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Atmospheric Measurement Techniques

A single gas chromatograph for accurate atmospheric mixing ratio measurements of CO_2, CH_4, N_2O, SF_6 and CO

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Abstract. We present an adapted gas chromatograph capable of measuring simultaneously and semi-continuously the atmospheric mixing ratios of the greenhouse gases CO_2, CH_4, N_2O and SF_6 and the trace gas CO with high precision and long-term stability. The novelty of our design is that all species are measured with only one device, making it a very cost-efficient system. No time lags are introduced between the measured mixing ratios. The system is designed to operate fully autonomously which makes it ideal for measurements at remote and unmanned stations. Only a small amount of sample air is needed, which makes this system also highly suitable for flask air measurements. In principle, only two reference cylinders are needed for daily operation and only one calibration per year against international WMO standards is sufficient to obtain high measurement precision and accuracy.

The system described in this paper is in use since May 2006 at our atmospheric measurement site Lutjewad near Groningen, The Netherlands at 6°21′ E, 53°24′N, 1 m a.s.l. Results show the long-term stability of the system. Observed measurement precisions at our remote research station Lutjewad were: ±0.04 ppm for CO_2, ±0.8 ppb for CH_4, ±0.8 ppb for CO, ±0.3 ppb for N_2O, and ±0.1 ppt for SF_6. The ambient mixing ratios of all measured species as observed at station Lutjewad for the period of May 2007 to August 2008 are presented as well.

1 Introduction

The effects of Global warming are becoming more and more notable every year. According to the Intergovernmental Panel for Climate Change (IPCC) eleven of the twelve years between 1995 and 2006 rank among the warmest years since 1850. The global average surface temperature has already increased by 0.74°C between the years 1906 and 2005 (IPCC, 2007). Most of the observed temperature increase since the mid-20th century can probably be attributed to the observed increase of anthropogenic greenhouse gas mixing ratios (IPCC, 2007). Since 1750, the radiative forcing caused by the long-lived greenhouse gases (LLGHGs) CO_2, CH_4 and N_2O is estimated to be: 1.66, 0.48 and 0.16 $\mathrm{Wm^{-2}}$, respectively, causing a combined radiative forcing of Earth's climate which is unprecedented in at least 10 000 years (IPCC, 2007).

Assessing the above, our goal was to develop a facility for measuring ambient mixing ratios of the three most important LLGHGs: CO_2, CH_4 and N_2O. This facility was to comply with the following: in-situ measuring the ambient mixing ratios with sufficient temporal resolution (at least several measurements per hour) and a high reliability, low in maintenance, relative easy to operate and autonomously operating. The latter is an essential feature at remote and unmanned stations. Furthermore it had to comply with the recommendations for measurement precision as given by the World Meteorological Organization's Global Atmosphere Watch (WMO-GAW). The WMO gives recommendations for inter-laboratory comparability as follows: CO_2±0.1 ppm, CH_4±2 ppb, N_2O±0.1 ppb, (WMO, 2005, 2001). Hence, measurement precision and accuracy for one single measurement has to meet at least these requirements. We further desired the system to be relatively inexpensive in order to be attractive (cost-benefit wise) for other research groups as well and potentially improve global data coverage.

Besides measuring CO_2, CH_4 and N_2O we desired the system also to measure two other components: CO and SF_6. CO is an important molecule in tropospheric chemistry mainly for its reaction with OH (Fishman and Crutzen, 1978). Because CO and CH_4 both are oxidized in the troposphere by

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the OH radical, changes in background mixing ratio of either one of them will affect the other. Moreover, since any carbon-containing fuel combustion process with CO_2 as an end product also delivers CO, the sources of CO are very closely linked to those of fossil fuel CO_2 (Gamnitzer et al., 2006). The ratio of CO: fossil fuel CO_2 is thus a direct measure for combustion quality on a regional scale (Zondervan and Meijer, 1996; Meijer et al., 1996). Once this ratio is known, CO can be used as a proxy for the fossil fuel part of CO_2. The fossil fuel part of atmospheric CO_2 can be determined very well using ^{14}C measurements (de Jong and Mook, 1982; Tans et al., 1979; Levin et al., 1980, 2008; Turnbull et al., 2006). The method is however too laborious and expensive to obtain continuous high precision measurements with a temporal resolution of a few hours or less (Gamnitzer et al., 2006). When CO is calibrated regularly to $^{14}CO_2$ measurements, it can easily be used as a proxy for $^{14}CO_2$ and supply a continuous fossil fuel CO_2 record (Gamnitzer et al., 2006; Bakwin et al., 1998).

SF_6 is an anthropogenically produced molecule which is mainly used as an electrical insulator in high voltage applications. It is of interest because even though the current atmospheric background concentration is very low (<7 ppt) it is an extremely effective greenhouse gas due to its strong infrared absorption and a long atmospheric lifetime of about 3200 yr (Maiss and Brenninkmeijer, 1998). Its global warming potential is estimated to be about 23 300 times that of CO_2 over a period of 100 years (IPCC, 2007). SF_6 is furthermore of interest because it can be used as an indicator for anthropogenic emissions (Turnbull et al., 2006; Rivier et al., 2006) since its sources (e.g. electricity plants) coincide with human activities.

High quality monitoring of the ambient mixing ratios of these five LLGHGs and tracers can greatly improve our knowledge of their regional sinks and sources and is needed to accurately determine their inter-annual variations. Several techniques currently exist to measure these five LLGHGs and tracers. CO_2 is mostly measured using a Non-Dispersive Infra-Red (NDIR) gas analyzer or with a Gas Chromatograph (GC). For both devices long term precisions of <0.1 ppm can be obtained. Extremely high measurement precision for CO_2 of about 0.003–0.01 ppm is reported with a LOFLO analyzer (Francey and Steele, 2003; WMO, 2005) which is basically a modified and improved commercial NDIR instrument. Analyzers for ambient measurements of CO_2 and CH_4 based on Cavity Ringdown Spectroscopy have recently become commercially available (Los Gatos Research Inc., CA, USA; Picarro, CA, USA) and analyzers using quantum cascade laser technology have also become available for ambient measurements of CO and N_2O. Although these new laser based instruments seem very promising (suggested precisions when averaging over 5 min are: <50 ppb for CO_2, <0.7 ppb for CH_4, <0.3 ppb for N_2O and <5 ppb for CO) there is, however, still little experience regarding long term performance (e.g. aging, mirror contamination, interference with other gases). Currently, CH_4 is mostly measured with a GC using a Flame Ionization Detector (FID). With this technique, measurement precision of <2 ppb is obtainable.

