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Guidelines for Measurements of Non-Methane Hydrocarbons in the Troposphere

WEATHER CLIMATE WATER

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GUIDELINES FOR MEASUREMENTS OF NON-METHANE HYDROCARBONS (NMHCs) IN THE TROPOSPHERE

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CONTENTS

1. GENERAL INTRODUCTION

Non-methane hydrocarbons (NMHCs) include short-chain (typically C_2 to ~C_{10}), high-vapour pressure alkanes, alkenes, alkynes, and aromatics. Together with the low boiling point oxygenated hydrocarbons (OVOCs, e.g. alcohols, ketones, aldehydes) they comprise 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) (*The changing atmosphere, an integrated global atmospheric chemistry observation theme for the IGOS partnership: report of the Integrated Global Atmospheric Chemistry Observation Theme Team* (WMO/TD No. 1235) 2004), VOCs are mainly related to air quality, oxidation capacity of the atmosphere, and chemistry-climate interaction. They are major precursors in photochemical ozone (O_3) and secondary organic aerosol (SOA) formation, they impact the oxidative capacity of the atmosphere and they are important tracers for emissions, transport, mixing, and chemistry. Some VOCs are also toxic or carcinogenic at high amount fractions and can directly impact human health.

NMHCs and OVOCs are emitted by the biosphere and by anthropogenic activities such as biomass burning, fossil fuel combustion and evaporation, and solvent usage. Their atmospheric lifetimes range from months in the case of ethane, to hours for the most reactive species such as alkenes (e.g. 1,3-butadiene or isoprene). The scientific rationale for 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 VOCs are among the long-term monitoring parameters in global and regional infrastructures such as the Global Atmosphere Watch or GAW (WMO, 2007b; GAW, 2017), the European Monitoring and Evaluation Programme (EMEP, 2008), the EU Aerosols, Clouds and Trace Gases Research Infrastructure (ACTRIS, 2017), and the US Environmental Protection Agency (EPA) Photochemical Assessment Monitoring Stations (PAMS) network (EPA, 2016).

Detailed NMHC measurement guidelines are provided here to the GAW community, focusing on the priority NMHC species identified in the GAW Report No. 171 *A WMO/GAW Expert Workshop on Global Long-term Measurements of Volatile Organic Compounds* (WMO/TD-No. 1373), (2007a; Table 1) and the GAW general quality assurance (QA) recommendations and strategic plan (WMO, 2007b). These measurement guidelines cover only the ground-based ambient measurements of NMHCs (C_2 to ~C_{10} hydrocarbons) by gas chromatography-flame ionization detection (GC-FID) and GC-mass spectrometry (GC-MS). For monoterpenes and OVOCs, as well as other analysis techniques (e.g. PTR-MS), separate measurement guidelines will be published in the future.

Table 1. Priority NMHCs listed in WMO (2007a) and modified in WMO (2017)
in order of increasing atmospheric lifetime

Molecule	Formula	Approx. lifetime
Isoprene (2-methylbuta-1,3-diene)	C_5H_8	3 hr
Toluene	C_7H_8	2 d
i-Pentane (2-methylbutane)	C_5H_{12}	3 d
n-Pentane	C_5H_{12}	3 d
i-Butane (2-methylpropane)	C_4H_{10}	5 d
n-Butane	C_4H_{10}	5 d
Benzene	C_6H_6	10 d
Propane	C_3H_8	11 d
Ethyne (acetylene)	C_2H_2	15 d
Ethane	C_2H_6	2–3 months

NMHCs are typically present in the atmosphere at low parts-per-billion to parts-per-trillion levels. Their analysis requires a sequence of steps that entails their extraction/ preconcentration from the bulk air constituents, gas chromatography separation, and detection. The measurement of NMHCs by gas chromatography generally includes these components and steps:

(1) Intake manifold and sampling line,

(2) Scrubbers and filters (traps) to remove particles, water, ozone and possibly CO_2,

(3) Sample preconcentration (followed by thermal desorption),

(4) Gas chromatographic separation,

(5) Detection / identification of eluting compounds,

(6) Data processing and data delivery.

A sample containing atmospheric NMHCs can be introduced to an analytical system directly from ambient air (online), or via a pre-filled sampling canister or an adsorptive sampling tube (offline). The sample is normally passed through a particle, moisture and/or ozone removal system and then concentrated in a freeze-out trap or on a chemical adsorbent medium that is cooled either cryogenically or using thermo-electric devices. There may also be an additional refocussing of analytes by a cooled secondary trap before injection of analytes in a narrow band onto the GC separation column. The concentrated sample is directly thermally desorbed onto the GC column, separated by chromatography, and finally quantified by FID, MS, or any other suitable detector, e.g. a photoionization detector (PID).

Throughout this document, the term ‘amount fraction’ is used instead of mole fraction, because amount fraction, unit mol mol^{-1}, is the preferred quantity for expressing gas mixture composition in metrology. As such we use pmol mol^{-1} instead of ppt or 1 part in 10^{12}, nmol mol^{-1} instead of ppb or 1 part in 10^9, and µmol mol^{-1} instead of ppm or 1 part in 10^6. The terms ppt, ppb and ppm are not recommended as their meanings are language dependent.

2. DATA QUALITY OBJECTIVES

Data quality objectives (DQOs) were introduced in the 2000–2007 strategic plan in WMO/GAW (WMO, 2001) and were first presented for NMHCs in the GAW Report 171 (WMO, 2007a). They define the quality and quantity of data required to support policy decisions and scientific research such as trend assessments, air quality studies and modelling. Table 2 shows the requirements for answering these specific questions. In Table 3, revised and more demanding DQOs (GAW target performance goals) are listed together with older values from WMO (2007a) (GAW basic performance goals). These DQOs are defined for measurements of NMHCs in compressed whole air test gases and they are used to assess inter-laboratory compatibility. They are expressed as an expanded uncertainty *U*, which defines an interval around the measurement result in which a large fraction of the measurand is expected to lie. The DQOs use a coverage factor $k = 2$, which corresponds to a level of confidence of ~95% that is required to answer specific scientific questions (see Table 2).

Table 2. Required data quality for NMHC measurements in ambient air, expressed as expanded uncertainties (k = 2) at levels of 100 pmol mol^{-1} or above.

Scientific question	Expanded uncertainty required*
- Decadal trends for changes of sources and environmental conditions - Source attribution studies	5%
- Modelling of tropospheric ozone and SOA - Total reactivity closure studies - Ambient air quality/health studies - Comparability between different studies	20–30%

* Minimum requirement for global sites.

For example, models that assess the impact of NMHCs on the formation of secondary pollutants and other atmospheric chemical processes often face large uncertainties due to the high regional and temporal variability of trace compounds and considerable uncertainties in rate constants. Models may also be limited by the fact that individual NMHC species generally have only a minor impact on integrated parameters such as the O_3 formation rate or oxidizing capacity. Accordingly, for studies including chemical models, a 20–30% expanded uncertainty is considered sufficient since the measurement uncertainty is rarely the most significant uncertainty factor (Table 2).

The rationale for the DQOs listed in Table 3 is driven by the scientific need to detect subtle 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. Within the EU for example, emissions of anthropogenic NMHCs (alkanes, alkenes, alkynes, aromatics) are regulated by the National Emissions Ceiling Directive (EMEP, 2008) and fall under the policy aegis of the Convention on Long-range Transboundary Air Pollution (CLRTAP, 2016). Emissions reduction goals of NECD and CLRTAP should lead to lower emissions, and these should be detectable at regionally influenced GAW sites. Such changes can only be detected when the overall measurement uncertainty is better than half of the expected trend. Minimizing the uncertainty is also important for correctly attributing sources, for example by source apportionment techniques such as Positive Matrix Factorization (PMF). Therefore, the expanded uncertainty for NMHCs in ambient air measurements should be lower than 5%.

Table 3. Data quality objectives (DQOs) for the measurements of NMHCs in whole air compressed test gases (inter-laboratory compatibility) expressed as expanded uncertainty (k = 2) and repeatability (k = 1).

The basic station performance requirements correspond to the former and weaker DQOs of GAW Report 171 (WMO, 2007a). For amount fractions < 100 pmol mol^{-1}, the DQOs are expressed in absolute pmol mol^{-1} (rather than as a percentage).

	GAW basic performance goal: Expanded uncertainty	GAW basic performance goal: Repeatability	GAW target performance goal: Expanded uncertainty	GAW target performance goal: Repeatability
Amount fraction >100 pmol mol^{-1}				
Alkanes	10%	5%	5%	2%
Alkenes including isoprene	20%	10%	5%	2%
Alkynes	15%	5%	5%	2%
Aromatics	15%	10%	5%	2%
Amount fraction <100 pmol mol^{-1}				
Alkanes	10 pmol mol^{-1}	5 pmol mol^{-1}	5 pmol mol^{-1}	2 pmol mol^{-1}
Alkenes	20 pmol mol^{-1}	10 pmol mol^{-1}	5 pmol mol^{-1}	2 pmol mol^{-1}
Alkynes	15 pmol mol^{-1}	5 pmol mol^{-1}	5 pmol mol^{-1}	2 pmol mol^{-1}
Aromatics	15 pmol mol^{-1}	10 pmol mol^{-1}	5 pmol mol^{-1}	2 pmol mol^{-1}

The determination of the system measurement uncertainty is commonly done by quantification and precision measurements of NMHCs from synthetic or whole air test gases in pressurized gas cylinders. The DQOs in Table 3 are for pressurized cylinder tests and are defined in absolute terms (rather than as a percentage) for amount fractions lower than 100 pmol mol^{-1}. This is justified by the increasing influence of uncertainty as concentrations approach the limits of detection, which are typically around 10 pmol mol^{-1} for NMHC measurement systems in the field. An intercomparison experiment conducted in the framework of the European ACTRIS project has shown that these GAW DQOs are achievable by a substantial number of different instruments and research groups (Hoerger et al., 2015).

3. NMHC MEASUREMENT SETUP

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

3.1 Facility requirements

Facility requirements include 24-hour available electricity and communications, and a building suitable for the instruments and staff. The facility and equipment should support 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 to be addressed as well as practical considerations such as funding and personnel. The sampling frequency should allow seasonal cycles and annual trends to be produced. For example, EMEP (2008) recommends performing regular offline sampling twice per week at local noon, and online sampling twice per day (at local noon and midnight) and preferably more frequently. However, it is recognized that this frequency of sampling may not be possible in all locations. Air sampling should be structured in a way to avoid local contamination sources (see Section 4). The laboratory building and inlet location should be set away from any other buildings, garages, parking lots, generators, or other emission sources, and any nearby areas where fossil fuels or biomass may be combusted or 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 a 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. Technicians should possess skills in: (1) analytical chemistry, particularly atmospheric composition; (2) electronics; and (3) information technology (IT), particularly instrument control, data acquisition, and data processing. It is recommended that the station staff participates in the GAWTEC training programme and other GAW specialist activities, or those of infrastructures associated with GAW, e.g. the European ACTRIS consortium.

Provisions should be made for backup staff to cover the periods when regular staff are away at training, annual leave, etc.

3.3 Occupational health and safety

The NMHC measurements may involve the 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 exist and appropriate occupational health and safety information, protective equipment and training is required.

3.4 Instrumentation requirements

The following supporting infrastructure is required for a reliable long-term NMHC monitoring station in GAW:

- Suitable inlet and NMHC 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 NMHC and O_3 removal, and, depending on the purpose, also H_2O removal (see Section 7);
- Sample path including inlet line and filters inert to NMHCs;
- Computer, instrument control and data acquisition interface;
- Internet connection/remote computer access;
- Uninterruptable power supply.

Equipment can vary in specification and performance; the World Calibration Centre (WCC), GAWTEC, and existing experienced GAW stations and laboratories can provide advice on instrumentation that has worked successfully in the past.

Manufacturers' instrument reference manuals must 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 need for a replacement. If the instruments' performance indicates the need for a replacement, the new and old system should run in parallel for some time, for at least six months if possible.

Since IT equipment is subject to faster evolution, backup 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 depend on the available manufacturers' software for the GC and the thermal desorption equipment, although typically both software packages run on the same PC.

3.4.3 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 composition 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.

3.4.4 Associated key measurements and logging requirements

Key measurements that will help in the interpretation of NMHC measurements include those used for processing the NMHC data, data selection and those related to NMHC chemistry. To understand the influence of nearby sources, undertake data selection according to meteorological conditions, and achieve optimal quality control, measurement of the following additional parameters are useful:

- Meteorological parameters (requirement for GAW stations (WMO, 2017b)): Wind speed, wind direction, air temperature, humidity, air pressure;
- 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 amount fractions;
- Particle number concentrations and speciation;
- ^{222}Radon concentration.

The measurement techniques for these parameters are defined in *Global Atmosphere Watch measurements guide* (GAW Report No. 143 (WMO/TD-No. 1073) 2001b) and in individual measurement guidelines (WMO, 2007a; WMO, 2010b; WMO, 2010c; WMO, 2011a).

An instrument logbook should be used to keep track of events which could influence the quality of the measurements (e.g. change of pumps and inlet lines for offline systems and change of instrument parts, instrument settings and gas replacements for online instruments, column changes, etc.). In addition, a station logbook should be used to follow external events, such as building activities and nearby local pollution (e.g. from fires and heavy-duty equipment).

3.5 Environmental issues that affect GAW stations and NMHC observations

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

- Inlet blockage due to ice riming and blowing snow
- Condensing water within the inlet system
- Pollution events from nearby roads, industry, agriculture, biomass burning, volcanoes, etc.
- Access limited by environmental conditions such as flooding, severe weather, etc.
- Tourist activities

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

4. SAMPLING OF NMHCS

NMHCs in sample air can be analysed online at the measurement site or offline using passivated or electropolished stainless steel canisters, glass flasks or adsorption tubes. Offline samples are subsequently transported to a central lab where they are analysed. The specific requirements of the different sampling methods are described in this Section.

4.1 Location of the inlet

The height of the air inlet is critical to sampling representative air. The optimum inlet height depends on the surrounding area (vegetation, orography, soil, water, snow). New stations should, if possible, sample NMHCs at 2–3 different heights for a trial period to determine which inlet height is suitable for minimizing local contamination. 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 two metres above the building where the sampling line is mounted, and at least five metres above ground. Stations on mountains may use lower inlets, if appropriately tested. These inlet location recommendations represent guidelines, but station PIs must demonstrate that the inlet is mounted such that it is not impacted by emissions from the station or point sources very close to the station.

4.2 Inlet manifold and sampling lines

Generally, a high flow inlet manifold is recommended to minimize the transport time from the inlet to the laboratory (<1 min). From there, small diameter and short sampling lines go to the sampling devices (e.g. canisters) or directly to the instruments. For NMHCs the manifold and sampling line should preferably consist of surface-passivated steel (e.g. silcosteel® or sulfinert®) or glass. If stainless steel is used, it should be electropolished and heated up to 70°C to prevent condensation of NMHCs on internal surfaces (Hopkins et al., 2011). Using untreated stainless steel is not recommended.

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 (typically 10 min at 30 ml/min are sufficient for NMHCs) to equilibrate surfaces. The residence time between the manifold and the instrument should not exceed a few seconds. Installing a particle filter is recommended (see Section 5.1.4).

In order to control the sampling flow, mass flow controllers (MFCs) or needle valves can be used. It is recommended to locate the MFC/needle valve downstream of the sampling device. If this is not possible, the MFC and valve material must be tested for sampling artefacts. If needle valves are used it is recommended to measure the sample flow downstream with a mass flow meter (MFM).

4.3 Offline sampling

Offline sampling should follow a station specific protocol. As generally only a limited number of offline samples are taken, these should characterize typical air masses at the station with little influence from local sources. For non-mountain stations, conditions around noon, e.g. between 12:00 and 14:00 local time, should be chosen because then a well-mixed boundary layer has developed. According to monitoring requirements, the sampling time may vary from seconds to several hours. At mountain stations (depending on their height and sampling time), free tropospheric, residual layer, or mixed-layer air can be sampled. Generally when an operator performs offline sampling, indications for local contamination from other online instruments at the station should be checked, e.g. NO_x or particle concentration (see Section 3.5). Furthermore, meteorological conditions that can lead to small local impacts, 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 or of stagnant wind conditions.

4.3.1 Electropolished stainless steel canisters and passivated stainless steel canisters

In the GAW Report No. 204 *Standard Operating Procedures (SOPs) for Air Sampling in Stainless Steel Canisters for Non-Methane Hydrocarbons Analysis* (WMO, 2012) a Standard Operation Procedure (SOP) is described for the sampling of a sub-group of NMHCs in electropolished stainless steel 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 the US-EPA (1998, 1999) on determination of NMHCs in ambient air.

The described procedures are appropriate for alkanes, alkenes, alkynes, and aromatic compounds with two to six carbon atoms (C_2 to C_6). Some NMHCs with more than six carbon atoms can be adsorbed on the canister surfaces and may only be partially recovered. The procedures are valid for analysing volatile alkanes, ethyne and isoprene amount fractions in continental background air with amount fractions at pmol mol^{-1} levels as well as for ambient air in and around urban areas in the range of µmol mol^{-1}. Under conditions of normal usage for sampling ambient air, most NMHCs can be recovered from canisters near their original concentrations after storage times of up to thirty days (US-EPA, 1999), however air sample storage time is recommended to be as short as possible before analysis. As an alternative to electropolished stainless steel, passivated stainless steel canisters e.g. by Silconert 2000®, SUMMA® treatment, can also be used.

4.3.2 Glass flasks

Glass flasks, as used in the NOAA Cooperative Air Sampling Network with the corresponding automatic sampling equipment, have been shown to provide high quality observations for analyses of C_2-C_6 NMHCs, including ethyne, and isoprene. This was verified in an ongoing comparative study with the online system at Hohenpeissenberg (Pollmann et al., 2006; Helmig et al., 2016, Blanchard et al., 2017; Hueber et al., 2017).

