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Wrocław, 13.12.2024

Dear Dr. Yoshiteru Iinuma,
Editor,
Atmospheric Measurement Techniques,

On behalf of my co-authors, I am pleased to submit revised version of the article entitled: “Simultaneous measurement of greenhouse gases (CH₄, CO₂ and N₂O) using a simplified gas chromatography system” by: Michał Bucha, Dominika Lewicka-Szczebak, Piotr Wójtowicz

Thank you very much for giving us the opportunity to provide the modified version of our manuscript. We did our best to incorporate all the reviewers comments and suggestions into the final manuscript. The critical reviews helped us to vastly improve our work and clearly indicate the possible applications of our new presented set-up. We are quite convinced that our work will be interested to other scientists working with GC measurements, since this presents new idea for alternative GC system, which has been not described in the literature before.

Please find our point-by-point response to the reviews including a list of all relevant changes made in the manuscript. No part of this manuscript has been published previously and all authors are aware of and accept responsibility for the manuscript.

Best regards,

Dr. Michał Bucha

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Reply to Reviewer #1

Thank you very much for your positive evaluation on our manuscript and the critical comments which helped us to prepare the improved version of our work.

Please find below our responses and clarifications (black font) and the changes that have been made in the manuscript (blue font).

Page 3, line 89

What SRI stand for? please write first

This is the name of the producer, we clarified exact name:

AS-210 Greenhouse Gas Autosampler (SRI Instruments Europe GmbH, Bad Honnef, Germany)

Page 3, line 90

Molecular sieve

Yes, the own name of the column was used. This sentence is now corrected with precise information :

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.

Page 3, line 95

The schematic configuration of GC system for simultaneously measurement of CO₂, CH₄, and N₂O should be provided to get better understanding of the this measurement

Thank you for this suggestion, this will be definitely helpful for the readers. The following scheme is added to Section 2.1, as Figure 1 as well Figure 2 which shows the details regarding flow parameters.

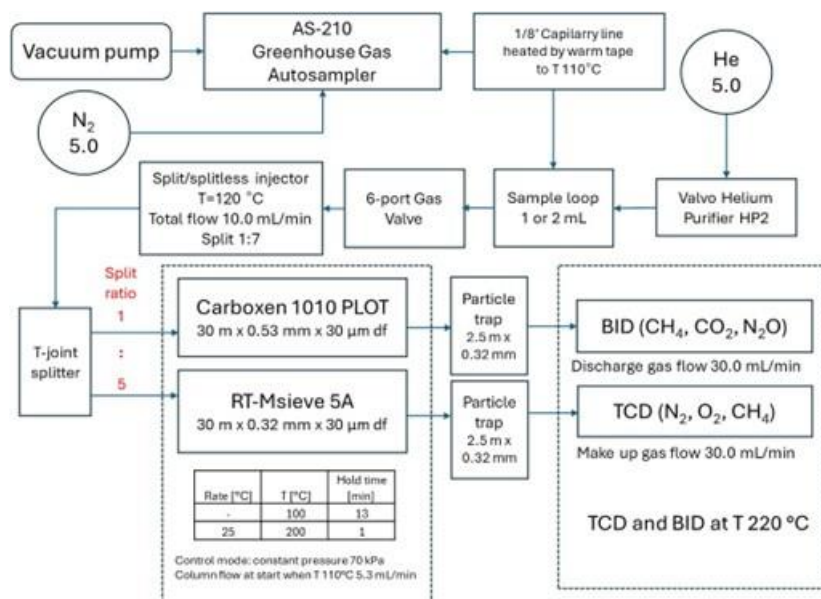


Figure 1: Configuration of GC system for measurement of CH₄, CO₂ and N₂O

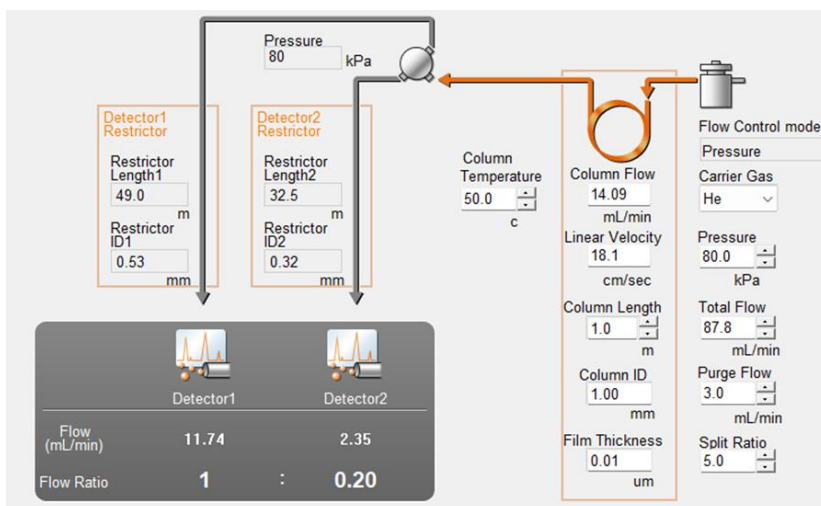


Figure 2: Detailed flow parameters in GC system configuration

Page 3, line 115

The statement of high sensitivity of BID and the usage of discharge flow, is there any references? (please cited in this statement)

This is information from Shimadzu Instruction Manual. The respective citation is added: Barrier Discharge Ionization Detector for GC-2010 Plus BID-2010 Plus Instruction Manual. Shimadzu Corporation 2013

Page 4, line 99

Liquid N2 (LN2)

The sentence is corrected:

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.

Page 4, line 107 and 108

Column has length 30 m, 0.32 mm inner diameter (i.d). Please provide also the information of thickness of stationery phase?

This missing information is now added and corrected as below:

Additionally, using a Tt-joint, the injection sample was then divided between two porous layer open tubular capillary columns filled molecular sieve 5A (RT-Msieve 5A 30 m x 0.32 mm x 30 µm; Restek, USA, Cat. No. #19722) and fused silica (Carboxen 1010 PLOT 30 m x 0.53 mm x 30 µm; Supelco, USA, Cat. No. #25467).

Page 4, line 113

Porous-layer open-tubular?

Yes, sentence and phrase are corrected to:

The presence of the traps protected the detectors from particles dislodging from the porous layer open tubular (PLOT) capillary column, which can cause spikes.

Page 4, line 124

Please express with the consistence significant figures of the mL value (two digit or one digit behind coma)

The values of flow parameters are corrected to one digit behind coma.

Page 4, line 128

the standard gas mixtures used in this study, is the certified standard gas mixtures or in-house standard gas mixtures developed by your institute?

Description regarding standards is improved:

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 (vapour), was stored in the 10 litres gas cylinder. The second standard was ordered in Messer Polska Sp. z o.o. and is the commercial product prepared in Switzerland according to the norm ISO6141:2015. This standard was prepared in pure N₂, without moisture, in volume of 8 litres and contains F10 filter, which protects outer valve from the possible vapour or solid particles.

Page 4, line 129:

Concentrations are the same as showed in the second columns in the Tables 1 and 2. The link to the values in respective tables will be added (Exact values in Table 1 and 3).

