Summary:

This report provides the description of a GCMS instrumentation for state-of-the art measurement of atmospheric OVOCs within the EU FP7 infrastructure project ACTRIS. The report contains the following topics:

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1. Introduction

Continuous measurements of atmospheric oxygenated volatile organic compounds (OVOCs) are only rarely continuously performed in global and regional networks, although an imminent need for such measurements exists. Atmospheric OVOCs mainly consist of alcohols, aldehydes, ketones, ethers, esters and organic acids. They are part of the group of the volatile organic compounds (VOCs), which are, besides CO, the major contributors of reduced gaseous carbon-containing compounds in the atmosphere. VOCs are emitted into the atmosphere by biogenic and anthropogenic sources (with largest sources from traffic and solvent usage). Typically, more than 100 VOCs can be detected with mixing ratios in the range from a few ppt up to some ppb. On a global scale, methanol, ethanol, acetone and formaldehyde are the most important OVOCs and have therefore been identified as high-priority compounds in the Global Atmosphere Watch (GAW) of the World Meteorological Organization (report #171, WMO, 2006). However, on the continental scale (i.e. Europe) also C₂-C₄ aldehydes, >C₅ alcohols, ethers and esters are in the focus of interest, as they contribute to the formation of tropospheric ozone (O₃) and secondary organic aerosols (SOAs) in the troposphere.

Gas chromatography-mass spectrometry (GC-MS) has been used for several decades to analyse these OVOCs in the atmosphere, ranging from the polar background regions to the most polluted urban environments. An extensive review of measurements in different environments can for example be found in Koppman and Wildt (2007). Until now GC-MS is the most general method for the analysis of atmospheric OVOCs. Therefore, GC-MS is the method of choice within ACTRIS and will be the main subject of this report on standardized measurements of OVOCs. However, other measurement methods for the analysis of specific OVOCs and groups of compounds (PTR-MS and HPLC) are also discussed.

The measurement of OVOCs by gas GC-MS is generally performed in the following steps.

1. An air sample is introduced to the analytical system from ambient by an intake manifold and sampling line.
2. The air sample is then passed through a moisture removal/ozone removal system.
3. OVOCs are preconcentrated on an adsorbent medium that is cooled using liquid nitrogen, liquid carbon dioxide, or thermoelectric closed-cycle coolers.
4. The concentrated OVOC sample is optionally refocussed cryogenically by a cooled secondary trap to narrow the band width for injection onto the capillary GC analytical column.
5. The OVOCs are then thermally desorbed into the analytical gas chromatographic (GC) column and finally analysed by mass spectrometry (MS).
6. For quantification a standard is used which contains mixing ratios of OVOCs in zero air or N₂ in the ppb (10⁻⁹) range. The standard has to be diluted with zero air or N₂ into a concentration which is in the range of those usually encountered at the specific station. For data processing and data delivery protocols should be used as specified below.

In the following the steps 1-6 are discussed in detail.
2. Sampling

For the analysis of all atmospheric OVOCs sampling has to performed directly at the measurement site. Off-line analysis with sampling of OVOCs on adsorbent-filled tubes or in stainless steel canisters is possible for certain types of OVOCs, but is not recommended for the analysis of the whole suite of OVOCs. However, for carbonyls only, a well-tested method exists with DNPH-coated tubes (see section 7.1).

For OVOCs the inlet line should be either silco-treated stainless steel or Teflon PFA). Transfer lines for the analysis of OVOC should be either made of silco-steel or PFA (Perfluoralkoxy) and not of stainless steel. Silco-treated steel should be humidified before first usage (e.g. by passing moist ambient air). The residence time in the inlet should not exceed a few seconds. Therefore, the inlet line has to be as short as possible and the diameter should not be larger than 1/8 inch in order to minimize the dead volume, unless it is permanently flushed with high volumes of air. It is recommended to have a Teflon mesh with a maximum of 5 µm mesh size included in the line for holding back particles. This has to be exchanged regularly. Experience from an urban site (Zurich) is that the grid has to be exchanged every 4 months.

3. Preconcentration

3.1. removal of water/O₃/CO₂

3.1.1 Water removal

The dew point should be defined and it should be at least 10°C lower than the trapping temperature in case of adsorptive sampling. Otherwise adsorbed water on the trap will lead to a smaller breakthrough volume or even a blockage of the trap. For cryogenic trapping the dew point should be below -30°C. Systems in use are (1) a precolumn with 0.6 g of Haysep-D (Legreid et al., 2007) and a water trap at subambient temperature, where water is adsorbed but not the analytes (Hopkins et al., 2011). Nafion® Dryers must not be used for water removal of OVOCs ambient air analysis as OVOCs tend to be lost within the Dyrer.

3.1.2 Ozone removal

As the reactive OVOCs are prone to be degraded by ozone during the sampling process, the O₃ in the sampled ambient air should be destroyed before trapping. Several methods exist:

- A heated stainless steel line or a metal grid in the ambient air flow (>70°C)
- The addition of a flow of NO (O₃ + NO→NO₂) into the ambient air flow
- Small cartridges filled with or filters impregnated with special salts like sodium thiosulfate or potassium-iodide

A compilation of available method and their evaluation can be found in Appendix 1 (Ozone removal techniques for GC analysis of OVOC (oxygenated volatile organic compounds) in ambient air samples.

3.1.3 CO₂ removal

If the trapping temperature is lower than -60 °C it is advisable to remove CO₂ (boiling point: -78 °C) either from the ambient air flow (by using an in-line adsorbent (e.g. Ascarite) or between trapping and analysis (e.g. by slowly heating the trap to a temperature high enough for the CO₂ to be released but not for the analytes). If CO₂ is trapped and released into the analytical system this could lead to distortion of chromatography and/or diminished sensitivity of the detector.
3.2. Trapping

As OVOCs are only occurring in the atmosphere in the ppt (parts per trillion, $1 \times 10^{-12}$) to ppb (parts per billion, $1 \times 10^{-9}$) range, they have to be preconcentrated before the analysis, using gas chromatography-mass spectrometry (GC-MS). Preconcentration of OVOCs is performed on a trap which contains enough of a suitable material or a combination of different adsorbents for fully retaining VOCs at a given temperature. In use are either a combination of week adsorbents with low sub-ambient temperature or a stronger adsorbent at ambient temperature, often also multi-bed adsorbents with increasing adsorbent strength in sampling flow direction. For each system breakthrough volumes have to be tested for the specific OVOCs, using either increasing amounts of humidified synthetic standards or ambient air spiked with standards.

