Application Note 10349

Analysis of Greenhouse Gases by a Turnkey GC Analyzer System

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Introduction

The sun rays warm the earth, and the heat from the earth travels back to the atmosphere. The gases in the atmosphere prevent some of the heat from escaping into space. These gases are called greenhouse gases, and this natural process that traps the heat in the earth's atmosphere is known as 'Greenhouse Effect'. This greenhouse effect causes global warming. The two most significant greenhouse gases in the atmosphere are carbon dioxide and water vapor. Water makes a greater contribution (about 60%) to the natural greenhouse effect. Between the absorptions caused by carbon dioxide (CO_2) and water, there is a 'window' where the majority of the infrared radiation can escape with relatively little absorption (except for a narrow band where ozone absorbs.) About 70% of Earth's radiation escapes into space through this 'window.' The other gases which cause greenhouse effect are methane, nitrous oxide (N_2O), ozone, SF_6, and chlorofluorocarbons (CFCs). Amongst them CO_2, methane, and N_2O are critically important and are being monitored for their effects in several environmental and agricultural studies all over the world. The effects of global warming are becoming more and more significant every year. Eleven years between 1995 and 2006 are recorded as the warmest years since 1850 according to Intergovernmental Panel for Climate change (IPCC) [1, 2]. Between the years 1906 to 2005, the average surface temperature of the earth has increased by 0.74 °C, which can be mainly attributed to the greenhouse effect due to industrialization and automobile fuel exhaust.

Greenhouse gas analysis is one of the most useful diagnostic tools in the fields of agricultural and environment monitoring. We present a specially configured gas chromatograph (GC) capable of simultaneously measuring the important greenhouse gases, including methane, CO_2, and N_2O, simultaneously, in a simple yet reliable manner with high accuracy and repeatability at trace levels of the component gases. The system is designed to work autonomously; hence the measurements can be made at remote stations.

The GC system involves a valve oven and two detectors, a flame ionization detector (FID) with methanizer and an electron capture detector (ECD). The FID with methanizer is used for determining CO_2 and CH_4 (methane). The ECD is used for determining trace levels of N_2O (nitrous oxide).

Methods

Sample Preparation

The calibration standard for the greenhouse gases is injected onto a GC analyzer. The FID with methanizer is used for determining CO_2 and CH_4, and the ECD is used for determining the traces of N_2O.

Instrumentation

The schematic diagram of the green house analyzer GC system involving the Thermo Scientific™ TRACE™ 1110 GC is shown in Figure 1. The GC system involves a heated valve oven and two detectors an FID with methanizer and an ECD.

GC Configuration and Analytical Conditions

The GC analytical conditions are given in following Table 1.

Table 1. GC Parameters.

TRACE 1110 GC

Oven Program:	60 °C, 10.0 min
Total Time:	10.0 min
Max Temp. :	200 °C
Cryo Temp. :	Disabled
Multi Cycle :	00/01

Injectors

Injector 1:	PK_ MPC
Set Temp:	50 °C
Control Mode:	Constant pressure
Carrier Gas:	Nitrogen
Injector Mode:	Through AGSV
Pressure:	1.8 bar
Column Flow:	25 mL/min
Column 1:	3' x 1/8'' Porapak Q +
Column 2:	8' x 1/8'' Porapak Q

Injector 2:	PK_ MPC
Set Temp:	50 °C
Control Mode:	Constant pressure
Carrier Gas:	Nitrogen
Injector Mode:	Through AGSV
Pressure:	1.4 bar
Column Flow:	25 mL/min
Column 1:	8' x 1/8'' Porapak™ Q
Sample loop/channel:	2 mL for FID Channel
	5 mL for ECD

Valve Oven

Injector 3:	Valve Oven
Valve Oven Temp:	60 °C

Detector

Detector 1:	Methanizer
Methanizer Temp:	380 °C (Det-1)
Hydrogen:	45 mL/min (from FID)