Gas	Concentration [% or ppm]
N ₂	78.084 %
O ₂	20.946 %
CH ₄	1.895 ppm
CO ₂	411 ppm
N ₂ O	0.339 ppm

Page 5, line 149

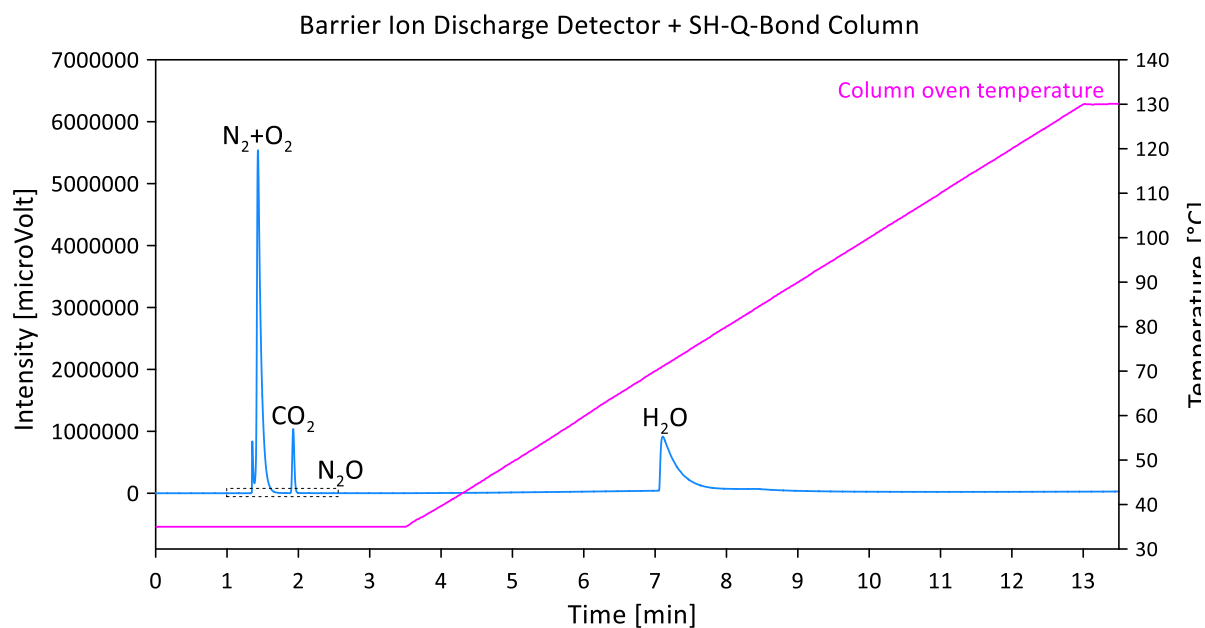
The peak label (name) for identification of gas component cannot be seen clearly (too small) both in the picture and inset of picture

Page 6, line 163

The peak label (name) for identification of gas component cannot be seen clearly (too small) both in the picture and inset of picture

The figures have been modified for better clarity and larger fonts were applied

3A



3B

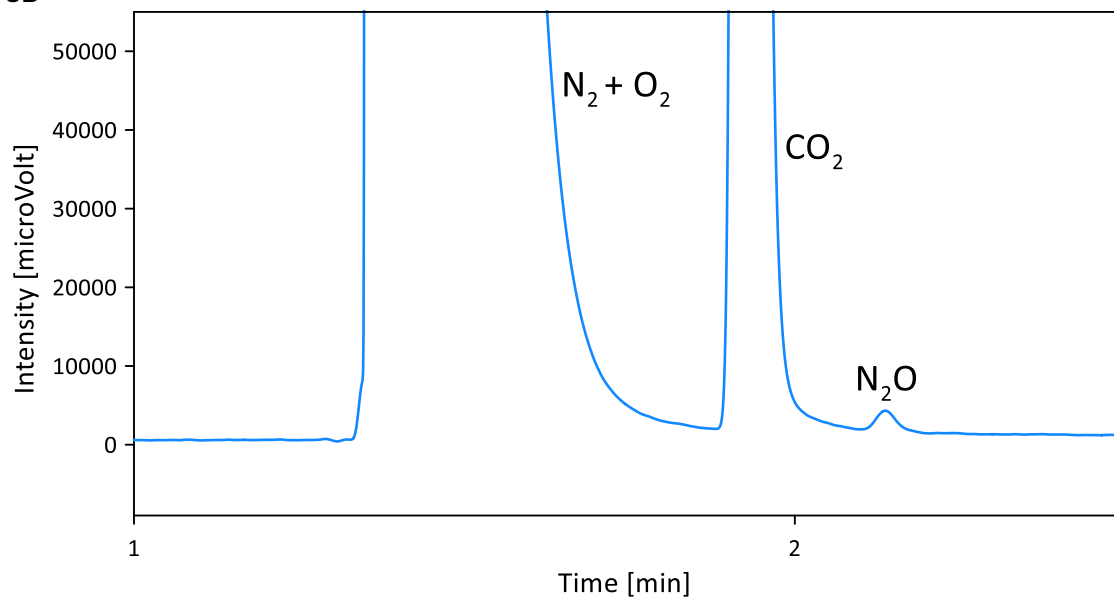


Figure 3: A - Chromatograms of ambient air gases separated using the SH-Q-BOND column and detected using BID; B - Zoomed chromatogram from Figure 3A

