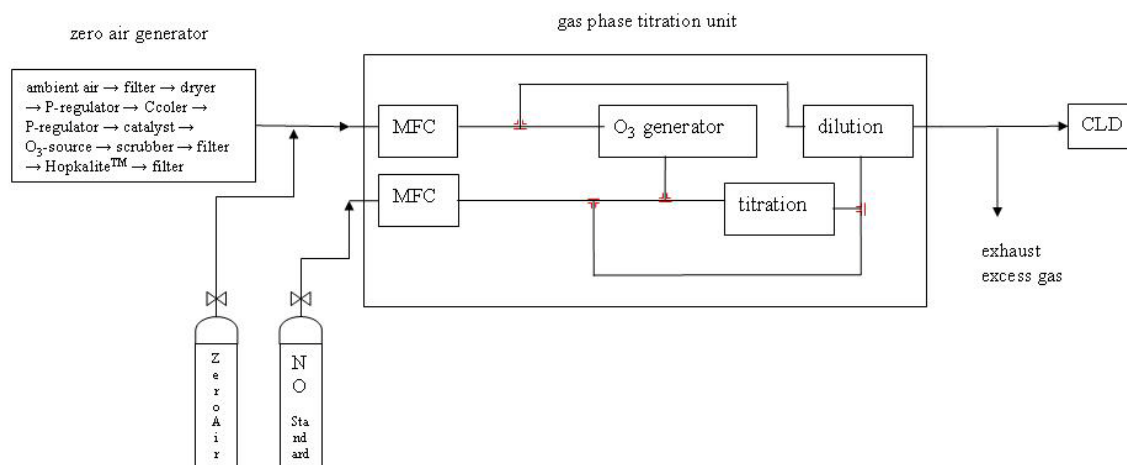
sketch of calibration configuration

For calibration, special equipment is needed and special care has to be taken to achieve reliable results: A zero air supply is needed (as the sketch indicates zero air in cylinders or alternatively a zero air generator should be used), which exceeds the gas consumption of the analyzer by about a factor of 2 and has a sufficiently high purity such that the remaining nitrogen oxides concentrations are less than the detection limit of the respective analyser (Hint: Eco Physics offers a zero air generator which provides nitrogen oxides free air (< 5 ppt). An alternative is the use of adsorbent traps (activated charcoal and Sofnofill[TM] or Hopkalit[TM]). The lifetime of these catalysts/absorbers strongly depends on quality of air which has to be cleaned, of course. If zero air has been o.k. for some time and then tends get measurable amounts of nitrogen oxides, change the cleaning cartridges.). Each station should have at least a laboratory standard by the CCL or traceable to the CCL and a second certified standard ("working-standard") as a check at each station. The NO working standard is used at the station for regular calibrations. It has to be diluted with zero-air to achieve a suitable concentration range. For this, a dilution unit with flow controllers or passive elements like critical orifices or restrictors has to be used which need to be carefully characterized to achieve the required dilution factors and accuracy. From comparisons between working standard and station-standard it has to be checked that no drift occurs.

During constant NO mixing ratios in ambient air (e.g. during night) the detector sensitivity to NO can also be determined by spiking with standard additions, using a known mixing ratio of NO in the low micromole/mole (ppmv) range, added at the inlet tip to the ambient air sample stream to produce a calibration in the low nmole/mole (ppbv) range. The advantage is calibrating in a real air matrix, so the data will not need to be corrected (at the given humidity) to account for ambient water vapor quenching effects according to Ridley et al. (1992) before being applied to the ambient data. The disadvantage is that this technique relies on constant ambient NO mixing ratios during calibration which means that it needs to be repeated several times (switching between ambient NO and spiked NO) and only if constant span factors are achieved it can be used.

When first attached to the NO standard cylinder pressure regulators must be flushed 4-5 times with cylinder contents. After that the regulators remain under pressure for at least 24 hours in order to achieve equilibrium. After again flushing 4-5 times they are ready for use. This procedure is required to prevent residual atmospheric O_2 from reacting with NO and altering the cylinder mixing ratio. The duration of the calibration procedure should be sufficient long to ensure a zero drift in the calibration signal.