A compilation of different trapping adsorbents and their usage is available in Appendix 2 (Adsorbents for sorbent-based enrichment of OVOCs (oxygenated volatile organic compounds) in ambient air samples

For the trapping procedure a pump should be used after the trap, which is connected to a critical orifice or a mass flow controller (or any other suitable instrument to regulate the flow over the trap). It is essential to determine the sampling volume with low uncertainty either by regularly calibrated mass flow controllers or by differential pressure measurement in a defined reference volume. If the pump is used before the trap it has to be ensured that it does not produce any additional contamination.

After trapping, the trap should be flushed in forward mode at the same temperature for an adequate amount of time to allow the purge out of remaining water and potentially adsorbed gases (e.g. CO$_2$, noble gases) from the trap.

Release of the analytes from the trap is normally done by heating the trap (either by ohmic resistance or by other means of heating) in counterflow. The final temperature should be reached as fast as possible and should be high enough to release all analytes from the trap. Analytes are transferred to the gas chromatography system by carrier gas flow. After transfer of the analytes the trap should be reconditioned (e.g. by flushing it further with carrier gas and heating it to a higher temperature than needed to release the analytes). The flow of cleaning gas is vented to the environment. If the injection of the OVOCs is not rapid enough to obtain sharp peaks (due to too large traps or to slow heating rates, a second focusing trap should be installed between preconcentration and column. This again may be adsorptive or cryogenic but needs to have a substantially smaller internal volume than the preconcentration trap.

3.3. capillary columns for GC analysis of OVOC

Several possible analytical columns are discussed in the Appendix 3 (chromatographic separation)

Compared to packed columns capillary columns exhibit better separation efficiencies and higher inertness. Despite their lower capacity they are suitable for most applications in atmospheric trace gas measurements. There are basically two types of capillary columns that are currently used for the analysis of OVOCs: 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 OVOCs at ambient and above ambient oven temperatures which reduces liquid nitrogen consumption that is necessary in case of WCOT columns. Special highly polar OVOCs PLOT columns do not retain saturated aliphatic NMHCs as they have little or limited interactions with the surface of the stationary phase. By this way OVOC are isolated and generally no co-elutions with NMHC will appear. Thus, in principle a non-specific detector (flame ionisation detector; FID) can be used as single detector.

The disadvantage of PLOT columns is the need for humidity management. Otherwise there would be a sharp water peak that co-elutes with OVOCs, e.g. propanal and acrolein on GS-OxyPLOT (Agilent) and for most PLOT columns a shift in retention times depending on the moisture content of the ambient air sample. Furthermore, some PLOT columns may occasionally lose particles of the stationary phase (problem especially for MS), but this effect was decreased by better bonding 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 rate of diffusion into the stationary phase and solubility according to the boiling points. The polar/non-polar interactions are much weaker than the adsorptive interactions in PLOT columns. There two types of films exist: 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 OVOCs with NMHC and so there is the need for a specific detector (MS). Another disadvantage is the low retention of alcohols on dimethylpolysiloxane columns. On the contrary on polyethylene glycol columns alcohols have high retention potential. Concurrently NMHC are emitted in a fast way, which leads to less co-elutions with OVOCs. But a drawback of the polar columns is the fact that aldehydes have also low retention volumes. Furthermore polyethylene glycol columns have short lifetimes, susceptible to damage upon overheating or exposure to oxygen and they cannot be operated at sub-ambient oven temperatures.

4. Analysis by GC-MS

As the sensitivity of the mass spectrometer decreases relatively rapidly, calibrations using a working standard have to be performed nearly as often as ambient air measurements. This ensures that the decline in sensitivity is accurately tracked. Furthermore, target tank measurements should be performed bi-weekly and blank measurements should be performed monthly. After a considerable change of the system (e.g. source replacement, changing of analytical column or trap) blank measurements have to be performed as soon as the system runs in a steady mode again.

The source has to be tuned after the loss of sensitivity has reached a certain degree, but at least every second month. If boundary conditions of the source (repeller voltage, lenses) do not allow a proper tuning of the source anymore it has to be cleaned using the procedure specified by the manufacturer.
5. Quality Assurance and Quality Control

Quality assurance (QA) follows the principles of the GAW QA system (see Figure 2 and http://www.wmo.int/pages/prog/arep/gaw/qassurance.html):

1. Network-wide use of only one reference standard or scale (primary standard). In consequence, there is only one institution that is responsible for this standard (CCL).
2. Full traceability to the primary standard of all measurements made by Global, Regional and Contributing GAW stations.
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. Establishment of MGs or SOPs for these measurements.
6. Use of detailed log books for each parameter containing comprehensive meta information related to the measurements, maintenance, and 'internal' calibrations.
7. Regular independent assessments (system and performance audits, Performance audit: check measurements versus DQOs and traceability System audit: overall conformity of a station with the principles of GAW).
8. Timely submission of data and associated metadata to the responsible World Data Centre as a means of permitting independent review of data by a wider community.

![Diagram of the GAW QA system](image)

Fig. 2: Principles of the GAW QA system.
5.1 Standards and Scale

The nomenclature of standards should be used as follows: The “primary standard”, “secondary standard” etc. should only be used at the Central Calibration Laboratory (CCL), they comprise a system of standards defining the “scale” for VOC in GAW.

Generally, “tertiary standards” are provided by the CCL to the stations and laboratories and they are used there as “laboratory standards” or “working standards”. The highest level standard at a given site is called the “laboratory standard” (the laboratory standard is not necessarily a tertiary standard from the CCL, though it is recommended). The laboratory standard is supplemented by a system of working standards at the stations that may consist of synthetic or whole air mixtures, certified or custom-made.

“Traveling standards” are generally working standards with reference mole fractions determined by the CCL, WCC or a certified laboratory used in comparisons and round robins.

The term “target gas” is used for a working standard which is treated as a sample of unknown compositions, e.g. the data evaluation procedures of a station are used to determine the VOC mixing ratios and the deviation from the assigned values is a test for the quality of measurements. Accordingly, a target gas should be close to ambient gas composition which means a whole air standard with similar concentration levels.

The scale is kept by the CCL by means of a system of standards (see above). The scale is transferred to the stations and labs by the tertiary standards. In case a station does not hold a tertiary standard by the CCL, it has to demonstrate that the laboratory standard is linked to the scale by regular and direct comparison.