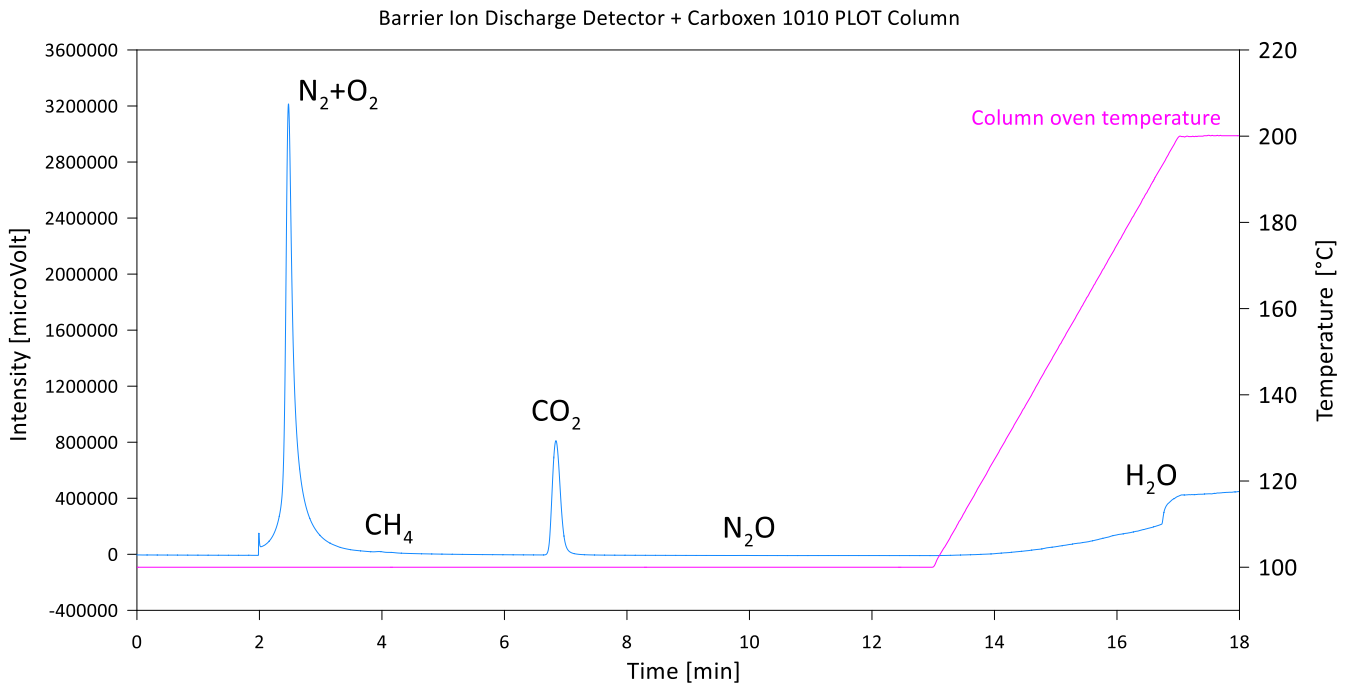


Figure 4: Chromatogram of special gas mixture separated using the Carboxen 1010 PLOT column and detected using BID

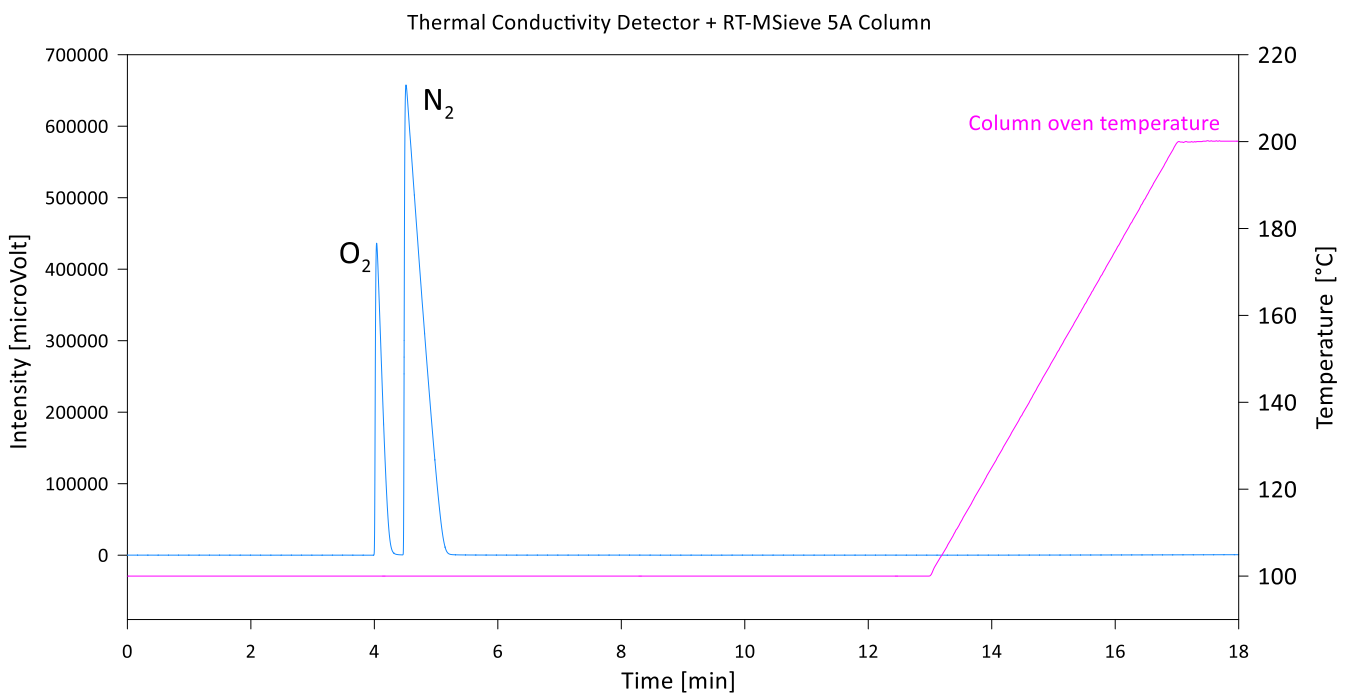


Figure 5: Chromatogram of ambient air separated using the RT-MSieve 5A column and detected by TCD

Page 6, line 164

Is the compressed air standard mixtures contained the moisture (dry or wet compressed air standard mixtures).

How the compressed air standard mixtures prepared should be explained in Materials and method section?

We clarified this question in section 2.3 as below:

The in-house standard of compressed air from Wrocław (Poland), which contained natural moisture (vapour), was stored in the 10 litres gas cylinder. It was prepared by oil-free compressor for diving cylinders.

Page 6, line 178

In this section, can O₂ and N₂ be separated well by the GC system and detected by TCD? because in section 3.1, the O₂ and N₂ peaks overlapped when analyzed with GC BID as seen in the chromatogram in Figure 2.

The separation is showed on newly added figure 5.

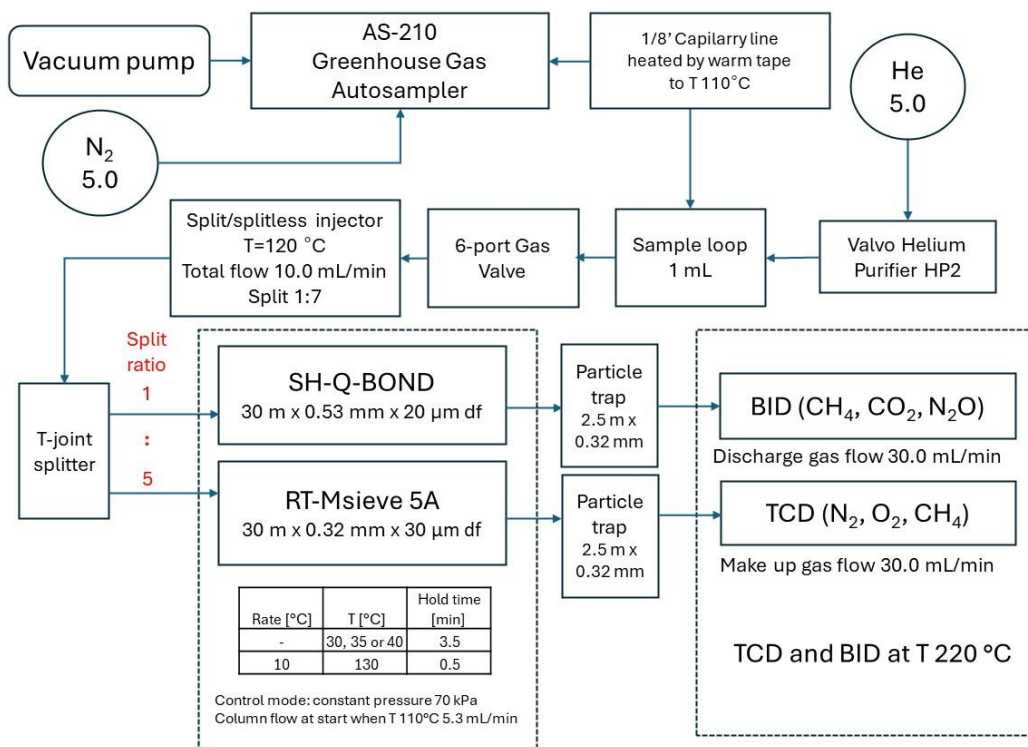
Are the conditions and setup of the GC system in sections 3.1 and 3.2 different?

