Deliverable 3.17. Updated Measurement Guideline for NOx and VOCs

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Summary

The updated Measurement Guideline for NO_x and VOCs (deliverable 3.17 of ACTRIS-2) is based on the original measurement guidelines for VOCs and NO_x, which were produced within the first ACTRIS project (Deliverable D4.9: Final SOPs for VOCs measurements and Deliverable D4.10: SOPs for NO_{xy} measurements). This updated measurement guideline provides recommendations for good measurement practice for the analysis of NO_x and VOCs under ACTRIS. The deliverable is separated in part 1 on NO_x and part 2 on VOCs.

Atmospheric volatile organic compounds (VOCs) and nitrogen oxides (NO_x) play an important role in the formation of secondary air pollutants such as ozone, secondary organic aerosols and short-lived climate forcers. Therefore, their continuous measurements contributes to the verification of emissions control measures and are valuable input variables for chemical models to forecast air pollution and the oxidative capacity of the atmosphere.

VOCs consist of low-boiling non-methane hydrocarbons (alkanes, alkenes, alkynes, aromatics, terpenes) and oxygenated hydrocarbons (alcohols, ketones, aldehydes). VOCs with lifetimes from minutes to months are emitted by both the biosphere and by anthropogenic activities, such as motor vehicle exhaust and solvent usage.

Priority VOCs to be measured within in-situ measurement systems have been identified in the GAW Report No. 171 and are the main focus of this measurement guideline (MG). In respect to the quality assurance the MG provides an update of the WMO report and will also build the basis of a future WMO guideline which is in progress, with members of the ACTRIS VOC community being among the drivers of this global effort.

NO_x consists of NO and NO_2. Whereas NO is emitted from the burning of fossil fuel, NO_2 is mainly formed in the atmosphere as secondary product from the photochemical destruction of VOCs.

Measurements of nitrogen oxides (NO_x) have been made for decades using a number of different techniques and calibration scales. This MG 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. This MG follows up the initial work on this topic in the GAW Report #195 and will build the basis for a future measurement guideline planned to be produced under the auspices of WMO.

PART 1 NOx

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1 Introduction

Long term observations of the chemical composition and physical properties of the atmosphere are crucial for understanding atmospheric chemistry and climate change. The Global Atmosphere Watch (GAW) Programme of the World Meteorological Organization (WMO) has been established to provide reliable and high quality data on a long term basis from regionally representative stations. One major focus is the monitoring of reactive gases such as nitrogen oxides. Especially nitric oxide (NO) and nitrogen dioxide (NO_2) ($NO_x = NO + NO_2$) play key roles in tropospheric (photo)chemistry controlling tropospheric ozone formation, the atmospheric self-cleaning capacity and air quality (for details see GAW report No. 195 (2011)). However, within GAW there are only a few sites performing continuous in situ measurements of nitrogen oxides, most of them located in Europe. Extension of the network is demanded followed by the indispensable need of data comparability between these stations.

2 Rationale and Objectives

Measurements of nitrogen oxides have been made for decades using different techniques and calibration scales. To ensure their intercomparibility and to detect global trends, harmonisation is essential for the compatibility between the stations and for the achievement of a high quality data set representative for the globe. To fulfill these needs, long term stability of the reference scale is required as well as standard operation procedures to be applied at the stations.

This report aims at documenting suitable in-situ measurement techniques for surface NO and NO_2 and to give recommendations for the design of the measurements, the required instrumentation and the data quality assurance and control. The Measurement Guidelines have to be applied at GAW sites and any other measurement platform with already existing NO_x measurement capabilities and in particular at facilities where such measurements have recently been added to the program or will be added in the foreseeable future. This report follows up the initial work on this topic in the GAW Report #195 (2011).

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].

Table 1 summarises the scientific needs, instrumental techniques, and sensitivity requirements for NO_x measurement station with different characteristics, including continental, continental background, and pristine marine locations. Table 1 presents initial DQO requirements which are expected to evolve in time for each site depending on developing user and scientific requirements. The scientific needs refer to (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) the investigation of photochemical processes, or the combination of these issues. More specifically, these needs relate to the following requirements:

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 a few minutes to days.

Continuous measurements are recommended.

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 mole fractions of NO$_x$.

Table 1 - Data Quality Objectives (DQOs) for NO and NO$_2$ under differing conditions

Level	**1 (basic)**	**2 (enhanced)**	**3 (high)**[1]
Site characteristics	Continental basic	Continental background	Pristine marine background, free troposphere
Mean mole fraction NOx	> 1 nmol/mol	0.1 – 1 nmol/mol	< 0.1 nmol/mol
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, 3σ)	NO: 50 pmol/mol NO$_2$:100 pmol/mol	NO: 10 pmol/mol NO$_2$:20 pmol/mol	NO: 1 pmol/mol NO$_2$:5 pmol/mol
uncertainty (1 hour, 2σ)[2]	NO: 40 pmol/mol or 3% NO$_2$:80 pmol/mol or 5%	NO: 8 pmol/mol or 3% NO$_2$:15 pmol/mol or 5%	NO: 1 pmol/mol or 3% NO$_2$:3 pmol/mol or 5%
uncertainty (1 month, 2σ)[3]	NO: 2.5% NO$_2$: 3%	NO: 2.5% NO$_2$: 3%	NO: 1 pmol/mol or 2.5% NO$_2$:3 pmol/mol or 3%
data coverage	66%		
suggested method[4]	CLD / PLC	CLD / PLC	CLD / PLC
Alternative / upcoming methods[5] (backup or QC reasons)	CRDS ; LIF ; DOAS ; TDLAS	CRDS ; LIF ; TDLAS	LIF

[1] *in pristine environments with NOx levels below 10 pmol/mol, the required detection limits and uncertainties would be 0.1 pmol/mol for NO and 0.3 pmol/mol for NO$_2$.*

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

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

[4] *see list of acronyms (Annex 1) for full method names*

[5] *methods that are either new and not yet fully tested for their long-term applicability or research type instrumentation that is demanding to operate, thus, prone to incorrect handling and therefore not fully suitable for long-term monitoring*

Commercial instruments are available with specifications meeting the requirements for both continental basic (Level 1, "basic") and continental background environments (Level 2, enhanced) but only research instruments developed by skilled investigators are capable of providing high-precision measurements in pristine conditions (Level 3).

In spite of clear scientific needs to incorporate the data quality objectives, the above formulated requirements will indeed present a measurement challenge given the low levels of NO and NO_2 expected at many GAW 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 by well-trained staff and thorough attention to details is required to achieve the DQOs necessary to make valuable measurements of NO and NO_2.

4 Measurement Setup

4.1 Basic measurement setup for monitoring surface NO and NO_2

The list below is a compilation of the needed infrastructure for in-situ NOx measurements at GAW-stations. More detailed information can be found in the following sections.

4.2 Location and site requirements

Location and site requirements have to be in compliance with GAW station standards:

- Representativeness for the region:

The station's location has to be regionally representative for the measured species, e.g. reflecting typical in population, vegetation, weather conditions, etc.

- Unaffected from local contamination sources:

The sample location has to be upwind of any buildings, garages, parking lots, generators or other emission sources – any nearby areas where fossil fuels or biomass may be combusted. Station personnel should remain downwind of sample collection and refrain from smoking.

- Infrastructure

Measurements sites should provide facilities which allow sound operation. This usually requires sufficient electrical power, a suitable data acquisition system and other supplies depending on the instrumentation. Furthermore, a controlled laboratory temperature (air-conditioning) is beneficial for the precision of most measurements and instrumentation should not be exposed to direct sunlight. Network connection for (automated) data transfer to the data processing and analysis centre as well as for remote access of the data acquisition system is highly recommended in particular for stations with infrequent operator presence. This ensures a timely backup of the measurement data, allows basic maintenance and potentially provides the opportunity for problem identification in case of instrumental issues.

4.3 Air inlet and sample line design

- Material:

Ambient NO and NO_2 mixing ratios can be altered inside the sample line by adsorption, absorption, diffusion and chemical reactions on the wall. PFA-Teflon tubing having a smooth (not prone to adsorption), non-porous (low absorption & diffusion) and inert (low reactions) surface are highly recommended for the use of the sample line. Teflon should also be used for all other components exposed to the ambient air probe. It is recommended to shield the PFA-Teflon tubing against light. In dark conditions the ambient $NO_2 + h\nu \rightarrow NO + O$ reaction is prevented, whilst the reaction $NO + O3 \rightarrow NO_2 + O2$ continues shifting NO towards NO_2. Under these clearly defined conditions and if the O3 concentration is known a correction factor can be derived (see section7.3).

- Sample line:

To minimise this correction factor, the residence time in the inlet line needs to be as short as possible. A residence time of less than 5 seconds is recommended. However, increasing flow rates also favours decreasing pressure in the inlet line shifting the gas-particle partitioning towards the gas phase e.g. HNO_3 (aq) ⇌ HNO_3 (g); PAN degradation or decomposition of $N_2O_5 \rightleftharpoons NO_2 + NO_3$. Increasing the sample line diameter will prevent a major pressure drop.

The performance of the inlet line can be tested by feeding a small tube (e.g. 1/16" or 1/8" tube into the existing ¼" or larger inlet line) with a constant calibration gas flow into the inlet line The mole fractions 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.

- Heating:

Controlled heating of the sample line of a few degrees (3-4°) above ambient temperature is recommended to prevent condensation of water, organic and inorganic volatile compounds and aerosol deposition. Temperature should stay below 50 °C, because otherwise thermal decomposition of other trace gases (e.g. PAN) will occur leading to an interference in the NO and/or NO_2 measurements.

- Sampling height:

Sampling height should be chosen that ambient air measurements are not affected by local contamination. GAW recommends the installation at least 2 meters, preferably 10 meters, away from the closest surface. Roofs can be appropriate when the inlet is situated well above its boundary layer.

- Inlet line filter:

The NO and NO_2 analyzers should be equipped with an inlet line filter made of Teflon with a pore size of 5 um. The filter should be changed on a regular time basis (see 7.1).

- Rain cover:

The inlet has to be shielded from liquid water entering the sample line, e.g. by using a Teflon funnel.

- Maintenance:

The properties of the inlet surfaces can change with time. Regular cleaning of the inlet line is advised depending on the site-specific conditions, e.g. once per year at remote, twice per year at clean rural and up to monthly at urban and sea spray influenced sites, respectively.

4.4 Instrumentation

For NO GAW recommends the chemiluminescence detection technique (CLD) with ozone and for NO_2 the photolytic conversion of NO_2 to NO, followed by the detection of NO (see section 5.2.1). The instruments have to be equipped with a "prechamber" mode to account for the well-known interference due to alkenes. Several manufactures are available and the more sensitive instruments (trace gas levels) should be chosen.

Uprising new techniques are promising for measurements of NO_2, but highly skilled personnel and frequent maintenance is required to achieve high quality measurements. Whilst GAW encourages the stations to exploit and develop these new techniques, for now the operational routine should be performed by photolytic converters coupled with CLD.

4.5 Personnel qualification

Well trained personnel are essential. The officers in charge should be aware of the whole complexity of the analysis system. The participation in dedicated training courses concerning nitrogen oxides such as the GAWTEC (GAW Training and Education Centre) training course on reactive gases is highly recommended.

4.6 Health and safety issues

GAW advises the participation in safety trainings depending on the site and the instrumentation used, such as handling of toxic and compressed gases, chemicals and electrical hazards. I.e. the detection of NO by CLD technique (see section 5.1) requires ozone in toxic concentrations and it must be ensured that the excess of ozone is treated accordingly (ozone destroying unit at exhaust).

5 Measurement Principle

5.1 Chemiluminesence techniques for NO

The chemiluminescence technique detects nitric oxide (NO) via the gas-phase reaction of NO with added O3 yielding to an exited NO_2^* (Fontijn et al., 1970). Ozone in excess (several ppm) is produced internally by an O_3 source, such as by corana discharge or an UV lamp. The exited NO_2^* is either quenched by N_2, O_2 and H_2O or emits a photon in the red/infrared wavelength, which is then detected by a photomultiplier (PMT):

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (1)$$

$$NO + O_3 \rightarrow NO_2^* + O_2 \qquad (2)$$

$$NO_2^* + M \rightarrow NO_2 \qquad , M = N2, O2, H2O(3)$$

$$NO_2^* \rightarrow NO_2 + h\cdot\nu \quad (590 \leq \lambda \leq 3000\ \text{nm}) \qquad (4)$$

In principle, the detector signal (counts / sec) is proportional to the ambient NO concentration if further corrections are applied (see below and section 7.3)

Prechamber Mode

CLD instruments for NO detection have to be equipped with a prechamber (see fig 1.) Besides NO, some hydrocarbons (alkenes) and other trace substances react with O_3 followed by chemiluminescence of OH in the red/infrared region adding to a non-NO PMT signal. However, these interferences can be minimized by using a prechamber. Since the reactions (5) are generally slower compared to reaction (2), the $NO+O_3$ reaction completes inside the prechamber so that only photons emitted from the slower reactions of O_3 with interfering agents are counted (prechamber mode). 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 must allow sufficient reaction time to completely remove 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 overestimated, leading to a systematic error and a higher detection limit. In case the residence time in the prechamber is too long, the interference signal is already reduced in the reaction chamber resulting in an underestimate of the interference and corresponding overestimate of NO. 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 decided 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. It is important to avoid changes in reaction chamber pressure induced by valve switching/flow conductance between background and signal measurement, as this can result in changes of the background signal induced by wall reactions of ozone, causing additional artefacts.

To minimize the quenching term (3) the reaction chamber is operated under low pressure. However, lowering the pressure decreases the number of molecules and therefore the number of excited NO_2*. An optimum of sensitivity is achieved usually around 15 hPa depending on the instrument design.

Ambient NO = (main chamber signal – prechamber signal) / sensitivity (5)

The detector signal (counts / sec) is then proportional to the ambient NO concentration. Correction for the quenching of ambient water vapour will be discussed in section 7.3.1.

The signals are given as counts measured by the photomultiplier tube (PMT), the sensitivity of the detector is provided as counts·nmol/mol.

The following sketches give a schematic overview of operating mode:

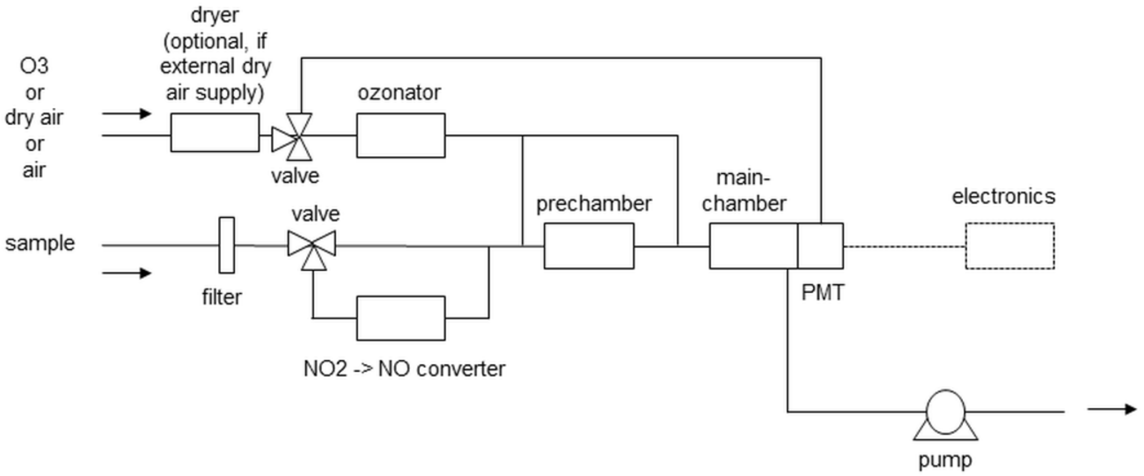

Fig. 1: Simplified flow scheme of a typical design of a chemiluminescence detector. Flow sensors, pressure sensors and flow restrictions (capillaries) are usually additionally implemented depending on the manufacturer and configuration. PMT: Photomultiplier tube.

The light released from reaction (4) passes a window, equipped with a red/infrared filter (optimized for the NO_2* emission spectrum and minimizing interference from short wavelengths) and enters the PMT connected to the reaction chamber. Since most of the emitted light is lost upon scattering, 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. To avoid condensation, the PMT window is continuously purged with dry air.

O_3 generator

In most instruments, the ozone generator provides high ozone levels (1-4%) by silent electrical discharges which are necessary for high sensitivity (signal ~ $k[NO][O_3]$). To achieve high ozone concentrations, 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. The supply with pure oxygen can be implemented with pressurized oxygen. Commercially available oxygen generators are also capable of producing oxygen of sufficient quality. Experience showed that the long term stability of the ozone generator could be enhanced by the use of a short piece (some 2 centimeter) 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 can be achieved by humidifying the oxygen/ozone flow before introducing it 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, if not done properly, can also cause some problems. It is recommended that above described adjustments are done only by experienced users.

Pressure

According to reaction (3), the majority of the excited NO_2^* molecules are deactivated by collision with N_2, O_2, or water molecules. To minimize this, a low reaction chamber pressure and therefore a strong pump is recommended. However, since a lower pressure in the reaction chamber corresponds to a shorter residence time, sensitivity will eventually begin to decrease due to incomplete NO conversion to NO_2 (depending on ozone concentration in the reaction chamber). The ideal reaction chamber pressure should therefore be optimized for each specific instrument design.

Detector artefact

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 (synthetic air), and alternating between sample and background (prechamber) modes. Artefact signals can arise from spurious CLD pressure differences between these two modes, outgassing of surfaces, 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 pmol/mol range. However, determination of detector artefacts is critical as determined differences might depend on moisture contents, e.g. differences between ultrapure air and the ambient air being measured. Thus, it is recommended to determine detector artefact levels at night as follows. For measurement sites far 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 equal zero due to reaction with ambient O_3. If ozone is > 10 to 20 nmol/mol, a comparison of the detector background signal to the ambient signal measured during nighttime should give a very good measure of the detector artefact signal.

Night time zero correction

If under the aforementioned conditions at night, a NO signal close to zero is measured but in zero gas measurements a significantly different signal, one should inspect the zero gas for possible leaks or exhausted cleaning cartridges. If substantial non zero and similar levels are measured for both, zero air and night-time ambient, it indicates a substantial detector artefact signal as it is very unlikely to have similar counts originating from NO residuals in zero air and from sources in ambient air).

By calculating the difference between "measurement mode", "prechamber mode" and "artefact signal" according to equation (5), a highly selective signal for the ambient NO mole fraction is achieved.

Principally this technique is only able to measure NO, all other nitrogen oxides must be converted.

5.1.1. Other techniques for NO

Recently, other techniques like Quantum Cascade Laser Absorption Spectroscopy (QCLAS) and Long Path Absorption Photometry (LOPAP) (measuring NO_2 directly and NO after conversion with dichromate) have proven their capabilities and have also been tested at a GAW station. First results look very promising. However, these instruments are currently not commercially available and/or very expensive and require well trained personnel. Furthermore, extended tests proving the applicability for long-term monitoring purposes are still outstanding. See also Chapter 5.3.3 for an extended list of new NO_2 measurement technologies that might be partly suitable for NO measurements, at least when combining with a NO to NO_2 converter prior to analysis.

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) to NO followed by CLD detection. Conversion is performed below 400 nm using an adequate broad band light source like Xenon high pressure, metal halide lamps or small band ultraviolet light-emitting diodes (UV-

LEDs), latter referred as “blue light converter” (BLC). Depending on the wavelength spectrum of the photolysis source, a fraction of ambient HONO can by photolysed to NO (http://joseba.mpch-mainz.mpg.de/spectral_atlas_data/cross_sections_plots/Nitrogen+compounds%28N,H,O%29/HONO_184-400nm_log.jpg) interfering with the NO_2 measurement. For a broadband photolysis spectrum similar to sunlight (e.g. from a Xe high pressure lamp), the photolysis frequency of HONO is 35% of that of NO_2 (Galbally et al, 1987). For the line spectrum of a BLC this interference may be as small as 5% depending on the LED used.

Subsequent to the conversion within the photolytic converter the sum of converted fraction of NO_2 and ambient NO is detected by the CLD. Ambient NO_2 is calculated by the difference of the total signal (NO.c) and ambient NO (Kley and McFarland, 1980) provided that the photolysis efficiency “S_C” of the converter is known. (For determination of Sc see section ….) The residence time in the photolysis chamber should be about one second, but is often longer. An extended residence time inside the photolytic converter increases the conversion efficiency but at the same time enhances the back reaction of NO with O_3. There are two different plumbing approaches: PLCs are typically equipped with a 3-way-solenoid and a bypass pump, at BLCs the LED can be switched on and off. This requires different approaches of calculating the ozone interferences (see section 7.3.2).

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

background measurement $\Rightarrow$ prechamber measurement $\Rightarrow$ bkgrd
NO measurement $\Rightarrow$ reaction chamber measurement $\Rightarrow$ NO
NO.c measurement $\Rightarrow$ converter + reaction chamber measurement $\Rightarrow$ 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 (Reaction (1)) in the inlet line and photolytic converter as well as quenching effects caused by water vapor, the formula given in section 7.3 must be used to calculate most accurate NO and NO_2 ambient air mole fractions. Quality-controlled H_2O and O_3 observations are required to accurately determine ambient NO and NO_2 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 can lead to substantial error in NO_2 up to 80% in rural/remote areas (see e.g. Steinbacher et al., 2007). For this reason it is NOT recommended to use chemical converters but instead PLC / BLC converters in networks like GAW.

The assessment of artefacts was deemed crucial for low-level measurements of NO_2. LEDs of 385-395 nm photolyse NO_2 into NO. However, also interference from HONO (overlap in spectrum) was witnessed at 395 nm wavelength. This artefact may compromise the measurement of NO_2. The spectra of systems in use should be checked and potential artefacts quantified and considered in the uncertainty estimates. Guidelines should consider spectral information and recommend LEDs least prone to artefacts (Reed et al., 2016). New BLC are being developed to overcome these issues. Another issue was surface artefacts due to surface adsorbed compounds and artefacts due to light from the converter LEDs. A discussion on collimation of the light beam in BLCs for minimizing wall effects and the use of quartz tubes instead of the metal chambers was not conclusive but several groups will continue work on this.

5.2.3. Other techniques for NO_2 detection

Other techniques such as laser induced fluorescence (LIF) (Thornton et al., 2000), Tunable Diode Laser Spectroscopy (TDLS) (Li et al., 2004), Quantum Cascade Laser Absorption Spectroscopy (QCLAS) (Tuzson et al., 2013), Cavity Ring Down Spectroscopy (CRDS) (Fuchs et al., 2009), Cavity Attenuated Phase Shift (CAPS) technology (Kebabian et al., 2008) and Long Path Absorption Photometry (LOPAP) (Villena et al., 2011) have also been applied to NO_2 detection at trace levels in the atmosphere. They have the advantage of directly measuring NO_2 and less prone to artefacts due to interference of other NO_y compounds. However, most of them are still research type instrumentation and commercial instruments are beginning to become available. Results of a comprehensive laboratory study comparing some of the above mentioned techniques can be found in Fuchs et al. (2010). However, these instruments first have to prove their suitability for long-term monitoring within the DQO specified in this document.

With ground-based Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) (Hendrik et al., 2014), the vertical profile and atmospheric NO_2 burden in the lowermost few hundred meters above ground can be monitored continuously. Such measurements complement the traditional ground-based in-situ observations, and provide a more integrated and more representative view on the NO_2 levels which are of interest for model and satellite validation. However, MAX-DOAS does generally not reach the DQOs for GAW in-situ observations and, though of interest for GAW, is not within the scope of this report.

6 Primary standards and calibration centre for NO and NO_2

Calibration gases

Calibration gases, traceable to the Central Calibration Laboratory (CCL) scale and a calibration unit with the possibility of gas phase titration (for calibration of NO_2) is needed.

Zero air

Recommended approach for producing zero air to be included in the measurement guidelines. Calibration gases, traceable to the Central Calibration Laboratory (CCL) scale and a calibration unit with the possibility of gas phase titration (for calibration of NO_2) is needed. Gases, calibration unit

Types and use of reference standards and the choice of regulators

It was suggested to include in the measurement guidelines about the types and use of reference standards including the choice of regulators. It was asked which manufacturers to buy from and whether it matter. It was noted that different cylinder types do have significant influences on preparative losses so it does matter where standard cylinders are purchased from. There was some discussion about whether cylinders need to be used lying on their sides or whether standing cylinders were fine to use. NPL commented that for the levels of uncertainty needed here there is not a difference so standing up cylinders is fine. It was also noted that cylinders are homogenised by rolling for 2 hours after initial preparation but do not need to be re-homogenised after this.

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-network can be made traceable [WMO, 2008] thus underpinning the long-term accuracy of data.

The National Physical Laboratory (NPL) has been assigned as CCL for NO and NO_2. Furthermore, a number of National Metrology Institutes already disseminate NO and NO_2 standards in nitrogen to meet the needs of the air quality monitoring community. The range and uncertainty in which these standards are available, have been peer reviewed and accepted, and are published together with the results of international comparisons to demonstrate their degrees of equivalence in the Key comparison database (KCDB) of the Bureau International des Poids et Mesures. A NO/N_2 comparison at 700 nmol/mol (CCQM-K26a) was coordinated by the National Physical Laboratory in 2004/5 [CCQM-K26.a]. Since then the state of the art for measurements of NO in N_2 has improved. In 2009, EURAMET 1084 [EURAMET 1084], a bilateral comparison at 200 nmol/mol NO in N_2 between the National Physical Laboratory (NPL) and Laboratoire National de Métrologie et d'Essais (LNE), demonstrated equivalence with relative expanded uncertainties less than 1%. Another key comparison was completed in 2013 [EURAMET.QM-K26.a] and focused on testing the analytical capabilities of National Metrology Institutes (NMIs) to analyse a NO/N_2 mixture at a nominal amount fraction of 450 nmol/mol. NPL used a Molbloc dilution facility to generate dynamic reference standards of NO in N_2 at 450 nmol/mol from a 10 µmol/mol primary reference gas mixture of NO in N_2. The dynamic facility was used to certify a suite of travelling NO in N_2 standards. The travelling standards were certified before and after distribution to participants and over a period of more than a year. These measurements were used to provide the reference values and to determine accurate drift rates so that any change in the amount fraction during the distribution period could be corrected. The estimated drifts of the travelling standards were distributed around a median value of -0.02 nmol/mol/day. This median drift corresponds to a drift of 0.8% over 6 months calculated at the nominal amount fraction of 450 nmol/mol. The comparison included the Hohenpeissenberg Meterological Observatory, DWD, Germany. Equivalence was demonstrated by 12 of the 15 laboratories.

At present only NO in nitrogen is used as a primary standard, usable also for NO_2 by gas phase titration (GPT) with ozone. NO in N_2 (≥ quality 5.0) is stable in the range of 450 nmol/mol ≤ m.r. ≤ 10 ‰ in specifically passivated cylinders. Drift at 50 ppm standard is about -0.2% - -0.02% year^{-1}.

Standards and calibration services for NO_2 in nitrogen standards are also available from National Metrology Institutes, with calibration of standards down to nominal mole fractions of 100 nmol/mol available with relative expanded uncertainties of 3%. The first international comparison of standards of NO_2 in nitrogen was completed in 2013 [CCQM-K74 Final Report] at a nominal mole fraction of 10 µmol/mol with the reference value set using a permeation facility for the generation of NO_2 standard mixtures [Flores at al., 2012] and achieving relative standard uncertainties of 0.4% The comparison demonstrated that standards in cylinders will generally contain trace levels of HNO_3 (in the range 100 nmol/mol to 300 nmol/mol for 10 µmol/mol NO_2 standards) due to residual water present in the standard preparation phase. The amount of HNO_3 present can be accurately quantified using FTIR techniques [Flores et al. 2013]. The next international comparison for NO_2 standards at the nominal mole fraction value of 1000 nmol/mol is planned for 2017.

6.2 World Calibration Centre (WCC)

The main task of WCC is to assist the GAW sites to achieve the data quality objectives described in chapter 3 and to document the respective status of data quality. Additionally the WCC links the in-situ observations to the primary standard. This should be done through regular calibrations, round robins, side-by-side measurements and audits. The role of WCC is described in detail in WMO/GAW Report No. 172 (WMO TD No. 1384, 2007).

The Research Centre Juelich (Germany) has been assigned by WMO to operate the WCC for NO_x in GAW.

7 Quality Assurance and Quality Control

7.1 Measurement and measurement protocol

Typically the chemiluminescence analyzers measure NO and NO_2 mole fractions 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 recommendations 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 acquisition) must be documented in a station logbook with the respective time. The time zone of the logbook entries should also be clearly documented. Special care has to be taken for the documentation of the material, dimension, flow, temperature, and pressure of all components of the inlet system from the inlet point to the NO analyser. Log books should be regularly copied for backup reasons. Data should be regularly backuped on an external memory device.

The following items should be checked on regular time intervals. The use of check lists is advised:

1.) Routine checks (e.g. every time the operator is on site):

Connections to the instrument:

- Electrical power: Is the cord really fixed?
- Data acquisition: 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 condensation in the inlet line? Are the flow and temperature(s) of the inlet line in the allowed range (control unit of inlet line)? (Hint: Measure the inlet flow at the beginning of the line and compare to the sum of individual instrument flows.)
- Dry air supply for flushing the PMT window: Is the dry air connected correctly? Is the drying unit working well, or does the silica gel cartridge need to be regenerated? It is very important to feed dry air into the CLD which is used for flushing the PMT window. Humidity leads to condensation at the PMT window followed by significant loss of sensitivity. Condensation from high humidity also can lead to failure of the PMT or connected electronics.
- In case the CLD is operated with pure oxygen for supplying the ozonizer **(Hint: To improve the sensitivity of CLD the ozone generator should be operated with pure oxygen)**: Is the oxygen supply correctly connected and is the pressure of the oxygen cylinder sufficient? Check for time to order a new oxygen cylinder (consider delivery time). Commercially available oxygen generators are also capable of producing oxygen of sufficient quality.
- Is the clock of the data acquisition system accurate and/or synchronized with a GPS signal?

Check of (meta)data:

All metadata should be stored, the use of data acquisition systems is recommended.

- Is the measurement system showing any errors / alarms / warnings?
- Are 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) within 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 2-10 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 (not all analyzer provide this information)? Problems might be a hint for a weakening of the ozone generator.
- Are there “artefact signals” during night (in the presence of ambient $O_3 > 20$ nmol/mol) and during 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 acquisition system? This is a simple and effective test whether the data flow from instrument to data storage is o.k.
-

2.) Routine 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 - in case of use of drying cartridges for dry air generation - capacity of drying cartridge): change of filters at dry air and oxygen inlet; regeneration of drying cartridge. First the CLD is shifted to standby 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 the 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 cartridge alone in this case the CLD does not need to be switched into stand-by mode. With this setup the Drierite cartridge has to be regenerated only every third month in a cabinet dryer.)
- Every 6th month (depending on pollution level): cleaning of reaction chamber, cleaning of photolysis chamber; (persistent loss in counting rate is an indication of a dirty cell, loss in conversion efficiency even when using a new lamp is an indication of a dirty photolysis chamber). Refer to instrument manual for disassembling reaction and photolysis chamber. Warning: The PMT, as long as under electrical power, will be destroyed by incident light. Once disassembled it is recommended to use the following cleaning procedure: First rinse with deionized water. For more persistent deposits use a lint-free cloth. Avoid scratching the walls or any glass part. Do not 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 fluctuating lamp intensity: Change of Xe-photolysis lamp, (other conditions and limits for other types of converters e.g. Blue Light Converter).
- Are the sensitivity values and conversion efficiencies drifting with time?
- How large is the enhancement of the zero mode by NO? This indicates declining O_3 generator performance.
- Some instruments require periodic replacement of consumables, e.g. valves, or maintenance of the pump (e.g. regular membrane replacements). 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 required uncertainty based on DQO. In continental atmosphere ($NO_x > 0.1$ nmol/mol), zero checks are typically not as important as span checks for instruments equipped with a prechamber. However, to ensure that zero air contains only traces of nitrogen oxides causing a signal well below the DQO detection limit, zero checks should always be performed together with span checks. For pristine locations ($NO_x < 0.1$ nmol/mol) the respective error analysis (section 7.5) will indicate growing impact of the zero-signal fluctuations and frequency of zero checks have eventually to be increased. 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. Given the instrument operates linear, it is recommended to calibrate the CLD at some 10-30 nmol/mol in order to have lower uncertainty of the span. The instrument linearity should be verified up to the maximum of the expected ambient mixing ratio range at least once a year. Nonlinear instruments indicate problems which should be solved (see maintenance). Measurements with nonlinear instruments require frequent calibration of the nonlinear behavior.

