https://doi.org/10.5194/egusphere-2024-2125
Preprint. Discussion started: 3 September 2024

Simultaneous measurement of greenhouse gases (CH_4, CO_2 and N_2O) at atmospheric levels using a gas chromatography system

Michał Bucha[1], Dominika Lewicka-Szczebak[1], Piotr Wójtowicz[2,3]

[1] Institute of Geological Sciences, University of Wrocław, pl. M. Borna 9, 50-204 Wrocław, Poland
[2] Department of Environmental Engineering, West Pomeranian University of Technology, Piastów 45, 70-311 Szczecin, Poland
[3] Shim-Pol A.M. Borzymowski, Official Shimadzu Distributor in Poland, ul. Kochanowskiego 49A, 01-864 Warszawa, Poland

Correspondence to: Michał Bucha (michał.bucha@uwr.edu.pl)

Abstract. This article presents a simple method for determining greenhouse gases (CH_4, CO_2, N_2O) at ambient atmospheric levels using a chromatographic system. The novelty of the presented method is the application of a Carboxen 1010 PLOT capillary column for separation of trace gases – CH_4, CO_2 and N_2O – from air samples and their detection using a barrier discharge ionisation detector (BID). Simultaneously, a parallel molecular sieve column connected to a thermal conductivity detector (TCD) allowed the determination of CH_4, N_2 and O_2 concentrations from 0.1 to 100 %. The system was equipped with an autosampler transferring the samples without air contamination thanks to a vacuum pump-inert gas flushing option. Method validation was performed using commercial gas standards and undertaking a comparison measurement with a reference method: optical methods applying Picarro isotope and concentration instruments with cavity ring-down spectroscopy for CO_2, CH_4 and N_2O. A three-day continuous measurement series of the lowest GHG concentrations in ambient air and tests of typical vial sample measurements with increased GHG concentrations were performed.

The advantage of this method is that the system is easy to set up and allows for simultaneous detection and analysis of the main GHGs in their ambient concentrations using one GC column and one detector, thereby omitting the need for an electron capture detector (ECD) containing radiogenic components for N_2O analysis and a flame ionisation detector (FID) with a methaniser for low-concentration CO_2 samples. The simplification of the system reduces analytical costs, facilitates instrument maintenance and improves measurement robustness.

1 Introduction

The reduction of greenhouse gas (GHG) emissions caused by human activity presents a major challenge that needs to be addressed in order to limit the effects of global warming. The main GHGs responsible for global warming are CO_2, CH_4 and N_2O (Lamb et al., 2021). Besides natural sources (e.g. volcanic activity, peat bogs, paddy soils, fresh and saltwater sediments etc.), human activity also contributes to increasing GHG emissions by having an impact on global carbon and nitrogen cycling.

Therefore, precise measurement of GHG concentrations from natural sources and the environment is crucial in order to quantify and estimate the contribution of different anthropogenic sources to worldwide emissions. The development of analytical equipment in recent years has allowed the application of user-friendly methods to determine trace gases and monitor slight changes in their concentrations precisely, even at the lowest levels expressed in units ppm and/or ppb (Zaman et al., 2021). In the very near future, it can be expected that analytical devices and their measurement precision will be enhanced further. Therefore, in order to maintain reliable continuity of measurement data on GHG concentrations in the atmosphere and in other elements of the earth's ecosystem, measurements should be performed with the utmost care using the most modern techniques and devices available. It is also important to maintain easy access to simple and relatively cheap analytical devices and their ease of use in order to obtain more statistical data.

Several methods are available for monitoring GHG based on optical techniques such as non-dispersive infrared spectroscopy (NDIR), Fourier-transform infrared spectroscopy (FTIR), photoacoustic spectroscopy (PAS), tunable laser absorption spectroscopy (TLAS), cavity ring-down spectroscopy (CRDS), and off-axis integrated cavity-output spectroscopy (OA-ICOS) (Zaman et al., 2021). Some of these laser instruments allow for simultaneous analyses of CH_4, CO_2, N_2O and NH_3 using the laser absorption spectroscopy method (e.g. Picarro G2509 Gas Concentration Analyzer). Although these devices guarantee the stability of continuous measurements, their measurement range is much lower than chromatographic systems equipped with typical detectors. For example, the Picarro G2509 operation range for CO_2 is 380-6000 ppm, for CH_4 1-800 ppm and for N_2O 0.3-200 ppm. Other versions of Picarro analysers have been developed to measure single GHG concentrations, e.g. of CH_4, CO_2 or N_2O, in combination with analyses of stable isotope composition of carbon or nitrogen from atmospheric air or headspace samples (SSIM module). These methods are recommended only for the measurement of a single gas compound at very specific concentrations. Thus the most reliable methods for checking samples in a very wide range of concentrations are chromatographic methods: gas chromatography and and/or gas chromatography coupled with mass spectrometry (GC-MS) (Ekeberg et al., 2004).