At most stations, N_2O is measured with a GC using an Electron Capture Detector (ECD) (WMO, 2001). Currently, GCs are for sale only with the newer type (micro) ECD which perform slightly worse than the original type. Still, precisions are obtainable of <0.5 ppb. Conveniently, analysis of SF_6 can also be done with the same detector (Maiss, 1992; Schmidt et al., 2001) with a measurement precision of <0.1 ppt.

Measuring ambient mixing ratios of CO with high precision at a continental site as Lutjewad can be challenging because of its large signal dynamics. CO mixing ratios can easily change by a factor of four from a clean background value of below 100 ppb up to 400 ppb (with polluted air masses) within short time. The corresponding variation of CO_2 is usually in the range of about 380 ppm to 430 ppm. This is in agreement with the finding that fossil fuel burning in the Netherlands on average delivers an amount of CO of roughly 1% of the amount of CO_2 (Meijer et al., 1996). Several techniques exist for measurements of ambient CO mixing ratios. Most of them are based on using gas chromatography or optical spectroscopy. When using the first, the GC can be equipped with a mercury oxide reduction detector (Gros et al., 1999; Seiler et al., 1980), an ECD (Hurst et al., 1997) or with a FID (Rasmussen and Khalil, 1981). Measurement precision os 1–5 ppb for these methods at current atmospheric background levels. Other frequently used techniques for ambient CO measurements include: resonance fluorescence in the fourth positive band of CO (VURF) and Gas Filter Correlation Radiometry (GFC). The precision using VURF is about 1.5 ppb at an atmospheric mixing ratio of 100 ppb (Gerbig et al., 1999). GFC is a Non-Dispersive Infra-Red (NDIR) technique. A precision of about 1.4 ppb was reported after improvement of a commercial analyzer by Parrish et al. (1994). Tunable diode laser spectroscopy (TDLS) offers a high sensitivity, a precision of about 1 ppb, and response times of a few seconds, but is still subject to relatively high costs and requires well-trained operators. For a review on these measurement techniques see also Novelli et al. (1999) and references therein.

Considering all of the above and our quest to develop a high-precision and cost-effective instrument for continuously measuring the ambient mixing ratios of CO_2, CH_4, N_2O, CO and SF_6, we decided to make use of gas chromatography. GC systems are very reliable and until now less difficult to operate and maintain than optical measurement systems and they require considerably less start-up costs than the laser-based technologies (WMO, 2001). Because all species can be analyzed with either an ECD or FID only two detectors are needed. The instrument presented here is capable of measuring all five species practically simultaneously and under the same circumstances. Furthermore, the use of gas chromatography ensures that only a small sample is needed, making this also an ideal facility for flask measurements. With the exception of maintenance work (e.g. replacement of carrier gas cylinders) the system reported here is designed to operate continuously without the need for intervention of an operator, making this instrument highly suitable for unmanned and remote stations. In this paper we present a detailed description of the complete setup, followed by the procedures for calibration of the system's response and the method for calculating the ambient mixing ratios. We will demonstrate that, after calibration against a suite of WMO reference standards, only two working standards (references) for daily use are needed to determine the ambient mixing ratios of CO_2, CH_4, N_2O, CO and SF_6. Using a well-known target cylinder, we will show the long-term stability over more than 2 years. Finally, we will present mixing ratios as measured at our site Lutjewad in The Netherlands at 6°21′ E, 53°24′ N.

2 Technical description and analysis of components

2.1 Description of the system

Our measurement system is based on a commercially available Agilent HP 6890N gas chromatograph (GC) which was modified to our purposes. For a detailed schematic diagram see Fig. 1. Our system is an improvement of other GC systems currently operational (Worthy et al., 2003; Ramonet et al., 2003; Thompson et al., 2009) which are limited to measuring 4 gases, i.e. N_2O and SF_6 in combination with CH_4 and CO_2 or CH_4 and CO simultaneously.

The basic principle of our system is as follows: first, a sample loop is flushed with the sample air. Secondly, the sample is transported with a carrier gas and led through a chromatographic column were separation of the gases takes place. The effectiveness of this separation is very sensitive to the gas flow, the temperature of the column and the type of column used. Finally, the individual components are analyzed by a detector. Two different detectors are used in this application: a Flame Ionization Detector (FID) for measuring CO_2, CH_4 and CO, and a micro Electron Capture Detector (μECD) for measuring N_2O and SF_6. CO_2 and CO are catalytically converted to CH_4 prior to the analysis by flushing the gas with hydrogen through a nickel powder filled methanizer at 370°C.

The sample air is introduced into the system by entering a 16-port, electrically driven Valco valve (V7), which is controlled via the external events output connector of the GC, and flushed through three sample loops. For analysis of CO_2, CH_4 and CO two 10 mL sample loops are used: sample loop 3 is used for CO_2 and CH_4 and sample loop 2 is used for CO. A 15 mL sample loop (sample loop 1) is used for N_2O and SF_6. All sample loops are temperature stabilized at 60°C. Two mass flow controllers (MFC) (max. 500 mL min^{-1}, Bronkhorst, Ruurlo, The Netherlands) are used to stabilize the flow of the sample loops. They are set to 300 mL min^{-1} for sample loop 1, and 450 mL min^{-1} for sample loops 2 and 3. All sample loops are flushed for 0.55 (metric) min which represents at least eleven times their own volume of sample air.

Five columns are used for separating the individual components from the air sample. They are temperature stabilized at 72°C. CO_2 and CH_4 are separated using a 10 feet Haysep Q column (3/16 inch o.d., mesh 80/100, column 5). CO is separated with a 6 feet Porapack Q pre-column (1/8 inch o.d., mesh 80/100, column 3) and a 4 feet Molsieve 5Å analytical column (1/8 inch o.d., mesh 60/60, column 4). The function of the pre-column is to separate CO_2 from the sample and by (back)flushing it at the right time preventing it from entering and degrading the Molsieve column. Besides CO also CH_4 is separated by column 3, but since it is partly flushed away when the pre-column is backflushed, the CH_4 analysis is of too low quality to be used for our purposes. N_2O and SF_6 are separated from the air sample using two Haysep Q columns (3/16 inch o.d., mesh 80/100). One column is 4 feet long (column 1) and is configured as a pre-column and the second column is 6 feet long (column 2) and is used as the main analytical column. The analytical column is connected to the μECD using a packed column adapter (Agilent part no. 19301-80530).