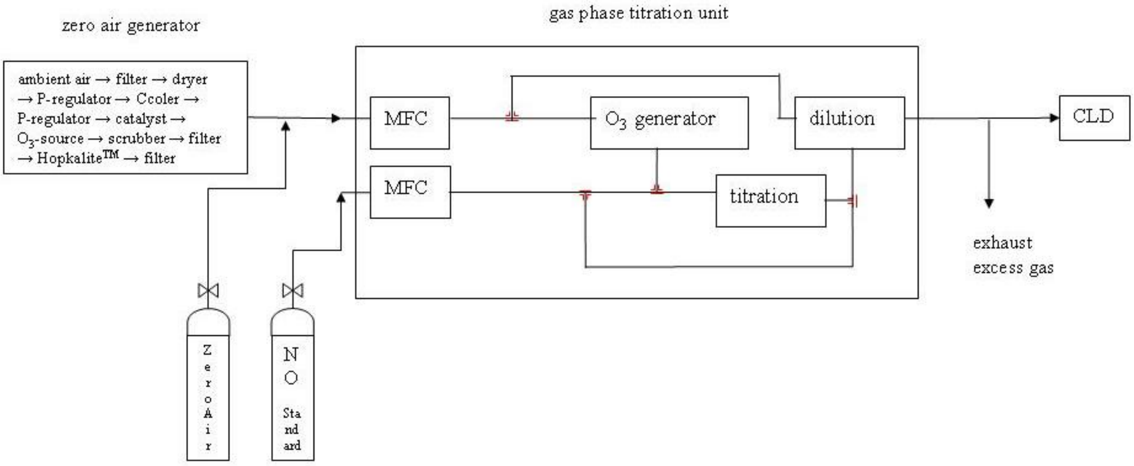

Fig. 2: sketch of calibration configuration

For calibration, special equipment is needed and special care has to be taken to achieve reliable results: A zero air, i.e. air without significant amounts of NO in it, 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 analyzer (Commercial zero air generators are available which provide nitrogen oxides free air (< 5 pmol/mol). An alternative is the use of adsorbent traps (activated charcoal and Sofnofill™ or Hopkalit™). The lifetime of these catalysts/absorbers strongly depends on the quality of air which has to be cleaned. If zero air has been sufficiently clean and then shows increasing amounts of nitrogen oxides, change the cleaning cartridges. Each station should have at least one laboratory standard by the CCL or traceable to the CCL and a second certified standard ("working-standard"). 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 needs to be carefully characterized to achieve the required dilution factors and accuracy. From comparisons between working standard and laboratory standard it has to be checked that no drift occurs.

When first attached to the NO standard cylinder, pressure regulators must be flushed 4-5 times with cylinder contents, in a way avoiding back-diffusion of residual air in the regulator, e.g. by initially evacuating the regulator. Then the regulators should remain under pressure for longer times, e.g. 24 hours, in order to achieve equilibrium. After another flushing for 4-5 times, they are ready for use. This procedure is required to prevent residual atmospheric O_2 in the regulator from reacting with NO and altering the cylinder mole fraction. 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 also be calibrated for NO_2. Since NO_2 is prone to instability in cylinders, it is recommended to produce NO_2 from 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 (GPT) 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 µmol/mol range. As the permeation device includes further error sources besides dilution, i.e. non-constant permeation rates and the need of a 2-step dilution owing to the high NO_2 concentration involved, these methods generally have larger uncertainties than the method recommended above. Accordingly, these should only be used as an additional 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 for manual calibration:

1. Insure that all instruments and tools needed for calibration are connected and working.
2. Warm-up time of GPT with ozone generator should be at least 1 hour. Flush the calibration unit with a high mole fraction of ozone (e.g. 100 nmol/mol) during that time (warm up of ozone source and cleaning of tubing).
3. Flow zero air for at least 20 min, connect calibration source to CLD and acquire zero air counts for at least 10 minutes (depending on type of CLD). For CLDs displaying the counts, compare the readouts (counts) of background 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) are an indication of NO_2 impurities in zero air. If it is not possible to look at the count rates change span to a high level and have a look on the “mole fractions” at the respective modes.) These NO or NO_2 impurities in zero gas will become critical if their amount exceeds the lower limit of detection of the instrument. In this case resolve problems in your zero air supply.
4. Adjust the desired span point and allow the system to run for at least 20 minutes until constant levels are achieved, then acquire the span air counts for at least 10 minutes.
5. After determination of the new calibration factors for NO, continue with NO_2 calibration.
6. Introduce the desired NO concentration (without ozone) into the system and acquire the data for NO- ($NO_{(1)}$) and NO_2 channel ($NO.c_{(1)}$) for at least 10 minutes each (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 converted to NO_2. Allow at least 20 minutes for the instrument 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 the inlet line, GPT unit and zero air supply are switched off and the pressure regulator of the standard gas cylinder is shut off.

Automated calibration:

The gas-phase titration unit and corresponding valves needs to be controlled by a computer with control software. The metadata of the unit should be recorded. Zero gas and calibration gas supply need to be switched by automated valves. The CLD inlet needs to be equipped with appropriate automated valves switching between ambient air inlet and gas-phase titration unit. Furthermore, an exhaust valve allowing purging of the GPT unit during equilibration times is to be installed. Times when no ambient measurements are performed must be automatically flagged in the data acquisition system of the NOx analyzer.

Follow the above manual procedure with following modifications:

In step 2: Automated Valve switching will supply gases to GPT unit and purge them to the exhaust valve.

In step 3: Open the valve from the gas-phase titration unit to the CLD, close the exhaust and the ambient air supply valves. Specify the purge and measurement times according to your specific set-up such that stable measurements are achieved in each mode.

In step 9: reverse automated valve switching to ambient measurements, switch off gas supply to gas-phase titration unit and switch off unit.

Zero, span and converter efficiency measurement data need to be evaluated and checked for stable conditions during data analysis. Zero correction and span must be applied off-line to the data.

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:

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

7.2.1. Span check in standard addition measurements

As a calibration check, NO can be added to the inlet air yielding 10-30 pmol/mol of NO (standard addition), under conditions of very low and constant ambient NO, e.g. during night or background sites with NO < 0.02 pmol/mol. This calibration check works in the same matrix as ambient air and corresponding water vapor quenching effects (section 7.3.1) are the same in span check and ambient measurements. Moreover, the flow path and inner surfaces are in contact with the same humidity and pressure/flow conditions as in ambient measurements. Disadvantage, however, is that this technique relies on constant or very low ambient NO mole fractions during span checks which means that it needs to be repeated several times (switching between ambient NO and standard addition NO) and only if constant span factors are achieved they can be used. With regular span checks, the calibration factors under zero gas conditions can be verified after applying the water vapor correction. Differences indicate matrix effects, e.g. artefacts on surfaces, and need to be resolved, e.g. by cleaning of the cells or leak checks.

In pristine environments with extremely low NO_x concentrations, it is recommended to operate the analyzer under constant matrix conditions in order to avoid equilibration phases after dry calibration gas exposure and minimize detector artefacts (section 5.2.1). Under such conditions, the regular calibration should proceed in this standard addition method and only in larger intervals should be checked by calibrations containing zero gas.

7.3 Corrective actions for interferences by water vapor and ozone

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 H2O molecules. For example this accounts for about 4%

signal loss due to an absolute humidity of 9 g/m³ (corresponds to 50% relative humidity at 20°C). Accordingly, a correction factor has to be applied:

$$[NO]_{H_2Ocorr} = [NO]\cdot(1+\alpha\cdot[H_2O]) \quad \text{with} \quad \alpha = (4.3\pm0.3)\cdot10^{-3}\cdot\frac{flow_{sampleair}}{flow_{ozone}+flow_{sampleair}}$$

Formula by Parrish et al (1991), adopted and modified by Franz Rohrer (WCC NOx).

$[H_2O]$ is in units of parts per thousand [‰] in this equation. One can use the ambient water mol fraction, e.g. calculated from relative humidity from the meteorological data set if the respective site.

However, for CLD instruments calibrated by standard addition (section 7.2.1), the calibration and measurements are performed at the same humidity in the reaction chamber. Thus, no water vapor correction needs to be applied for such calibrated instruments, given that the frequency of calibrations tracks the changes in ambient humidity.

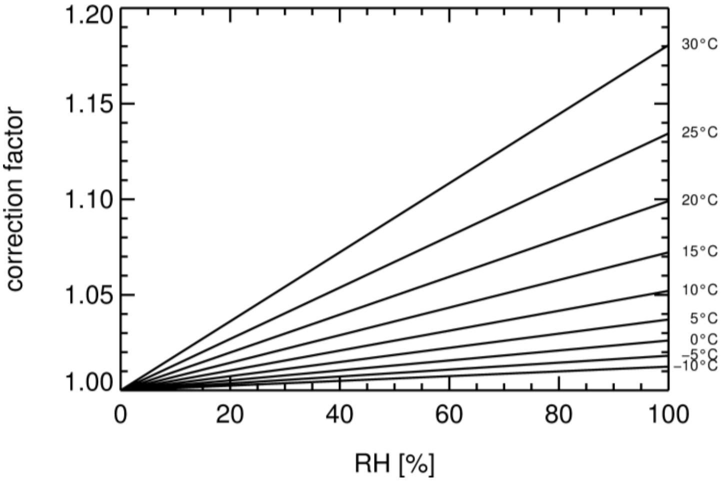

Fig. 3: correction factor (1+α· [H2O]) of the NO chemiluminescence signal for quenching by H2O (at 1013 hPa).

7.3.2. Artefacts caused by ozone

As mentioned in chapter 4.2., when ambient air enters the inlet line, NO_2 photolysis is stopped whereas the reaction of NO and O_3 continues, leading to overestimation of NO_2 and underestimation of NO. To correct for this effect, the following formulae should be used to convert the measured raw 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 [nmol/mol] without photolytic converter (LED off in BLC, or bypass in PLC)
$[NO]_{E2}$: measured NO signal [nmol/mol] 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 [nmol/mol] 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 (BLC for LED off) or bypass line (PLC)
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} : $k(O_3+NO)*[O_3]*10^{-9}*M$

First, the readout values 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 formulae for calculating the NOx mole fractions without ozone correction.

J_c is the photolysis rate inside the PLC and $[NO]_{PSS}$ and $[NO_2]_{PSS}$ are the equilibrium mole fractions of NO and NO_2 inside the PLC, respectively ("PSS" stands for photo stationary state).

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

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

in photolytic converter

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

in photolytic converter

From these quantities, one can calculate the NO and NO_2 mole fraction 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:

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

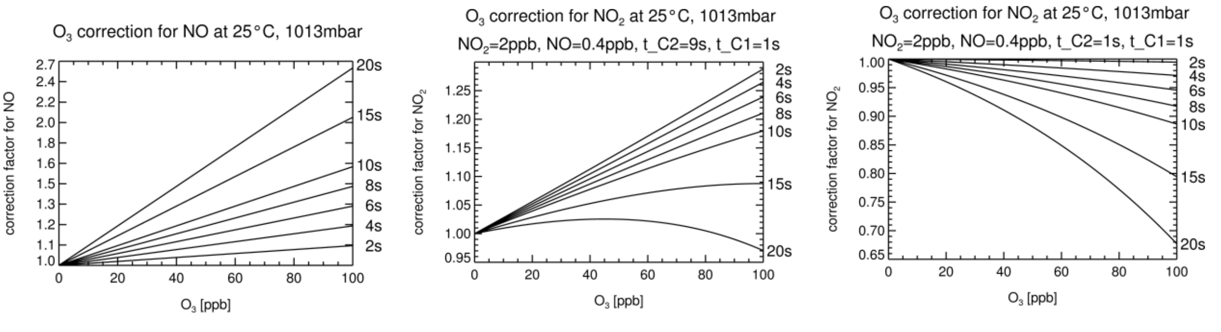

Fig 4: Correction factors for NO and NO_2 due to reactions of O_3 in the inlet line and in the photolytic converter. The values at the right side of each panel denote the residence time in the inlet line. S_c is set to 50%.

7.4 Quality control procedures

Besides routine calibration and quality checks, comparisons, exchange of experience, and data control workshops are essential for compatible, quality proofed data. Main comparison procedures are: round robin, side-by-side experiments in controlled environments (simulation chambers or manifolds) or in the field (many instruments at one site), and audits with comparison to reference instruments at a given station.

7.4.1. Round Robins

NO in N_2 mixtures in the µmol/mol range are used as test gases. Participants are asked to analyse the sent gas mixture following a well described procedure. Results are submitted by the participants using form sheets to achieve comparable methods of data and uncertainty evaluation. Such round-robins are organised within projects, e.g. ACTRIS performed a 18 lab-round robin in 2012 overseen by DWD Hohenpeissenberg, or by WCC-NOx. Such intercomparisons ensure the traceability of the used laboratory standards. This is the basic requirement for comparable measurements. However, round-robins lack a check of the applied dilution systems and thus are not able to ensure traceable calibration factors. This shall be overcome in future by routine use of target gas measurements at the stations. Another procedure under development is the use of tracer substances added to the calibration gas cylinders. It is tested to use CO2 which can be measured highly accurate by cavity ring down systems that exist at most GAW stations.

7.4.2. Outlook - Target gases

The concept of target gases shall be taken over from the climate gas community. Target gases are high pressure cylinders containing some 100 nmol/mol NO/N2 mixtures purchased from gas suppliers, checked for stability and certified by a reference laboratory. This process is overseen by the WCC. Such cylinders are shipped to the stations and used in monthly measurements, i.e. they are switched directly (manually or by automated valve) to the CLD and measured after a stabilization time for some 10 min. Before emptied or after maximum 2 years, they are replaced by new target gases. The used ones are sent back to the reference laboratory and re-checked for potential drift. Data of target gas measurements are flagged in the records and delivered together with ambient data to WCC and WDCRG for evaluation.

7.4.3. Outlook - Side-by-side-comparisons

Side-by-side intercomparisons take advantage of identical samples being analysed by collocated instruments. In easiest case, this can be achieved by instruments sampling in ambient air side-by-side assuming identical sample gas, however, this approach lacks control of the range of encountered conditions and shall therefore only be used for basic comparisons of very few, mostly 2, instruments or in station audits (section 7.4.4). Instead, approaches of multiple instruments sampling from a common manifold or connected to an atmospheric simulation chamber are favoured. Advantages are 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. Furthermore, it enables to test in real ambient air measurements conditions and in spiked ambient measurements. Several side-by-side experiments focusing on NOx took already place in the past and it is recommended to organize more experiments in the future aiming at a strong participation of many GAW stations. This will be task of the WCC to organize and oversee such intercomparisons.

7.4.4. Audits

Audits are a most powerful QA/QC tool. The NO and NO_2 measurements itself as well as all parameters which influence the measurements or the quality of measurements are under examination at the station. Station audits are performed by the WCC-NOx, the FZ Jülich. The first audit has taken place in July 2014 at the Hohenpeissenberg Meteorological Observatory.

7.4.5. Outlook - Data processing and QC tools

The WCC-NO_x has developed a systematic data evaluation and visualization tool. This tool can either be used by the stations or stations can send their raw data including all necessary metadata to the WCC for this processing. It is recommended to be used by the stations supplying data to the GAW Datacenter for Reactive Gases (WDCRG) but not mandatory, i.e. well experienced stations shall follow their own procedures.

7.4.6. Outlook - Data workflow and issue tracker

The processed data are quality checked by GAW experts coordinated and overssen by WCC-NOx. This initiates a review process. Issues indicating problems or questionable data are commented and sent to the station. The station re-checks instrumental conditions and questionable data and answers the raised issues. It proposes a procedure to overcome the issue, e.g. checked and ok, questionable and flagged, questionable and uncertainty enlarged and flagged, or rejected. The station answer and measures taken are again reviewed by WCC and experts, either settled or commented again. Usually, it is aimed for solving issues and have accepted data. If the process does not come to an agreement, WCC and experts have the right to flag the questionable data at the WDCRG. The review (issue-tracker) will be stored at the WDCRG and available to users.

7.4.7. Outlook - Data control and evaluation workshops

One step in the data workflow (section above) will be a yearly data workshop. This will bring together the station PIs, WCC-NOx and NOx experts to evaluate and discuss station data with respect to quality and open issues. Generally, the workshop shall discuss data after data processing according to section 7.4.5. It is central part of the data workflow and enables discussion of the issues identified so far and to raise new issues with the data.

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 NO_2 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 errors in corrections applied to the data as described in section 7.3, especially for O_3 in the inlet line and PLC and water vapor in the CLD measurement chamber.

The uncertainty analysis should separately determine systematic uncertainties and random uncertainties. Systematic uncertainties are due to the laboratory standard and systematic effects of the dilution system applied. Other uncertainties are typically evaluated in multiple determinations and thus random in nature. Gaussian error propagation assuming independent errors is assumed.

Each measurement needs to be supplemented by its total uncertainty (coverage factor k=2) and the random part expressed by the standard deviation. These informations are supplied to WDCRG.

8 Data Management (has to be adapted to GAW needs)

The format used by **WDCRG for the data is plain ASCII encoded text in tabular form (NASA AMES),** preceded by a section **containing metadata**. Quality checks performed by WDCRG currently include consistency checks as well as checks on data integrity. WDCRG uses unique identifiers to indicate missing values. Data submitters are advised to consult the WDCRG data submission guidelines and to contact WDCRG prior to data submission.

8.1 Data evaluation, flagging and control

Each station should develop a detailed procedure for evaluating the measurement data or use the procedure developed by WCC-NOx (Section 7.4.5). 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 running averages of these values and accordingly running 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 required 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 or dedicated scripts, 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 can 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 require additional 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 NO_2) 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 measurements of NO or NO_2.

Data of NO and NO_2 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 nmol/mol) 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 NO_2 and lower levels of ozone, in case of local pollutions the NO and NO_2 signals are highly variable and anti-correlated with ozone, NO_2 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 Ancillary data and metadata

Ancillary data are instrument and station specific parameters that should be recorded along with the trace gas readings to keep track of the instrument performance and the environmental conditions which might be useful for data evaluation and flagging. Essential ancillary data are: PMT temperature, reaction cell pressure, ambient ozone concentration, ambient temperature and humidity and other meteorological data. It is also recommended to carefully document useful metadata such as integration time, high voltage of PMT, chamber/instrument temperatures, (all) calibration factors, and length and inner 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. WDCGG accepts irregularly spaced data (such as events, flask samples) and continuous data. Of the latter, hourly data as well as higher aggregates (daily, monthly averages) along with associated standard deviations are collected. 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). Near-Real-Time data are currently not implemented in the WDCGG.

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

Flag	**Data Valid / Invalid**	**Description**
000	**V**	**Valid measurement**
120	V	Sample reanalyzed with similar result
185	V	Possible local contamination indicated by wind direction or velocity
380	V	More than 50% of measurements below detection limit
382	V	More than 75% of measurements below detection limit
390	V	Data completeness less than 50%
392	V	Data completeness less than 75%
394	V	Data completeness less than 90%
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 activity nearby
659	I	Unspecified instrument / sampling anormaly
660	V	Unspecified instrument / sampling anormaly
780	V	Value below detection or quantification limit, data element contains estimated or measured value
797	V	Data element taken from co—located instrument
899	I	Measurement undefined, unspecified reason
980	I	Missing due to calibration or zero/span check
999	I	Missing measurement, unspecific reason

Table 2: data quality flags as recommended by EBAS

All ACTRIS nitrogen oxides data are reported to, and stored in the EBAS atmospheric database http://ebas.nilu.no The EBAS database, originally designed for the European Monitoring and Evaluation Programme (EMEP), today archives data on atmospheric composition from ground stations around the globe, as well as aircraft and ship platforms. All datasets in EBAS are associated to one or more projects/frameworks, having individual rules for data disclosure. Most data stored in EBAS are originating from programs encouraging an unlimited and open data policy for non-commercial use. Offer of co-authorship is made through personal contact with the data providers or owners whenever considerate use is made of their data. In all cases, an acknowledgment must be made to the data providers or owners and to the project name when these data are used within a publication.

The ACTRIS data portal links EBAS data, together with data from the two other ACTRIS databases, EARLINET and CloudNet, into one common data portal. The portal facilitates the combined analysis of all ACTRIS data, offering advanced tools for plotting and combining ACTRIS data from the three fundamental databases, and mapping tools for user defined visualization of distribution atmospheric sites and variables across networks and projects.

The following section provides a summary of the data submission procedures for nitrogen oxide data to EBAS. The text below only address the main points as defined by August 2014, for a complete and, at any time, updated document please reference http://ebas-submit.nilu.no/

Nitrogen oxide in situ data are qualified as ACTRIS data only if the measurement data are reported to EBAS by using the templates recommended by the ACTRIS trace gas community, and following the procedures described in the current document. ACTRIS partners shall label their contribution to EBAS with project/framework "ACTRIS". The data can also be associated to other programs and frameworks like GAW-WDCGG-node, EMEP, etc. Data submitted to EBAS need to be formatted in the EBAS NASA-Ames format by the data provider. The EBAS NASA-Ames format is based on the ASCII text NASA-Ames 1001 format, but contains additional metadata specifications ensuring proper documentation of the setup and procedures for each measurement principle. Specific templates for each of measurement principle are available from http://ebas-submit.nilu.no/ under the tab Submit Data -> Regular Annual Data Reporting -> NOx (regular).

An EBAS NASA Ames file consist of two parts; a metadata header and a column formatted data part. The header section contains a number of important metadata items describing the measurement site, data variable, instrument, measurement principle and operating procedure. If nothing change in the measurement set up, the header will remain the same from year to year, and the measurement data will be visible as one continuous dataset in the database. The data section of an EBAS NASA Ames file consists of a fixed column number format ASCII table, including time stamp, data value and flag for each single measurement point or data average point. The data formatting templates give the user a detailed line-by-line explanation of what metadata that should be included on which line of the header, in terms of correct procedure and wording. Further information are available by clicking on the respective line number from the template. Flagging of data should be done according to the ACTRIS nitrogen oxides and EMEP guidelines. For time being only flags from the tables at the format template pages are recommended, but a complete list of flags available in EBAS is located at http://www.nilu.no/projects/ccc/flags/flags.html

The data centre recommends to first create the data table and then add the header. Name the file over using the filename stated in the header.

The data submission deadline for the ACTRIS project is following the EMEP submission deadline, for time being (August 2014) this is 31.July for data from the year before. Example: 31.July 2014 is reporting deadline for 2013 data. The files containing the data submissions must be uploaded to the EBAS anonymous FTP site, accessible at:

ftp://ebas-submissions.nilu.no/incoming using the submitters email as password.

This site is for security reasons a blind drop page, so the submitter will not be able to see the data after submission, but an auto-mail from the system will be sent to the data submitter if the submission was successful.

All ACTRIS partners and associated partners operating one or more instrument measuring trace gases are expected to report their data within the reporting deadline, following the guidelines.

After the data submission all datasets will be handles by the data format checker in EBAS, and contact between the data submitter and the EBAS team will be established. Feedback is given to the data submitter if critical errors in the file format or in the data part are detected. Data submitted to EBAS can be expected available in the EBAS and ACTRIS data portals around to months after the submission.

The EBAS database team provides support on data formatting, data submission and use of EBAS, and can be contacted by e-mail at ebas@nilu.no

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 References

GAW Report 195, WMO/GAW Expert Workshop on Global Long-term Measurements of Nitrogen Oxides and Recommendations for GAW Nitrogen Oxides Network (Hohenpeissenberg, Germany, 8-9 October 2009), (WMO/TD-No. 1570), February 2011.

WORLD METEOROLOGICAL ORGANIZATION, GLOBAL ATMOSPHERE WATCH , No. 172: WMO Global Atmosphere Watch (GAW) Strategic Plan: 2008 – 2015, A Contribution to the Implementation of the WMO Strategic Plan: 2008-2011, WMO TD NO. 1384, pp16, 2007.

ACTRIS-Report: WP4 – NA 4: Trace gases networking: Volatile organic carbon and nitrogen oxides; Deliverable D4.4: Results of Round Robin exercise of NO, April 2013

ACTRIS-Report: WP4 – NA 4: Trace gases networking: Volatile organic carbon and nitrogen oxides; Deliverable D4.6: Results of NOx side-by-side inter-comparison exercise of ambient air and test gases, April 2013

Thornton, J. A., P. J. Woolridge, R. C. Cohen, 2000. Atmospheric NO_2: In situ laser-induced fluorescence detection at parts per trillion mixing ratios. Analytical Chemistry, 72, 528–539.

Tuzson B., K. Zeyer, M. Steinbacher, J. B. McManus, D. D. Nelson, M. S. Zahniser, L. Emmenegger, 2013. Selective measurements of NO, NO_2 and NOy in the free troposphere using quantum cascade laser spectroscopy, Atmospheric Measurement Techniques, 6, 927-936.

Fuchs H., W. P. Dube, B. M. Lerner, N. L. Wagner, E. J. Williams, S. S. Brown, 2009. A Sensitive and Versatile Detector for Atmospheric NO_2 and NOx Based on Blue Diode Laser Cavity Ring-Down Spectroscopy, Environmental Science and Technology, 43, 7831-7836.

Kebabian, P. L., E.C. Wood, S.C. Herndon, A. Freedman, 2008. Practical Alternative to Chemiluminescence Detection of Nitrogen Dioxide: Cavity Attenuated Phase Shift Spectroscopy, Environmental Science and Technology, 42, 6040-6045

Villena, G., I. Bejan, R. Kurtenbach, J. Kleffmann, 2011. Development of a new Long Path Absorption Photometer (LOPAP) instrument for the sensitive detection of NO2 in the atmosphere, Atmospheric Measurement Techniques, 4, 1663-1676.

Fuchs, H., et al., 2010, Intercomparison of measurements of NO_2 concentrations in the atmosphere simulation chamber SAPHIR during the NO3Comp campaign, Atmospheric Measurement Techniques, 3, 21-37.

Hendrick, F., J.-F. Müller, K. Clémer, P. Wang, M. De Mazière, C. Fayt, C. Gielen, C. Hermans, J. Z. Ma, G. Pinardi, T. Stavrakou, T. Vlemmix, M. Van Roozendael, 2014. Four years of ground-based MAX-DOAS observations of HONO and NO_2 in the Beijing area, Atmospheric Measurement Techniques, 14, 765-781.

Galbally, I.E., J. R. Freney, W. A. Muirhead, J. R. Simpson, A. C. F. Trevitt, P. M. Chalk, 1987, Emission of nitrogen oxides (NO_X) from a flooded soil fertilized with urea: Relation to other nitrogen loss processes. J. Atmos. Chem., 5, 343-365.

CCQM-K74 Final Report: Flores E., Idrees F., Moussay P., Viallon J., Wielgosz R., Fernández T., Ramírez S., Rojo A., Shinji U., Waldén J., Sega M., Sang-Hyub O., Macé T., Couret C., Qiao H., Smeulders D., Guenther F.R., Thorn III W.J., Tshilongo J., Godwill Ntsasa N., Štovcík V., Valková M., Konopelko L., Gromova E., Nieuwenkamp G., Wessel R.M., Milton M., Harling A., Vargha G., Tuma D., Kohl A., Schulz G., Final report on international comparison CCQM-K74: Nitrogen dioxide, 10 µmol/mol, *Metrologia,* 2012, **49**, *Tech. Suppl.,* 08005

CCQM-K26.a Final report: http://kcdb.bipm.org/appendixB/anmol/molresults/ccqm-k26.a/ccqm-k26.a_final_report.pdf;

EURAMET 1084 report: http://www.euramet.org/index.php?id=tc-mc-projects&tx_nneurametctcp_projects%5Baction%5D=show&tx_nneurametctcp_projects%5Bcontroller%5D=Project&tx_nneurametctcp_projects%5Bproject%5D=850&cHash=9178d5a58c84fd182cc7c247cb68ee43

EURAMET.QM-K26.a Final report: http://kcdb.bipm.org/appendixB/anmol/molresults/ccqm-k26.a/ccqm-k26.a_final_report.pdf

Flores E., Idrees F., Moussay P., Viallon J., Wielgosz R., Highly accurate nitrogen dioxide (NO_2) in nitrogen standards based on permeation, *Anal. Chem.,* 2012, 84, 23, 10283-10290

Flores Jardines E., Viallon J., Moussay P., Wielgosz R.I., Accurate Fourier transform infrared (FT-IR) spectroscopy measurements of nitrogen dioxide (NO_2) and nitric acid (HNO_3) calibrated with synthetic spectra, *Applied Spectroscopy,* 2013, 67, 10, 1171-1178

Appendix

Measurement Techniques

Overview

The existing measurement techniques for detection of nitrogen oxides can be separated into three main groups: passive, active and remote sensing techniques. Principally, active techniques draw the air sample through the detector or sampling device by a pump, whereas passive techniques use the diffusion of air to the sampling device. In remote sensing techniques, e.g. satellite, FTIR (Fourier transform infrared spectroscopy) or MAXDOAS (multi-axis differential absorption spectroscopy), sampled air and detector are at different locations. Passive and wet chemcial techniques are not considered appropriate for GAW NOxc measurements (GAW Report #195, 2011). Figure 1 presents an overview of current techniques.

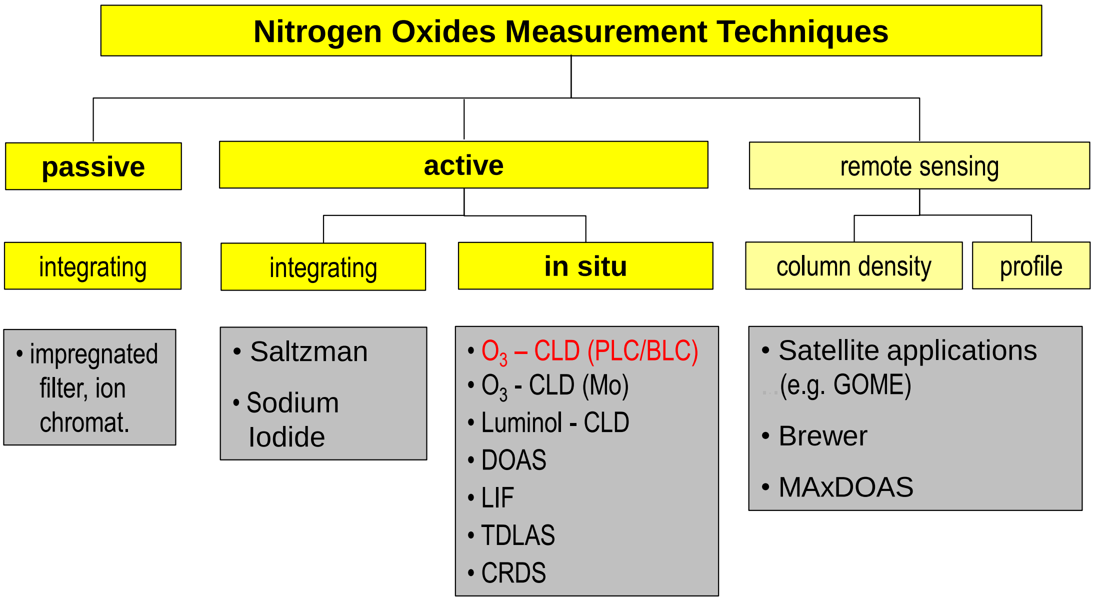

Fig. 1: summary of NOx measurement techniques. See text for explanation of acronyms.

The active techniques can be divided into integrating and “in-situ” techniques, with the integrating techniques consisting of a sampling step usually involving liquid-phase sample collection and off-line analysis, whereas in-situ (continuous) measurements directly analyse the sample air. Active integrating methods comprise the well-known Saltzman method and related methods like the Griess or Sodium Iodide method. The latter is being used in the EMEP network (European Monitoring and Evaluation Programme). Due to the high reactivity of NOx, flask sampling followed by quantitative off-line analysis is impossible.

“In-situ” techniques comprise the ozone chemiluminescence detection (CLD), which detects NO directly and NO_2 after suitable conversion to NO with a photolysis converter (PLC) or blue light converter (BLC). The Luminol-CLD measures NO_2 directly and NO indirectly after oxidation. Also, very selective and partly new optical absorption techniques for NO_2 detection have been developed including tuneable diode laser absorption spectroscopy (TDLAS), differential optical absorption spectroscopy (DOAS), laser induced fluorescence (LIF), and cavity ring down spectroscopy (CRDS).