It is recommended that each station or laboratory holds the following Calibration Gases:

1. A laboratory standard which should be a multi-component laboratory standard (synthetic mixture) that covers the main components and should presumably be produced by the CCL (NPL) or another (NMI) linked to the CCL.
2. A certified multi-component working standard (synthetic mixture with certified mixing ratios) with similar components as the laboratory standard.
3. Multi-component working standards that cover all components measured and which are calibrated versus laboratory standard, travelling standards, or other methods (Carbon response FID, permeation/diffusion source, mixtures). One of these working standards should be of high mole fractions (upper nmol/mol range) for standard addition measurements.
4. A Target Gas which is a whole-air working standard calibrated versus laboratory standard, other standards or by other means

Though not recommended, there are minimum requirements for a station that need to be fulfilled:

1. A laboratory standard to define the scale for each component measured at the station
2. One working standard (which may be custom-made) to check for drifts in the scale. In case of a GC-FID where calibration can in many cases be reasonably transferred from the laboratory standard to other compounds not present in the laboratory standard by means of the carbon response concept, a well documented procedure to assign calibration factors and uncertainties to these compounds are needed.
3. A target gas which is presumably whole air but could also be a synthetic mixture
5.2 Zero Gas

“Zero gas” is a hydrocarbon free gas from either catalytically cleaned ambient air (Pt or Pd catalyst at 400°C) or alternatively, not as good but easier to handle, synthetic gas of at least 5.0 quality. Catalytically cleaned air is preferred as this is identical to the sample gas matrix. Often, trace amounts of hydrocarbons in the pmol/mol range are present as impurities in the zero gas. Stations should go for optimum zero gases by comparing the blank values obtained in measurements of different hydrocarbon free gases aiming at the lowest levels.

The regular measurement of zero gas is part of the QA program to be followed at all stations. It yields information about artifacts due to release of adsorbed hydrocarbons or leaks in the sample path. Blank values should be as low as possible. Zero gas should be applied at the inlet of the sampling system (on-line system) or to flasks and canisters via any used sampling line under field use conditions. Often a high flow inlet manifold is used which cannot be easily flushed by zero gas, then zero gas can be introduced after the sampling split to the instrument, but checks with independent sampling not over the routinely used inlet should be performed.

5.3 Data Quality Objectives

The GAW data quality objectives have been approved by the GAW-VOC expert group. The enhanced uncertainty/repeatability is envisaged for the best ACTRIS measurements. Below 0.1 ppb an absolute value below the numbers in the table should be achieved.

<table>
<thead>
<tr>
<th>OVOCs</th>
<th>GAW uncertainty</th>
<th>GAW repeatability</th>
<th>ACTRIS: Enhanced uncertainty</th>
<th>ACTRIS: Enhanced repeatability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mole fraction</td>
<td>+/- 20 ppt</td>
<td>+/- 15 ppt</td>
<td>+/- 10 ppt</td>
<td>+/- 5 ppt</td>
</tr>
<tr>
<td>&lt; 0.1 ppb</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The enhanced DQOs are the objective for good performing stations. Within ACTRIS, generally the GAW DQO shall be reached. These stated DQOs are valid for individual ambient air measurements. This is different from the interlaboratory comparability objectives used in the greenhouse gas community where the objectives refer to uncertainties in measurements of standards comprising multiple measurements.

5.4 Method for Measurement of Standards

Generally it is recommended to leave pressure regulators and transfer lines attached to the working standard/target gas cylinders in order to minimize the risk of contamination and reduce equilibration times. Laboratory gloves (i.e. powder-free latex) should be worn whenever working with parts in contact with test gases in order to avoid contamination. Furthermore, it is strongly recommended to use no liquid leak tester solutions as they might contaminate the system.

If a working standard/target gas cylinder is newly connected, the pressure regulator and the transfer line with capped fitting on the GC connection side should be mounted at least 24 hours before the measurement. The transfer line should be made of Silcosteel or Sulfinert or other stainless steel tubing with a passivated internal surface. The use of Vespel/Graphite (VG) ferrules is recommended as these provide a tight sealing while not damaging the tubing. They can be used several times and should only be replaced in case that sealing or contamination problems are present (follow the mounting instructions of the manufacturer). After installation, the regulator needs to be flushed. For this, the transfer line is uncapped, the regulator’s low pressure port is gently opened and
the cylinder valve is opened very short such that the primary pressure jumps up and goes down again to ambient. This procedure should be repeated at least 2 times. After flushing, plug the transfer line and pressurize the pressure regulator another time by shortly opening the cylinder valve. Check the pressure for a few minutes; if not constant, tighten the 30 mm nut and repeat until pressure is constant. Then, apply a low pressure (0.2-0.5 bar) to the transfer line, as well. As an initial leak check, close the regulator. After it is closed, watch the low pressure port for some 10 min. If not constant, check plug and connection to the transfer line, tighten gently, and repeat the check. Finally, 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 loosing sample through possible leakages. This setup also serves as a static leak test as the upstream regulator pressure should not change during the 24 h equilibration period. Connect the test gas cylinder to an appropriate instrument inlet port. Then flush the whole inlet line for at least another 3 times and leave the gas cylinder connected to your instrument. It is recommended to open the standard cylinder valve only during the sampling periods unless you use an automated measurements sequence in unattended operation.

In many set-ups the standard cylinder is permanently connected to the GC system. The measurement of the standard gas should be performed after an initial flushing period through the GC valve system which is sufficiently long to achieve equilibration in the lines (typically 10 min with 30 ml/min). To stay within the DQQ, the sensitivity of a GC system should not drift by more than 3% between calibrations. Similarly, blank values (see below) and reproducibility should not change such that they introduce more than 3 % effects on the measured data. As both, calibration and target gas measurements enable to detect drifts in the system it is up to the operators to decide the share of these measurements. Another issue is the reproducibility of such standard measurements. Often, first measurements are off in a set of measurements due to insufficient equilibration of internal surfaces of sampling lines. For such conditions, series of standard measurements are to be performed containing at least one appropriate measurement.

If a drift in the laboratory standard is observed as determined by a drift / inconsistency with a working standard or a discrepancy with a new laboratory standard beyond the combined uncertainties, the discrepancy has to be resolved as soon as possible. Options in such a situation are to send the laboratory standard for recalibration to the CCL or WCC, ask other stations for a high level standard for an independent check, or check available results from past intercomparisons. Anyways, station operators should try to identify where the drift occurred and apply a correction for those periods in which the drift can be well described. If this is not possible, the uncertainty during this period needs to cover the range of unexplained drift.