If NO_2 is measured at the site, the PLC-CLD system must be calibrated also for NO_2. Since NO_2 is generally not stable in cylinders, it is recommended to produce NO_2 out of NO standard gas by gas phase titration with ozone (it is not recommended to buy gas mixtures, which contain both NO and NO_2 since the O_2 added to stabilize NO_2 would react with NO to form NO_2). Thus, a gas phase titration unit is needed, which consists of a dilution unit (which is also needed for the NO calibration, see above) and an ozone generator. The GPT ozone source must be very stable over time. Irradiation of zero air with the 185 nm

UV output from a temperature-controlled Hg pen-ray lamp has proved to be suitable. Silent electrical discharge is not appropriate for ozone production because it is not stable enough for GPT and generates small amounts of NO_2.

Other methods for calibration of NO_2 include permeation sources or high pressure cylinders with NO_2 concentrations in the high ppm range. As the permeation device includes further error sources than dilution, e.g. the uncertainty of a constant permeation rate and the dilutions from NO_2-mixtures requires a second dilution step due to the high concentration involved, these methods generally have higher uncertainties than the methods recommended above. Accordingly, these should only be used as an extra quality check.

Calibrations should be performed under the same conditions as the ambient air measurements. Generally the NO_2 calibration should always immediately follow the NO calibration as it includes the NO chemiluminescence sensitivity.

Practical procedure:
1. Check that all instruments and tools needed for calibration are connected and work.
2. Warm-up time of GPT with ozone generator should be at least 1 hour. Rinse the calibration unit with a high mixing ratio of ozone (e.g. 100 ppb) during that time (warm up of ozone source and cleaning of tubing).
3. Flow of zero air for at least 20 min, connect CLD with calibration source and acquire zero air counts for at least 10 minutes (depending on type of CLD). (Hint: Compare the readouts (counts) of prechamber mode and measurement mode: Significant higher levels during measurement mode are an indication of NO impurities in zero air, higher levels only during NO.c measurement mode (sample flowing through PLC/BLC) is an indication of NO_2 impurities in zero air. If it is not possible to look at the count rates (e.g. TE 42) change span to a high level and have a look on the "mixing ratios" at the respective modes.) These NO or NO_2 impurities in zero gas will become critical if their amount exceeds the LDL of the respective system. In this case inspect your zero air supply.
4. Adjust the desired span point and allow the system to run for at least 20 minutes, then acquire the span air counts for at least 10 minutes.
5. After determination of the new calibration factors for NO, one can continue with NO_2 calibration.
6. Let the desired NO concentration (without ozone) flow into the system and acquire the data for NO- ($NO_{(1)}$) and NO_2 channel ($NO.c_{(1)}$) for at least 10 minutes each (Hint: Higher $NO.c_{(1)}$ signal compared to $NO_{(1)}$ is an indication of NO_2 impurities in the standard gas and/or zero air).
7. Choose an ozone concentration so that 80% of the primary NO amount is titrated. Give the system at least 20 minutes to stabilize.
8. After stabilisation acquire the data for the NO- ($NO_{(2)}$) and NO_2- ($NO.c_{(2)}$) channel for at least 10 minutes (each).
9. Subsequently the NO_x analyzer is reattached to inlet line, GPT unit and zero air supply are switched off and pressure reducer of standard gas cylinder is shut off.

