



Simultaneous measurement of greenhouse gases (CH₄, CO₂ and N₂O) using a simplified gas chromatography system

Michał Bucha¹, Dominika Lewicka-Szczebak¹, and Piotr Wójtowicz^{2,3}

¹Institute of Geological Sciences, University of Wrocław, pl. M. Borna 9, 50-204 Wrocław, Poland

²Department of Environmental Engineering, West Pomeranian University of Technology, Piastów 45, 70-311 Szczecin, Poland

³Shim-Pol A.M. Borzymowski, Official Shimadzu Distributor in Poland, ul. Kochanowskiego 49A, 01-864 Warsaw, Poland

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

Received: 9 July 2024 – Discussion started: 3 September 2024

Revised: 13 December 2024 – Accepted: 19 December 2024 – Published: 25 February 2025

Abstract. This article presents a simple method for determining greenhouse gases (CH₄, CO₂ and N₂O) using an alternative new set-up of the chromatographic system. The novelty of the presented method is the application of a Carboxen 1010 PLOT capillary column for separation of trace gases – CH₄, CO₂ and N₂O – from air samples and their detection using a barrier discharge ionisation detector (BID). Simultaneously, a parallel molecular sieve column RT-Msieve 5A connected to a thermal conductivity detector (TCD) allowed the determination of CH₄, N₂ and O₂ concentrations from 0.2 % to 100 %. The system was equipped with an autosampler transferring the samples without air contamination thanks to a vacuum pump and inert gas flushing. Method validation was performed using commercial gas standards and comparative measurement of CO₂, CH₄ and N₂O concentrations applying cavity ring-down spectroscopy (CRDS). A 3 d continuous measurement series of greenhouse gas (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 using one gas chromatography (GC) column and one detector, thereby omitting the need for an electron capture detector (ECD) containing radiogenic components for N₂O analysis and a flame ionisation detector (FID) with a methaniser for low-concentration CO₂ 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 CO₂, CH₄ and N₂O (Lamb et al., 2021). Besides natural sources (e.g. volcanic activity, peat bogs, paddy soils, and freshwater and saltwater sediments), 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 of parts per million (ppm) and/or parts per billion (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. Often the analytical devices providing very precise measurements have limitations in the analytical range and do not allow for observations of GHGs in a wide range of concentrations observed in nature. Therefore, the development of a new analytical method that is characterised by relatively high sensitivity in the range from the lowest to the highest concentrations is a desirable feature but quite difficult to achieve in a single device.

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 CH₄, CO₂, N₂O and NH₃ using the laser absorption spectroscopy method (e.g. Picarro G2509 gas concentration analyser). 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 CO₂ is 380–6000 ppm, for CH₄ it is 1–800 ppm and for N₂O it is 0.3–200 ppm. Other versions of Picarro analysers have been developed to measure single-GHG concentrations, e.g. of CH₄, CO₂ or N₂O, 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 GHGs measurements in a very wide range of concentrations are chromatographic methods (Ekeberg et al., 2004). Another important limitation of the laser-based system is the sample matrix, which should be stable and most similar to standard ambient air composition. Hence, these methods are not well suited for untypical gas samples, like mine gases, or samples originating from laboratory experiments, e.g. with a He atmosphere.

Gas chromatography with automated sampling injections is a very common, flexible and user-friendly technique. The most common GHG measurement systems have been developed with a thermal conductivity detector (TCD; measurement of CH₄ and CO₂), flame ionisation detector (FID; measurement of CH₄ and CO₂ using a methaniser) and electron capture detector (ECD; measurement of N₂O) (Hedley et al., 2006; Loftfield et al., 1997; Wang and Wang, 2003). The gas chromatography (GC) systems can be dedicated for specific gases at ambient concentrations with precision similar to or even better than that achieved by optical techniques. Van der Laan et al. (2009) developed the GC system which allows for simultaneous measurement of CH₄, CO₂, N₂O, CO and SF₆

using one gas chromatograph and single injection that allows the measurement of GHGs from ambient air at remote stations. However, the system is characterised by a quite complex set-up with multiple gas valves, columns, a methaniser, a ECD and a FID.

The most popular analytical technique for determining N₂O 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, special safety requirements have to be 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 N₂O 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 a minimum of three gas tanks (carrier gas He, Ar, or N₂; synthetic air; H₂ or H₂ generator; make-up gas for ECD N₂ of 6.0 purity, min. 99.9999 %), whereas for BID only a He tank is required.

Separation of CH₄, CO₂ and N₂O from one sample can be done using, for example, a system of two columns with 10-port valves (Scion Instruments, 2023) or a single column, e.g. a micropacked ShinCarbon ST or RT-Q-Bond column (Shimbo and Uchiyama, 2022). Methods using a single-column micropacked ShinCarbon ST or RT-Q-Bond are typically applied by Shimadzu using a Nexis GC-2030 gas chromatograph equipped with a dielectric barrier discharge ionisation detector (BID) dedicated to trace compounds (Shimbo and Uchiyama, 2022). This set-up using a single column and single BID detector is commonly used for determination of CH₄ and CO₂ at very low atmospheric concentrations (Gruca-Rokosz et al., 2020). Unfortunately, the retention times for CO₂ and N₂O are often insufficient for correct measurement, especially by high CO₂ concentrations, when CO₂ tailing can even cover the N₂O 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 a Car-

boxen 1010 PLOT column for CH₄, CO₂ and N₂O separation.