In Figure 3 an example of a series of working standards measured at Hohenpeissenberg (DWD, Germany) is shown. Here, the determined mixing ratios for all analysed compounds are plotted over time in a log scale. Relative changes should become detectable by non-constant values. The Figure shows an example for NMHCs.
5.5. Method for Measurement of zero gas (blanks)

For blank measurements, a zero gas is sampled via the usual air sample path. Thus, it passes the ozone and particle filter, the water trap and sampling unit just like ambient air samples. At Hohenpeissenberg, Helium is applied at an open “T” into the 1/8” sampling line at a flow rate of about 100 ml/min yielding a sample flow of about 80 ml/min towards the GC and 20 ml/min towards the ambient air sample manifold. A similar amount of zero gas is analysed as in the ambient air samples. For convenience, we use purified He 5.0 (charcoal and mole sieve at -40°C) as zero gas as we use the same gas as carrier gas and purge gas. Occasionally, we also test the same line using catalyst-purified ambient air (Pd at 400°C) and essentially observe the same results as with He.

The Figure 4 gives an example of the behaviour of NMHC blanks over time. Peaks in benzene are occasionally observed and are generally associated to some kind of overheating of traps but the nature of this contamination is not really understood. Additionally, it can not be excluded that small amounts of ambient air diffuse into the He against the He flow (at the open “T”) and some of the ethane, ethylene, propane and benzene is attributed to ambient air mixing into the He.
5.6. Method for Detecting Effects of Ozone on Reactive Compounds

In order to check for interferences with ozone and other reactive constituent of the ambient air sample gas, it is suggested to perform standard addition measurements. In these, an amount of standard is added via a fused silica capillary into the ambient air sample flow, so that roughly 2-10% of the ambient air matrix (including ozone) is formed by the standard. It is not so important to know the flows exactly, as the mixing ratios of alkanes with low concentrations in ambient air and no reactivity towards ozone (e.g. n-hexane, benzene) can be used to scale the mixing (if incorporated in the OVOC standard). Then the ratios of the mixing ratios in standard addition measurement compared to a pure standard are plotted after normalizing them to the corresponding ratios of the above mentioned compounds (Fig. 4). Some of them have fairly high contributions from ambient air but the important OVOCs are clearly dominated by the added standard. If ozone interferences (losses) exist, these OVOCs should show lower ratios than 1.

5.7 Logs at each station

It is required that each station has the following logs either in electronic or paper-based form:

1. Instrument Log with all operation parameters, significant changes, characterizations, tests results, etc.
2. Measurement Log with all measurements including the type of measurement, the time of measurement in UTC (start sampling, end sampling, start GC run), sampled volume (dry volume), and comments (anything unusual)
3. A Log of the used calibration factors and blank value determinations from zero gas measurements
4. A Log of all working standard and target gas measurements
5. An Error Log with ascribed uncertainty contributions to compound measurements due to peak-overlap, scatter of blank values, unusual low reproducibility, instable sensitivity a.s.o. as well as all other unexplained deviations from normal instrument performance.
6. Meteorological data Log (temp, hum., wind velocity and dir.)

6. Post-measurement analysis

6.1 Data checks of final mixing ratio data

OVOCs should be grouped in a convenient number (typically 3 or 4) of functionally similar compounds, e.g. alcohols or ketones, in a log plot over a time interval of half a year or a year. The procedure is illustrated in the Figure 5, where the quality checks were performed for the Hohenpeissenberg data in year 2009 for NMHCS.

Generally, it is expected that the variability of the data should increase with higher reactivity (variability-lifetime-relation) and changes should be more pronounced for shorter lived compounds (lower background). Spikes in positive direction may be attributed to plumes with local/regional pollution and should be checked for consistency with other compounds from similar sources, if not consistent, the raw data should be rechecked. Spikes in negative direction stand for clean air and should again be checked for consistency with other compounds from similar sources. If they are found to be not consistent with other compounds, the peak integration has to be checked.
Fig. 6: Time series (annual cycle) of C2-C4 alkanes measured at Hohenpeissenberg, generally, measurements from 1:00 and 13:00 CET are shown.

**xy-plots for the data evaluation (used at Rigi, Switzerland by Empa)**

A similar approach as used at Hohenpeissenberg is applied at the Rigi site by Empa. In addition many xy-plots are produced to check for consistency with former years and within the year. In Figure 7 and 8 an example is shown of a correlation plot using benzene vs. acetylene.

Fig: 7: acetylene vs benzene at Rigi (Switzerland). Blue 2011 data, brown 2008-2011 data
6.2 Uncertainty evaluation

This section describes the routine assessment of measurement precision and uncertainty. While the precision reflects random errors in the measurement process, the uncertainty includes also possible systematic errors in the measurement. In the following it is illustrated which factors influence precision and uncertainty and how they are derived following the concept of the “Guide to the Expression of Uncertainty in Measurement” (GUM, 2008).

Derived uncertainty values are 1-sigma errors, for the expanded uncertainty the values have to be multiplied by the coverage factor $k=2$ (representing the 2-sigma error). The error calculation is based on the calculation of mixing ratios for linear detection systems as presented in section 6.2.1.

6.2.1. Calculation of mixing ratios for linear detection systems

For substances quantifiable via a standard gas mixture, the mixing ratio $X_{\text{sample},i}$ of a compound “i” in a sample is calculated via:

$$X_{\text{sample},i} = \frac{A_{\text{sample},i} - A_{\text{blank},i}}{A_{\text{cal},i} - A_{\text{blank},i}} \times X_{\text{cal},i}$$

where:
- $A_{\text{sample},i}$ = peak area of sample measurement of compound “i”
- $A_{\text{cal},i}$ = peak area of calibration gas measurement of compound “i”
- $A_{\text{blank},i}$ = possible blank value of compound “i” determined in zero gas measurements
- $X_{\text{cal},i}$ = certified mixing ratio of calibration gas standard

6.2.2 Determination of Precision

The precision can either be derived from the target gas or working standard (whole air) measurements or series of air samples taken in similar, stable air mass conditions (meteorological and chemical) in series of 5 or more measurements.

