A gas chromatographic system for high-precision quasi-continuous atmospheric measurements of CO_2, CH_4, N_2O, SF_6, CO and H_2

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Abstract: The set up of an automated gas chromatographic system (Combi-GC), combining one HP 5890II and one Trace Analytics RGA-3 (resp. a Peak Performer 1) instrument is presented. The system is designed to perform quasi-continuous simultaneous measurements of CO_2, CH_4, N_2O, CO, H_2 and SF_6 with one single sample injection at a temporal resolution of 5 minutes. Except for SF_6, the GC is able to measure atmospheric mixing ratios in ambient air as well as from flask samples and high pressure cylinders close to the precision recommended by WMO for monitoring of background air in the Northern Hemisphere. The reproducibility (1 σ) of duplicate measurements on different days is for CO_2: ±0.06ppm; CH_4: ±1.7ppb; N_2O: ±0.11ppb; CO: ±1.7ppb; H_2 ±2.1ppb; SF_6 ±0.06ppt. The Combi-GC as described here has been continuously running in Heidelberg for more than three years with only short interruptions covering less than 5% of the time. The long-term stability of all components, as monitored with a daily measured target gas of elevated mixing ratios, has been better than the precision values cited above, and did not show any trends. With the Peak Performer 1 instrument, now installed at the GAW station Schauinsland, the precision of the CO and H_2 measurements was improved by a factor of 5 and 2.5 respectively compared to the RGA3 system.

1.   Introduction

In the last decade, considerable world-wide effort has been put into setting up new monitoring stations for atmospheric greenhouse gases and other traces species, particularly in continental areas [Dolman et al., 2008]. The aim of these observational networks is to quantify regional budgets of these trace gases in combination with regional or global atmospheric transport modelling. But long-term measurements over continents can also provide observational constraints on anthropogenic greenhouse gases emissions reductions as anticipated in the framework of the Kyoto Protocol [e.g. Schmidt et al., 2001; Levin and Rödenbeck, 2008]. However, unlike many classical short-lived atmospheric pollutants, most greenhouse gases have long residence times in the atmosphere and thus relatively high background mixing ratios. Therefore, and due to the vigorous mixing of the atmosphere, temporal and spatial gradients caused by regional sources and sinks are often only small. This is true on the global scale, but also over continents despite often large anthropogenic emissions of these gases. In order to quantify these gradients, and be able to detect respective changes, high precision and well comparable measurements are required for these species. This is even more crucial if measurements from various laboratories shall be combined into one network as is the case for example in Europe [Nisbet et al. 2008]. For reliable long-term high-precision observations, therefore dedicated instrumentation is required, which for most greenhouse gases is not commercially available for immediate application.

Here we describe the gas chromatographic system used in Heidelberg for continuous trace gases observations in ambient air as well as for analysis of flask samples from a small global network. The original Heidelberg GC system was set up in 1994 for measurement of CO_2, CH_4, N_2O and SF_6 [Levin et al., 1999, Schmidt et al., 2001]. It has now been completely re-furnished and extended to also measure CO and H_2 on the same air sample. The Reduction Gas Analyser (RGA) system which was used in earlier work as a separate device only for CO analysis [Gamnitzer et al., 2006], has now been combined with the greenhouse gases GC and also optimised for analysis of molecular Hydrogen (H_2). The Heidelberg Combi-GC system has been cloned with modern instrumentation (HP6890 and Peak Performer 1), and was recently installed at the GAW station Schauinsland run by the German Umweltbundesamt. In particular the precision for CO and H_2 measurements was largely improved with this system. A detailed description of the instrumental design, the parameters used, the long-term performance and calibration of the Heidelberg system, including the non-linearity of the detectors is given. The improvements obtained with the new instrumentation run at the Schauinsland site are also reported.

2. Instrumental setup

The combined Heidelberg gas chromatographic system (Combi-GC) is designed for the simultaneous analysis of CO_2, CH_4, N_2O, SF_6, CO and H_2. For each trace gas the Combi-GC is optimised to measure ambient concentration levels. Due to short term concentration variations of these trace gases in ambient air, particularly in polluted or semi-polluted areas simultaneous instead of sequential analysis is mandatory to be able to compare the measured mixing ratios of different gases with each other. At the same time a reduction of sample amount needed for a single analysis e.g. of a flask sample collected at a remote site is achieved. The Combi-GC consists of two commercial gas chromatographs, a HP5890II (Hewlett-Packard) and a Reduction Gas Analyser, RGA-3 (Trace Analytics Inc.). These GCs are equipped with three detectors: (1) a Flame Ionisation Detector (FID) to analyse CO_2 and CH_4, (2) an Electron Capture Detector (ECD) for N_2O and SF_6, and (3) a Reduction Gas (HgO) Detector for the measurement of CO and H_2.

2.1 Sample inlet system

We distinguish between three different atmospheric sample types: Flask samples, high pressure cylinders (i.e. calibration gases) and ambient air. These samples are connected via different lines to the GC inlet system (Figure 1). Ambient air (in Heidelberg) is sampled routinely from either one (SW) or two (SW and SE) intake lines. These two intake lines are located on the south-western (SW) and the south-eastern (SE) corners of the institute's rooftop, approx. 30 m above local ground level. Having two redundant ambient air intake lines generally allows for detecting technical problems of the air intake system, but in Heidelberg with this set-up we are also able to detect very local contamination e.g. from the building itself. For applications at a tower site, one would add here more intake lines to allow for the (consecutive) measurement of vertical profiles. Ambient air is pumped with a high flow rate (of approx. 50 litres per min) through half inch stainless steel tubes to the laboratory. From these permanently flushed intake lines by-pass air is collected with separate pumps (Neuberger Type 13593-86, EPDM membrane), at a smaller flow rate of 330 ml/min through a cooling trap at approx. -40°C, before entering the sample inlet system at the GC at ports 5 and 7 of the sample selection valve V2 (Figure 1). These lines are also permanently flushed and the excess air is released through an overpressure release valve. Permanent flushing of all intake lines and the cooling trap ensures a small residence time of the sample air in all lines (< 10 seconds) and "fresh" dried, ambient air at the GC sample inlet at any time.

The other ports of V2 are connected to the working standard gas (p1), a target gas (p3) and three optional gas cylinders (p9, p11, p13), while p15 is connected to a second sample selection valve V1. At V1 twelve inlet ports are set up to connect either flask samples or cylinders to the inlet system (4 ports remain un-used). To avoid contamination and reduce the flushing volume of the sample when measuring flasks, all sample inlet lines at V1 can be separately evacuated via a three-way magnetic valve V3 mounted between the outlet of V1 and the inlet of V2. Each flask tubing contains a cooling trap to allow drying of the flask air to a dew point of approximately -70°C with an isopropanol dry-ice mixture.

2.2   Trace gas separation and detection

Following the sample selection part, the GC setup consists of three independent branches, one for each detector. The corresponding sample loops of all three detector branches are connected in series and the selected sample is purged through the respective sample loops in the load position of the injection valves V5-V7. Sample flow is controlled by an electronic pressure controller (EPC) mounted in front of the first injection valve V5. The sample loops are purged for 108 s with a total gas volume of approx. 150 ml, requiring a permanent overpressure of at least 350 mbar during flushing. After the sample purge is finished the EPC is closed and the gas in the sample loops equilibrates to ambient temperature and pressure for 120s. The complete sample inlet system is located in a closed wooden compartment to prevent short-term temperature variations.