A simple chromatographic system is presented here for a quick and accurate analysis of GHG using the TCD and BID of the Nexis GC-2030 gas chromatograph combined with an AS-210 greenhouse gas autosampler (SRI Instruments Europe GmbH, Bad Honnef, Germany) at a wide range of concentrations from ambient to higher fluxes observed for different emission sources.

The GC separation columns used in this study were performed with a porous layer open tubular column (Carboxen 1010 PLOT) and a molecular sieve column (RT-MSieve 5A), which assured the full separation of the analysed gases. The results of the experimental data were compared with the concentrations obtained for CH₄, CO₂ and N₂O using the CRDS technique by Picarro analysers (G2201-i for CO₂ and CH₄; G5131-i for N₂O).

2 Materials and methods

2.1 Gas chromatography system

This chromatographic system was built based on the Shimadzu Nexis GC-2030 equipped with two parallel detectors: BID and TCD (Fig. 1). 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.

The gas chromatograph oven was equipped with an additional cryogenic option (CRG) where liquid nitrogen (LN₂) was used as a cooling agent, which allowed for separation at below-ambient temperatures. The samples from the AS-210 greenhouse gas autosampler (SRI Instruments Europe GmbH) were transferred to the sampling valve through a stainless-steel transfer line continuously warmed to 110 °C with heating tape to prevent moisture contamination. The presence of moisture in the samples results in the 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 or 2 mL) through the injector at a total flow of 10 mL min⁻¹ and was then split 1 : 7 just before the column inlet. This was sufficient to achieve a good peak shape with sufficient area.

Additionally, the injection sample was then divided with using a T-joint connector between two porous layer open tubular capillary columns filled molecular sieve 5A (RT-MSieve 5A 30 m × 0.32 mm × 30 μm; Restek, USA, catalogue no. 19722) and fused silica (Carboxen 1010 PLOT 30 m × 0.53 mm × 30 μm; Supelco, USA, catalogue no. 25467). 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 (Fig. 2).

Extremely low baseline noise (signal-to-noise ratio (S/N) always above 10) was achieved by a combination of two factors: a high-purity carrier gas helium of grade 5.0 connected to the Valco helium purifier HP2 (VICI, Valco Instruments Co. Inc.) and particle traps (2.5 m × 0.32 mm o.d.) mounted on the columns' outlets. The presence of the traps protected the detectors from particles dislodging from the porous layer open tubular (PLOT) capillary column, which can cause spikes.

Both of 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 to 30 mL min⁻¹, which is the lowest possible flow. Below this value the plasma flame is not stable and tends to flicker or is extinguished. Detection levels did not need to be taken into consideration with the TCD.

The linearity of both detectors' response was controlled and maintained during all the measurements with minimal $R^2 = 0.99$ applying at least two standard gases and zero point.

2.2 Parameters of the separation and detection methods

The temperature programme for gas chromatography analyses started at 100 °C for 13 min and later increased to 200 °C at a rate of 25 °C min⁻¹ with the oven set at 200 °C for 1 min. The temperature of the split/splitless injector was 120 °C. The TCD and BID were at an equal temperature of 220 °C. The carrier gas pressure was 70 kPa and the column flow was 5.3 mL min⁻¹. Linear velocity was 41.2 cm s⁻¹ and purge flow was 1 mL min⁻¹. 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⁻¹, 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 N₂, O₂, CH₄, CO₂ and N₂O at ambient atmospheric concentrations) and a special gas mixture from Messer (CH₄ 10 ppm, CO₂ 1000 ppm, N₂O 50 ppm, diluted in pure N₂). The in-house standard of compressed air from Wrocław (Poland), which contained natural moisture (water vapour), was stored in the 10 L gas cylinder. It was prepared using an oil-free compressor for diving cylinders. The second standard was ordered for Messer Polska Sp. z o.o. and is the commercial product prepared in Switzerland according to ISO6141:2015. This standard was prepared in pure N₂, without moisture, and in a volume of 8 L, and it contains an F10 filter, which protects the outer valve from the possible water vapour or solid particles. The standards were directly connected by a 1/8 in. capillary to the AS-210

