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Application News

No. GC-2202

System GC

Rapid Greenhouse and Inorganic Gas Analysis via GC-2030

■ Background

A novel design was created for the rapid analysis of Greenhouse gases, which are those that trap the infrared energy in the atmosphere and induce the greenhouse effect. Accurate and reliable monitoring of emissions and removals of the main greenhouse gases to and from the atmosphere is a crucial step in the overall management of climate forcers.

The gas chromatograph system described here enables the qualitative and quantitative analysis of three major greenhouse gases: methane, carbon dioxide, and nitrous oxide; light hydrocarbons: ethane and ethylene; and inorganic gases: hydrogen, oxygen, and nitrogen, with a simplified design.

■ Instrumentation

The GC-2030 is equipped with two capillary columns, an ECD Exceed-2030, FID-2030 with a Jetanizer™, an in-jet methanizer, a 6-port gas loop sampling valve and a 6-port switching valve. Additionally, a solenoid valve is connected on the FID line to heart cut analytes such as hydrogen sulfide or acetylene to vent before eluting to the Jetanizer™-FID. The 6-port gas switching valve is used to cut inorganic gas to the TCD for quantitation. An overview of the instrument design is provided in Figure1.

The system is designed to accommodate various sample types including summa canisters, Tedlar™ bags, and gas-tight syringe injections via manual injection or from an autosampler. With the addition of the AOC-6000 Plus autosampler, Exetainer™ vials can be sampled directly, allowing for increased sample throughput and ease of sample collection.

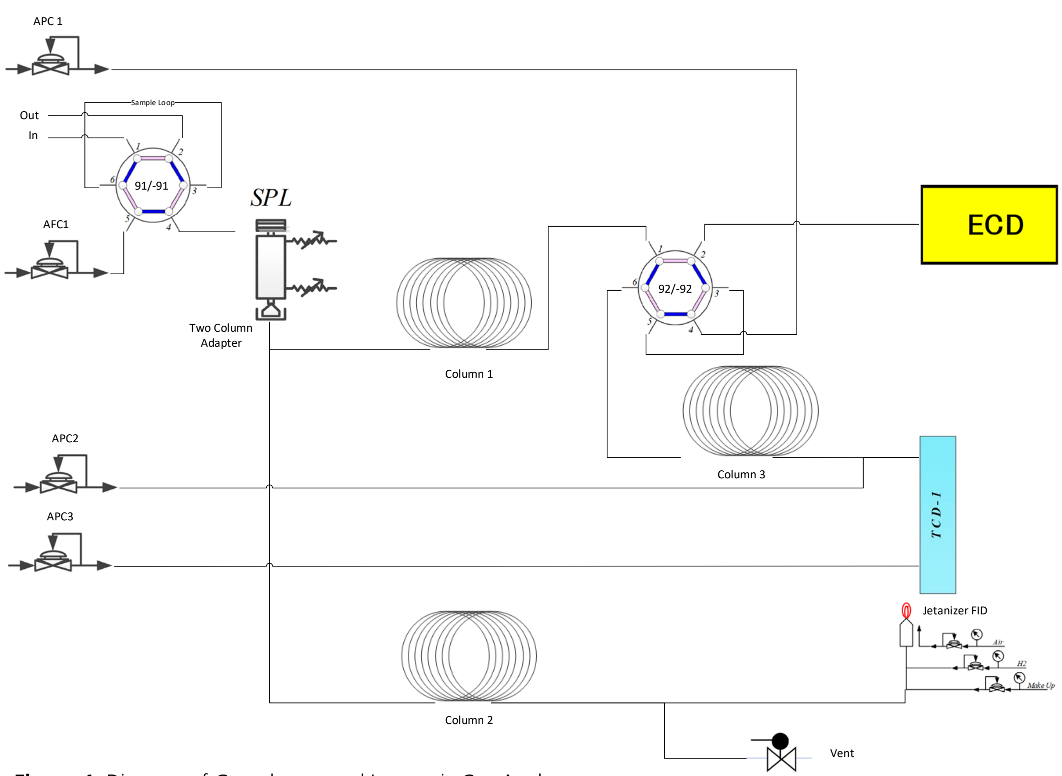

Figure 1: Diagram of Greenhouse and Inorganic Gas Analyzer

■ Experimentation and Observation

Four standards were analyzed to demonstrate the performance of the turnkey system; composition of the standards is listed in Table 1. Calibration curves, limits of detection, and limits of quantification were calculated using the four standards.