The converter efficiency is calculated as follows:
The effective produced NO_2 amount results from: $[NO_2] = [NO_{(1)} - NO_{(2)}]$
The converted NO_2 amount by PLC is calculated by: $[(NO.c_{(2)} - NO_{(2)}) - (NO.c_{(1)} - NO_{(1)})]$
Accordingly the efficiency factor is calculated by:

$$S_C = \frac{[(NO.c_{(2)} - NO_{(2)}) - (NO.c_{(1)} - NO_{(1)})]}{[NO_{(1)} - NO_{(2)}]} = 1 - \frac{NO.c_{(1)} - NO.c_{(2)}}{NO_{(1)} - NO_{(2)}}$$

7.3. Corrective actions facing possible interferences
7.3.1. Interferences caused by water vapor

Since water vapor is an effective quenching substance in the CLD reaction chamber parts of the excited NO_2 molecules are quenched by H_2O molecules. For example this accounts for about 4% signal loss due to an absolute humidity of 9 g/m³ (corresponds to 50% RH at 20°C). Accordingly, a correction factor has to be applied:

$$[NO]_{H_2Ocorr} = [NO] \cdot (1 + \alpha \cdot [H_2O]) \quad \text{with} \quad \alpha = (4.3 \pm 0.3) \cdot 10^{-3} \cdot \frac{flow_{sampleair}}{flow_{ozone} + flow_{sampleair}}$$

Ridley et al, 1991, adopted and modified by Franz Rohrer (WCC NOx)

7.3.1. Interferences caused by ozone

As mentioned in chapter 4.2. after entering the inlet line NO_2 photolysis is stopped whereas reaction of NO and O_3 continues, leading to overestimation of NO_2 and underestimation of NO.

To allow for this, the following formulae should be used for back calculating the measured signal to ambient air concentrations:

S_C : conversion efficiency of PLC or BLC
J_C : photolysis rate of NO_2 in converter
$[NO]_M$: analyzers readout for NO
$[NO_2]_M$: analyzers readout for NO_2
$[NO]_{E1}$: measured NO signal [ppb] without photolytic converter (LED off or bypass)
$[NO]_{E2}$: measured NO signal [ppb] with photolytic converter
$[NO]_0$: NO mole fraction at the entry of inlet line
$[NO_2]_0$: NO_2 mole fraction at the entry of inlet line
$[NO]_L$: NO mole fraction at the entry of converter at time t_L
$[O_3]_0$: O_3 mole fraction [ppb] at the entry of inlet line
t_L : time [sec] from entry inlet line to entry of converter
t_{C1} : duration of stay [sec] in converter or bypass line (in case of LED off or bypass)
t_{C2} : duration of stay [sec] in converter
t_{E1} : $t_L + t_{C1}$
t_{E2} : $t_L + t_{C2}$
$k(O_3+NO)$: reaction rate constant for $NO+O_3$
k_{O3} : $k(O_3+NO) * [O_3] * 10^{-9} * M$

In first step the analyzers readout for NO and NO_2, $[NO]_M$ and $[NO_2]_M$, respectively, have to be reconverted to the related NO signals $[NO]_{E1}$ and $[NO]_{E2}$.

$$[NO]_M = [NO]_{E1} \qquad \text{and} \qquad [NO_2]_M = \frac{[NO]_{E2'} - [NO]_{E1}}{S_C}$$

These are the typical formulae for calculating the NOx mixing ratios without ozone correction.

With the intermediate parameters J_c; which is the photolysis rate in PLC and $[NO]_{PSS}$ and $[NO_2]_{PSS}$, which are the equilibrium mixing ratios of NO and NO_2 in PLC, respectively,

$$J_c = \frac{-\ln(1 - S_C)}{t_{C2}}$$

$$[NO]_{PSS} = \frac{J_C}{J_C + k_{O3}} \cdot ([NO]_0 + [NO_2]_0) \qquad \text{in photolytic converter}$$

$$[NO_2]_{PSS} = \frac{k_{O3}}{J_C + k_{O3}} \cdot ([NO]_0 + [NO_2]_0) \qquad \text{in photolytic converter}$$

one can calculate the NO and NOx mixing ratio at the entrance of the inlet line, $[NO]_0$ and $[NO_2]_0$:

⇨ **Calculation of NO:**

$$[NO]_0 = [NO]_{E1} \cdot \exp\{k_{O3} \cdot t_{E1}\}$$

⇨ **Calculation of NO$_2$:**

$$[NO_2]_0 = \left(\frac{J_C + k_{O_3}}{J_C}\right) \cdot \left(\frac{[NO]_{E2} - [NO]_{E1} \cdot \exp\{-(k_{O3} \cdot (t_{C2} - t_{C1}) + J_C \cdot t_{C2})\}}{1 - \exp\{-(k_{O3} + J_C) \cdot t_{C2}\}}\right) - [NO]_0$$

7.4. Audit , round robin, side-by side measurement procedures

Besides routine calibration and quality checks, intercomparisons are essential for intercomparable, quality proofed data. Main intercomparison procedures are: round robin, side-by-side experiments and audits.