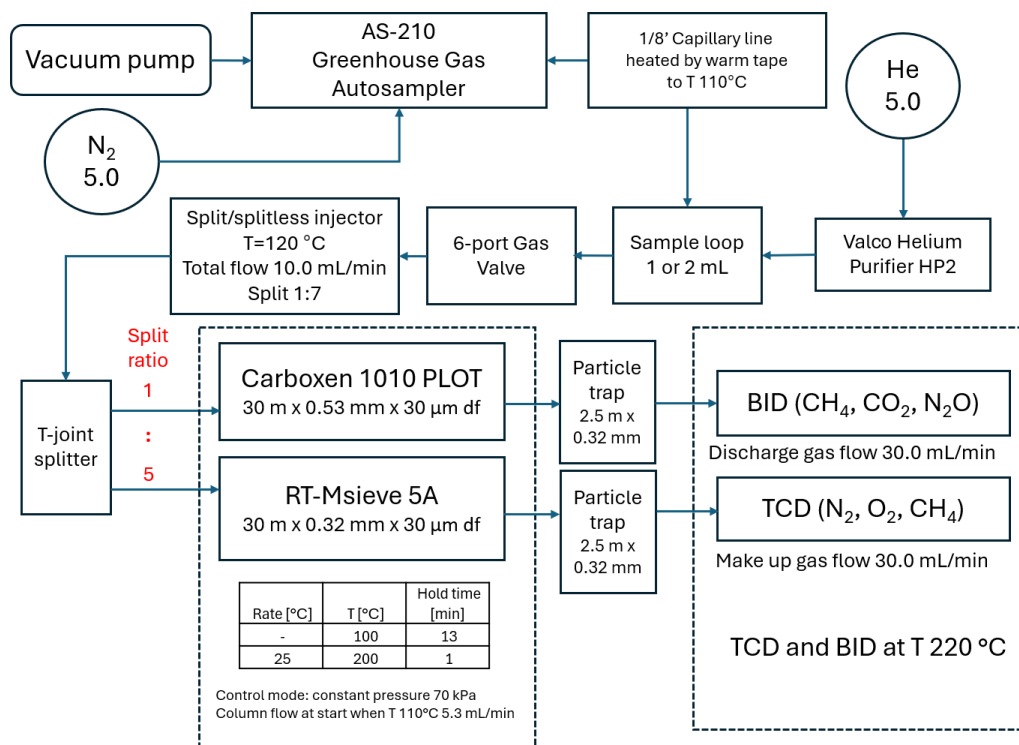


Figure 1. Configuration of the GC system for measurement of CH_4 , CO_2 and N_2O .

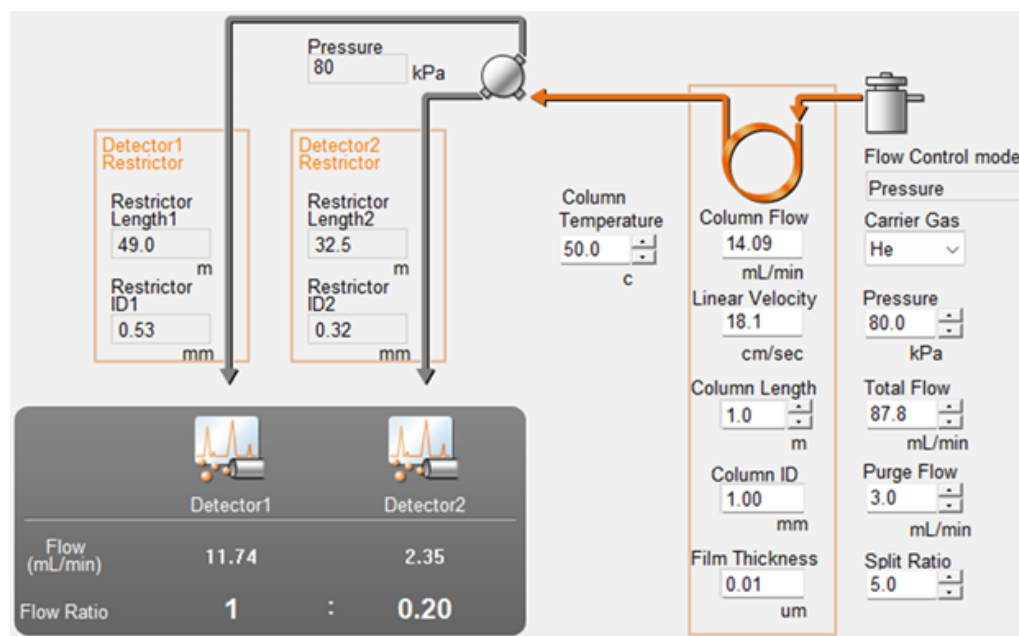


Figure 2. Detailed flow parameters in GC system configuration.

greenhouse gas autosampler. The sample loops used for tests of standard gases were 1 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.

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 and 2 mL sample loops.

Gas	Conc.		1 mL sample loop					2 mL sample loop		
			Split					Split		
			1	2	3	4	5	3	4	5
		Repetitions	<i>n</i> = 3	<i>n</i> = 10	<i>n</i> = 20	<i>n</i> = 20	<i>n</i> = 20	<i>n</i> = 10	<i>n</i> = 20	<i>n</i> = 10
CH ₄	1.895 ppm	Area	33 294	24 249	25 271	20 085	16 269	25 535	23 758	23 195
		SD	2580	802	1859	1365	1394	386	381	640
		CV [%]	7.75	3.31	5.95	6.79	8.57	1.51	1.59	2.76
CO ₂	411 ppm	Area	10 900 323	8 015 901	5 742 835	4 525 868	3 658 827	10 274 295	6 900 992	6 295 494
		SD	99 092	84 289	162 281	58 578	79 062	155 997	45 587	117 747
		CV [%]	0.91	1.05	2.83	1.29	2.16	1.52	0.57	1.87
N ₂ O	339 ppb	Area	7801	4732	3572	2565	2080	5565	4610	3306
		SD	714	955	554	289	323	705	317	329
		CV [%]	9.15	20.19	15.51	11.26	15.55	12.67	7.09	9.95
O ₂	20.946 %	Area	4 317 080	3 030 077	2 147 582	1 660 466	1 340 040	4 513 907	3 322 830	2 523 219
		SD	9241	5136	7177	4196	2088	10 598	3298	7454
		CV [%]	0.21	0.17	0.33	0.25	0.16	0.23	0.11	0.30
N ₂	78.084 %	Area	1 652 2678	11 587 989	8 205 177	6 343 410	5 119 796	17 338 000	12 684 872	9 709 091
		SD	42 456	21 960	27 025	16 376	8251	31 998	12 603	38 248
		CV [%]	0.26	0.19	0.33	0.26	0.16	0.15	0.13	0.39