Method conditions

Method conditions (Table 2) were optimized for the separation of the permanent gas composite peak from carbon dioxide and nitrous oxide. The ECD line was timed to fore flush inorganic gases to the TCD for separation and rotate the 6-port gas switching valve to the positive position to allow elution of nitrous oxide to the ECD.

The vent valve on the Jetanizer/FID line was timed to cut acetylene to vent; however, this can be quantified by the Jetanizer/FID if required. The repeatability of the instrument as well as the calculated limits of detection and quantitation were determined based on triplicate injections of Standard 1 and Standard 3. Representative chromatograms of Standard 1 and Standard 4 with different detectors are shown in figures 2 to 6.

Table 1: Standards used for analysis

ANALYTE	STANDARD 1 CONCENTRATION (PPM)	STANDARD 2 CONCENTRATION (PPM)	STANDARD 3 CONCENTRATION (PPM)	STANDARD 4 CONCENTRATION (PPM)
CARBON DIOXIDE	600	600	400	20000
METHANE	5	5	100	4200
NITROUS OXIDE	1	1	-	-
HYDROGEN	-	-	100	4200
OXYGEN	200000	-	2500	125000
NITROGEN	Balance	Balance	16900	Balance
CARBON MONOXIDE	200	200	100	4200
ETHYLENE	-	-	100	4200
ACETYLENE	-	-	100	4200
ETHANE	-	-	100	4200
SULFUR HEXAFLUORIDE	1	-	-	-
ARGON	-	-	Balance	-

Table 2: Method Parameters

Parameter	Value
Column Used	SH-RT-Q-BOND 30 m x 0.53 mm x 20 um (P/N 221-75765-30) RT-QS-BOND 30 m x 0.53 mm x 20 um (P/N 220-97805-01) RT-MS-5A 15 m x 0.53 mm x 20 um (P/N 220-94805-02)
Injection Volume	1 mL gas sampling loop
Injector Temperature	100 °C
Linear Velocity	33.9 cm/sec Ar
Split Ratio	5:1
Oven Ramp	35 °C for 2 min; 7 °C/min to 70 °C for 1 min
FID Temperature	400 °C
FID Gas Flows	Makeup (Ar): 20 mL/min, H_2: 32 mL/min, Air: 200 mL/min
ECD Temperature	325 °C
ECD Gas Flow	15 mL/min (P5)
ECD Current	1.5 nA
TCD Makeup Gas Pressures	Makeup Pressure (Ar): 52 kPa, Reference (Ar): 66.5 kPa
TCD Temperature	100 °C
TCD Current	70 mA