Following the separation of the air sample, the species are analyzed with the FID and the μECD. The temperatures of the detectors are stabilized at 250°C for the FID and 300°C for the μECD. The flame of the FID is fed by clean air (300 mL min^{-1}) and hydrogen (90 mL min^{-1}).

Nitrogen (quality 5.0) is used as carrier gas (and backflush gas in case of CO) for all species which are analyzed with the FID (CO_2, CH_4 and CO). It is led through a purifier (Aeronex 500k, Sigma-Aldrich, The Netherlands) in order to ensure stable baseline conditions. A mixture of Argon (95%) and Methane (5%) (quality 6.0, AirLiquide, Eindhoven, The Netherlands) is used as the carrier gas and backflush gas for both species which are analyzed with the μECD (N_2O and SF_6).

Five 6-port 2-way Valco valves (V1, V2, V3, V4 and V5), one 10-port 2-way Valco valve (V6) and four 2-port solenoid valves (V1_2, V8_1, V8_2 and V8_3) are used in the application. V1_2 is electrically connected with V1 and they are controlled simultaneously. The purpose of V1_2 is to prevent wasting of the relative costly Argon/Methane mixture when V1 is switched on. V8_1, V8_2, V8_3 are also electrically connected to each other and controlled simultaneously. V8_1 and V8_2 are used to close sample loop 3 in order to prevent the sample from leaking out (see process scheme). V8_3 is mounted between V7 and the MFCs as an extra prevention of potential leakage of the reference gases. Two valves (V5 and V6) are mounted on top of the GC for practical reasons due to limited space in the internal valve box of the GC. By placing them on top of the methanizer not only the tubing length is minimized but also the temperature of these valves

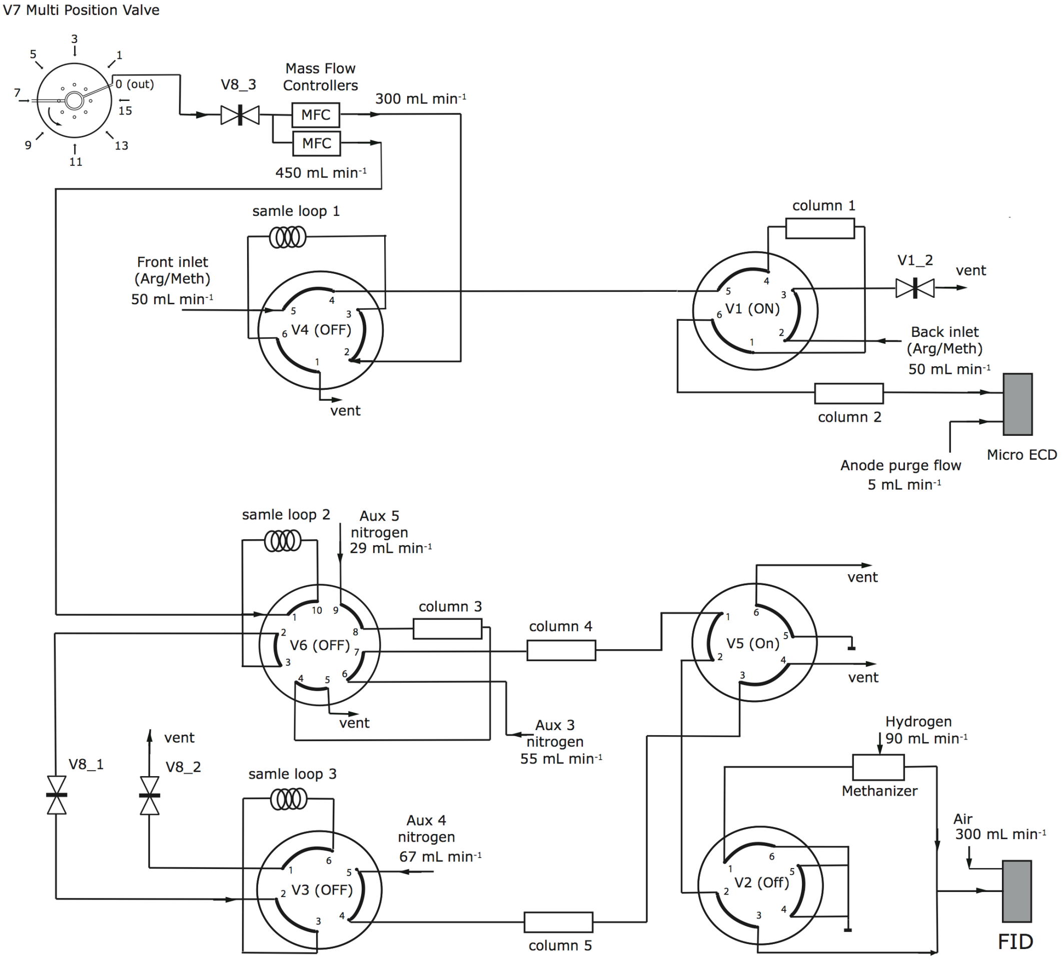

Fig. 1. Schematic design of the GC. The air sample enters the system through multivalve V7 and is stabilized with two Mass flow controllers. CO_2 and CH_4 are separated from the sample air using a Haysep Q column (column 5) and analyzed with the FID. CO is separated from the sample using a Porapack Q column (column 3) and a Molsieve 5Å column (column 4) and is also analyzed by the FID. N_2O and SF_6 are separated with two Haysep Q columns (columns 1 and 2) and analyzed with the μECD. Valves V8_1, V8_2 and V8_3 are simultaneously controlled. V1_2 is simultaneously controlled with V1. All valves are drawn in their starting position.

is stabilized at about 70°C by using the waste heat of the methanizer. All valves are controlled with Chemstation software (Agilent Technologies, v. B.01.01) using a sequence list containing all consecutive methods (i.e. measurement and analysis procedures). At the end of the list, the sequence is restarted by an external Delphi program. Chemstation is also used for the analysis of the chromatograms.