2.2.1   FID branch

For the FID branch, nitrogen (5.0) is used as carrier gas with a flow rate of 24.4 ml min^{-1}. CO_2 and CH_4 are separated on a Hayesep Q (1.8 m; T = 40°C) column. The CH_4 peak elutes first from the Hayesep Q column and is directly passed to the FID. The detection principle of the FID relies on the thermal ionisation of the investigated substance in the plasma of a hydrogen flame. Surrounding the flame there is a cylindrical electrode, and high voltage is applied between the FID jet and the electrode to collect the ions. For a detailed description of the FID refer to Scott [2003]. The FID can only detect reduced carbon compounds, therefore the CO_2 peak is re-directed (via V9) to a Ni catalyst, operating at 350°C in an H_2 environment. On the Ni catalyst CO_2 is reduced and subsequently detected as CH_4 by the FID. The quantitative reduction of CO_2 is checked once per month. The catalyst is replaced if the conversion rate drops below 95%.
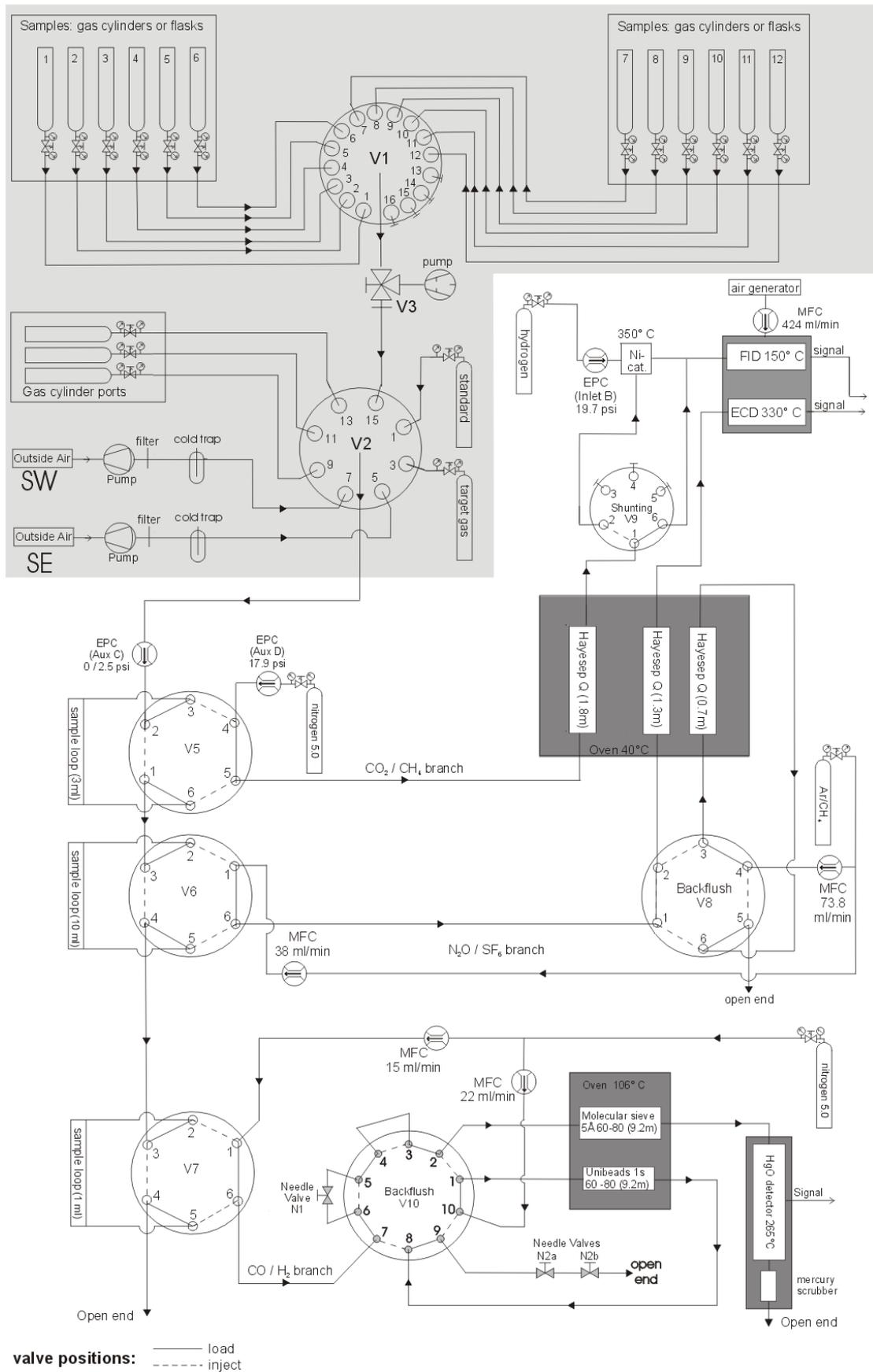
Figure1: Setup of the Combi-GC system. The grey shaded area represents the sample inlet section of the GC system. For a detailed list of parts and parameters see Table 1.

Sample selection:	
selection valve (V1)	16 port / 16 position; *VICI AG*
selection valve (V2)	8 port / 16 position ; *VICI AG*
magnetic valve (V3)	2 way; *Fluid Automation Systems*
vaccum pump	Vacuubrand RD4, *Brand*
sample pressure	2.5 psi (83 ml/min); electronic pressure controller(EPC); *Hewlett-Packard*
FID branch:	
carrier gas	nitrogen (purity 5.0)
N_2 carrier flow	24.4 ml/min; electronic pressure controller(EPC); *Hewlett-Packard*
sample loop volume	3 ml
sample loop valve (V5)	six port / two position; *VICI AG*
analytical column	Hayesep Q (1.8 m)
column temperature	40° C
shunting valve	six port / two position; *VICI AG*
catalyst	Nickel
catalyst temperature	350° C
detector type	flame ionisation detector (FID)
detector temperature	150° C
combustion gases	Hydrogen (5.0) and synthetic air
H_2 pressure	19.7 psi; electronic pressure controller(EPC); *Hewlett-Packard*
air flow	424 ml/min; mass flow controller; *MKS Instruments, Inc.*
ECD branch:	
carrier gas	$ArCH_4$ (purity 3.5/4.8)
$ArCH_4$ carrier flow	38 ml/min; mass flow controller; *MKS Instruments, Inc.*
sample loop volume	10 ml
sample loop valve (V6)	six port / two position; *VICI AG*
pre-column	Hayesep Q (0.7 m)
analytical column	Hayesep Q (1.3 m)
column temperature	40° C
backflush valve (V8)	six port / two position; *VICI AG*
backflush gas	$ArCH_4$ (purity 3.5/4.8)
$ArCH_4$ backflush flow	73.8 ml/min; mass flow controller; *MKS Instruments, Inc.*
detector type	electron caption detector (ECD)
detector temperature	330° C
RGA branch:	
carrier gas	synthetic air (purity 5.0)
Synth. air carrier flow	14.4 ml/min; mass flow controller; *Bronkhorst High-Tech BV*
sample loop volume	1 ml
sample loop valve (V7)	six port / two position; *VICI AG*
pre-column	Unibeads 1s, 60-80 (30 1/4")
analytical column	molecular sieve 5Å, (30 1/4")
column temperature	106° C
backflush valve (V10)	ten port / two position; *VICI AG*
backflush gas	synthetic air (purity 5.0)
Synth. air backflush flow	22 ml/min; mass flow controller; Brooks
detector type	reduction gas detector
detector temperature	265° C