Gas chromatography with automated sampling injections is very common and user friendly. The most common GHG measurement systems have been developed with two detectors: a flame ionisation detector - FID (measurement of CH_4 and CO_2 using a methaniser) and electron capture detector - ECD (for N_2O measurement) (Hedley et al., 2006; Loftfield et al., 1997; Wang and Wang, 2003). Other systems for CH_4 or CO_2 analyses are equipped with a thermal conductivity detector (TCD) connected to, for example, a Carboxen 1010 PLOT column or a FID system equipped with a methaniser (for reduction of CO_2 to CH_4 with H_2 supply). The most popular analytical technique for determining N_2O concentration is gas chromatography equipped with ECD using Porapak Q or Hayesep Q columns (Rapson and Dacres, 2014).

However, the use of an ECD is associated with additional difficulties. The main disadvantage of the ECD is its poor stability over a long period of time. During ongoing analyses, the cell interior may become contaminated and natural wear may occur. This can result in an increasing response to the tested concentrations. Consequently, within a week a significant increase in the measured area may be observed for the same analysed concentrations. This drift can be compensated for by the addition of an internal standard. Moreover, due to the presence of radioactive material in the ECD detector, special safety requirements have

https://doi.org/10.5194/egusphere-2024-2125
Preprint. Discussion started: 3 September 2024

to been taken into account. According to current regulations, the purchase of a new unit, its possession and the disposal of a used detector cell involve a number of formal requirements.

In the case of the dielectric barrier discharge ionisation detector (BID), there are no such limitations and restrictions. The only requirement is to ensure a supply of helium of appropriate purity (99.9999 %). The detector is incredibly stable and maintenance-free for a very long period of time. Application of the BID for N_2O measurements has the advantages of avoiding radiogenic compounds present in the ECD and reducing the number of gases required. Combination of ECD+FID requires installation of minimum 3 gas tanks (carrier gas He, Ar, or N_2; synthetic air; H_2 or H_2 generator; make-up gas for ECD N_2 of 6.0 purity, min. 99.9999%), whereas for BID only He tank is required.

Separation of CH_4, CO_2, and N_2O from one sample can be done using, for example, a system of two columns with 10-port valves (Scion Instruments, 2023) and/or a single column e.g. Micropacked ST Shin Carbon (Shimbo and Uchiyama, 2022) or RT Q-Bond column. Methods using a single-column Micropacked ST Shin Carbon or RT Q-Bond are typically applied by Shimadzu using a GC Nexis 2030 gas chromatograph equipped with a dielectric barrier discharge ionisation detector (BID) dedicated to trace compounds (Shimbo and Uchiyama, 2022). This set-up is commonly used for determination of CH_4 and CO_2 at very low atmospheric concentrations (Gruca-Rokosz et al., 2020), as well as CH_4, CO_2, and N_2O in the system, using FID-BID detectors (Shimbo and Uchiyama, 2022) Unfortunately, the retention times for CO_2 and N_2O are often insufficient for correct measurement, especially by high CO_2 concentrations, when CO_2 tailing can even cover the N_2O peak. This separation can be enhanced by application of cryogenic methods for decreasing oven temperature. However, these methods are time-consuming and expensive. The present study tested an alternative solution that involved the application of Carboxen 1010 PLOT for CH_4, CO_2 and N_2O separation.

A simple chromatographic system is presented here for quick and accurate analysis of GHG using TCD and BID detectors of the GC Nexis 2030 gas chromatograph combined with an SRI autosampler at ambient concentrations observed in the earth's atmosphere. The GC separation columns used in this study were a Carboxen 1010 PLOT and a RT-MSieve 5A, which assured the best separation of the analysed gases. The results of the experimental data were compared with the concentrations obtained for CH_4, CO_2 and N_2O using the CRDS technique by Picarro analysers.