4.3.3 Adsorption tubes

Though offline 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 to meet the DQOs. While the method is used widely in areas such as occupational health, these studies are often concerned with much higher concentrations of NMHCs than are found at GAW stations. One of the main problems associated with adsorption tubes are artefacts due to poor blanks (especially for aromatic compounds), often in a similar range of amount fractions as those encountered at clean background sampling sites.

4.4 Online sampling for quasi-continuous observations

While online sampling avoids storage issues, minimizes leak issues, and increases the time resolution of data, it requires an analytical system located at the sampling site and is limited in terms of sampling intervals by the capabilities of the analytical system. During online sampling, air is directly transferred via a sampling line into the GC. Use of online systems is encouraged at all GAW global stations if the following criteria are met: well-trained personnel, the appropriate equipment and the resources necessary for QA/QC including regular zeroing, calibration procedures installed, and target gas measurements available. Otherwise, it is recommended to use offline sampling and perform the analyses in an experienced laboratory.

4.5 Determination of the sampling volume

The sampling volume can be determined either with a MFM or a reference volume.

4.5.1 Determination of sampling volume using a reference volume

If sampling into a known reference volume is applied, the sample volume (V_{sample}) can be determined by the pressure and the temperature changes in a defined reference volume:

$$V_{sample} = \left[\frac{p_{end}}{T_{end}} - \frac{p_{start}}{T_{start}}\right] * T_0 * \frac{m_0}{p_0} \quad \text{(F1)}$$

with

p_{end}, T_{end} = pressure and temperature in the reference volume at the end of the sampling

p_{start}, T_{start} = pressure and temperature in the reference volume at the beginning of the sampling

p_0 ,T_0 = Standard pressure 1013,25hPa and temperature 273.15K

m_0 = Reference volume under conditions p_0 and T_0

The advantage is that temperature and pressure sensors have high accuracy and low drifts, especially as this method uses differential values. The derived sample volume has a high accuracy and high stability. It is sufficient to check the pressure sensor and its calibration every few years or in case of issues with the sample volume (e.g. drifts, instabilities, etc.)

The disadvantage of this method is that it requires a more sophisticated instrumental set-up.

4.5.2 Determination of sampling volume by MFC/MFM

Using a mass flow controller / mass flow meter (MFC/MFM) for sampling, the sample volume is determined by

$$V_{sample} = t * F \quad \text{(F2)}$$

with

t = duration of sampling

F = mass flow through the trap/sampling device

The advantage of this method is its simple set-up.

The disadvantage is that mass flow meters are prone to drifting, have a lower accuracy compared to pressure sensors and require frequent calibrations. The accuracy of an MFC/MFM is usually defined relative to its full scale. Therefore, it is recommended to use MFC/MFM suitable to the range of the sampling flow (e.g. for 80 ml min^{-1} of sampling flow apply a 0–100 ml min^{-1} MFM) and to check/calibrate MFMs versus a stable standard twice a year. Stable standards are e.g. DryCal.

5. MEASUREMENT TECHNIQUES FOR ANALYSIS OF NMHCS

For online and offline in situ analyses of C_2 to C_{10} NMHC species from ambient air, different measurement techniques are available (Table 4). Gas chromatography (GC) systems are currently the method of choice. The advantages are medium cost, high sensitivity, excellent reproducibility, and, depending on the applied chromatographic details, resolving power to speciate many different VOCs. Disadvantages are the restricted time resolution (due to the chromatography) and possible artefacts or losses in the necessary preconcentration step. An alternative with a high time resolution is the proton-transfer reaction mass spectrometer (PTR-MS; Lindinger et al., 1998), which can be applied to analyse NMHCs with alternating double bonds (e.g. aromatics or 1,3-butadiene). PTR-MS and other chemical ionization – mass spectrometry systems will be covered in a separate Measurement Guidelines report. Other NMHC measurement techniques are evolving (e.g. CRDS, chemiluminescence) but are currently not considered in these guidelines since the methods are still under development and detection limits are still too high.

Table 4. Measurement techniques available for C_2 to C_{10} NMHCs.

Instrument type	Detection limit	Compounds	Guidelines
GC-FID, GC-MS	≤10 pmol mol^{-1}	C_2 to C_{10}	Here
PTR-MS	≤10 pmol mol^{-1}	Aromatics, alkenes with alternating double bonds	In preparation
PTR-TOF-MS	≤10 pmol mol^{-1}	See PTR-MS + separation of isobaric compounds possible	In preparation
CRDS	1 nmol mol^{-1}	Single NMHCs e.g. ethane	-
Chemiluminescence	~1 nmol mol^{-1}	Isoprene	-
Electrochemical gas sensors	~1 μmol mol^{-1}	Single NMHCs (e.g. benzene, ethane)	-

NMHC amount fractions in the remote atmosphere typically range from pmol mol^{-1} or less, to >10 nmol mol^{-1}. As a result of these potentially 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 must be pre-concentrated before GC analysis in order to increase signals above the instrumental detection limits. Preconcentration of NMHCs is performed on a so-called trap, consisting of a tube packed with adsorbent material held at a low, often sub-ambient, controlled temperature (Section 5.2). After heating the trap, the pre-concentrated compounds are subsequently transferred 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 with an appropriate detector (FID or MS, see Section 5.4.1 and 5.4.2).

5.1 Removal of water / ozone / carbon dioxide / particles

Prior to preconcentration, additional scrubbing devices may be required. Water in ambient air affects the adsorption capacity of the preconcentration trap (see Appendix 2), the chromatography (peak shapes) and retention times, and leads to ice formation in the preconcentration unit when temperatures < 0°C are applied. Co-sampled ozone may react with alkenes during the preconcentration step. Ozone can react with the adsorbent material itself (see Appendix 1), producing additional organic compounds. Adsorbed carbon dioxide can distort the chromatography on porous layer GC columns or affect detector sensitivity. Furthermore, when adsorption temperatures are <–78°C the sampling trap can be blocked. Finally, particle filters are recommended to avoid contamination of the system and blockages of lines and valves.

5.1.1 Water removal / management

Water management is used to reduce the dew point of the atmospheric sample. This can be achieved by different methods such as a cold trap or a Nafion® dryer (Table 5). The use of cold traps is recommended because these systems are less prone to artefacts and analyte losses when compared to Nafion (in which case appropriate care has to be given to the characterization of blanks and analyte losses). The use of chemical water traps (e.g. $Mg(ClO_4)_2$) is not recommended for NMHC sampling because they increase the risk of poor blanks and artefacts. Furthermore, these materials can form a solution which can be transported through parts of the inlet after reacting with water. Regardless of which water management system is chosen, its efficiency, potential artefacts (e.g. blank values) and the recovery of the target NMHCs need to be tested (see Standard addition measurements in Section 7.1.4).

If *hydrophobic adsorbents* (see Appendix 2) and trapping at above ambient air temperature are used in the preconcentration trap, prior water removal is potentially not necessary, assuming a dry purging step subsequent to desorption is performed. This can be done by flushing the preconcentration trap in the sample flow direction with dry gas, e.g. purified helium. However, this treatment is applicable only for C_4 and higher boiling compounds.

Table 5: Methods to remove water from air samples

Method	Comments	Recommended for
Cold trap @ $T < T_{ambient}$ typically consisting of a PFA tube, a passivated steel tube, or a small volume glass flask and a cooling device	H_2O (but not the target analytes) is adsorbed or frozen-out. The dew point should be measured and appropriate for the capacity of the preconcentration trap and GC columns (typically below -30°C; e.g. Hopkins et al., 2003).	NMHCs and monoterpenes, some OVOCs
Nafion ® Dryer with a volumetric counter-flow of dry air or N_2, which is around three times higher than the flow of humid ambient air*	Removes H_2O effectively, but also part 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 depending on the specific Nafion dryer specs.

5.1.2 Ozone removal

To avoid artefact formation from the reaction of unsaturated, reactive NMHCs with co-sampled ozone, several methods are available to eliminate ozone from the sample stream (Table 6). A more thorough compilation of available methods and their evaluation can be found in Appendix 1.

Table 6. Common ozone removal methods and recommendations for NMHC sampling

Method	Comments/References
(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 to be checked for adsorptive losses and lower volatility NMHCs

5.1.3 Carbon dioxide removal

The operation of preconcentration traps at temperatures where CO_2 is retained is a risk with respect to breakthrough and losses of low boiling NMHCs. Different approaches are used to minimize the effect of CO_2 (Table 7): (1) The trapping temperature can be held high enough that only a minor acceptable portion of CO_2 is trapped; (2) CO_2 can be chemically removed before the trap; or (3) the dimension of the trap is large enough to quantitatively trap NMHCs without interference from CO_2. For (3) the CO_2 may need 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 7. CO_2 management

Method	Comments	Recommended for
CO_2 trap Removal of CO_2 before trapping using a cartridge with Ascarite	Ascarite is hygroscopic, so a trap should be installed behind a water trap to avoid liquefaction; artefacts are possible and need to be checked; a trap needs to be changed regularly	Offline 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 depending on the trapping material. Regular checks have to be performed to check full trapping and desorption of C_2 NMHCs	Online systems/ offline systems

Method	Comments	Recommended for
High-volume preconcentration trap CO_2 is held back at the trap but the volume of the trap is high enough to not loose NMHCs	The preconcentration trap is slowly heated to a temperature high enough for CO_2 to be released but not the analytes (Miller et al., 2008)	Online systems/ offline systems

5.1.4 Particle filters

In order to avoid contamination of the analytical systems with particles, filters should be used on the inlets (Table 8) but they have to be checked carefully for adsorptive artefacts of less volatile and of more polar compounds. Polytetrafluoroethylene (PTFE) membrane filters are recommended. Stainless steel screens with a mesh size and thickness of a few µm are recommended for coarse filtering of larger particles. 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-impacted site at least every four months.

Table 8. 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. Not suitable for OVOCs	NMHCs (C_2-C_{14})
Stainless steel screens	Several µm thickness and mesh size, only for coarse particles > several µm	NMHCs (C_2-C_{14}) BVOCs

5.2 Sample preconcentration and transfer to the analytical system

No single solution for sample preconcentration is prescribed in these guidelines. Cryogenic adsorption on glass beads, a combination of weak adsorbents with low sub-ambient trapping temperature, or stronger adsorbents with higher (up to ambient) temperature can all work well. A compilation of different trapping adsorbents and their usage is provided in Table 9 and in Appendix 2. A thorough review of possibilities for the trapping of NMHCs from air can be found in Helmig et al. (1999). Often, multibed adsorbents are used with the weakest adsorbent at the beginning and the strongest at the end of the sampling trap. In this way, the NMHCs with the highest boiling point are adsorbed on the weakest adsorbent at the beginning of the trap and those with low boiling point will be trapped at the end. Hence, when the analytes are released with a counter-purge of carrier gas, adsorption will be minimized. For each system, breakthrough volumes and desorption efficiency have to be tested for the different NMHCs, using either increasing amounts of humidified synthetic standards or ambient air spiked with standards (Section 7.1.4). At very low temperatures (e.g. when cooling is done with liquid nitrogen) care has to be taken to remove adsorbed oxygen and noble gases prior to desorption (see below).

For sampling, a pump should be used, preferably downstream of the preconcentration trap and 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 to a low uncertainty either by regularly calibrating the mass flow controllers or by using a pressure rise measurement in a defined reference volume. If the pump is used upstream of the

preconcentration trap, in a pressurizing manner, it has to be ensured that no artefacts are produced by the pump and that no leaks draw air from around the pump itself.

After sampling of a known volume of gas, 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 for removal of remaining water, oxygen, and potentially adsorbed non-VOC gases (e.g. CO_2, noble gases) from the trap. This helps prevent the formation of artefacts from reactions of the aforementioned gases with adsorbent material, as well as degradation of the chromatography.

NMHCs are normally transferred from the preconcentration trap to the analytical system by heating the trap (electrically or by other means) in a counter-flow of gas, passed through a transfer line capillary made from inert materials. The final temperature of the trap should be reached as fast as possible (within seconds) and should be high enough to release all NMHCs in one analysis step. Analytes are transferred to the GC system by carrier gas flow. After this transfer, the preconcentration trap has to be reconditioned by heating it to a higher temperature than needed to release the NMHCs and by flushing it backwards with carrier gas. In the case that NMHC injection is not rapid enough to obtain sharp chromatographic peaks, which may be due to large preconcentration trap volumes or a slow heating rate of the trap, a second focusing-trap should be installed between the preconcentration trap and the analytical column. This trap may again be adsorptive or cryogenic, but it needs to have a substantially smaller internal volume than the preconcentration 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 preconcentration trap is first heated up and then the well-mixed desorbed NMHCs in the carrier gas are injected onto the column in an injection band that 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 inherent loss of sensitivity using a split mode is in conflict with the low atmospheric mixing ratios of NMHCs (Hoerger et al., 2015). Therefore, it is recommended to use direct on-column injection.

Table 9. Examples of successfully employed preconcentration systems (and thermo-desorption (TD) 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 (LN_2 cooling) Des. 340°C and 5ml/min dry purge 1min @ 10ml/min He	750 ml	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	600 ml	Rigi, Empa*	NMHCs (C_2-C_8)
Carbopack®BHT	Ads. -120°C Des. 200°C	400 ml	WCC-VOC, KIT Garmisch*	NMHCs (C_2-C_6)

Adsorbents	Temperature and flows	Sample Volume	Systems	Recommended for
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	1500 ml	Hohenpeißenberg	NMHCs (C_4-C_{14})
Commercial preconcentration systems				
Markes UNITY TD Carbopack®B, Carboxen®1000	Ads. -30°C Des. 350°C	800 ml	Cape Verde, (Hopkins et al., 2003) Empa	NMHCs (C_2-C_8)
ENTECH TD Glass beads	Ads. -120°C Des. 70°C***	360 ml	IMT Lille Douai	NMHCs (C_2-C_8)
Medusa Hayesep®D	Ads. -160°C Des. 100°C	1000 ml	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

*** Refocussing on glass beads, Tenax®, Ads. -50°C, Des. 220°C

5.3 Capillary columns for the GC analysis of NMHCs

Two types of capillary columns are widely used for the GC analysis of NMHCs: PLOT (Porous Layer Open Tubular) and liquid film columns (Helmig, 1999). Table 10 lists a number of columns which are successfully employed in NMHC analysis. Further analytical column possibilities are listed in Appendix 3, in Helmig (1999) and in Hoerger et al. (2015).

Table 10. List of recommended NMHC columns for GC analysis.

analytes	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***	Ethyne 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 NMHCs difficult, applicable for BVOCs	Riemer et al., 1998
	DB-5**		50m x 0.25mm		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

*** For FID systems, the 0.53mm diameter is commonly used in ambient air measurements. The column diameter affects the separation and retention times of peaks, the carrier flowrate but also requires a higher pressure. Smaller diameters it might be useful to limit the carrier gas flow (e.g. for MS systems) or improve the peak separation.

5.4 Detection principles for NMHCs

Two detection principles are mainly used for the analysis of atmospheric NMHC species: Flame Ionization Detection (FID) and Mass Spectrometry (MS). This section describes the operational conditions of these detectors and their advantages and disadvantages (Table 11). For the calculation of molar ratios using these two detectors, see Section 7.

Table 11. Advantages and disadvantages of flame ionization detection (FID) and mass spectrometry (MS). QA = quality assurance.

	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 of non-specifically calibrated VOCs with effective carbon number (ECN) concept + ECN, allows effective QA (see Section 7.3.1) + 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 specificity + Substance-specific quantification (overlaying peaks can be separated by compound specific mass tracks) + Up to 10x more sensitive than FID when using Single Ion Mode monitoring
Disadvantages	- Not substance-specific, identification just by retention time - Co-eluting peaks can only be quantified after post-treatment - Because of reduced sensitivity compared to MS operated in SIM mode, need to preconcentrate more sample	- Each substance needs individual calibration - Variable sensitivity requires more frequent calibration measurements - Instruments need regular tuning - Expensive - May show non-linear behaviour if the concentration range is extremely large

FID is the preferred detection system whenever identification of NMHCs 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 a detector for its compound identifying capabilities.

5.4.1 Flame Ionization Detector (FID): Operating conditions

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

An FID needs a supply of clean dry air, H_2 to produce the flame and a make-up gas to sweep the internal volume of the detector. The flow rates should be tightly controlled to achieve stable operation of the detector (Table 12), although in practice most modern GC systems do this automatically to high precision.

Table 12. Operating conditions for FIDs.

Gas	Supply	Flow rate*	Temperature
Air	Synthetic air (min. quality 5.0) or compressed (compressor, oil free) ambient air catalytically cleaned (Pd or Pt catalyst at 350°C-450°C) or Zero air generator (quality generated 5.0 or higher)	300–350 ml/min	T_{FID} ** ≥ $T_{column,max}$ to avoid or minimize deposition of column residues
H_2	Cylinders or generator, quality 5.0 or higher	30 ml/min	
Make-up gas (e.g. N_2)	Cylinders or generator, quality 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 margins specified by the FID manufacturer.

** Follow specification of the manufacturer.

FID systems are highly linear (concentration range of ~10^7; Baars and Schaller, 1994) and the sensitivity is generally sufficient for analysis in background atmospheres at pmol mol^{-1}levels, e.g. detection limits of GC-FID systems when pre-concentrating 1 litre of air are typically better than 3 pmol mol^{-1} (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

Gas chromatographic-mass spectrometry (GC-MS) is a powerful analytical technique that has both advantages and disadvantages for ambient air analysis. There are many types of mass spectrometers on the market that can be interfaced to a GC including quadrupole GC-MS, ion trap GC-MS (GC-IT-MS) and time-of-flight MS (GC-ToF-MS) varieties. Both chemical and electron ionization (EI) schemes can be used to ionize the sample prior to entering the MS filter. Recently, the GC-ToF-MS has been gaining in popularity but by far the most common GC-MS systems for ambient VOC analyses use a quadrupole mass spectrometer with electron ionization as the ionizing source, and we will restrict the discussion here to this method. GC-MS instruments provide two separate dimensions of information about the components in the sample: GC retention times and electron ionization (EI) mass spectra (EI-MS). This can have high utility when analysing urban- or fire-impacted samples that may contain species that cannot be chromatographically separated but whose EI-MS is unique as discussed further below.