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 i.d. × 20 μm df; catalogue no. 221-75765-30) from Shimadzu, which allows for separation of CH₄, CO₂ and N₂O and is resistant to water vapour contamination. The scheme showing the GC configuration for testing of SH-Q-BOND and RT-Msieve 5A is presented in Appendix A (Fig. A1). In this configuration most of the parameters were exactly the same (length of the column, diameter, film thickness, flow parameters, split ratio) as in the configuration using the Carboxen 1010 PLOT column. The only differences were the usage of a SH-Q-BOND column for separation of CH₄, CO₂, and N₂O and a different column oven temperature programme.

Separation of these gases was tested at different low temperatures of the column oven (30, 35 and 40 °C). The lowest temperature (30 °C) was difficult for the oven to achieve quickly without using a cryogenic trap. At the laboratory's normal temperature (22 °C), it was possible to decrease the oven temperature rapidly to 35 and 40 °C, but unfortunately both temperatures were insufficient to separate CO₂ from N₂O at a retention time interval longer than 30 s, which appeared very problematic while analysing real samples of elevated CO₂ concentration. When the CO₂ concentration was

high (e.g. 700 ppm), the tail of the CO₂ peak partially covered the N₂O peak, as shown below in Fig. 3a and b, and ultimately the N₂O peak area was understated. Moreover, this set-up did not allow detection of CH₄ in atmospheric concentrations.

Therefore, after basic tests of the SH-Q-BOND column at different temperatures, it was decided to check the retention times of individual CH₄, CO₂ and N₂O gases on the Carboxen 1010 PLOT column. The Carboxen 1010 PLOT column offered very good separation of CO₂ from N₂O, even at a very high concentration (CO₂ 1000 ppm), as shown in Fig. 4 (peaks of CH₄ and N₂O are visible only when zoomed). Moreover, the ambient CH₄ was very well separated from the N₂+O₂ peak (Fig. 4). The longer programme of separation guaranteed the ideal separation of CH₄, CO₂ and N₂O (more than 2 min between each gas). The time for one single analysis is 18 min, 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⁻¹) 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 water vapour. Therefore, before starting the analyses, all lines of the AS-210 greenhouse gas 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. The parallelly connected column Rt-Msieve 5A

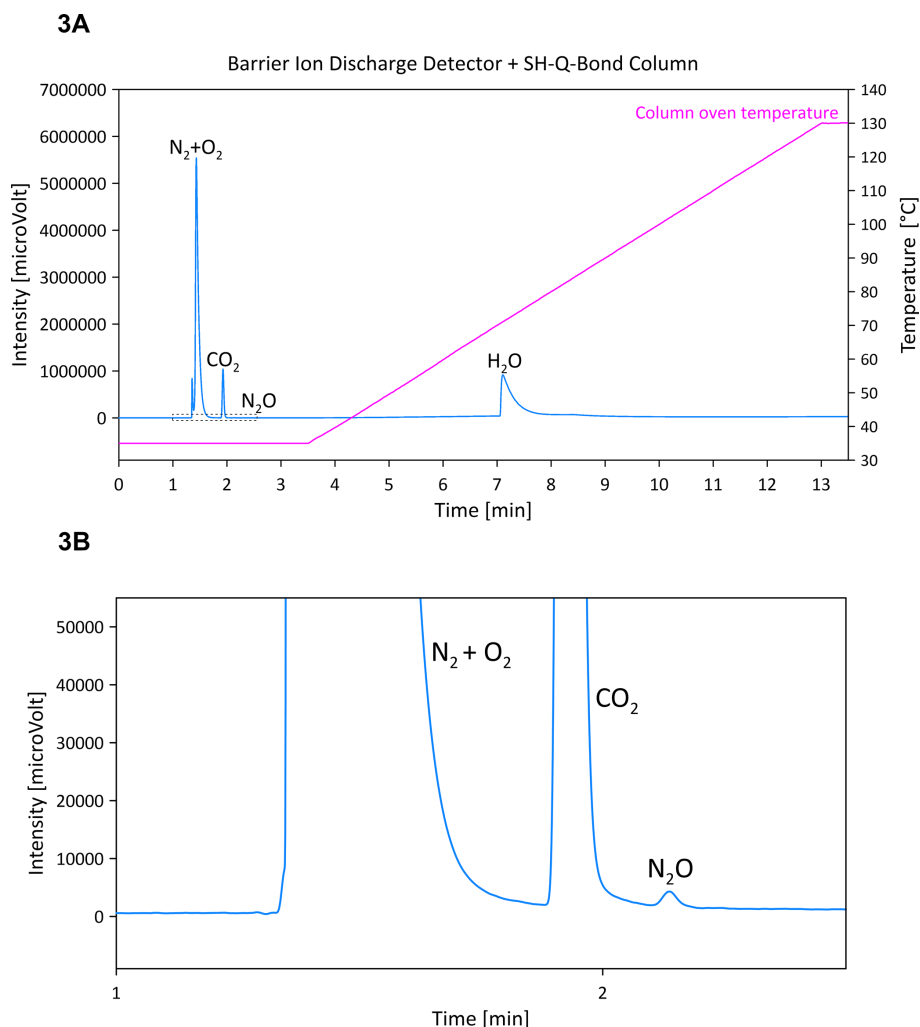


Figure 3. (a) Chromatograms of ambient air gases separated using the SH-Q-BOND column and detected using BID; (b) zoomed chromatogram from panel (a).

and TCD allow for determination of N_2 and O_2 (and if necessary CH_4) concentrations in the range from 0.2 % to 100 % (example shown in Fig. 5).