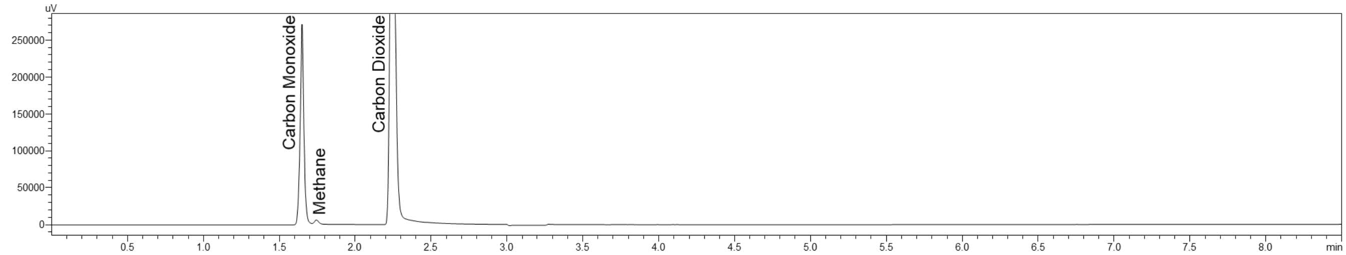

Figure 2: Representative chromatogram of Standard 1 on Jetanizer™-FID

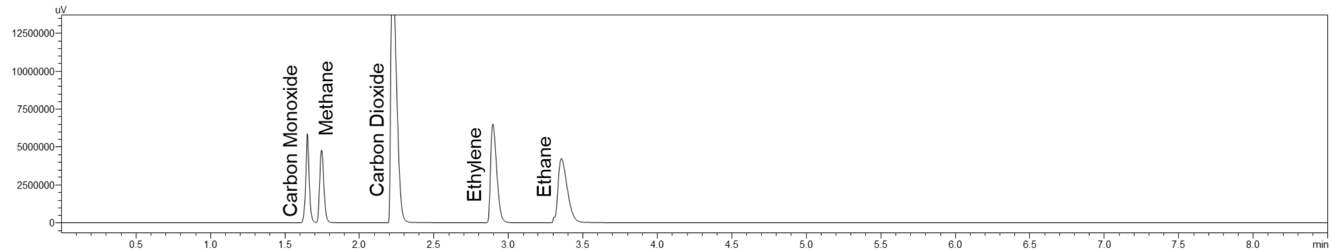

Figure 3: Representative chromatogram of Standard 4 on Jetanizer™-FID

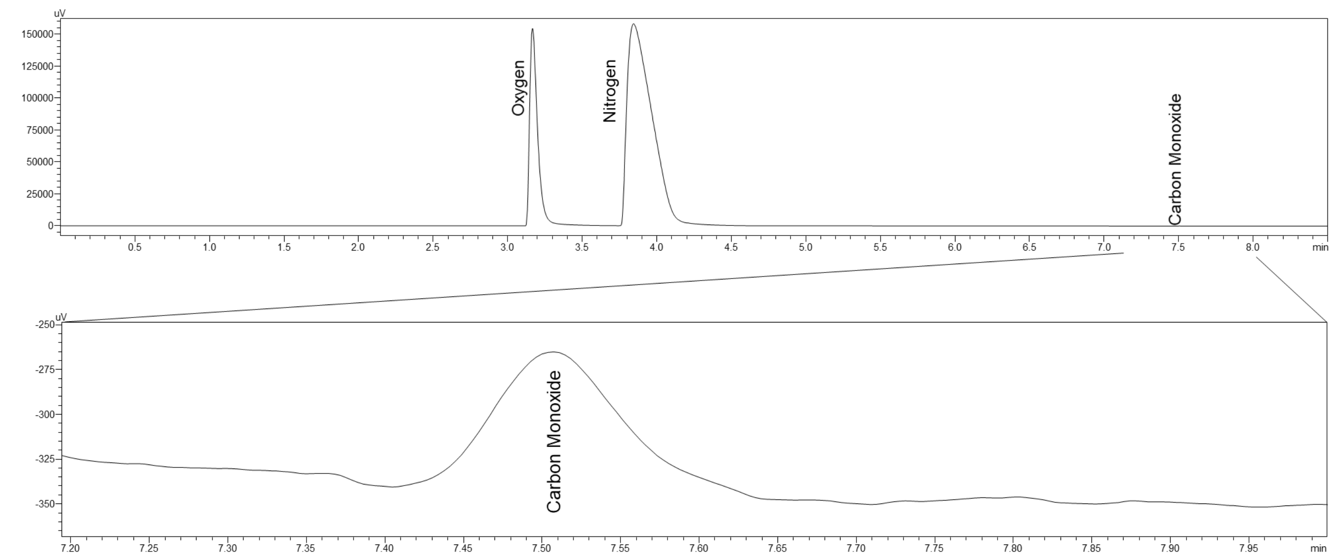

Figure 4: Representative chromatogram of Standard 1 on TCD

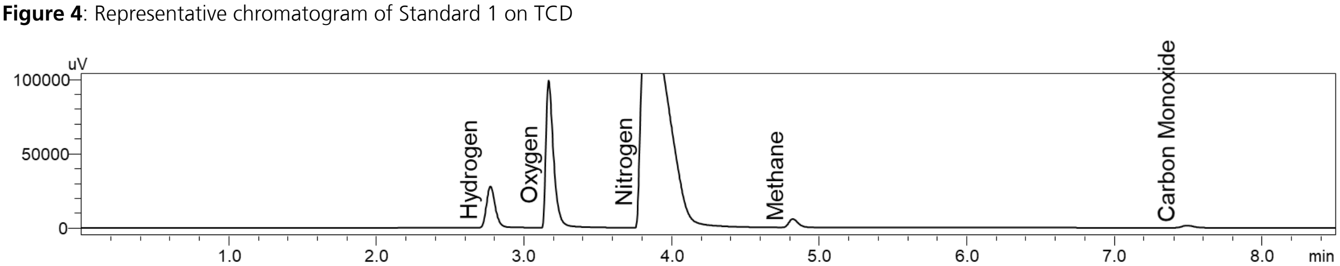

Figure 5: Representative chromatogram of Standard 4 on TCD

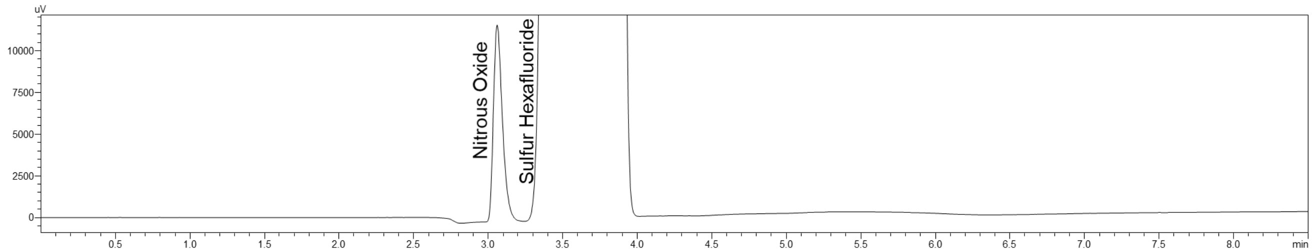

Figure 6: Representative chromatogram of Standard 1 on ECD

■ Results

A run time of less than 8 minutes was achieved with the optimized conditions with fully resolved peaks for carbon monoxide, methane, carbon dioxide, ethane, ethylene, hydrogen, oxygen, nitrogen, nitrous oxide, and sulfur hexafluoride.

Calibration curves were created for the analytes using the four standards. Linear regression curves were created with an R^2 value of 0.99999 or better for all analytes on the FID and 0.99 or better for all analytes on the TCD. Analytes with only a one or two-point calibration curve could not generate a meaningful R^2 value and are not shown. Representative calibration curves are displayed in figures 7 and 8.

The system displayed repeatability under 1.5% relative standard deviation for all analytes except for methane on the tail of a larger carbon monoxide peak. Calculated limits of quantitation are below 0.4 ppm for all components on the Jetanizer™- FID. On the ECD, the calculated limit of quantitation for nitrous oxide was 10 ppb. The limit of quantitation for sulfur hexafluoride and the limit of detection for nitrous oxide and sulfur hexafluoride were not calculated due to the high concentrations of these analytes in the standards. The calculated limits of quantitation on the TCD were 8 ppm for hydrogen, 80 ppm for oxygen, and 110 ppm for nitrogen. The calculated LOQ and LOD together with retention time, average peak area with %RSD, and S/N are included in Tables 3 and 4.