Table 1: Parameters and parts of the Heidelberg Combi-GC system

A FID chromatogram of the working standard is displayed in Figure 2a. The first peak corresponds to oxygen and is neglected, the second peak is CH_4. Due to the switching of valve V9, the baseline is perturbed at 0.05 and 1.32 min. The large CO_2 peak is recorded after 1.9 min and is approximately 200 times larger than the CH_4 peak.
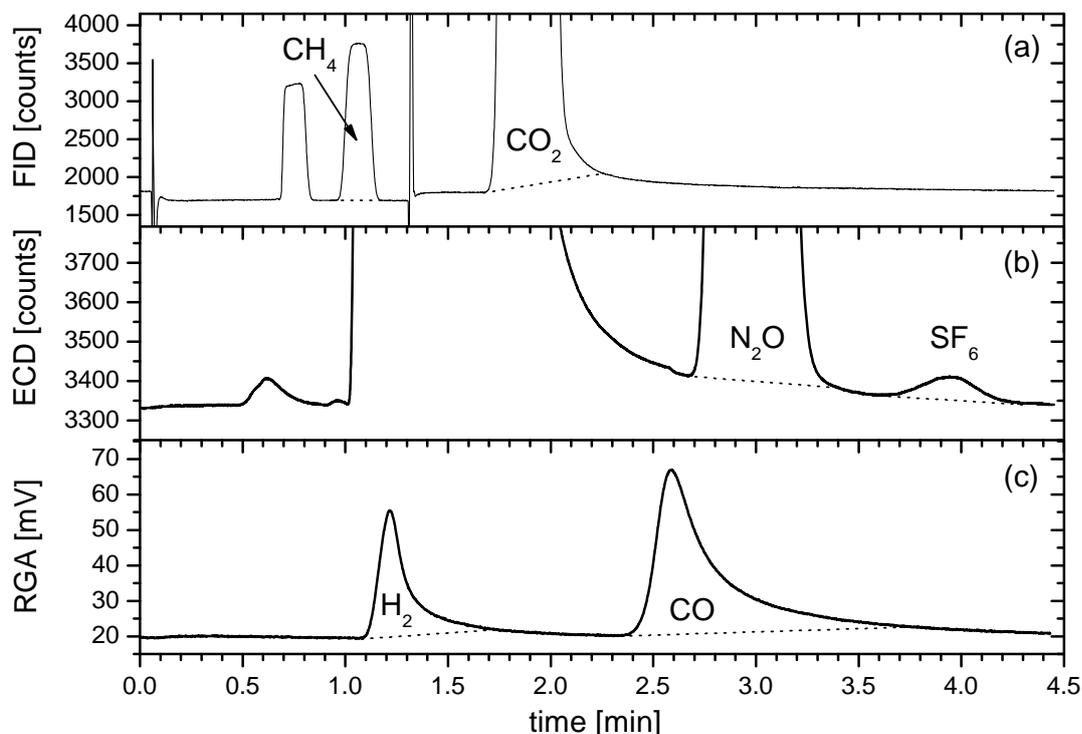

Figure 2: Typical chromatograms of our working standard (a) FID signal of 1838.8 ppb CH_4 and 379.13 ppm CO_2. The first peak corresponds to oxygen. The spikes at 0.05 min and 1.35 min are caused by switching the catalyst valve V9. (b) ECD signal with 316.35 ppb N_2O and 5.72 ppt SF_6. The large peak before the N_2O peak is again caused by oxygen. (c) HgO-D signal with 595.3 ppb H_2 and 275.8 ppb CO.

2.2.2 ECD branch

The ECD branch uses Ar/CH_4 (5% CH_4 (3.5) in Ar (4.8)) as carrier gas with a flow rate of 38 ml min^{-1}. The sample first passes the pre-column (Hayesep Q (0.7 m; T = 40°C)). After 2.55 min when N_2O and SF_6 have eluted, the pre-column is back-flushed (V8) for 2.45 min, with a flow rate of 73.8 ml min^{-1} to avoid contamination of the analytical column and the ECD with compounds that have a longer retention time than SF_6, and reduce analysis time. N_2O and SF_6 are then directed through the analytical column (Hayesep Q (1.3 m; T = 40°C)) to improve peak separation and subsequent detection at the ECD operating at 330°C. The ECD detector uses electrons released by a beta source (^{63}Ni, 610 MBq) which are attracted to a positively charged anode. As the sample is transferred into the detector, the electronegative sample molecules capture the electrons and reduce the current between the collector anode and a

cathode [Scott, 2003]. The electron capture probability varies with the amount of sample molecules in the detector, the response function of the ECD is, thus, non-linear. In addition to this non-linearity of the ECD for N_2O the cross-sensitivity to CO_2 has to be taken into account (Section 2.4.2). Compared to N_2O and SF_6, molecular oxygen has a short retention time on the columns used here and due to its abundance in the sample causes a huge peak in the ECD chromatogram (compare Figure 2b). The peaks of N_2O and SF_6 are located on the tailing of the oxygen peak.

2.2.3 HgO-D branch

For the HgO-D branch we use synthetic air (5.0, hydrocarbon free) as carrier gas with a flow rate of 14.4 ml min^{-1}. The original set up of the RGA-3 instrument with one 10 port valve for the sample loop and the back-flush was modified by adding a separate sample injection valve (V7). This was necessary to be able to place all sample loops close to each other in the wooden compartment, thereby minimising the volume that needs to be flushed in the sample inlet part. It additionally allowed decoupling the back-flush time from the sample injection time. The sample is flushed to the pre-column (Unibeads 1s, 60-80 Mesh (30 1/4"); T = 106°C) and after 1.55 min, when the H_2 and CO peaks have eluted, the pre-column is back-flushed (V10) with a flow rate of 22 ml min^{-1}. CO and H_2 are then directed to the analytical column (molecular sieve 5Å, (30 1/4"); T = 106°C) and are subsequently detected with the HgO detector. According to reaction (1), H_2 and CO (here replaced by X) get fully oxidised when they come into contact with a heated (265°C) mercury oxide bed in the detector

$$X + HgO_{solid} \rightarrow XO + Hg_{gas} \qquad\qquad (1)$$

The mercury vapour which is generated by this reaction is flushed into an absorption cell illuminated by a mercury lamp. According to the Beer-Lambert-law the excitation of the mercury atoms in the vapour reduces the intensity of the light passing through the cell. This reduced intensity is a measure of the initial content of reduced species (H_2 resp. CO) passing the mercury bed. Due to the exponential shape of the Beer-Lambert-law the response function of this detector is non-linear.

The additional needle valves N1, N2a and N2b (Figure 1) are adjusted to reduce internal pressure variations caused by switching of valve V10. This is necessary to maintain a stable baseline because the HgO detector is very sensitive to pressure, respectively flow changes.

These alter the residence time of Hg vapour in the absorption cell leading to changes in the detector signal. Figure 2c shows a typical chromatogram of the HgO detector.

2.2.4   HgO-D branch in the modified Combi-GC systems of Schauinsland

At the GAW station Schauinsland we use a Peak Performer 1 instrument for the HgO-D branch to measure H_2 and CO. Unlike the Heidelberg system the combined GC system at the Schauinsland uses only one 10 Port valve as a combined sample loop/back flush valve instead of valve V7 and V10 in Heidelberg. Compared to the old RGA3 the new Peak Performer 1 has several different features: (1) Unlike the RGA-3 the Peak Performer 1 does not have a separate reference cell, so that only the beginning of each method is corrected for changes in intensity of the UV-Lamp. (2) The photo diode showed a sensitivity to changes in ambient light conditions which we mitigated by additional light protection. (3) Gas flow rate through the detector is controlled by a mechanical pressure controller, and depends on primary pressure as well as on the resistance of tubing, columns, needle valves etc. (4) We observed that gas flow through the detector is very sensitive to even small changes in ambient air temperature. As the detector signal depends on the number of Hg-Atoms per time in the detector cell, this effect leads to drifts of the baseline. We addressed this problem by two means: We added more thermal isolation and light shield and replaced the 1ml sample loop with a 2ml one to get a better signal to noise ratio.

We investigated the effects of detector temperature, column temperature and carrier gas flow rates on sensitivity (peak height for given mixing ratio), reproducibility (standard deviation of repeated measurements of the same sample), amplitude and stability of non-linearity. We found a detector temperature of 265°C, column temperature of 95°C and carrier gas flow rate of 18 ml min^{-1} as optimum setting for the range of ambient air concentrations we expect at the GAW station. With this setting we reach a precision of ±0.8 ppb for H_2 and ±0.3 ppb for CO. As the optimum settings amongst others depend on the properties and condition of the HgO-bed they vary for each Peak Performer and probably also with time.

2.3   Instrument control and data processing

2.3.1   Automated measurement procedures

The main sample selection valve V2 is controlled directly by the host computer via the COM-port. The valves V1 and V5-V10 are all controlled by an analogue-digital (AD) converter/control unit (Agilent Technologies Inc. 35900E). This AD converter is connected to a host computer by a 10 Mbit/sec Ethernet interface using TCP/IP. Communication with the valves is established by open collector outputs and an eight channel relay box. The AD converter serves to convert the analogue output of the HgO detector to a digital signal at a rate of 20Hz. The communication between the host computer and the HP5890II GC, including the FID and ECD, is handled by a GPIB PCI board (Agilent Technologies Inc., Part No. G1680-63715). The control of the entire system and the processing of the detector output signals are performed by the Agilent ChemStation software (Vers. B.01.03). The ChemStation software offers the possibility of switching the valves according to a prescribed time table. An example of such a time table for one injection is given in Table 2, it is called *method*.