Conditions and setup of testing with SH-Q-BOND were exactly the same (injector, TCD, BID configuration, presence of MSieve 5A, the splitting), the only difference was oven temperature programme which was as below:

Rate	Temperature	Hold Time
-	35.0	3.50
10.00	130.0	0.50

The following scheme was added to supplementary materials.

The notification regarding this scheme is added to the text in the section 3.1



The separation chromatogram for analysis in the GC system in section 3.2 can be displayed

It is showed in the Figure 5.

Page 7, line 194

For the better understanding, the data can be added with split ratio of 1,2 at 2 mL sample loops

We decided not to do it, because the amount of water vapour which can be transferred through the column after injection of 2 ml of ambient air sample would be destructive for the column's filling phase (will shorten its proper functioning). Material used for Carboxen columns is known as very sensitive for water vapour – in the past its filling was used as water adsorber – please see:

Fastyn P., et al. 2003: Adsorption of water vapour from humid air in carbon molecular sieves: Carbosieve S-III and Carboxens 569, 1000 and 1001 - Analyst (RSC Publishing)

Page 7, line 189

The detection limit of simultaneous analysis N₂O, CH₄, CO₂ using GC BID can be provided further to get the information of the characteristics of this GC system

In case of CH₄ and N₂O we are working at very low levels for BID, almost at the limit of detectability. For CH₄ it is 1.8 ppm and for N₂O 339 ppb. The precision error of N₂O at such low concentration is 5%. We are aware that this precision is not really satisfactory for measuring slight variations of ambient levels, however can be very well applied to determine environmental fluxes. We are still working on improvements, and we will test some modifications few more modifications, e.g. installing additional valve to allow for more gas measurements combinations and temperature controlling of sample loop and injection valves to better control the water level. With this manuscript we intended to publish the first idea of the system with Carboxen column and BID detector already applicable for many environmental studies. Hopefully in near future we can report better precision.

Page 7, line 194

Why the special gas mixture used in this analysis do not contain the same matrices as compressed air or ambient air (it means the CH₄, CO₂, and N₂O is in air matrices)

This results from the process of preparing the calibration mixture by the manufacturer. To obtain the appropriate accuracy, the manufacturer uses pure gas that does not contain the analyte, which is to be added in high dilution.

Our aim was to use the GC system also for samples from laboratory incubation studies with partially anoxic conditions. For such experiments it is important to determine the low oxygen levels, therefore we needed a gas standards with no and low O₂ concentration. To reduce the amount of necessary standards tanks we simultaneously varied O₂/N₂ levels and levels of GHGs possibly widest range of concentrations of all gases with lowest amount of tanks.

Page 10, line 238

How about the comparison of precision from this GC system and CRDS Picarro in CO₂ and CH₄ measurement (standard deviation, %relative standard deviation, error)?

For these comparison measurements we could only determine % error, because we measured atmospheric ambient air and it shows natural diurnal variations, we compared the results point by point and not the means and standard deviations. This could be only done this way because CRDS Picarro is dedicated mostly to ambient air samples, and it is not possible to insert special gas samples.

Page 10, line 248

Regarding the upper detection limit, How much the upper detection limit of this simultaneous measurement of CH₄, CO₂, N₂O by the GC system in this study?

We can state at this moment that concentrations which can be measured using our GC system are:

CH₄ 1.8 ppm to 4000 ppm (using BID), and 0.2% to 100% (using TCD)

CO₂ 411 ppm to 4000 ppm (0.4%) – according to Shimadzu specifications of BID detector

N₂O 0.330 ppm (339 ppb) to 4000 ppm – according to Shimadzu specifications of BID detector

Additional information:

O₂ – 0.2 to 100% (using TCD)

N₂ – 0.2 to 100% (using TCD)

The information regarding the detection limits is added to the conclusions.

Response to Reviewer #2

General comments

This paper reports a method for analyzing three greenhouse gases simultaneously using a relatively simple GC system. The strength of this paper is that the developed method enables us to separate and quantify CH₄, CO₂, and N₂O in air samples on a single column with a single detector. This technique would reduce sample size, time, and resources for the gas analyses. A shortcoming of this paper is that the precision or repeatability of the method is insufficient for atmospheric monitoring at background concentration level. In this regard, I think the title is misleading and should be revised to mean that the method is most suitable for source gases such as soil emission. Another concern is that the results of experiments for optimizing the GC setting are mainly discussed in the context of CV without further consideration of sensitivity of the detector. I believe combination of split ratio and sample size affect the amount/concentration of the target species delivered to the detector. For example, split ratio of 1 with 1-mL sample loop should give peak area that is equal to the area obtained at split ratio of 3 with 2-mL loop. In Table 1, I see results of CO₂ and N₂ are consistent with this idea, but it is not the case for other gases.

In summary, I recommend the publication of this paper after the authors address the issues above and specific points below.

Thank you very much for your positive evaluation on our manuscript and the critical comments which helped us to prepare the improved version of our work. Yes, definitely we proposed inappropriate title for this manuscript, this will be changed to: "**Simultaneous measurement of greenhouse gases (CH₄, CO₂ and N₂O) using a simplified gas chromatography system**". Our initial idea was to test this system for ambient air measurements and although so far the precision is not sufficient for precisely measure the small atmospheric variations, it can be very well applied for measurements of atmospheric fluxes. We missed to review our title before the final submission.

The answer for questions regarding the sensitivity of the BID detector is based on the analysing S/N (signal/noise) ratio for the selected peak. Generally, S/N above 3 allows for identification of the peak, whereas S/N above 10 allows for quantitative determination of concentration. For 339 ppb N₂O analysis at split ratio 5 we achieved the ratio S/N usually between 12-15. The S/N ratio for 50 ppm N₂O standard was usually above 250. The method how we calculated SD and CV [%] is described in the detailed answers to Reviewer's comments. We presented the equations and method of obtaining the CV [%] for this data. The very high peak area of O₂ (Table 1, sample loop 2 ml, split 1) was incorrect (mistake during preparation of the final table) and the corrected value 4513907 will be inserted in the table, which is similar to value 4317080 obtained with split 1 and sample loop 1.

Generally, transferring of the sample from the columns should be very fast to avoid the flattening of the peaks. The sample is transported from the sample loop to the column at total flow speed. Total flow is mainly dependent on the split value: total flow = column flow + split ratio x column flow + purge flow (3ml/min). Therefore, the larger the split value, the faster the sample reaches the column. The narrower band in which the sample hits the column makes the peaks narrower and higher than with lower split values, even though less sample hits the column. However, this is one of the rules that must be checked experimentally each time to find appropriate values for the experiment being conducted.