2 Materials and methods

2.1 Gas chromatography system

This chromatographic system was built based on the Shimadzu GC Nexis 2030 equipped with two parallel detectors: BID and TCD. The carrier gas was controlled by an advanced flow controller (AFC) connected to a split/splitless injector. Between the AFC and the injector, a two-position six-port valve with a 1 mL (or 2 mL) sample loop was placed on the carrier line.

https://doi.org/10.5194/egusphere-2024-2125
Preprint. Discussion started: 3 September 2024

The gas chromatograph oven was equipped with an additional cryogenic option (CRG) where LN_2 was used as a cooling agent, which allowed for separation at below-ambient temperatures. The samples from the headspace sampler SRI AS-210 autosampler (SRI Instruments GmbH) were transferred to the sampling valve through a stainless steel transfer line continuously warmed with heating tape to prevent moisture contamination. The presence of moisture in the samples results in loss of sorption capacity of carbon molecular sieves which are used commonly for separation of gases (Fastyn et al., 2003). The injection was performed by valve rotation. The sample was transferred from the loop (1 mL or 2 mL) through the injector at a total flow of 10 mL/min, and was then split 1:7 just before the column inlet. This was sufficient to achieve a good peak shape with sufficient area.

Additionally, using a t-joint, the injection sample was then divided between two columns: a Molecular Sieve 5A 30 m x 0.32 mm and a Carboxen 1010 PLOT 30 m x 0.53 mm. The dimensions of the columns were selected to achieve a splitting ratio of 1:5, directing most of the sample to the Carboxen 1010 PLOT and BID. Corresponding calculations were performed in Shimadzu AFT (Advanced Flow Technology) software.

Extremely low baseline noise was achieved by a combination of two factors: a high purity carrier gas helium grade 5.0 connected to the Valco Helium Purifier HP2 (VICI Valco Instruments Co. Inc.) and particle traps (2.5 m x OD 0.32 mm) mounted on the columns' outlets. The presence of the traps protected the detectors from particles dislodging from the PLOT column, which can cause spikes.

Both the detectors used are concentration dependent; therefore to obtain the highest sensitivity on the BID channel, the discharge gas flow rate was decreased from a default of 50 mL/min to 30 mL/min, which is the lowest possible flow. Below this value the plasma flame is not stable and tends to flicker or extinguish. Detection levels did not need to taken into consideration with the TCD.

2.2 Parameters of the separation and detection methods

The temperature programme for gas chromatography analyses started at 100 °C for 13 minutes, and later increased to 200 °C at a rate of 25 °C/min with the oven set at 200 °C for one minute. The temperature of the split/splitless injector was 120 °C. The TCD and BID detectors were at an equal temperature of 220 °C. The carrier gas pressure was 70 kPa and the column flow was 5.25 mL/min. Linear velocity was 41.2 cm/s and purge flow was 1 mL/min. The total flow for split ratios 1, 2, 3, 4 and 5 was 11.5, 16.8, 22.0, 27.3 and 32.5 mL/min, respectively.

2.3 Standard gas mixtures

Standard gas mixtures used for testing and final determination of the measurements precision were atmospheric air from Wrocław (Poland) (analyses of N_2, O_2, CH_4, CO_2 and N_2O at ambient atmospheric concentrations) and a special gas mixture from Messer (CH_4 10 ppm, CO_2, 1000 ppm, N_2O 50 ppm, diluted in pure N_2). The standards were directly connected by 1/8' capillary to the SRI instrument. The sample loops used for tests of standard gases were 1 mL and 2 mL. The atmospheric air was tested for splits 1, 2, 3, 4 and 5. The special gas mixture from Messer was tested for splits 3, 4 and 5.

3 Results and Discussion

3.1 Basic testing of the SH-Q-BOND and Carboxen 1010 PLOT columns and BID detector

The chromatographic system for GHG analyses using a single BID was initially tested for application of the SH-Q-BOND column (30 m, 0.53 mm ID, 20 um df) from Shimadzu, which allows for detection of CH_4, CO_2 and N_2O, and is resistant to water contamination. Separation of these gases was tested at different low temperatures of the column (30 °C, 35 °C and 40 °C). The lowest temperature (30 °C) was difficult to achieve quickly by the oven without using a cryogenic trap. At the laboratory's normal temperature (22 °C), it was possible to decrease the oven temperature rapidly to 35 °C and 40 °C, but unfortunately both these temperatures were insufficient to separate CO_2 from N_2O at a retention time interval longer than 30 seconds, which appeared very problematic while analysing real samples of elevated CO_2 concentration. When the CO_2 concentration was high (e.g. 700 ppm), the tail of the CO_2 peak partially covered the N_2O peak, as shown below in Figure 1, and ultimately the N_2O peak area was understated. Moreover, this set-up did not allow detection of CH_4 in atmospheric concentrations.