At present, the only mature technique that can compete in meeting GAW requirements is the ozone-induced chemiluminescence NO detection (CLD) measurement of NO. Recent developments in cavity ring-down spectroscopy (CRDS) for measurement of NO_2 and of NO as NO_2 after oxidation by ozone are promising but long-term applicability such as stability of instrument sensitivity has not yet been demonstrated. Passive and active integrating methods should be avoided in the GAW Programme for their inappropriate selectivity and time resolution (GAW Report #195, 2011).

Annex I Abbreviations and acronyms

CLD	chemiluminescence detector
PLC	photolysis detector
BLC	blue light detector
CRDS	cavity ring down spectroscopy
LIF	laser induced fluorescence
DOAS	differential optical absorption spectroscopy
TDLAS	tunable differential laser absorption spectroscopy
CAPS	cavity attenuated phase shift (spectroscopy)
DQO(s)	data quality objective(s)

LDL, PAN, DWD, NPL, EMEP, GAW, …

PART 2: VOCs

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1. General introduction

Non-methane hydrocarbons (NMHCs) contain short-chain, high-vapour pressure alkanes, alkenes, alkynes, and aromatics. Together with the low-boiling oxygenated hydrocarbons (e.g. alcohols, ketones, aldehydes) they build the group of volatile organic compounds (VOCs). With respect to the four grand challenges in atmospheric chemistry identified within the Integrated Global Atmospheric Chemistry Observations (IGACO), VOCs are mainly related to air quality, oxidation capacity of the atmosphere, and chemistry-climate interaction. They are major precursors in photochemical O_3 formation, impact the oxidative capacity of the atmosphere, and are important precursors of secondary organic aerosols (SOAs). Furthermore, they are important tracers for emissions, transport, mixing, and chemistry.

VOCs are emitted by the biosphere and by anthropogenic activities, such as motor vehicle exhaust and solvent usage. A complex mixture of several hundred VOCs is existing in the atmosphere with lifetimes ranging from several months in the case of ethane, to hours for the most reactive ones, such as alkenes (e.g., 1,3-butadiene or isoprene). VOCs are removed from the atmosphere predominantly by their reaction with hydroxyl radicals – a process which forms intermediate oxygenated organic compounds. However, reaction with ozone, nitrate and halogen radicals and photolysis can also be important sinks, depending on the VOC species, location, season and time of day. In populated areas VOCs and their degradation products are responsible, together with NO_x, for the photochemical production of ozone (O_3) and other photo-oxidant pollutants, including peroxyacyl nitrates (PANs) and secondary organic aerosols (SOAs). The scientific background for the need of monitoring atmospheric VOCs in global and regional networks has been extensively presented (e.g. WMO, 1995; WMO, 2007a; WMO, 2012; Helmig et al., 2009) and measurements of VOCs are among the long-term monitoring parameters in global and regional infrastructures, such as GAW (WMO, 2007b; GAW Reactive Gases Bulletin No. 1, 2017), EMEP (Directive 2008/50/EC on ambient air quality and cleaner air for Europe), the EU Infrastructure Network ACTRIS (Aerosols, Clouds and Trace Gases), and the US EPA PAMS network (ref: https://www3.epa.gov/ttnamti1/pamsmain.html).

Priority substances of NMHCs, oxygenated VOCs (OVOCs), and biogenic VOCs (BVOCs, mainly isoprene and terpenes) have been identified in the GAW Report No. 171 (WMO, 2007a) and are shown in Table 1. Detailed guidelines have to be provided to the GAW community for their measurements, following the general quality assurance (QA) recommendations and the strategic plan by GAW (GAW Report 172, WMO, 2007b). This measurement guideline covers only the ground-based ambient measurements of NMHCs (C_2-C_9 hydrocarbons) by gas chromatography-flame ionization detection (GC-FID) and gas chromatography-mass spectrometry (GC-MS). For monoterpenes and oxygenated VOCs (OVOCs) as well as other analysis techniques (e.g. PTR-MS) separate measurement guidelines will be published within GAW.

Table 1 The list of priority VOCs focused in the GAW report No. 171 (WMO, 2007a) and modified in the reactive gases bulletin No.1 (WMO, 2017).

Molecule	**Approximate Lifetime**	**Importance in Atmospheric Research and for GAW**
Terpenes	1-5 hours	Plant emissions, sensitive to temperature, land use, and climate change, precursors of organic aerosols
Isoprene	3 hours	Plant emissions, sensitive to temperature, land use, and climate change, ozone precursor, formaldehyde precursor
Formaldehyde	1 day	Indicator of isoprene oxidation, biomass burning, source of free radicals in remote areas
Dimethyl Sulfide (DMS)	2 days	Major natural sulfur source, sulfate aerosol precursor, tracer of marine bioproductivity
Toluene	2 days	Precursor of organic aerosol, ratio with benzene used to determine age of air plume

Iso/n-pentane	3 days	Tracer for petrochemical emissions, isomeric ratio indicates impact of halogen chemistry
Ethanol	4 days	Tracer for biofuel production and use
Iso/n-butane	5 days	Tracer for natural gas extraction and use and chemical processing, precursor of ozone, isomeric ratio indicates impact of halogen chemistry
Benzene	10 days	Tracer of fossil and biofuel combustion, biomass burning
Propane	11 days	Tracer for methane sources, natural sources, biomass burning, regional fossil fuel emission trends
Methanol	12 days	Biological sources, oxidation product from methane and other VOCs, exchange with ocean
Acetylene	15 days	Motor vehicle emissions, biomass burning, ratio to other hydrocarbons (age of air plume), regional trends
Ethane	1.5 months	Tracer for methane sources, biomass burning, hemispheric fossil fuel emission trends
Acetone	1.7 months	Oxidation product from other VOCs, source of free radicals in the upper troposphere
Acetonitrile	0.5-1 year	Biomass burning and biofuel burning indicator

The measurement of NMHCs by GC is generally performed in a series of steps with (1) intake manifold and sampling line, (2) traps to remove water, ozone and possibly CO_2, (3) sample pre-concentration, (4) gas chromatographic separation, (5) analysis in detector, and (6) data processing and data delivery. A sample of atmospheric VOCs can be introduced to the analytical system directly from ambient air (on-line), or via a canister or an adsorptive sampling tube (off-line). The sample is normally passed through a moisture and/or ozone removal system and then concentrated in a freeze-out trap or on an adsorbent medium that is cryogenically cooled, using liquid nitrogen, liquid carbon dioxide, compressor, thermoelectric (Peltier), or closed-cycle coolers (e.g. Stirling coolers). The sample may also be refocussed cryogenically by a cooled secondary trap to narrow the band width before injection onto the GC separation column. The concentrated sample is then thermally desorbed, separated on the GC column and finally analysed by flame ionization detection (FID) or mass spectrometry (MS) (or any other suitable detectors, e.g., a photoionization detector (PID)).

2. Data Quality Objectives

In WMO/GAW, data quality objectives (DQOs) were introduced in the 2000-2007 strategic plan (WMO, 2001). These DQOs define the quantity and the quality of data required to yield information to support policy decisions. In particular, DQOs specify tolerable levels of uncertainty in the data, required completeness, and comparability. The rationale for the setting of NMHC DQOs is related to answering specific scientific questions that were outlined in the GAW Report 171, and are revised in this section with new and more demanding DQOs (Table 2). DQOs are defined for measurements of VOCs in whole air compressed test gases and describe an inter-laboratory compatibility. The DQOs are first expressed as expanded combined uncertainty (coverage factor k=2), required to answer specific scientific questions. This includes the repeatability of measurements, which is indicated with a coverage factor of k=1. (Both are listed in Table 3 with relative values above 100 pmol/mol and absolute DQOs (pmol/mol) below 100 pmol/mol.

The rationale for these numbers is related to the ability to detect annual and decadal trends related to changing anthropogenic and biogenic emissions, changing patterns in atmospheric transport and mixing, and changing lifetimes related to potential variations in the oxidative capacity of the atmosphere. Anthropogenic NMHCs (alkanes, alkenes, alkynes, aromatics) are regulated by EU Directives, (2008/50/EC) and come under the policy aegis of the Convention on Long-range Transboundary Air Pollution (CLRTAP, UNECE,VOC Protocol, Gothenburg Protocol and follow up Protocols). Emissions reduction goals can act as a facilitator for changes in emissions, which should be detectable at a regionally influenced GAW site. These envisaged emission reductions have been and are typically in the range between 10-20% per decade. Such changes can only be detected when the overall measurement uncertainty is better than half of the expected trend, e.g. 5%, at a specific site. Furthermore, the attribution of source types to the measured NMHC profiles is important for the understanding of changing emissions. Source apportionment attribution e.g.by positive matrix factorisation (PMF) methods, and the relative changes of these sources over time, have to be provided with an uncertainty of less than 10% per decade. Such analyses critically depend on the measurement uncertainties, which should be below 5% for the less reactive and more abundant NMHCs, especially the C_2-C_5 hydrocarbons and benzene, in order to achieve uncertainties in ratios of hydrocarbons of less than 10%.

Models used to assess the impact of NMHCs on formation of secondary pollutants and atmospheric chemical processes, often face large uncertainties of about 50% due to the high regional and temporal variability of the reactive NMHCs, the uncertainties in rate constants (typically larger than 20%), and the fact that individual NMHC species have only minor impact on integrated parameters such as the O_3 formation rate or oxidizing capacity. Accordingly, for studies including chemical models a 20-30% uncertainty is considered sufficient.

Table 2 DQOs for NMHC measurements in ambient air, related to scientific questions and expressed as expanded combined uncertainties (k=2) at levels above 100 pmol/mol.

Scientific question	Overall uncertainty needed*
Decadal trends for changes of sources/environmental conditions Source attribution studies	C_2-C_5-alkanes, acetylene, benzene: 5% Other NMHCs and isoprene 10%
Modelling of tropospheric ozone Modelling of secondary organic aerosols Total reactivity closures Ambient air quality/health studies Comparability between different studies	20-30%

* Minimum requirement for global sites

For practical reasons, assessing the compliance of a station to these DQOs by parallel measurements with a reference system can generally not be achieved, as GC reference systems cannot be transported to stations with reasonable efforts. As an alternative, synthetic or whole air test gases from pressurized cylinders are used to check the compatibility of stations with respect to the DQOs in ambient air. DQOs in pressurized cylinders are shown in Table 3 and are identical to those in ambient air, except for the group of the other NMHCs (e.g. including alkenes). Here the combined uncertainty is also set to 5%, as the dependence on ambient ozone and possibly humidity are absent. For measured mole fractions which are lower than 100 pmol/mol absolute uncertainty goals are defined in Table 3. This is justified by the growing influence of the limits of detection, which are typically around 10 pmol/mol for NMHC measurement systems in the field.

For trend studies and source allocation measurements performed at a GAW site the more stringent GAW DQOs have to be applied. Basic station DQOs are useful for atmospheric chemical process studies. An intercomparison experiment conducted in the framework of the European ACTRIS project has shown that these GAW DQOs are achievable (Hoerger et al., 2015).

Table 3 Data quality objectives (DQOs) for the measurements of NMHCs in whole air compressed test gases (inter-laboratory compatibility) expressed as the expanded combined uncertainty (k=2) and the repeatability (k=1; standard deviation). The basic station performance requirements correspond to the former and weaker DQOs of GAW Report 171 (2006).

	GAW basic performance expanded combined uncertainty	GAW basic performance repeatability	GAW target performance expanded combined uncertainty	GAW target performance repeatability
Alkanes	10%	5%	5%	2%
alkenes incl. isoprene	20%	10%	5%	2%
Alkynes	15%	5%	5%	2%
Aromatics	15%	10%	5%	2%
mole fraction (1) <100 pmol/mol	10/15/20 pmol/mol	5/10 pmol/mol	5 pmol/mol	2 pmol/mol

(1)*For mole fractions below 100 pmol/mol, the DQO are expressed in pmol/mol, reference is the above stated relative value at 100pmol/mol e.g. for alkanes basic performance 10 pmol/mol.*

3. NMHC Measurement Setup

The GAW Programme consists of global, regional and local stations as well as stations from contributing networks (WMO, 2017). The essential characteristics of a GAW regional or contributing station include regional representativeness, which is not influenced by significant local pollution for the measured variables (WMO, 2017).

3.1 Facility requirements

Facility requirements include 24-hour available electricity and communications, a building suitable for the instruments and staff. The facility and equipment should be suitable to sustain long-term observations with greater than 90% data capture (i.e. <10% missing data). For NMHCs, there is no strict sampling frequency to be followed by the stations; this depends on the scientific and societal questions addressed. It should at least be once per week in order to analyse annual cycles and trends. However, with weekly sampling only limited representativeness can be achieved. Thus, it is recommended to perform regular off-line sampling twice per week at local noon, and on-line sampling at least twice per day, at local noon and midnight, preferably more frequent. The sampling of the air should be structured in a way to avoid local contamination sources (see section 4). The laboratory building and inlet location have to be set upwind of any other buildings, garages, parking lots, generators, other emission sources – any nearby areas where fossil fuels or biomass may be combusted and where intensive agriculture is undertaken. Station personnel should also remain downwind of the sampling inlet and refrain from smoking. Within the analytical laboratory, temperature control and clean lab environment are required. Instrumentation should not be exposed to direct sunlight.

3.2 Personnel requirements

Each set of measurements at a GAW station should be conducted under the guidance of a designated Principal Investigator (PI). For NMHCs, it is recommended that the PI has training in atmospheric chemistry, meteorology, and atmospheric composition monitoring. There are requirements for technicians with skills in (1) analytical chemistry, particularly atmospheric composition, (2) electrics and electronics, and (3) IT, particularly instrument control, data acquisition, and data processing. It is recommended that the station staff participate in the GAWTEC training programme and other GAW specialist activities, or those of infrastructures associated to GAW, e.g. the European ACTRIS (Aerosol, Clouds, and Trace gases Research Infrastructure Consortium).

Provision should be made for back up staff to cover the periods when regular staff is away at training, annual leave etc.

3.3 Occupational health and safety

The NMHCs measurement includes use of following issues that potentially can cause occupational health and safety issues:

- High voltages;
- High-pressure gas lines (for example associated with the zero air generator or gas cylinders);
- Noise;
- Heavy equipment.

Other hazards may occur and appropriate occupational health and safety information, protective equipment and training is required.

3.4 Instrumentation requirements

The following instrumentation is required for a reliable long-term NMHCs monitoring station in GAW:

- Suitable inlet and NMHCs analysis system as described in Sections 4 and 5. This system must be calibrated as recommended in Sections 7 and 8 of this measurement guideline;
- Zero gas supply that includes NMHCs and O_3 removal, depending on purpose also H_2O removal (see Section 7);
- Sample path including inlet line and filters inert to VOCs;
- Computer, instrument control and data acquisition interface;
- Internet connection/remote computer access;
- Uninterruptable power supply.

Equipment varies in specification and performance. The WCC, GAWTEC, existing well experienced GAW stations and laboratories can provide advice on instrumentation that has performed successfully.

Manufacturers' instrument manuals have to be available for all instruments used at the site.

3.4.1 Instrument replacement

As long as an instrument performs within the specifications and the DQOs (Section 2), there is no necessity for replacement. If the instrument performance requires a replacement, the new and old system should run parallel for some time. If possible this parallel operation should be for at least 6 months.

Since IT equipment is subject to fast evolution, back-up equipment should be available and appropriate updates should be carried out depending on the availability of financial resources.

3.4.2 Instrument control and data acquisition software

Instrument control and data acquisition usually depends on the available manufacturers' software for the NMHCs instrument.

3.5 Air inlet and sample lines

The air inlet is an essential component of the GAW monitoring system. There are two key components of the inlet system, the location of the inlet and the flow rate and materials of the inlet. In analytical chemistry terminology, the location of the inlet is an aspect of sampling and the passage of the air through the inlet corresponds to pre-treatment of the sample. See Section 4 for details.

3.6 Associated key measurements and logging requirements

Key measurements that will help in the interpretation of NMHCs measurements include those used for processing the NMHCs data, data selection and those related to NMHCs chemistry. To understand the influence of nearby sources, to undertake data selection according to meteorological conditions and to quality control, the following additional parameters are useful but not a requirement:

- Meteorological parameters: Wind speed, wind direction, air temperature, humidity, boundary layer height;
- Spectral distribution of solar radiation (suitable for determining molecular photolysis rates)/solar radiation.
- O_3/CO/CH_4/CO_2 /NO_x (and further if available: SO_2/OH/RO_2/HO_2/NO_3…) mole fractions;

- Particle number concentrations and speciation ;
- Radon concentration.

Where NMHC measurements are undertaken at GAW stations, consideration should be given to measurement of these additional parameters and long-term data storage together with the NMHC data. The measurement techniques for these parameters are defined in GAW Report No.143 (Global Atmosphere Watch Measurements Guide, WMO 2001b) and in individual measurement guidelines (WMO, 2007a; WMO, 2010b; WMO, 2010c; WMO, 2011a). Furthermore, an instrument log book has to be used to keep track of events which could influence the quality of the measurements (e.g. change of pumps and inlet lines for off-line systems and change of instrument parts, instrument settings and gas replacements for on-line instruments. In addition, a station log book has to be used to follow external events, such as building activities and nearby local pollution (e.g. from fires and heavy duty equipment).

3.7 Environmental issues that affect GAW stations and VOCs observations

The environmental conditions/hazards that affect VOCs observations include the following:

- Inlet blockage at polar and high-altitude sites, due to ice riming and blowing snow;
- Pollution events by nearby roads, industry, agriculture, biomass burning, volcanoes, etc.;
- Access limited by environmental conditions such as flooding, severe weather etc.;
- Tourist activities.

Consideration should be given to minimising the effect of the factors listed above where possible when setting up the station, while it is clear that the impact of natural hazards cannot be completely avoided.

4. Sampling of NMHCs

The air from which NMHCs is analysed can be sampled and analysed on-line at the measurement site, or off-line, using either adsorption tubes, (passivated) stainless steel canisters, or glass flasks. Off-line samples are subsequently transported to the lab, where they are analysed. The specific requirements of the different methods are described below.

4.1 Location of the inlet

The height of the air inlet is critical to the sampling of representative air. The optimum inlet height depends on the surrounding area (vegetation, orography, soil, water, snow). New stations should, if possible, for a trial period sample NMHCs at 2-3 different heights to determine which inlet height is suitable. The lowermost height of the inlet should be well above upwind structures, such as buildings or trees, and it should be mounted on the predominant upwind side of the building. It is recommended to be at least 2 m above the building where the sampling line is mounted, and at least 5 m, above ground. Stations on mountains may use lower inlets, if appropriately tested. These inlet location recommendations represent guidelines but station PIs have to prove that the inlet is mounted such that it is not impacted by emissions due to the station or point sources very close to the station.

4.2 Inlet manifold and sampling lines

Generally, it is recommended to use a high flow inlet manifold to transfer samples with short residence time from the inlet to the laboratory (<1 min). From there, small diameter and short sampling lines go to the sampling devices or directly to the instruments. For NMHCs the manifold and sampling line should preferentially consist of surface passivated steel (e.g. silcosteel^R or sulfinert^R) or glass. If stainless steel is used, it should be electro-polished and heated up to 70°C to prevent condensation of NMHCs on internal surfaces (Hopkins et al., 2011). It is not recommended to use untreated stainless steel.

The inlet line connecting the instrument to the manifold should be optimized for minimum surface area and residence time, and it should be flushed prior to sampling for a sufficient time to equilibrate surfaces. The residence time between the manifold and the instrument should not exceed a few seconds. It is recommended to install an aerosol filter (see Section 5.1.4).

4.3 Off-line sampling

Off-line sampling should follow a station specific protocol. As generally only few samples are taken, e.g. twice per week, these should then characterise typical air masses at the stations with little influence from local sources. For flat-land stations, conditions at noon, e.g. between 12:00 and 14:00 local time, should be chosen because then a well-mixed boundary layer has developed. At mountain stations and depending on their height and sampling time, free tropospheric, residual layer, or mixed-layer air can be sampled. Generally, when an operator performs the off-line sampling, indications for local contamination from other on-line instruments at the station should be checked, as e.g. NO_x or particle concentration (see section 3.6). Furthermore, meteorological conditions in favour of small local impact, e.g. certain wind sectors or wind speed > 2 m s^{-1} should be specified in the corresponding protocol. The sampling needs to be well documented, including metadata, i.e. observation of potential local pollution sources.

4.3.1 Adsorption tubes

Though off-line sampling of NMHCs by adsorption tubes is an established method, it is not recommended for use in the GAW NMHC network. It has not been thoroughly tested in intercomparison exercises and its suitability has not been unambiguously proven suitable with respect to the DQOs. One of the main problems associated with adsorption tubes are artefacts due to blanks (especially for aromatic compounds) in the range of mole fractions encountered at clean background sampling sites. However, for some compounds like terpenes, adsorption tubes might be useful to generally characterise the abundance of this compound class, which is often not routinely analysed with on-line GC-systems.

4.3.2 Stainless steel canisters and passivated stainless steel canisters

In the GAW Report No. 204 (WMO, 2012) a Standard Operation Procedure (SOP) is described for the sampling of a group of NMHCs in canisters. This measurement guideline is largely based on the recommendations from the “Accurate Measurements of Hydrocarbons in the Atmosphere” project AMOHA (Plass-Dülmer et al., 2006) and from US-EPA (1998, 1999) on determination of NMHCs in ambient air. This technique is recommended only for C_2-C_6 alkanes, isoprene and benzene. Instead of stainless steel, also passivated stainless steel canisters e.g. by Silconert 2000®, SUMMA® treatment, can be used.

4.3.3 Glass flasks

Glass flasks, as used in the NOAA Cooperative Air Sampling Network with the corresponding automatic sampling equipment, have been shown to provide quality observations for analyses of C_2-C_6 NMHC, including ethyne, and isoprene. This was verified in an ongoing comparative study with the on-line system at Hohenpeissenberg (Pollmann et al., 2006; Helmig et al., 2016, Blanchard et al., 2017; Hueber et al., 2017). The equipment uses a PTFE sampling line, an inlet at a height of 2 m, a high-purity membrane pump to pressurize the sample, a condenser to remove water, tapered leak-tight PTFE-glass connectors, and Pyrex glass flasks of 2.5 litre volume. The flasks are locked by Teflon valves, purged prior to sampling for 5 min and pressurized to about 2500 hPa (abs.) (see References).

4.4 On-line sampling for quasi-continuous observations

On-line sampling avoids storage issues and minimizes leak issues, however, requires an analytical system at the sampling site and thus restricts the sampling intervals to the capabilities of the analytical system. The air sample is directly transferred via a sampling line into the NMHC instrument. Use of on-line systems is encouraged at all GAW global stations if the required, well trained personal, the appropriate equipment and the resources necessary for QA/QC including regular zero, calibration, and target gas measurements are available. Otherwise, it is recommended to use off-line sampling and have the analyses done by an experienced laboratory.

5. Measurement techniques for analysis of NMHCs

For on-line and off-line in-situ analyses of C_2-C_9 NMHC species from ambient air, different measurement techniques are in principal available (Table 4). GC systems are currently the method of choice. The advantages are medium cost, high sensitivity, excellent reproducibility, and, depending on the applied chromatographic details, large resolving power. Disadvantages are the restricted time resolution and possible artefacts or losses in the necessary pre-concentration step. An alternative for aromatics (e.g. toluene) and alkenes with alternating double-bonds (e.g. 1,3-butadiene) are the PTR-MS systems with high time resolution. However, PTR-MS cannot separate compounds with identical molecular masses, though recent developments in selective reagent ion (O_2^+, NO^+ and H_3O^+) and high resolution PTR-TOF-MS have overcome this problem for isobaric but not for isomeric compounds. PTR-MS system will be covered in a separate MG. Other NMHC measurement techniques are evolving (e.g. CRDS, chemiluminescence) but are currently not considered in this guideline since the method is still under development and detection limits are still too high.

Table 4 Measurement techniques available for C_2-C_9 NMHCs.

Instrument type	Detection limit	Compounds	Guidelines
GC-FID, GC-MS	≤10 pmol/mol	C_2-C_9	In here
PTR-MS	≤10 pmol/mol	Aromatics, Alkenes with alternating double bonds	in preparation
PTR-TOF-MS	≤10 pmol/mol	See PTR-MS + separation of isobaric compounds possible	in preparation
CRDS	1 nmol/mol	Single NMHCs e.g. ethane	-
chemiluminescence	~1 nmol/mol	isoprene	-
electrochemical gas sensors	~1μmol/mol	Single NMHCs (e.g. benzene, ethane)	-

NMHCs are found in the atmosphere in the range of pmol/mol (ppt) up to some nmol/mol (ppb). As a result of these low mixing ratios, other trace gases with higher concentrations (e.g. H_2O, CO_2) have to be separated from the gas flow so that they do not interfere with the analysis of the NMHCs (Section 5.1). As ambient concentrations of NMHCs are generally too low for direct analysis they have to be pre-concentrated before GC analysis in order to increase the signals above the instrumental detection limits. Pre-concentration of NMHCs is performed on a so-called trap, consisting of a tube packed with adsorbent material held at a controlled temperature (Section 5.2). After heating the trap the pre-concentrated compounds are subsequently injected onto the analytical column where they are separated depending on the characteristics of the chosen column (Section 5.3). In the final step they are analysed on an appropriate detector (FID or MS, see Section 5.4).

5.1 Removal of water/ozone/carbon dioxide/particles

Prior to pre-concentration, additional scrubbing devices may be required: Water (H_2O) in ambient air affects the adsorption capacity of the pre-concentration trap (see Appendix 2), the chromatography (peak shapes), and retention times, and leads to ice formation in the pre-concentration unit, when temperatures <0 °C are applied. Ozone may react with alkenes during the pre-concentration step. Furthermore, ozone could react with the adsorbent material itself (see Appendix 1). CO_2 can distort the chromatography or effect detector sensitivity in case of sample pre-concentration at adsorption temperature <-78 °C. Furthermore, particle filters are recommended to avoid contamination of the system.

5.1.1 Water removal/management

Water management can be achieved by different methods such as a Nafion® dryer or a cold trap (Table 3). The use of cold traps is recommended because these systems are less prone to artefacts. Nafion may be an alternative, however, it is more prone to artefacts and analyte losses, therefore appropriate care has to be given for the characterization of blanks and of analyte losses. It is not recommended to use chemical water traps in VOC sampling by unexperienced users, e.g. $Mg(ClO_4)_2$, because increased blanks and artifacts may occur. Furthermore, these materials together with water can form a solution which might be transported through parts of the inlet. Regardless which water management system is chosen, its efficiency, potential artefacts (e.g. blank values) and the recovery of the NMHC intended to be measured need to be tested (see Standard-addition measurements in Section 7.1.3).

If *hydrophobic adsorbents* (see Appendix 2) at above ambient air temperature are used in the pre-concentration trap, prior water removal is not necessary if a dry purging step (flushing of the pre-concentration trap in the sample flow direction with dry gas, e.g. purified helium (He 5.0 or He 6.0) subsequent to sampling is performed. However, this kind of sampling is applicable only for C_4 and higher boiling compounds.

Table 4: Methods to remove water from the sample.

Method	Comments	Recommended for
Cold trap @ $T < T_{ambient}$ typically consisting of a passivated steel tube or a small volume glass flask and a cooling device	H_2O is adsorbed or frozen-out but not the analytes. The dew point should be measured and it should be appropriate for the capacity of the pre-concentration trap and GC columns, typically below -30°C. (e.g. (Hopkins et al., 2003)).	NMHCs and monoterpenes
Nafion ® Dryer with a volumetric counter-flow of dry air or N_2, which is around 3 times higher than the flow of humid ambient air*	removes H_2O effectively and substantial parts of the polar OVOCs and monoterpenes. Potential artefacts in C_2-C_4- alkenes may occur depending on the status of the Nafion® Dryer. ((Gong and Demerjian, 1995; Plass-Dülmer et al., 2002) and references therein).	NMHCs C_2-C_7 (sometimes C_8)

*Has to be adjusted dependent on the specific Nafion dryer specs.

5.1.2 Ozone removal

To avoid artefact formation from the reaction of unsaturated, reactive NMHCs with ozone (O_3), several methods are available to eliminate ozone from the sample. Table 5 lists the most common methods. A more thorough compilation of available methods and their evaluation can be found in Appendix 1.

Table 5: Ozone removal methods and recommendations for NMHC sampling.

Method	Comments

(e-polished) stainless steel @ T > 70°C	Has to be regularly checked (at least once per month) for efficiency (Hellén et al., 2012)
Cartridges filled or filters impregnated with	
sodium thiosulfate ($Na_2S_2O_3$)	Helmig, 1997; Plass-Dülmer et al., 2002
sodium sulfite (Na_2SO_3)	Efficiency depends on H_2O vapour content of air stream, humidity increases efficiency (Helmig, 1997).
Manganese-Oxide	Needs check for adsorptive losses and lower volatility NMHC

5.1.3 Carbon dioxide removal

The operation of pre-concentration traps at temperatures where CO_2 is retained is a risk with respect to breakthrough and losses of low boiling NMHCs. Different approaches are in use to minimize the effect of CO_2 (Table 6). (1) The trapping temperature can be hold high enough that only a minor, acceptable portion of CO_2 is trapped or (2) CO_2 can be chemically removed before the trap or (3) the dimension of the trap is big enough to quantitatively trap NMHCs without interference of CO_2. For (3) the CO_2 may have to be removed prior to transfer of NMHCs to the analytical system by moderately heating the trap to temperatures high enough to volatize the CO_2 only.

Table 6: CO_2 management

Method	**Comments**	**Recommended for**
CO_2 trap: Removal of CO_2 before trapping using a cartridge with Ascarite	Ascarite is hygroscopic, trap should be installed behind a water trap to avoid liquefaction; artefact are possible and need to be checked, CO_2 trap needs to be exchanged regularly	NMHCs, off-line systems
Trap temperature management: trap is only as cold as it is needed for complete NMHC trapping	There may be a gap between temperatures needed to fully trap the most volatile C_2-NMHCs and CO_2 dependent on the trapping material. Regular checks have to be performed to check full trapping and desorption of C_2-NMHCs	NMHCs, on-line systems/off-line systems
High-volume pre-concentration trap: CO2 is hold back at the trap but the volume of the trap is high enough to not loose NMHCs	May be needed to slowly heat the preconcentration trap to a temperature high enough for CO_2 to be released but not for the analytes (Miller et al, 2008)	NMHCs, on-line systems/off-line systems

5.1.4 Particle filters

In order to avoid contamination of the system with particles, filters (Table 7) should be used in the analysis of VOCs but have to be checked carefully for adsorptive artefacts of less volatile and more polar compounds. PTFE membrane filters are recommended. Stainless steel screens with few µm mesh size and thickness are recommended for coarse filtering of large particles. These can be used in fittings. Bulky filters, however, with large surface area (metal meshes or sintered materials) should be avoided. Filters have to be changed at regular intervals depending on the aerosol loading, e.g. at an urban site every 4 months.

Table 7: Particle filters used in GC systems.

Method	**Comments**	**Recommended for**

PTFE membrane filter	Pore size: 20-30 µm, e.g. Metron Technology, Aschheim, Germany (used at Hohenpeißenberg) No artefacts are detected for recommended compounds (see Section 6.6.). Not suitable for OVOCs.	NMHCs (C_2-C_{14}) BVOCs
Stainless steel screens	Several µm thickness and mesh size, only for coarse particles > several µm	NMHCs (C_2-C_{14}) BVOCs

5.2 Sample pre-concentration and transfer to the analytical system

Either cryogenic adsorption on glass beads, a combination of weak adsorbents with low sub-ambient temperature or stronger adsorbent with higher, up to ambient temperature can be chosen. A compilation of different trapping adsorbents and their usage is provided in Table 8 and in Appendix 2. A thorough review of possibilities can be found in Helmig et al. (1999). Often, multi-bed adsorbents with increasing adsorbent strengths in sampling flow direction are used. For each system, break-through volumes and desorption efficiency have to be tested for the different NMHCs, using either increasing amounts of humidified synthetic standards or of ambient air spiked with standards (Section 7.6). At very low temperatures (e.g. when cooling is done with liquid nitrogen) care has to be taken to remove adsorbed oxygen and noble gas prior to desorption (see below). In addition, trapping efficiency of NMHCs could also be affected if large volumes of these gases are adsorbed and hence has to be tested.