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 (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 (411 ppm), the CV ranged from 0.91 % to 2.83 % for the 1 mL sample loop and from 0.57 % to 1.87 % for the 2 mL sample loop. The CV of the N_2O measurement was lower for the 2 mL sample loop and ranged from 7.09 % 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 water vapour contained in the sample partially 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 unnecessary contamination of the column.

The gases analysed using the TCD, 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 2 mL sample loop, where the peak area was

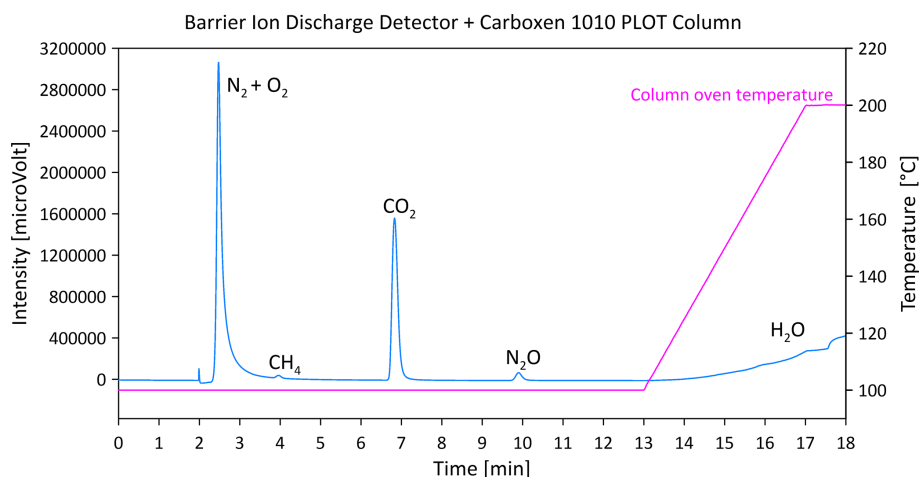


Figure 4. Chromatogram of special gas mixture separated using the Carboxen 1010 PLOT column and detected using BID.

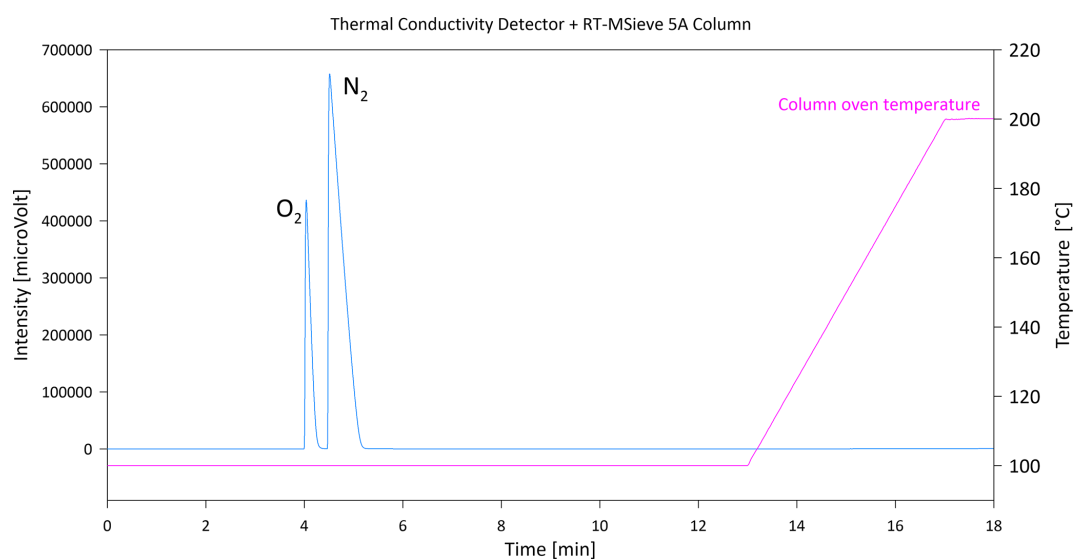


Figure 5. Chromatogram of ambient air separated using the RT-Msieve 5A column and detected by TCD.

very large. The results of the measurement (peak area, SD, CV) are presented in Table 1.

3.3 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 it was 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 0.18 % to 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 repeatable results. Table 2 shows all the data of the standard gas mixture testing measurements.

3.4 Direct measurement of ambient laboratory air using the AS-210 greenhouse gas autosampler

Another testing of the GC system was carried out with the application of splits 3, 4 and 5 with a 2 mL sample loop (Table 3). The ambient air from the laboratory on 1 d was anal-

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 1 and 2 mL sample loops.