For the Combi-GC system a nested injection procedure is used, meaning the next sample is already flushed through the inlet system and the equilibrium with ambient pressure and temperature is established while the first sample is being analysed. This parallel processing of flushing and analysing allows for sample injections every five minutes, although the complete analysis time for one sample is ten minutes. Figure 3 shows a sketch of the injection procedure. After the end of every method, all recorded chromatograms are analysed by an automated post-processing integration method. This ensures the same integration parameters for all samples. The integration results are stored together with the raw data in individual sub-folders. The disadvantage of nested injections is that the number of methods needed for n ports increases from n to n(n−1).
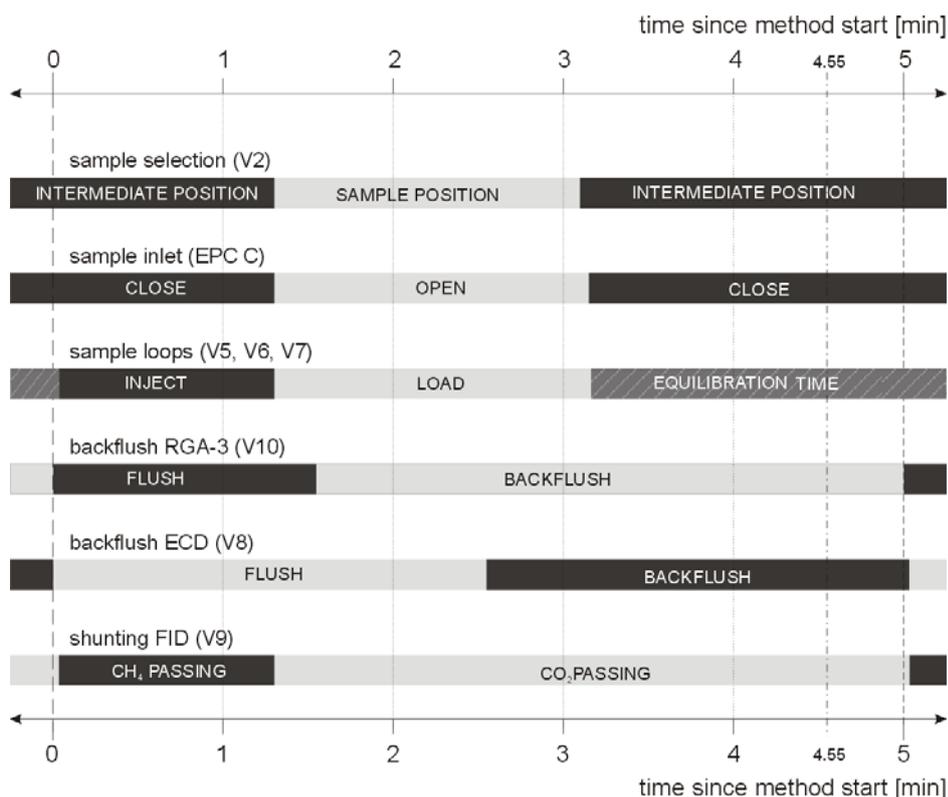
Figure 3: Valve switching sketch for the nested injections used at the Combi-GC system. The sample is injected on the chromatographic columns from 0.06 min to 1.30 min. While the chromatograms of this sample are recorded, the next sample is already flushed through the sample-loops and from 3.2 min onwards, equilibration to ambient pressure and temperature takes place. At 4.55 min, the post-processing analysis methods start to analyse the recorded chromatograms.

Time	Specifier	Parameter	Comments
0.01	V8	in line	ECD backflush valve in inject position
0.01	V10	in line	HgO backflush valve in inject position
0.06	V1	select	Additional port valve goes to required position
0.06	V9	Direct	Shunting valve goes in direct position
0.06	V5,V6,V7	Inject	Sampling valves into Inject position
1.28	V2	Connected	Sample selection valve goes connected position
1.30	V9	Catalyst	Shunting valve into catalyst position for CO_2 peak
1.30	V5,V6,V7	Load	Sampling valves into load position
1.30	Aux C	2.5 psi	Sample inlet pressure controller goes to 2.5 psi
1.55	V10	Backflush	HgO backflush valve into backflush position
2.55	V8	Backflush	ECD backflush valve in backflush position
3.08	V2	intermediate	Sample selection valve goes to intermediate position
3.08	Aux C	0 psi	Sample inlet pressure controller closes and sample loop equilibrium takes place

Table 2: Timed events and valve switching table during one method

Caution is required when chaining single methods to so-called *sequences*. Thus, a GC configuration software was written which allows the user to simply select the required sequence. Several different sequences for all 19 ports and different purposes are available. These sequences can easily be combined by the user to perform individual measurement programs. Thus, a completely autonomous run of the GC system up to four days is possible. The internal structure of all sequences has the common order

working standard → sample → air → working standard → sample → air

The *working standard* is injected every 15 min; *sample* can either be a flask sample, a high pressure cylinder or ambient air. In total, we are thus able to analyse eight unknown samples per hour. In the Heidelberg set-up, at least one ambient Heidelberg *air* injection from the SW line is measured every 15 minutes.

2.3.2 On-line determination of measured mixing ratios

The online determination of the measured mixing ratios is performed using the self-developed software Combi-GC-Organizer. This software is based on the software GC-Organizer developed by Glatzel-Mattheier [1997]. The mixing ratios C_{sample} of the unknown samples are calculated according to

$$C_{sample} = C_{std} \cdot \frac{A_{sample}}{A_{std}^{int}} \qquad (2)$$

Where C_{std} is the mixing ratio of the standard, A_{std}^{int} is the linearly interpolated area of the working standards peaks measured before and after the sample, and A_{sample} is the area of the sample peak. The peak area is dependent on the number of molecules of the investigated species. The number of trace gas molecules in the fixed sample loop volume changes not only with mixing ratio of the gas in the sample loops but, since the gas in the sample loops equilibrates with ambient conditions, also with ambient pressure and temperature. In our air-conditioned laboratory, the temperature variations between two standard injections (15 min) are smaller than 0.05 K while pressure variations, even during frontal passages with fast pressure changes, are smaller than 0.5 hPa, so that all relevant environmental changes are well captured and corrected for by normalisation of the sample peak areas to those of the two bracketing standard measurements according to equation (2). No additional elaborate pressure and temperature control of the sample loops is, therefore, required.

2.4   Calibration and non-linearity

2.4.1   Calibration procedures

All measured mixing ratios are determined relative to one working standard. The working standard consists of ambient Heidelberg air dried to a dew point of less than -55°C (15 ppm) and compressed into a 40 litre high pressure cylinder at 200 bar. We use a diving compressor (Bauer Group, Purus 10) and replace the molecular-sieve-charcoal cartouche mounted in the high-pressure stage of the compressor by silica gel. Using real ambient air working standards minimises possible matrix effect differences between sample and standard gas, as well as possible interference of other trace components present in the samples. Mixing ratios of all six trace gases in the working standard are close to those measured in the samples minimising the non-linearity corrections necessary for the ECD and the HgO-D. One working standard tank normally lasts for more than one year of continuous measurements. Working standards are filled well in advance of their usage to allow frequent checks of their stability over at least six months. New and running working standards are calibrated against a set of primary laboratory standards. Table 3 lists the calibration scales, the calibrated concentration ranges as well as the number of primary laboratory standards used to transfer the internationally agreed scales to our measurements. For CO_2, CH_4 and N_2O the calibration tanks are identical. All primary laboratory standards are measured approximately every three months against the current working standard to check the stability of the system over the whole calibration scale. In addition, every working standard is monitored approximately once per month with one of the primary laboratory standards to detect potential drifts.

Component	Scale	Range	No. of tanks
CO_2	WMO-2007[a]	348 to 422 ppm	8
CH_4	WMO X-CH₄[b]	1764 to 1935 ppb	6
N_2O	WMO 2006[c]	307 to 327 ppb	5
SF_6	Heidelberg[d]	2.2 to 15.8 ppt	6
CO	MPI-Mainz/UBA[e]	55 to 900 ppb	6
H_2	EuroHydros 2007[f]	220 to 822 ppb	6

Table 3: Calibration scales (a: Tans et al., 2007; b: Dlugokencky et al., 2005; c: Hall et al., 2007; d: Maiss et al., 1996; e: Brenninckmeijer et al., 2001; f: Jordan, A., 2006) and ranges together with the number of available primary laboratory standards for the different components measured at the Heidelberg Combi-GC system. For H_2 and CO the calibration cylinders are identical to the span gas cylinders (see Sec. 2.4.4).