A GC-MS quadrupole mass analyser can be operated in two modes: SCAN and selection monitoring (SIM). In the SCAN mode, the quadrupole continuously and repeatedly ramps the monitored mass to charge (*m/z)* ratio from a pre-set lower limit to a pre-set upper limit, generating a series of complete mass spectra. At the conclusion of each individual scan, the intensities of all the *m/z* ratios within the scan are summed, giving a total ion current. A chromatogram is then constructed by plotting the series of total ion current versus retention time. This plot is called the total ion chromatogram, or TIC. The mass spectrum obtained in full scan mode yields information about the atomic composition of species as they elute from the column which, when interpreted, most commonly by way of matching to a mass spectral library, can be used for species identification of closely eluting or even completely overlapping chromatographic peaks, provided that the mass spectra of the closely eluting species are distinct. Methods have been described (e.g. EPA TO-15) for doing quantitative analysis in the SCAN mode. For GAW analyses, we recommend that all quantitative analyses be done in the SIM mode (newer MS systems allow dual SIM/SCAN). In this case, the quadrupole remains fixed on a small set of *m/z* ratios, effectively allowing only those predetermined masses to pass through the MS filter to the detector, substantially increasing the sensitivity over the SCAN mode (often more than 10x higher) so high signal to noise ratios are achievable on smaller sample sizes. To operate in the SIM mode the compounds that one wishes to analyse in a sample must be pre-selected; the approximate retention times of the species of interest and the fragment ion (or ions) with specific *m/z* ratios from the EI-MS that will be used for quantification must be known. When analysing a complex sample, overlapping peaks (e.g. MBO – methyl butene -ol and heptane) can still be quantified by targeting and calibrating for the specific *m/z* ratios characteristic of individual species that co-elute.

Unlike the FID, the MS requires no gases for operation other than the carrier gas to transfer the analytes from the preconcentration system to the MS detector. This carrier gas, most commonly Helium or Hydrogen, has to be of ultra-high purity. The temperature of the transfer line (capillary which transfers the sample from the column to the ion source) must be higher than the highest GC oven temperature to minimize adsorption effects.

The MS should be tuned regularly. During continuous operation, each week an autotune should be performed. This is commonly done through software in which the ion source, lenses, and multiplier voltages are optimized at different *m/z* ratios throughout the range of *m/z* ratios of interest. It is necessary to establish that the GC/MS meets tuning and standard mass spectral abundance criteria prior to initiating any analysis of blanks, standards, or air samples.

A certified calibration standard is required for each compound that one wishes to quantify in the air analysis. A discussion of calibration standards and frequency can be found in Section 7.

System blanks (Section 7) using clean humidified air should be obtained prior to analyses of ambient samples and run periodically to ensure that the system is clean.

6. REFERENCE GASES

The Central Calibration Laboratory (CCL) is the GAW Central Facility that maintains the primary standard that defines the calibration scale for GAW stations. For NMHCs, the CCL is the National Physical Laboratory in the United Kingdom (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 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 its own laboratory standard is linked to the calibration scale by direct comparisons in time intervals that correspond to the stability of the standard mixture. This non-CCL standard will have a higher uncertainty relative to the GAW calibration scale than that produced by the CCL, as uncertainties increase the further you move down the traceability chain away from the primary GAW standard.

Minimum standard requirements for a GAW (World and/or Regional) station:

1. A (secondary) **laboratory standard** that has to be a multicomponent standard (synthetic mixture), produced and certified by the CCL (recommended), or at least traceable to the CCL standard, 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 which are used for regular calibration of the measurements, as well as 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, as well as compressed whole air, that are calibrated by a reference laboratory (CCL or World Calibration Centre (WCC) (recommended), but which are at least calibrated by the station against the **laboratory standard**.

3. A **target gas mixture** that 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. The target gas 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 amount fraction. Monitoring the target gas concentrations yields information about the performance of the instrument, drifts of the laboratory standard, and potential instrument problems.

7. QUALITY ASSURANCE

This quality assurance (QA) section comprises all the principal actions needed to achieve the required quality of GAW NMHC measurements. The evaluation of the acquired data and related data quality checks are described in Section 8 (data management).

Quality assurance follows the principles of the GAW QA system as outlined in:

Quality Assurance | World Meteorological Organization (wmo.int) and summarized in the box below. The principles apply to GAW Contributing Stations, which are directly traceable to or linked to the CCL standard.

Principles of NMHC quality assurance for GAW Contributing Stations:

(1) Network-wide use of only one reference standard or scale (primary standard). Therefore, there is only one institution that is responsible for this standard (CCL).

(2) Full traceability of all measurements made by Global, Regional and Contributing GAW stations to the primary standard.

(3) The definition of data quality objectives (DQOs).

(4) 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).

(5) Use of detailed logbooks for each parameter containing comprehensive meta information related to the measurements, maintenance, and 'internal' calibrations.

(6) Regular independent assessments (System and Performance Audits, where a Performance Audit is measurement checks with respect to DQOs and traceability, and a System Audit is overall conformity of a station with the principles of GAW).

(7) Timely submission of data and associated metadata to the responsible World Data Centre as a means of enabling independent access to the data by a wider community.

For the calibration of NMHC measurements under the GAW framework, each station needs to have a system of laboratory standards, working standards and target gases (see Section 6 for definitions and Section 7.1 and 7.2 for the procedure). If target gas measurements are not within the DQOs, the instrument and quality assurance systems should be further optimized in order to achieve improved results. In parallel, a robust procedure is needed to detect any NMHCs found in blank (zero air) samples and any artefacts or losses of specific species when the system is running (see Section 7.2). Table 13 recommends sampling frequencies for the various standard measurements.

Table 13: Recommended frequencies for standard, blank and target gas measurements
(the minimum acceptable frequencies are specified in parentheses for periods without GC system irregularities)

System	Lab. Standard	Working Standard	Blank	Target gas	Stand. Add.**
GC-FID	2/year (1/year)*	2/month (1/month)*	1/week (1/month)	1/month*	1/year*
GC-MS	2/year (1/year)*	Every 2–4 samples (1/day)	1/week (1/month)	1/month*	1/year*

* Measurement series with 3–5 replicates

** Standard additions are recommended for checking artefacts/losses, but comparisons to measurements at similar sites with different measurement systems are also possible.

7.1 Calibration procedure

Regular calibration using working standards is essential for achieving good quality measurements. The sensitivity of a GC system should be stable and well within the DQOs between calibrations. Similarly, blank values and results of the target gas measurements (see below) and their reproducibility should not change substantially, i.e. less than specifications for < 100 pmol mol^{-1} in DQOs. Both calibration and target gas measurements enable the detection of any drifts in the measurement system which, when they occur, should be diagnosed and minimized (see Section 8.1).

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

- To send the laboratory standard for recalibration to the CCL or WCC
- To request a high-level standard from another station to carry out an independent check with
- To check available results from past intercomparison exercises

Station operators should try to identify at what point in time 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 assigned during this period needs to be increased to include the range of the unexplained drift. A drift in a standard can be identified by comparing two different calibration gases: if the difference (e.g. amount fraction, C-response factor, see Section 7.3) between two cylinders reveals a drift for one or just a few compounds, it is likely that the reason is not a change of instrument characteristics, but rather a change in the standard gases themselves. It is impossible to work through every possible calibration scenario, but it is quite common in a multicomponent standard containing 20–30 different NMHCs species for 1 or 2 compounds to drift outside of tolerances over a period of time. Pragmatic solutions are often needed, for example calibrating those NMHC species for which no standard is available with the nearest and most similar NMHC with the same carbon number (Section 7.3.2).

For linear detectors like the FID a linear calibration curve can be assumed (see Section 7.3.1) and a standard gas at one concentration level is sufficient. However, in case of a non-linear detector behaviour (e.g. MS) or to verify the linearity of your system, full calibration curves must be constructed using certified standards at three to five concentrations that encompass the range of anticipated amount fractions in the ambient samples. The preferred method is to dynamically dilute a standard to achieve the desired amount fractions. Suitable dynamic dilution methods have been described in the literature (Apel et al., 2003). Full calibrations should be performed prior to conducting any ambient analyses and repeated periodically.

7.1.1 Measurements of laboratory standards, 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.

Several other issues should be considered:

- *Transfer line and ferrule material*

  - Silconert® 1000/2000 or other stainless steel tubing with a passivated internal surface is recommended.

  - The use of Vespel/Graphite® (VG) ferrules is recommended as these provide a tight seal while not damaging the tubing. They can be used several times and should only be replaced when sealing or contamination problems are present (follow the manufacturers' instructions).

- *Installation of a new standard gas cylinder*

  - The pressure regulator and transfer line with capped fitting on the GC connection side should be fitted at least 24 hours before the measurement.

  - After installation, the regulator and transfer line need to be flushed (by pressurizing and releasing pressure without allowing air to enter the line) at least three times with the calibration gas.

  - Initial leak check: After flushing, the pressure regulator (cylinder pressure) and the plugged transfer line should be pressurized (at the level of pressure which is needed for the measurement set-up). With the cylinder valve closed, the pressure should be checked for at least 10 minutes; if it is not constant, all connections should be checked and gently tightened, and the leak check should be repeated.

- *Equilibration*

  For equilibration of gases with surfaces, the pressure regulator and the transfer line (plugged at the end) should be 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 set-up 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*

  To connect the test gas cylinder, attach it to an appropriate instrument inlet port and then flush the whole inlet line at least three times. It is recommended to only open the standard cylinder valve during the sampling periods, unless an automated measurement sequence is used in unattended operation. Leaving the standard cylinder permanently connected to the GC system is also recommended. If this is not possible, leave the pressure regulator mounted on the cylinder, keep it pressurized, and repeat the "connection to the instrument" procedure every time the cylinder is connected to the standard port.

  If the pressure regulator needs to be disconnected, follow the complete "installation of a new gas cylinder" procedure every time.

- *Measurement procedure*

  The standard gas measurement should follow the typical measurement procedure. However, it should be performed after an initial flushing period through the GC valve system that is sufficiently long so as to achieve equilibration in the lines (typically 10 min at 30 ml/min is sufficient for NMHCs). A series of 3–5 standard measurements is sufficient.

7.1.2 Checks for blanks, artefacts and losses

This section outlines procedures for checking blanks, which are impurities within the measurement system. A method for detecting artefacts and losses is also described. Data series of these tests build the basis for the data evaluation described in Section 8.1.

7.1.3 Measurement of zero-gas (blanks)

In this context, “zero-gas” is a VOC-free gas. The routine measurement of zero-gas is part of the quality assurance (QA) program to be followed at all stations. It yields information about artefacts due to the release of adsorbed hydrocarbons or from leaks in the sample path. Measured NMHC concentrations in the blank values should be as low as possible. Zero gases can be:

- Catalytically cleaned ambient air (Pt or Pd catalyst at 400°C), at concentrations very close to the sample gas and with similar humidity levels.

- Synthetic gas (e.g. He or N2) of at least 5.0 or higher quality. In N2 5.0 quality, traces of VOCs (e.g. methanol, xylenes) are potentially present. To reduce impurities in synthetic gases, a post-clean is recommended (commercial systems or home-made systems, based on e.g. cooled charcoal and molecular sieve cartridges).

In the case of synthetic zero-gas, it is recommended to humidify it by passing it over a film of water, especially for offline sampling, in order to passivate active surface sites and thereby minimize surface artefacts. Humidification requires high purity water (e.g. HPLC grade, or deionized water). The humidification device should be flushed with the zero-gas for at least 2 hours in order to remove potentially dissolved compounds.

Often, trace amounts of VOCs, in the pmol mol^{-1} 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 must be taken to identify the origin of impurities found in zero-gas measurements. Stations should test zero gases by comparing the blank values obtained in measurements of different hydrocarbon-free gases, aiming to achieve the lowest levels possible.

As blank values can vary over time, it is recommended to conduct weekly zero-gas measurements. Some commonly observed NMHCs in blank samples are listed in Table 14.

Table 14. Occasionally observed NMHCs in blank samples.

Compound	Cause
Various (e.g. cyclic siloxanes)	Column bleed, leakages, contamination
Benzene	Potentially associated with new traps or overheated traps, Viton o-rings
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 filters (if present), the water trap, and the sampling unit just like ambient air samples. The sample volume for zero-gas should be the same as for ambient air samples. Further information can be found in the literature (e.g. Englert et al., 2018 and references therein).

7.1.4 The Standard Addition Method for detecting reaction artefacts during sampling

Reactions between unsaturated NMHCs (alkenes, alkynes) might occur in the presence of ozone or other reactive constituents of the ambient air sample 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, for example by adding a high amount fraction standard gas mixture (e.g. NMHCs at 100 nmol mol^{-1}) into the ambient air stream with a low-volume flow so that the ambient air peak areas are negligible yet the gas matrix is dominated by ambient air (e.g. >90%). Ideally the ambient air should contain ozone at amount fractions that are typical of local high ozone conditions, and 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, but, instead of the zero-gas, the high amount fraction standard is added. It is recommended to use a quartz capillary without a needle valve for the application of the standard.

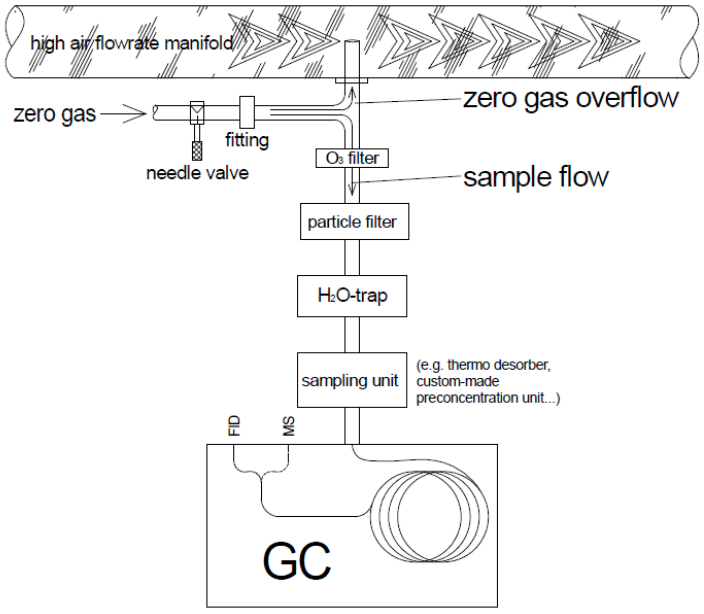

Figure 1 Example of a zero-gas measurement set-up with a high flow inlet manifold. The same set-up and also be used for standard addition measurements. The sequence of the filters can be changed depending on the individual system requirements.

7.2 Audit procedures

Audits are performed by the WCC-VOC (currently hosted by Forschungszentrum Jülich GmbH FZJ, Jülich, contact Dr Ralf Tillmann). Audits check for the conformity of a station to GAW QA system, including recommendations of the Measurement Guidelines, and the conformity of test gas measurements with targeted values within the DQOs (see definitions and procedures of performance and system audits in GAW Report No. 228, WMO 2017b). 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, logbooks, the scientific use of the data, and the overall equipment of the station.

7.3 Calculation of amount fractions and measurement uncertainties

In this section, the routine determination of atmospheric amount fractions is described together with the calculation of the measurement uncertainty. Each station needs to assess its measurement uncertainty in order to state the level of quality associated with the data over time, given the method used and its performance. In this section, references to the document 'Evaluation of measurement data – Guide to the Expression of Uncertainty in Measurement' or 'GUM' in short, are made in brackets [] with the number referring to the section as in GUM.

The process for calculation of the measured amount fraction and its associated uncertainty follows GUM [Chap. 8, p. 28] as well as the EURACHEM guide (QUAM: 2012.P1, p. 10):

- Step1: Specification of the measurand (i.e. the amount fraction of a given substance). In this step the equation describing the measured quantity is written. The equation should represent the relationship between the measurand and the input quantities (e.g. measured areas, sample volume) or, in other words, the influence of input quantities on the sample amount fraction.

- Step 2: Identification of uncertainty sources. A list is established with the possible sources of uncertainties affecting the parameters stated in Step 1, and additional uncertainties, if any.

- Step 3: Quantification of uncertainty components. Each potential source of uncertainty, listed in Step 2, is quantified.

- Step 4: Calculation of the combined uncertainty. The uncertainties quantified in Step 3 are here combined using rules for uncertainty propagation. Finally, the obtained standard uncertainty is transformed into the expanded uncertainty by multiplication with a coverage factor (usually 2 that represents the 95% confidence interval).

7.3.1 Step 1: Calculation of amount fractions for linear detection systems

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

$$\chi_{sample} = \frac{A_{sample} - A_{blank}}{A_{cal} - A_{blank}} * \frac{V_{cal}}{V_{sample}} * \chi_{cal} \qquad \text{(F3a)}$$

Amount fraction of the sample, mol/mol

Ratio of areas, no units

Ratio of volumes, no units

Amount fraction of the standard, mol/mol

This can be re-arranged to:

$$\chi_{sample} = \frac{A_{sample} - A_{blank}}{V_{sample}} * f_{cal} \qquad \text{(F3b)}$$

with the calibration factor f_{cal} defined as:

$$f_{cal} = \frac{V_{cal} * \chi_{cal}}{A_{cal} - A_{blank}} \qquad \text{(F4)}$$

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 amount fraction of calibration gas

V_{cal} = sample volume of calibration gas

V_{sample} = sample volume of sample

In cases when some NMHCs are not present in the standard reference gas mixture (laboratory and working standard), their respective calibration factors may be scaled by calibration factors of physically similar-behaving compounds present in the standard (Sections 7.1 and 7.5.2). This, however, is only possible in FID systems and is an option for less abundant compounds. Stations should, however, favour complete substance mixtures in their working standards. For MS systems this technique is not recommended.