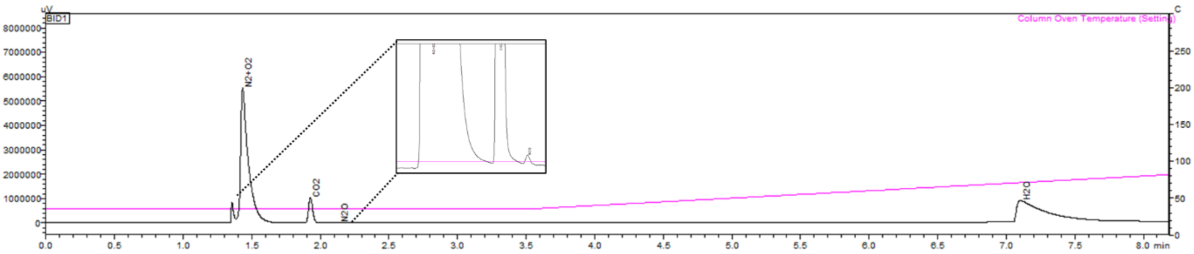

Figure 1: Chromatogram of ambient air gases separated using the SH-Q-BOND column and detected using BID

Therefore, after basic tests of the SH-Q-BOND column at different temperatures, it was decided to check the retention times of individual CH_4, CO_2 and N_2O gases on the Carboxen column. The Carboxen 1010 PLOT column offered very good separation of CO_2 from N_2O, even at a very high concentration (CO_2 1000 ppm), as shown in Figure 2. Moreover, the ambient CH_4 was very well separated from the N_2+O_2 peak (Fig. 2). The longer programme of separation guaranteed the ideal separation of CH_4, CO_2 and N_2O (more than two minutes between each gas). The time of one single analysis is 18 minutes, but this is necessary because a low flow of the carrier gas is recommended for the Carboxen column by its manufacturer. A carrier gas flow that is too high (e.g. above 20 mL/min) causes faster destruction of the column and contamination of the particle trap, and subsequently of the detector, with fragments of the column filling. However, the disadvantage of the application of the Carboxen column is also its low resistance to vapour. Therefore, before starting the analyses, all lines of the SRI autosampler as well as the sample loop were carefully heated using heating tape and a gun heater to remove water from the stainless steel capillaries and metal parts of the valves.

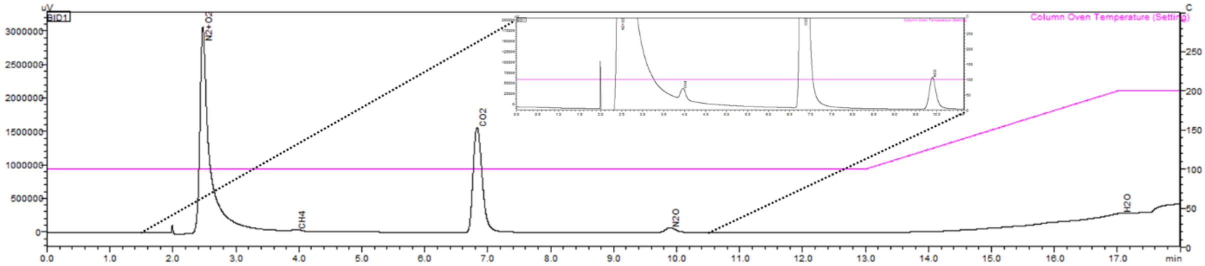

Figure 2: Chromatogram of special gas mixture separated using the Carboxen 1010 column and detected using BID

3.2 Compressed air standard measurements

The analyses of the compressed air standard with split ratios 1, 2, 3, 4 or 5 and using 1 and 2 mL sample loops showed a different precision, expressed as a coefficient of variation (CV: calculated as the standard deviation divided by the mean value, expressed in %). The CV of the CH_4 measurement (mean = 1.895 ppm) was in the range of 3.31 to 8.57 % for the 1 mL sample loop and 1.51 to 2.76 % for the 2 mL sample loop. In the case of CO_2 (mean = 411 ppm), the CV ranged from 0.91 to 2.83 % for the 1 mL sample loop and from 1.42 to 1.87 % for the 2 mL sample loop. The CV of the N_2O measurement was significantly lower for the 2 mL sample loop, and ranged from 2.76 to 12.67 %, compared with the 1 mL sample loop where the CV of the N_2O measurement ranged from 9.15 to 20.19 %. Generally, it was observed that gases at low detection limits (CH_4, CO_2) were measured more precisely using the 2 mL sample loop.

Measurement of N_2O in split ratio 3 resulted in a significantly higher CV when compared with the results obtained in split ratios 4 and 5 (Table 1). This is because the injection of a higher amount of vapour contained in the sample covered the peak area of the N_2O (by increasing the baseline level), similarly to the measurement in split ratio 2 (CV 20.19 %). In this case the lower CV at split ratio 1 was only calculated for three measurements to avoid contamination of the column.