The detection principles of both, the ECD as well as the HgO detector comprise a nonlinear response function. After determination of the mixing ratios according to Eq. (2) which

assumes a linear response function, a non-linearity correction needs to be applied for N_2O, SF_6 CO and H_2. For the calibrated range, this correction function could, in principle, be obtained from the primary laboratory standards (Table 3). We additionally determined the non-linearity for H_2, CO, and N_2O by diluting a high concentration cylinder with "zero" air. For this purpose a cylinder was filled in Heidelberg during a pollution event in April 2006 in Heidelberg. This high concentration cylinder is step-wise diluted with the "zero" air cylinder using two mass flow controllers. Since the FID has proven to be linear over the whole range [Glatzel-Mattheier, 1997], which was confirmed for the calibrated ranges of CH_4 and CO_2 by our primary laboratory standards (Table 3), the measured CH_4 mixing ratio of the diluted sample can be used to calculate the mixing proportions of the two cylinders.

2.4.2   Non-linearity of the ECD for N_2O

Schmidt et al. [2001] have reported a cubic non-linearity correction for the Heidelberg ECD detector over the whole range from ambient N_2O mixing ratios down to zero ppb (upper stratospheric mixing ratio). The results of the new full range calibration are compared here to the findings from 1996. The differences (N_2O_{calc} - N_2O_{meas}) between the calculated and measured N_2O mixing ratios for each dilution step are plotted in Figure 4 as a function of the measured mixing ratios. In order to obtain a non-linearity correction a polynomial function was fitted through all data points. The original non-linearity function reported by Schmidt et al. [2001] is also plotted in Figure 4. The non-linearity of the ECD obviously did not change by more than 1.5 ppb over the last ten years, and the whole range of mixing ratios. In the narrow concentration range of 307 to 327 ppb (i.e. tropospheric N_2O mixing ratios of the last 10 years) the dilution samples suggest a linear correction function which is confirmed by the primary laboratory standards. The full range calibration has shown that this linear correction function can also be applied to the wider concentration range between 300 and 400 ppb. Only for concentrations below 300 ppb the cubic function according to Eq. (3) is used

$$\Delta N_2 O^{non-lin}(calc-meas) = A + B \cdot N_2 O_{meas} + C \cdot (N_2 O_{meas})^2 + D \cdot (N_2 O_{meas})^3 \qquad (3)$$

Because of the good stability of the ECD non-linearity for N_2O in the tropospheric concentration range, we apply a temporally constant non-linearity correction to all N_2O measurements.

In addition to the non-linearity of the ECD detector the N_2O mixing ratio is altered by the cross-sensitivity to CO_2. For ambient mixing ratios this correction is small compared to the

non-linearity correction. For 100 ppm CO_2 difference between the sample and the working standard the N_2O cross-sensitivity correction is ≈ 0.6 ppb. For the Heidelberg GC we found that above 100 ppm CO_2 the cross-sensitivity can be described as a linear relation according to Eq (4) depending on the CO_2 difference between sample and working standard and the N_2O mixing ratio of the sample [Glatzel-Mattheier, 1997]. To avoid the influence of the CO_2 cross-sensitivity for the dilution experiments, the CO_2 mixing ratio of the "zero" air tank was adjusted to the approximate CO_2 mixing ratio of the high concentration cylinder.

$$\Delta N_2O^{cross} = \left(CO_2^{std} - CO_2^{sample}\right) \cdot \frac{0.12 + 0.0016 \cdot N_2O^{sample}}{100} \tag{4}$$
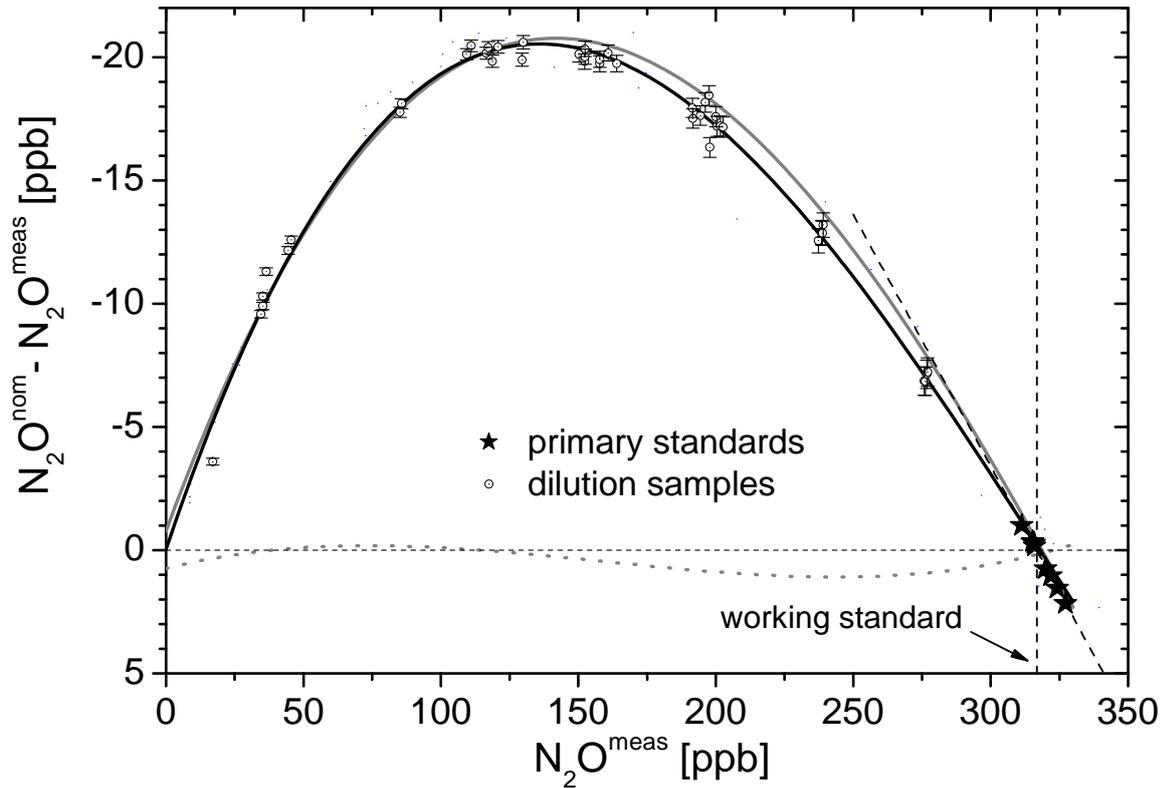

Figure 4: Non-linearity of the ECD for N_2O in the range from 330 ppb to 0 ppb. The deviation from a linear detector response in 2006 (open symbols, black fit curve) is compared to the deviations determined in 1996 (grey fit curve). Both non-linearity functions have been derived with a cubic polynomial according to Eq. (3). The residual deviation between the two fits (grey dotted line) is smaller than ±1.5 ppb over the whole range. For the ambient concentration range the results of our primary laboratory standards are given (black stars). A linear regression for these cylinders is displayed as dashed black line.