For sampling, a pump should be used (preferably) downstream of the pre-concentration-trap connected to a critical orifice or a mass flow controller (or any other suitable instrument) to regulate the flow through the trap. It is essential to determine the sampling volume with low uncertainty either by regularly calibrating the mass flow controllers or by pressure rise measurement in a defined reference volume. If the pump is used upstream of the pre-concentration-trap it has to be ensured that no artefacts are produced by the pump.

After sampling, the trap should be flushed with the carrier gas in forward mode (same flow direction as during the sampling) at the same temperature for an adequate amount of time (see Table 7, dry purge) to allow removal of remaining water, oxygen, and potentially adsorbed non-VOC gases (e.g. CO_2, noble gases) from the trap. This prevents formation of artefacts due to reactions of the aforementioned gases with adsorbent material, and degradation of the chromatography.

NMHCs are normally transferred from the pre-concentration trap to the analytical system by heating the trap (electrically or by other means) in counter-flow. The final temperature should be reached as fast as possible and should be high enough to release all NMHCs. Analytes are transferred to the gas chromatography system by carrier gas flow. After this transfer, the pre-concentration-trap has to be reconditioned by heating it to a higher temperature than needed to release the NMHCs and flushing it backwards with carrier gas. In case that NMHC injection is not rapid enough to obtain sharp chromatographical peaks, which may be due to large pre-concentration-trap volumes or slow heating rate of the trap, a second focusing-trap should be installed between the pre-concentration-trap and the analytical column. This again may be adsorptive or cryogenic but needs to have a substantially smaller internal volume than the pre-concentration-trap. Another option to achieve better peak shapes is to use a trap-circuit separated by a 4-port, 2 position valve. In such a configuration, the pre-concentration-trap is first heated up and then the well mixed desorbed VOCs in carrier gas are injected onto the column in an injection band which is determined by the ratio of the gas volume in the trap circuit and the carrier gas flow rate.

Split injection is commonly used to improve the shapes of chromatographic peaks in many applications. However, the inherently involved loss of sensitivity is in conflict with the low atmospheric mixing ratios of NMHCs (Hoerger et al., 2015). Therefore it is recommended to use direct column injection.

Table 8: Examples of successfully employed pre-concentration systems (and thermo-desorption systems) (Hoerger et al., 2015).

Adsorbents	Temperature and flows	Sample Volume	Systems	Recommended for
custom made preconcentration systems				
Glass beads in 1/8" Silcosteel tubing	Ads. -180°C and 50 ml/min (LN2 cooling) Des. 340°C and 5ml/min dry purge 1min @ 10ml/min He	750ml	Hohenpeißenberg, DWD (Plass-Dülmer et al., 2002)*	NMHCs (C_2-C_8)
Fused Silica beads, Carboxene®1003, Carboxene®1016, Carbosieve®S-III	Ads. -45°C Des. 235°C	600ml	Rigi, Empa*	NMHCs (C_2-C_8)
Carbopack®BHT	Ads. -120°C Des. 200°C	400ml	WCC-VOC, KIT Garmisch*	NMHCs (C_2-C_6)
Tenax TA/Carbopack X/ Carboxene®569 in fritted glass tube	Ads. 30°C, 80 ml/min Des. 200°C, 20 ml/min** dry purge 8 min @ 10ml/min He	1500ml	Hohenpeißenberg	NMHCs (C_4-C_{14})
Commercial preconcentration systems				
Markes UNITY TD Carbopack®B, Carboxen®1000	Ads. -20°C Des. 350°C	1000ml	Cape Verde, (Hopkins et al., 2003) Empa	NMHCs (C_2-C_8)
ENTECH TD Glass beads	Ads. -120°C Des. 70°C****	360ml	IMT Lille Douai	NMHCs (C_2-C_8)
Medusa Hayesep®D	Ads. -160°C Des. 100°C	1000ml	Medusa/AGAGE (Miller et al, 2008)	NMHCs (C_2-C_5), aromatics

* Reference systems during ACTRIS intercomparison (Hoerger et al., 2015).
** Refocussing on Methyl Silicone Capillary, ads. -180°C 20ml/min, des. 60°C, 2.5ml/min
*** needs to be tested regularly, depletion process increases with age of td tube
**** Refocussing on glass beads, Tenax®, Ads. -50°C, Des. 220°C

5.3 Capillary columns for GC analysis of NMHCs

Capillary columns exhibit better separation efficiencies and higher inertness compared to packed columns. Despite their lower capacity they are suitable for most applications in atmospheric NMHC analysis. There are two types of capillary columns that are most widely used for the analysis: PLOT (Porous Layer Open Tubular), WCOT (Wall Coated Open Tubular) and liquid film columns (Helmig, 1999). Table 9 lists a number of columns which are successfully employed in NMHCs analysis. More possible analytical columns are listed in the Appendix 3, in Helmig (1999) and in Hoerger et al. (2015).

Table 9: List of recommended NMHC columns.

VOCS	Column	T_{range}	Typ. Dim	Comments	Citation
NMHCs C_2-C_8	AL_2O_3/KCL PLOT	~40°C – 200°C	50m x 0.53mm	Acetylene losses may occur, check response factors	Plass-Dülmer et al., 2002 Hoerger et al., 2015

NMHCs C_2-C_8	AL_2O_3/Na_2SO_4 PLOT	~40°C – 200°C	50m x 0.53mm		Hoerger et al., 2015
NMHCs C_5 and higher	DB-1**	-60°C – 350°C	50m x 0.32mm	Co-elution with OVOCs, separation of light NMHC difficult, applicable for BVOC	Riemer et al., 1998
	DB-5**		50m x 0.22mm		Hoerger et al., 2015

* or similar columns as listed in table 1 in Appendix 3
** or similar columns as listed in table 2, in Appendix 3

5.4 Detection of NMHCs

Two different detection principles are used for the analysis of atmospheric NMHC species: Flame Ionization Detection (FID) and Mass Spectrometry (MS). In this section the operation conditions of these detectors are described together with their advantages and disadvantages (Table 10). For the calculation of molar ratios from these two detectors see Section 7.

Table 10: Advantages and disadvantages of flame ionization (FID) and mass spectrometric (MS) detection

	FID	**MS**
Advantages	+ sensitive, robust, simple in design and easy to use + very stable performance with typically less than 2% sensitivity drift over one month + response of NMHC is proportional to the mass or carbon number and allows easy quantification + quantification other VOCs with effective carbon number (ECN) concept + ECN , allows effective QA (see Section 8.1.1) + not sensitive to traces of water, N_2, O_2, and noble gases + relatively low costs	+ compound identifying capabilities + second dimension (mass tracks) for better resolution + substance-specific quantification (overlaying peaks can be separated by compound specific mass tracks)
Disadvantages	- not substance-specific, identification just by retention time -Co-eluting peaks cannot be quantified individually	- each substance needs individual calibration - variable sensitivity requires more frequent calibration measurements, generally, calibration of each sample run is recommended - instruments need regular tuning - expensive - may show non-linear behaviour

FID is the favourable detection system whenever identification can be achieved simply based on the retention times. If the resolution of the chromatographic system does not allow unambiguous identification of different compounds based on retention time alone, a mass spectrometer is recommended as detector for its compound identifying capabilities. Other possible detectors are currently not advantageous and are falling short with respect to sensitivity, robustness, ease of use and stability.

5.4.1 Flame Ionization Detector (FID): Operating conditions

The operation principle is based on the ionization of organics in a hydrogen flame. The abundance of formed ions is proportional to the concentration of organic species and its number of carbons.

A FID needs air and H_2 to produce the flame and a make-up gas for proper operation; the flow rates should be well controlled to achieve stable operation of the detector (Table 11). It is essential to have low NMHCs levels or at least low fluctuation in NMHCs levels in the operating gases.

Table 11: Operating conditions for FID

Gas	**Supply**	**Flow rate***	**Temperature**
Air	Synthetic air (quality 5.0) or ambient air catalytically cleaned (Pd or Pt catalyst at 350°C-450°C)	300-350 ml/min	T_{FID} **>= $T_{column,max}$ to avoid or minimize deposition of column residues
H_2	Cylinder (H_2 quality 5.0) or H_2 generator	30 ml/min	
Make Up Gas (e.g. N_2)	Cylinders, grade 5.0 or higher	30 ml/min	

*The suitable flows might vary depending on the FID used; it is important to check the total flows of the individual gases, including the carrier gas, and stay within the specified margins by the FID manufacturer.
**Follow specification of the manufacturer

FID systems are highly linear ($\sim 10^7$, Baars and Schaller, 1994) and the sensitivity is generally sufficient to do analysis in background atmosphere at pmol/mol levels (ppt), e.g. detection limits of GC-FID systems for analysing 1 litre of air are typically better than 3 pmol/mol (e.g. Plass-Dülmer et al., 2002; Hoerger et al., 2015).

For GC-FID systems, it is recommended to perform calibration, zero and target gas measurements regularly (see section 7.1).

5.4.2 Mass Spectrometer (MS): Operating conditions

In a MS the analytes are ionized in the ion source either by chemical (CI) or electron ionization (EI). EI is normally used for analysis of NMHCs. The resulting gas-phase ions are measured depending on their specific mass-to-charge ratio. Thus, even overlying peaks can be separated by analysing different, compound specific mass tracks.

Concerning operating temperatures of a MS refer to the specs of the specific system. However, for the transfer line (capillary which transfers the sample from the column to the ion source) and the ion source a temperature $T \geq T_{column,max}$ should be chosen in order to minimize deposition of column residues, residence time and adsorption effects.

The sensitivity of a MS is not stable and the signal depends on a set of tuneable parameters (e.g. repeller, lenses, and multiplier voltages), which influence ionization and ion transmission process as well as the detection of the charged ions at an electron multiplier. Usually a decrease of MS sensitivity is observed over time which results in a decrease of peak area. Three measures are thus required:

i) Tracking the sensitivity with frequent working standard measurements. The frequency of the working standard measurements should ensure that the decline in sensitivity is accurately tracked over time (e.g. if continuous measurements are performed it is recommended to perform a working standard measurement every 2-4 sample; at least daily, close to the ambient air sample).

ii) Regular auto-tuning of the MS: Weekly to monthly, depending on the drift strength observed in the individual systems but at least every second month.

iii) If the tuning does not yield sufficient results, the ion source has to be cleaned using the procedure specified by the manufacturer.

Note: Often the MS software has a minimal signal threshold set. If this is activated and set to > zero, this influences the signal noise and may affect the Detection limit and thus the determination and integration of small peaks. For ambient air measurements at background level it is recommended to de-activate the signal threshold or set it to zero.

6. Reference materials

The Central Calibration Laboratory (CCL) maintains the primary standard that defines the calibration scale for GAW sites. For NMHCs, the CCL is the National Physical Laboratory (NPL; http://www.npl.co.uk/). The calibration scale is transferred to the stations and laboratories through laboratory standards that are prepared by the CCL and that are directly traceable to the primary standard. In case a station does not use a laboratory standard from the CCL, it has to demonstrate that the laboratory standard used is linked to the calibration scale by direct comparisons in time intervals that correspond to the stability of the standard mixture. This standard will have a higher uncertainty than the laboratory standard produced from the CCL as uncertainties increase the further you move down the traceability chain away from the primary standard.

Minimum requirements for a station that need to be fulfilled:

1. A (secondary) **laboratory standard** which has to be a multi-component standard (synthetic mixture), produced and certified by the CCL (recommended), or at least traceable to the CCL, for ensuring traceability of the measurements to the WMO GAW calibration scale.

2. One or more (tertiary) **working standards** that cover most (ideally all) components measured and are used for regular calibration of the measurements, regular or high consumption applications like standard addition or dilution series, etc. These working standards can be either other certified or custom made synthetic mixtures and are calibrated versus the laboratory standard.

3. A **target gas** which is preferably compressed whole air but could also be a synthetic mixture calibrated by a reference laboratory (CCL or WCC) (recommended) but at least calibrated by the station against the laboratory standard: it is used to check the assigned values of the calibration mixtures and the calibration process itself and is treated as an air sample with unknown mole fraction. Monitoring of the target gas results yields information about the performance of the instrument, drifts of the laboratory standard and potential instrumental problems.

7. Quality assurance

Quality assurance comprises the actions required to achieve the requested quality of GAW NMHC measurements. It also includes the methods of how to control the quality and the frequency of their use. The evaluation of data and of quality control actions is described in section 8 below.

Quality assurance (QA) follows the principles of the GAW QA system (http://www.wmo.int/pages/prog/arep/gaw/qassurance.html):

i) Network-wide use of only one reference standard or scale (primary standard). In consequence, there is only one institution that is responsible for this standard (CCL).
ii) Full traceability to the primary standard of all measurements made by Global, Regional and Contributing GAW stations.
iii) The definition of data quality objectives (DQOs).
iv) Establishment of guidelines on how to meet these quality targets, i.e., harmonized measurement techniques based on Measurement Guidelines (MGs) and Standard Operating Procedures (SOPs).
v) Establishment of MGs or SOPs for these measurements.
vi) Use of detailed log books for each parameter containing comprehensive meta information related to the measurements, maintenance, and 'internal' calibrations.
vii) Regular independent assessments (system and performance audits, Performance audit: check measurements versus DQOs and traceability System audit: overall conformity of a station with the principles of GAW).
viii) Timely submission of data and associated metadata to the responsible World Data Centre as a means of permitting independent review of data by a wider community.

As part of QA, each station performing NMHC measurements needs to have a system of laboratory and workings standards, target gases and a procedure to perform blank measurements (all specified below). Table 12 lists recommended frequencies of the respective measurements. Target gases are whole air mixtures in pressurized cylinders with specified mixing ratios. They are used in regular quality control. If results of target gas measurements are not within the DQOs, the instrument and quality assurance system have to be optimized in order to achieve better results with potential consequences on more frequent calibration, blank and target gas measurements. Another QC procedure is standard addition measurements to characterize artefacts of more reactive NMHC compounds (see below).

Table 12: Recommended frequencies for standard, blank and target measurements (in parenthesis the minimum acceptable frequencies are specified for periods without irregularities of the GC system).

System	Laboratory Standard	Working Standard	Blank	Target
GC-FID	2/year (1/year)*	2/month (1/month)*	1/week (1/month)	1/month*
GC-MS	2/year (1/year)*	Every 2-4th sample (1/day)	1/week (1/month)	1/month*

*Measurement series with 3-5 replicates

7.1 Calibration procedure

Regular calibration is essential for performing good quality measurements. To stay within the DQOs, the sensitivity of a GC system should be stable well within the DQOs between calibrations. Similarly, blank values (see below) and their reproducibility should not change substantially, i.e. less than specifications for < 100 pmol/mol in DQOs. Both, calibration and target gas measurements enable the detection of drifts in the measurement system which, in case of their occurrence, should be understood and minimized.

If a drift in the working or laboratory standard is observed or a discrepancy with a new laboratory standard beyond the combined uncertainties occurs, the discrepancy has to be resolved as soon as possible. Options in such a situation are:

- send the laboratory standard for recalibration to the CCL or WCC
- ask other stations for a high level standard for an independent check
- check available results from past comparisons

Station operators should try to identify when the drift occurred and apply a correction for those periods in which the drift can be well described. If this is not possible, the uncertainty during this period needs to be increased to include the range of the unexplained drift. A drift in a standard can be identified by comparison of two different calibration gases: If the difference (e.g. mole fraction, C-response factor, see 7.4) between two cylinders reveals a drift for one or few compounds, it is likely that the reason is not a change of instrument characteristics.

In case stations use working standards/target gases not comprising all components measured, it is justified to determine the sensitivity drift of the instrument by this reduced compound mix if it comprises major constituents of the various groups of NMHCs and it covers the range of volatility and polarity encountered in the samples. Calibration factors of compounds not present in the working standard may then be scaled by calibration factors of physically similar behaving compounds present in the standard (7.4.2).

Low volatile NMHCs might show a lower repeatability and reproducibility as surface equilibria need more time to be established and slight changes in pressure and temperature may affect these equilibria. Frequently used dynamic dilution systems might require substantial warm-up times and it is recommended to heat lines and valves, and keep dilution systems running all time.

7.1.1 Measurements of secondary laboratory, tertiary working standards and target gases

Generally it is recommended to leave pressure regulators and transfer lines attached to the laboratory/working standard/target gas cylinders in order to minimize the risk of contamination and reduce equilibration times. Laboratory gloves (i.e. powder-free latex) should be worn whenever working with parts in contact with test gases in order to avoid contamination.

Furthermore, several issues should be considered:

- *Transfer line and ferrule material:*
    - Silconert 1000/2000 or other stainless steel tubing with a passivated internal surface.
    - The use of Vespel/Graphite (VG) ferrules is recommended as these provide a tight sealing while not damaging the tubing. They can be used several times and should only be replaced in case that sealing or contamination problems are present (follow the mounting instructions of the manufacturer).

- *Installation of a new standard gas cylinder*
    - Pressure regulator and the transfer line with capped fitting on the GC connection side should be mounted at least 24 hours before the measurement.
    - After installation, the regulator and transfer line need to be flushed (pressurize and release pressure without allowing air to enter line) at least 3 times with the calibration gas.
    - Initial leak check: After flushing, pressurize the pressure regulator (cylinder pressure) and the plugged transfer line (at the level of pressure which is needed for the measurement set

up). With the cylinder valve closed, check the pressure for at least 10 minutes; if not constant, check all connections, tighten gently, and repeat the check.

It is strongly recommended to use no liquid leak tester solutions (e.g., snoop) as they might contaminate the system.

- *Equilibration*
  For equilibration keep the pressure regulator and the transfer line (plugged at the end) pressurized with the standard gas for at least 24 hours. During this equilibration time, the cylinder valve is closed to avoid back diffusion of potential contaminants into the cylinder and to avoid losing sample through possible leakages. This setup also serves as a static leak test as the upstream regulator pressure should not change during the 24 h equilibration period.

- *Connection to the instrument*
  Connect the test gas cylinder to an appropriate instrument inlet port. Then flush the whole inlet line for at least another 3 times and leave the gas cylinder connected to your instrument. It is recommended to open the standard cylinder valve only during the sampling periods unless you use an automated measurements sequence in unattended operation. It is recommended to leave the standard cylinder permanently connected to the GC system. If this is not possible:
  a. Leave the pressure regulator mounted on the cylinder, keep it pressurized and repeat the "connection to the instrument" method every time you connect the cylinder to the standard port.
  b. If you have to disconnect the pressure regulator, it is recommended to follow the complete "installation of a new gas cylinder" – method every time.

- *Measurement procedure*
  The standard gas measurement should follow the typical measurement procedure. However, the measurement of the standard gas should be performed after an initial flushing period through the GC valve system which is sufficiently long to achieve equilibration in the lines (typically 10 min with 30 ml/min are sufficient for NMHCs). A series of standard measurements must be performed containing at least two appropriate measurements; often a series of 3 measurements is sufficient.

7.1.2 Measurement of zero gas (blanks)

In this context, "Zero gas" is a hydrocarbon free gas. The routine measurement of zero gas is part of the QA program to be followed at all stations. It yields information about artefacts due to release of adsorbed hydrocarbons or leaks in the sample path. Blank values should be as low as possible. "Zero gases" can be:

- catalytically cleaned ambient air (Pt or Pd catalyst at 400°C), which is very close to the sample gas with similar humidity.
- synthetic gas (e.g. He or N_2) of at least 5.0 or higher quality.

This method is not as good but easier to handle. In N_2 5.0 quality, traces of VOC, e.g. methanol can be present. To reduce impurities in synthetic gas a post-cleaning is recommended (e.g. cooled charcoal and molecular sieve cartridges).

- In case of synthetic zero gas, it is recommended to humidify it, especially for offline sampling, as surface artefacts are minimized due to passivation of active surface sites. Humidification requires high purity water (e.g. HPLC grade, or deionized water). The humidification device has to be flushed with zero gas at least 2 hours in order to remove compounds potentially dissolved.

Often, trace amounts of hydrocarbons in the pmol/mol range are present as impurities in the zero gas. This creates an inherent problem: blank values caused by impurities cannot easily be separated from blank artefacts as mentioned before. Accordingly, care has to be taken to identify the origin of blanks found in zero gas measurements. Stations have to test zero-gases by comparing the blank values obtained in measurements of different hydrocarbon free gases aiming at the lowest levels.

As blank values might vary over time, it is recommended to conduct weekly zero gas measurements.

Some occasionally observed blank substances are listed in table 13 below.

Table 13: Occasionally observed NMHCs in blank samples.

Compound	**Cause**
Various	column bleeding, leakages, contamination
Benzene	Potentially associated with new traps or overheated traps
C_2-C_4 alkenes	often observed in systems using Nafion® Dryers ((Gong and Demerjian, 1995; Plass-Dülmer et al., 2002, Hoerger et al., 2015) and references therein)

For blank measurements, a zero gas is sampled via the usual air sample path. Thus, the zero gas passes the ozone and particle filter (if present), the water trap, and sampling unit just like ambient air samples. The sample volume for zero gas should be the same as for ambient air samples.

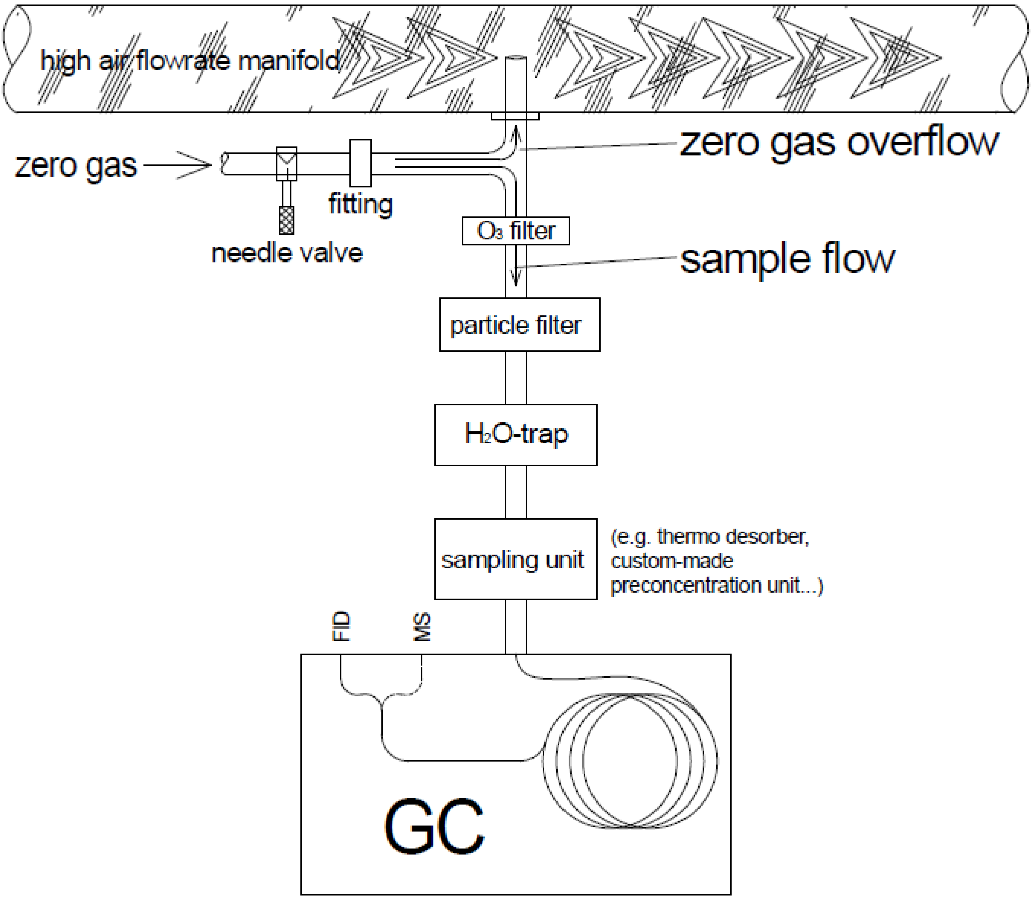


Figure 1: Example for a zero gas measurement set-up with a high flow inlet manifold. The sequence of the filters can be changed depending on the individual system requirements.

7.1.3 The Standard Addition Method for Detecting Reaction Artefacts during Sampling

Reactions between unsaturated VOCs (alkenes, alkynes) might occur in the presence of ozone or other reactive constituents of the ambient air sample gas during the sampling process. Therefore, an O_3 filter is recommended (see Section 5.1.2.). The performance of this filter should be checked regularly by standard addition measurements. This can for example be tested by adding a high concentrated standard gas mixture (e.g. VOCs at 100 nmol/mol level) into the ambient air stream with a low volume flow that the ambient air peak areas are negligible, while the gas matrix itself is dominated by ambient air (e.g. >90%). Ideally the ambient air should contain ozone at mixing ratios which are typical for local high ozone conditions. The standard mixture should contain ozone reactive compounds (e.g. alkenes). If the peak area ratio of the standard addition and a pure standard measurement are identical for all compounds and as defined by the dilution factor, no corresponding artefacts exist under the tested conditions.

The set up shown in Figure 1 can be used for the standard addition measurements. Instead of the zero gas, the high concentrated standard is added. It is recommended to use a quartz capillary without needle valve for the application of the standard.

7.2 Audit procedures

Audits are performed by the WCC-VOC (KIT Garmisch). Audits check for the conformity of a station to GAW QA system including recommendations of this Measurement Guideline, and the conformity of a measurement of test gases with targeted values within the DQOs (see definitions and procedures of performance and system audits in GAW Report No. 142, WMO 2001) The reference for conformity of a station will evolve as the GAW QA system evolves, however, it will check all parts of the sampling and instrument set-up; the calibration and zero gas systems; the QA, training and instructions at the station; the calibration, zero gas, target gas, and standard addition data; the data delivery; the results from intercomparison exercises, the uncertainty evaluation; the logbooks (see next section 7.3); the scientific use of the data; and the overall equipment of the station.

7.3 Measurement protocol

It is required that each station has the following log sheets/book either in electronic or paper-based form:

1. Instrument logbook with all operation parameters, significant changes, characterisations, tests results, etc.
2. Measurement logbook with all measurements including the type of measurement, the time of measurement in UTC (start sampling, end sampling, start GC run), sampled volume (dry volume), and comments (anything unusual).
3. A log of the used calibration factors and blank value determinations from zero gas measurements.
4. A log of all working standard and target gas measurements.
5. An error log with ascribed uncertainty contributions to compound measurements due to peak-overlap, scatter of blank values, unusual low reproducibility, unstable sensitivity and so on as well as all other unexplained deviations from normal instrument performance.
6. It has to be assured that the station records representative meteorological data (temp, humidity, wind velocity and direction).

7.4 Mole fractions and measurement uncertainties

This section describes the routine determination of mole fractions and the assessment of measurement uncertainty. Each site has to assess the measurement uncertainty in order to provide over the time the level of quality associated to the data, regarding the method used and its performance.

Note: in the following section all formula are given for compound “i”, but the index “i” is not indicated):

7.4.1 Calculation of mole fractions for linear detection systems

For substances quantifiable via a standard reference gas mixture, the mole fraction χ_{sample} of a compound in a sample is calculated as:

$$\chi_{sample} = \frac{A_{sample} - A_{blank}}{V_{sample}} * f_{cal} \qquad \text{(F1)}$$

With the calibration factor

$$f_{cal} = \frac{V_{cal} * \chi_{cal}}{A_{cal} - A_{blank}} \qquad \text{(F2)}$$

A_{sample}= peak area of sample measurement

A_{cal} = peak area of calibration gas measurement
A_{blank}=possible blank value determined in zero gas measurements
χ_{cal} = certified mole fraction of calibration gas
V_{cal} = sample volume of calibration gas
V_{sample} = sample volume of sample

In few cases, the blank values obtained in zero gas measurements can be significantly higher than the determined peak areas yielding negative mole fractions according to (F1) and (F2). Then the zero gas procedure and further potential sources of blank values have to be checked and appropriate uncertainties of the blank values have to be estimated.

In case of few substances not present in the standard reference gas mixture (laboratory and working standard), the respective calibration factors of those compounds may be scaled by calibration factors of physically similar behaving compounds present in the standard (section 7.1 and 7.4.2)). This, however, is only possible in FID systems and is an exception for few and less important compounds. Stations should favour complete substance mixtures in their respective working standards. For MS systems and the above given DQOs, it is not possible to quantify substances that are not present and calibrated in the working standards. Thus, MS systems need to have working standards covering all compounds to be measured.

7.4.2 FID: effective carbon number

The effective carbon number concept (ECN) (Sternberg et al., 1962, Dietz et al., 1967) states that the response (peak area) of the FID is proportional to the number of molecules times the effective number of carbon atoms per analyte molecule. This holds for single hydrogen-carbon bonds. If other bonds in a specific molecule occur, the response of the respective carbon atom is adjusted to yield an effective carbon number. The carbon response factor C_{resp} is expressed as:

$$C_{resp} = \frac{A_{cal} - A_{blank}}{C_{num} * y * V_{cal} * \chi_{cal}} = \frac{1}{C_{num} * y * f_{cal}} \quad \text{, with} \qquad \text{(F3)}$$

C_{num} = Number of C atoms in the molecule (e.g. for n-Pentane, C_{num} = 5)
and
Y is the ECN contribution, *i.e*. 1.0 for carbon in aliphatic and aromatic bonds, 0.95 per C in olefinic bonds, 1.3 in acetylenic bonds (Sternberg et al., 1962).

The C-response factor C_{resp} is derived for each compound from the measurement of the certified standard reference gas mixture. Using the ECN-concept, reliable calibration factors can also be estimated for compounds not present in the calibration gas mixture. In this case, the mole fraction is calculated via the mean C-response factor $\overline{C}_{resp}$, which is determined from selected compounds in the standard gas measurements averaging the C_{resp} factors for those substances.

The mole fraction of a substance is then

$$\chi_{sample} = \frac{A_{sample} - A_{blank}}{V_{sample} \times C_{num} \times \bar{C}_{resp} \times y} \qquad \text{(F4)}$$

7.4.3 Determination of the uncertainty

The uncertainty reflects combination of both random and systematic errors in the measurement process. The main factors influencing the uncertainty of the measurements are:

- the reproducibility of the measurement method $u\chi_{prec}$
- uncertainty due to measurements close to limit of detection $u\chi_{zero}$
- uncertainty due to the uncertainty of the calibration gas $u\chi_{cal}$
- uncertainty due to systematic errors of the measurement system used $u\chi_{instr}$, namely:
  - integration errors (due to peak overlay, tailing, bad peak separation) $u\chi_{\text{int}}$
  - systematic errors in sample volume determination $u\chi_{vol}$
  - further instrumental problems (e.g. sampling line artefacts, carry over, changes of split flow rates) $u\chi_{instrument}$
  - error due to linearity issues (especially for the MS instruments) $u\chi_{lin}$
- when off-line method is used, the errors due to the sampling device have to be considered (e.g. sampling volume accuracy, storage issues, sampler blank) $u\chi_{sampling}$

According to the “Guide to the Expression of Uncertainty in Measurement” (JCGM 100, 2008), the combined uncertainty is calculated using the law of propagation of the uncertainties (considering that the standard uncertainties are not correlated):

$$u\chi^2_{sample} = u\chi^2_{prec} + u\chi^2_{cal} + u\chi^2_{instr} + u\chi^2_{sampling} \qquad \text{(F5)}$$

where

$$u\chi^2_{instr} = u\chi^2_{\text{int}} + u\chi^2_{vol} + u\chi^2_{instrument} + u\chi^2_{lin} \qquad \text{(F6)}$$

The standard uncertainties are determined individually for each analysed compound.

- $u\chi_{prec}$, the precision reflects the variability of the measurement system due to random errors. It can be derived from series of target gas (whole air) or working standard measurements. The mole fractions of NMHC measured should reflect the amounts that are normally measured at a given location. Generally, these series should use the identical sample path as ambient air samples, e.g. like shown for standard addition measurements in Fig. 3.

  Precision covers the random error contributions due to the sampling volume, the integration (only random errors of volume determination and peak integration are captured, the systematic errors are considered thereafter), blank variation, and the sampling system (in case of identical sample paths, see above).

The precision $u\chi_{prec}$ has to be evaluated in reproducibility conditions (ISO 5725-1, 1994), using the relative standard deviation $\left(\sigma_{series}^{rel}\right)$ of at least 6 individual measurements of target gas or working standard over the considered interval. (Note: this does not aim for the lowest possible precision but a realistic precision applicable for single measurements of a given ambient air sample).

Since usually working standards are in a higher concentration range than air samples, the precision will be underestimated for small concentrations close to the detection limit χ_D. Therefore, it is necessary to include the error for low concentration represented by the standard deviation of blanks which are commonly used to determine the detection limit.