7.4.1. Draft Standard Operating Procedure for Round Robin of NO in cylinders

This Standard Operating Procedure (SOP) provides recommendations for consistent and comparable round robin measurements of nitric oxide (NO). The SOP is structured in four paragraphs: The equipment, preparation of the measurements, the measurement procedure itself and the post-measurement procedures.

This SOP should be used with the following round robin cylinders and regulators (examples of the ACTRIS Round Robin in 2012):

Cylinder	Corresponding pressure regulator
ACTRIS #1 NO in N$_2$ standard	CONCOA, Type: 3322 862-01-D14
	Ser.-No.: 1180JRTP
ACTRIS #2 NO in N$_2$ standard	CONCOA, Type: 3322 862-01-D14
	Ser.-No.: 1180JRTQ

Round Robin Equipment (per unit):

2 shipping container (for cylinder and pressure regulator, respectively)
1 gas cylinder
1 pressure regulator
1 PFA tubing ☐ 1m length with 1/8" Swglock fitting female and 1/8" blind cap male.
"Parafilm" tape
1 log table

Picture 1)   Round robin gas cylinder and pressure regulator with PFA tubing

The equipment is stored and shipped in transport boxes. Please use only the provided pressure regulator and transfer line. A log table is connected to the cylinder. Please fill in measurement dates, cylinder pressure, operators name, etc.

Preparation of measurements

Please use laboratory gloves (i.e. latex) in order to avoid contamination of the equipment!!

i) At least 24 hours before the measurement:

Mount the pressure regulator onto the gas cylinder and connect the transfer line with the 1/8" (Swagelok etc.) outlet port of the pressure reducer. The transfer line is made of PFA (Perfluor-Alkoxy-Teflon) and stainless steel fittings.

ii) When the regulator and the transfer line are fixed, please, flush the regulator:

First, uncap the transfer line and open the regulator's low pressure port, thus, a flow through the regulator and transfer line is allowed. For flushing, open the cylinder valve and close it again quickly (seconds; in order to avoid back diffusion of potential contaminants into the cylinder). Wait until the pressure has released through the low pressure port (until primary pressure goes down to ambient). Repeat this procedure at least another 2 times.

After flushing, plug the transfer line and pressurize the pressure regulator another time by shortly opening the cylinder valve. Check the pressure for a few minutes; if not constant, tighten the nut and repeat. Write the cylinder pressure into the log (pressure at first use). Apply a low pressure (2-3 bar) to the transfer line, as well. As an initial leak check, close the regulator. After it is closed, watch the low pressure port for some 10 min. If not constant, check plug and connection to the transfer line and tighten gently and repeat the check.

Please, do not use liquid leak tester solutions as they might contaminate the system!

iii) Equilibration:

Keep the pressure regulator and the transfer line pressurized with the ACTRIS Round robin gas for at least 24 hours. The cylinder valve has to be closed during that time to avoid back diffusion of potential contaminants into the cylinder and loosing sample through possible leakages. This setup also serves as a static leak test (the upstream regulator pressure should not change during the 24 h equilibration period)!

Comment: During transport, the pressure regulator's surface was in contact with air of different humidity and composition. As the pressure regulator is made of stainless steel, it provides an active surface. Thus flushing the regulator with the sample gas and applying an equilibration time is necessary to yield good measurement results.

iv) Before starting the measurements connect the transfer line to your gas dilution system and flush the system as long as needed to get into equilibrium (time depends on type of gas dilution system).