2.2 Process flow scheme

A detailed description of the process flow scheme is given in Fig. 2 (see also Fig. 1). Each run starts by switching V1 and V5 to "on", and the four solenoid valves: V1_2, V8_1, V8_2 and V8_3 to "open". All other valves are switched off. Now, all sample loops are flushed with sample air and all columns are flushed with the carrier gases. After 0.55 (metric) min V7 switches to a closed position in order to equilibrate the pressure in the sample loops with the room pressure. In this way, the sample loops contain virtually the same amount of molecules when either measuring ambient air samples or reference gases, provided the time between their consecutive measurements is kept short compared to atmospheric pressure changes. To prevent contamination with outside air due to backflow long capillary tubing is connected to the flushing outlets.

At 1.10 min 6-port, 2-way valve V4 and 10-port, 2-way valve V6 are switched on and the samples are flushed from sample loops 1 and 2 to the pre-columns. The sample from sample loop 3 is not flushed yet. To prevent the sample from diffusing out of this sample loop, V8_1 and V8_2 are closed. At 2.42 min V6 is switched off in order to backflush column 3. At 2.85 min V2 is switched on, and the sample leaving column 4 is led through the methanizer allowing CO to be converted to CH_4. The CH_4 in the sample air which elutes

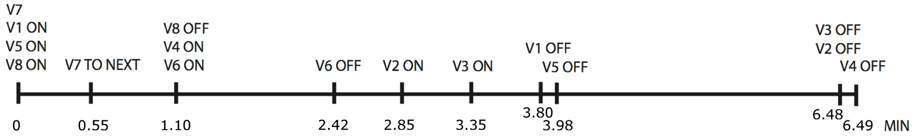

Fig. 2. Process flow scheme indicating the switch time of all the valves. The starting position of V7 is determined prior to the run. V8 represents the three coupled solenoid valves V8_1, V8_2 and V8_1, and V1 represents both V1 and solenoid valve V1_2.

from the column prior to CO will also pass through the methanizer but this way we ensure the baseline to be undisturbed around the small CO peak. At 3.35 min V3 is switched on and the sample from sample loop 3 is injected into column 5 where CO_2 will be separated from the air sample. The FID is still connected to column 4 until V5 is switched off. This way, the FID first analyzes CO eluting from column 4 and sequentially analyzes CH_4 and CO_2 which will elute from column 5. At 3.98 min V5 is switched off and the FID is connected to column 5 just in time to detect CH_4, followed by CO_2. The exact switching time is chosen such that oxygen, which precedes CH_4, will not enter and degrade the methanizer by oxidizing the nickel catalyst powder. Meanwhile, at 3.80 min V1 was switched off in order to flush column 1 and allowing N_2O and SF_6 to be further separated from the sample in column 2. Following the separation, they are measured by the μECD. Finally, at 6.48 min V2 and V3 return to their original (off) positions again, and V4 is switched off at 6.49 min. The total analytical procedure of one sample takes only 6.5 min, which makes it possible to do about 9 measurements of all 5 gases in one hour.

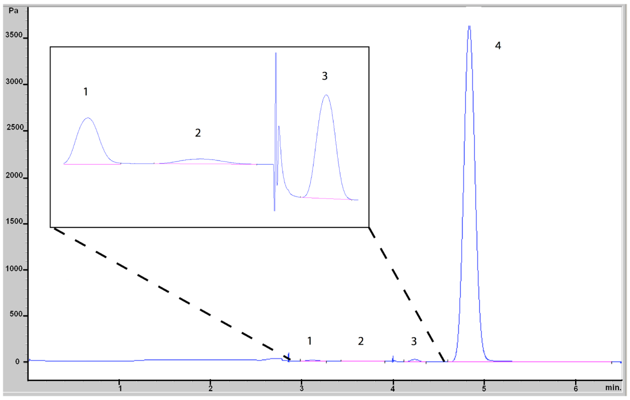

Fig. 3. Chromatogram of the FID with from left to right: CH_4 (1) and CO (2) followed by a spike caused by switching V5 and then CH_4 (3) and CO_2 (4). Only the latter CH_4 is used for further analysis.

2.3 Chromatograms

The results of a typical run are shown in Figs. 3 and 4. The FID's response is in pA, the response of the μECD is in Hz. Figure 3 shows the chromatograms from analysis with the FID. From left to the right (inset) first CH_4 (not used for further analysis) and CO are seen, followed by a short spike which is caused by the switching of V5. This spike is closely followed by CH_4 and CO_2 (the largest peak). Figure 4 shows the output of the μECD. First a large O_2 peak is detected which is considered a by-product of the method. This peak is followed by the N_2O peak and finally the much smaller peak of SF_6. For the analysis of the peaks of CO_2, CH_4 and N_2O, integration of their areas is used. The peaks of SF_6 and CO are relatively wide compared to their heights. Therefore, they are more sensitive to small disturbances in the baseline and higher precision is obtained by using their peak heights for analysis. Typical peak characteristics are given in Table 1.

2.4 Additional remarks

Before entering the GC the ambient air has to be pre-dried. At our station we use Nafion membrane pre-dryers (MD 110-72-S, Perma Pure, Toms River, New Jersey) which remove up to 50% of the water vapor from the ambient sample. The majority of the air which is not used is pumped back to the nafion to dry the new incoming air, preventing any concentration gradient in one of the measured gases over the membrane. To freeze out the remaining water vapor from the sample air, we use cold traps made of glass which effectively dry the air to a dewpoint of −50°C and which are cleaned again automatically. The lower 15 cm of the cold traps are immersed in a silicone-oil-based thermofluid (M60.115.05, Renggli, Rotkreuz, Switzerland); each in a separate 2-L stainless steel dewar vessel. By using two identical sides, the water from one of the cryo-traps can be removed while the other is drying the air streams at a temperature of around −50°C. The water is removed from the traps by back-flushing with air while the temperature of the thermo fluid is around +40°C. This drying system does therefore not need servicing in the form of replacing cryo-traps and can run unattended during long periods of time. More details are given by Neubert et al. (2004).

Regular service is needed to supply the argon/methane mixture (about 95 L day^{-1}) and nitrogen (about 35 L day^{-1}), as well as water for the hydrogen generator (about 0.2 L day^{-1}). The usage of the reference cylinders is about 6.5 L day^{-1} and for the target tank 2.7 L day^{-1}. For a 50 L reference cylinder this represents over 2 years of continuous measurements.