The gases analysed using the TCD detector, O_2 and N_2, were characterised by a narrow CV ranging from 0.10 to 0.39 %. The highest CV (0.39 %) was observed for the N_2 measurement with the sample loop 2 mL, where the peak area was very large. The results of the measurement (peak area, SD, CV) are presented in Table 1.

Table 1: Peak area, SD (standard deviation) and CV (coefficient of variation) of standard atmospheric gas measurements at split ratios 1, 2, 3, 4, and 5 with 1 mL and 2 mL sample loops

			Sample loop 1 mL					Sample loop 2 mL		
Gas	Conc.		Split					Split		
			1	2	3	4	5	3	4	5
		Repetitions	n=3	n=10	n=20	n=20	n=20	n=10	n=20	n=10
CH_4	1.895 ppm	Area	33294	24249	25271	20085	16269	25535	23758	23195
		SD	0.15	0.06	0.11	0.13	0.16	0.03	0.04	0.05
		CV [%}	7.75	3.31	5.95	6.79	8.57	1.51	2.49	2.76
CO_2	411 ppm	Area	10900323	8015901	5742835	4525868	3658827	10274295	6900992	6295494
		SD	3.74	4.32	11.61	5.32	8.88	6.24	5.84	7.69
		CV [%}	0.91	1.05	2.83	1.29	2.16	1.52	1.42	1.87
N_2O	339 ppb	Area	7801	4732	3572	2565	2080	5565	4610	3306
		SD	0.03	0.07	0.05	0.04	0.05	0.04	0.01	0.03
		CV [%}	9.15	20.19	15.51	10.14	13.46	12.67	2.76	9.95
O_2	20.946%	Area	4317080	3030077	2147582	1660466	1340040	12767184	3322830	2523219
		SD	0.04	0.04	0.07	0.05	0.03	0.08	0.02	0.06
		CV [%}	0.21	0.17	0.33	0.25	0.16	0.10	0.11	0.30
N_2	78.084%	Area	16522678	11587989	8205177	6343410	5119796	17338000	12684872	9709091
		SD	0.20	0.15	0.26	0.20	0.13	0.12	0.10	0.31
		CV [%}	0.26	0.19	0.33	0.26	0.16	0.15	0.13	0.39

The main atmospheric gases had the lowest SD for split ratio 5 – more than three times better precision than for split ratio 3. It was observed that in split ratios 1-3, the baseline was noised by vapour from the gas samples, and therefore the standard deviation was higher. The increasing dilution of the sample reduces the amount of water vapour entering the chromatography column, and hence the measurement is more accurate. However, if the sample is diluted too much, the amount of N_2O will not be sufficient for precise measurement or N_2O will be below the detection limit. The present results showed that with split ratio 4, the amount of gas in the column was sufficient to detect CH_4, CO_2 and N_2O at atmospheric levels and obtain satisfactory measurement precision.

3.2 Standard gas mixture measurements

The CH_4, CO_2 and N_2O measurements of the special gas mixture standard at split ratios 3, 4 and 5 were characterised by a repeatable CV within a narrow range from 0.11 to 3.22 %. The CV of the CH_4 measurement (10 ppm) using the 1 mL sample loop ranged from 0.11 to 0.55 %, while for the 2 mL sample loop the CV was in the range of 0.34 to 1.79 %. The CV of CO_2 (1000 ppm) for the 1 mL sample loop was between 2.05 and 3.08 % and for the 2 mL sample loop between 1.57 and 3.22 %.

The N_2O measurement (50 ppm), which is a very high concentration (rare in the natural environment), was characterised by a CV in the range of between 0.18 and 0.44 % for the 1 mL sample loop and 0.85 to 2.14 % for the 2 mL sample loop. These values clearly show that measurements of the gas mixtures with relatively high concentrations of N_2O using BID were repeatable for all splits 3, 4 and 5, and were slightly better using the 1 mL sample loop. However, the application of the sample loops (1 and 2 mL) at split ratios 3, 4 and 5 guaranteed the achievement of reportable results. Table 2 shows all the data of the standard gas mixture testing measurements.