Finally $u\chi_{prec}$ is thus calculated as:

$$u\chi_{prec}^2 = \left(\chi_{sample} * \sigma_{series}^{rel}\right)^2 + \left(\frac{\chi_D}{3}\right)^2 \qquad \text{(F7)}$$

- $u\chi_{cal}$ *the standard uncertainty for the single point calibration is given as:*

$$u\chi_{cal} = \frac{A_{sample} * V_{cal}}{V_{sample} * A_{cal}} * u_{cal} \qquad \text{(F8)}$$

where u_{cal} is the certified uncertainty of the standard gas (or the working standard) and it includes the possible drift of the standard. Please note that the standard gas concentration is generally given with an expanded uncertainty having a coverage factor of k=2. The standard uncertainty u_{cal} is thus half of the expanded uncertainty.

- $u\chi_{\text{int}}$, the standard uncertainty due to the integration is determined based on the equation F3 and is equal to :

$$u\chi_{\text{int}}^2 = \left(\frac{f_{cal}}{V_{sample}} * uA_{\text{int},sample}\right)^2 + \left(\frac{A_{sample} * V_{cal} * \chi_{cal}}{V_{sample} * A_{cal}^2} * uA_{\text{int},cal}\right)^2 \qquad \text{(F9)}$$

where $uA_{\text{int},cal}$ reflects the potential error in peak area due to integration of the calibration measurement and $uA_{\text{int},sample}$ the potential integration error of the sample measurement, respectively. Examples of determination of these uncertainties are given in the appendix 4.

- $u\chi_{vol}$, the systematic error of the sample volume, can be neglected when $V_{sample} = V_{cal}$. When the sample volume and calibration volume are different, a linearity check should be performed to calculate the relative deviation of the two volumes from linearity. This value will be $u\chi_{vol}$. The random volume error is covered by the measurement precision for measurement systems having a flow controller that corrects for temperature and pressure (e.g. Mass Flow Controller, critical orifices). Mass Flow Controllers are prone to drift, therefore it is important to take this into account or to calibrate the measurement system regularly. For off-line sampling using sorbent tubes, the uncertainty of the volume sampled depends on the sampling flow rate and sampling time, both associated with uncertainties that need to be estimated.

- $u\chi_{instrument}$, the standard uncertainty due to specific instrumental problems (e.g. sampling line artefacts, carry over, changes of split flow rates) has to be evaluated for each site specifically. This uncertainty can be derived from tests, audits or intercomparison results.
- $u\chi_{lin}$, the standard uncertainty due to lack of linearity of the measurement system. This can be calculated by fitting a linear regression function of the measured amount fractions against calibrated amount fractions. At least 4 standard amount fractions should be available. They can be obtained for example
  * by dynamic dilution (ISO 6145 series) of a gravimetrically prepared (ISO 6142-1, 2015) standard gas (or working standard) or
  * a set of calibrations gases covering the whole measurement range or
  * injecting a calibration gas or working standard at different sample volumes

  The uncertainty $u\chi_{lin}$ corresponds to the relative residual from the linear regression function having the largest value

- $u\chi_{sampling}$, the standard uncertainty due to application of off-line sampling techniques depends on the technique used. Contributions to the uncertainty common to all off-line techniques (cleaning of the samplers, storage, adsorption effects, etc.) should be evaluated case-by-case and per individual component. If not available in literature, a proper validation of the sorbent tubes is recommended prior to their use in the field to establish the efficiency of adsorption/desorption and the safe sampling volume at different composition levels and atmospheric conditions.

Finally, the overall uncertainty (or the combined standard uncertainty) is multiplied by a coverage factor k=2 to provide the expanded uncertainty ($U\chi_{sample}$):

$$U\chi_{sample} = 2 \times u\chi_{sample} \tag{F10}$$

An example of calculation is given in the appendix.

For data submission $u\chi_{prec}$ will be reported as well as the total expanded uncertainty $U\chi_{sample}$.

7.4.4 Determination of detection limit

Due to impurities, electronics or other analytical problems the baseline of gas chromatographic systems is to a certain degree noisy. Thus, the lowest quantifiable quantity of a substance - the detection limit of the measurement system – is different from zero.

Measurements at very low levels are required for systems with very low detection limits. The detection capability, i.e. detection limit χ_D [pmol/mol], is defined by IUPAC as the smallest measure that can be detected with reasonable certainty for a given analytical procedure.

The general concept to determine the detection limit according to IUPAC has to consider several potential impacts on the measuring system as there are matrix effects of the sample gas (humidity, oxygen, …), impurities in the test measurements to determine blank values, the linearity and reproducibility of the system response etc. Thus, conditions in measurements to determine blanks need to be as close as possible to ambient air sample measurements. Given that conditions are comparable, the system response is highly reproducible, and the probability functions are normal distributed for a zero determination and a small peak determination with the same variance, then the limit of detection LD can be approximated by (Currie, 1995):

$\chi_D = 2t_{1-\alpha,\nu}\ \sigma_0$

With σ_0 is the standard deviation of determined blank values (integration of blank peaks or blank baseline for intervals of peak widths if the peak is absent), $t_{1-0.05,\nu}$ is the student's-t for 5% probability, for 25 blank determinations it becomes 1.71 and for 10 repetitions 1.83 (9 degrees of freedom). Thus, using 10 blank determinations and all assumptions valid, the above equation is reduced to:

$\chi_D = 3.7\ \sigma_0$

In the preceding section, in (F7) an approximation with factor 3 was used.

8. Data Management

In this chapter all data related procedures and recommendations are given from QC measures using calibration gas and ambient air measurements to the final data submission to the data centre.

8.1 Data evaluation

This section gives examples of QC tools which are recommended for regularly checking the quality of the GAW NMHC measurements. It comprises visualizations of the results of FID-C-response factors in working standard measurements, the results of target and standard addition measurements, and gives QC plots of the final data evaluation with focus on correlated behaviour between selected NMHCs with respect to time and concentration.

8.1.1 Time series of calibration gas measurements

Time series of the calibration factor, peak area or especially for GC-FID systems the C-response factor are valuable tools to monitor the system status over time.

A GC-FID system can be characterized for adsorptive losses or artefacts (e.g. poor peak separation) by making use of the known carbon response C_{resp} (see Section 7.4.2, F3) (Plass-Duelmer et al., 2002). When the carbon responses for the various organic compounds are calculated, they should agree within a few percent for C_2-C_8 NMHC, except for ethyne (Burns et al., 1983; Dietz, 1967; Faiola et al., 2012; Gong and Demerjian, 1995; Scanlon and Willis, 1985; Sternberg et al., 1962). Deviations are often due to poor peak separation, adsorptive losses in the system, artificial changes at active sites, or FID operation conditions not in the optimum range as specified by the manufacturer. Efforts should be taken to optimize the system. As long as the FID conditions do not change, the C-response factor is expected to be constant.

Since a MS is more variable these time series are expected to show drifts and steps due to sensitivity changes. But as for the C-response factor, a similar behaviour is expected for similar compounds.

In Figure 2, a time series of C-response factors for a number of NMHCs is shown. Several features can be observed in this example: With the exception ethyne, all shown substances agree within 3% and resemble the same behaviour over time. A reason for the drift (~ -4%) might be e.g. a slow change of FID characteristics which are, however, captured by the frequent standard measurements.

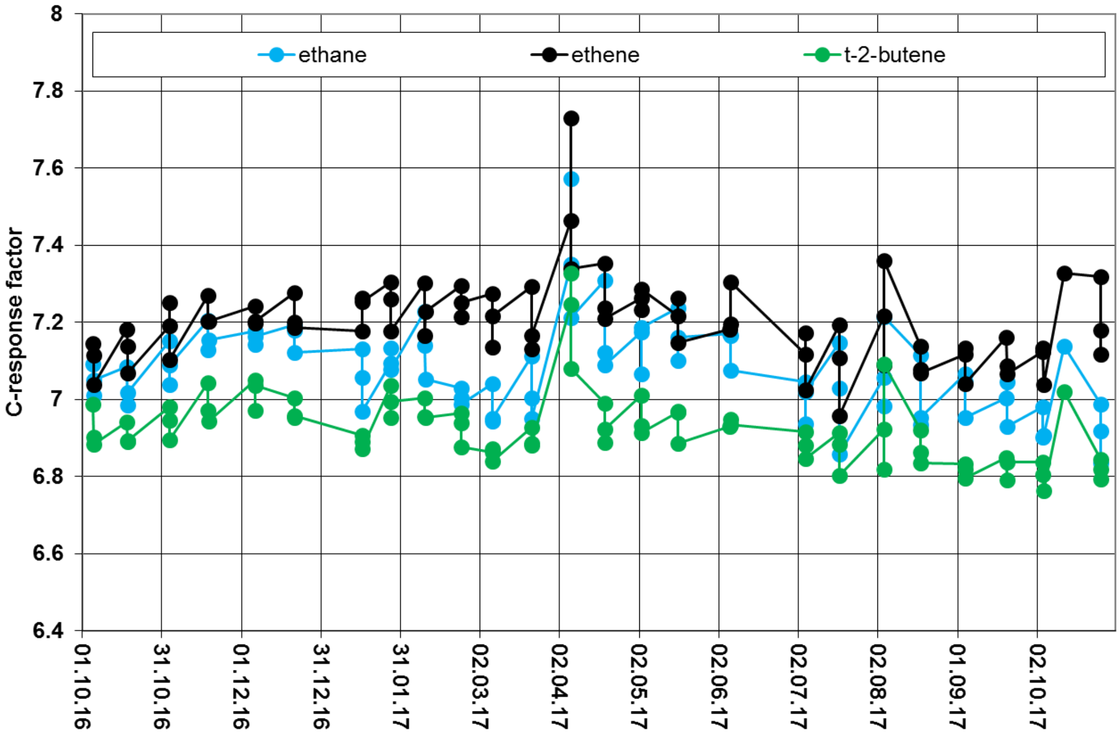


Figure 2: Time series of C-response factors of ca. 1 nmol/mol working standard measurements (bi-weekly) with a GC-FID system.

8.1.2 Target gas measurements

In Figure 3, a series of target gas measurements (whole air) is shown. Here, the determined mole fraction for selected analysed compounds is plotted over time in a log scale. Relative changes are detectable as deviations from constant values. The plot shows compounds with mole fraction of more than 50 pmol/mol. Except for 2-methylpropene (due to blank values), it should be pointed out that reproducibility gets poorer for compounds with higher molecular weight and towards lower mole fractions. However, the reproducibility is still mostly within 2 pmol/mol or a few percent. This plot shows monthly repeatability of a series of 5 replicates, and monthly reproducibility throughout the year for ambient air mole fraction levels and ambient air matrix.

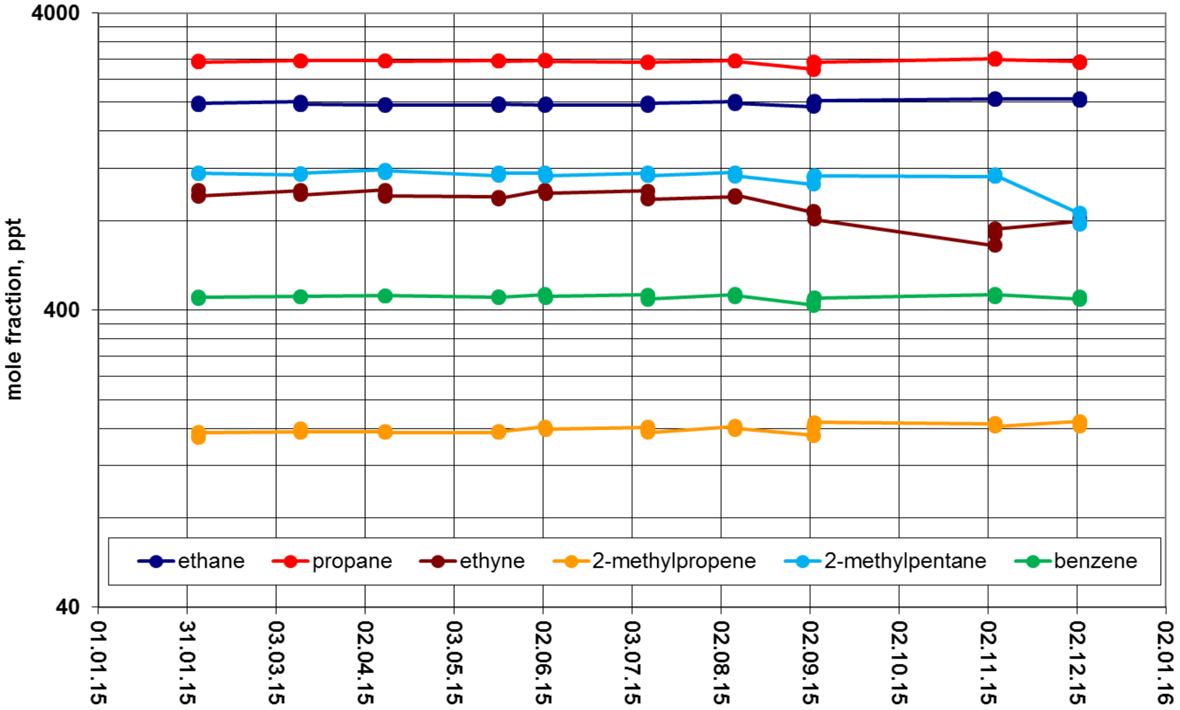


Figure 3: Examples of measurements of compressed whole air from a cylinder through 2015; 3 replicates are measured once a month. Mole fractions are plotted on a log scale versus time. Except for ethyne and 2-methylpentane, the observed mole fractions are stable. In this case, for those two substances and the period after Sep 2015, the system has to be checked. However, in general this plot indicates good calibration procedure and performance of the system.

8.1.3 Results of standard addition measurements

The standard addition measurement (“add”) is compared to a pure standard (“pure”) measurement of the same standard gas mixture. If the O_3 rich ambient air matrix does not have an effect on the sample, the calibration factor (for FID systems the C-response factor) must be the same for both measurements and thus

$$1 = \frac{\frac{A_{add}}{A_{pure}}}{\left[\frac{A_{add}}{A_{pure}}\right]_{avg}}$$

With $\left[\frac{A_{add}}{A_{pure}}\right]_{avg} = \frac{flow_{add}}{flow_{total}}$ being the average peak area ratio for non O_3-reactive compound with low mole fraction in the ambient air (e.g. alkanes like heptane). This concept is applicable for all VOC compounds in linear GC-systems for which the ambient air concentration is negligible versus the standard addition concentration. An advantage is that the exact flow in standard addition does not need to be known because it is determined from the peak area ratios.

In Figure 4, results of monthly performed standard addition measurements (set-up see Figure 1) are shown. Plotted is the normalized peak ratio as described above. Positive deviations from 1 are possible if the substance has a relevant contribution from ambient air. However, generally results should vary within a few percent around 1 as indicated for n-heptane (green).

The here shown alkenes are clearly dominated by the added standard. If ozone interferences (losses) exist, these reactive alkenes should show lower ratios than 1. None of the alkenes shows any significant deviations from 1 and thus no indication of reactive losses with O_3. In case alkene measurements exhibit a normalized peak area ratio $r_{norm} < 1$, the GC system is further checked and if necessary the O_3 filter is replaced.

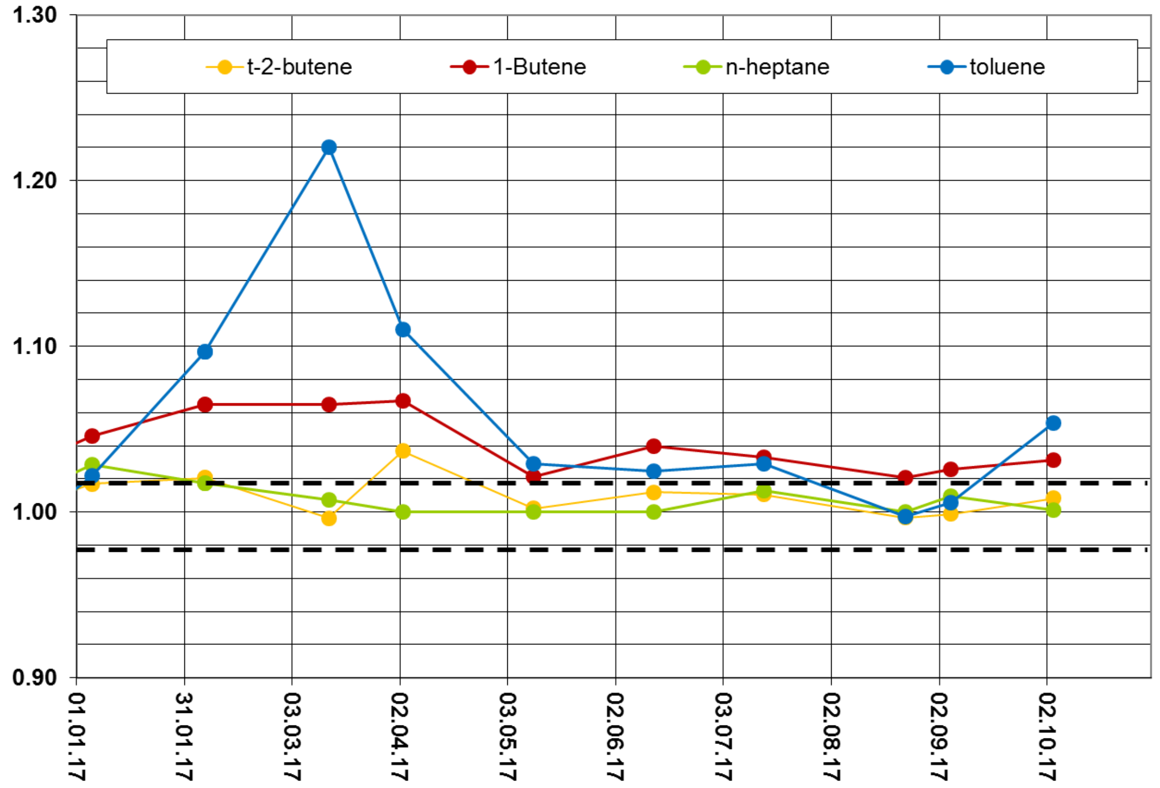


Figure 4: Results of a 100ppb-NPL standard addition measurements performed once per month with a set-up described in Section 7.1.3. 1ml/min of NPL was added into an 80ml/min ambient air sample flow. On the y-axis the peak area ratios are given as stated in the text. Dashed line marks a 2% interval, normalization was made to the respective ratios of 2-methylpentane, n-heptane and n-octane.

8.1.4 Data checks of final mole fraction data

NMHCs should be grouped in a convenient number (typically 3 or 4) of functionally similar compounds, e.g. alkanes or alkenes, in a plot over a time interval of half a year or a year. The procedure is illustrated in Figure 5.

Generally, it is expected that the variability of the data should increase with higher reactivity (variability-lifetime-relation) and changes should be more pronounced for shorter lived compounds (lower background). Spikes in positive or negative direction may be attributed to plumes with local/regional pollution or very clean conditions, respectively, and should be checked for consistency with other compounds from similar sources. If not consistent, the raw data should be rechecked, especially the peak integration, breakthrough in trap, adsorption/desorption effects or other potential problems should be checked.

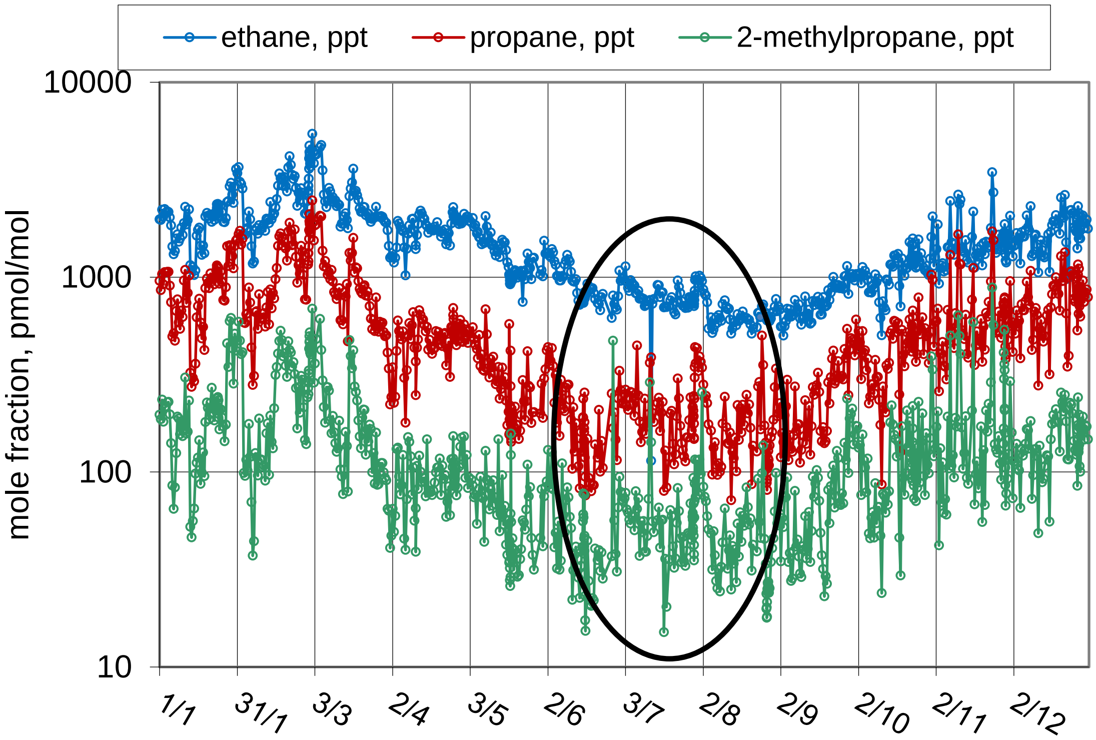
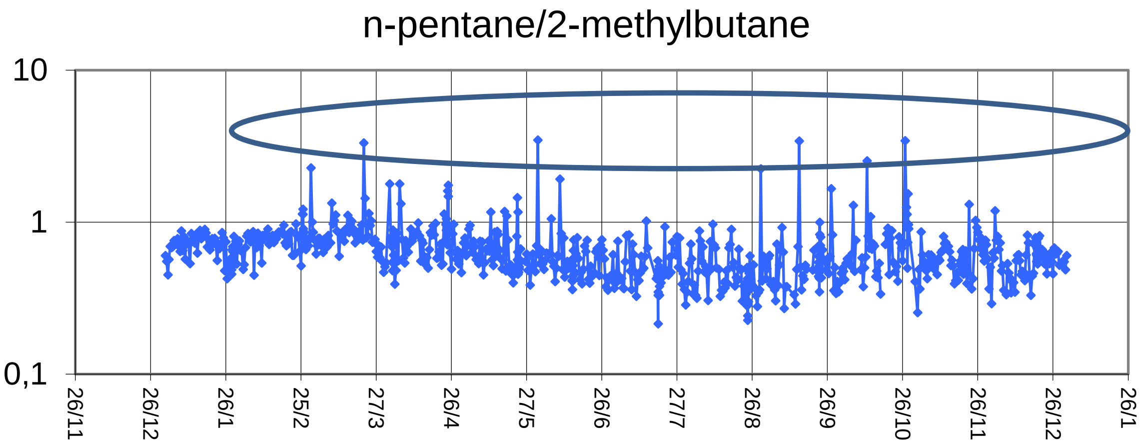


Figure 5: An example for time series (annual cycle) of C_2-C_4 alkanes. On the y-axis the mole fraction in pmol/mol is given in a log-scale. E.g. the negative spike for ethane in July and positive spikes for 2-methylpropane in June to August should be checked.

For compounds with similar relative annual cycles, due to similar sources or similar lifetimes it is valuable to look at time series of their ratio (example given in Figure 6) or plot the correlation (example in Figure 7). Useful NMHC pairs are listed in Table 14. Such tracer NMHC pairs can reveal a very compact correlation and their ratio can be constant or show a specific behaviour over time at a station. Of course, when compounds have more than one potential source, the scatter plot can be sparse or multi-distributed. Further, it might not be representative due to a technical issue. In some cases it can be specific to one site due to its specific situation (source/sink distribution, topography, etc.) and in such case the year to year shape of the cloud is interesting to be checked.

For distinct deviations observed in control plots as shown in Figures 5 to 7 it is recommended to perform following checks:

i) logbook entries to identify irregular operation conditions
ii) peak integration
iii) other compounds deviating in these individual measurements and try to identify the reason for the spike



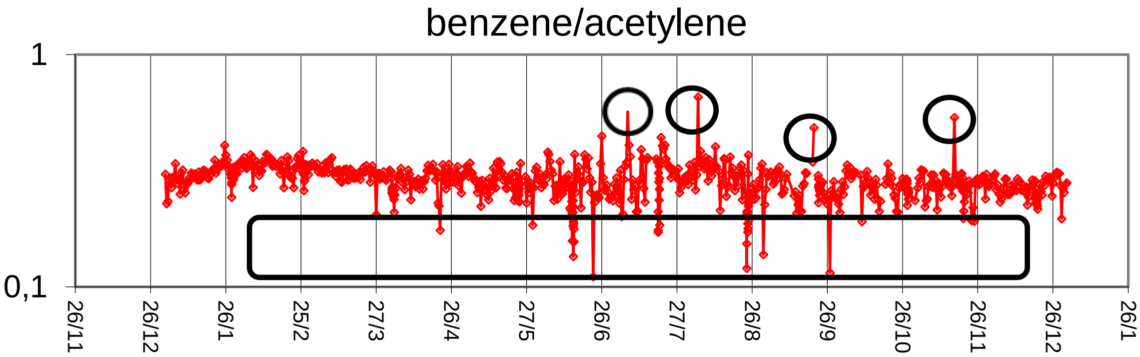


Figure: 6 Time series of ratios between pairs of hydrocarbons with similar structure. On the y-axis the ratio between the compounds is given. Marked data points should be checked as they either point to a specific local situation (meteorological situation, local sources) or a technical issue.

Table 14: Useful tracer-tracer correlation pairs of NMHCs.

Tracer/tracer	**description**
propane/ethane	Both due to natural gas losses, fossil fuel exploration, refineries, biological processes, and both with fairly long lifetimes
n-butane/ethane	natural gas leakage, butane is also emitted from fuel evaporation
propane/n-butane	Butane emitted from fuel evaporation and propane from natural gas leakage
2-methylpropane/n-butane	Isomers, fuel evaporation tracers
2-methylbutane/n-pentane	Isomers, fuel evaporation tracers
propene/ethene	Combustion, very reactive species
ethyne/ethene	Combustion, ethene more reactive than ethyne
ethyne/ benzene	Very compact correlation, same sources (incomplete combustion), very similar lifetimes

butenes/ethene	reactive species, combustion sources, butenes can also be emitted from fuel evaporation sources
pentenes/ethene	reactive species, combustion sources, pentenes can also be emitted from fuel evaporation sources
ethenes/butenes	Combustion, very reactive species
methylpropane/2-methylbutane	Fuel evaporation sources
1,3-butadiene/ethene	Combustion sources
n-hexane/n-pentane	Fuel evaporation
isohexane/n-hexane	Isomers
toluene/benzene	Both aromatics, similar combustion sources but different lifetime, toluene with additional source due to solvent and fuel evaporation in summer time.
m,p-xylene/benzene	Both aromatics, similar combustion sources but different lifetime, m,p-xylene with additional source due to solvent and fuel evaporation in summer time.
ethylbenzene/m,p-xylene	Both aromatics, similar sources like combustion, solvent and fuel evaporation
o-xylene/m,p-xylene	Isomers emitted from the same sources
o-xylene/ethylbenzene	Both aromatics, similar sources like combustion, solvent and fuel evaporation

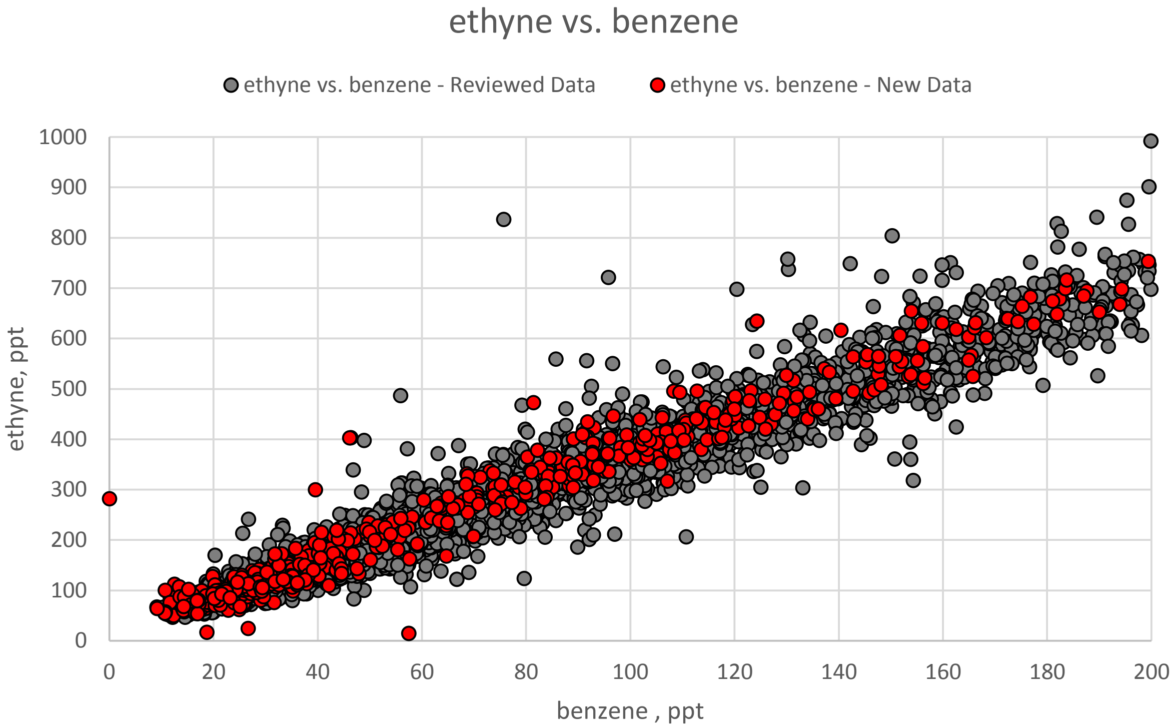


Figure 7: Example for a xy-plot: Ethyne vs benzene at one single measurement site. Reviewed data 2012-2016 are shown in grey, new 2017 data in red. Points falling apart from the tight correlation should be checked.

8.1.5 QC in repeatability and reproducibility

The plausibility of the random uncertainty estimation can be assessed from the combined repeatability (sets of 3-5 measurements each) and reproducibility (monthly or bimonthly), i.e. standard deviations of available target gas measurements of a given period. In this example (Figure 8), all measurements of 3 different target gases of one complete year are shown. The absolute (pmol/mol) standard deviations are plotted versus the mole fraction for all identified compounds. Expected is a constant absolute variability at low mole fractions close to the detection limit (F9), and constant relative variability at higher mole fractions (F7 and F8) (see section 7.1.6). Such a presentation helps to identify reproducibility problems with individual compounds. Dashed lines represent variability defined in the DQOs (Table 3). For most compounds the GAW target performance (in green) represents a good fit all points fall below or on the green line. However, some of the compounds exhibit higher scatter but are generally within the GAW basic performance of 5% (yellow line) for alkanes and 10% for alkenes, alkynes and aromatics (red line), which still is a quite good level for the reproducibility of measurements of cylinder gases and within the DQOs as shown in Section 2. Compounds with higher deviations should be checked to identify the reason of the deviation. Often peak-overlap or –integration problems are associated with worse reproducibility. Also, heavier compounds tend to be less reproducible due to adsorption/desorption problems.