It covers the random errors of peak integration, volume determination and blank variation. In case of canister or adsorption tube sampling it includes the reproducibility of the sampling system as well.

The Precision $\delta X_{\text{prec}}$ is determined as the standard deviation of a series of measurements of a sample:

$$\delta X_{\text{prec}} = \sigma X_{\text{sample}}$$

6.2.3 Determination of Uncertainty

The total uncertainty $\Delta X_{\text{unc}}$ of a measurement does not only include the random errors described by the precision but also the systematic errors $\Delta X_{\text{systematic}}$ of the measurement.
Possible systematic errors are:

- The uncertainty in the standard gas mixing ratio $\delta \chi_{\text{cal}}$
- Systematic integration errors (due to peak overlay or bad peak separation) $\delta A_{\text{int}}$
- Systematic errors in sample volume determination $\delta V$
- Further instrumental problems (e.g. sampling line artefacts, possible non-linearity of the Detector (MS), changes of split flow rates) $\delta \chi_{\text{instrument}}$

Following Gaussian error propagation, the overall systematic error is then described as

$$\Delta \chi_{\text{systematic}} = \Delta \chi_{\text{cal}} + \Delta \delta_{\text{int}} + \Delta \chi_{\text{cal}} + \Delta \chi_{\text{instrument}}$$

Referring to equations F1 to F3, the single error contributions are determined for each analysed compound as

$$\Delta \chi_{\text{cal}} = \frac{A_{\text{sample}} \cdot V_{\text{cal}} \cdot \chi_{\text{cal}}}{V_{\text{sample}} \cdot A_{\text{cal}}}$$

where $\delta \chi_{\text{cal}}$ includes the certified relative uncertainty of the standard gas (or the working standard) and possible drifts of the standard.

$$\Delta \chi_{\text{int}} = \left( \frac{f_{\text{cal}}}{V_{\text{sample}}} \cdot \delta A_{\text{int, sample}} \right)^2 + \left( \frac{A_{\text{sample}} \cdot V_{\text{cal}} \cdot \chi_{\text{cal}}}{V_{\text{sample}} \cdot A_{\text{cal}}} \cdot \delta A_{\text{int, cal}} \right)^2$$

where $\delta A_{\text{int, cal}}$ represents the relative error in peak area due to integration of the calibration measurement and $\delta A_{\text{int, sample}}$ the integration error of the sample measurement, respectively.

$\Delta \chi_{\text{cal}}$, the systematic error of the sample volume, can be neglected, since $\delta V_{\text{sample}} = \delta V_{\text{cal}}$, and thus the error cancels in equation F1. The statistic volume error is covered by the measurement precision.

$\Delta \chi_{\text{instrument}}$, the error in mixing ratio due to specific instrumental problems has to be evaluated for each site individually. These errors can be derived by tests or intercomparison measurements.

### 6.2.4 Determination of detection limit

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

A simple way to calculate the detection limit is, to integrate a baseline signal over a time interval similar to the average peak width. This integration is performed for a statistically significant number of times (min 10 times). The derived standard deviation of the integrated area multiplied by a factor of 3 represents the detection limit.
6.3 Data submission

Data submission has to be performed using the template provided by EBAS using the website: http://ebas-submit.nilu.no/. The deadline for submission for data from one year, is 31 July of the following year.

7. Additional methods

Carbonyl OVOCs (aldehydes/ketones) by 2,4-Dinitrohydrazine (DNPH) impregnated cartridge sampling and subsequent analysis by HPLC. Furthermore, for formaldehyde and the relatively new on-line method PTR-MS. As gas chromatography is most widely used, this method will be in the focus of this measurement guideline but the other techniques are also covered.

7.1. Liquid Chromatography method for carbonyl OVOCs (DNPH-sampling)

Off-line sampling of carbonyl OVOCs (ketones/aldehydes) by 2,4-Dinitrophenylhydrazin (DNPH)-coated samplers with subsequent liquid chromatography is a well-established method within EMEP. Therefore, analyses using this method should be performed according to the method description of the chapter 3.8 (Determination of aldehydes and ketones in ambient air) of the EMEP manual for sampling and chemical analysis (Revision nov 2001).

7.2 PTR-MS (provided by R. Holzinger Uni Utrecht and T. Petäjä)

Many OVOCs can also be measured using proton transfer reaction mass spectrometry (PTR-MS). The advantage of PTR-MS is that it is an online method that does not require the preconcentration of samples. However, there are potential interferences from isomeric compounds. The following recommendations provide a rough guideline for using a PTR-MS for the measurements of OVOCs from ambient air. It is not as elaborated as the GC-MS based guideline above, as PTR-MS based measurements are not in the primary focus of this guideline.

Inlet (recommendation):
~4mm ID PFA tubing, max 15m, flow 2 L/min, protected by PFA filter holder with 47mm PTFE filter 5 μm pore size
PTR-MS samples from this inlet line with a short low volume (1/8"or 1/16”) line. Recommended materials: PFA, PEEK

Background determination:
The 2L main sample flow is passed through a Pt catalyst at a temperature of 350 C.

Critical instrument settings (recommendation):
Drift tube pressure: 2.2 mbar
Drift tube voltage: 600V
Drift tube temperature: 50C
Voltage between last drift ring and exit lense: 30V (instrument dependent, maybe define a procedure to optimize this)
Ratio O2+/H3O+ below 0.03
**PTR-TOF-MS:**
- SV valve setting (describe optimization procedure)
- Peak shape standards
- MCP voltage

**Q-PTR-MS**
- Tuning of mass scale and resolution
- SEM voltage

**Working standard (recommendation)**
Methanol, m33; Acetonitrile, m42; Acetaldehyde, m45; Acetone, m59; MBO, m87, m69, m41; MVK, m71; MEK, m73; Benzene, m79; Toluene, m93; Xylene, m107, TMB, m121; a-pinene, m137, m81, Trifluorobenzene, m133; Trichlorobenzene, m181, m183, m185

**Intercalibration standard (recommendation): same compounds**
Prepared and distributed by EMPA twice per year. (I think it is not necessary to ship pressurized cylinders ~1-2 liters of gas standard should be sufficient)

**In field operation:**
Perform regular background measurements, working standard measurements and full mass scan

**Calculation of VMR** according to the literature (rate constants, transmission)
8. References


9. Appendices

Appendix 1: Ozone removal techniques for GC analysis of OVOC

Appendix 2: Adsorbents for sorbent-based enrichment of VOCs and OVOCs (oxygenated volatile organic compounds) in ambient air samples