7.3.2 FID: Effective carbon number

The effective carbon number (ECN) concept states that the response (peak area) of the FID is proportional to the number of molecules times the number of carbon atoms per analyte molecule (Sternberg et al., 1962, Dietz et al., 1967). 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:

$$C_{resp} = \frac{A_{cal} - A_{blank}}{C_{num} * y * V_{cal} * \chi_{cal}} = \frac{1}{C_{num} * y * f_{cal}} \quad \text{(F5)}$$

where

C_{num} = number of C atoms in the molecule (e.g. 5 for *n*-pentane)

y = ECN contribution (1.0 per carbon in aliphatic and aromatic bonds, 0.95 in double bonds, and 1.3 in triple bonds; Sternberg et al., 1962).

The carbon-response factor 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 amount fraction is calculated via the mean carbon-response factor, $\overline{C}_{resp}$, which is determined from selected compounds in the standard gas measurements by averaging the C_{resp} values for those NMHCs. The amount fraction of a given compound is then:

$$\chi_{sample} = \frac{A_{sample} - A_{blank}}{C_{num} * y * V_{sample} * \bar{C}resp} \quad \text{(F6)}$$

7.3.3 Step 2: Identification of the uncertainty sources

The uncertainty in reported NMHC values should reflect the combination of both random and systematic errors during the measurement process. Hereafter we use lower case '*u*' to describe a standard uncertainty or uncertainty expressed with a coverage factor of 1 (written k=1, usually known as 'one sigma') and we use upper case '*U*' to describe an expanded uncertainty, expressed with a coverage factor of 2 (k=2 or '2 sigma', which represents approximately a 95% confidence interval for a Gaussian distribution).

The main factors influencing the uncertainty (*u*) of the measurements are:

- The combination of the reproducibility and the detection limit of the measurement method: defined here as 'precision'. $u\chi_{prec}$
- Uncertainty due to the accuracy of the calibration gas $u\chi_{cal}$
- Integration errors (due to peak overlay, tailing, bad peak separation) $u\chi_{\text{int}}$
- Systematic errors in sample volume determination $u\chi_{vol}$
- Error due to linearity issues (especially for the MS instruments) $u\chi_{lin}$

- Other instrumental problems (e.g. sampling line artefacts, carry over, changes of split flow rates, column degradation) $u\chi_{instrument}$
- When offline methods are used, errors due to the sampling canisters also have to be considered (e.g. storage issues, sample contaminants) $u\chi_{sampling}$

7.3.4 Step 3 and 4: Quantification of uncertainty components and calculation of the combined uncertainty

The standard uncertainties are determined individually for each VOC measured and it is common for there to be a range of different uncertainties for each VOC even if measured on a common GC system. According to the "Guide to the Expression of Uncertainty in Measurement" (JCGM, 2008), the combined uncertainty is calculated using the law of propagation of uncertainties (assuming that the standard uncertainties of each factor are not correlated) [GUM, 5.1.2].

$$u^2_{\chi sample} = u^2_{\chi prec} + u^2_{\chi cal} + u^2_{\chi int} + u^2_{\chi vol} + u^2_{\chi lin} + u^2_{\chi instrument} + u^2_{\chi sampling} \quad \text{(F7)}$$

F7 has to be multiplied by a coverage factor $k=2$ to provide the expanded uncertainty ($U\chi_{sample}$):

$$U\chi_{sample} = 2 \times u\chi_{sample} \quad \text{(F8)}$$

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

The terms of equation F7 are explained in Appendix 4. Furthermore, a step-by-step example of the calculation is given in Appendix 4.

7.3.5 Determination of Limit of Detection (LOD)

The limit of detection (LOD) is one of the parameters describing the method performance characteristics. The LOD is defined as 'the smallest measure that can be detected with reasonable certainty for a given analytical procedure' [IUPAC, Gold Book].

Due to impurities, electronics or other analytical interferences the baseline of gas chromatographic peaks is to a certain degree noisy. Thus, the lowest quantifiable amount of a substance –the detection limit of the measurement system – is different from zero. The detection limit should be chosen to keep the risk of not detecting a substance, while the substance is present, lower than 5% (or 1%). It means that if a sample with a concentration exactly at the LOD is measured multiple times, in average 5% (or 1%) of the sample will be 'undetected' and 95% (or 99%) or the sample will be detected and assigned an amount fraction).

The suggested procedure to quantify the LOD is based on the baseline noise and is described in the appendix.

8. DATA MANAGEMENT

This section gives recommendations for data evaluation and checks, using measurement data from calibration gases and ambient air (Section 8.1), for (1) periodically checking the performance of the analytical system and (2) before final data submission to the data centre (Section 8.2). Before final submission, data have to be flagged either as valid or invalid, using flags defined by the World Data Centre for Reactive Gases (WDCRG) EBAS database, which is hosted by the Norwegian Institute for Air Research (NILU) and listed at:

http://ebas-submit.nilu.no/Submit-Data/Data-Reporting/Templates/Category/Trace-Gases/VOC/NMHC/level2.

To help master the data evaluation and data submission process, GAW station personnel are encouraged to attend training courses by WDCRG/EBAS and GAWTEC.

8.1 Data evaluation

This section gives examples of quality checking (QC) tools that are recommended for inspecting the quality of the GAW NMHC measurement data. It comprises visualizations of the time series of working standard measurements using carbon-response factors for FIDs, or NMHC specific peak areas for GC-MS measurements (Sections 8.1.1); the usage of target and standard addition measurements (Section 8.1.2); and the application of x/y-plots of the NMHC data with a focus on correlations between selected NMHCs with similar sources and atmospheric lifetimes (Section 8.1.3).

8.1.1 Inspecting time series of calibration gas measurements

A GC-FID system can be characterized for adsorptive losses, artefacts and poor peak separation by using the carbon-response factor (C_{resp}; Section 7.3.2) (Plass-Duelmer et al., 2002). When the carbon-responses for the various organic compounds are calculated, they should agree within to a few percent for C_2 to - C_{10} NMHCs, 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). In Figure 2, a time series of carbon-response factors for a number of NMHCs is shown. In cases of deviations, as occurs shortly after 02.04.17 in the example of Figure 4, efforts should be taken to optimize the GC-FID system.

For GC-MS the sensitivity changes quickly and the time series of calibration gas measurements are expected to show drifts and steps. But for the carbon-response factor, a similar behaviour is expected for similar compounds.

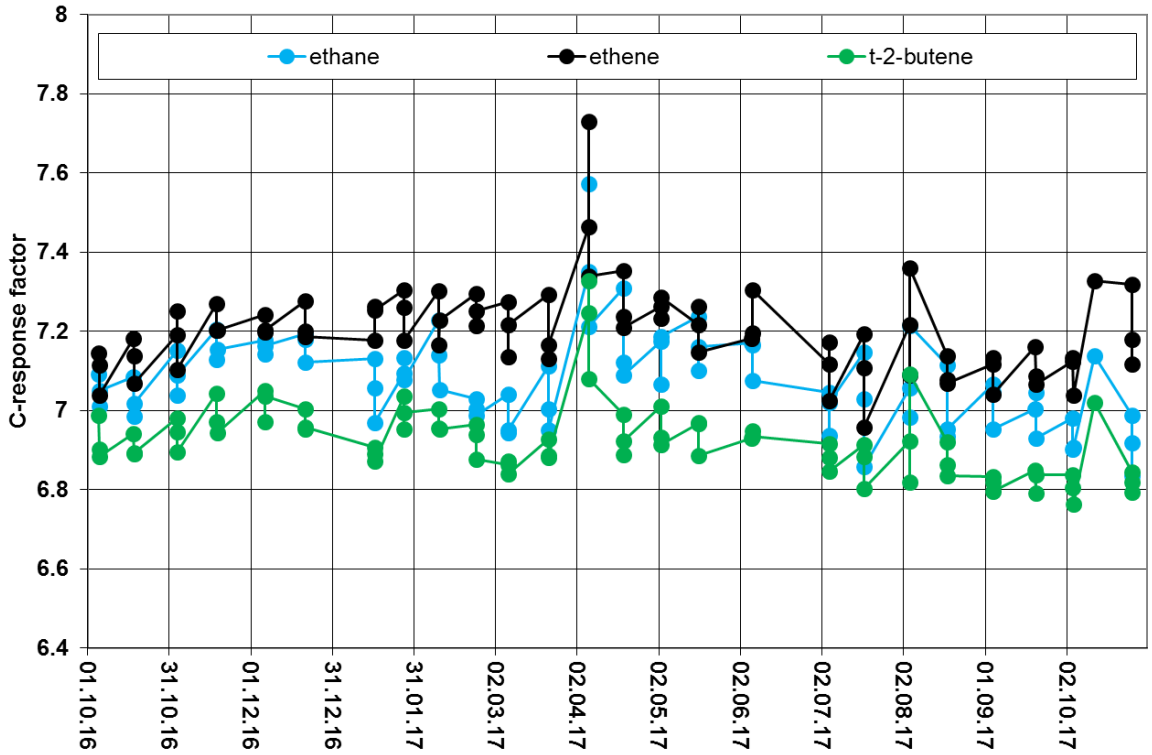

Figure 2. Time series of carbon-response factors for ~1 nmol mol^{-1} working standard measurements (biweekly) with a GC-FID system.

8.1.2 Target gas measurements and standard addition

In Figure 3, a time series of target gas measurements (whole air) is shown, in which the determined amount 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 the monthly repeatability of a series of five replicates, and the monthly reproducibility throughout the year for ambient air amount fractions. Except for ethyne and 2-methylpentane, the observed amount fractions are stable. In this case, the system has to be checked for those two substances for the period after September 2015. However, in general, this plot indicates good calibration procedure and performance of the system.

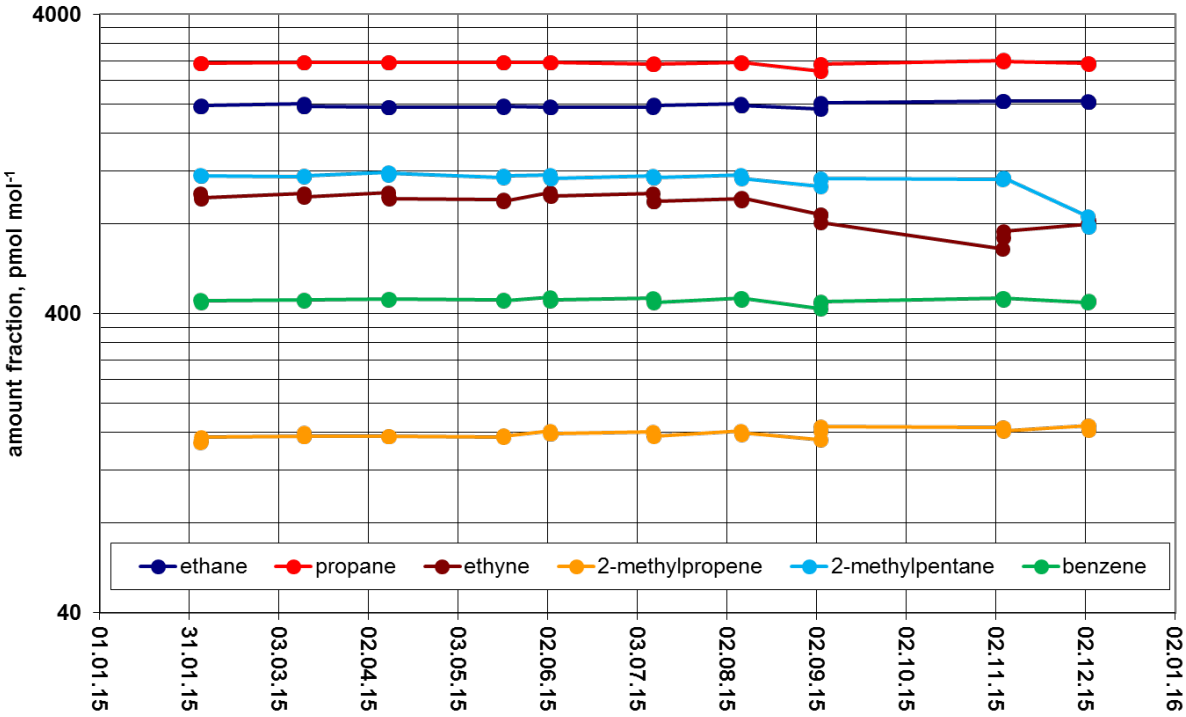

Figure 3. Examples of measurements of compressed whole air from a cylinder through 2015

Three replicates were measured once a month. Amount fractions are plotted on a log scale versus time.

As discussed in Section 7.1.4, the standard addition method tests for reaction artefacts during sampling, for example reactions between unsaturated NMHCs and ozone. The standard addition measurement ("add") can be compared to a pure standard ("pure") measurement of the same standard gas mixture. If the ozone-rich ambient air matrix does not have an effect on the sample, the calibration factor (for FID systems the carbon-response factor) is the same for both measurements and thus:

$$1 = \frac{\frac{A_{add}}{A_{pure}}}{\left[\frac{A_{add}}{A_{pure}}\right]_{avg}} \qquad \text{(F9)}$$

where $\left[\frac{A_{add}}{A_{pure}}\right]_{avg} = \frac{flow_{add}}{flow_{total}}$ is the average peak area ratio for non O_3-reactive compounds with low amount fraction in the ambient air (e.g. alkanes like *n*-heptane). This concept is applicable for all NMHCs for which the ambient air concentration is negligible compared to 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.

Results of standard addition measurements performed monthly are shown in Figure 4. The normalized peak ratio is plotted as described in Equation F9. Positive deviations from one are possible if the substance has a relevant contribution from ambient air, as in the case of toluene (Figure 4). However, results should generally vary within a few percent around 1 as indicated for *n*-heptane (green). The alkenes are clearly dominated by the added standard. If ozone interferences (losses) exist, these reactive alkenes should show ratios lower 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 should be further checked and, if necessary, the O_3 filter replaced.

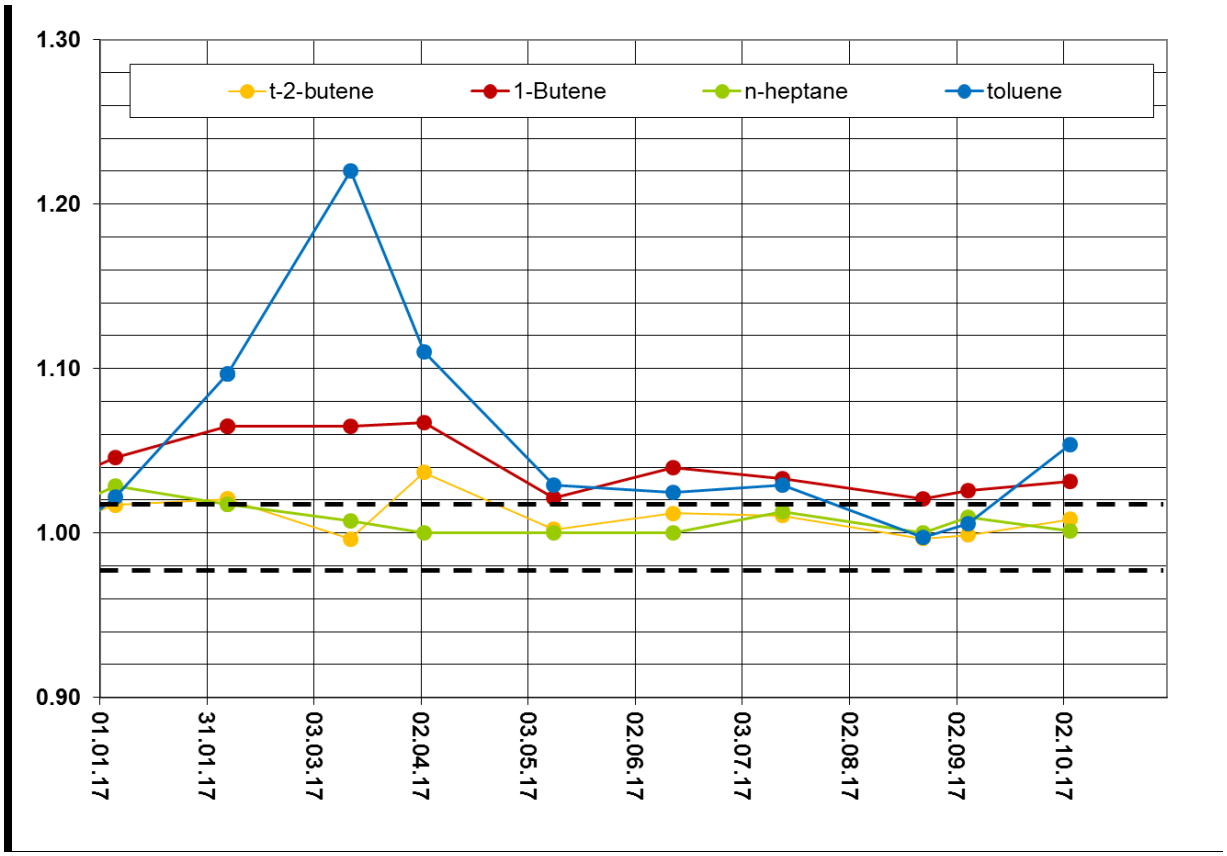

Figure 4. Results of 100 nmol mol^{-1}-NPL standard addition measurements performed once per month with a set-up described in Section 7.1.1.
1ml/min of NPL standard was added into an 80ml/min ambient air sample flow. On the y-axis the peak area ratios are given as stated in formula (F9) using the average peak area ratio of 2-methylpentane, n-heptane and n-octane for normalization. Those compounds are expected to be neither influenced by trap breakthrough or ozone artefacts and have a low concentration in ambient air. Dashed lines mark a 2% interval above and below 1.00.