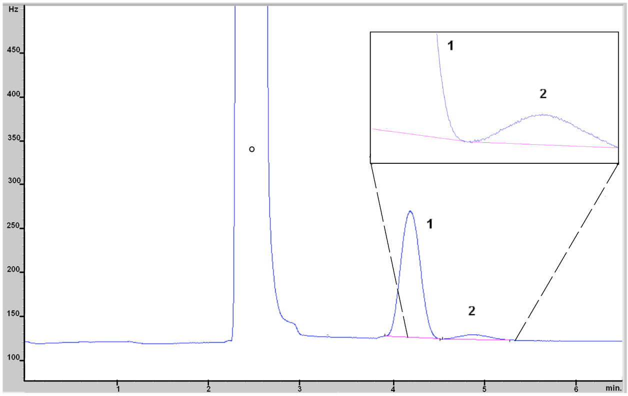

Fig. 4. Chromatogram of the μECD. An oxygen peak (0, not used for analytical purposes) is followed by: N_2O (1) and SF_6 (2).

Table 1. Typical peak characteristics.

	CO_2	CH_4	CO	N_2O	SF_6
Retention time	4.8 min	4.2 min	3.6 min	4.2 min	4.9 min
Width	0.13 min	0.09 min	0.18 min	0.24 min	0.27 min
Area	33 914 pA s	166.3 pA s	16.1 pA s	2085 Hz s	93.7 Hz s
Height	3892 pA	27 pA	1.2 pA	139 Hz	4.4 Hz
Baseline noise	0.01 pA	0.01 pA	0.01 pA	0.2 Hz	0.2 Hz

The efficiency of the methanizer needs to be tested on a regular basis. An interrupt of the hydrogen supply to the methanizer, e.g. by a FID-safety shutdown during power failure, can cause degradation of the methanizer if it is still at operational temperature. Ambient O_2 molecules diffuse into the FID outlet and oxidize the nickel powder, reducing the methanizer efficiency. Without action taken, recovery from 40% efficiency back to 100% can take several weeks. The efficiency of the methanizer can be tested by examining the response/concentration ratio of CO_2 to that of CH_4 for a well-known cylinder, since for a given cylinder the ratio of the mixing ratios of CO_2 to CH_4 is constant and thus should also be the ratio of their responses. In Sect. 4.1 we will give an example of this and the effect of the methanizer on the measurement precision.

Measuring at remote stations can be a costly and time-consuming task. For example, we've encountered several power failures at our station and breakdown of equipment or leakages in one of the valves or connectors can be a potential source of data loss. Because of the relatively low ambient mixing ratio of N_2O and the high sensitivity of the μECD, N_2O can be applied as a very cheap and effective tool to check the whole system for any leakages (i.e. leaking room-air into the system). Even a very small leak will result in a significant increase in the response of the μECD when emitting some N_2O into the room. Since in most whipped cream cans N_2O is used as a propellant this can be a very cheap solution to test the system for any leakages.

3 Sampling strategy and calibration

Two reference cylinders with known mixing ratios are used to normalize the response of the detectors to an internationally recognized scale. This scale is provided by the World Meteorological Organization (WMO). One reference cylinder ($\text{Ref.}_{\text{high}}$) contains relatively high mixing ratios, the other one (Ref._{low}) contains relatively low mixing ratios. The mixing ratios are preferably at the high- and low end of the current ambient mixing ratios. They range from: 364 ppm to 408 ppm for CO_2, 1758 ppb to 2133 ppb for CH_4, 303 ppb to 326 ppb for N_2O, 113 ppb to 323 ppb for CO and 6 ppt to 7 ppt for SF_6. Both reference cylinders, as well as a third target cylinder which is used for quality control, are periodically calibrated on the WMO scale using five primary calibration cylinders provided by the National Oceanic and Atmospheric Administration/Earth Systems Research Laboratory (NOAA/ESRL, Boulder, Colorado, USA). They range from: 353 ppm to 426 ppm for CO_2, 1739 ppb to 2107 ppb for CH_4, 305 ppb to 326 ppb for N_2O, 89 ppb to 404 ppb for CO and 4 ppt to 8 ppt for SF_6.

During normal operation, the typical measurement sequence is deployed as:

$$\text{Ref.}_{\text{high}}-\text{S}-\text{S}-\text{S}-\text{Ref.}_{\text{low}}-\text{S}-\text{S}-\text{S}-\text{Ref.}_{\text{high}}$$

in which "S" is a sample measurement. The responses of the two references are linearly interpolated in time to obtain reference values for each measured sample. One full analysis of either a sample or reference requires 6.5 min, hence every 26 min a reference standard is measured. This method largely reduces the errors caused by short-term variations (e.g. changes in ambient pressure) and still allows six sample measurements per hour. Three times a day, a sample analysis is substituted by a well-known target cylinder analysis for the purpose of quality control. Close observation of the target cylinder is key in detecting any potential problems (e.g. drift in one of the cylinders) at an early stage.

The concentration-response curves for CO_2, CH_4 and SF_6 are to a very good approximation linear. The maximum difference compared to using a quadratic fit was $<$0.01 ppm for CO_2, $<$0.4 ppb for CH_4 and $<$0.002 ppt for SF_6 for the full range of our WMO standards. Therefore, the mixing ratio of a sample can simply be calculated by linear interpolation between the two references. The non-linear character of the concentration-response curves of CO and N_2O was significant (max. 0.5 ppb for N_2O and 1.4 ppb for CO on the full range) therefore we decided to use a second order polynomial function for their representation:

$$C_x = \alpha R_x^2 + \beta R_x + \gamma \tag{1}$$

Where C_x is the mixing ratio of a sample and R_x is the detector's response for a sample measurement and α, β and γ are the fit parameters of the polynomial concentration-response curve. Since the response of the FID is very linear for the other species, the non-linearity of CO is most likely caused by its high dynamical range (over a factor of 4 difference between the two reference cylinders compared to 20–25% for CO_2 and CH_4). Probably, the response of the μECD is non-linear for SF_6 as well, but this is apparently not noticeable in the low-response range of SF_6.