Measurements

The measurements should cover:

1.   zero air
2.   site's laboratory standard (used as highest level standard at station)
3.   zero air
4.   Round Robin test gas

5.   zero air
6.   site's laboratory standard
7.   zero air

The frequent zero air measurements are necessary to prove that there is no calibration gas left in the tubing / dilution system. The check of the site's standard before and after ACTRIS standard is for tracking a possible drift in sensitivity.

Leave the gas cylinder connected to your instrument and measure the required series using the routine procedures that you apply in your laboratory for gas standard measurements. It is recommended to open the test gas cylinder valve only during the sampling periods.

We ask you to perform a series of at least 3 "normal" measurements, but please restrict the total consumption of ACTRIS test gas, e.g. no more than 30 litres of the test gas (corresponds to 3 bar pressure drop in cylinder) should be used, preferably much less. If problems in the series of 3 measurements occur, please add more measurements so that in total 3 "normal" measurements are available.

Comment: Besides having more robust statistics, running a series enables the detection of possible drifts. This SOP should provide a reasonable concept for consistent and constant measurement of NO.

Finalization of the measurement

After the measurement, please, make the requested notes into the log, close the cylinder valve and release the pressure from the regulator. Then, to check the close-position of the cylinder valve, turn the pressure regulator off and watch the pressure gauge of the regulator for 10 min (it should not go up). Dismount the pressure regulator from the cylinder. Seal all openings with plugs, caps or "parafilm" (see picture). It is important to cap the cylinder outlet to avoid loss of sample gas due to potentially leaking cylinder valves. The cylinder connector of the pressure regulator has to be sealed with Parafilm tape or anything similar. Store the equipment in the transport boxes.

Picture 2) cylinder connector sealed with Parafilm tape.

Update the log table connected to the gas cylinder! Possible log entries of interest are listed in the following list:

+ arrival date of shipment
+ cylinder pressure at first usage
+ cylinder pressure at end of usage
+ measurement dates, instrument, operator names
+ general comments as general condition of shipment/cylinder and equipment
+ approximate date of outgoing shipment

Send the corresponding information also to the organizer of the round robin such that he can keep track on the progress of the round robin.

Report of participants' round robin results

For the participants' results submission, the following template data sheets should be used:

Actris Round Robin Data sheet 2012

site:
name:

site standard (label informations):
ACTRIS Standard No.:

¹ˢᵗ intercomparison

date / time from:	to:

time from:	to:	item	flow zero air	flow cal. gas	purging time	measuring time	expected NO m.r. [ppb]	measured NO m.r. [ppb]
		zero air						
		site standard						
		zero air						
		ACTRIS ①					–	
		zero air						
		ACTRIS ②					–	
		zero air						
		site standard						
		zero air		–			0.00	

⇨   calculated mixing ratio of ACTRIS standard: [ppm]

comments: (e.g.: what kind of zero air, how is dilution archieved, are the MFC's calibrated and when;

measuring conditions (e.g. temperature fluctuations in lab during measurement) ; …)

Uncertainty evaluation of participants' round robin results

At most stations, dilution systems are used to dilute the test gas with zero gas to ppb level mixing ratios. For such stations, an example of the uncertainty evaluation is set up below.

The uncertainty includes the uncertainty of the laboratory standard, the dilution system,

i) uncertainty of dilution factor: The standard deviations of dilution gas and of calibration gas flow measurements (repeatability) have to be combined with the relative uncertainty of the site's flow controllers (declaration by manufacturer); typical: 0.8% of reading + 0.2% of max. flow.

ii) uncertainty of calibration standard: see label of calibration gas cylinder (consider that these are generally given with a coverage factor k=2, but here only the standard deviation is needed, thus devide by 2)

iii) uncertainty of analyzer: the analyzer has been calibrated by the site's laboratory standard, thus it comprises the uncertainty of the dilution factor, the standard's certified mole fraction, and the repeatability of the measurements.