8.1.3 Data checks of final amount fraction data

As a check on final amount fractions, NMHCs should be grouped in a convenient number (typically 3 or 4) of functionally similar compounds with similar atmospheric lifetime, 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, the variability of the data is expected to increase with higher reactivity (inverse variability-lifetime relation) and changes should be more pronounced for shorter lived compounds (which have a lower background). Positive or negative variations may be attributed to plumes with local/regional pollution or to 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.

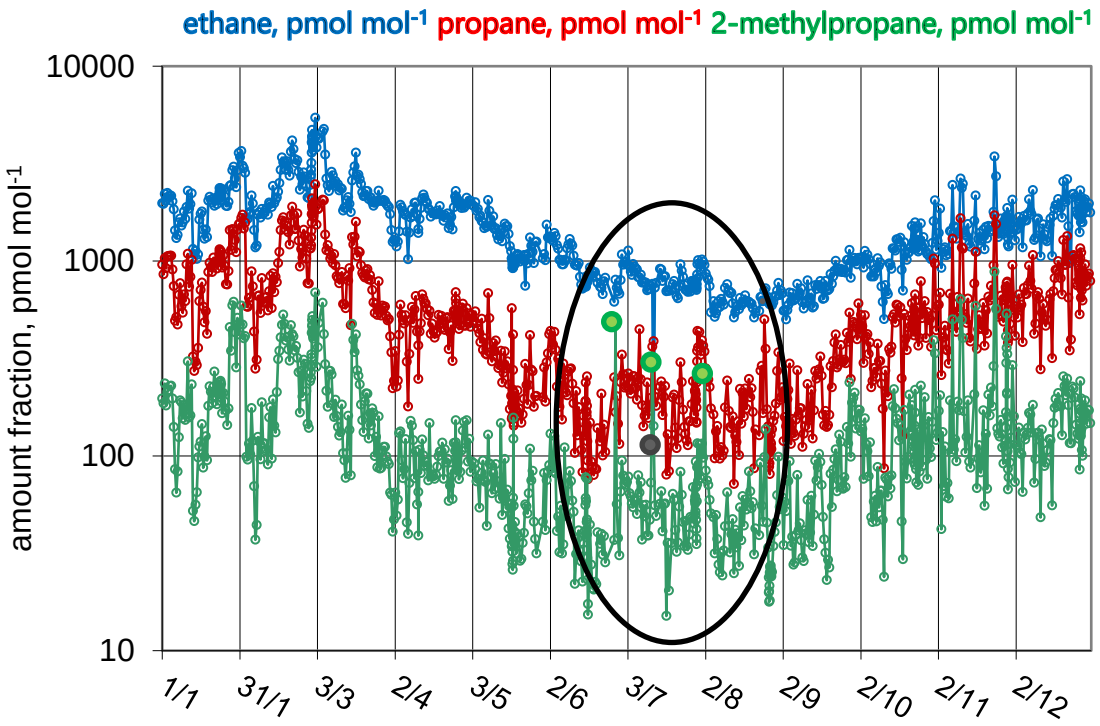

Figure 5. A sample time series (annual cycle) for C_2-C_4 alkanes (note the log scale on the y-axis).

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 plot a time series of their ratios (Figure 6) and/or their correlation (Figure 7). Ratios with different lifetimes are also useful in NMHC analysis (e.g. toluene/benzene, ethyne/ethene), for example as an indicator of air mass freshness. Useful NMHC pairs are:

- C_3-C_5 alkanes/ethane
- 2-methylpropane/*n*-butane
- 2-methylbutane/*n*-pentane
- C_3-C_5 alkenes/ethene
- Ethyne/ethene
- Ethyne/benzene
- 2-methylbutane/*n*-pentane
- 2-methylpentane/*n*-hexane
- Toluene/benzene
- *M,p*-xylene/toluene
- Ethylbenzene/*m,p*-xylene
- *O*-xylene/*m,p*-xylene
- *O*-xylene/ethylbenzene

Such tracer 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 multidistributed. Further, the plot might not be representative due to a technical issue. In some cases, it can be site-specific (e.g. based on

source/sink distribution, topography, etc.) and in such a case the current year's distribution can be checked against data from former years at the same site.

For distinct deviations observed in as the examples shown in Figures 5 to 7, the following checks are recommended:

(i) Logbook entries to identify irregular operation conditions

(ii) Peak integration

(iii) Other compounds deviating in these individual measurements, to try to identify the reason for the spike

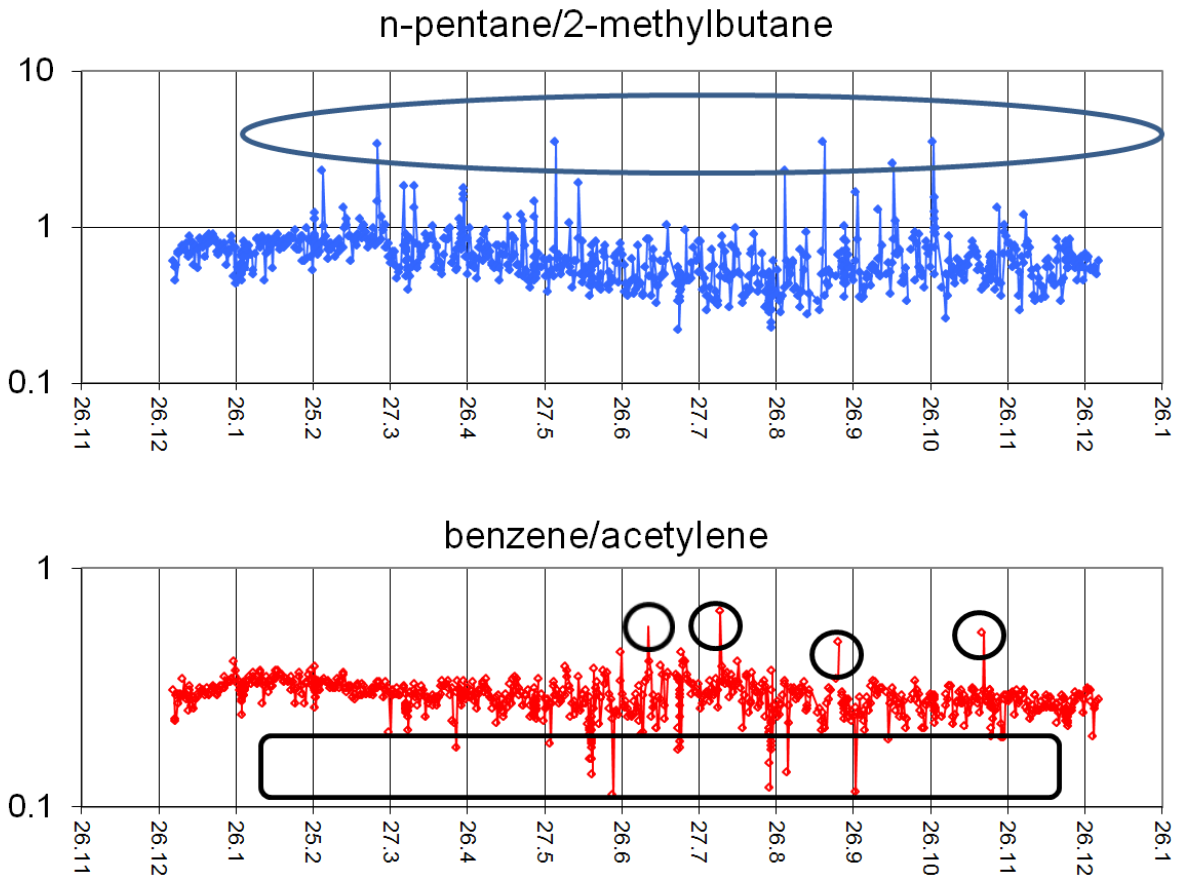

Figure 6. Time series of ratios between hydrocarbon pairs with similar lifetimes.

The y-axis is the compound ratio. Marked data points should be checked as they either point to a specific local situation (meteorological situation, local sources) or a technical issue.

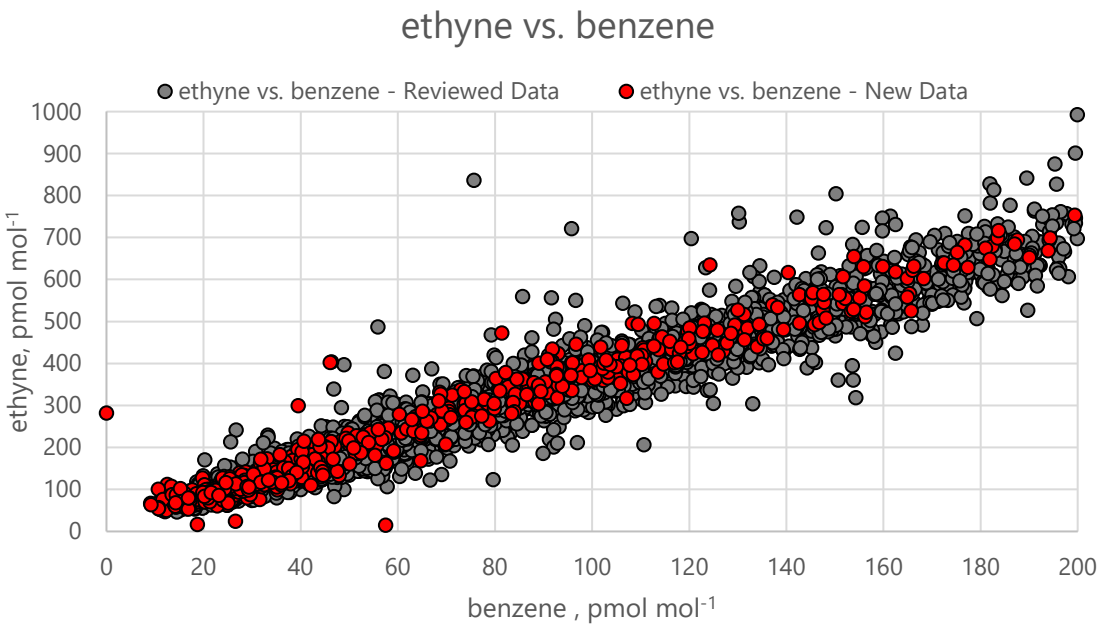

Figure 7. Example of an x/y-plot: Ethyne vs benzene at one single measurement site
Quality-checked data from 2012–2016 are shown in grey, and new 2017 data in red. Points that deviate from the tight correlation should be checked.

8.2 Data Submission to GAW-World Data Centre for Reactive Gases (WDCRG)

As stated earlier in Section 8, the global data archive for VOC measurements is the WDCRG EBAS database, which is maintained by 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. For example, the target date for final data submission is 31 December for data from the year before (i.e. 31 December 2017 is the preferred reporting deadline for all 2016 data).

A file format checker and submission tool are available at the EBAS 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 this check, the files can be submitted to EBAS directly through the submission tool.

An expanded set of guidelines, templates and explanations for data submission is available on the EBAS web pages. Data submitted to EBAS need to be formatted by the data provider in the EBAS NASA-Ames format, which is based on the ASCII text NASA-Ames 1001 format but contains additional metadata specifications ensuring proper documentation. The webpage http://ebas-submit.nilu.no/ provides links to data templates for reporting VOC data to EBAS.

Furthermore, 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 set-up and procedures for each measurement technique (online and offline traps and offline canisters).

Continuous and quasi-continuous data may be reported as hourly averages (preferred) or higher aggregates. The data must be accompanied by appropriate metadata. The WDCRG also accepts flask and field campaign data. Data submitters should consult the WDCRG data submission guidelines (WMO, 2009c) and submit data to EBAS with the GAW-WDCRG label.

Tables of recommended data flags are available from each individual template, but a complete list of flags available in EBAS is located at http://www.nilu.no/projects/ccc/flags/.

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9. Appendices

9.1 Appendix 1: Ozone Removal Techniques for GC Analysis of Volatile Organic Compounds in Ambient Air Samples

Reactions of concentrated VOCs with ozone during the 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, respectively. 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 these reactions leading to artefacts like methacrolein and methyl vinyl ketone. 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. graphitized 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 also a widely used and applied technique to remove ozone.

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, leads to nickel tubing being 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 µmol mol^{-1} 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 one-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 artefacts (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. It 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 fibre 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 fibre 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 A1).

In-line O_3 scrubbers like granular KCl and crystalline Na_2SO_4 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 fibre filter	Sodium thiosulphate ($Na_2S_2O_3$)	High capacity, also reduces sampling artefacts 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

Technique	Agent	Characteristics
Gas-phase ozone titration	Nitric oxide (NO)	Very efficient, quantitative recovery of formaldehyde, formation of artefacts 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 pre-treatment of the adsorbent, improved monoterpene recovery
Spiked cartridge	$Na_2S_2O_3$	Interferences eliminated

9.2 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) online 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) offline pumped (active) or diffusive (passive) sampling onto adsorbent tubes or cartridges held at ambient temperature. In the case of offline 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 graphitized 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. graphitized 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 multibed 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 very volatile analytes. In multibed 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 graphitized 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 graphitized 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 graphitized 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 adsorption is too strong to release most of the analytes with only heat. However, they are sometimes used in multiadsorbent traps for very volatile analytes e.g. Halocarbon 12 and Chloromethane. Charcoals are hydrophilic (Brown and Shirey, 2001).

Multiadsorbent 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 multiadsorbent 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). Multiadsorbent traps used for NMHCs are, for example, Carbopack™ B : Carboxen™ 1000, 90 mg in total (Hopkins et al., 2003) or Carbopack™ B : Carbosieve™ S-III 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.

The most 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 minimize back pressure
Carbograph™ 2TD Carbopack™ C	Graphitized carbon black	Weak	>450	C_8-C_{20}	Very inert, hydrophobic, minimal inherent artefacts, friable, 40/60 mesh recommended to

Adsorbent	Class	Strength	Max. Temp. [°C]	Relative analyte size to n-alkanes	Characteristics
Carbotrap™ C					minimize 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™	Graphitized carbon black	Weak/ medium	>450	$C_{5/6}$-C_{14}	Hydrophobic, minimal inherent artefacts, friable, formation of fines, 40/60 mesh recommended to minimize 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	Graphitized carbon black	Medium/ strong	>450	$C_{3/4}$-C_8	Hydrophobic, minimal inherent artefacts, friable, formation of fines, 40/60 mesh recommended to minimize back pressure, retention of very volatile compounds e.g. 1,3-butadiene

Adsorbent	Class	Strength	Max. Temp. [°C]	Relative analyte size to n-alkanes	Characteristics
Carbopack™ X	Graphitized carbon black	Medium/ strong	>450	C_3-C_9	Hydrophobic, minimal inherent artefacts, friable, formation of fines, 40/60 mesh recommended to minimize back pressure, retention of very volatile compounds e.g. 1,3-butadiene, no O_3 artefacts (Lee et al., 2006)
Carboxen™ 569	Carbonized molecular sieve	Strong	>450	C_2-C_5	Inert, less hydrophilic than most carbonized molecular sieves, minimal inherent artefacts
Unicarb™	Carbonized 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	Carbonized 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™ S-III	Carbonized 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

Adsorbent	Class	Strength	Max. Temp. [°C]	Relative analyte size to n-alkanes	Characteristics
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

9.3 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 usually used to isolate OVOCs and generally avoid 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 with PLOT columns may be occasionally occurring mobilization of particles from the stationary phase (a 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 are 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). Contrary to Dimethylpolysiloxane columns, NMHCs have lower retention on polyethylene glycol columns. 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 cannot be operated at sub-ambient oven temperatures.