Appendix 3: Chromatographic separation
APPENDIX 1: OZONE REMOVAL TECHNIQUES FOR GC ANALYSIS OF OVOC (OXYGENATED VOLATILE ORGANIC COMPOUNDS) IN AMBIENT AIR SAMPLES

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

Ozone reactions during cryogenic enrichment of OVOC:

Ozone melting and boiling points (at atmospheric pressure) are at -192.1°C and 111.9°C. During cryogenic freezeout of OVOC 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 OVOC with ozone occur when heating the cryogenic trap to transfer the analytes to the GC system. Alkenes, such as isoprene and monoterpenes can be depleted in this reactions leading to artefacts like methacrolein and methylvinylketone. By collecting ambient air into stainless steel canisters prior to the analysis with cryogenic freezeout techniques this effect is reduced because of the short lifetime of ozone in these canisters (HELMIG, 1997; GREENBERG et al., 1992). But this method is not suitable for oxygenated VOC because of the high reactivity of these compounds on unheated stainless steel surfaces.

Ozone reactions during solid adsorbent sampling of OVOC:

Ozone artefacts are formed on and with some sorbents (e.g. graphitised carbon sorbents and Tenax® TA) leading to both OVOC 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, 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.

Catalytic destruction of ozone on metal surfaces:

Aluminium, 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 acquirement of some metals is used e.g. by nickel tubing, which reduces 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 OVOC on the surface of stainless steel even at high temperatures (150°C).

**Ozone removal by nitric oxide (NO) titration:**

Titration of the ambient air sample with a few ppm of NO prior to the concentration step is a very efficient method to remove ozone. Ozone deletion performance depends on sufficient reaction time and NO concentration in the mixing chamber. An example is the titration of the ambient air sample for 20 seconds in a 1 litre glass reaction vessel with a small flow of 200 ppm NO in nitrogen resulting in a NO concentration of 2 ppm. NO reacts with ozone to nitrogen dioxide (NO2) and oxygen (O2) (HELMIG, 1997). The reaction is: \( \text{O}_3 + \text{NO} \rightarrow \text{O}_2 + \text{NO}_2 \).

Disadvantage: slow reaction, potential alcohol losses (but constant)

**Ozone removal by potassium iodide (KI):**

In many cases KI is used for ozone removal. This technique is very effective at ambient humidity levels while capacity is reduced in dry air respected in following equation (HELMIG, 1997):

\[ \text{O}_3 + 2\text{KI} + \text{H}_2\text{O} \rightarrow \text{O}_2 + \text{I}_2 + 2\text{KOH}. \]

KI reacts with ozone to potassium oxide (K2O) and elemental iodine.

Example: PTFE-lined stainless steel or Silcosteel 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)

**Ozone removal by sodium sulphite (Na\(_2\)S\(_2\)O\(_3\)):**

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 ozone in a humid ambient air stream but inconsistent removal efficiencies from different suppliers and from different batches – testing of individual ozone traps is required (HELMIG, 1997)

Example: ¼” glass tube filled with 1 g of Na\(_2\)SO\(_3\) anhydrous crystals held in place by glass wool plugs and maintained at 100°C to prevent clumping of the Na\(_2\)S\(_2\)O\(_3\)

Disadvantage: removal of methylvinylketone and methacrolein.
**Sodium thiosulphate (Na2S2O3):**

The reaction between thiosulfate and ozone produces tetrathionate oxygen and water: \( 2S_2O_3^- + O_3 + 2H^+ \rightarrow S_4O_6^{2-} + O_2 + H_2O \)

Example: ozone filters were prepared by flowing a 10% solution of aqueous Na\(_2\)S\(_2\)O\(_3\) through commercial glass fiber filters followed by dry purge with nitrogen and had capacities in excess of 1 m\(^3\) air at ambient ozone levels (HELMIG, 1997)

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

Other ozone removal agents are copper oxide (CuO), magnesium sulphate (MgSO\(_4\)), manganese dioxide (MnO\(_2\)), potassium carbonate (K\(_2\)CO\(_3\)) and TPDDC (see table 1).

In-line ozone scrubbers like granular KCl and crystalline Na\(_2\)S\(_2\)O\(_3\) are prone to artefacts and require regular maintenance so that they are not suited to long-term instrument deployments (HOPKINS et al., 2011).