In this method we also consider the amount of water vapour, which is transferred to the column. It is important to find the ideal compromise between the appropriate amount of gas supplied to the column and obtaining a strong signal, especially for the lowest concentrations using BID. Therefore, we assume that the peak areas are not consistent with idea of the Reviewer mainly due to the difference in the speed of transferring through the columns. The additional calculation is showed below to compare all uncertainties. The difference between obtained peak areas is showed in the table as column C, and its absolute value in column D. Then in column E we showed that the value A (difference of the peak area expressed in %) is much higher for smaller peaks (CH₄ and N₂O, 23.30 and 28.66%, respectively). For larger peaks of CO₂, O₂ and N₂ the difference E is equalled around 5%. Therefore, it is very important to monitor parameter of S/N ratio when analysing low concentration samples.

	A	B	C	D	E [%]
Gas	Peak area at split 1 sample loop 1mL	Peak area at split 3 sample loop 2mL	C=A-B	Absolute value of C	$E=(A*100)/D$
CH ₄	33294	25535	7759	7759	23.30
CO ₂	10900323	10274295	626028	626028	5.74
N ₂ O	7801	5565	2236	2236	28.66
O ₂	4317080	4513507	-196427	196427	4.55
N ₂	16522678	17338000	-815322	815322	4.93

Please find below our responses to the specific points and clarifications (black font) and the changes that have been made in the manuscript (blue font).

Specific comments

L40–41. I think “the most modern techniques and devices” should be adopted only if they provide results with precision and accuracy that are sufficient for the purpose.

We agree with this comment and we are aware it is not suitable for measuring minimal changes in greenhouse gas concentrations in ambient air over time (and such measurements are required for monitoring climate change). Therefore we decided to change the manuscript title which is now:

“Simultaneous measurement of greenhouse gases (CH₄, CO₂ and N₂O) at atmospheric levels using a simplified gas chromatography system”

We also improved the description of our GC configuration, showed possible applications and underline its strengths and weakness.

L46. I think a chapter from an e-book is referred here. Correct the citation information in the References section.

You have right. This is a chapter from the e-book. Citation is corrected in the reference list.

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., Müller, C., 2021. Methodology for Measuring Greenhouse Gas Emissions from Agricultural Soils using Non-Isotope techniques. 11-209. In: Zaman M, Kleineidam K, Bakken L, Berendt J, Bracken C, Butterbach-Bahl K, Cai Z, Chang SX, Clough T, Dawar K, Ding WX, Dörsch P, dos Reis Martins M, Eckhardt C, Fiedler S, Frosch T, Goopy J, Görres C-M, Gupta A, Henjes S, Hofmann MEG, Horn MA, Jahangir MMR, 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, Müller C (2021) 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>.

L53–55. I think mass spectrometer is one of the detectors used in gas chromatography. I cannot understand why the mass spectrometry is specifically noted.

You have right, we deleted the part of the sentence “gas chromatography and/or gas chromatography coupled with mass spectrometry (GC-MS)”. Corrected sentence is:

Thus, the most reliable methods for GHGs measurements in a very wide range of concentrations are chromatographic methods (Ekeberg et al., 2004).

L56–63. This paragraph is difficult to read because there is a lot of duplication. It seems that the authors try to list several types of “systems”, but they just mention detectors and GC columns.

You have right. We corrected and improved this paragraph to avoid duplication.

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), electron capture detector - ECD (for N₂O measurement) (Hedley et al., 2006; Loftfield et al., 1997; Wang and Wang, 2003).

L64. What does “natural wear” mean? Because the half-life of the radiation source Ni-63 is 100 years, I wonder other factors are meant.

The ECD detector cell is a consumable part. The cells should be replaced every 2-5 years. Moreover, the ECD is very sensitive to oxygen, which oxidizes the nickel foil. Using poor quality nitrogen, e.g. 5.0, which contains trace amounts of oxygen, is enough to shorten the cell's life. Before the ECD, oxygen traps are used that must be replaced regularly. In addition, the ECD gets dirty with the stationary phase from the column. In general, the thicker the film inside the chromatography column, the faster the cell wears out. The ECD also gets dirty simply with the measured analytes. The ECD cell can no longer be disassembled and cleaned. Theoretically, it can be sent to service for cleaning, but the price is so prohibitive that it is not worth doing (the price of cleaning ~ the price of buying a new cell). The ECD can only be annealed. On the other hand, the BID is a maintenance-free detector, by definition it does not get dirty due to the dielectric barrier.

L78. It is not clear what “and/or” means. In a certain case, both the two-column system and the single-column system are required?

You have right, this I misleading phrase. The corrected sentence is:

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. Micropacked ST Shin Carbon or RT Q-Bond column (Shimbo and Uchiyama, 2022).

L81–83. This sentence is difficult to understand. For example, what is compared using “as well as”?

The corrected sentence is:

This set-up using 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).

L95. I recommend to add a schematic figure showing the GC system.

The new, two figures are added to the text – scheme of GC configuration and details parameters of the flow. Moreover, the scheme of the GC configuration with column SH-Q-BOND is showed in the Appendix and mentioned in the section 3.1.