Gas	Conc.		1 mL sample loop			2 mL sample loop		
			Split			Split		
			3	4	5	3	4	5
	Repetitions	<i>n</i> = 5	<i>n</i> = 4	<i>n</i> = 3	<i>n</i> = 10	<i>n</i> = 10	<i>n</i> = 10	
CH ₄	10 ppm	Area	149 922	118 357	96 007	278 296	207 227	161 265
		SD	831	133	318	1067	707	2895
		CV [%]	0.55	0.11	0.33	0.38	0.34	1.79
CO ₂	1000 ppm	Area	13 522 596	11 079 679	8 993 195	21 485 425	17 323 467	13 525 917
		SD	331 786	341 314	184 053	337 763	331 554	435 439
		CV [%]	2.43	3.08	2.05	1.57	1.91	3.22
N ₂ O	50 ppm	Area	629 251	497 331	402 025	1 171 624	867 747	673 486
		SD	2801	1782	729	9975	11 510	14 360
		CV [%]	0.44	0.36	0.18	0.85	1.33	2.14

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 a 2 mL sample loop.

Gas	Conc.		2 mL sample loop		
			Split		
			3	4	5
	Repetitions	<i>n</i> = 20	<i>n</i> = 20	<i>n</i> = 20	
CH ₄	1.895 ppm	Area	27 007	24 994	23 355
		SD	919	1047	957
		CV [%]	3.40	4.19	4.10
CO ₂	411 ppm	Area	8 297 069	6 787 524	5 351 342
		SD	190 315	89 672	97 529
		CV [%]	2.29	1.31	1.82
N ₂ O	339 ppb	Area	5736	4479	3359
		SD	232	139	111
		CV [%]	4.04	3.11	3.31
O ₂	20.946 %	Area	4 466 737	3 319 922	2 493 245
		SD	6357	4415	4366
		CV [%]	0.14	0.13	0.17
N ₂	78.084 %	Area	17 054 807	12 671 953	9 517 713
		SD	23 464	15 061	15 702
		CV [%]	0.14	0.12	0.16

used directly from the AS-210 greenhouse gas 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 CH₄ was in the range of 3.40 % to 4.10 % (the highest value for split 4). The CV of CO₂ was in range of 1.31 % to 2.29 %, whereas for N₂O it was between 3.11 % and 4.04 %. These CV values are close to the results obtained during measurements of the compressed air standard (Sect. 3.3, Table 1). The difference between the two experiments is that compressed air always had the same composition and gas concentrations, whereas the CH₄ and CO₂ con-

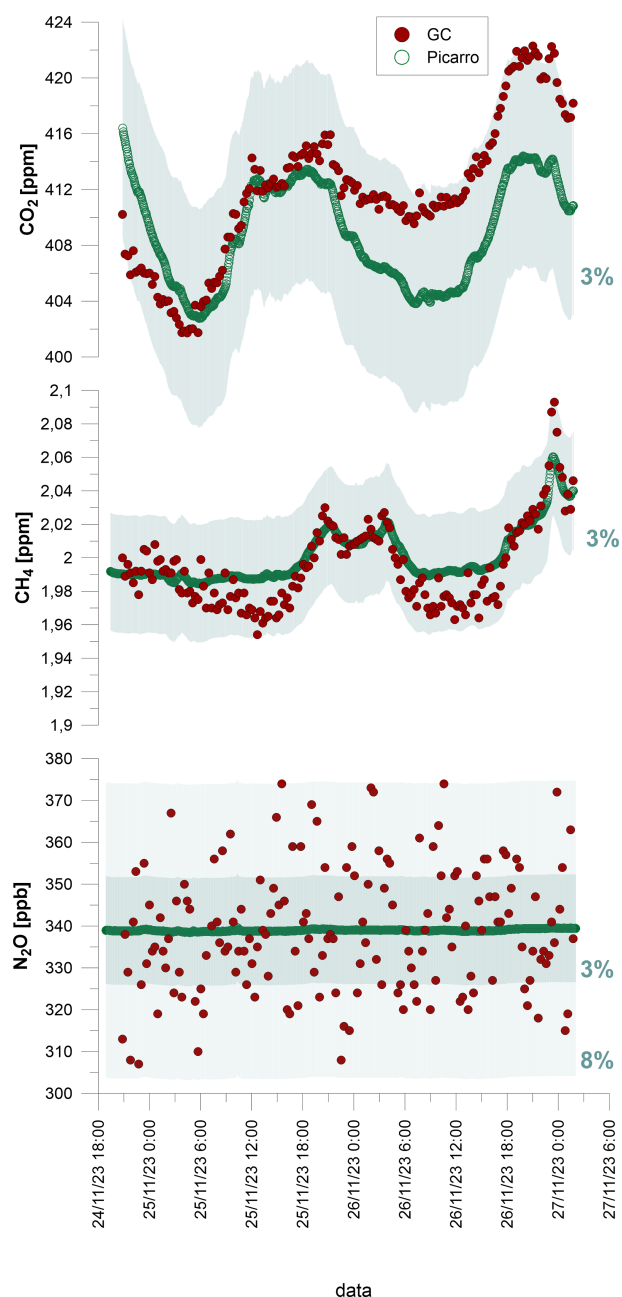


Figure 6. Comparison of CH_4 , CO_2 and N_2O variations in ambient air measured using a Picarro analyser and the GC system.

concentrations in ambient air could change slightly over time (daily variability).

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 h long measurement series of ambient laboratory air was performed.