(example: u(lab-standard, k=2)=4%, u(flow zero gas)=1%, u(flow lab-standard)=1.5%, repeatability(measurements of lab-standard, 1 min)=3%

Measurements of laboratory standard have been performed for 10 min, no drift discernable:

error of mean in measurements of lab-standard (10 min)=1/SQRT(9) x 3%=1%

u(analyzer, 1 min)=(2%^2+1%^2+1.5%^2+3%^2)^0.5=4%

u(analyzer, 10 min average)=(2%^2+1%^2+1.5%^2+1%^2)^0.5=2.9%

corresponds to an expanded uncertainty with coverage factor k=2: u(exp, 10 min)=5.8%)

iv) standard uncertainty of the determination of the mol fraction of the unknown round robin gas: Combination of the uncertainty of the analyzer, the uncertainty of the dilution factor, and of the repeatability of the unknown standard

(example: the lab standard has been measured for 10 min total without a drift in 1 min intervals and the unknown round robin gas also for 10 min with a standard deviation of the 1 min values of 4% and the same dilution factors as used for the laboratory standard:

u(round robin gas, 10 min average)=(2.9%^2+1%^2+1.5%^2+1.3%^2)^0.5=3.6%, corresponds to expanded uncertainty with coverage factor k=2 of 7.3%)

7.4.2. Side-by-side-experiment

Side-by-side intercomparisons should guarantee that identical samples are analysed by collocated instruments. This is either achieved by instruments sampling in ambient air side-by-side assuming homogenous trace gas distribution at the sample gas intakes, or by instruments sampling from a common manifold or atmospheric simulation chamber. One of the advantages of side-by-side intercomparisons is that much more complex sample gas matrixes can be analyzed and also the mole fractions can be varied in a controlled manner such that a range from the detection limits of the instruments to polluted conditions is encountered. This enables a full characterization of the detection limit, the linear range, the span, and of potential artifacts of interfering gases which are present in the complex test gas mixtures used.

7.4.3. Audit

Station audits are performed by the designated WCC for NOx, the FZ-Juelich.

7.5. Measurement uncertainties

Measurement uncertainty is defined as the parameter associated with the result of a measurement that characterized the dispersion of the values that could be reasonably attributed to the measurand. The uncertainty is estimated following the "Guide for expressing uncertainty in measurements" (GUM).

The uncertainty contributions in NO calibration measurements are the flow rates of mass-flow regulating devices, the uncertainty of certified reference material, the zero gas purity, the repeatability of the analyzer, and drifts of the analyzer. Additionally, for NO2 the photolytic converter efficiency has to be included.

In ambient measurements the uncertainty contributions due to zero, span, and repeatability of the measurements have to be considered, additionally that of corrections applied to the data as described in section 7.3, especially for O3 in the inlet line and PLC and water vapor in the CLD measurement chamber.

8   Data Management

8.1. Data evaluation, flagging and control

A detailed procedure is developed for evaluating the measurement data. It contains statistical analysis of the span-factors, zero gas readings and converter efficiency analyses supported by visual inspection of the temporal development over longer time periods, e.g. typically a year. The time series are checked versus the instrument-Log and discontinuities in the time series should be associated to documented

instrument changes. In case a discontinuity cannot be attributed to documented instrumental changes, other explanations for the behavior of the instrument have to be analyzed by careful inspection of the meta-data like chamber pressure or flow rate. In case no explanation for a discontinuity can be identified, an uncertainty contribution in the same magnitude as the discontinuity has to be considered. Generally, the zero gas readings should be in the range of the expected detection limit and the standard deviation of span factors and converter efficiencies in the range of estimated uncertainties, e.g. typically a few percent.

The calibration data are then used to determine a best fit to the span function of the instrument in time: usually, the scatter in the calibration data in frequent span and zero measurements is larger than the drift in floating averages of these values and accordingly floating averages of the span factors should be used in data evaluation.

The instrument readings in ambient measurements are transformed to mole fraction values using the above described averaged span factor functions in time. It is recommended to evaluate the mole fractions, repeatability of measurements and the uncertainty together with the flags in one step, e.g. by use of spread sheet calculations, and using the information from the Log. Thus, discontinuities in the time series are apparent and can directly be attributed to the log and be associated with higher uncertainties and corresponding flags.