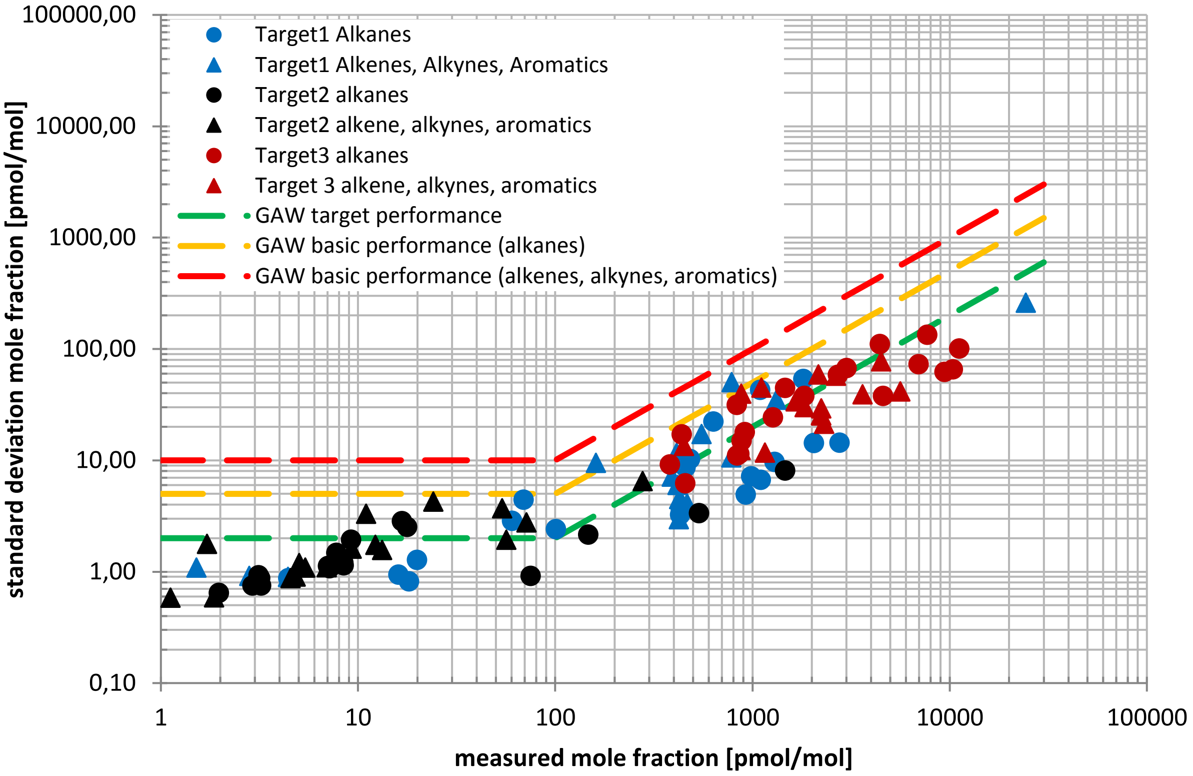


Figure 8: Standard deviations obtained from all measurements of target gases (whole air) in one year versus compounds' mole fractions in pmol/mol in the respective standard; Dashed lines represent variability defined in the DQOs (Table 3) with 2% (2ppt below 100ppt) in green, 5% (5ppt below 100ppt) in yellow and 10% (10ppt below 100ppt) in red. Data for each target gas have been splitted into alkanes (circles) and alkenes, alkynes and aromatics (triangles).

8.1.6 Recommended QC and flagging of the data

Recommended QC is to visually control time series of calibration gas (7.2), target gas (7.3), and ambient air measurements (7.5) and to generate xy-plots for the above mentioned compounds (7.6) and to compare the data to previous years.

Data flagging is defined by the WDCRG data base (EBAS, NILU Norway). The flags commonly used for VOCs and NMHCs in EBAS are listed at http://ebas-submit.nilu.no/Submit-Data/Data-Reporting/Templates/Category/Trace-Gases/VOC/NMHC/level2

Station personnel are encouraged to attend training courses and QC workshops by WDCRG and GAWTEC.

8.2 Meta data

Data submitted to EBAS need to be formatted in the EBAS NASA-Ames format by the data provider. The EBAS NASA-Ames format is based on the ASCII text NASA-Ames 1001 format, but contains additional metadata specifications ensuring proper documentation. The page http://ebas-submit.nilu.no/ provides links to data reporting templates for reporting VOC data to EBAS.

8.3 Ancillary data

See section 3.6.

8.4 Data archiving at the station or laboratory

It is recommended to perform daily backups of the raw data.

8.5 Data submission

The global data archive for VOC measurements is the World Data Centre for Reactive Gases (GAW-WDCRG) under the EBAS database, which is maintained by the Norwegian Institute for Air Research (NILU). All VOC data obtained as part of the GAW programme should be submitted within one year to the WDCRG using the specific submission tool available at http://ebas-submit.nilu.no. Continuous and quasi-continuous data may be reported as hourly averages (preferred) or higher aggregates. The data must be accompanied with appropriate metadata. The WDCRG also accepts flask and campaign data. Submittal of ancillary data is encouraged, of meteorological data mandatory. Data submitters should consult the WDCRG data submission guidelines [WMO, 2009c] and submit data to EBAS with the GAW-WDCRG label.

GAW and the European ACTRIS (Aerosols, Clouds and reactive Trace gases Research Infrastructure Consortium), work together on the development of procedures described in the following. The data providers are responsible for the quality of the data submitted and the templates ensure proper and sufficient documentation of the data.

An expanded set of guidelines, templates and explanations for data submission is available on EBAS's web pages. Data submitted to EBAS need to be formatted in the EBAS NASA-Ames format by the data provider. All information on how to report data to EBAS is available from the page http://ebas-submit.nilu.no/Submit-Data/Getting-started . This includes online data reporting templates with proper documentation for the setup and procedures for each measurement principle (online and offline traps and offline canisters).

The reported data can be associated to programs and frameworks like GAW-WDCRG, EMEP, ACTRIS, InGOS, etc. (e.g. GAW stations should label their data files submitted to EBAS with project/framework "GAW-WDCRG"), defined in the metadata by the data provider.

An EBAS NASA Ames file consists of two parts; a metadata header and a column formatted data part. The header section contains a number of important metadata items describing the measurement site, data variable, instrument, measurement principle and operating procedure. If nothing changes in the measurement set up, the header will remain the same from year to year, and the measurement data will be visible as one continuous dataset in the database. The data section of an EBAS NASA Ames file consists of a fixed column number format ASCII table, including time stamp, data value (mole fraction, precision, total expanded uncertainty) and flag for each single measurement point or data average point. The data formatting templates give the user a detailed line-by-line explanation of what metadata shall be included in which line of the header, dare needs to be taken to follow the correct procedure and use the correct wording. For this, metadata information is available by clicking on the respective line number from the template. Tables of recommended flags are available from each individual template, but also a complete list of flags available in EBAS is located at http://www.nilu.no/projects/ccc/flags/flags.html

The data centre recommends first to create the data table and then add the header. Name the file overusing the filename stated in the header.

The final data submission deadline is May 31 for data from the year before. Example: 31. May 2017 is reporting deadline for all 2016 data. In areas and for stations where data quality control workshops are part of the QC, the entire data need to be submitted by March 31, and revisions following an issue tracked will be possible with a final submission by May 31.
A file format checker and submission tool is available at the data centre. This tool, located at http://ebas-submit-tool.nilu.no/ is designed to give the data submitter feedback on the file format prior to data

submission, so that only correct files are uploaded. After checking, the files can be submitted to EBAS directly through the submission tool.

An auto-mail from the system will be sent to the data submitter if the submission was successful.
The submitted data will be collected, checked and inserted to EBAS. The data submitter will be notified in case of needs for correction in the submitted data.

9. References

Apel, E.C. et al. (2003): A fast-GC/MS system to measure C_2 to C_4 carbonyls and methanol aboard aircraft. Journal of Geophysical Research 108 (D20): 15-1 – 15-12.

Baars, B. and Schaller, H. (1994), Fehlersuche in der Gaschromatografie, VHC Verlagsgesellschaft mbH.

Barkley, C.S. et al. (2005): Development of a Cryogen-Free Concentration System for Measurements of Volatile Organic Compounds. Analytical Chemistry 77 (21): 6989-6998.

Blanchard et al. (2017): Atmospheric Isoprene in the NOAA/INSTAAR Global Greenhouse Gas Reference Network . Presentation at the GAW VOC expert meeting, Boulder, May 2017.

Blake, R. S., Monks, P. S., Ellis, A. M. (2009): Proton- Transfer Reaction Mass Spectrometr. Chem. Rev. 109: 861 - 896.

De Gouw, J., Warneke, C. (2007): Measurements of volatile organic compounds in the earth's atmosphere using proton-transfer-reaction mass spectrometry. *Mass Spectrom. Rev*. 26 (2): 223–257.

Dietz W.A. (1967): Response factors for gas chromatographic analyses, J. of Gas Chromatography 5, 68.

Graus, M., Müller, M., Hansel, A. (2010): High Resolution PTR-TOF: Quantification and Formula Confirmation of VOCS in Real Time. *J. Am. Soc. Mass Spectrom*. 21 (6): 1037–1044.

Greenberg, J.P., Zimmermann, P.R., Pollock, W.F., Lueb, R.A., Heidt, L.E. (1992): Diurnal variability of atmospheric methane, nonmethane hydrocarbons, and carbon monoxide at Mauna Loa. Journal of Geophysical Research 97: 10,395-10,413.

Hellén, H., P. Kuronen, and H. Hakola (2012): Heated stainless stell tube for ozone removal in the ambient air measurements of mono- and sesquiterpenes. Atmospheric Environment 57: 35-40, DOI:10.1016/j.atmosenv.2012.04.019.

Helmig, D., Greenberg, J.P. (1994): Automated in situ gas chromatographic-mass spectrometric analysis of ppt level volatile organic trace gases using multistage solid-adsorbent trapping. Journal of Chromatography A 677: 123-132.

Helmig, D. (1997): Ozone removal techniques in the sampling of atmospheric volatile organic trace gases. Atmospheric Environment 31 (21): 3635-3651.

Helmig, D. (1999): Air analysis by gas chromatography. Journal of Chromatography A 843(1-2): 129-146.

Hoerger, C. C., A. Claude, C. Plass-Duelmer, S. Reimann, E. Eckart, R. Steinbrecher, J. Aalto, J. Arduini, N. Bonnaire, J. N. Cape, A. Colomb, R. Connolly, J. Diskova, P. Dumitrean, C. Ehlers, V. Gros, H. Hakola, M. Hill, J. R. Hopkins, J. Jäger, R. Junek, M. K. Kajos, D. Klemp, M. Leuchner, A. C. Lewis, N. Locoge, M. Maione, D. Martin, K. Michl, E. Nemitz, S. O'Doherty, P. Pérez Ballesta, T. M. Ruuskanen, S. Sauvage, N. Schmidbauer, T. G. Spain, E. Straube, M. Vana, M. K. Vollmer,R. Wegener, and A. Wenger (2015), ACTRIS none-methane hydrocarbon intercomparison experiment in Europe to support WMO GAW and EMEP observation networks. Atmos. Meas. Tech. 8, 2715-2736, DOI:10.5194/amt-8-2715-2015.

Hopkins J.R., Lewis A.C., Read K.A. (2003): A two-column method for long-term monitoring of non-methane hydrocarbons (NMHCs) and oxygenated volatile organic compounds (o-VOCs). Journal of Environmental Monitoring, volume 5, issue 1.

Hopkins, J.R., Jones, C.E., Lewis, A.C. (2011): A dual channel gas chromatograph for atmospheric analysis of volatile organic compounds including oxygenated and monoterpene compounds. Journal of Environmental Monitoring DOI: 10.1039/c1em10050e.

Hueber et al., (2017): Monitoring of Atmospheric Acetylene from the Global Greenhouse Gas Reference Network. Presentation at the GAW VOC expert meeting, Boulder, May 2017.

Komenda, M., Schaub, A., Koppmann, R. (2003): Description and characterization of an on-line system for long-term measurements of isoprene, methyl vinyl ketone, and methacrolein in ambient air. Source of the Document Biochimica et Biophysica Acta - Bioenergetics 1605 (1-3): 55-66

Koppmann, R., Johnen, F.J., Khedim, A., Rudolph, J., Wedel, A., Wiards, B. (1995): The influence of ozone on light nonmethane hydrocarbons during cryogenic preconcentration. Journal of Geophysical Research 100: 11,383-11,391.

Kuster, W.C, Goldan, P.D., Albritton, D.L. (1986): Ozone interferences with ambient dimethyl sulfide measurements: The problem and a solution. Eos 67: 887.

Lee, J.H., Batterman, S.A., Jia, C., Chernyak, S. (2006): Ozone artifacts and carbonyl measurements using Tenax GR, Tenax TA, Carbopack B, and Carbopack X adsorbents. Journal of the Air & Waste Management Association 56: 1503-1517.

Leibrock E. (1996): Entwicklung eines gaschromatographischen Verfahrens zur Spurenanalytik von oxidierten Kohlenwasserstoffen in Luft, Wissenschafts-Verlag Maraun, Frankfurt a.M., McClenny, W.A., Pleil, J.D., Evans, G.F., Oliver, K.D., Holdren, M.W., Winberrry, W.T. (1991): Canister-based method for monitoring toxic V0Cs in ambient air, J. Air Waste Manage. Assoc. 41, 1308-1318

McClenny W.A., Pleil J.D., Evans G.F., Oliver K.D., Holdren M.W., Winberry W.T. (1991): Canister-based method for monitoring toxic VOCs in ambient air J. Air Waste Man. Ass., 41, 1308–1318.

Miller, B.R., Weiss, R.F., Salameh, P.K., Tanhua, T., Greally, B.R., Mühle, J., Simmonds P.G. (2008) Medusa: A sample preconcentration and GC/MS detector system for in situ measurements of atmospheric trace halocarbons, hydrocarbons, and sulfur compounds, Anal. Chem., 80 (5), 1536-1545.

Palluau F., Ph Mirabel , M Millet (2007): Influence of ozone on the sampling and storage of volatile organic compounds in canisters, Environ Chem. Lett. 5, 51–55.

Plass-Dülmer, C.; Michl, K.; Ruf, R.; Berresheim, H. (2002), C_2 - C_8 hydrocarbon measurement and quality control procedures at the Global Atmosphere Watch Observatory Hohenpeissenberg. J. Chromatogr. 953, 175-197.

Plass-Dülmer C., N. Schmidbauer J. Slemr, F. Slemr, H. D'Souza (2006): European hydrocarbon intercomparison experiment AMOHA part 4: Canister sampling of ambient air, J. Geophys. Res., 111, D04306, doi:10.1029/2005JD006351.

Pollmann J., D. Helmig, J. Hueber, Ch. Plass-Dülmer, P. Tans (2008): Sampling, storage, and analysis of C_2–C_7 non-methane hydrocarbons from the US National Oceanic and Atmospheric Administration Cooperative Air Sampling Network glass flasks, J. Chromatogr., A 1188, 75-87.

Sternberg J.C., W.S. Gallaway and D.T.L. Jones, in N. Brenner (1962), The mechanism of response of Flame Ionization Detectors, in J. Callen and M.D. Weiss (Editors) Gas-Chromatography, Academic Press, New York, p. 231-267.

Taipale, R., Ruuskanen, T. M., Rinne, J., Kajos, M. K., Hakola, H., Pohja, T., Kulmala, M. (2008): Technical Note: Quantitative long-term measurements of VOCS concentrations by PTR-MS – measurement, calibration, and volume mixing ratio calculation methods. Atmospheric Chemistry and Physics 8, 9435-9475.

US-EPA (1998): Technical assistance document for analysis of ozone precursors, US-Environmental Protection Agency, EPA/600-R-98/161.

US-EPA TO-14A (1999): Compendium of methods for the determination of toxic organic compounds in ambient air: determination of volatile organic compounds (VOCs) in ambient air using specially prepared canisters with subsequent analysis by gas chromatography, US-Environmental Protection Agency, Method TO-14A, 2nd ed., EPA/625/R-96/010b.

Wisthaler, A. et al. (2006): Recent developments in proton-transfer-reaction mass spectrometry. Photonic, Electronic and Atomic Collisions, 24th International Conference on Photonic, Electronic and Atomic Collisions, Rosario, Argentina: 462-469. Doi: 10.1142/9789812772442_0060.

WMO (1995), WMO-BMBF Workshop on VOCs - Establishment of a „World Calibration/Instrument Intercomparison Facility for VOCs“ to serve the WMO Global Atmosphere Watch (GAW) Programme, WMO Report, 111.

WMO (2001): Strategy for the Implementation of the Global Atmosphere Watch Programme (2001 – 2007), GAW Report No. 142 (WMO TD No. 1077), 62 pp., World Meteorological Organization, Geneva, Switzerland.

WMO (2001b): Global atmosphere watch measurements guide, GAW Report No. 143 (WMO TD No. 1073), 87 pp., World Meteorological Organization, Geneva, Switzerland.

WMO (2007a): A WMO/GAW Expert Workshop on Global Long-Term Measurements of Volatile Organic Compounds, Geneva, Switzerland.

WMO (2007b): WMO Global Atmosphere Watch (GAW) Strategic Plan: 2008-2015, Geneva, Switzerland.

WMO (2009): GAW Report 188: Revision of the World Data Centre for Greenhouse Gases Data Submission and Dissemination Guide, Geneva, Switzerland.

WMO (2012): GAW Report 204: Standard Operating Procedures (SOPs) for Air Sampling in Stainless Steel Canisters for Non-Methane Hydrocarbons Analysis (prepared by R. Steinbrecher and E. Weiss), 28 pp., Geneva, Switzerland.

WMO (2017): Reactive Gases Bulletin No.1, Highlights from the Global Atmosphere Watch Programme, April 2017

Zhao, J. and R. Zhang, 2004: Proton transfer reaction rate constants between hydronium ion (H3O+) and volatile organic compounds. Atmospheric Environment, 38, 2177–2185.

10. Appendices

Appendix 1: Ozone removal techniques for GC analysis of oxygenated volatile organic compounds (OVOCs) in ambient air samples

Appendix 2: Adsorbents for sorbent-based enrichment of VOCs and OVOCs in ambient air samples

Appendix 3: Chromatographic separation

Appendix 4: Uncertainty calculation

APPENDIX 1: OZONE REMOVAL TECHNIQUES FOR GC ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR SAMPLES

Reactions of concentrated VOCs with ozone during sampling process may alter the quantities of the target analytes and also contribute to the formation of artefacts which may mistakenly be interpreted as atmospheric constituents.

Ozone reactions during cryogenic enrichment of VOCs:

Ozone melting and boiling points (at atmospheric pressure) are at -192.1°C and 111.9°C. During cryogenic freeze-out of VOCs from ambient air samples ozone is concentrated together with the target analytes, whereas the main constituents of air nitrogen and oxygen do not condense under these conditions (boiling point of liquid nitrogen -196°C). Reactions of VOCs with ozone occur when heating the cryogenic trap to transfer the analytes to the GC system. Alkenes, such as isoprene and monoterpenes can be depleted in this reactions leading to artefacts like methacrolein and methylvinylketone. By collecting ambient air into stainless steel canisters prior to the analysis with cryogenic freeze-out techniques this effect is reduced because of the short lifetime of ozone in these canisters (Helmig, 1997; Greenberg et al., 1992).

Ozone reactions during solid adsorbent sampling of VOCs:

Ozone artefacts are formed on and with some sorbents (e.g. graphitised carbon sorbents and Tenax® TA) leading to both VOCs losses and formation (Lee et al., 2006; McClenny et al., 2001). Adsorbed unsaturated hydrocarbons might for example undergo reaction with ozone during ambient sampling leading to diminished alkene concentrations and the formation of oxygenated reaction products e.g. acetaldehyde and formaldehyde. Products from ozone - Tenax® reactions include benzaldehyde, phenol, acetophenone and n-aldehydes (Helmig, 1997).

Reactions with ozone can be reduced by selectively removing the oxidant in the sample flow prior to the concentrating of the analytes of interest. The ozone removing system should be easy to use, inexpensive, and efficient in the ozone removal rate and have a high scrubbing capacity, long lifetime and eliminate the effects of ozone without interfering with the analytes of the target compounds and without introducing contaminants. Furthermore, it should be universally applicable to allow the analysis of a wide range of compounds. Commonly reported techniques for ozone scrubbers include impregnated filters, impregnated glass wool, coated tubes, and coated annular denuders. Titration with nitric oxide (NO) is a widely used and applied technique to remove ozone, too.

Catalytic destruction of ozone on metal surfaces:

Aluminum, copper, lead and tin have low ozone depletion efficiency whereas silver, iron, zinc, gold, nickel, mercury and platinum have high ozone destruction capacities. The ozone removal capability of some metals e.g. nickel tubing is used, to reduce ozone levels to less than 20 % of ambient air level (Helmig, 1997). Koppmann et al. (1995) found up to 50% destruction of ambient ozone by pulling the sample air through stainless steel inlet lines kept at 67°C.

Hopkins et al. (2011): All gas transfer lines within the system are made from stainless steel and heated to 70°C to reduce ozone mixing ratios.

Disadvantage: Loss of OVOCs on the surface of stainless steel even at high temperatures (150°C).

Ozone removal by nitric oxide (NO) titration:

Titration of the ambient air sample with a few ppm of NO prior to the concentration step is a very efficient method to remove ozone. Ozone (O_3) deletion performance depends on sufficient reaction time and NO concentration in the mixing chamber. An example is the titration of the ambient air sample for 20 seconds in a 1 litre glass reaction vessel with a small flow of 200 ppm NO in nitrogen resulting in a NO concentration of 2 ppm. NO reacts with O_3 to nitrogen dioxide (NO_2) and oxygen (O_2) (Helmig, 1997). The reaction is: $O_3 + NO \rightarrow O_2 + NO_2$.

Disadvantage: slow reaction, alcohol losses (but constant)

Ozone destruction by potassium iodide (KI):

In many cases KI is used for O_3 removal. This technique is very effective at ambient humidity levels while capacity is reduced in dry air respected in following equation (Helmig, 1997): $O_3 + 2KI + H_2O \rightarrow O_2 + I_2 + 2KOH$. KI reacts with O_3 to potassium oxide (K_2O) and elemental iodine.

Example: PTFE-lined stainless steel or Silco steel capillary, OD 1/4″ , 5 cm filled with KI-coated glass wool.

Disadvantage: formaldehyde and acetaldehyde blank values, alcohol losses (Helmig and Greenberg, 1994; Leibrock, 1996), production of iodated artifacts (Helmig and Greenberg ,1995)

Sodium sulphite (Na_2SO_3):

Most efficient in the presence of atmospheric water vapour and hence has to be positioned upstream of a water trap – was found to remove 99% of the O_3 in a humid ambient air stream but inconsistent removal efficiencies from different suppliers and from different batches – testing of individual O_3 traps is required (Helmig, 1997)

Example: ¼“ glass tube filled with 1 g of Na_2SO_3 anhydrous crystals held in place by glass wool plugs and maintained at 100°C to prevent clumping of the Na_2SO_3

Disadvantage: removal of methyl vinyl ketone (MVK) and methacrolein.

Sodium thiosulphate ($Na_2S_2O_3$):

The reaction between thiosulfate and O_3 produces tetrathionate oxygen and water depends on the pH level: $2S_2O_3^{2-} + O_3 + 2H^+ \rightarrow S_4O_6^{2-} + O_2 + H_2O$

Example: O_3 filters were prepared by flowing a 10% solution of aqueous $Na_2S_2O_3$ through commercial glass fiber filters followed by dry purge with nitrogen and had capacities in excess of 1 m^3 air at ambient O_3 levels (Helmig, 1997)

Advantage: this glass fiber filters also reduce sampling artefacts from reactions with halogens

Other O_3 removal agents are copper oxide (CuO), magnesium sulphate ($MgSO_4$), manganese dioxide (MnO_2), potassium carbonate (K_2CO_3) and TPDDC (see Table 1).

In-line O_3 scrubbers like granular KCl and crystalline Na2SO4 are prone to artefacts and require regular maintenance so that they are not suited to long-term instrument deployments (Hopkins et al., 2011).

Table A1: Ozone removal techniques for VOCS monitoring and their characteristics.

Technique	**Agent**	**Characteristics**
Coated annular denuder	Potassium iodide (KI)	Very efficient
Cellulose filter	KI	Improved formaldehyde and acetaldehyde recovery

Packed Teflon tubing	Crystalline KI	Quantitative transmission of formaldehyde and acetaldehyde, partial loss of methacrolein and methyl vinyl ketone (MVK)
Impinger	KI	2% aqueous, buffered KI solution
Impregnated glass wool	KI	Quantitative O_3 removal, iodated artefacts
Coated tubing	KI in copper tubing	
Commercial scrubber	KI in polyethylene cartridge	Low capacity at 5% RH
Impregnated glass fiber filter	Sodium thiosulphate ($Na_2S_2O_3$)	High capacity, also reduces sampling artifacts from reactions with halogens
Coated copper screen	Manganese dioxide (MnO_2)	High capacity, possible losses of terpenes (e.g. camphor, linalool), loss of formaldehyde
Packed copper tubes	Anhydrous 20-60 mesh potassium carbonate (K_2CO_3), crystalline	100% transmittance of light hydrocarbons
Packed Teflon tubing	K_2CO_3	ozone and water removal, 100% transmission of light hydrocarbons
Packed glass tube	Crystalline sodium sulphite (Na_2SO_3)	Loss of unsaturated compounds prevented, most efficient in the presence of atmospheric water vapour
Cartridge	Copper oxide (CuO), crystalline	No losses of carbonyl compounds
Trap	Crystalline magnesium sulphate ($MgSO_4$)	Removal of at least 100 ppb, loss of O_3 removal efficiency with sampling length
Gas-phase ozone titration	Nitric oxide (NO)	Very efficient, quantitative recovery of formaldehyde, formation of artifacts on Tenax exposed to elevated NO_x levels, possible chromatographic interferences of NO and NO_2 with NMHCS (Kuster et al., 1986), losses of alcohols, slow reaction (Pollmann et al. 2005)
Metal tubing	Nickel (Ni)	O_3 reduced to less than 20% of ambient level
Spiked cartridge	TPDDC (Tetramethyl-1,4-phenylenediamine dihydrochloride)	Sampling of carbonyl compounds on microcartridges containing porous glass particles impregnated with dansylhydrazine (DNSH), agent added to the reagent solution at the time of cartridge preparation to serve as an O_3 scavenger
Spiked cartridge	5% $Na_2S_2O_3$ aqueous solution on Tenax	Direct pretreatment of the adsorbent, improved monoterpene recovery
Spiked cartridge	$Na_2S_2O_3$	Interferences eliminated

APPENDIX 2: ADSORBENTS FOR ADSORBENT-BASED ENRICHMENT OF VOCS IN AMBIENT AIR SAMPLES

Sampling of ambient air with adsorbent tubes or traps and subsequent thermal desorption to transfer the sampled compounds to a GC system is widely-used for trace gas analysis of VOCs because of the high sensitivity of this method.

There are two different adsorbent-based sampling strategies: (1) on-line sampling of ambient air directly onto (cooled) adsorbent focusing traps or transfer of air samples from containers (stainless steel canisters or PTFE bags) onto these (cooled) traps; and (2) off-line pumped (active) or diffusive (passive) sampling onto adsorbent tubes or cartridges held at ambient temperature. In the case of off-line sampling VOCs are transferred in a second step into a cooled focusing device (e.g. adsorbent trap). For reactive VOCs a method with short transfer from sampling device to the analysis system is important because of the high losses of these analytes on surfaces, especially on unheated and not inert ones like untreated surfaces of stainless steel.

When selecting a suitable adsorbent or adsorbent combination for the target VOCs several factors have to be considered including adsorbent strength, artefacts, hydrophobicity, inertness, thermal stability and friability. It has to be verified that there is no breakthrough (most critical are C_2 compounds), getting stuck or back-diffusion of target compounds. Some special, low volatile analytes may also be lost through aerosol formation.

The adsorbents must be strong enough to retain target analytes from a specific sample volume but must also be weak enough to release them during thermal desorption. Adsorbent strength is measured in terms of breakthrough volumes that are defined as the litres gas per gram adsorbent required to elute VOCs off 1.0 gram adsorbent at an indicated temperature. This capacity of solid adsorbents depends on temperature and is typically specified at 20°C. It approximately halves for every 10°C rise. Therefore, cooling the trap during sampling increases/improves adsorbent performance. The lowest possible temperature is limited by the dew point of the sampled air (Brown and Shirey, 2001; Helmig and Greenberg, 1994; Woolfenden, 2010b).

When using hydrophilic adsorbents (molecular sieves) or temperatures below the dew point for ambient air samples some kind of water trap has to be installed in the sampling line. Otherwise there would be a reduction of adsorbent performance that might reach a factor of 10 at high humidity conditions (90% RH) and after desorption of the trapped water moisture might interfere with the following chromatographic analysis. Weak and medium strength adsorbents (porous polymers and graphitised carbon blacks) are hydrophobic and so they prevent trapping of excess water.

Some adsorbents especially carbon blacks contain chemically active materials (trace metals) and are unsuitable for reactive species. Most porous polymers except for Tenax® TA have high inherent artefacts with blank peaks at 5-10 ng levels (Woolfenden, 2010b).

Ozone (O_3) artefacts are formed on and with some adsorbents (e.g. graphitised carbon adsorbents and Tenax® TA) leading to both losses and increases of oxygenated VOCs (Lee et al., 2006; McClenny et al., 2001). So the aspect of O_3 removal has to be considered in adsorbent-based ambient air sampling.

Quartz wool or silica beads are not able to retain most of the compounds. They are usually used in multi-bed traps to prevent very high boilers from coming in contact with a stronger adsorbent (Pollmann et al., 2006).

Porous polymers are weak or medium strength adsorbents. None of them can retain the very volatile analytes. In multi-bed traps they are often the first adsorbent in sampling direction for the mid and higher boiling point analytes beginning from benzene. Porous polymers are hydrophobic and so are adequate for humid ambient air samples.

CarbopackTM, CarbotrapTM and CarbographTM are graphitised carbon blacks. The three different types differ in mesh sizes. They are suitable for most of the VOCs depending on their different adsorbent strength. The strongest CarbopackTM X should have a weaker adsorbent in front of it when sampling very high boiling point analytes. All graphitised carbon blacks are hydrophobic like porous polymers and so are adequate for humid ambient air samples (Brown and Shirey, 2001).

CarboxenTM and CarbosieveTM adsorbents are very strong and not appropriate for analytes with boiling points higher than benzene because they have very small pores. They should always be used with a weaker adsorbent (porous polymer or graphitised carbon black) placed in front. Pore shape of the CarbosievesTM is different from the CarboxensTM. Pores of CarbosievesTM may be blocked by analytes with high boiling points. Both CarboxensTM and CarbosievesTM are not hydrophobic and so do need water removal for sampling humid ambient air samples.

Charcoals are not suitable for thermal desorption because their adsorbtion is too strong to release most of the analytes with only heat. However, they are sometimes used in multi-adsorbent traps for very volatile analytes e.g. Halocarbon 12 and Chloromethane. Charcoals are hydrophilic (Brown and Shirey, 2001).

Multi-adsorbent traps with up to four different adsorbents allow a wide range of volatile compounds to be enriched simultaneously. Adsorbents are arranged in order of increasing adsorbent strength from the sampling end. Thermal desorption is in reverse direction to sampling flow so that low-volatile compounds do not come in contact with the stronger adsorbent for highly volatile analytes. Care should be taken when choosing adsorbents for multi-adsorbent traps or tubes. The temperature required for conditioning the most thermally-stable adsorbent must not exceed the maximum temperature of any other. Migration of loosely bound analytes from weak to strong adsorbent (e.g. from Tenax® TA to a carbon molecular sieve) has to be inhibited by extending the bed length of the weaker adsorbent or inserting a medium strength adsorbent between (Woolfenden, 2010b). Multi-adsorbent traps applied for NMHCs are for example Carbopack^{TM} B : Carboxen^{TM} 1000, 90 mg in total (Hopkins et al., 2003) or Carbopack^{TM} B : Carbosieve^{TM} SIII tubes (e.g Air Toxics traps).

There are different adsorbent bed sizes and densities depending on application and analytes. To allow high sampling flow rates coarse adsorbent grain sizes (20/40 mesh) have to be used (Helmig and Greenberg, 1994). Another important consideration in the selection of adsorbent materials is how stable the particles of the adsorbent are. Some materials, such as Carbosieve, exhibit good adsorption properties, but they might degrade during preparation or over time.

Important characteristics of the most common adsorbents are summarized in Table A2.

Table A2: most common adsorbents.