**Table 1: Ozone removal techniques for VOC monitoring and their characteristics.**

<table>
<thead>
<tr>
<th>Technique</th>
<th>Agent</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coated annular denuder</td>
<td>Potassium iodide (KI)</td>
<td>Very efficient</td>
</tr>
<tr>
<td>Cellulose filter</td>
<td>KI</td>
<td>Improved formaldehyde and acetaldehyde recovery</td>
</tr>
<tr>
<td>Packed Teflon tubing</td>
<td>Crystalline KI</td>
<td>Quantitative transmission of formaldehyde and acetaldehyde, partial loss of methacrolein and methylvinylketone</td>
</tr>
<tr>
<td>Impinger</td>
<td>KI</td>
<td>2% Aqueous, buffered KI solution</td>
</tr>
<tr>
<td>Impregnated glass wool</td>
<td>KI</td>
<td>Quantitative ozone removal, iodated artefacts</td>
</tr>
<tr>
<td>Coated tubing</td>
<td>KI in copper tubing</td>
<td></td>
</tr>
<tr>
<td>Commercial scrubber</td>
<td>KI in polyethylene cartridge</td>
<td>Low capacity at 5% RH</td>
</tr>
<tr>
<td>Impregnated glass fiber filter</td>
<td>Sodium thiosulphate (Na(_2)S(_2)O(_3))</td>
<td>High capacity, also reduces sampling artifacts from reactions with halogens</td>
</tr>
<tr>
<td>Coated copper screen</td>
<td>Manganese dioxide (MnO(_2))</td>
<td>High capacity, possible losses of terpenes (e.g. camphor, linalool), loss of formaldehyde</td>
</tr>
<tr>
<td>Packed copper tubes</td>
<td>Anhydrous 20-60 mesh potassium carbonate (K(_2)CO(_3)), crystalline</td>
<td>100% transmittance of light hydrocarbons</td>
</tr>
<tr>
<td>Packed Teflon tubing</td>
<td>K(_2)CO(_3)</td>
<td>ozone and water removal, 100% transmission of light hydrocarbons</td>
</tr>
<tr>
<td>Packed glass tube</td>
<td>Crystalline sodium sulphite</td>
<td>Loss of unsaturated compounds</td>
</tr>
<tr>
<td>Cartridge</td>
<td>(Na₂SO₃)</td>
<td>prevented, most efficient in the presence of atmospheric water vapour</td>
</tr>
<tr>
<td>------------------</td>
<td>----------</td>
<td>---------------------------------------------------------------------</td>
</tr>
<tr>
<td>Copper oxide (CuO), crystalline</td>
<td>No losses of carbonyl compounds</td>
<td></td>
</tr>
<tr>
<td>Trap</td>
<td>Crystalline magnesium sulphate (MgSO₄)</td>
<td>Removal of at least 100 ppb, loss of ozone removal efficiency with sampling length</td>
</tr>
<tr>
<td>Gas-phase ozone titration</td>
<td>Nitric oxide (NO)</td>
<td>Very efficient, quantitative recovery of formaldehyde, formation of artefacts on Tenax exposed to elevated NOx levels, possible chromatographic interferences of NO and NO₂ with NMHC (KUSTER et al., 1986), losses of alcohols, slow reaction</td>
</tr>
<tr>
<td>Metal tubing</td>
<td>Nickel (Ni)</td>
<td>Ozone reduced to less than 20% of ambient level</td>
</tr>
<tr>
<td>Spiked cartridge</td>
<td>TPDDC (Tetramethyl-1,4-phenylenediamine dihydrochloride)</td>
<td>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 ozone scavenger</td>
</tr>
<tr>
<td>Spiked cartridge</td>
<td>5% Na₂S₂O₃ aqueous solution on Tenax</td>
<td>Direct pretreatment of the adsorbent, improved monoterpene recovery</td>
</tr>
<tr>
<td>Spiked cartridge</td>
<td>Na₂S₂O₃</td>
<td>Interferences eliminated</td>
</tr>
</tbody>
</table>
APPENDIX 2 (ADSORBENTS FOR SORBENT-BASED ENRICHMENT OF OVOCs (OXYGENATED VOLATILE ORGANIC COMPOUNDS) IN AMBIENT AIR SAMPLES

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

For oxygenated VOC 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. Ambient air is drawn through an on-a (cooled) sorbent preconcentration trap. When selecting a suitable sorbent or sorbent combination for OVOCs several factors have to be considered including sorbent strength, artefacts, hydrophobicity, inertness, thermal stability and friability. It has to be verified that there is no breakthrough (most critical compounds methanol and acetaldehyde), getting stuck or back-diffusion of target compounds. Some special, low volatile analytes may also be lost through aerosol formation.

The sorbents 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. Sorbent strength is measured in terms of breakthrough volumes that are defined as the litres gas per gram adsorbent required to elute an OVOC off 1.0 gram adsorbent at an indicated temperature. This capacity of solid sorbents depends on the temperature and is typically specified at 20°C. It approximately doubles for every -10°C. Therefore, cooling the traps during sampling increases adsorbent performance. The lowest possible temperature is limited by the dewpoint of the sampled air (BROWN and SHIREY, 2001; HELMIG and GREENBERG, 1994; WOOLFENDEN, 2010b).

When using temperatures below the dew point some kind of water trap has to be installed in the sampling line when analyzing ambient air samples. Otherwise a reduction of sorbent performance might occur, which could 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 sorbents (porous polymers and graphitised carbon blacks) are hydrophobic and so they prevent trapping of excess water.

Some sorbents especially carbon blacks contain chemically active materials (trace metals) and are unsuitable for labile (reactive) species. Most porous polymers except from Tenax® TA have high inherent artefacts with blank peaks at 5-10 ng levels (WOOLFENDEN, 2010b). Ozone artefacts are formed on and with some sorbents (e.g. graphitised carbon sorbents and Tenax® TA) leading to both OVOC losses and buildings (LEE et al., 2006; McCLENNY et al., 2001). So the aspect of ozone removal has to be considered in sorbent-based ambient air sampling.

Porous polymers are weak or medium strength sorbents. None of them could retain the very volatile analytes. In multi-bed traps they are often the first sorbent 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, CarbosieveTM and CarbographTM are graphitised carbon blacks. The three different types differ in mesh sizes. They are suitable for most of the VOC depending on their different sorbent strength. The strongest CarbopackTM X should have a weaker adsorbent in front of it when sampling very high boiling point analytes. All graphitised carbon blacks are hydrophobic like porous polymers and so are adequate for humid ambient air samples (BROWN and SHIREY, 2001).
CarboxenTM and CarbosieveTM adsorbents are very strong and not appropriate for analytes with boiling points higher than benzene because they have very small pores. They should always be used with a weaker adsorbent (porous polymer or 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.

Multi-adsorbent traps with up to four different sorbents allow a wide range of volatile compounds to be enriched simultaneously. Sorbents are arranged in order of increasing sorbent 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 sorbents for multi-adsorbent traps or tubes. The temperature required for conditioning the most thermally-stable sorbent 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 sorbent or inserting a medium strength sorbent between (WOOLFENDEN, 2010b). Multi-adsorbent traps applied for oxygenated VOC are for example CarboblockTM B : CarboxenTM 1000, 90 mg in total (HOPKINS et al., 2003), 75 mg CarbopackTM B : 5 mg CarbopackTM X (ROUKOS et al., 2009) or 70 mg Tenax® TA : 110 mg CarbosieveTM SIII (Folgers, 2002).

There are different adsorbent bed sizes and densities depending on application and analytes. To allow high sampling flow rates coarse sorbent grain sizes (20/40 mesh) have to be used (HELMIG and GREENBERG, 1994).