Determining the coefficients α, β and γ of Eq. (1) requires at least three references, preferably more. We determined the coefficients periodically using the five WMO standards, during the same exercise in which we (re)determined the values of our high and low reference cylinders and of our target.

However, for the daily maintenance of our calibration, we decided to use no more than two cylinders, just as in the cases of the linear responses. This strategy functions well, as the contribution of the 2nd-order term of the response curve is minor and has been relatively constant over the years that our system has been operational. Hence, the shape of the response curve does not change significantly over time, or its effect on the final mixing ratios is relatively small at the most. In this case, the information of the response curve Eq. (1), combined with the well-known mixing ratios of two references, yields the mixing ratios of a sample C_x as follows:

$$C_x = C_1 + (C_2 - C_1)\frac{\alpha\left(R_x^2 - R_1^2\right) + \beta\left(R_x - R_1\right)}{\alpha\left(R_2^2 - R_1^2\right) + \beta\left(R_2 - R_1\right)} \tag{2}$$

Where C_1 and C_2 are the mixing ratios of the reference gases and C_x is the mixing ratio of a sample. R_1 and R_2 are the response values corresponding to C_1 and C_2 and R_x is the response of a sample measurement. α and β are the fit parameters of the 2nd-order polynomial concentration-response curve, which are determined at the site using the five WMO standards.

Applying Eq. (2), and assuming the shape of the concentration-response curve remains intact, necessitates only two well-known reference standards. However, although the shape of the response curve remains the same, the values of the fit parameters will vary over time because of changes in the response, especially for longer periods of several weeks or months for example due to reduced efficiency of the methanizer. Therefore we define: α' and β' as the actual fit parameters at a certain time of a measurement during daily operation. We further introduce $r_{x,1,2}$ as the responses of a sample or a reference standard at a certain time of a measurement during daily operation. R_1 and R_2 are now defined as the response values of two reference standards at the time of calibration (when the concentration-response curve and its fit parameters were determined with the five WMO standards). And C_1 and C_2 are their corresponding mixing ratios.

Assuming the shape of the response curve to be stable over time (i.e. the relative contribution of the 2nd-order term is constant), the change over time of the response (from R to r) is then the result of a linear transformation only. The response of a reference (e.g.) during daily operation (r) and its response at the time of calibration (R) are then related as follows:

$$r_{1,2} = qR_{1,2} + k \rightarrow R_{1,2} = \frac{r_{1,2} - k}{q} \tag{3}$$

Hence, the response at a certain time (r) can have an offset (k) compared to its original response (R) and can be multiplied with a certain sensitivity/response factor (q).

From Eq. (3a) we find for k:

$$k = r_2 - qR_2 = r_1 - qR_1 \tag{4}$$

And for q:

$$q = \frac{r_2 - r_1}{R_2 - R_1} \tag{5}$$

Substituting Eq. (3b) and (3c) in Eq. (1) we find:

$$\alpha' = \frac{\alpha}{q^2} = \frac{\alpha}{\left(\frac{r_2 - r_1}{R_2 - R_1}\right)^2} \tag{6}$$

And:

$$\beta' = \frac{\beta}{q} - \frac{2\alpha k}{q^2} = \frac{\beta}{\left(\frac{r_2 - r_1}{R_2 - R_1}\right)} - \frac{2\alpha\left(r_1 - \frac{R_1(r_2 - r_1)}{R_2 - R_1}\right)}{\left(\frac{r_2 - r_1}{R_2 - R_1}\right)^2} \tag{7}$$

α' and β' are the fit parameters now determined continuously by the measurement of the low and high reference cylinders, They are adapted to the linear transformation of the response. Through the linear extrapolation of the responses of the reference cylinders these coefficients are available for any point in time, and the mixing ratios for a given sample at a certain time and using only two reference cylinders, can thus be calculated as follows:

$$C_x = C_1 + (C_2 - C_1)\frac{\alpha'\left(r_x^2 - r_1^2\right) + \beta'\left(r_x - r_1\right)}{\alpha'\left(r_2^2 - r_1^2\right) + \beta'\left(r_2 - r_1\right)} \tag{8}$$

So far, we have (re)calibrated the response of Eq. (1) for N_2O and CO three times at the site (December 2006, August 2007 and July 2008), and observed that the change of shape of the response is indeed below significance. Furthermore, the measurement of the target serves as a permanent check of the measurement quality, and it would thus also reveal the eventual variation in the shape of the quadratic calibration curve.

4 Results

4.1 Measurement performance

The system as described in this paper has been operational at our atmospheric measurement station Lutjewad since May

2006. Since August 2006 two reference standards are available and calculation of the mixing ratios is performed as described above. A target cylinder has been measured since July 2007 every 7 h to validate the long-term reproducibility of the measurements.

As explained in Sect. 2.4 an interrupt of the hydrogen supply to the methanizer, if at operational temperature, can have an effect on the measurement performance of the GC. Figure 5 shows the mixing ratio of CO_2 as determined from the target cylinder and the efficiency of the methanizer from September to December 2007 after a power failure at the station on 5 September. The efficiency of the methanizer slowly increases from about 65% to 100% during a period of about two months. A similar effect on the CO measurements was not observed. Because of its much lower mixing ratio no saturation takes place: there is still enough non-oxidized nickel powder left to convert all of the CO molecules to CH_4. The concentration-dependency introduces a non-linearity in the response. When only one reference standard would be available, the accuracy for CO_2 would be off by about 0.8 ppm at a methanizer efficiency of about 65%. Although scatter is observed at a methanizer efficiency of $<$90%, when using two references the measurement performance is still acceptable. Because the recovery of the methanizer (and thus its efficiency change) is slow compared to the measurement rate of the references, and because the effect of the lower efficiency on the CO_2 measurement is to a good approximation linear within the range of the two references, the effect is canceled out when applying Eq. (6). Using only one reference implies the interpolation between that reference value and the origin (i.e. CO_2 mixing ratio = 0), and over this long range the methanizer loss of efficiency clearly is not linear, but shows a kind of saturation behavior.