Table 2: Peak area, SD (standard deviation) and CV (coefficient of variation) of special gas mixture measurements at split ratios 3, 4, and 5 with sample loops 1 mL and 2 mL

			Sample loop 1 mL			**Sample loop 2 mL**		
Gas	**Conc.**		**Split**			**Split**		
			3	**4**	**5**	**3**	**4**	**5**
		Repetitions	**n=5**	**n=4**	**n=3**	**n=10**	**n=10**	**n=10**
CH_4	**10 ppm**	**Area**	149922	118357	96007	278296	207227	161265
		SD	0.06	0.01	0.03	0.04	0.03	0.18
		CV [%]	0.55	0.11	0.33	0.38	0.34	1.79
CO_2	**1000 ppm**	**Area**	13522596	11079679	8993195	21485425	17323467	13525917
		SD	24.54	30,81	20.47	15.72	19.14	32.19
		CV [%]	2.43	3.08	2.05	1.57	1.91	3.22
N_2O	**50 ppm**	**Area**	629251	497331	402025	1171624	867747	669861
		SD	0.22	0.18	0.09	0.43	0.66	1.07
		CV [%]	0.44	0.36	0.18	0.85	1.33	2.14

3.4 Direct measurement of ambient laboratory air using the SRI autosampler

Another testing of the GC system was carried out with the application of splits 3, 4 and 5 and sample loop 2 ml (Table 3). The ambient air from the laboratory on one day was analysed directly from the SRI autosampler (empty plate for vials, which enabled direct sampling of the ambient air from the needle to the line connected with the GC's sample loop). The tests were performed with splits 3, 4 and 5 (splits 1 and 2 were omitted to avoid excessive introduction of air containing natural moisture into the Carboxen column).

The CV of CH_4 was in the range of 3.40 to 7.44 % (the highest value for split 5). The CV of CO_2 was in range of 1.31 to 2.29 %, whereas for N_2O it was between 3.11 and 7.70 %. These CV values are close to the results obtained during measurements of the compressed air standard (Section 3.3, Table 1). The difference between the two experiments is that compressed air always had the same composition and gas concentrations, whereas the CH_4 and CO_2 concentrations in ambient air could change slightly over time (daily variability).

Table 3: Peak area, SD (standard deviation) and CV (coefficient of variation) of direct measurements of laboratory air at split ratios 3, 4, and 5 with sample loop 2 mL

			Sample loop 2 mL		
Gas	Conc.		Split		
			3	4	5
		Repetitions	n=20	n=20	n=20
CH_4	1.895 ppm	Area	27007	24994	23355
		SD	0.06	0.08	0.14
		CV [%]	3.40	4.19	7.44
CO_2	411 ppm	Area	8297069	6787524	5351342
		SD	9.43	5.43	7.49
		CV [%]	2.29	1.31	1.82
N_2O	339 ppb	Area	12589404	4479	3359
		SD	26.10	10.53	11.23
		CV [%]	7.70	3.11	3.31
O_2	20.946%	Area	4466737	3319922	2493245
		SD	0.03	0.03	0.04
		CV [%]	0.14	0.13	0.17
N_2	78.084%	Area	17054807	12671953	9517713
		SD	0.11	0.09	0.13
		CV [%]	0.14	0.12	0.16

3.5 Experimental measurement series comparing the GC results with the reference method (Picarro analyser)

To verify the long-term stability of the measurements and the system performance for real samples, a 55-hour-long measurement series of ambient laboratory air was performed. The subsequent air samples were measured in parallel with the GC setup and with the optical instruments dedicated to analyses of GHG concentrations and isotopic signatures (Picarro G5131-i for isotopic N_2O and Picarro G2201-i for CO_2 and CH_4) (Picarro, Santa Clara, USA). The reference methods were applied to check whether slight changes in GHG concentrations over the day/night period can be monitored well with this GC system. The reference instruments – isotopic Picarro – showed a quite narrow range of possible concentration measurements (Picarro G5131-i isotopic N_2O up to 2000 ppb, Picarro G2201-i up to 2000 ppm CO_2 and up to 12 ppm CH_4) but a very high precision for ambient concentrations, without the need for calibration. Therefore they served here as an ideal reference method.