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	+	+	-

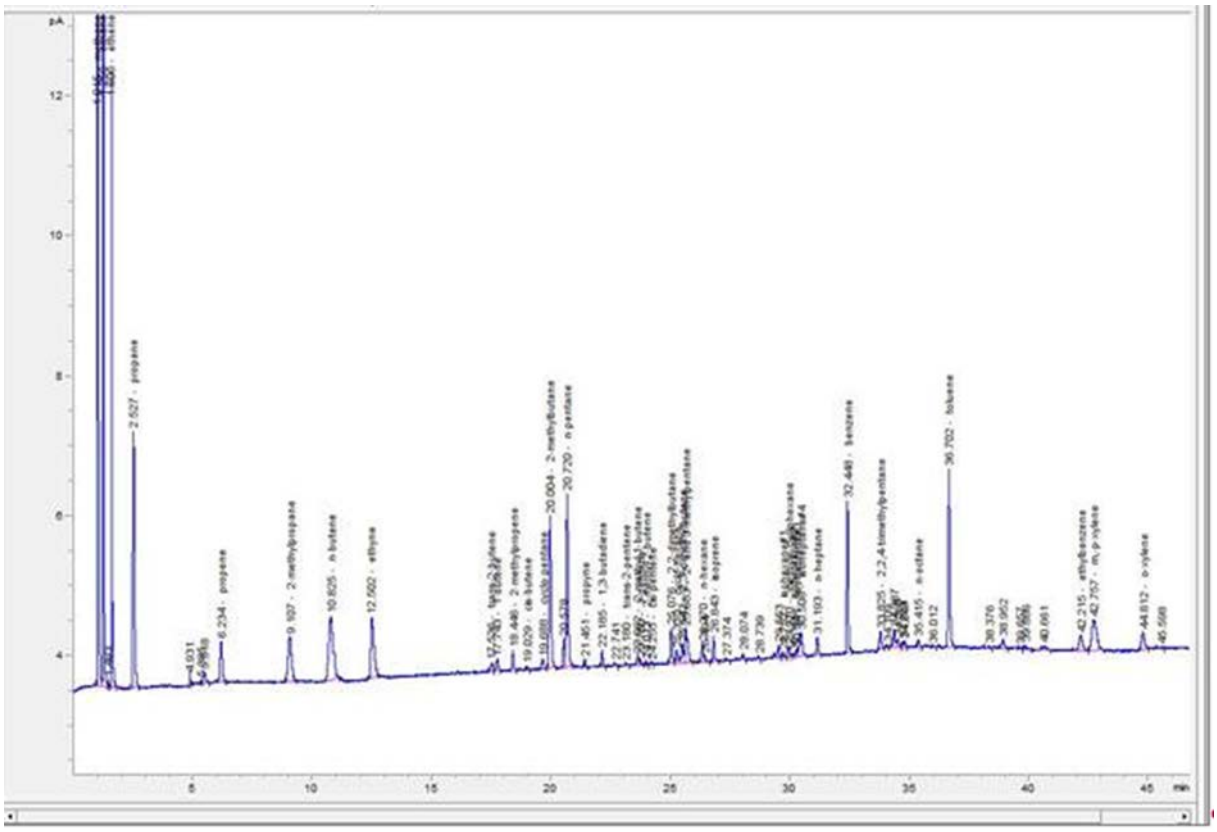
PLOT column equivalents	GS-OxyPLOT (Agilent), CP-LowOx (Varian)	CP-PoraBOND U (Agilent resp. Varian)	AlO_3 PLOT (Agilent resp. Varian)
Analysis of ethers	+	+	-
Analysis of esters	+	+	-
Analysis of aromatics	+	+	+
Analysis of alkanes	-	+	+
Analysis of terpenes	+/-	+	
Analysis of nitriles	+	+	
Expected 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

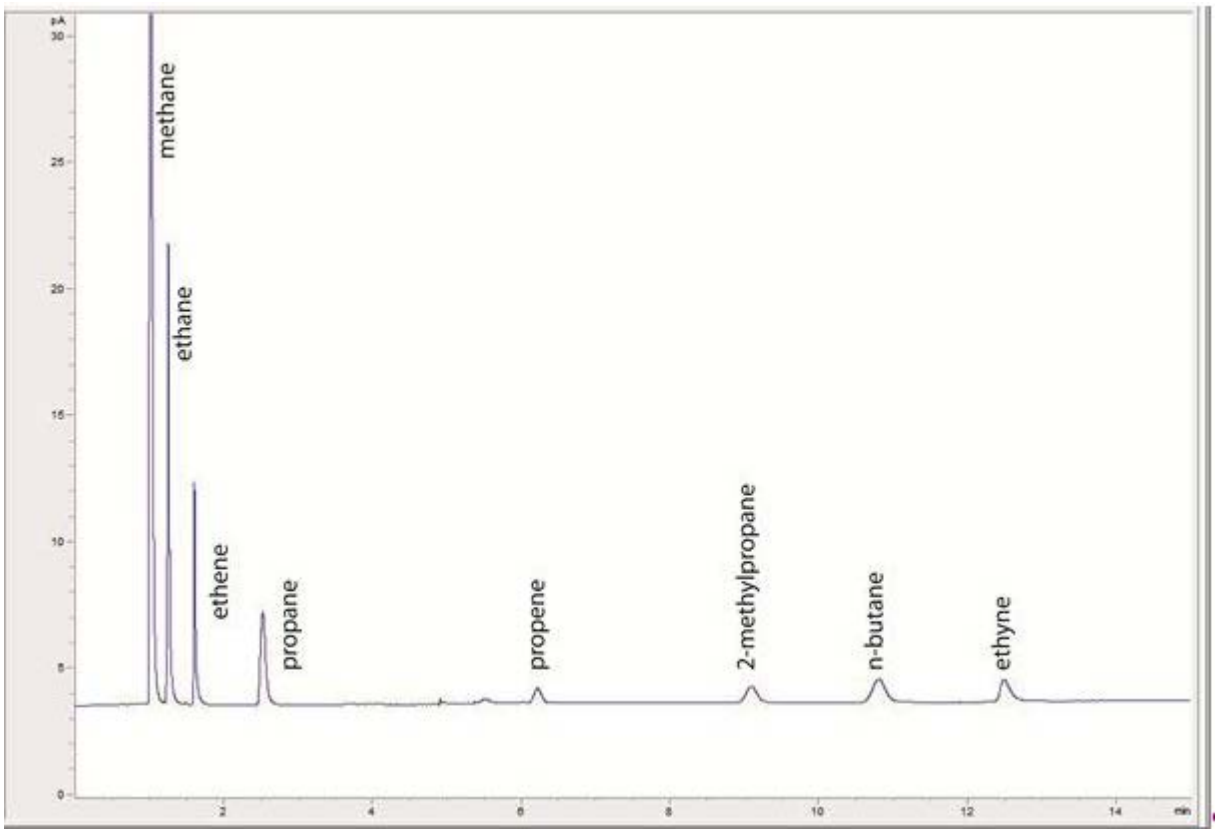
\+ suitable for measurement of mentioned compound groups

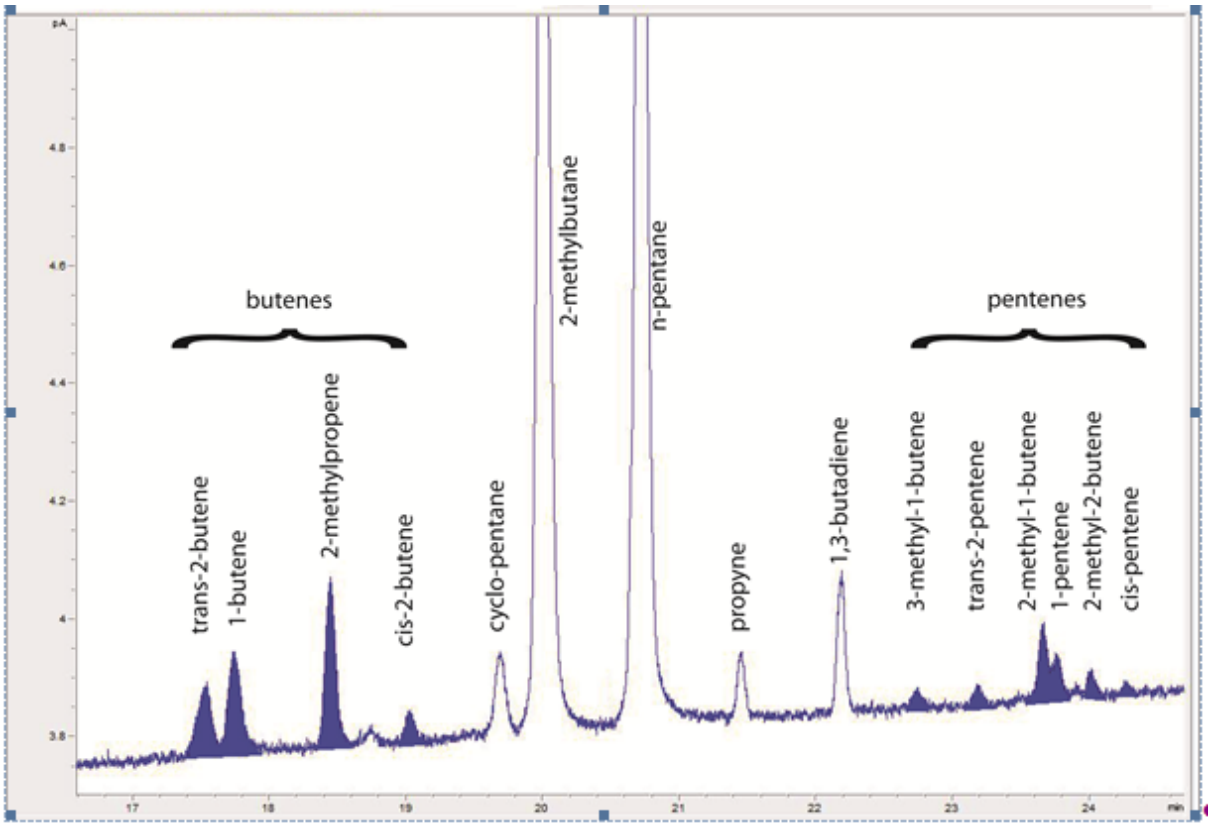
\- unsuitable for measurement of mentioned compound groups

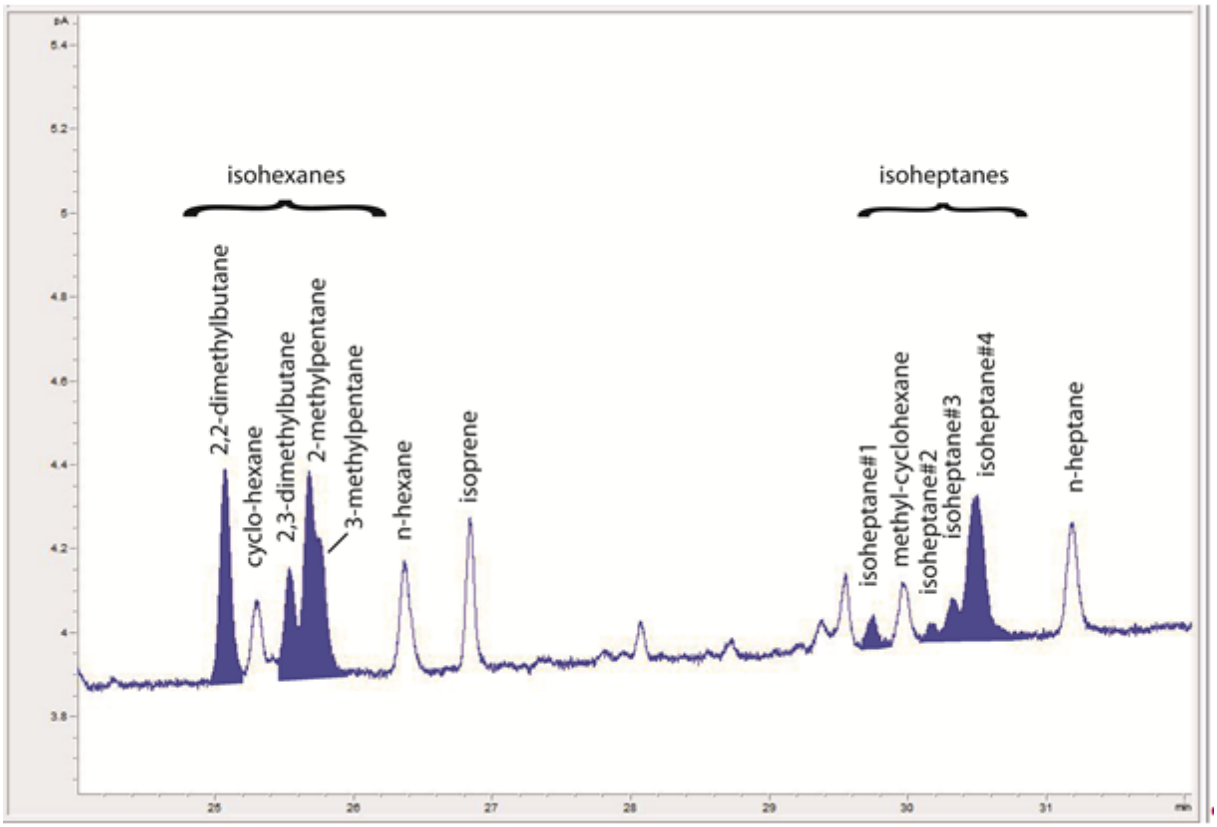
Examples of ambient air chromatograms

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






butenes
pentenes
trans-2-butene
1-butene
2-methylpropene
cis-2-butene
cyclo-pentane
2-methylbutane
n-pentane
propyne
1,3-butadiene
3-methyl-1-butene
trans-2-pentene
2-methyl-1-butene
1-pentene
2-methyl-2-butene
cis-pentene


isohexanes
isoheptanes
2,2-dimethylbutane
cyclo-hexane
2,3-dimethylbutane
2-methylpentane
3-methylpentane
n-hexane
isoprene
isoheptane#1
methyl-cyclohexane
isoheptane#2
isoheptane#3
isoheptane#4
n-heptane

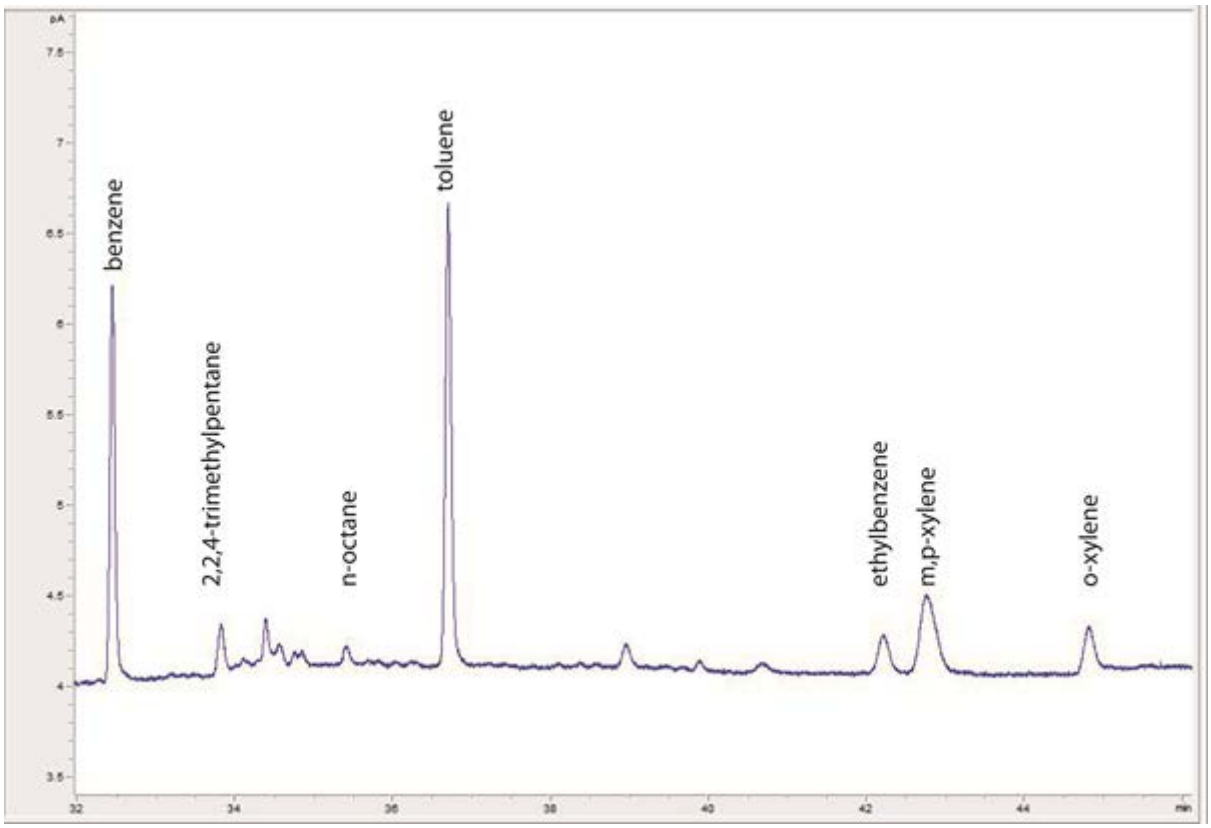


Figure A1. Al_2O_3 (KCl): a typical chromatogram at Rigi (Switzerland)

1B) LowOx

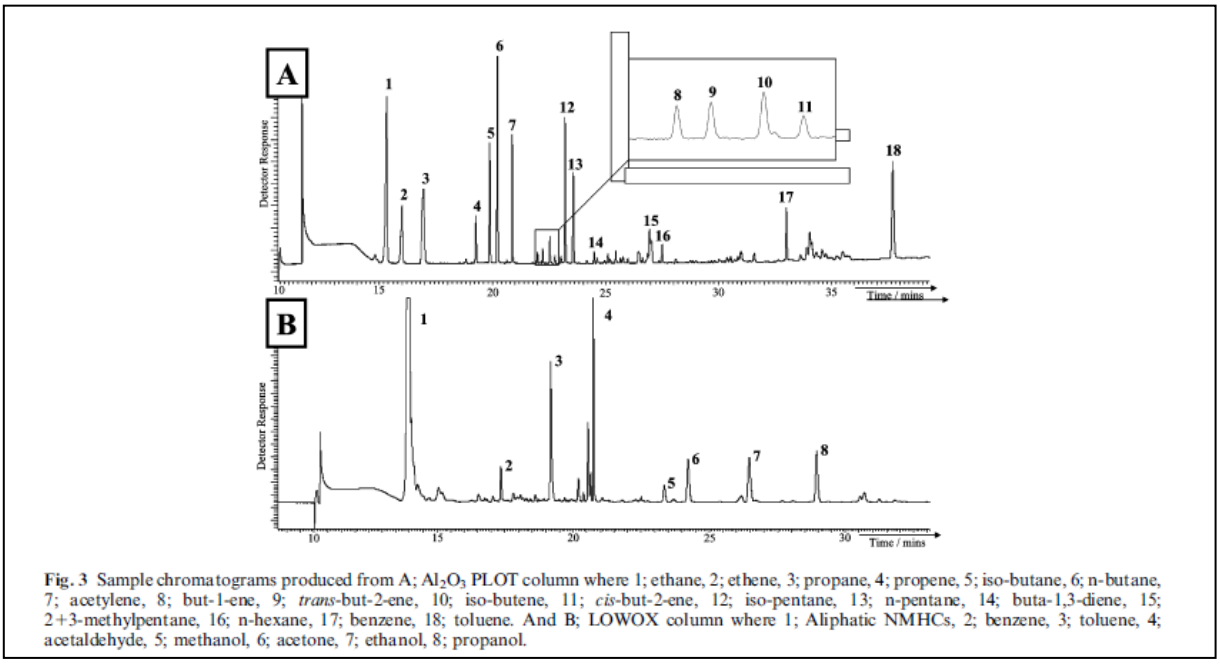


Fig. 3 Sample chromatograms produced from A; Al_2O_3 PLOT column where 1; ethane, 2; ethene, 3; propane, 4; propene, 5; iso-butane, 6; n-butane, 7; acetylene, 8; but-1-ene, 9; *trans*-but-2-ene, 10; iso-butene, 11; *cis*-but-2-ene, 12; iso-pentane, 13; n-pentane, 14; buta-1,3-diene, 15; 2+3-methylpentane, 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)