The reproducibility of measurements could either be determined by multiple measurements of a highly diluted calibration gas and assessing additional impacts due to fluctuations in the zero and due to interfering species in ambient air, or, what is recommended here, by extracting appropriate periods from routine, continuous ambient air measurements. The latter has a number of advantages as (1) it characterizes the scatter for real ambient air, (2) it is available in the data sets and does not need extra measurements, and (3) it can be automatically withdrawn from the measurement series by statistical criteria. The procedure shall evaluate all series of 10 consecutive measurements (both NO and NO2) and determine their absolute scatter by means of the standard deviations in nmol/mol. Then, an average of those 10 periods with the lowest standard deviation is built and used as the reproducibility of ambient NO or NO2 measurements, respectively.

Data of NO and NO2 are plotted together with ozone (and an anthropogenic tracer as black carbon or CO, if available) in quality-check-charts covering periods of typically 2 weeks. These data are checked for NO periods at night which are obtained with ambient ozone present (> 10 ppb) and under conditions of fairly low scatter. In such situations the NO should go down to zero, if not there is a zero off-set in the data and a correction has to be applied covering the deviation from zero and a corresponding uncertainty has to be considered in these measurements. Pollution episodes are characterized by elevated NO2 and lower levels of ozone, in case of local pollutions the NO and NO2 signals are highly variable and anti-correlated with ozone, NO2 may occasionally be negative. Such episodes should be flagged as polluted data but should be left in the data set.

Furthermore, annual cycles should be plotted and compared to corresponding cycles from recent years, wind roses shall demonstrate no local or strongly inhomogenous source patterns in the surrounding of the station, and percentile distributions of monthly values help to identify periods of unusual instrument operation.

8.2. Metadata and ancillary data

Data sets have to be sent to the EBAS (see 8.3 below) data centre, for which the traceability of the "final" level-2 data is achieved by a clear procedure based on the "raw" (level-0) or "original" data and metadata. Essential metadata are: PMT temperature, reaction cell temperature, reaction cell pressure, inlet flow, ambient ozone concentration ambient temperature and humidity. Very useful metadata are other meteorological data, integration time, high voltage of PMT, chamber/instrument temperatures, (all) calibration factors, and length and diameter of inlet line.

8.3. Data archiving and data submission

The global data archive for in situ nitrogen oxides data is the World Data Centre for Greenhouse Gases (WDCGG) maintained by the Japan Meteorological Agency (JMA, http://gaw.kishou.go.jp/wdcgg). All NO and NO_2 data obtained as part of the GAW programme should be submitted without undue delay (attempts should be made to update the archives every one year or more often) to the responsible

World Data Centre (WMO 2009). WDCGG accepts irregularly spaced data (such as events, flask samples) and continuous data. Of the latter, hourly data as well as higher aggregates are archived. In addition to the NO/NO$_2$ data, WDCGG also encourages submission of meteorological data.

The format used by WDCGG for the data is plain ASCII encoded text in tabular form, preceded by a section containing metadata. Quality checks performed by WDCGG currently include consistency checks as well as checks on data integrity. WDCGG uses "-9(99…)" with different numbers of digits depending on the field to indicate missing values. Data submitters are advised to consult the WDCGG data submission guidelines (WMO/GAW Report no. 188) or to contact WDCGG prior to data submission.

All data (raw and final data including all metadata at highest time resolution) must be stored on different data storage media stored at different locations (not only at respective site).

For European data, there was an agreement between EBAS (NILU) and the WDCGG (Tokyo) that all European data shall be submitted to EBAS according to their rules developed during the European infrastructure project ACTRIS and they will be mirrored by EBAS to WDCGG. EBAS foresees data submission with three data levels: Level-0, -1 and -2. Basic hereby is a regular, annual data submission of final, fully quality assured 1-hour averaged data (NO, NO$_2$, NO$_{2+}$, NO$_y$ in ppb), including uncertainty, reproducibility, variability and data flagging (Level-2 data). The deadline for submission depends on the framework (GAW, EMEP, …) reported to, but for EMEP and ACTRIS data it is 31 July of the following year.