Pneumatic Diagram

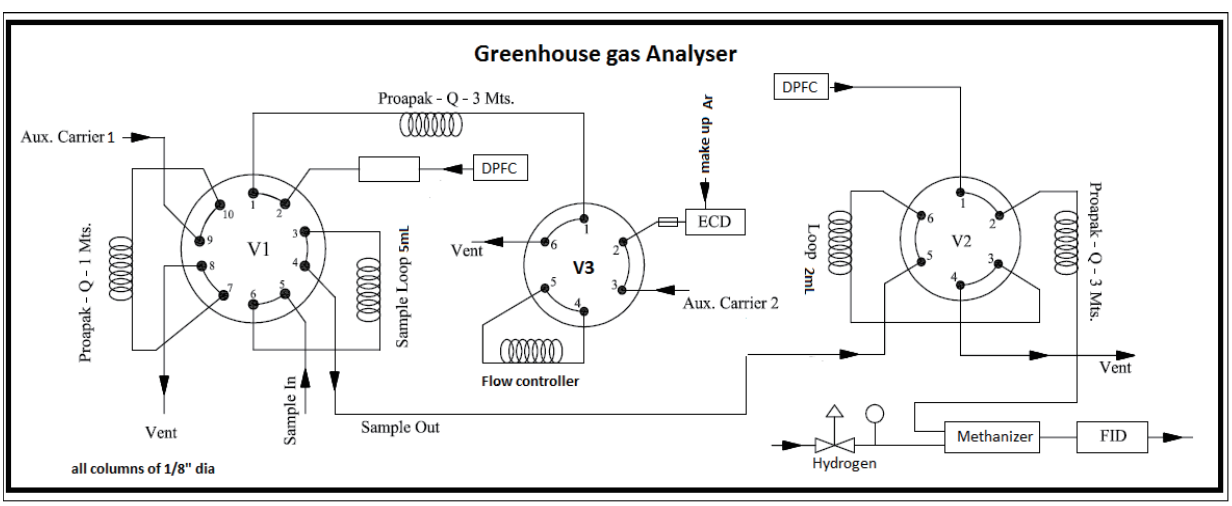


Figure 1. Schematic diagram showing the pneumatics of the GC system.

Column 1: 3 ft. × 1/8 in. Porapak™ Q short column to trap moisture and then vent
Column 2: 8 ft. × 1/8 in. Porapak Q long column main analysis column for CH_4 and CO_2
Column 3: 8 ft. × 1/8 in. Porapak Q long column main analysis column for N_2O in ECD
Note: Hydrocarbon components are analyzed on methanizer + FID with channel 1, and N_2O is analyzed on ECD with channel 2.

Detector 3:	SFID_EPC
Det. Set Temp:	250 °C
Baseline:	2 mV
Range:	10^0
Flame Status:	Off
Detector Gas Flows	
Make Up Gas:	10 mL/min
Air:	300 mL/min
Hydrogen:	45 mL/ min

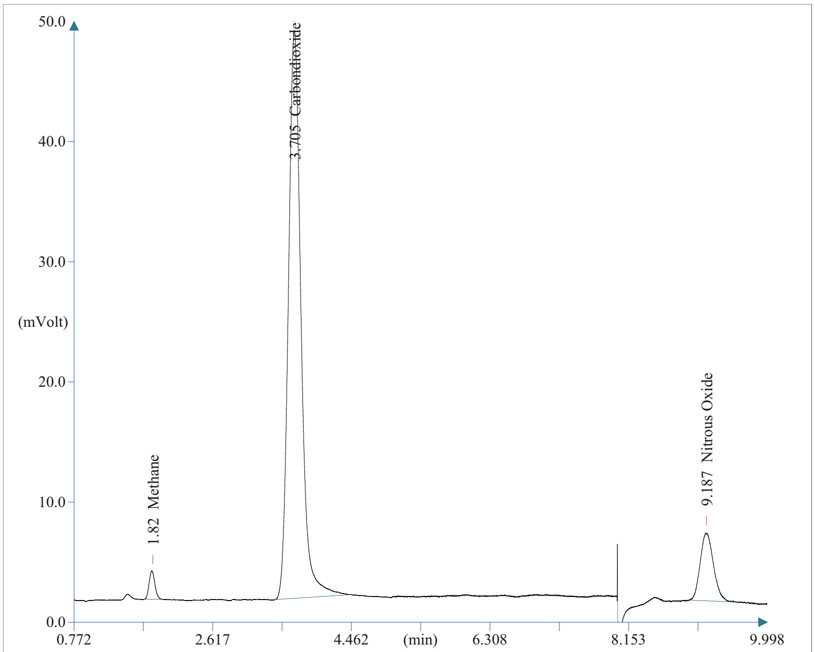
Detector 4:	ECD_EPC
Det. Set Temp:	350 °C
ECD Cell Temp:	330 °C
ECD Current:	0.5 nA
Baseline mV:	5.0 mV
Detector Gas Flows	
Make Up Gas (N_2) :	15 mL/min