Figure 6 shows the results for the target cylinder measurements for the period of July 2007 to August 2008. The mixing ratios of the target as determined by calibration with the WMO standards is illustrated by the lines drawn in the middle and is: 379.00 ppm for CO_2, 1859.9 ppb for CH_4, 149.2 ppb for CO, 314.3 ppb for N_2O and 6.06 ppt for SF_6. The lines above and below represent the upper and lower boundaries (1σ standard deviation) of the target based on the measurement precision. Our observed measurement precision was: ±0.06 ppm for CO_2, ±0.8 ppb for CH_4, ±1.7 ppb for CO, ±0.4 ppb for N_2O and ±0.10 ppt for SF_6. The average mixing ratios of the target cylinder and the 1σ standard deviations for this period were found to be: 379.01±0.06 ppm for CO_2, 1860.0±0.9 ppb for CH_4, 148.6±1.8 ppb for CO, 314.3±0.4 ppb for N_2O and 6.03±0.11 ppt for SF_6.

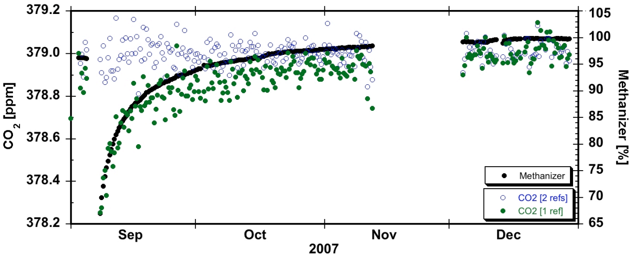

Fig. 5. Efficiency of the methanizer and the CO_2 mixing ratio of a target cylinder using one (open dots) or two reference cylinders. The accuracy and precision are strongly affected when only one reference cylinder is used, but remains acceptable when using two references.

During the period of July 2007 to August 2008, various technical problems were encountered at the station, which is why there are some gaps in the dataset. For example: malfunction of our air-drying apparatus (resulting in wet air getting into the columns), failure of the air compressor which supplies the FID (causing oxidation of the methanizer) and several electrical power failures were encountered. Although the results in Fig. 6 show that accurate and reliable measurements with our GC are still possible under such harsh conditions, the situation was clearly sub-optimal. For a subset of Fig. 6, during optimal conditions we find the following "best case" 1σ standard deviations: ±0.04 ppm for CO_2, ±0.7 ppb for CH_4 and ±0.8 ppb for CO based on the data of the month December 2007, and ±0.3 ppb for N_2O (October and November 2007), and ±0.09 ppt for SF_6 (July and August 2007).

4.2 Ambient measurements

Figure 7 shows the results of the measurements of all five species in ambient samples from the total period of May 2006 to August 2008. The thick line in the plots is a least squares regression fit on data indicated with the highlighted dots. These data represent non-polluted marine background values. In order to get the background mixing ratios we selected only day-time data for which the wind speed was $>$3.5 m s^{-1} and the ^{222}Radon (^{222}Rn) mixing ratio was $<$0.33 Bq m^{-3}. ^{222}Rn is a radioactive noble gas (its radioactive half-life time is 3.8 days) which is produced at a constant rate from ^{226}Radium which is relatively uniformly distributed in all soils. It is measured at our station since September 2005. It can be used as an indicator for background mixing ratios because air has high ^{222}Rn mixing ratios when it has been in close contact for some time with the continental (polluted) surface. With strong atmospheric mixing the air is diluted with air from the free troposphere which contains virtually no ^{222}Rn because most of it has already been decayed. Since water prevents the ^{222}Rn to emanate, air from the clean marine sector will also have very low mixing ratios of ^{222}Rn.

Our two reference standards were available only from August 2006 on, before this period the data was calculated with only one reference standard. This prevents us also to use a quadratic function to calculate the CO and N_2O mixing ratios. Although the lack of a target cylinder for this period prevents us from knowledge about the reliability of the data,

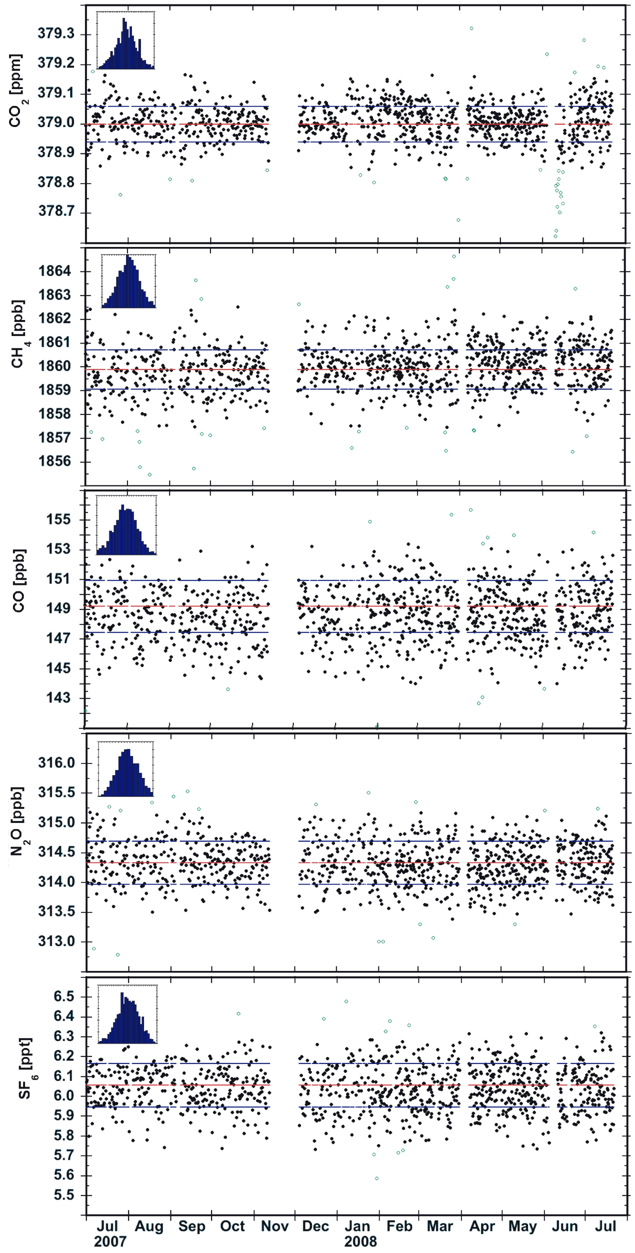

Fig. 6. Target measurements of all measured species for the period of July 2007 to August 2008. The known mixing ratios of the target are illustrated by the lines in the middle and the lines above and below represent the upper and lower boundaries based on the measurement precision. The observed measurement precision was: ±0.06 ppm for CO_2, ±0.8 ppb for CH_4, ±1.7 ppb for CO, ±0.4 ppb for N_2O and ±0.10 ppt for SF_6 for the whole period.