In Advanced Data Reporting, the traceability of data back to the time of measurement shall be achieved by submitting raw data (instrument reading) in high time resolution (1 min) accompanied by a list of metadata to characterize the instrumental status. Time for reporting is UTC and no corrections are applied for data below the detection limit (take data as they are) (Level-0). With the same time resolution, level-1 are supplied that have the same time resolution as the raw data (level-2) but with evaluated mol fractions.

Near-Real-Time data reporting should be available to the user within max. 3 hours of measurement. Data are processed and screened automatically by the data supplier, they have lower quality and higher uncertainty as with regularly reported data.

The following list of flags shall be used in NOx data reporting:

Flag	Data Valid (V) / Invalid (I)	Description
000	V	Valid measurement
120	V	Sample reanalysed with similar result.
185	V	Possible local contamination indicated by wind direction or velocity
420	V	Preliminary data
457	V	Extremely low value, outside four times standard deviation in a lognormal distribution
458	V	Extremely high value, outside four times standard deviation in a lognormal distribution
459	I	Extreme value, unspecified error
460	I	Contamination suspected
651	V	Agricultural activity nearby
652	V	Construction/acitivity nearby
659	I	Unspecified instrument/sampling anomaly
660	V	Unspecified instrument/sampling anomaly
780	V	Value below detection or quantification limit, data element contains estimated or measured value
899	I	Measurement undefined, unspecified reason
980	I	Missing due to calibration or zero/span check
999	I	Missing measurement, unspecified reason

394 V Data completeness less than 90%

392 V Data completeness less than 75%

390 V Data completeness less than 50%

382 V More than 75% of the measurements are below detection limit

380 V More than 50% of the measurements are below detection limit

797 V Data element taken from co-located instrument

8.4. Data revision

Data providers can revise their data that have been submitted to EBAS by changing the data, adjusting the revision data, and increasing the version number in the EBAS data submission templates.

9   Outlook

In the course of ACTRIS, vertical information of NO2 remote sensing instruments from ground (MAXDOAS and FTIR) as well as from satellite measurements will be linked to the ground based measurements described in this measurement guideline.

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Annex I   Abbreviations and acronyms

BBCEAS   Broad Band Cavity Enhanced Absorption Spectroscopy
BLC   Blue Light Converter
CCL   Central Calibration Laboratory
CLD   Chemiluminescence Detection
CMDL   Climate Monitoring and Diagnostics Laboratory, NOAA (now Global Monitoring Division of the Earth System Research Laboratory, NOAA ESRL)
DQO   Data Quality Objectives
DWD   National Meteorological Service of Germany
EMEP   Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe
Empa   Swiss Federal Laboratories for Materials Testing and Research
ESRL   Earth System Research Laboratory, NOAA
GAW   Global Atmosphere Watch (WMO Programme)
GAWG CCQM   Gas Analysis Working group
GAWSIS   GAW Station Information System
GG or GHG   Greenhouse Gases
GMD   Global Monitoring Division (as part of NOAA ESRL)
ICOS   Integrated Cavity Output Spectroscopy
ISO   International Organization for Standardization
LIF   Laser-Induced Fluorescence
MG   Measurement Guidelines
NMI   National Metrology Institute, National Measurement Institute
NPL   the National Physical Laboratory, UK
PLC   Photolytic Conversion
QA   Quality Assurance
QC   Quality Control
QA/SAC   Quality Assurance/Science Activity Centre
RG   Reactive Gases
SAG   Scientific Advisory Group
SOP   Standard Operating Procedure
SRM   Standard Reference Material
TDLAS   Tuneable Diode Laser Absorption Spectroscopy
WCC   World Calibration Centre
WDCGG   World Data Center for Greenhouse Gases
WMO   World Meteorological Organization

Annex II   List of contributors

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