Time Event Table

Event	ON time [min]	Off time [min]	Function
1	0.15	2.30	Valve # 1 Sampling in Col-1 FID channel and backflush of moisture and heavier at 2.30
2	0.30	2.00	Valve # 2 Sampling in Col-2 ECD channel.
3	3.0	10.00	Valve # 3 Bypass of Col-1 & Col-2 in series with Methanizer FID

Results and Discussion

The typical GC analysis chromatogram acquired on the TRACE 1110 GC pertaining to greenhouse calibration gas mixture is shown in Figure 2. The repeatability data for the retention time (RT), area counts, and concentrations for the greenhouse gas components are given below in Tables 2 and 3.



Retention Time (min)	Area (.1*uV*sec)	PPM	Component Name
1.820	125504	2.054	Methane
3.705	5505016	191.309	Carbondioxide
9.187	692805	2.093	Nitrous Oxide

Warning Chromatogram has been subjected to data manipulation.

Figure 2. Typical GC chromatogram of greenhouse gases calibration gas mixture.

Note: Methane and CO_2 are analyzed on a methanizer + FID with channel 1, and nitrous oxide (N_2O) is analyzed on ECD with channel 2. A combined report is generated by combining channels 1 and 2.

Table 2. Repeatability data on retention time (RT) for the greenhouse gas components.

Group	Filename	Methane [min]	Carbon Dioxide [min]	Nitrous Oxide [min]
3	Ch_GHA_std042	1.820	3.700	9.187
3	Ch_GHA_std043	1.820	3.705	9.208
3	Ch_GHA_std044	1.820	3.700	9.190
3	Ch_GHA_std045	1.820	3.705	9.208
3	Ch_GHA_std046	1.820	3.705	9.187
3	Ch_GHA_std047	1.820	3.702	9.188
3	Ch_GHA_std048	1.820	3.705	9.208
3	Ch_GHA_std049	1.820	3.705	9.208
3	Ch_GHA_std050	1.820	3.705	9.187
3	Ch_GHA_std051	1.820	3.705	9.187
	Average	1.820	3.704	9.196
	STDEV	0.000	0.002	0.011
	% RSD	0.00%	0.06%	0.12%
	Conclusion : Retention time RSD is better than 0.2%			

Table 3. Repeatability data for area counts for the greenhouse gas components.

Group	Filename	Methane [area cts]	Carbon Dioxide [area cts]	Nitrous Oxide [area cts]
3	Ch_GHA_std042	124755	5778805	661623
3	Ch_GHA_std043	126266	5714866	664228
3	Ch_GHA_std044	123156	5554882	683062
3	Ch_GHA_std045	128623	5715180	661081
3	Ch_GHA_std046	129730	5793584	664675
3	Ch_GHA_std047	123527	5551651	683293
3	Ch_GHA_std048	124306	5622573	661926
3	Ch_GHA_std049	125326	5526518	671365
3	Ch_GHA_std050	124584	5552617	692428
3	Ch_GHA_std051	125504	5505016	692805
	Average	125577	5631569	673648
	STDEV	2119	109285	12977
	% RSD	1.69%	1.94%	1.93%
	Conclusion : Concentration RSD is better than 2%			

Conclusion

The advanced TRACE 1110 GC system offers a fast, accurate, reproducible, rugged and simple analytical tool for the analysis of the greenhouse gases, including CO_2, CH_4, and N_2O. The system shows excellent reproducibility with good RSD values for retention time and peak area/concentration, which is well within expected limits and at the expected trace levels with high accuracy and precision.

References

[1] IPCC: Technical summary, in: Climate Change 2007, The Physical Science Basis, 4th Assessment Report of the Intergovernmental Panel on Climate Change, Edited by Soloman S. et al., Cambridge University Press UK, and NY, USA, 2007.

[2] Van der Laan, S.; Neubert, R.E.M.; Meijer, H.A.J., Atmospheric Measurement Discussions, 2009, 2, 1321-1349.

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