2.4.3 Non-linearity of the ECD for SF_6

The non-linearity of the ECD for SF_6 measurements within our measurement precision, is only significant at mixing ratios higher than the standard mixing ratio of 5.7 ppt. Considering, however, the occurrence of mixing ratios in Heidelberg which can exceed 60 ppt when the air is influenced by local point sources (compare Figure 8), points to the necessity to extend the calibration range for SF_6, if such events shall be quantitatively evaluated.
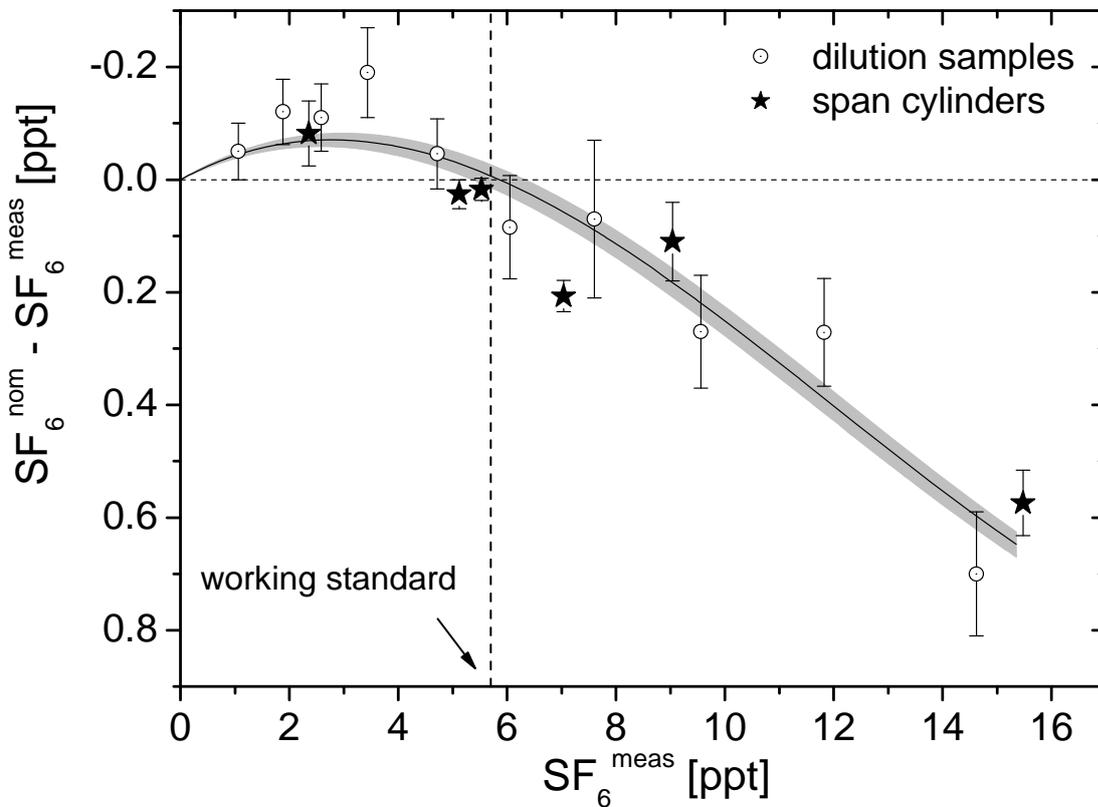

Figure 5: Non-linearity of the ECD for SF_6 in the range of 0 to 15 ppt. Open symbols originate from dilution experiments, stars represent the results of our six span gas cylinders. All data are fitted using a cubic polynomial similar to Eq. (3). The shaded area indicates a 1 σ confidence interval of the fit.

2.4.4 Non-linearity of the HgO detector for CO and H_2

The non-linearity of the HgO detector originates from Hg atom absorption of photons in the absorption cell of the detector emitted by a Hg-lamp. The intensity of the transmitted light depends on the number of absorbing atoms and their residence time in the cell. It is described by the Beer-Lambert law and thus decreases exponentially with an increasing number of absorbing atoms. The initial mixing ratio calculation (Eq. (2)) is based on the assumption of a

linear detector response. The non-linearity correction $\Delta C_x = C_x^{nominal} - C_x^{measured}$ for x = H_2 or CO is thus a combination of an exponential and a linear function [Schmitt, 2007]

$$\Delta C_x = A \cdot \exp\left(\frac{-C_x^{meas}}{B}\right) + C \cdot C_x^{meas} + D \qquad (5)$$

If no instrument blank is present, parameters A and D are equal and the non-linearity vanishes for $\Delta C_x = 0$ ppb. Equation (5) can then be simplified to

$$\Delta C_x = A \cdot \left(1 - \exp\left(\frac{-C_x^{meas}}{B}\right)\right) + C \cdot C_x^{meas} \qquad (6)$$

The difference of A and D is thus a measure for the instrument blank. (Refer to Schmitt [2007] for a detailed derivation of Eq.(6).)

Contrary to the ECD, the non-linearity of the HgO detector is not constant in time. We, therefore, measure six span gas cylinders at least once per month, to keep track of these changes. An example of the temporally changing non-linearity function for CO is given in Figure 6a, for H_2 in Figure 6b. For urban pollution events in the range of 1000 ppb CO resp. H_2, the correction increases up to 10% of the measured H_2 mixing ratios and up to 20% for CO.

The accuracy of the parameters A, B, C and D in the non-linearity correction function Eq. (5) is dependent on the number of calibration points taken. Typically, the error of each parameter is of order 3%. The error of an actual corrected measurement can then be calculated by standard error propagation of the actual measurement error and the uncertainty of the non-linearity correction. The uncertainties of the corrected values over the whole calibrated range are between 1% and 3% for CO and 0.7% and 2.6% for H_2, respectively.
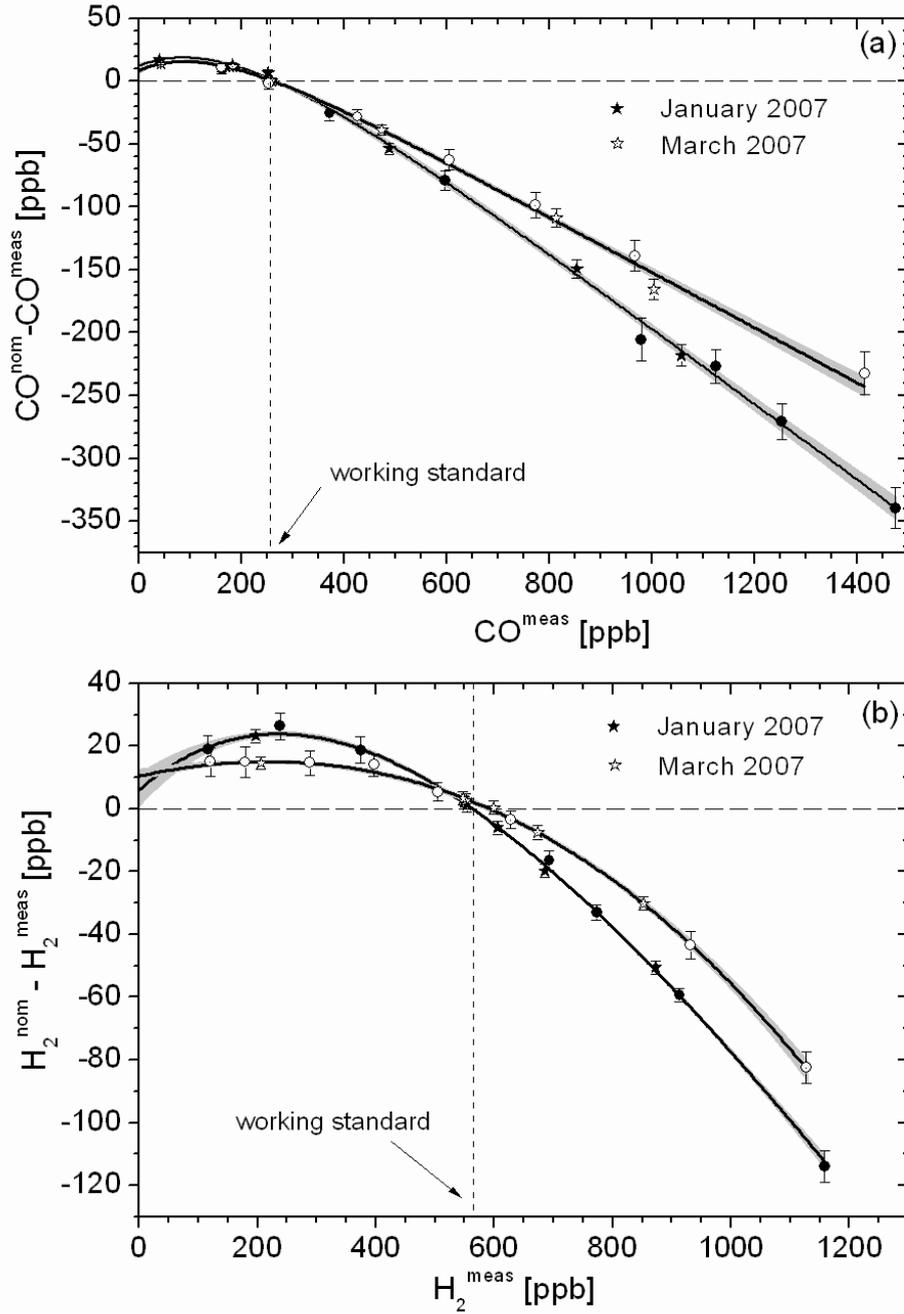
Figure 6: Typical non-linearity correction functions of the HgO detector for (a) CO and (b) H_2. The correction functions are derived from a combination of both, regular dilutions of a high mixing ratio cylinder (circles), and the six span gases (stars) (Table 3). The different curves represent different correction functions valid for different time periods one in January 2007 (closed symbols) and one in March 2007 (open symbols). For each time period a linear-exponential fit according to Eq. (5) is applied. The shaded areas represent 1 σ confidence intervals of the fits.