Table 3: Relative standard deviation and calculated limits of detections and quantitation for Standard 1

ANALYTE	DETECTOR	RETENTION TIME (MIN)	AVERAGE PEAK AREA	RSD% (N=3)	S/N	CALCULATED LOQ (PPM)	CALCULATED LOD (PPM)
CARBON MONOXIDE	Jetanizer™-FID	1.650	458,005	0.813	7760	0.27 (±0.06)	0.09 (±0.02)
METHANE	Jetanizer™-FID	1.746	13,627	3.903	172	0.39 (±0.08)	0.13 (±0.03)
CARBON DIOXIDE	Jetanizer™-FID	2.246	145,7267	0.799	17282	0.36 (±0.07)	0.12 (±0.02)
NITROUS OXIDE	ECD	3.060	49,468	0.173	1579	0.01 (±0.01)	-
SULFUR HEXAFLUORIDE	ECD	3.562	35,195,631	0.392	283787	-	-

Table 4: Relative standard deviation and calculated limits of detections and quantitation for Standard 3

ANALYTE	DETECTOR	RETENTION TIME (MIN)	AVERAGE PEAK AREA	RSD% (N=3)	S/N	CALCULATED LOQ (PPM)	CALCULATED LOD (PPM)
CARBON MONOXIDE	Jetanizer™-FID	1.649	219945	0.127	2638.50	0.37 (±0.01)	0.12 (±0.01)
METHANE	Jetanizer™-FID	1.751	219895	0.174	2615.32	0.38 (±0.01)	0.12 (±0.01)
CARBON DIOXIDE	Jetanizer™-FID	2.252	964044	1.244	9664.31	0.41 (±0.01)	0.14 (±0.01)
ETHYLENE	Jetanizer™-FID	2.918	442544	0.972	4055.49	0.25 (±0.01)	0.08 (±0.01)
ETHANE	Jetanizer™-FID	3.393	435339	0.194	2989.69	0.33 (±0.01)	0.11 (±0.01)
HYDROGEN	TCD	2.762	2739	0.142	120.02	8 (±1)	3 (±1)
OXYGEN	TCD	3.181	6892	0.634	298.45	80 (±10)	30 (±10)
NITROGEN	TCD	4.042	37892	0.386	1430.60	110 (±20)	40 (±10)