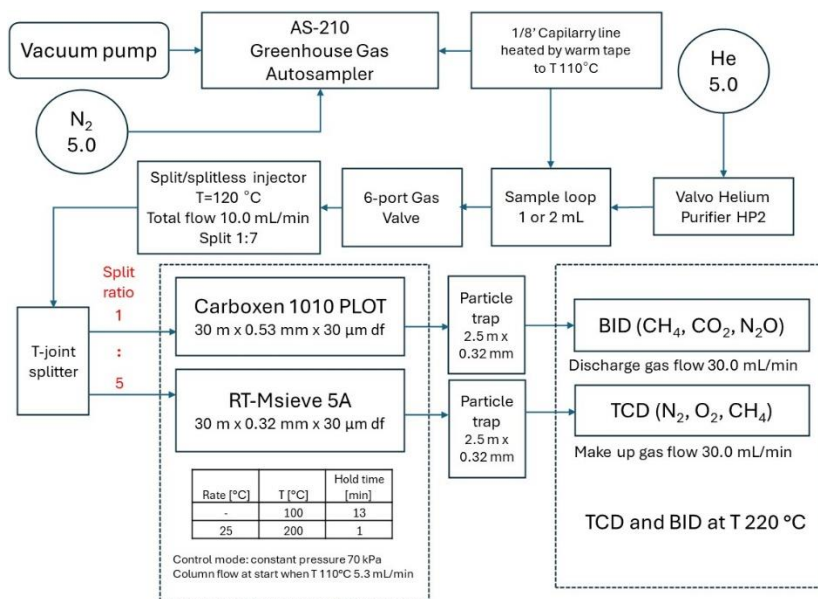


Figure 1: Configuration of GC system for measurement of CH₄, CO₂ and N₂O

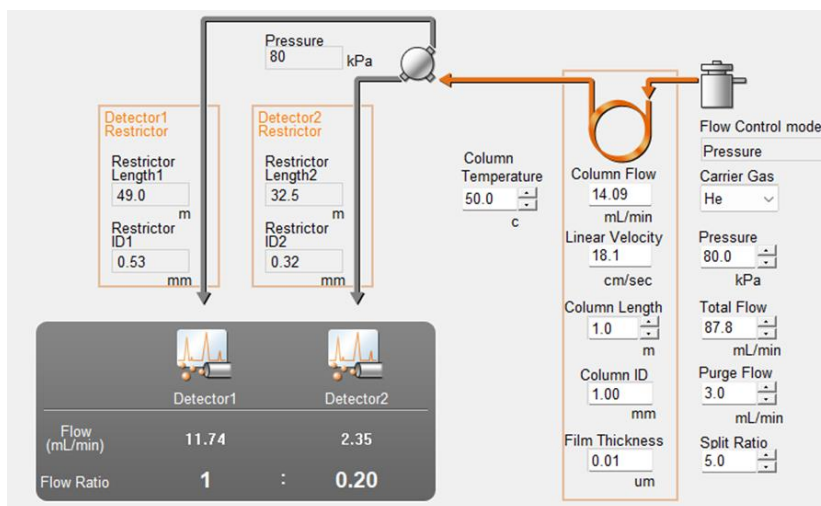
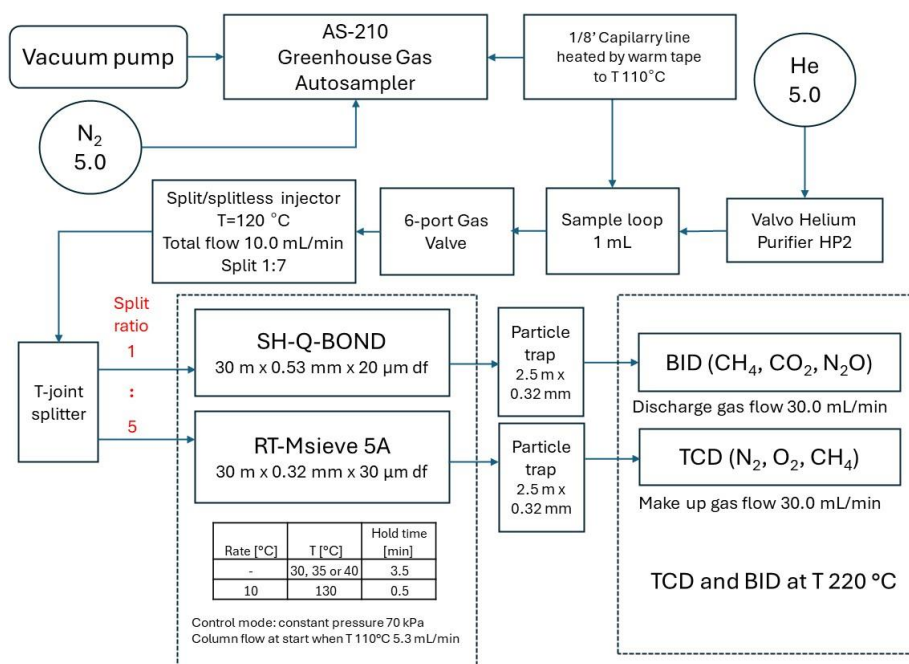


Figure 2: Detailed flow parameters in GC system configuration

Appendix 1

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



L101–102. “warmed” at what temperature?

It was 110°C. This information is added to the text and is shown on scheme of the GC system.

L102–103. This means gas sample with high moisture (e.g., soil gas) might cause problems. Is the system designed for already dried samples or does it withstand moist samples?

We tested Messer standard which doesn’t contain water vapour as well environmental samples with natural, high moisture (collected from the soil after rainfall etc.). Generally for samples with

significantly higher concentrations of CH₄, CO₂ and N₂O presence of moisture does not significantly affect the measurement. However, for samples with ambient concentrations of N₂O and with high moisture the baseline (and noise) should be checked to be sure that the signal of N₂O is enough to measure the concentrations. Shimadzu recommends that S/N (signal/noise) ratio should be above 10 to be sure that determination is correct. For 339 ppb N₂O analysis at split ratio 5 we achieved the ratio S/N usually between 12-15. The S/N ratio for 50 ppm N₂O standard was usually above 250.

The analysis of gas samples with natural moisture will lead to faster decay of the column filling (film) and accumulation of the solid parts in the particle trap, as a result, to a rise of the baseline, which has the greatest impact on the determination of samples with extremely low concentrations. For prevention we are actually testing different moisture traps (connected to the capillary between GC and autosampler). This is to minimize the presence of water vapour inside the system (such as the sample loop).

L107–110. I guess the length and inner diameter of the columns are described here, but the splitting ratio of 1:5 cannot be achieved with the dimensions shown here. Add other parameters such as thickness of the inner coating of the columns. Also, combination of column and detector should be clearly described or shown using a figure. Is the TCD connected to the molecular sieve column?

We will modify the description in the text as well showed basic information on GC scheme. The corrected text will be as below:

Additionally, using a T-joint, the injection sample was then divided between two porous layer open tubular capillary columns filled molecular sieve 5A (RT-Msieve 5A 30 m x 0.32 mm x 30 µm; Restek, USA, Cat. No. #19722) and fused silica (Carboxen 1010 PLOT 30 m x 0.53 mm x 30 µm; Supelco, USA, Cat. 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).

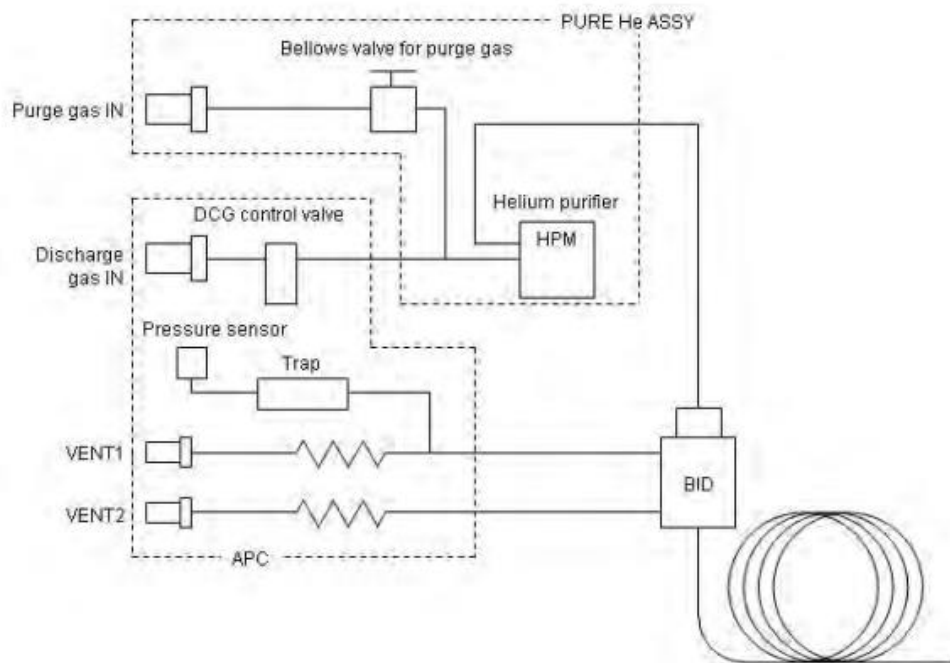
L111. Quantitative information should be given instead of “extremely low baseline noise”.