Adsorbent	**Class**	**Strength**	**Max. Temp. [°C]**	**Relative analyte size to n-alkanes**	**Characteristics**
Quartz wool/silica beads	Fused silica	Very weak	>450	C_{30}-C_{40}	Very inert, non-water retentive, hydrophobic, minimal inherent artefacts, friable, 40/60

					mesh recommended to minimise back pressure
Carbograph™ 2TD Carbopack™ C Carbotrap™ C	Graphitised carbon black	Weak	>450	C_8-C_{20}	Very inert, hydrophobic, minimal inherent artefacts, friable, 40/60 mesh recommended to minimise back pressure, O_3 artefacts
Tenax® TA	Porous polymer	Weak	350	C_6-C_{30}	Too weak for acetone and n-pentane, high benzene blank value, inert, hydrophobic, low inherent artefacts (e.g. aldehydes - Helmig and Greenberg, 1994), NMHCS, aldehyde and ketone artefacts in combination with O_3 (Lee et al., 2006), prone to chemical degradation and aging effects (Helmig and Greenberg, 1994)
Carbograph™ 1TD Carbograph™ B Carbopack™ B Carbotrap™	Graphitised carbon black	Weak/medium	>450	$C_{5/6}$-C_{14}	Hydrophobic, minimal inherent artefacts, friable, formation of fines, 40/60 mesh recommended to minimise back pressure, aldehyde and ketone artefacts in combination with O_3 (Lee et al., 2006)
Chromosorb® 102	Porous polymer	Medium	225	C_5-C_{12}	Inert, hydrophobic, high inherent artefact levels
PoraPak™ Q	Porous polymer	Medium	250	C_5-C_{12}	Inert, hydrophobic, high inherent artefact levels
Chromosorb® 106	Porous polymer	Medium	225	C_5-C_{12}	Inert, hydrophobic, high inherent artefact levels
PoraPak™ N	Porous polymer	Medium	180	C_5-C_8	Inert, hydrophobic, high inherent artefact levels
HayeSep™ D	Porous polymer	Medium	290		Inert, hydrophobic, high inherent artefact levels
Carbograph™ 5TD	Graphitised carbon black	Medium/strong	>450	$C_{3/4}$-C_8	Hydrophobic, minimal inherent artefacts, friable, formation of fines, 40/60 mesh recommended to minimise back pressure, retention of very volatile

					compounds e.g. 1,3-butadiene
Carbopack™ X	Graphitised carbon black	Medium/strong	>450	C_3-C_9	Hydrophobic, minimal inherent artefacts, friable, formation of fines, 40/60 mesh recommended to minimise back pressure, retention of very volatile compounds e.g. 1,3-butadiene, no O_3 artefacts (Lee et al., 2006)
Carboxen™ 569	Carbonised molecular sieve	Strong	>450	C_2-C_5	Inert, less hydrophilic than most carbonised molecular sieves, minimal inherent artefacts
Unicarb™	Carbonised molecular sieve	Strong	>450	C_3-C_8	Inert, hydrophilic, performance weakened in humid conditions, individual inherent artefacts, must be conditioned slowly, requires extensive purge to remove permanent gases
Carboxen™ 1003	Carbonised molecular sieve	Very strong	>450	C_2-C_5	Inert, hydrophilic, performance weakened in humid conditions, individual inherent artefacts, must be conditioned slowly, requires extensive purge to remove permanent gases
Carbosieve™ SIII	Carbonised molecular sieve	Very strong	>450	C_2-C_5	Inert, minimal inherent artefacts, significantly water and CO_2 retentive, performance weakened in humid conditions, cold trap not lower than 0°C, easily and irreversibly contaminated by higher boiling components – protect with front bed of weaker adsorbent
Molecular sieve 5Å	Molecular sieve	Very strong	>400	C_2-C_5	High inherent artefacts, significantly hydrophilic, not suitable in humid conditions, easily and irreversibly contaminated by higher boiling components

Molecular sieve 13x	Molecular sieve	Very strong	>400	C_2-C_5	High inherent artefacts, significantly hydrophilic, not suitable in humid conditions, easily and irreversibly contaminated by higher boiling components
Charcoal	Activated carbon	Very strong	>400	C_2-C_4	Limited to solvent extraction (too strong and reactive for thermal desorption – metal content), hydrophilic, poor sensitivity – only for ppm level concentrations, analytical interference when using MS detection

Trademarks:
Tenax® TA - Buchem bv, Netherlands
Chromosorb® - Celite Corporation, USA
PoraPak™ – Waters Corporation, USA
Carbograph™ – LARA s.r.l., Italy
UniCarb™ – Markes International Ltd.UK, USA
HayeSep™ – Hayes Separations Inc., USA
Carbotrap™, Carbopack™, Carboxen™ and Carbosieve™ – Sigma-Aldrich, USA

APPENDIX 3: CHROMATOGRAPHIC SEPARATION

There are two types of capillary columns that are most widely used for the analysis of volatile organic compounds (VOCs): PLOT (Porous Layer Open Tubular) and WCOT (Wall Coated Open Tubular) columns.

PLOT columns feature a solid stationary phase consisting of a thin layer of small and porous particles (adsorbent) adhered to the surface of the tubing. Chromatographic results are achieved by adsorption of the analytes on the surface of the stationary phase by either surface charge interactions or shape selectivity and size exclusion interactions. PLOT columns in contrast to weaker retaining dimethylpolysiloxane columns are able to separate VOCs at ambient and above ambient oven temperatures which reduces liquid nitrogen consumption that is necessary in case of WCOT columns. Be aware, that special highly polar PLOT columns do not essentially retain most NMHCs as they have little or limited interactions with the surface of the stationary phase (those columns are ususally used to isolate OVOCs and generally avoide co-elutions with NMHCs).

The disadvantage of PLOT columns is the need for water removal from the sample gas, since most PLOT columns are sensitive to water with respect to shifts in retention times depending on the moisture content of the ambient air sample. Another issue of PLOT columns may be occasionally occurring mobilisation of particles from the stationary phase (problem especially for MS), but this effect has decreased due to better bonding of the porous polymer layer.

WCOT columns have a liquid stationary phase. They separate the solutes with different polarities and solubility depending on the physical properties of the stationary phase, e.g. in non-polar films the analytes dissolve according to the boiling points. The polar/non-polar interactions are much weaker than the adsorptive interactions in PLOT columns. There a two types of films: non polar dimethylpolysiloxane or polar polyethylene glycol. Dimethylpolysiloxane columns are versatile, very stable and can be operated at very low temperatures. But there are co-elution problems of NMHCs with OVOCS and so there is the need for a specific detector (MS).

On the contrary on polyethylene glycol columns NMHCs have lower retention. Concurrently alcohols have high retention so that there are less co-elutions with OVOCs. But a drawback is the fact that aldehydes have also low retention. Furthermore, polyethylene glycol columns have shorter lifetimes, are susceptible to damage upon overheating or exposure to oxygen and they cannot be operated at sub-ambient oven temperatures.

1. PLOT columns

Table A3: PLOT columns

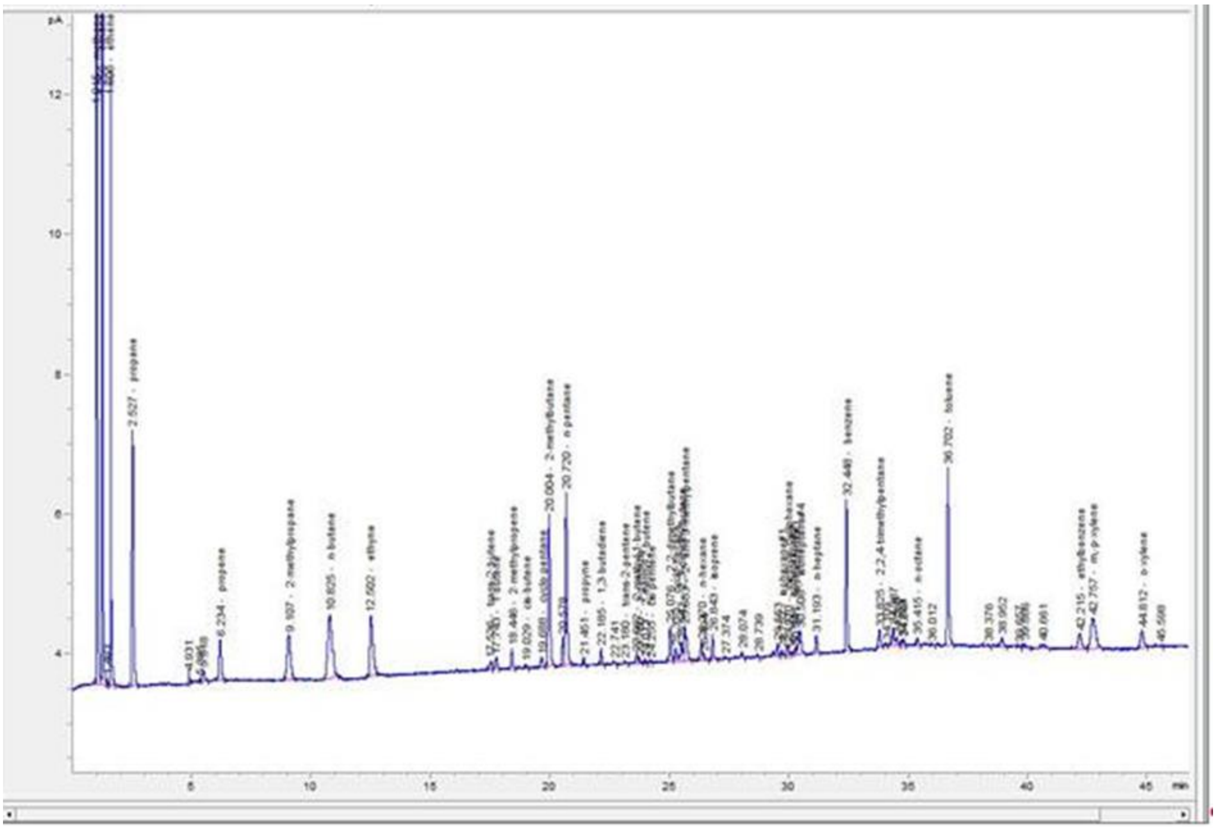
PLOT column equivalents	**GS-OxyPLOT (Agilent), CP-LowOx (Varian)**	**CP-PoraBOND U (Agilent resp. Varian)**	**AlO$_3$ PLOT (Agilent resp. Varian)**
Polarity	High polar	Midpolar	High polar
Composition	Proprietary, salt deactivated	Styrene-glycol methacrylate copolymer	Proprietary, salt deactivated
temperature range	0°C to 350°C	-100°C to 300°C	-100°C to 200°C
Analysis of alcohols	+	+	-
Analysis of aldehydes	+	+	-
Analysis of ketones	+	+	-

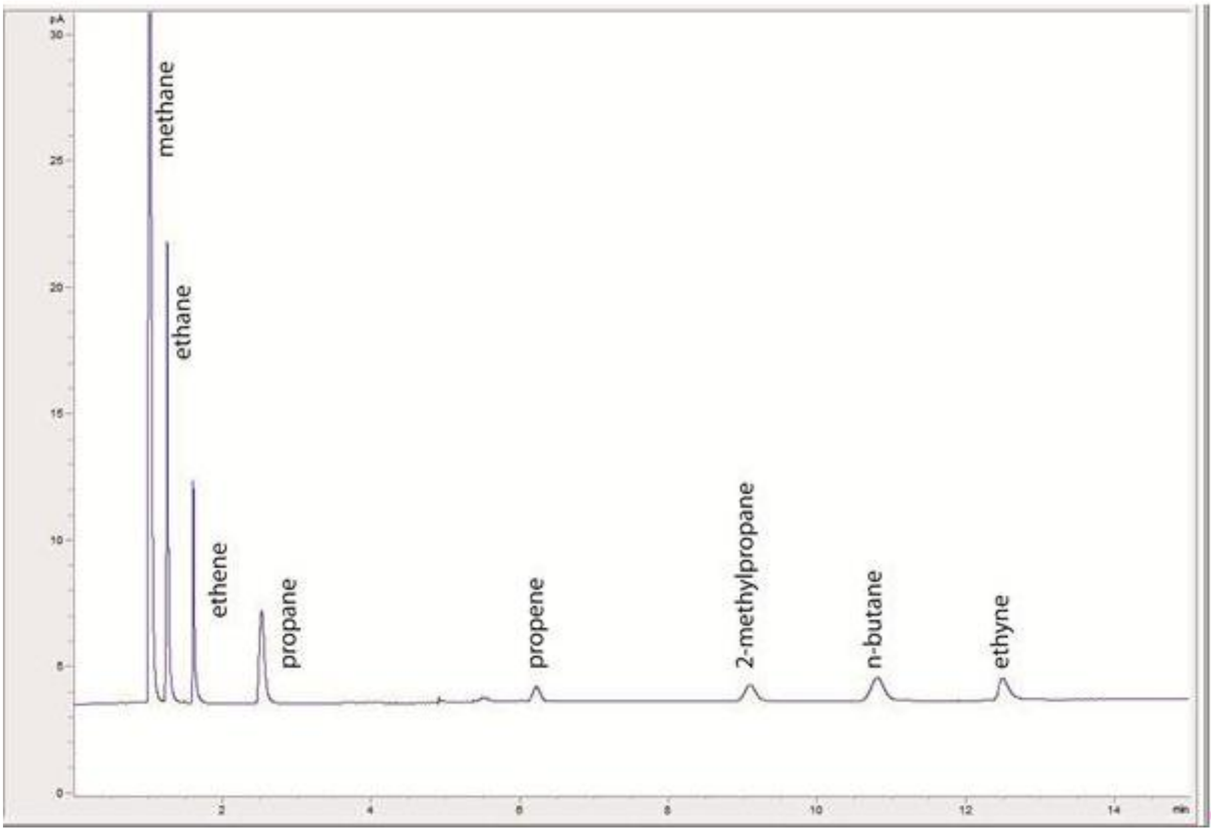
Analysis of ethers	+	+	-
Analysis of esters	+	+	-
Analysis of aromatics	+	+	+
Analysis of alkanes	-	+	+
Analysis of terpenes	+/-	+	
Analysis of nitriles	+	+	
Expected co-elution problems	Ethyl acetate+MVK+MEK (2-butanone), water peak+propanal and acrolein	Methanol+n-butane, butanal+benzene+ ethylacetate+MVK, 2-butanol+MEK, butylacetate+ ethylbenzene+m+p-xylene+n-hexanal, pentanal+toluene	n-butane and ethyne isohexanes isoheptanes m/p-xylene
Advantage	Strong selectivity to OVOCs, high retention of OVOCs even at above ambient oven temperatures, no retention of saturated aliphatic NMHCs, long lifetime	Water resistance, retention times not influenced by water, long lifetime	Strong selectivity on light hydrocarbons
Disadvantage	retention of water, tailing of unsaturated OVOCs, unsaturated NMHCs and aromatics with C>11 stick in the column	Co-elutions of OVOCs with aliphatic NMHCs, retention of water	Not useful for OVOCs

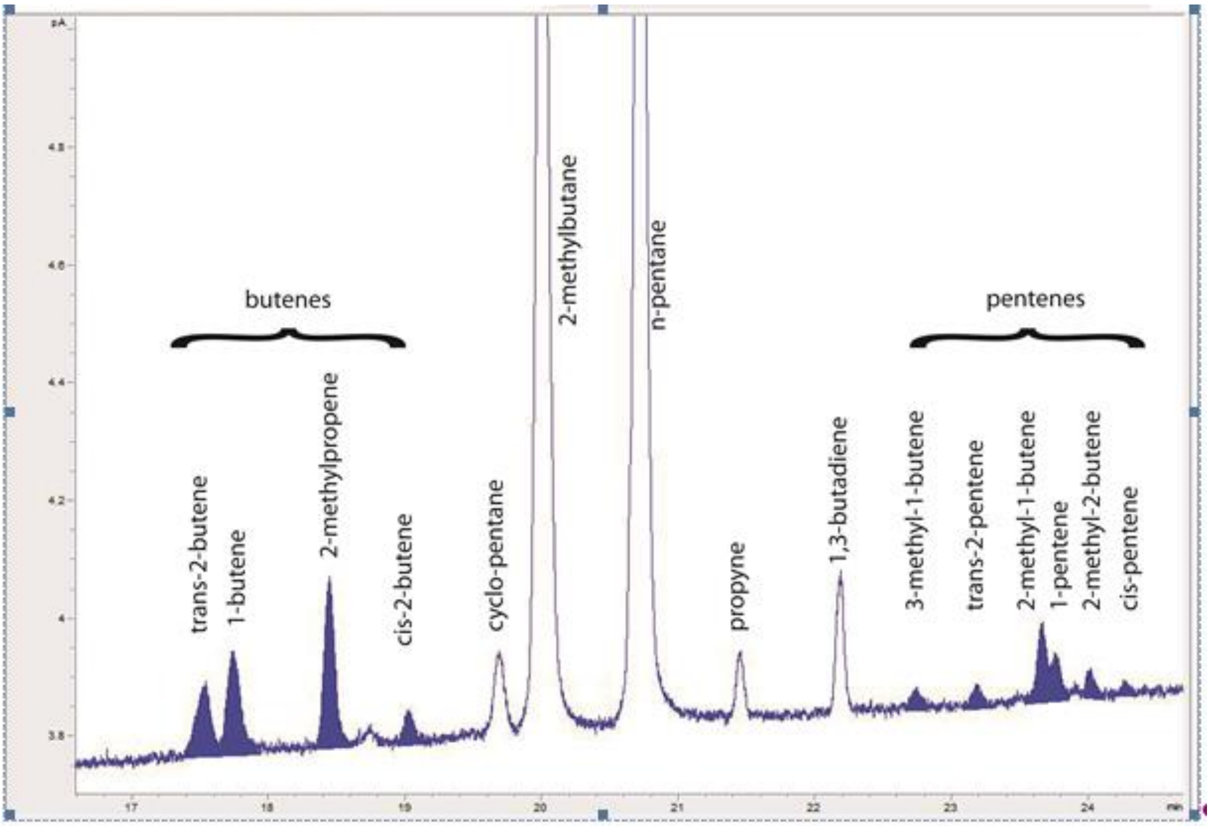
+: suitable for measurement of mentioned compound groups
-: unsuitable for measurement of mentioned compound groups

Examples of ambient air chromatograms

1A) Al_2O_3 (KCl) (from Rigi, Switzerland, Empa)






pA
4.8
4.6
4.4
4.2
4
3.8
butenes
trans-2-butene
1-butene
2-methylpropene
cis-2-butene
cyclo-pentane
2-methylbutane
n-pentane
propyne
1,3-butadiene
pentenes
3-methyl-1-butene
trans-2-pentene
2-methyl-1-butene
1-pentene
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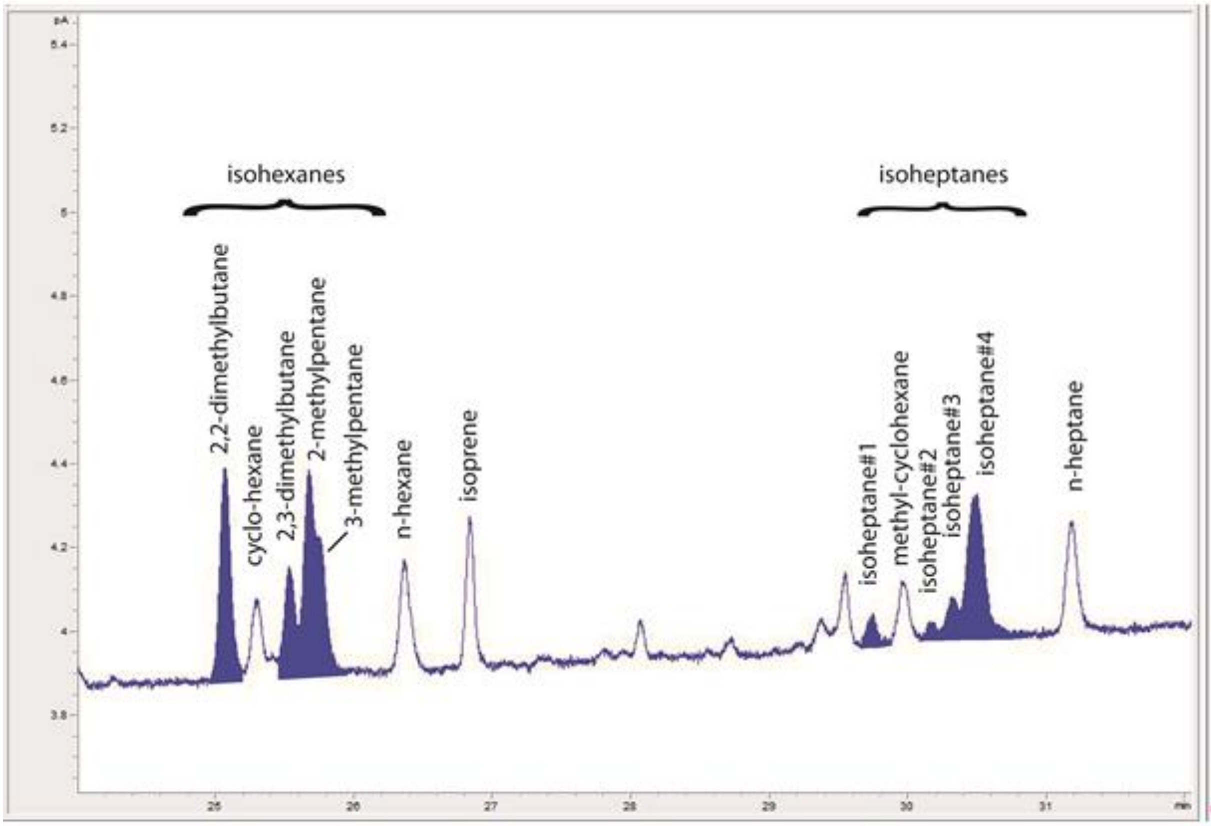
cis-pentene
17
18
19
20
21
22
23
24
min


pA
5.4
5.2
5
4.8
4.6
4.4
4.2
4
3.8
isohexanes
2,2-dimethylbutane
cyclo-hexane
2,3-dimethylbutane
2-methylpentane
3-methylpentane
n-hexane
isoprene
isoheptanes
isoheptane#1
methyl-cyclohexane
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28
29
30
31
min

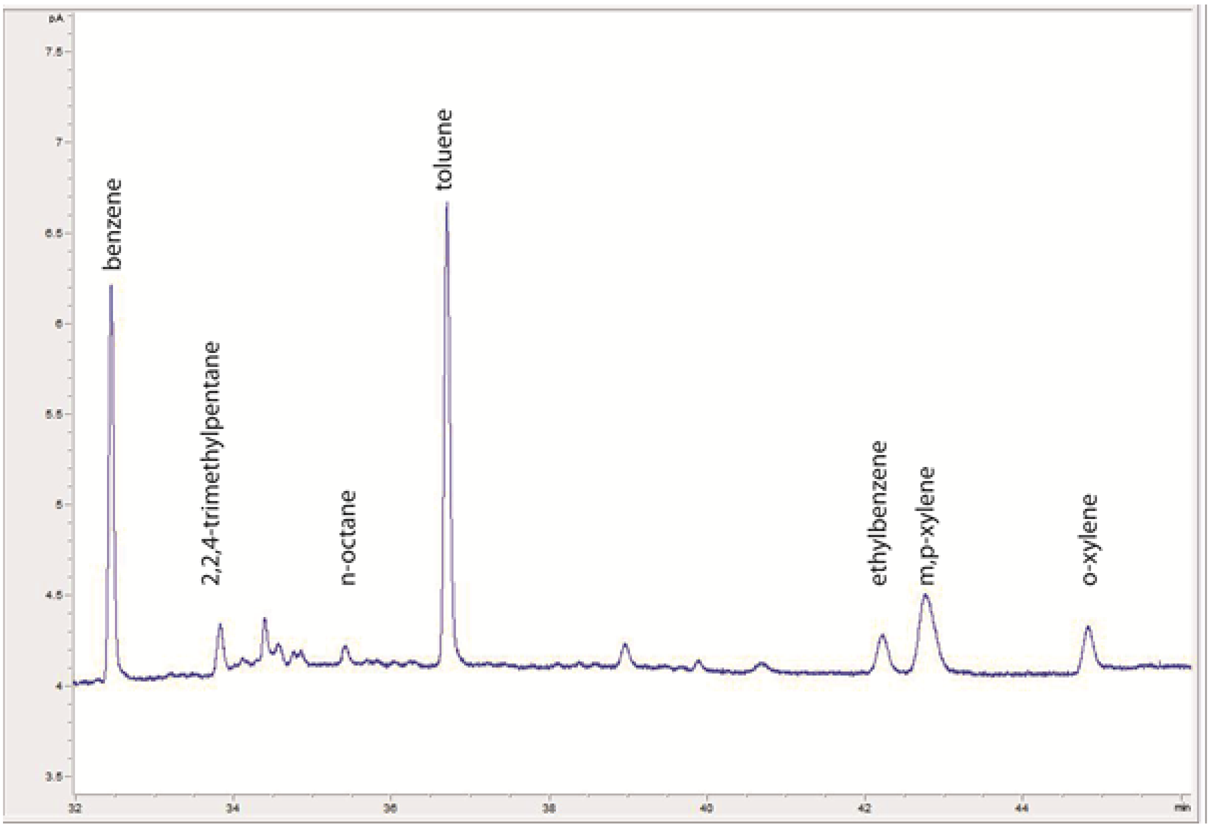

Figure A1: Al_2O_3 (KCl): a typical chromatogram at Rigi (Switzerland).

1B) LowOx

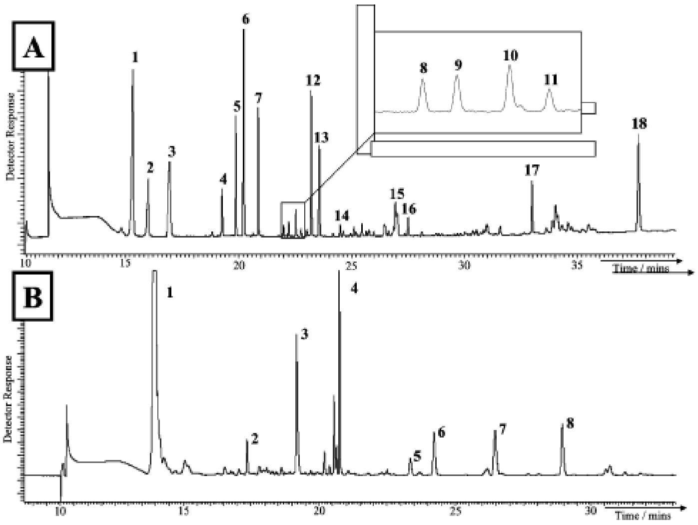

Fig. 3 Sample chromatograms produced from A; Al_2O_3 PLOT column where 1; ethane, 2; ethene, 3; propane, 4; propene, 5; iso-butane, 6; n-butane, 7; acetylene, 8; but-1-ene, 9; *trans*-but-2-ene, 10; iso-butene, 11; *cis*-but-2-ene, 12; iso-pentane, 13; n-pentane, 14; buta-1,3-diene, 15; 2+3-methylpentane, 16; n-hexane, 17; benzene, 18; toluene. And B; LOWOX column where 1; Aliphatic NMHCs, 2; benzene, 3; toluene, 4; acetaldehyde, 5; methanol, 6; acetone, 7; ethanol, 8; propanol.

Figure A2: CP-LowOx (Varian), 10 m x 0.53 mm x 10.0 µm (Hopkins et al., 2003).

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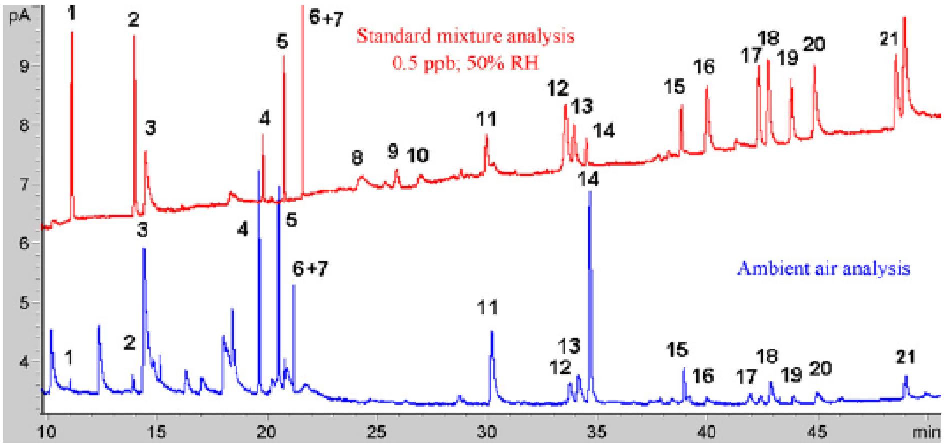


Fig. 9. Comparison of an analysis of ambient air and a standard mixture (0.5 ppb). Peak numbers are in Table 1.

Figure A3: CP-LowOx (Varian), 30 m x 0.53 mm x 10.0 µm (Roukos et al., 2009).

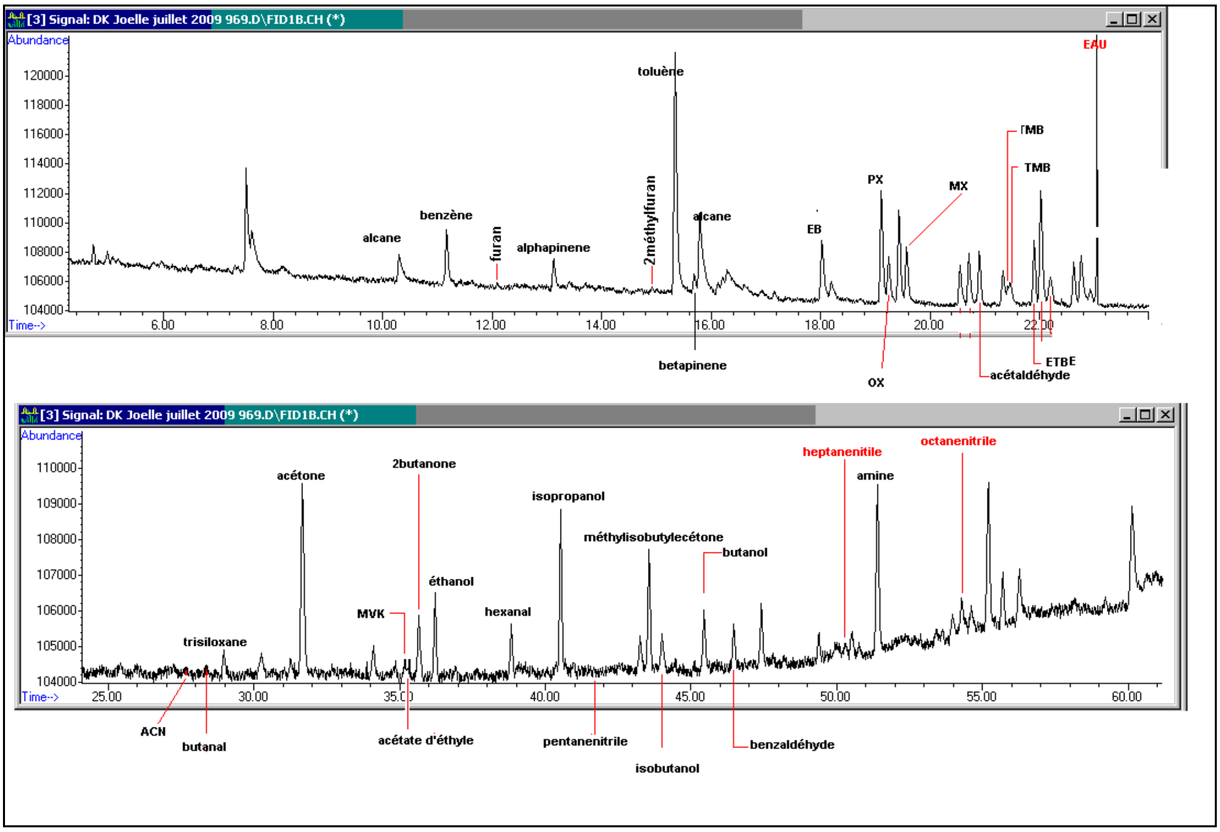


Figure A4: CP-LowOx (Varian), 30 m x 0.53 mm x 10.0 µm (measurements École des Mines de Douai, Environmental & Chemistry Department, site: Paris suburban, 2010).