2.5   Reproducibility and long-term stability of the system

2.5.1   Reproducibility of measurements on high pressure cylinders, flask samples, and ambient air

To assess the quality of the measurements performed with the Combi-GC system three different quality issues have to be considered: (1) the internal reproducibility of the measurements, (2) the traceability of the calibration to international scales, and (3) the long term stability of the whole system. In Table 5 the reproducibility of the Heidelberg Combi-GC is summarized along with the WMO targets for inter-laboratory comparability which may serve as a first evaluation of the precision achieved [WMO, 2008]. The reproducibility for the different gases is determined as the standard deviation of a routine cylinder measurement (40 consecutive injections) with ambient mixing ratios. Apart from SF_6, the reproducibility of the measurements is comparable to the WMO target. Note, however, that the Heidelberg Combi-GC system was not designed for background monitoring of SF_6, as respective analysis of our remotely collected samples is performed with a dedicated high-precision $SF_6 - GC$ system using pre-concentration of a sample of 15 ml volume [Maiss et al., 1996].

	$1\,\sigma$ Reproducibility (40 measurements)	Pair difference of duplicate flask measurements	WMO inter-laboratory comparability target for the Northern Hemisphere
CO_2	0.04 ppm	0.08 ppm (0.06 ppm)	0.1 ppm
CH_4	2 ppb	2.4 ppb (1.7 ppb)	2 ppb
N_2O	0.07 ppb	0.15 ppb (0.11 ppb)	0.1 ppb
SF_6	0.1 ppt	0.09 ppt (0.06 ppt)	0.02 ppt
CO	1.5 ppb	2.4 ppb (1.7 ppb)	2 ppb
H_2	2 ppb	3.0 ppb (2.1 ppb)	2 ppb

Table 5: Mean reproducibility of tank measurements and difference of duplicate flask measurements performed with the Combi-GC system for samples with typical atmospheric mixing ratios (CO_2 = 380 ppm, CH_4 = 1800 ppb, N_2O = 318 ppb, SF_6 = 6 ppt, CO = 120 ppb, H_2 = 500 ppb). The WMO target precision for inter-laboratory comparability of background measurements in the Northern Hemisphere [WMO, 2008] is given in the last column. Numbers in brackets (third column) give an indication of the typical reproducibility of atmospheric measurements performed on different days, as approximated from the mean difference of duplicate measurements

The precision of flask measurements was estimated as the mean pair difference of all duplicate flask analyses performed since 2005. These duplicate measurements were carried out on different days and hence under different environmental conditions. The difference of duplicate flask measurements is larger than its repeatability, and, thus, larger than the

reproducibility of a repeated cylinder measurement. The reproducibility of flask measurements can, however, be approximated by the pair difference divided by 1.4 (numbers in brackets in Table 5). This number is slightly larger than the reproducibility of tank measurements which can be attributed to the additional parts in the sample intake line when measuring flasks (cooling traps, tubing, valves). We assume these values also as a good estimate of the uncertainty of typical direct ambient air measurements. For CO and H_2 the final uncertainty of the mixing ratio measurement is larger than noted in Table 5 due to the non-linearity correction (see Sec. 2.4.2). Error propagation leads to a mean uncertainty for both gases of 1 to 2 %, depending on the mixing ratio.

2.5.2   Long-term stability of the system

The long-term stability of the Combi-GC system is monitored with a so-called target gas and a second sub-target gas. The target gas is measured once per day with 6 to 12 injections, whereas the sub-target is measured only once per month. The life time of the target gas is 3-4 years; it thus allows for the detection and quantification of system drifts or scale shifts due to working standard changes or other reasons. The mixing ratios of the target gas (listed in Table 6) are elevated compared to the working standard (except for CO). The reason is that this also allows monitoring changes in the non-linearity of the GC system. Figure 7 shows the long-term trend from January 2005 to April 2008 of the measured target gas mixing ratios. In Table 6 the standard deviation of all daily mean values over this more than 3-years period is given. As can be seen in Figure 7 e and f, the major problem with the long-term stability of H_2 and CO is the temporally changing non-linearity of the HgO detector. The influence of the non-linearity increases with mixing ratio difference relative to the working standard, thus the influence on H_2 in the target gas with a mixing ratio of almost 1300 ppb is very large.

	Target gas mixing ratio	Long term stability (1σ)	Long term stability (%)
CO_2	406.21 ppm	0.02 ppm	0.005%
CH_4	1996.6 ppb	0.5 ppb	0.025%
N_2O	331.73 ppb	0.07 ppb	0.02%
SF_6	6.06 ppt	0.03 ppt	0.5%
CO	116.5 ppb	2.3 ppb	2.0%
H_2	1293.5 ppb	14 ppb	1.1%