The subsequent air samples were measured in parallel with the GC set-up 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 h time series, the Picarro measurement was performed every 3 min and the GC measurement every 19 min. 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. 6). Importantly, it was observed for CO_2 that after 24 h the measurements were slightly recalibrated and shifted in relation to the reference method. This indicates the need for repeated calibration at least every 24, 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 h of measurement was 0.24 ppb, which represents less than 0.1 % error. However, for typical N_2O measurements of unknown sample 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 simply using a RT-Msieve 5A column. The chromatographic system can be improved by the addition of a second gas valve

aimed at transferring CO₂ to the TCD after separation using the Carboxen column. This would allow further improvement of this chromatographic system for the maximum range of measured GHG concentrations.

4 Conclusions

This article outlined a simple method for determination of CH₄, CO₂ and N₂O concentrations from ambient air. The main advantage is that the use of at least two separate detectors can be avoided, including the ECD that contains radioactive materials and the FID with a methaniser to measure CO₂. A single-column Carboxen 1010 PLOT can be successfully used for separation of GHG (CH₄, CO₂, N₂O) in the time interval enabling measurement of each gas separately without the effect of peak overlapping. In parallel a connected Rt-MSieve 5A column allows for determination of higher CH₄ concentrations as well control of the O₂ and N₂ concentrations in the sample. The main disadvantage of the method is the lack of direct measurement of samples with high CO₂ concentrations (above 4000 ppm) in the set-up presented here, which is the upper detection limit for the BID. In summary the detection limits of the simplified GC system are 1.8 ppm–100 % for CH₄, 411–4000 ppm for CO₂, 339–4000 ppm for N₂O, 0.2 %–100 % for O₂ and 0.2 %–100 % for N₂. Further reconstruction with an additional valve directing the separated CO₂ to the TCD would allow additional analyses of higher CO₂ concentrations.

Based on performed tests, it is recommended that atmospheric GHGs be 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 water vapour; therefore, splits 1–3 should not be considered for the measurement of environmental gas samples. In this chromatography system, the CV of N₂O measurement at atmospheric level was 11 %–15 % (1 mL sample loop) and around 7 %–9 % (when using the 2 mL sample loop), the CV of CH₄ measurement at atmospheric level was near 7 % (1 mL sample loop) and below 3 % (when using the 2 mL sample loop), and the CV of the CO₂ measurement at atmospheric level was near 2 % (1 mL sample loop) and around 1.5 % (when using the 2 mL sample loop). The diurnal variations for CO₂ and CH₄ can be monitored well with the precision below 3 % error, whereas for N₂O measurements 8 % error must be taken into account.

The presented results for the measurement precision are satisfactory for the most analytical needs for determining GHG fluxes in field studies or laboratory incubation experiments. However, this GC system is not designed for the most precise analyses at ambient concentration and monitoring daily changes or long-term periods. Its measurement accuracy is not sufficient for such purposes when compared with instruments using optical techniques or automated GC systems dedicated for GHG at ambient air concentration. The greatest advantage of the proposed GC system is the ability to measure GHGs at the widest possible concentration, from the near-ambient concentrations to 100 %, and in any sample matrix, without the risk of damaging or decalibration of the equipment. It is easy to use and relatively cheap. Therefore, it can be successfully used for analyses of the gas samples with unknown GHG concentrations, e.g. from soil chamber measurements, laboratory incubation studies, biogas plants, waste dumps, burning coal heaps, mines, or monitoring of environmental GHGs fluxes.

Appendix A

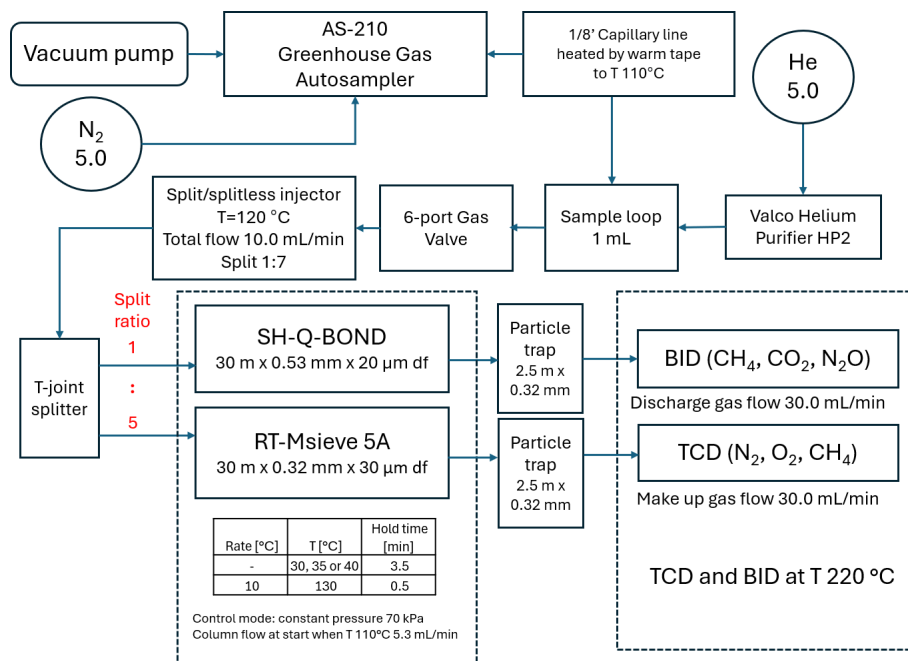


Figure A1. The scheme of GC configuration for testing with columns SH-Q-BOND and RT-Msieve 5A.