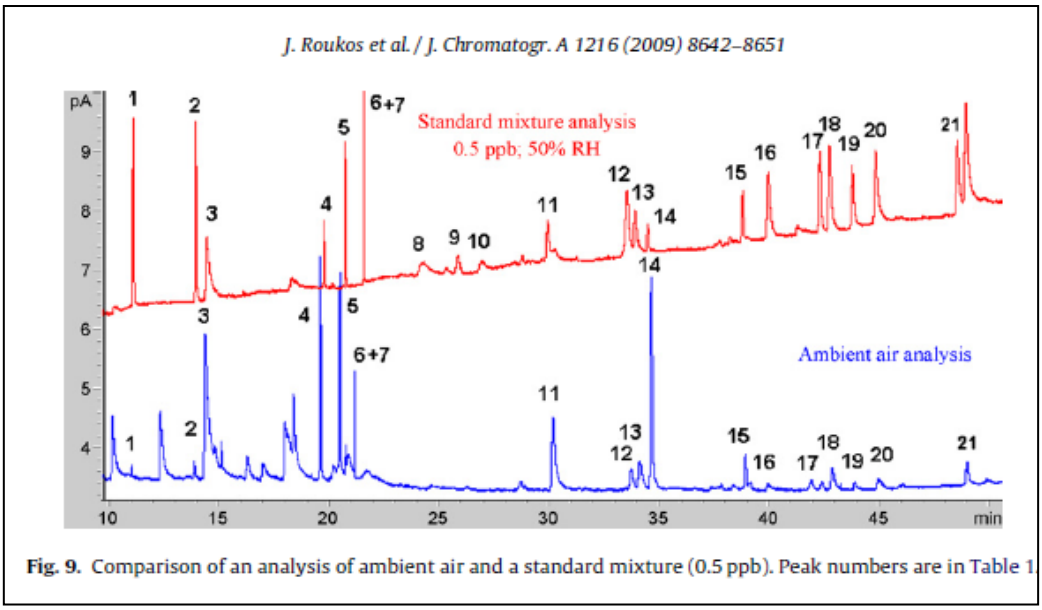


Fig. 9. Comparison of an analysis of ambient air and a standard mixture (0.5 ppb). Peak numbers are in Table 1.

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

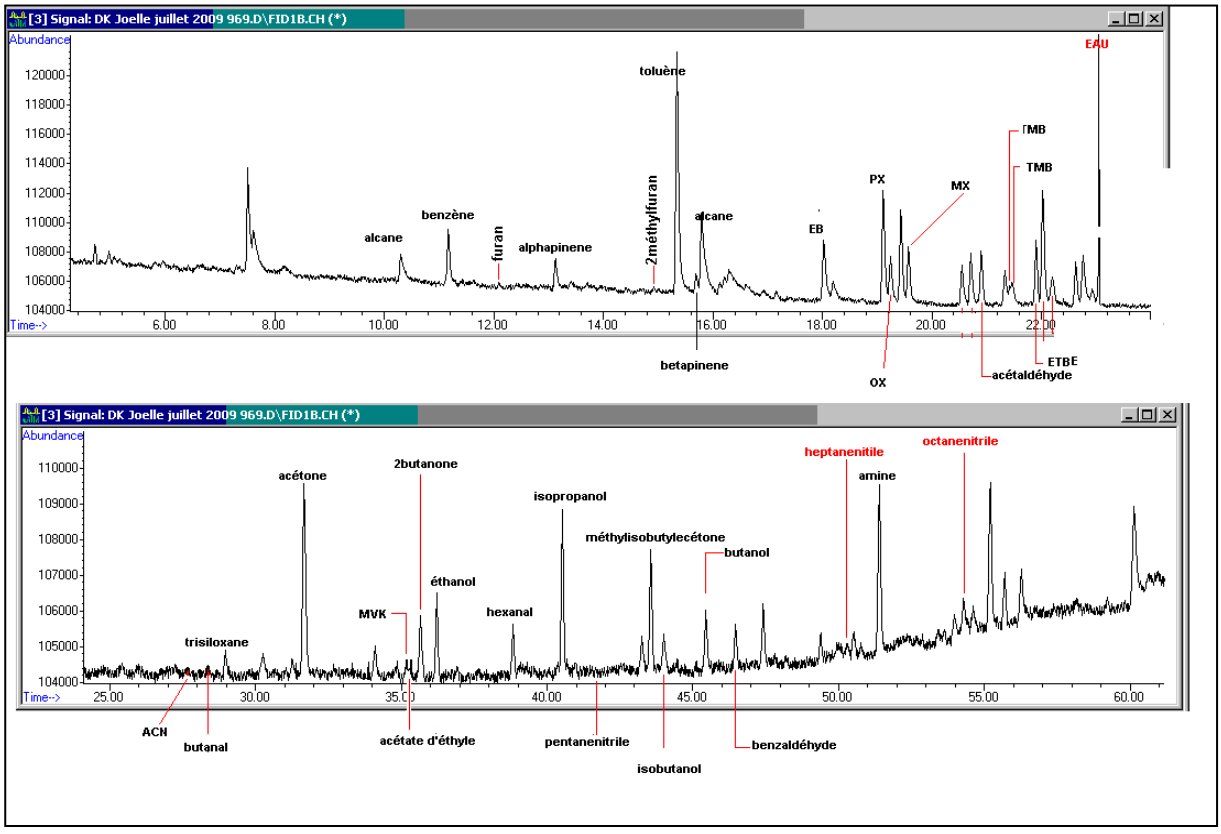


Figure A4: CP-LowOx (Varian), 30 m x 0.53 mm x 10.0 µm
(measurements École des Mines de Douai, Environmental & Chemistry Department, site: Paris suburban, 2010)

1C) PoraBOND U

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.

Dimethylpolysiloxane column

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

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)
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

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
t-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

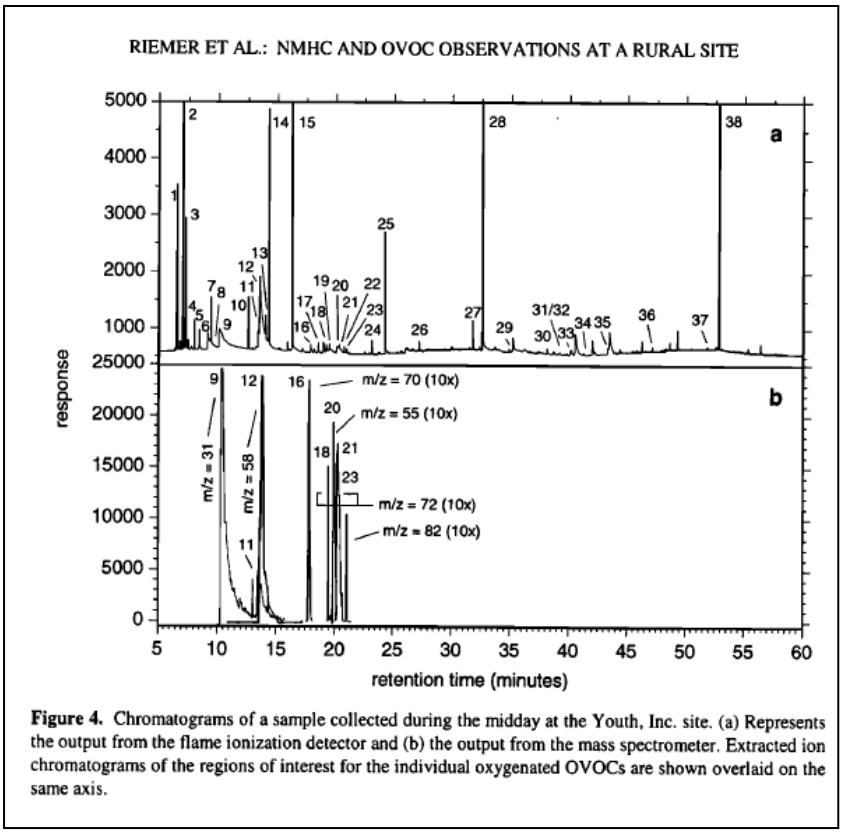


Figure 4. Chromatograms of a sample collected during the midday at the Youth, Inc. site. (a) Represents the output from the flame ionization detector and (b) the output from the mass spectrometer. Extracted ion chromatograms of the regions of interest for the individual oxygenated OVOCs are shown overlaid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

Figure A5. DB-1 (Agilent J&W), 100 m x 0.25 mm x 0.5 µm
(Riemer et al., 1998)

2B) Rtx-1

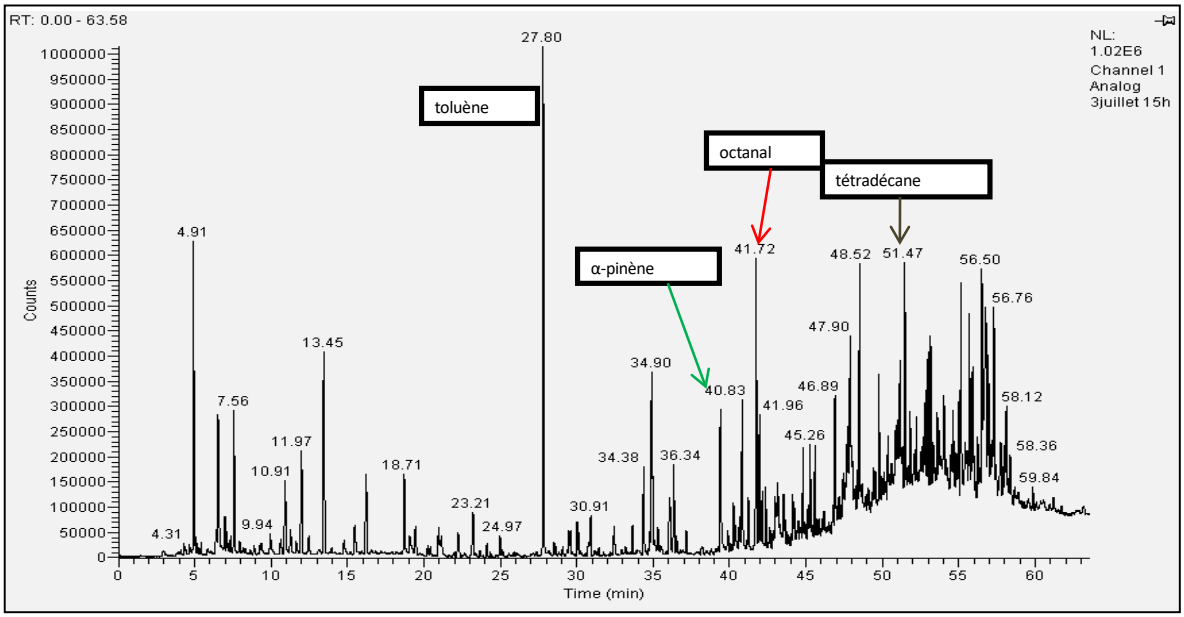


Figure A6. Rtx-1

2C) BPX-5

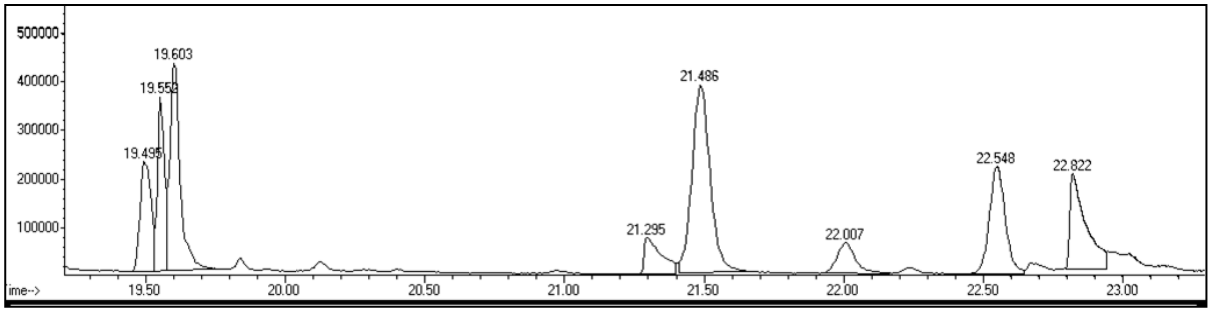


Figure A7. BPX-5 (SGE), 50 m x 0.22 mm x 1.0 µm
(measurements at Hohenpeissenberg Meteorological Observatory, 2011): 19.49 min isobutene + methanol, 19.55 min acetaldehyde, 19.60 min n-butane, 21.29 min ethanol, 21.49 min isopentane, 22.01 min CCl_3F, 22.55 min n-pentane, 22.67 min acrolein, 22.82 min acetone.

2D) DB-624

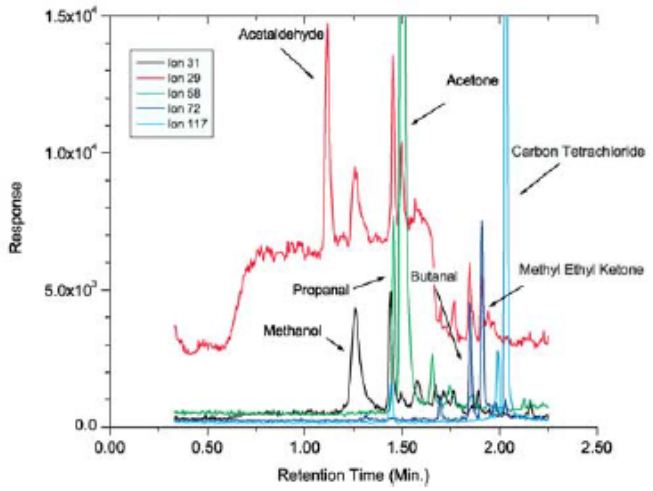


Figure 10. Typical chromatogram, obtained during the TRACE-P mission, of a subset of the targeted compounds. Ions used for quantification for individual compounds are color-coded.

Figure A8. DB-624 (Agilent J&W), 10 m x 0.18 mm x 1.4 µm
(Apel et al., 2003)

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	+

WCOT column equivalents	DB-WAX (Agilent), CP-WAX 52 CB (Varian), Rtx-WAX (Restek), BP-20 (SGE), SUPELCOWAX 10 (Supelco)
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

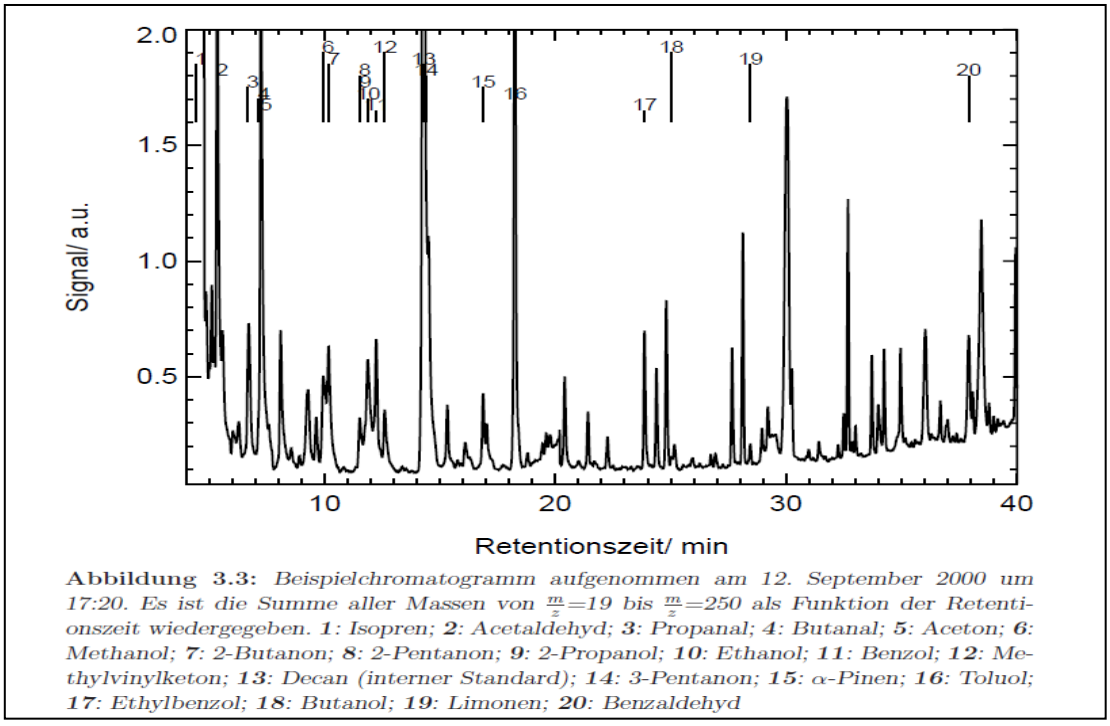


Abbildung 3.3: *Beispielchromatogramm aufgenommen am 12. September 2000 um 17:20. Es ist die Summe aller Massen von $\frac{m}{z}$=19 bis $\frac{m}{z}$=250 als Funktion der Retentionszeit wiedergegeben.* ***1****: Isopren;* ***2****: Acetaldehyd;* ***3****: Propanal;* ***4****: Butanal;* ***5****: Aceton;* ***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 A9. CP-WAX 52 CB (Varian), 60 m x 0.25 mm x 0.5 µm
(Folkers, 2002)