During this 55-hour time series, the Picarro measurement was performed every three minutes and the GC measurement every 19 minutes. For GC measurements, split 4 was applied. The concentration trends for CO_2 and CH_4 were observed to be generally in good agreement and the N_2O concentration was very stable (Fig. 3). Importantly, it was observed for CO_2 that after 24 hours the measurements were slightly recalibrated and shifted in relation to the reference method. This indicates the need for repeated calibration at least every 24 hours, especially for CO_2. However, even without recalibration, the maximum difference between the GC measurement and the reference value was below 3 % for both CO_2 and CH_4. The largest variations in the GC results were observed for N_2O, especially when comparing them to the very stable Picarro measurements. This is the most challenging analysis, since N_2O ambient concentrations are lowest and hardest to measure correctly. The maximum difference between the GC measurement and the reference value for N_2O was around 8 % and the standard deviation of GC measurements was 15 ppb, which represents a 4.4 % error. This is quite high when compared with Picarro statistics where the standard deviation over 55 hours of measurement was 0.24 ppb, which represents less than 0.1 % error. However, for typical N_2O measurements with GC techniques, a 5 % error is a satisfactory result, typically given as an accepted GC measurement error in research studies (Arnold et al., 2001; Harvey et al., 2020). The precision obtained for ambient air measurements is similar for CO_2 and CH_4 compared with classical FID measurements, with an error of around 2 % (Loftfield et al., 1997), but is lower when compared with ECD measurements, for which a 1.2 % error has been reported (Loftfield et al., 1997). Usually systems that enable the simultaneous measurement of CH_4 and CO_2 are very accurate, but the main limitation is the upper detection limit. For example, Wang and Wang (2003) achieved a CH_4 precision error in a range from 3.37 % (ambient concentration) to 0.05 % (60 ppm), or for CO_2 from 0.66 % (ambient concentration) to 0.04 % (4000 ppm). In the present system, higher concentrations of CH_4 can be measured by the TCD detector simply using a Molecular Sieve 5A column. The chromatographic system can be improved by the addition of a second gas valve aimed at transferring CO_2 to the TCD detector after separation using the Carboxen column. This would allow further improvement of this chromatographic system for the maximum range of measured GHG concentrations.

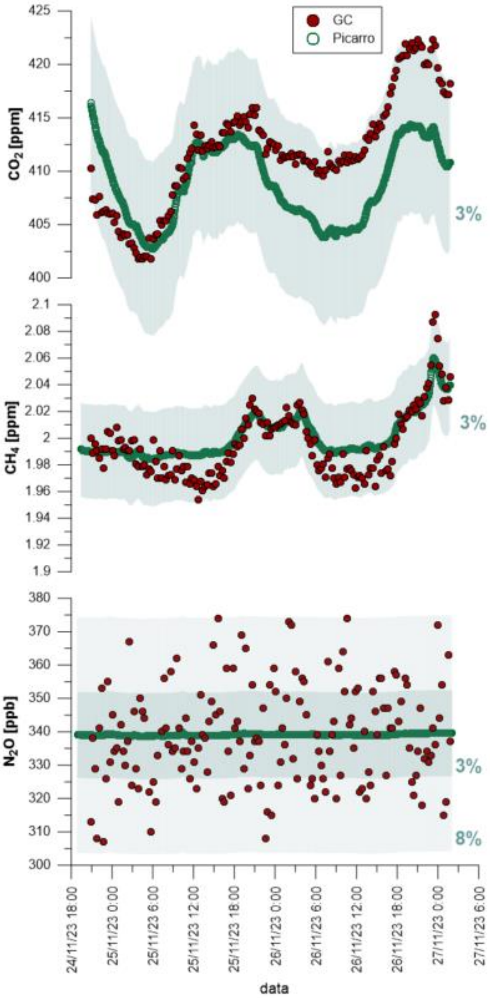

Figure 3: Comparison of CH_4, CO_2 and N_2O variations in ambient air measured using a Picarro analyser and the GC system

3. Conclusions

This article outlined a simple method for determination of CH_4, CO_2 and N_2O concentrations from ambient air. The main advantage is that the use of three separate detectors can be avoided, including the ECD detector that contains radioactive materials. A single column Carboxen 1010 PLOT can be successfully used for very good separation of ambient GHG, and in parallel a connected MSieve column allows for determination of higher CH_4 concentrations as well control of the O_2 and N_2 concentrations in the sample. The main disadvantage of the method is the lack of direct measurement of samples with high CO_2 concentrations (above 4000 ppm) in the set-up presented here, which is the upper detection limit for the BID. Further reconstruction with an additional valve directing the separated CO_2 to the TCD as well would allow additional analyses of higher CO_2 concentrations.

Based on these tests, it is recommended that atmospheric GHGs are analysed using a BID at split ratio 4 or 5 and with a sample loop of 2 mL volume. This would help avoid unnecessary contamination of the Carboxen column with vapour, therefore splits 1-3 should not be considered for the measurement of environmental gas samples. In this chromatography system, the CV of N_2O measurement at atmospheric level was near 10 % (sample loop 1 mL), or even around 3 % (when using the 2 mL sample loop), CV of CH_4 measurement at atmospheric level was near 7 % (sample loop 1 mL), or even below 3 % (when using the 2 mL sample loop), CV of CO_2 measurement at atmospheric level was near 2 % (sample loop 1 mL), or even around 1.5 % (when using the 2 mL sample loop). The diurnal variations for CO_2 and CH_4 can be monitored well with the precision below 3% error, whereas for N_2O measurements 8% error should be taken into account.