We corrected the sentence and added information regarding S/N ratio (signal/noise ratio):

Extremely low baseline noise (signal/noise ratio (S/N) always above 10) 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.

L115–117. It is not clear at which position the discharge gas is added to the flow system.

Discharge gas is connected and passed from the top, it is used to create plasma, below is a technical scheme from Shimadzu manual instruction:



Please see also link to the Shimadzu website [BID | Research & Development | SHIMADZU CORPORATION](#) with details regarding BID.

L117. I cannot understand what this sentence means.

On the TCD channel satisfactory sensitivity was achieved with standard settings - current 80 mA value and make-up gas 8 mL/min. Generally, in TCD, sensitivity can be adjusted by changing the type of carrier gas, make-up and current.

We added citation to the description of the method (information from the instruction manual of GC-2010 Nexis):

Barrier Discharge Ionization Detector for GC-2010 Plus BID-2010 Plus Instruction Manual. Shimadzu Corporation 2013)

L121-122. Do the authors mean the final temperature of 200C is kept for 1 min? Revise the sentence.

Yes. The final temperature is called "hold time". The temperature program is also now showed on the figure with GC Scheme.

L123-124. As described in the previous section, the flow after sample injection was divided into two columns. Are these flow parameters common to them?

It is necessary to add 2.5m particle traps with a diameter of 0.32mm to the columns. For a column with a diameter of 0.32mm, we added 2.5m which gives 32.5m. The column of 0.53mm should be theoretically extended by 19m, therefore 2.5m x 0.32mm gives the same resistance as 19m x 0.53mm, therefore the second column has a entered length of 49m. The details are showed in the new Figure 2 (previously showed in the response).

L140. Decrease from what temperature?

What we mean here is a quick stabilization of the oven temperature. Temperature stabilization. 35° is the lowest temperature that can be practically achieved in our laboratory without using liquid nitrogen for cooling. The temperature reduction that we mention here concerned the standard temperature of 40°C (at which we most often tested the SH-Q-Bond column).

The oven programme and configuration of SH-Q-BOND is showed in the new Appendix 1 (previously showed in the response).

Figures 1 and 2. Labels on the x and y axis are difficult to read.

The Figures are corrected with larger size fonts.

L158. Does “vapour” mean water vapor? Please specify. Also, do the authors mean that the retention time of H₂O peak shown in Figure 2 changes depending on the amount of water in the sample?

Yes, vapour means water vapour (natural moisture). The H₂O peak appeared usually when the oven temperature reached 115°C – it is not perfectly visible because the oven temperature was rising (and thus the baseline level too).

To be more precise, we have corrected in the whole manuscript ‘vapour’ to ‘water vapour’.

L165. It is not clear to me for what purpose the authors made experiments with different combinations of split ratio and sample size. I think the amount of sample (and water vapor) injected to the column is determined by the two parameters. For example, if 1 mL sample is processed with split ratio of 1, the amount of sample injected to the column is $1 \times 1 / (1+1) = 0.5$ mL. If 2 mL sample is processed with split ratio of 3, the amount would be $2 \times 1 / (1+3) = 0.5$ mL, which is the same as the first case.

We tested different split settings and loop volumes to find a compromise between the amount of sample analyzed and the speed of sample transport to the chromatography column. If we use a 2 mL loop, we can dose a larger amount of sample onto the column, which we want to transport to the column as quickly as possible. If we do it slowly, then the peaks will be broad and low, we will lose sensitivity. Hence, although the amount is identical, the flow through the column will differ between these settings.

L177 and elsewhere. Since TCD, FID, and ECD are acronyms of “xxx detector”, notation like “TCD detector” is awkward.

Thank you for this comment. We corrected these mistakes.

Table 1. It seems “SD” does not show the standard deviation of peak area, because dividing this value with “area” gives much smaller CV value. This is also the case for Tables 2 and 3. Please correct.

You have right. We suppose that these ambiguities resulted from the different way for presentation of the data (SD and CV) and lack of a clear presentation of the used calculation method in the table’s legends. In the original manuscript SD showed the standard deviation of the calculated concentration. First, we measured the same standard 3, 4, 5, 10 or 20 times. Then, this raw data of measured peak area was used for calculation of mean peak area typical for concentration at different and known levels (calibration). Concentrations were calculated according to equation:

Concentration [%] = (measured peak area * known concentration of the standard) / (calculated mean peak area from 3, 4, 5, 10 or 20 analyses)

SD = standard deviation of concentrations calculated for 3, 4, 5, 10 or 20 analyses

$CV = (SD * 100) / (\text{mean peak area from 3, 4, 5, 10 or 20 analyses})$

In the manuscript we corrected all the tables according to Reviewer's suggestion.

L185. Specify "the main atmospheric gases".

We mean O₂ and N₂. We will correct the paragraph because the measurement of these two compounds was performed with TCD – in our system is dedicated to a gases of higher concentrations than 0.2% (2000 ppm). Therefore the comparison of the SD obtained from BID which is much more sensitive in our opinion it is not recommended. New paragraph is corrected:

The gases analysed using the TCD detector, O₂ and N₂, were characterised by a narrow CV ranging from 0.10 to 0.39 %. The highest CV (0.39 %) was observed for the N₂ 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.

L202. What does "reportable results" mean?

This was a mistake, most probably made by autocorrection. We should use the phrase "repeatable results" – the achieved precision of N₂O analysis is considered as sufficient for determining environmental gas samples, e.g. from soil experiments and measurements of gas emissions from natural sources such as peat bogs.

L212–214. If the authors use the system for soil gases, should the sample be dried before analysis?

No, we recommend to use original sample and eventually trap the water moisture (using sorbents) – but these sorbents needs to be tested in order to check potential influence on the concentrations of other gases (e.g. sorption of CO₂ or N₂O). The best way is to analyse pure samples, and find the conditions when water moisture does not affect the precision of GC measurements.

Table 3. Is the area for N2O at split ratio of 3 correct? It is extremely higher than those obtained at split ratio of 4 and 5.

Thank you for this comment. This is mistake. The values in the table are corrected. The correct value of area= 5552, SD=30.6, CV [%]=9.02.

L234 split ratio of 4

It is corrected.

L235–237. I cannot understand these sentences. Do the authors mean the "GC" results of CO2 obtained after 25/11/23 18:00 (Figure 3) have a systematic error due to a shift in sensitivity of the detector?

Yes, some shift occurred, eg. due to change in air moisture, this was Friday evening after all people left laboratory. But importantly, with new calibration the both measurements would stay in very good agreement.

One of the reason why Picarro is much more precise could be amount of sample analysed. Picarro analyses at least 20mL of sample for constant measurement, which make a single measurement every few seconds. Our GC system is sampling air in the volume of 1 or 2 mL. By design, such a

measurement will not be as accurate in the long-term run as a device specifically dedicated to analyzing CO₂ or N₂O fluctuations in the atmosphere. But simultaneously, our system is not limited to low concentrations of GHG's, which is why it stands out from other special devices.