3B) Rtx-WAX

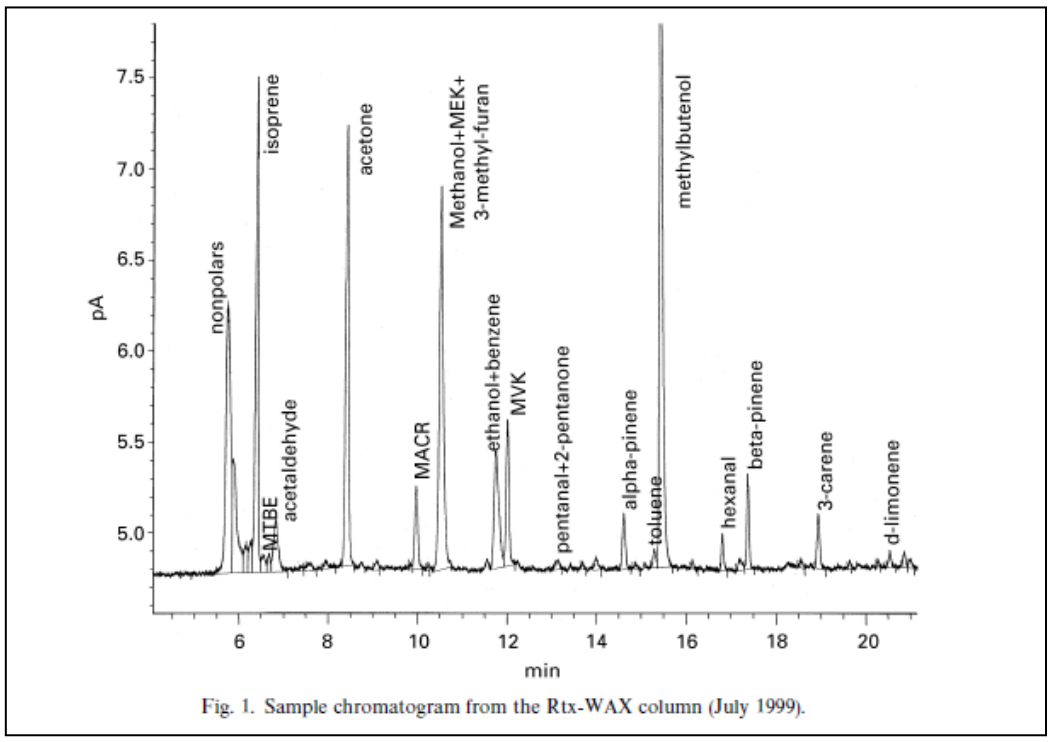


Figure A10. Rtx-WAX (Restek), 60 m x 0.53 mm x 0.5 µm
(Goldstein and Schade, 2000)

3C) DB-WAX

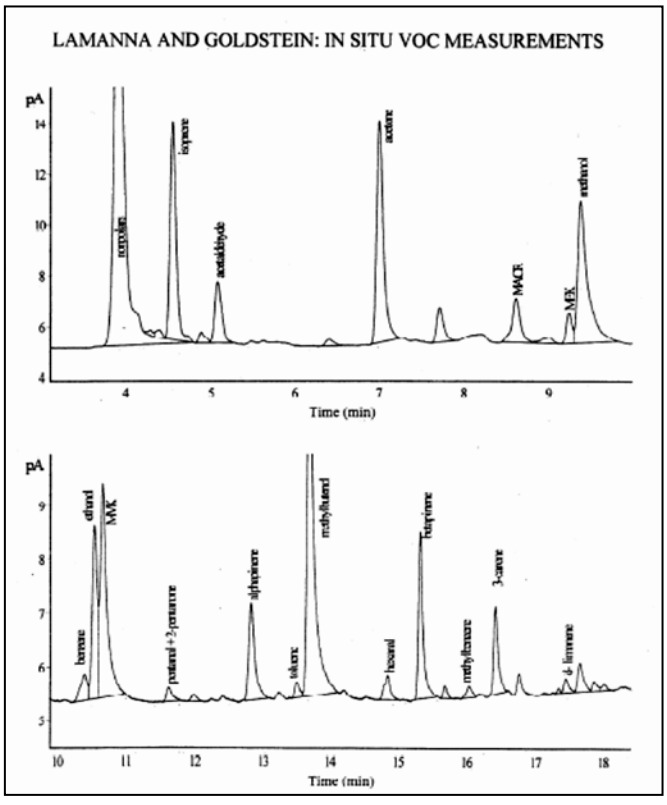


Figure A11. DB-WAX (Agilent J&W), 60 m x 0.32 mm x 0.5 µm
(Lamanna and Goldstein, 1999).

9.4 Appendix 4. The uncertainty calculation

According to the "Guide to the Expression of Uncertainty in Measurement (GUM)" (JCGM, 2008), the combined uncertainty is calculated using the law of propagation of uncertainties (assuming that the standard uncertainties of each factor are not correlated) [GUM, 5.1.2]:

$$u^2_{\chi sample} = u^2_{\chi prec} + u^2_{\chi cal} + u^2_{\chi int} + u^2_{\chi volume} + u^2_{\chi lin} + u^2_{\chi instrument} + u^2_{\chi sampling} \quad \text{(F7)}$$

The standard uncertainties are determined individually for each VOC measured and it is common for there to be a range of different uncertainties for each VOC even if measured on a common GC system. A GUM-conforming but also pragmatic "fit-for-purpose" approach for each uncertainty contribution is given in the following.

- $u\chi_{prec}$ **, *the precision*** (in this guideline "precision" is used as a short version for "measurement precision" as defined in the VIM) reflects the variability of the measurement system due to random uncertainty components. It can be derived from a series of working standards or from target gas measurements. The amount fractions of NMHCs in the whole air or working standards used in precision testing should reflect the amounts that are normally measured at a given location. Generally, these tests should use identical sample path as for ambient air samples, e.g. like shown for standard addition measurements in Fig. 1 (Section 8.1.2).

  Precision covers the random uncertainty contributions due to:

  - The reproducibility of the sampling volume and calibration gas volume
  - The reproducibility in peak integration for both sample area and calibration gas area, including noise in baseline determination and noise in peak separation (the systematic errors are considered below)
  - Blank variation
  - The sampling system (in the case of identical sample paths, see above)
  - Any additional random noise affecting the measurement system

  The precision $u\chi_{prec}$ should be evaluated using the reproducibility conditions set out in ISO 5725–1, 1994. In practical terms for GAW stations this means calculating the relative standard deviation $\left(\sigma^{rel}_{series}\right)$ [GUM, 4.2.2] of measurements of a target gas or a working standard (see Table 13) representative of the calibration period (at least six replicates).

  Since working standards are usually at a higher amount fractions than ambient air samples, the precision will likely be underestimated for low atmospheric concentrations close to the limit of detection (LOD, Section 7.3.5). Therefore, it is necessary to include the uncertainty for low amount fractions represented by the standard deviation of blanks which are commonly used to determine the detection limit (see Appendix 10.5).

  $$u\chi^2_{prec} = \left(\chi_{sample} * \sigma^{rel}_{series}\right)^2 + \left(\frac{LOD}{3}\right)^2 \quad \text{(F10)}$$

  The relative standard deviation $\left(\sigma^{rel}_{series}\right)$ in F10 is calculated based on the calibration measurements used to derive the calibration factor or a series of target gas measurements within the respective calibration period.

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

$$u^2_{\chi cal} = \left(\frac{A_{sample} - A_{blank}}{A_{cal} - A_{blank}} * \frac{V_{cal}}{V_{sample}}\right)^2 * u^2_{cal} \quad \text{(F11)}$$

where u_{cal} is the certified standard uncertainty (k=1) of the calibration gas (or the working standard) including the possible long-term drift of the standard. Please note that the calibration gas amount fraction 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.

If the relative certified uncertainty of the standard $u^2_{cal,rel}$ is given, F7 simplifies to

$$u^2_{\chi cal} = (\chi_{sample} * u_{cal,rel})^2 \qquad \text{(F 11.1)}$$

- $u\chi_{\text{int}}$, the ***standard uncertainty due to the peak integration*** is determined based on equation F1a to F2 and is equal to:

$$u\chi^2_{\text{int}} = \left(\frac{f_{cal}}{V_{sample}} * uA_{\text{int},sample} \right)^2 + \left(\frac{A_{sample} * V_{cal} * \chi_{cal}}{V_{sample} * A^2_{cal}} * uA_{\text{int},cal} \right)^2 \qquad \text{(F12)}$$

where $uA_{\text{int},cal}$ reflects the potential error in peak area due to integration of the calibration measurement and $uA_{\text{int},sample}$ is the potential integration error of the sample 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 A12a and A12b. After determination of a maximum (a_{max}) and a minimum peak area (a_{min}), the deviation from the average peak area can be calculated as $d_{int} = \frac{a_{min} - a_{max}}{2}$, which is a very conservative value corresponding to 3 σ. Since we are looking for a 1σ value d_{int} has to divided by 3 and $u_{int} = \frac{d_{int}}{6}$.

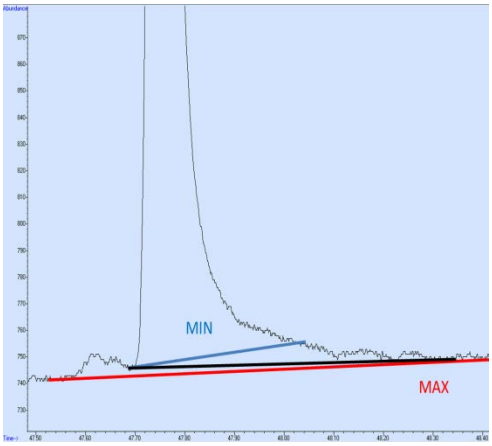


Figure A12a. Example of tailing peaks

The black baseline represents the best fit. Red and blue lines illustrate the baselines to derive the maximum and minimum peak area, respectively.

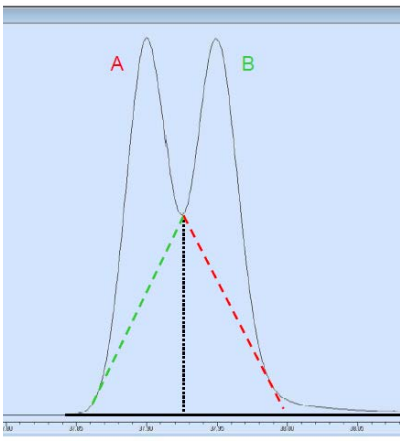


Figure A12b. Example for not separated peaks

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.

- $u\chi_{vol}$, the error contribution due to a ***systematic error of the sample volume***:

$$u^2_{\chi vol} = \left(\frac{A_{sample}-A_{blank}}{V^2_{sample}} * f_{cal} * u_{vol,sample}\right)^2 + \left(\frac{A_{sample}-A_{blank}}{A_{cal}-A_{blank}} * \frac{\chi_{cal}}{V_{sample}} * u_{vol,cal}\right)^2 \quad \text{(F13)}$$

$u\chi_{vol}$ can be neglected when $V_{sample} = V_{cal}$, since the systematic effects will cancel out.

When the sample volume and calibration volume are different, $u_{vol,sample}$ and $u_{vol,scal}$ have to be assessed. The errors of sampling volume are mainly related to the uncertainty of the measurement device to determine the sampling volume (e.g. accuracy of the mass flow controller to determine the sample flow, see F2, or the pressure sensors and temperature sensors, see F1, to determine the sample volume).

The random volume error is already covered by the measurement precision.

- $u\chi_{instrument}$, 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 four 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,
* by a set of calibrations gases covering the whole measurement range or,
* by 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 offline sampling techniques, depends on the sampling technique used. Contributions to the uncertainty common to all offline techniques (cleaning of the samplers, storage, adsorption effects, etc.) should be evaluated case-by-case and per individual component. If not available in the 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 given by (F7) multiplied by a coverage factor *k*=2 to provide the expanded uncertainty ($U\chi_{sample}$):

$$U\chi_{sample} = 2 \times u\chi_{sample} \quad \text{(F8)}$$

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

Example of the calculation of amount fractions and their uncertainty calculation for an online GC/FID:

A simple example is available online: UncertaintyExampleWMOGAWMGVOC_Excel file.

In the example the different uncertainties components are derived using equations presented in Section 7.3 and Appendix 10.4 of this document. The following settings are given:

- The system is linear and does not show specific instrumental issues; sampling errors are neglectable: $u\chi_{lin} = 0$; $u\chi_{inst} = 0$; $u\chi_{sampling} = 0$
- Two compounds are shown, 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 the same and estimated with the same device, thus no systematic volume error is accounted for.
- The reproducibility of the method has been determined with two series of three replicates of the working standard.
- Each individual compound amount fraction has been calculated using equation F3.
- The random changes in baseline position contributing to the integration error are included in the uncertainty of the repeatability of the measurement.
- A systematic integration error due to tailing and superimposition is assumed for one of the compounds.

9.5 Appendix 5. Limit of detection

A thorough definition of the Detection Limit and its determination and application is given in the literature (e.g. Currie et al., ISO 1995). Here we give two pragmatic approaches to derive a LOD from routine measurements performed at the stations.

Method 1

Using blank measurements: In the case of FID analysis, even when there is no analyte the measured signal (in mV) is usually not zero. This is due, for example, to detection of column bleeding and impurities in the carrier gas. Therefore, it is valid to assume that the noise of the baseline signal measurement is Gaussian and symmetric around the baseline average value.

In this case, an estimate of the LOD can be obtained based on the standard deviation of the mean baseline [EURACHEM MV guide]:

$$LOD = 2 * t_{(1-\alpha),v} * \sigma_{conc_{baseline}}$$

where $t_{(1\text{-alpha},v)}$ is the one-tailed Student t-value corresponding to the number of measurements n-1 = v, at a significance level α =0.05 (or 5%). This means that for a sample that contains the analyte, at the chosen LOD there will be statistically a 5% error of declaring the sample free of the analyte (also known as false negative).

A straightforward approach for estimating the LOD is explained in Figure A13. For the estimation of the substance-specific LOD, the baseline noise is manually integrated during the substance-specific retention time of the peak width at the base of the measurement peak (w_0). After several repetitions with slightly differing manual integrations, the resulting standard uncertainty in ppt $\sigma_{conc_{baseline}}$ is multiplied with the Student t-value (i.e. 4.04 for 6 repetitions and 3.31 for 10 repetitions).

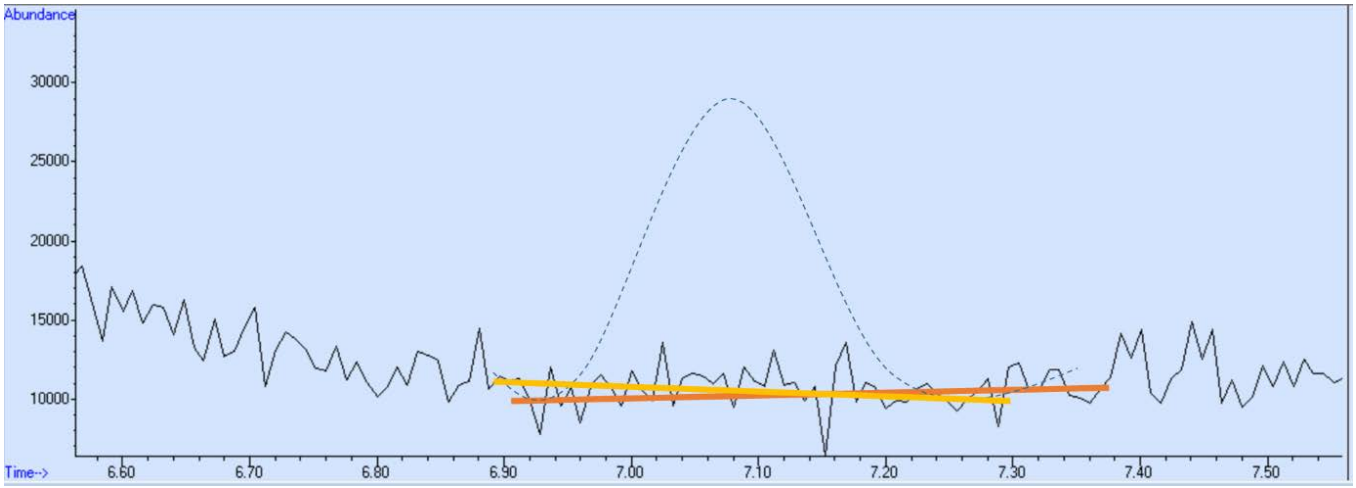


Figure A13. Integration of the noise signal in a blank measurement
blank chromatogram (black line) with two possible baseline realizations (yellow and brown lines) at the retention time window of a target substance (dotted line), which is not evident in the blank.

Method 2

A practical realization of detection limits for NMHCs may be based on the smallest integrate-able GC peak that can be reliably detected and its area then integrated. This is to a large degree a function of the software and user, but having determined the smallest integrate-able GC peak, the detection limit is commonly calculated based on the standard deviation of the mean of this smallest peak amount fraction $\sigma_{\chi_{LOD}}$:

$$\chi_{LOD} = \sigma_{\chi_{LOD}} * 2 * t_{(1-\alpha),\upsilon}$$

where $t_{(1-\alpha,\nu)}$ is the one-tailed Student t-value corresponding to the number of measurements n-1 = ν, at a significance level α =0.05 (or 5%). The t-value can be taken from tabulated values. In essence, Method 2 is therefore also based on the assumption that the standard deviation of the smallest peak is representative of the standard deviation at the LOD and at the baseline.

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