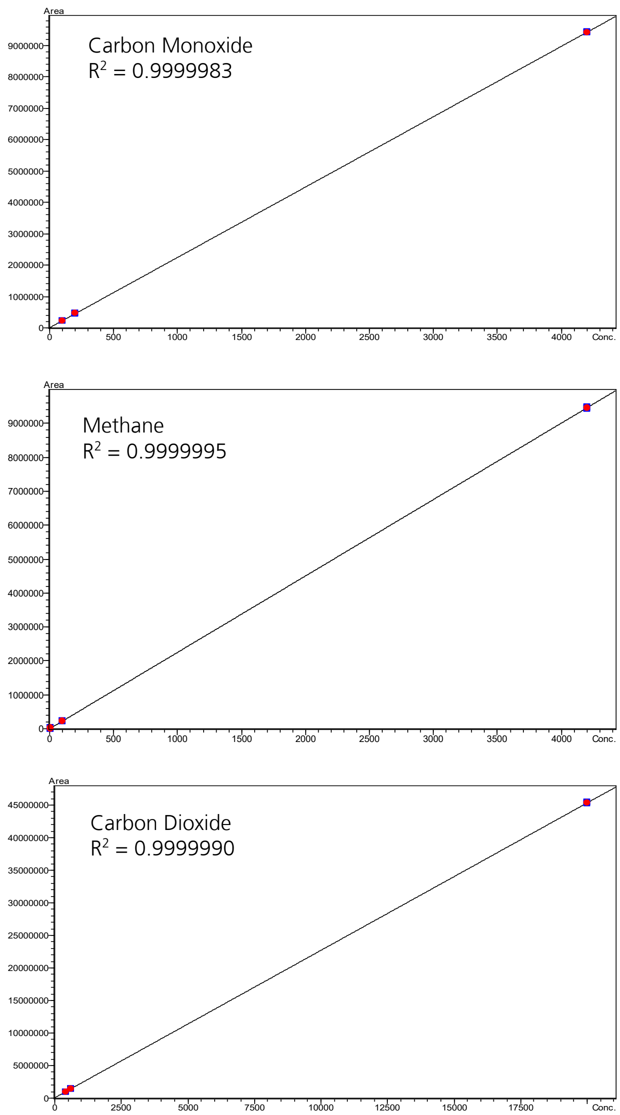

Figure 7: Calibration Curves for the FID

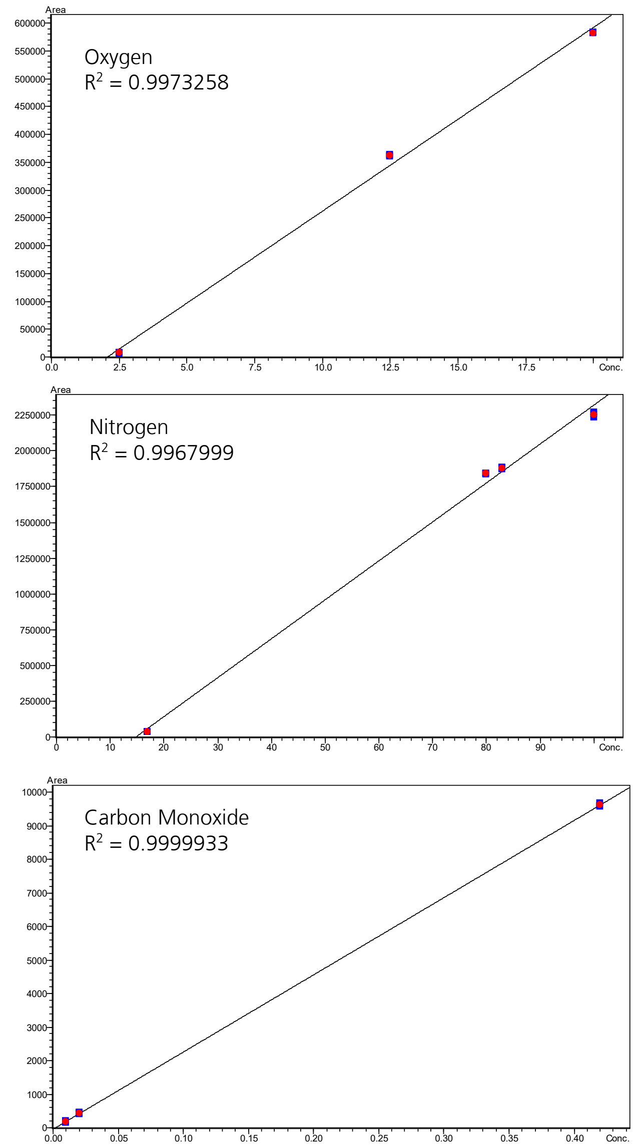

Figure 8: Calibration Curves for the TCD

■ Conclusion

The capillary greenhouse gas system provided a highly repeatable and rapid analysis. With a method under 8 minutes for carbon monoxide, methane, carbon dioxide, ethylene, ethane, nitrous oxide, sulfur hexafluoride, hydrogen, oxygen, and nitrogen, high throughput with excellent sensitivity and linearity can be achieved. The design is highly expandable with both the ability to quantify additional analytes and to incorporate the AOC-6000 Plus autosampler to sample directly from Exetainer™ vials.

This applicated GC system, with its simple flow path using independent columns for each analytical line and heart cutting, is highly sensitive, repeatable, linear, and robust for ensuring the fast analysis of greenhouse and inorganic gases.

First Edition: April 2022

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