Data availability. Original data are available at <https://doi.org/10.5281/zenodo.14905756> (Bucha, 2025).

Author contributions. MB and PW constructed the analytical setup; MB and DLS planned the measurement campaign; MB, DLS and PW performed the measurements; MB and DLS analysed the data; MB, DLS and PW wrote the manuscript draft; MB, DLS and PW reviewed and edited the manuscript.

Competing interests. The contact author has declared that none of the authors has any competing interests.

Disclaimer. Publisher's note: Copernicus Publications remains neutral with regard to jurisdictional claims made in the text, published maps, institutional affiliations, or any other geographical representation in this paper. While Copernicus Publications makes every effort to include appropriate place names, the final responsibility lies with the authors.

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

Review statement. This paper was edited by Yoshiteru Iinuma and reviewed by three anonymous referees.

References

- Arnold, S. L., Parkin, T. B., Doran, J. W., Eghball, B., and Mosier, A. R.: Automated gas sampling system for laboratory analysis of CH₄ and N₂O, *Commun. Soil Sci. Plan.*, 32, 2795–2807, <https://doi.org/10.1081/CSS-120000962>, 2001.
- Bucha, M.: Simultaneous measurement of greenhouse gases (CH₄, CO₂ and N₂O) using a simplified gas chromatography system, In *Atmospheric Measurement Techniques*, Zenodo [data set], <https://doi.org/10.5281/zenodo.14905756>, 2025.
- Ekeberg, D., Ognér, G., Fongen, M., Joner, E. J., and Wickstrøm, T.: Determination of CH₄, CO₂ and N₂O in air samples and soil atmosphere by gas chromatography mass spectrometry, *GC-MS*, *J. Environ. Monitor.*, 6, 621–623, <https://doi.org/10.1039/b401315h>, 2004.
- Fastyn, P., Kornacki, W., Kardaś, M., Gawłowski, J., and Niedzielski, J.: 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>, 2003.
- Gruca-Rokosz, R., Szal, D., Bartoszek, L., and Pękala, A.: 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>, 2020.

- Harvey, M. J., Sperlich, P., Clough, T. J., Kelliher, F. M., McGeough, K. L., Martin, R. J., and Moss, R.: 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>, 2020.
- Hedley, C., Sagar, S., and Tate, K.: 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>, 2006.
- Lamb, W. F., Wiedmann, T., Pongratz, J., Andrew, R., Crippa, M., Olivier, J. G. J., Wiedenhofer, D., Mattioli, G., Al Khourdajie, A., 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., and Minx, J.: A review of trends and drivers of greenhouse gas emissions by sector from 1990 to 2018, *Environ. Res. Lett.*, 16, 1–31, <https://doi.org/10.1088/1748-9326/abee4e>, 2021.
- Loftfield, N., Flessa, H., Augustin, J., and Beese, F.: 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>, 1997.
- Rapson, T. D. and Dacres, H.: Analytical techniques for measuring nitrous oxide, *TrAC – Trends Anal. Chem.*, 54, 65–74, <https://doi.org/10.1016/j.trac.2013.11.004>, 2014.
- Scion Instruments: Analysis of Greenhouse Gas by Gas Chromatography, Application Note AN012, 1–2, 2023.
- Shimbo, E. and Uchiyama, S.: Application News: Simultaneous Analysis of Three Greenhouse Gas Components, CH₄, CO₂, and N₂O, Shimadzu Corporation, Application Note 01-00363A, 1–3, 2022.
- van der Laan, S., Neubert, R. E. M., and Meijer, H. A. J.: A single gas chromatograph for accurate atmospheric mixing ratio measurements of CO₂, CH₄, N₂O, SF₆ and CO, *Atmos. Meas. Tech.*, 2, 549–559, <https://doi.org/10.5194/amt-2-549-2009>, 2009.
- Wang, Y. and Wang, Y.: Emissions from a Short-Plant Ecosystem, *Adv. Atmos. Sci.*, 20, 842–844, <https://doi.org/10.1007/BF02915410>, 2003.
- Zaman, M., Kleineidam, K., Bakken, L., Berendt, J., Bracken, C., Butterbach-Bahl, K., Cai, Z., Chang, S. X., Clough, T., Dawar, K., Ding, W. X., Dörsch, P., dos Reis Martins, M., Eckhardt, C., Fiedler, S., Frosch, T., Goopy, J., Görres, C.-M., Gupta, A., Henjes, S., Hofmann, M. E. G., Horn, M. A., Jahangir, M. M. R., Jansen-Willems, A., Lenhart, K., Heng, L., Lewicka-Szczebak, D., Lucic, G., Merbold, L., Mohn, J., Molstad, L., Moser, G., Murphy, P., Sanz-Cobena, A., Šimek, M., Urquiaga, S., Well, R., Wrage-Mönnig, N., Zaman, S., Zhang, J., and Müller, C.: Methodology for Measuring Greenhouse Gas Emissions from Agricultural Soils using Non-Isotope techniques, 11–209, in: *Measuring Emission of Agricultural Greenhouse Gases and Developing Mitigation Options Using Nuclear and Related Techniques*, Springer, ISBN 978-3-030-55395-1, <https://doi.org/10.1007/978-3-030-55396-8>, 2021.