1C) PoraBOND U

Fig. 5: CP-PoraBOND U (Varian), 25 m x 0.32 mm x 7.0 µm (measurements Empa 2012; system description: Ledreid, 2006):

4.0 min Methylether, 5.0 min Methanol, 5.1 min n-Butane, 5.5 min. 1,3-Butadiene, 5.9 min Acetaldehyde, 7.9 min Ethanol, 9.2 min Isoprene, 9.9 min Acrolein, 10.0 min Propanal, 10.6 min Methylacetate, 10.8 min Isopropanol, 11.1 min Acetone, 13.0 min MTBE, 13.3 Methacrolein, 12.6 n-Propanol, 14.8 Ethylacetate, 14.9 Butanal + Benzene, 15.1 MVK, 15.5 2-Butanol, 15.6 MEK, 17.1 2-Methyl-3-butene-2-ol, 17.8 n-Butanol, 19.8 Pentanal + Toluene, 24.1 Butylacetate + Ethylbenzene + m+p-Xylene + n-Hexanal, 24.8 o-Xylene, 29.0 Benzaldehyde.

2. *Dimethylpolysiloxane columns*

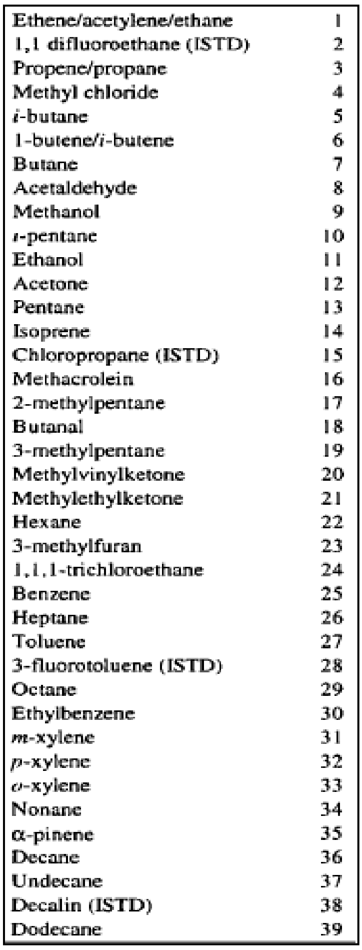
Table A4: Dimethylpolysiloxane columns

WCOT column equivalents	**DB-1 (Agilent), CP-Sil 5 CB (Varian), Rtx-1 (Restek), BP-1 (SGE), SPB-1 (Supelco)**	**HP-5ms resp. DB-5 (Agilent), CP-Sil 8 CB (Varian), Rtx-5ms (Restek), BPX-5 (SGE), SPB-5 (Supelco)**	**DB-624 (Agilent resp. Varian), Rtx-624 (Restek)**
Polarity	Non-polar	Non-polar	Midpolar
Composition	100% Dimethylpolysiloxane	5%-Phenyl-95%-methylpolysiloxane	6% Cyanopropylphenyl-94%-dimethylpolysiloxane
Operable temperature range	-60°C to 350°C	-60°C to 350°C	-20°C to 260°C
Analysis of alcohols	Tailing	Tailing	+
Analysis of aldehydes	+	+	+
Analysis of ketones	+	+	+
Analysis of ethers	-	-	-
Analysis of esters	+	+	+
Analysis of aromatics	+	+	+
Analysis of alkanes	+	+	+
Analysis of terpenes	+	+	+
Analysis of nitriles	-	+	+
Expected co-elution problems	Propanal+acetone, ethanol+acetone, n-pentane+acetone, n-butane+ acetaldehyde, OVOCs+ NMHCs	n-butane+acet-aldehyde+ methanol, isobutene+ methanol, ethanol+isopentane, acetone+propanal+ isopropanol, butanal+MEK, OVOCs+NMHCs	Propanal+acetone, OVOCs+NMHCs
Advantage	High thermal stability	More selective than DB-1, high thermal stability	Good retention of alcohols, good selectivity, good thermal stability
Disadvantage	Low selectivity, tailing of alcohols and ketones, co-elutions of OVOCs with NMHCs	Tailing of alcohols and ketones, co-elutions of OVOCswith NMHCs	Co-elutions of OVOCs with NMHCs

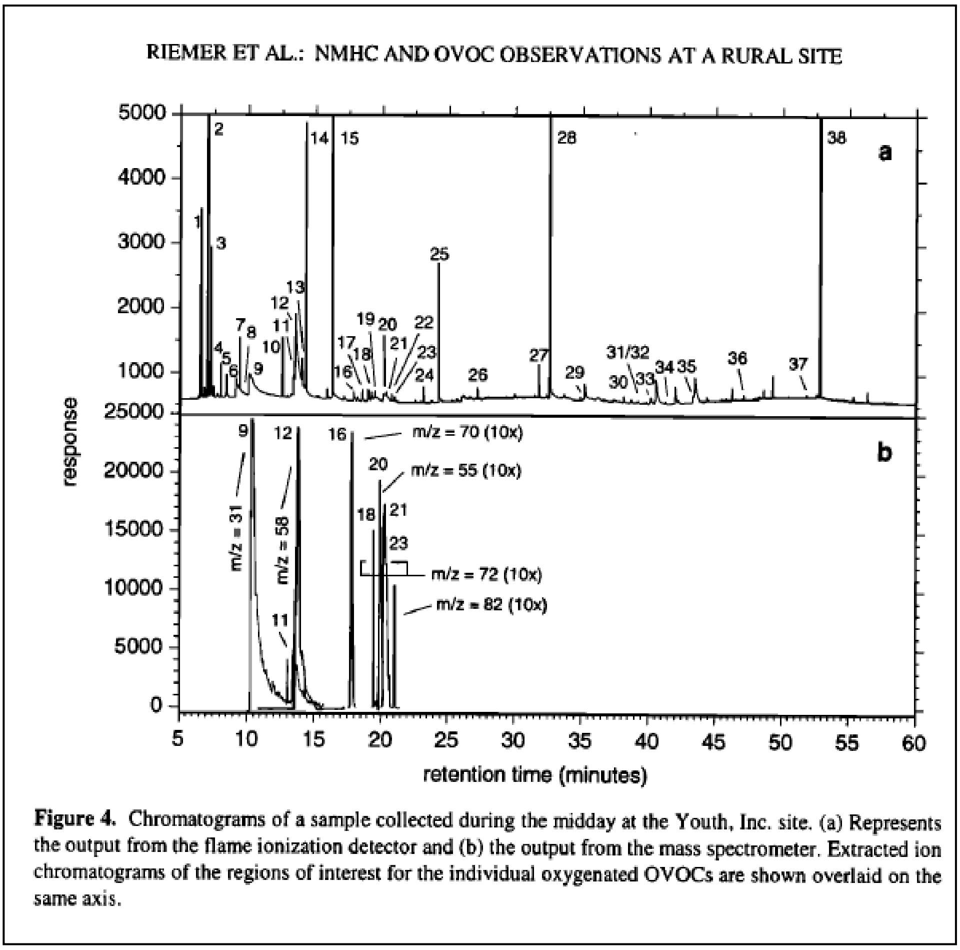
+: suitable for measurement of mentioned compound groups
-: unsuitable for measurement of mentioned compound groups

2A) DB-1

Figure A6: DB-1 (Agilent J&W), 100 m x 0.25 mm x 0.5 µm (Riemer et al., 1998).



Ethene/acetylene/ethane	1
1,1 difluoroethane (ISTD)	2
Propene/propane	3
Methyl chloride	4
i-butane	5
1-butene/*i*-butene	6
Butane	7
Acetaldehyde	8
Methanol	9
i-pentane	10
Ethanol	11
Acetone	12
Pentane	13
Isoprene	14
Chloropropane (ISTD)	15
Methacrolein	16
2-methylpentane	17
Butanal	18
3-methylpentane	19
Methylvinylketone	20
Methylethylketone	21
Hexane	22
3-methylfuran	23
1,1,1-trichloroethane	24
Benzene	25
Heptane	26
Toluene	27
3-fluorotoluene (ISTD)	28
Octane	29
Ethylbenzene	30
m-xylene	31
p-xylene	32
o-xylene	33
Nonane	34
α-pinene	35
Decane	36
Undecane	37
Decalin (ISTD)	38
Dodecane	39



RIEMER ET AL.: NMHC AND OVOC OBSERVATIONS AT A RURAL SITE

Figure 4. Chromatograms of a sample collected during the midday at the Youth, Inc. site. (a) Represents the output from the flame ionization detector and (b) the output from the mass spectrometer. Extracted ion chromatograms of the regions of interest for the individual oxygenated OVOCs are shown overlaid on the same axis.

2B) Rtx-1

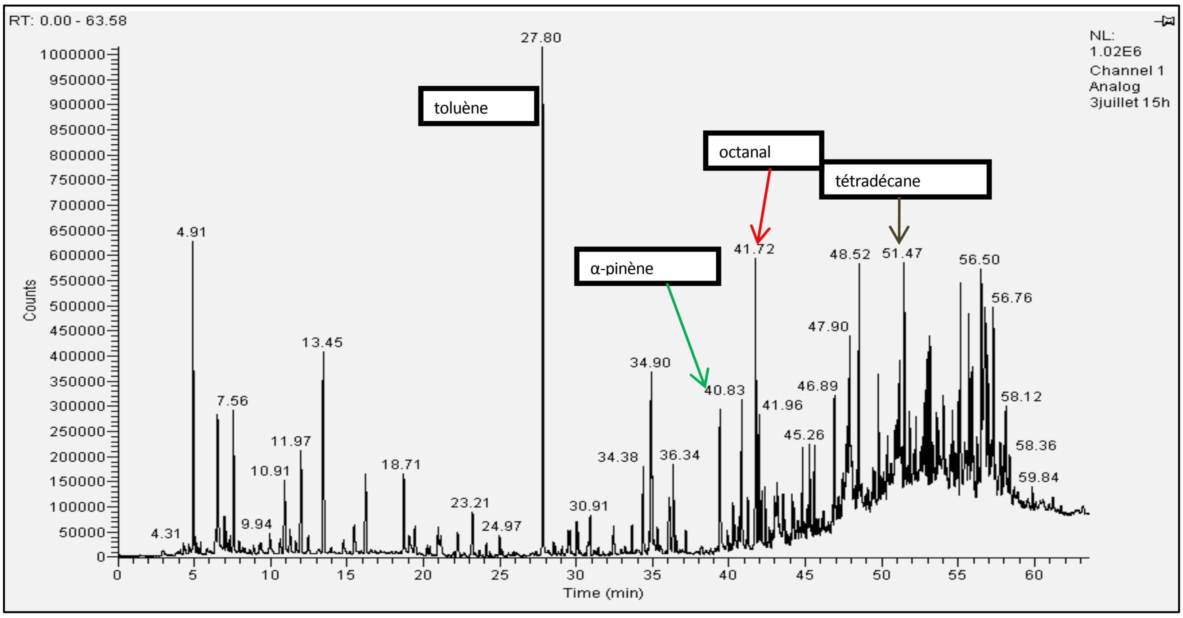


Figure A7: Rtx-1:

2C) BPX-5

Figure A8: BPX-5 (SGE), 50 m x 0.22 mm x 1.0 µm (measurements at Hohenpeissenberg Meteorological Observatory, 2011): 19.49 min isobutene + methanol, 19.55 min acetaldehyde, 19.60 min n-butane, 21.29 min ethanol, 21.49 min isopentane, 22.01 min CCl_3F, 22.55 min n-pentane, 22.67 min acrolein, 22.82 min acetone.

2D) DB-624

Figure A9: DB-624 (Agilent J&W), 10 m x 0.18 mm x 1.4 µm (Apel et al., 2003).

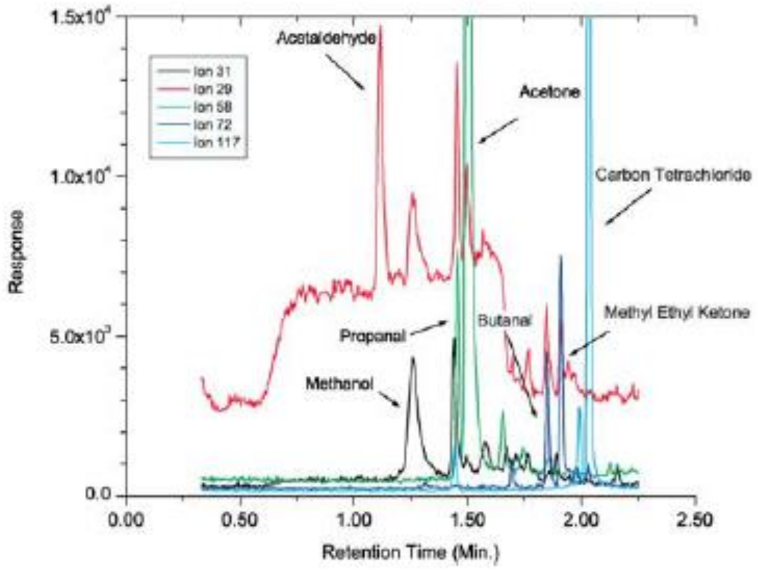


Figure 10. Typical chromatogram, obtained during the TRACE-P mission, of a subset of the targeted compounds. Ions used for quantification for individual compounds are color-coded.

3. *Polyethylene glycol column*

Table A5: Polyethylene glycol column

WCOT column equivalents	**DB-WAX (Agilent), CP-WAX 52 CB (Varian), Rtx-WAX (Restek), BP-20 (SGE), SUPELCOWAX 10 (Supelco)**
Polarity	High polar
Composition	Polyethylene glycol
Operable temperature range	20°C to 260°C
Analysis of alcohols	+
Analysis of aldehydes	+/-
Analysis of ketones	+
Analysis of ethers	+
Analysis of esters	+
Analysis of aromatics	+
Analysis of alkanes	+/-
Analysis of terpenes	+
Analysis of nitriles	-
Expected co-elution problems	Butanal+acetone, methanol+MEK+3-methylfuran, ethanol+benzene+MVK, methylbutenol+toluol, 2-pentanone+pentanal
Advantage	High retention of alcohols, low retention of alkanes (less co-elution problems)
Disadvantage	Low retention of aldehydes, short lifetime of the column, cannot be operated at sub-ambient temperatures

3A) CP-WAX 52 CB

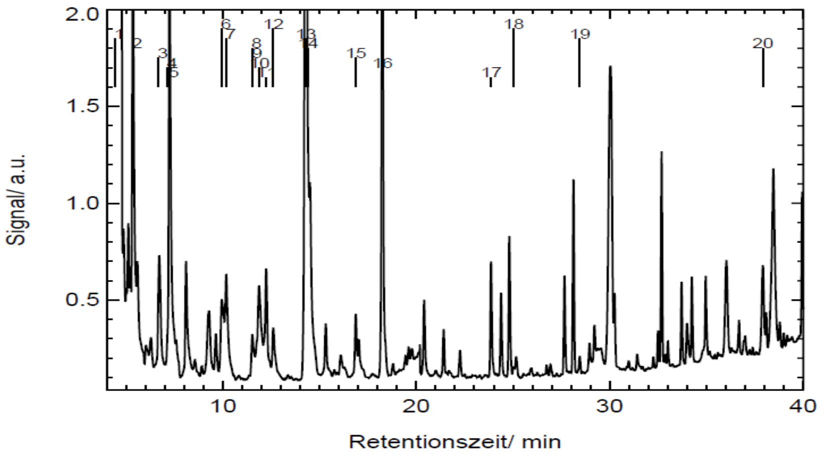


Abbildung 3.3: *Beispielchromatogramm aufgenommen am 12. September 2000 um 17:20. Es ist die Summe aller Massen von $\frac{m}{z}$=19 bis $\frac{m}{z}$=250 als Funktion der Retentionszeit wiedergegeben.* ***1***: *Isopren;* ***2***: *Acetaldehyd;* ***3***: *Propanal;* ***4***: *Butanal;* ***5***: *Aceton;* ***6***: *Methanol;* ***7***: *2-Butanon;* ***8***: *2-Pentanon;* ***9***: *2-Propanol;* ***10***: *Ethanol;* ***11***: *Benzol;* ***12***: *Methylvinylketon;* ***13***: *Decan (interner Standard);* ***14***: *3-Pentanon;* ***15***: *α-Pinen;* ***16***: *Toluol;* ***17***: *Ethylbenzol;* ***18***: *Butanol;* ***19***: *Limonen;* ***20***: *Benzaldehyd*

Figure A10: CP-WAX 52 CB (Varian), 60 m x 0.25 mm x 0.5 µm (Folkers, 2002).

3B) Rtx-WAX

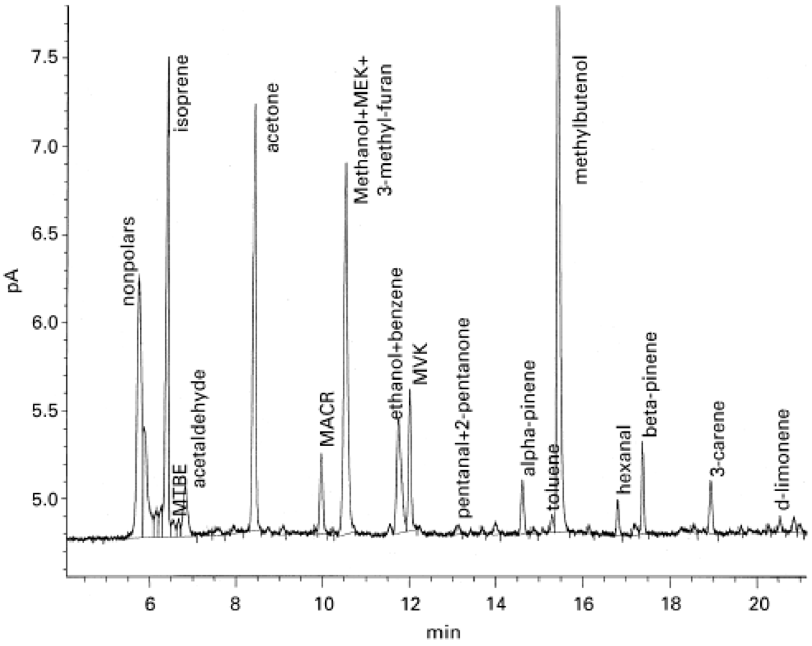


Fig. 1. Sample chromatogram from the Rtx-WAX column (July 1999).

Figure A11: Rtx-WAX (Restek), 60 m x 0.53 mm x 0.5 µm (Goldstein and Schade, 2000).

3C) DB-WAX

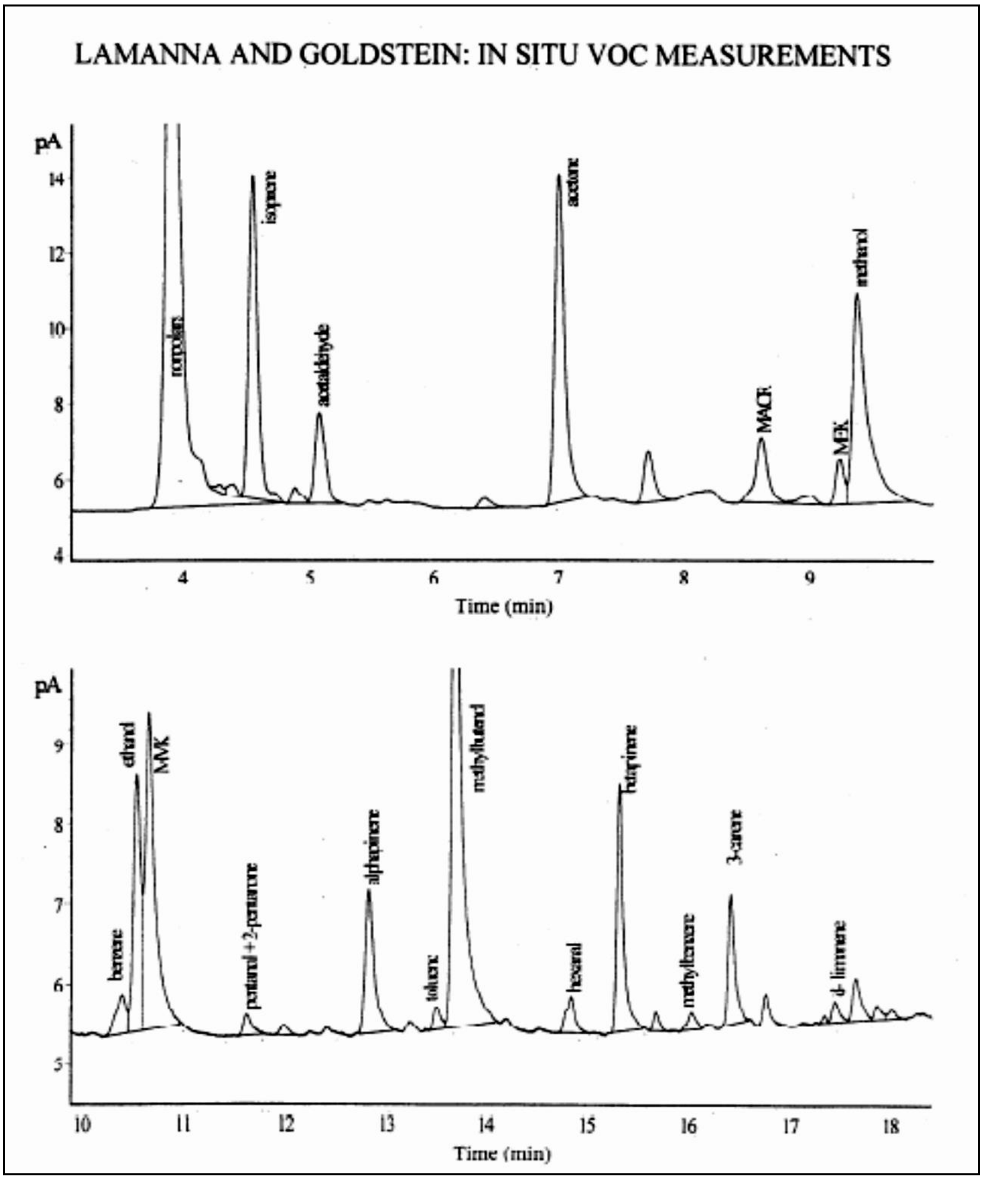


Figure A12: DB-WAX (Agilent J&W), 60 m x 0.32 mm x 0.5 µm (Lamanna and Goldstein, 1999).

References Annex:

Apel, E.C. et al. (2008): Intercomparison of oxygenated volatile organic compound measurements at the SAPHIR atmosphere simulation chamber. Journal of Geophysical Research 113 (D20307).

Apel, E.C. et al. (2003): A fast-GC/MS system to measure C_2 to C_4 carbonyls and methanol aboard aircraft. Journal of Geophysical Research 108 (D20): 15-1 – 15-12.

Apel, E.C. et al. (1998): Measurements comparison of oxygenated volatile organic compounds at a rural site during the 1995 SOS Nashville Intensive. Journal of Geophysical Research 103 (D17): 22,295 – 22,316.

Folkers, A. (2002): Oxygenated volatile organic compounds in the troposphere: Development and employment of a gas chromatographic detection method. Report of the Research Centre Jülich 3998. Dissertation University of Köln, Jülich.

Goldan, P.D., Kuster, W.C. (2004): Nonmethane hydrocarbon and oxy hydrocarbon measurements during the 2002 New England Air Quality Study. Journal of Geophysical Research 109 (D21309).

Goldstein, A.H., Schade, G.W. (2000): Quantifying biogenic and anthropogenic contributions to acetone mixing ratios in a rural environment. Atmospheric Environment 34: 4997-5006.

Helmig D. and Greenberg J. (1995) Artifact formation from the use of potassium iodide (KI) based ozone traps in atmospheric sampling. J. High Res. Chrom. 18, 15-18.

Helmig, D. (1999): Review: Gas chromatography air analysis. Journal of Chromatography A 843: 129-146.

Hopkins, J.R., Lewis, A.C., Read, K.A. (2003): A two-column method for long-term monitoring of non-methane hydrocarbons (NMHCs) and oxygenated volatile organic compounds (o-VOCs). Journal of Environmental Monitoring 5: 8-13.

Komenda, M., Schaub, A., Koppmann, R., 2003. Description and characterization of an on-line system for long-term measurements of isoprene, methyl vinyl ketone, and methacrolein in ambient air. Journal of Chromatography A 995, 185-201.

Lamanna, M.S., Goldstein, A.H. (1999): In situ measurements of C_2-C_{10} volatile organic compounds above a Sierra Nevada ponderosa pine plantation. Journal of Geophysical Research 104 (D17): 21,247-21,262.

Legreid, G. (2006): Oxygenated volatile organic compounds (OVOCs) in Switzerland: From the boundary layer to the unpolluted troposphere. Dissertation ETH No. 16982, Zürich, Dübendorf.

Leibrock, E., Slemr, J. (1997): Method for measurement of volatile oxygenated hydrocarbons in ambient air. Atmospheric Environment 31 (20): 3329-3339.

Leibrock, E. (1996): Development of a gas chromatography system for trace analysis of oxygenated volatile organic compounds in air. Scientific journal 40, Fraunhofer-Institute for Atmospheric Environmental Research, Garmisch-Partenkirchen. Dissertation Hamburg University of Technology, Hamburg-Harburg.

Lewis, A.C. et al. (1995): Programmed temperature vaporization injection (PTV) for in situ field measurements of isoprene, and selected oxidation products in a eucalyptus forest. Atmospheric Environment 29 (15): 1871-1875.

Miller, B.R., Weiss, R.F., Salameh, P.K., Tanhua, T., Greally, B.R., Mühle, J., and Simmonds, P.G. (2008) Medusa: A sample preconcentration and GC/MS detector system for in situ measurements of atmospheric trace halocarbons, hydrocarbons, and sulfur compounds, Anal. Chem., 80 (5), 1536-1545.

Pollmann J., Ortega J., and Helmig D. (2005) Analysis of atmospheric sesquiterpenes: sampling losses and mitigation of ozone interferences. Environ. Sci. and Technol. 39, 9620-9629.

Pollmann J., Helmig D., Hueber J., Tanner D., and Tans P. (2006) Evaluation of adsorbent materials for cryogen-free trapping-one stage-GC analysis of atmospheric C_2-C_6 non-methane hydrocarbons. J. Chrom., 1134, 1-15.

Pollmann J., Helmig D., Hueber J., Plass-Duelmer C., and Tans P. (2008) Sampling, storage, and analysis of C2-C7 non-methane hydrocarbons from the US National Oceanic and Atmospheric Administration Cooperative Air Sampling Network glass flasks. J. Chrom., 1188, 75-87.

Riemer, D. et al. (1998): Observations of nonmethane hydrocarbons and oxygenated volatile organic compounds at a rural site in the southeastern United States. Journal of Geophysical Research 103 (21): 28,111 – 28,128.

Roukos, J. et al. (2009): Development and validation of an automated monitoring system for oxygenated volatile organic compounds and nitrile compounds in ambient air. Journal of Chromatography A 1216: 8642-8651.

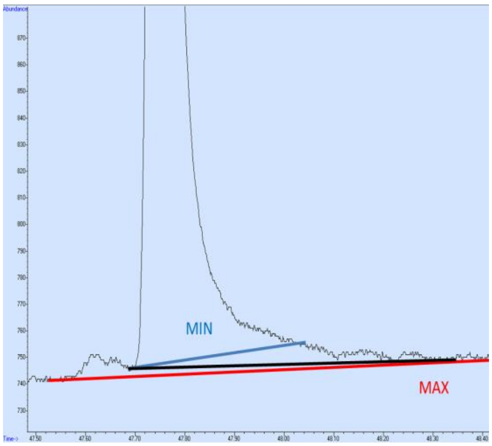
Zou, Y., Cai, M. (2008): Investigation of the unique selectivity and stability of Agilent GS-OxyPLOT columns. Agilent Technologies Application. Shanghai, China. Access: http://www.chem

APPENDIX 4: Example for uncertainty calculation

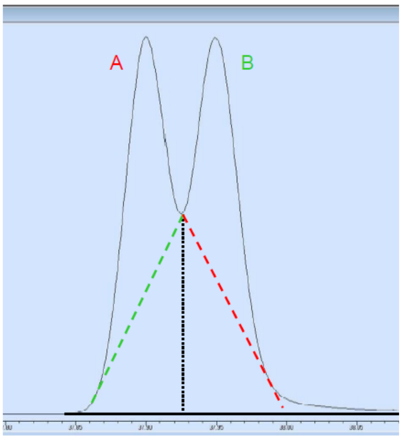
Please note that:

- Each variable of the uncertainty calculation is introduced in Table 1. The different uncertainties components are derived using equations presented in section 7.4 of the document.
- The uncertainty assessment is conducted using on-line GC/FID analysis. No linearity deviation, specific instrumental issues, and sampling device influence are taken into account.

- Two compounds are shown as example, both of them being present in the calibration gas mixture. In this case, an NPL standard and its certified concentrations and uncertainties are used.
- The sampling and calibration volume are estimated with the same device, thus no systematic error is accounted for.
- The reproducibility of the method has been determined with 2 series of 3 replicates of the working standard. Each individual compound concentration has been calculated using equation F1.
- The random changes in baseline position contributing to the integration error are included in the uncertainty of the repeatability of the measurement.
- For peaks strongly deviating from the theoretically expected Gaussian peak form (e.g. pronounced tailing or overlapping peaks) a systematic integration error is estimated. This can be achieved by integrating corresponding peaks manually such that an extreme minimum and maximum peak area is determined as depicted in figures 1 and 2. After determination of a maximum and a minimum peak area, the difference between max and min (d_{int}) of the derived peak areas is calculated. Then, $u_{\mathrm{int}} = \frac{d_{\mathrm{int}}}{6}$



<u>Figure 1</u>: example of tailing peaks. The black baseline represents the best fit. Red and blue lines illustrate the baselines to derive the maximum and minimum peak area, respectively.



<u>Figure 2</u>: example for not separated peaks. The baseline in black (straight line) yields the area of peak A and B. Applying a baseline drop in the peak valley (black dotted line) will separate the peak areas and yield the best estimate for the overlaid peaks. Dotted baselines in green and red can be used to derive the maximum and minimum expected peak areas.

<u>Table 1</u>: Example of uncertainty calculation for an on-line GC/FID

ACTRIS (www.actris.eu) is supported by the European Commission under the Horizon 2020 – Research and Innovation Framework Programme, H2020-INFRAIA-2014-2015, Grant Agreement number: 654109

Variable	*Description of the variable*	Ethane	Propane
A_{sample}	peak area of a sample measurement	17892	20101
A_{blank}	peak area of the blank (zero air) measurement	0	1873
A_{cal}	peak area of calibration gas measurement of compound	44149	55771
V_{sample}	sample volume (ml) 20 ml/min during 30min	600	600
V_{cal}	sample volume of calibration gas (ml)	600	600
$f_{cal,i}$	the calibration factor (see Eq F2)	54.36	44.53
$\chi_{cal,i}$	certified mole fraction of calibration gas (ppt)	4000	4000
$\chi_{sample,i}$	**the mole fraction in the sample (see Eq F1) (ppt)**	**1621**	**1353**
DL	detection limit of the measurement method (ppt)	9	7
(σ^{rel})	the relative standard deviation of 2 series of 3 replicats of the working standard	0.8%	1.3%
$u\chi_{prec}$	**combine the reproducibility and the Detection limit (see Eq F7) (ppt)**	**13**	**17**
ucal	certified uncertainty of the standard, Ucal given by the certificate divided by 2 (ppt)	40	40
$u\chi_{cal}$	uncertainty due to the calibration (see Eq F8) (ppt)	16	14
uV	systematic errors in sample volume determination Vsample=Vcal, neglected (ppt)	0	0
$u\chi_{instrument}$	further instrumental problems (ppt)	0	0
$uA_{\text{int},cal}$	potential error in peak area due to integration of the calibration (Amax-Amin)/6	759	876
$uA_{\text{int},sample}$	potential integration error of the sample (Amax-Amin)/6	128	992
$u\chi_{\text{int}}$	The Standard uncertainty due to the integration (See Eq F9) (ppt)	30	77
$u\chi_{lin}$	error due linearity issue (especially for the MS instruments) (ppt)	0	0
$u\chi_{sampling}$	sampling volume accuracy, storage issue, sampler blank, in this example blank (ppt)	0	0
$u\chi_{sample}$	The combined uncertainty of the mole fraction measured for the sample (see Eq F5) (ppt)	37	80
$U\chi_{sample}$	**The expanded uncertainty of the mole fraction measured for the sample (ppt) (eqF10)**	**73**	**161**
$U\chi_{sample}$	**The expanded uncertainty of the mole fraction measured for the sample (%)**	**4.5**	**11.9**

For the data submission, **X_{sample}, u_{prec} and $U_{Xsample}$** are reported, e.g. for ethane **1621, 13 and 73** respectively (in ppt)

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