L243–245. Although it is not clear what “typical N₂O measurements” means, 5% error is NOT satisfactory if one would like to know diurnal/seasonal cycle or secular trend of atmospheric N₂O at background level.

Yes, we agree with this comment. However, for measurement of larger fluxes, like e.g. soil gases such error is accepted by scientific community. Many scientists are working with such precision (as the cited papers), if these measurements are not related to very precise monitoring of ambient N₂O concentrations. Also, for higher concentrations our errors are much lower. We have now emphasised this difference in applications in the manuscript.

L250–251. Since no TCD chromatogram is shown, this statement cannot be verified.

We added the chromatogram with TCD to the manuscript as below:

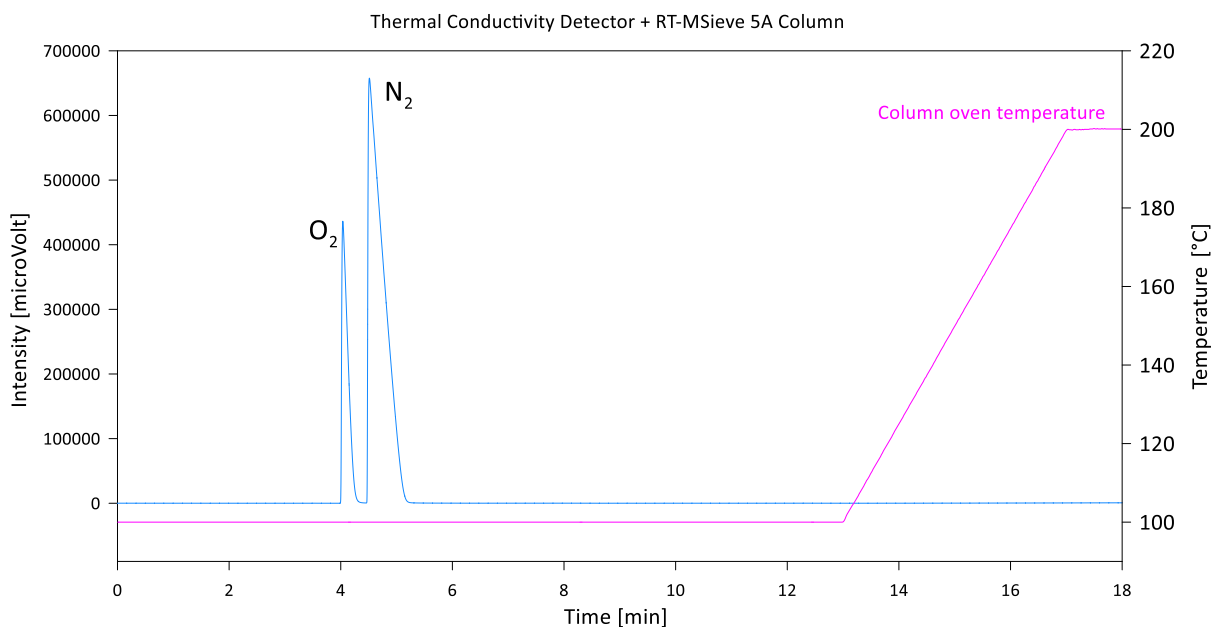


Figure 5: Chromatogram of ambient air separated using the RT-Msieve 5A column and detected by TCD

L261. Consider other quantitative or scientific expression for “very good”.

The sentence is corrected:

A single column Carboxen 1010 PLOT can be successfully used for separation of GHG (CH₄, CO₂, N₂O) in time interval enabling measurement of each gas separately without the effect of peak overlapping.

L268. water vapour?

Yes, we added clarification. The paragraph is corrected:

Based on performed 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 water vapour, therefore splits 1-3 should not be considered for the measurement of environmental gas samples.

Response to Reviewer #3

I am afraid I have to reject this paper in its present form, simply because to my opinion the instrument in its present state lacks being fit-for-purpose in any application.

While the simultaneous detection of the three anthropogenic greenhouse gases using just one detector and only He is an improvement compared to previous GC systems, the precision and accuracy is much too poor for any application, most certainly for atmospheric measurements. Compare for instance to van der Laan et al (2009): A single gas chromatograph for accurate atmospheric mixing ratio measurements of CO₂, CH₄, N₂O, SF₆ and CO. Atmospheric Measurement Techniques 2, 549–559 (2009). (not cited in the paper). They use two detectors, FID and EC, but they reach precisions : ±0.04 ppm for CO₂, ±0.8 ppb for CH₄, ±0.8 ppb for CO, ±0.3 ppb for N₂O, and ±0.1 ppt for SF₆, which are within the reach of the WMO recommendations for atmospheric monitoring. The present instrument gets uncertainties more than two orders of magnitude worse!

If the authors have other applications in mind, soil air or agricultural greenhouse air for example (as several of the papers they cite, and which is hinted at by the values for their reference cylinder with strongly enhanced concentrations compared to ambient), then they should make that very clear in the paper. Furthermore, I think that even for these applications the present quality is not good enough.

The authors should compare their instrument, with a proper, regular calibration scheme in place (periodically, with at least two reference cylinders, preferably more) for a longer time, with a Picarro, or with cylinder air input, and then show the uncertainty (in ppm / ppb), stability and linearity (!) of the system.

Thank you very much for your time and careful consideration of our manuscript and all the critical comments. According to the decision of the Editor of the Atmospheric Measurement Techniques we submitted revised version of the manuscript, which is significantly improved and takes into account all Reviewer's comments. The new title of the manuscript is "Simultaneous measurement of greenhouse gases (CH₄, CO₂ and N₂O) at atmospheric levels using a simplified gas chromatography system".

In the revised version we added scheme of GC configuration and details regarding flow parameters, new chromatograms, revised all the data including calculation of standard deviation, errors, discussed other systems (also proposed by the Reviewer – discussed in the article of van der Laan et. al 2009). In Appendix 1 we showed the GC configuration used for testing of SH-Q-BOND column. We also showed the possible applications of our simplified GC system in the conclusions section. We underline that proposed method is suitable for measurement of wide range GHGs concentrations, not for monitoring the slight changes in ambient air. Therefore, we assume that GC system can be shared to scientific community and help in development of alternative methods for GHGs measurement. We believe that this system has significant potential in the future not as the world's most precise instrumentation for ambient measurements but as simple device for detection of GHG's gases in large range of possible concentrations, hence dedicated for flexible and distinct applications.

We have also tested the system linearity, which was very good in range of the tested standards. This information was added in the manuscript.

In this manuscript we present the new idea of the system construction and the truly attainable precisions, which are indeed not so good for low N₂O levels. For higher N₂O concentrations and for CO₂ and CH₄ we get really satisfactory results in the whole measurement range. We believe, although this method do not provide the worlds-best precision, it is still worth publishing, because it presents new idea of the GC system set-up and maybe some scientists would decide this can be applicable for their needs (e.g. for CO₂ and CH₄ only, or for higher N₂O fluxes). It can be also further developed or refined, maybe in future better results can be obtained. Moreover, this is a documentation of how this set-up works – if anybody would like to construct similar system, with our work he can obtain the initial information how this can be done and which precision has been obtained.