Table 6: Long term stability of the Combi-GC system: 1σ standard deviation of the daily mean target gas values for all six components.
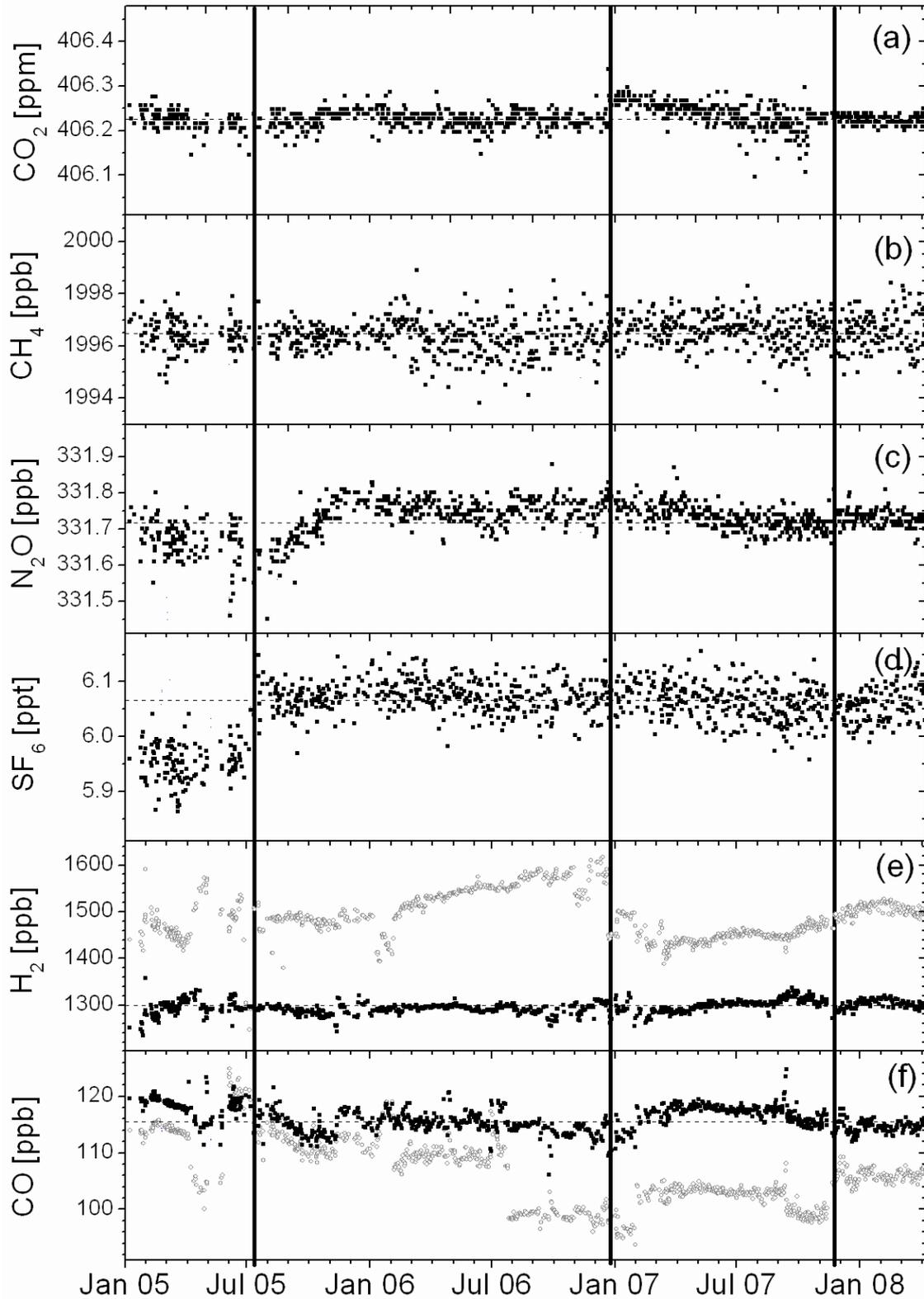
Figure 7: Long-term measurement of the target gas to check the stability of the complete measurement system. Horizontal bars mark working standard changes. For CO and H_2 (panel e and f) the uncorrected values of the target gas are shown as open circles. The non linearity function for both gases changes considerably in time. The non linearity-corrected results for CO and H_2 are given in black.
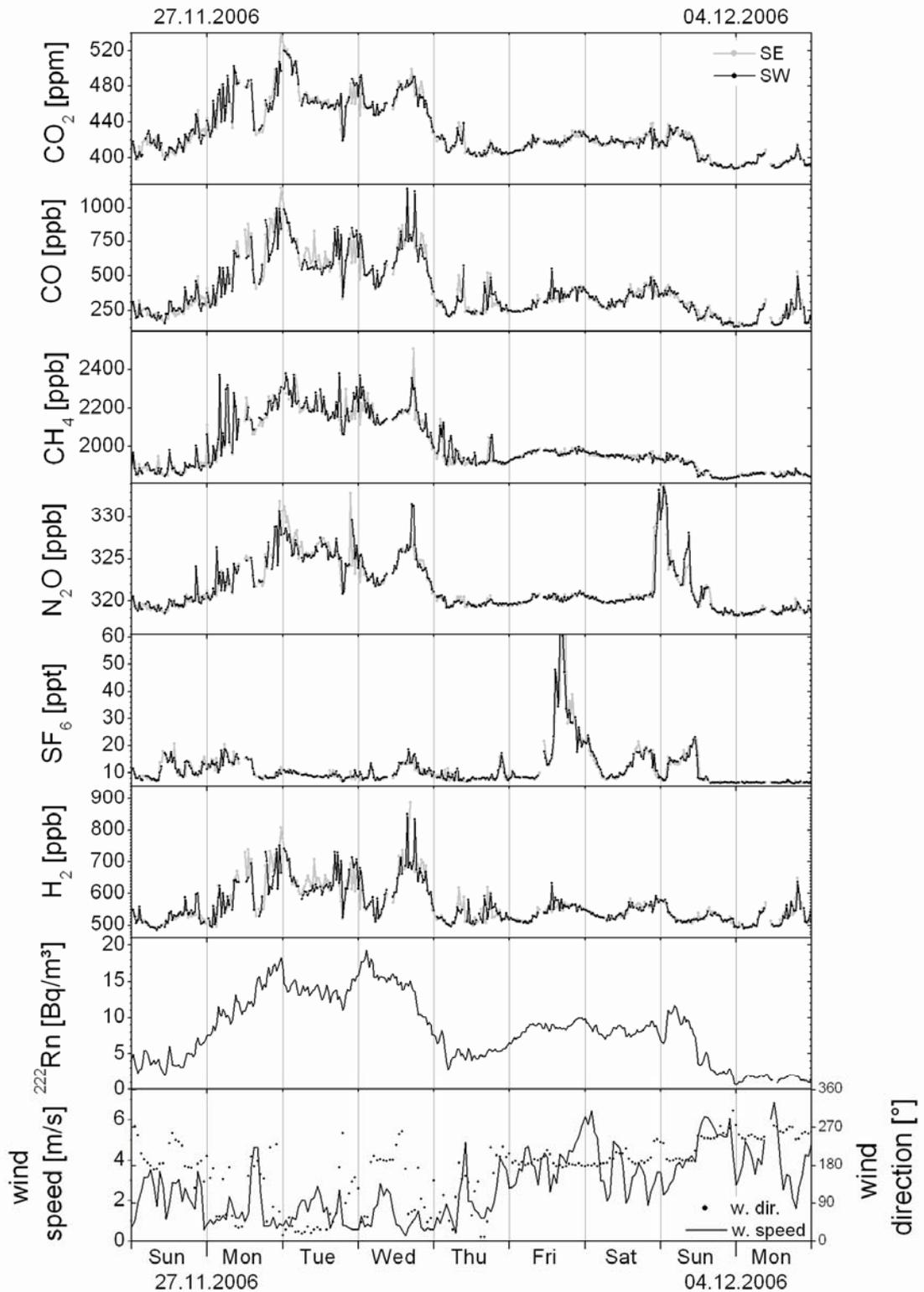
3. Example of ambient air measurements in Heidelberg

Figure 8: Nine days of half-hourly mean values of CO_2, CO, CH_4, N_2O, SF_6, and H_2 measured with the Heidelberg GC system, together with ^{222}Radon, wind velocity and wind direction. Data from both intake lines are shown in different "colours".

Ambient air measurements in Heidelberg of all trace gases analysed with our Combi-GC system show a very large range of mixing ratios (Figure 8). In particular during high pressure situations with a strong influence of continental air masses and low wind speed (first four days of the period displayed in Figure 8) mixing ratios of all components can be highly elevated due to local and regional source influence. However, during strong south-westerly winds (December 4, 2006) we also observe relatively clean well-mixed air (except for two local rush-hour peaks visible in the CO_2, CO and H_2 records). It is, thus, interesting to see, how all components which have more or less homogeneously distributed (soil-borne) sources - comparable to ^{222}Radon which is naturally emitted from all soils - show highly correlated changes. Gases jointly emitted from combustion sources like CO_2, CO and H_2, show strong similarities of their short-term variability; the same is true for gases mainly emitted from agriculture like CO_2, N_2O and CH_4. But there are also exceptions, as for N_2O on December 3 and SF_6 on December 1st, 2006, which are obviously emitted from single sources which can be localised by trajectory analyses (e.g. N_2O from the industrial area of Mannheim-Ludwigshafen, about 20 km north-west of Heidelberg [Schmidt et al., 2001]). Figure 8 also illustrates that, with few exceptions when the variability of mixing ratios is large, both intake lines on the roof of the Institute building show very similar values, indicating no direct contamination of the measurements from the building.

4.   Conclusions

To our knowledge the original set-up of the Heidelberg GC was one of the first which combined ambient air analyses for CO_2, CH_4, N_2O and SF_6 in one instrument. Respective simultaneous measurements have proven to be a powerful tool for disentangling the influences of various sources and sinks on a regional scale [Schmidt, 2001]. This earlier approach was now extended with additional simultaneous CO and H_2 measurements which, in particular when applied to regional studies in semi-polluted areas, are powerful tracers for separating the CO_2 component from fossil fuel sources [Gamnitzer et al. 2006; Levin and Karstens, 2007]. With respect to a possibly emerging H_2 economy measuring this trace gas in addition may become very important for future assessments of respective emissions impacts on the climate system. We could, however, show that the good long-tem stability of these measurements could only be achieved with a regular determination of the non-linearity of the HgO detector.

Although our Heidelberg instrumentation is pretty old (which is a disadvantage for the Reduction Gas Analyser part of the system), other components, i.e. CO_2 and in particular N_2O do not suffer from this. Contrary, for N_2O our detector seems to be more sensitive and stable

than many of the new electron capture detectors commercially available to date (<mark>reference</mark> ???).

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