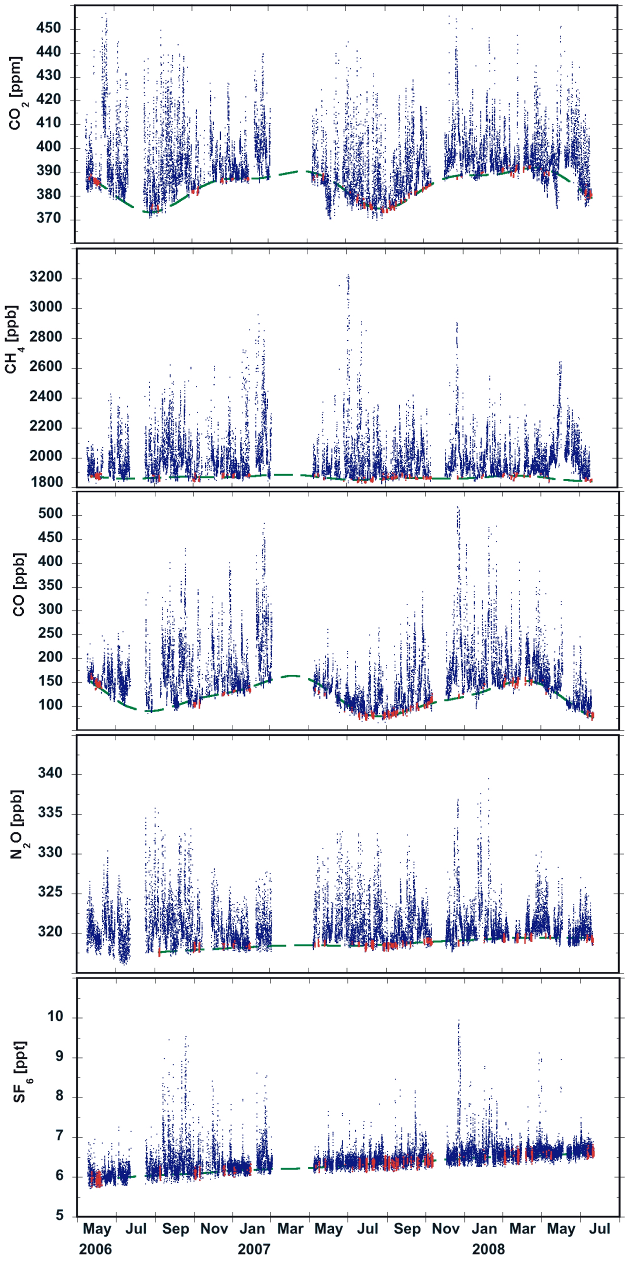

Fig. 7. Ambient mixing ratios of CO_2, CH_4, N_2O, SF_6 and CO measured at Lutjewad, The Netherlands. Average yearly trends were estimated to be: +1.5 ppm for CO_2, −8 ppb for CH_4, −10 ppb for CO, +1.0 ppb for N_2O and +0.3 ppt for SF_6.

most of the data is acceptable. N_2O however, is probably about 1.5 ppb too low. Therefore, the N_2O data before august 2006 are not used for determination of the background mixing ratio. The data for CO are more easily acceptable due to its much larger dynamical range and low relative precision.

Typical diurnal cycles are indicated by the high peaks for all species. These diurnal variations in the mixing ratios are dominantly caused by atmospheric stability, i.e. decreasing of the planetary boundary layer height at nights when turbulent mixing is absent. With northern winds we sample marine background air masses, and with southern winds we sample more polluted continental influenced air. Agriculture is a large source of CH_4 and N_2O emissions in The Netherlands, and many agricultural areas are in the north of the country, where our station is located (Van der Laan et al., 2009). For SF_6 we seem to have a very local source since the highest values are mostly found in the same wind sector (west-south west). For CO_2 the seasonal cycle representing the biospheric activity is clearly present. A seasonal cycle is also visible for CO and to a much less extent (relatively) for CH_4, caused by a strong seasonality in their lifetimes. The average amplitudes of the seasonal cycles for the total period were estimated to be: 7 ppm for CO_2, 11 ppb for CH_4 and 35 ppb for CO. Average annual trends for this period were estimated to be: +1.5 ppm for CO_2, −7.5 ppb for CH_4, −10 ppb for CO, +1 ppb for N_2O and +0.3 ppt for SF_6.

The sudden decline in CO_2 mixing ratio at the beginning of June 2007 is remarkable. This is not an artefact as it is also reported at station Cabauw near Utrecht, in the centre of The Netherlands (A. Vermeulen, personal communication, 2007). A more detailed analysis of our measurements is to follow in another paper.

5 Conclusions

We developed a measurement system based on one single Gas Chromatograph for simultaneously measuring ambient mixing ratios of CO_2, CH_4, N_2O, CO and SF_6 with high precision and accuracy. Our observed measurement precision over a year of observations (including non-optimal conditions) was: ±0.06 ppm for CO_2, ±0.8 ppb for CH_4, ±1.7 ppb for CO, ±0.4 ppb for N_2O and ±0.10 ppt for SF_6. For a shorter but more optimal period we find "best case" 1σ standard deviations of: ±0.04 ppm for CO_2, ±0.7 ppb for CH_4 and ±0.8 ppb for CO, ±0.3 ppb for N_2O and ±0.09 ppt for SF_6.

We have demonstrated that, together with a target cylinder for quality control, only two local reference cylinders are needed for daily routine. Our system has been stable enough to deliver high quality measurements with only one calibration per year against international WMO standards.

The facility is very cost effective: relatively low purchase costs, low in maintenance, and it is designed to operate fully automatically. The system is reliable, easy to operate, can operate autonomously and is able to do several measurements per hour. Our GC has proven its robustness by performing well under harsh conditions (i.e. several power failures). Only taking care for continuous gas supplies and some planned maintenance, our results have demonstrated that GC's can ensure a high measurement precision and accuracy and that they have the advantage of being able to measure multiple components simultaneously.

In total, the system is an ideal solution for measurements at remote and unmanned stations.

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