Important characteristics of the most common sorbents and their adequacy for OVOC analysis are summarized in the following Table.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Class</th>
<th>Strength</th>
<th>Max. Temp. [°C]</th>
<th>Reference</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>CarbographTM 1TD</td>
<td>Graphitized carbon black</td>
<td>Weak/medium</td>
<td>&gt;450</td>
<td>(HOPKINS et al., 2003; ROUKOS et al., 2009)</td>
<td>Hydrophobic, minimal inherent artefacts, friable, formation of fines, 40/60 mesh recommended to minimise back pressure, aldehyde and ketone artefacts in combination with ozone (LEE et al., 2006)</td>
</tr>
<tr>
<td>CarbographTM B</td>
<td>Porous polymer</td>
<td>Medium</td>
<td>225</td>
<td>Inert, hydrophobic, high inherent artefact levels</td>
<td></td>
</tr>
<tr>
<td>CarbopackTM B</td>
<td>Porous polymer</td>
<td>Medium</td>
<td>250</td>
<td>Inert, hydrophobic, high inherent artefact levels</td>
<td></td>
</tr>
<tr>
<td>CarbotrapTM</td>
<td>Porous polymer</td>
<td>Medium</td>
<td>225</td>
<td>Inert, hydrophobic, high inherent artefact levels</td>
<td></td>
</tr>
<tr>
<td>Chromosorb® 102</td>
<td>Porous polymer</td>
<td>Medium</td>
<td>225</td>
<td>Inert, hydrophobic, high inherent artefact levels</td>
<td></td>
</tr>
<tr>
<td>PoraPakTM Q</td>
<td>Porous polymer</td>
<td>Medium</td>
<td>180</td>
<td>Inert, hydrophobic, high inherent artefact levels</td>
<td></td>
</tr>
<tr>
<td>HayeSepTM D</td>
<td>Porous polymer</td>
<td>Medium</td>
<td>290</td>
<td>Inert, hydrophobic, high inherent artefact levels</td>
<td></td>
</tr>
<tr>
<td>polymer</td>
<td>inherent artefact levels</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------------------------------</td>
<td>--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbograph™ STD</td>
<td>Hydrophobic, minimal inherent artefacts, friable, formation of fines, 40/60 mesh recommended to minimise back pressure, retention of very volatile compounds e.g. 1,3-butadiene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbopack™ X</td>
<td>Hydrophobic, minimal inherent artefacts, friable, formation of fines, 40/60 mesh recommended to minimise back pressure, retention of very volatile compounds e.g. 1,3-butadiene, no ozone artefacts (LEE et al., 2006)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carboxen™ 569</td>
<td>Inert, less hydrophilic than most carbonised molecular sieves, minimal inherent artefacts</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unicarb™</td>
<td>Inert, hydrophilic, performance weakened in humid conditions, individual inherent artefacts, must be conditioned slowly, requires extensive purge to remove permanent gases</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carboxen™ 1003</td>
<td>Inert, hydrophilic, performance weakened in humid conditions, individual inherent artefacts, must be conditioned slowly, requires extensive purge to remove permanent gases</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbosieve™ SIII</td>
<td>Inert, minimal inherent artefacts, significantly water and CO₂ 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 sorbent</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Trademarks: Tenax® TA - Buchem bv, Netherlands; Chromosorb™ - Celite Corporation, USA; PoraPak™ – Waters Corporation, USA; Carbograph™ – LARA s.r.l., Italy; UniCarb™ – Markes International Ltd., UK, USA; HayeSep™ – Hayes Separations Inc., USA; Carbotrap™, Carbopack™, Carboxen™ and Carbosieve™ – Sigma-Aldrich, USA
## APPENDIX 3: CHROMATOGRAPHIC SEPARATION

1. PLOT columns

### Table 1: PLOT columns

<table>
<thead>
<tr>
<th>PLOT column equivalents</th>
<th>GS-OxyPLOT (Agilent), CP-LowOx (Varian)</th>
<th>CP-PoraBOND U (Agilent resp. Varian)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polarity</td>
<td>High polar</td>
<td>Midpolar</td>
</tr>
<tr>
<td>Composition</td>
<td>Proprietary, salt deactivated</td>
<td>Styrene-glycol methacrylate copolymer</td>
</tr>
<tr>
<td>Operable temperature range</td>
<td>0°C to 350°C</td>
<td>-100°C to 300°C</td>
</tr>
<tr>
<td>Analysis of alcohols</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Analysis of aldehydes</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Analysis of ketones</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Analysis of ethers</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Analysis of esters</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Analysis of aromatics</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Analysis of alkanes</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Analysis of terpenes</td>
<td>+/-</td>
<td>+</td>
</tr>
<tr>
<td>Analysis of nitriles</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Expected co-elution problems</td>
<td>Ethyl acetate+MVK+MEK (2-butanone), water peak+propanal and acrolein</td>
<td>Methanol+n-butane, butanal+benzene+ ethylacetate+MVK, 2-butanol+MEK, butylacetate+ ethylbenzene+m+p-xylene+n-hexanal, pentanal+toluene</td>
</tr>
<tr>
<td>Advantage</td>
<td>Strong selectivity to OVOC, high retention of OVOC even at above ambient oven temperatures, no retention of saturated</td>
<td>Water resistance, retention times not influenced by water, long lifetime</td>
</tr>
<tr>
<td>Disadvantage</td>
<td>Need for humidity management, retention of water, tailing of unsaturated OVOC due to reactions with the polar column, unsaturated NMHC and aromatics both with carbon atom numbers higher than eleven stick in the column</td>
<td>Co-elutions of OVOC with aliphatic NMHC, retention of water</td>
</tr>
</tbody>
</table>

Examples of ambient air chromatograms for OVOCs using PLOT columns

Fig.1: CP-LowOx (Varian), 30 m x 0.53 mm x 10.0 µm (ROUKOS et al., 2009).
Fig. 2: 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).

Fig. 3: 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).
### Dimethylpolysiloxane columns

#### Table 2: Dimethylpolysiloxane columns

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

Fig. 4: DB-1 (Agilent J&W), 100 m x 0.25 mm x 0.5 µm (RIEMER et al., 1998).

Fig. 5: Rtx-1:
Fig. 6: BPX-5 (SGE), 50 m x 0.22 mm x 1.0 µm (own 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 CCl₃F, 22.55 min n-pentane, 22.67 min acrolein, 22.82 min acetone.

Fig. 7: DB-624 (Agilent J&W), 10 m x 0.18 mm x 1.4 µm (APEL et al., 2003).
### Polyethylene glycol columns

#### Table 3: Polyethylene glycol columns

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

Fig. 8: CP-WAX 52 CB (Varian), 60 m x 0.25 mm x 0.5 µm (FOLKERS, 2002).

Fig. 9: Rtx-WAX (Restek), 60 m x 0.53 mm x 0.5 µm (GOLDSTEIN and SCHADE, 2000).
Fig. 10: DB-WAX (Agilent J&W), 60 m x 0.32 mm x 0.5 μm (LAMANNA and GOLDSTEIN, 1999).