Authors contributions:

MB and DLS planned the campaign; MB, DLS and PW performed the measurements; MB and DLS analyzed the data; MB, DLS, and PW wrote the manuscript draft; MB, DLS and PW reviewed and edited the manuscript.

Competing interests:

The authors declare that they have no conflict of interest.

Funding:

This study was financially supported by the "Polish Returns" programme of the Polish National Agency of Academic Exchange and the grant Opus No. 2021/41/B/ST10/01045 funded of the National Science Centre Poland.

References

Arnold, S.L., Parkin, T.B., Doran, J.W., Eghball, B., Mosier, A.R., 2001. Automated gas sampling system for laboratory analysis of CH4 and N2O. Commun. Soil Sci. Plant Anal. 32, 2795–2807. https://doi.org/10.1081/CSS-120000962

Ekeberg, D., Ogner, G., Fongen, M., Joner, E.J., Wickstrøm, T., 2004. Determination of CH4, CO2 and N2O in air samples and soil atmosphere by gas chromatography mass spectrometry, GC-MS. J. Environ. Monit. 6, 621–623. https://doi.org/10.1039/b401315h

Fastyn, P., Kornacki, W., Kardaś, M., Gawlowski, J., Niedzielski, J., 2003. Adsorption of water vapour from humid air in carbon molecular sieves: Carbosieve S-III and Carboxens 569, 1000 and 1001. Analyst 128, 198–203. https://doi.org/10.1039/b209296d

Gruca-Rokosz, R., Szal, D., Bartoszek, L., Pękala, A., 2020. Isotopic evidence for vertical diversification of methane production pathways in freshwater sediments of Nielisz reservoir (Poland). Catena 195, 104803. https://doi.org/10.1016/j.catena.2020.104803

Harvey, M.J., Sperlich, P., Clough, T.J., Kelliher, F.M., McGeough, K.L., Martin, R.J., Moss, R., 2020. Global Research

Alliance N2O chamber methodology guidelines: Recommendations for air sample collection, storage, and analysis. J. Environ. Qual. 49, 1110–1125. https://doi.org/10.1002/jeq2.20129

Hedley, C., Saggar, S., Tate, K., 2006. Procedure for fast simultaneous analysis of the greenhouse gases: Methane, carbon dioxide, and nitrous oxide in air samples. Commun. Soil Sci. Plant Anal. 37, 1501–1510. https://doi.org/10.1080/00103620600709928

Lamb, W.F., Wiedmann, T., Pongratz, J., Andrew, R., Crippa, M., Olivier, J.G.J., Wiedenhofer, D., Mattioli, G., Khourdajie, A. Al, House, J., Pachauri, S., Figueroa, M., Saheb, Y., Slade, R., Hubacek, K., Sun, L., Ribeiro, S.K., Khennas, S., De La Rue Du Can, S., Chapungu, L., Davis, S.J., Bashmakov, I., Dai, H., Dhakal, S., Tan, X., Geng, Y., Gu, B., Minx, J., 2021. A review of trends and drivers of greenhouse gas emissions by sector from 1990 to 2018. Environ. Res. Lett. 16. https://doi.org/10.1088/1748-9326/abee4e

Loftfield, N., Flessa, H., Augustin, J., Beese, F., 1997. Automated Gas Chromatographic System for Rapid Analysis of the Atmospheric Trace Gases Methane, Carbon Dioxide, and Nitrous Oxide. J. Environ. Qual. 26, 560–564. https://doi.org/10.2134/jeq1997.00472425002600020030x

Rapson, T.D., Dacres, H., 2014. Analytical techniques for measuring nitrous oxide. TrAC - Trends Anal. Chem. 54, 65–74. https://doi.org/10.1016/j.trac.2013.11.004

Scion Instruments, 2023. Analysis of Greenhouse Gas by Gas Chromatography.

Shimbo, E., Uchiyama, S., 2022. Application News: Simultaneous Analysis of Three Greenhouse Gas Components, CH4, CO2, and N2O.

Wang, Yuesi, Wang, Yinghong, 2003. Emissions from a Short-Plant Ecosystem. Adv. Atmos. Sci. 20, 842–844.

Zaman, M., Heng, L., Müller, C., 2021. Measuring emission of agricultural greenhouse gases and developing mitigation options using nuclear and related techniques: Applications of nuclear techniques for GHGs, Measuring Emission of Agricultural Greenhouse Gases and Developing Mitigation Options using Nuclear and Related Techniques: Applications of Nuclear Techniques for GHGs. https://doi.org/10.1007/978-3-030-55396-8