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Application News

System GC

Rapid Greenhouse Gas Analysis via the Nexis™ GC-2030 Gas Chromatograph

■ Background

Greenhouse gases are those that are found in the atmosphere that induce the greenhouse effect, which is an absorbance and emission of infrared energy emitted by the Earth. As sunlight strikes the surface of the Earth, some of the infrared light is reflected into the atmosphere. These greenhouse gases absorb that infrared energy and reflect it back towards the Earth. The gas chromatograph system described below enables the easy qualitative and quantitative analysis of three major greenhouse gases: methane, carbon dioxide, and nitrous oxide.

■ 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 to vent before eluting to the Jetanizer™-FID. The 6-port gas switching valve is used to vent permanent gas, water, and other analytes from the ECD. An overview of the instrument design is provided in Figure1 below.

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.

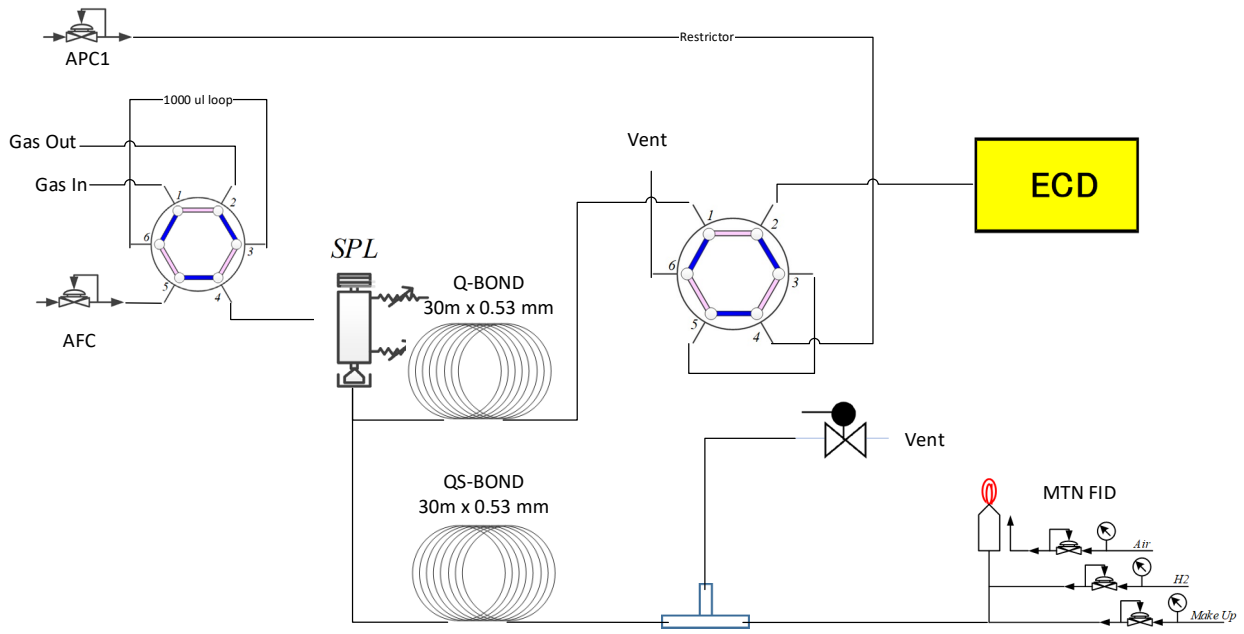

Figure 1: Diagram of Greenhouse Gas Analyzer

■ Experimentation and Observation

Two standards were used for this analysis. Standard 1 was used to determine limits of detection (LOD) and quantitation (LOQ). Standard 2 was used to verify the viability of the heart cut to vent.

Table 1: Standards used for analysis

ANALYTE	STANDARD 1 CONCENTRATION (PPM)	STANDARD 2 CONCENTRATION (PPM)
CARBON DIOXIDE	600	20000
METHANE	5	4200
NITROUS OXIDE	1	Not listed
HYDROGEN	Not Listed	4200
OXYGEN	Not Listed	125000
NITROGEN	Balance	Balance
CARBON MONOXIDE	Not Listed	4200
ETHYLENE	Not listed	4200
ACETYLENE	Not listed	4200
ETHANE	Not listed	4200

Method conditions

Method conditions were optimized for the separation of the permanent gas composite peak from carbon dioxide and nitrous oxide. The ECD line was timed to foreflush all permanent gas components to vent, rotate the 6-port gas switching valve to the positive position to allow elution of nitrous oxide to the ECD, and then rotate the 6-port gas switching valve back to the negative position to vent all heavier analytes.

The repeatability of the instrument as well as the calculated limits of detection and quantitation were determined based on triplicate injections of the standard. Representative chromatograms of Standard 1 are shown in Figures 2 and 3.

The analysis resulted in fully resolved peaks for methane, carbon dioxide and nitrous oxide and was completed in under three minutes.

Table 2: Method Parameters

PARAMETER	VALUE
Column Used	SH-Q-BOND 30 m x 0.53 mm x 20 µm (P/N 221-75765-30) SH-QS-BOND 30 m x 0.53 mm x 20 µm (P/N 220-36366-01)
Injection Volume	1 mL gas sampling loop
Injector Temperature	250 °C
Linear Velocity	35.7 cm/sec N_2
Split Ratio	5:1
Oven Ramp	Isothermal 35 °C
FID Temperature	400 °C
FID Gas Flows	Makeup (He): 24 mL/min, H2: 32 mL/min, Air: 250 mL/min
ECD Temperature	325 °C
ECD Gas Flow	15 mL/min (P5)
ECD Current	2.0 nA

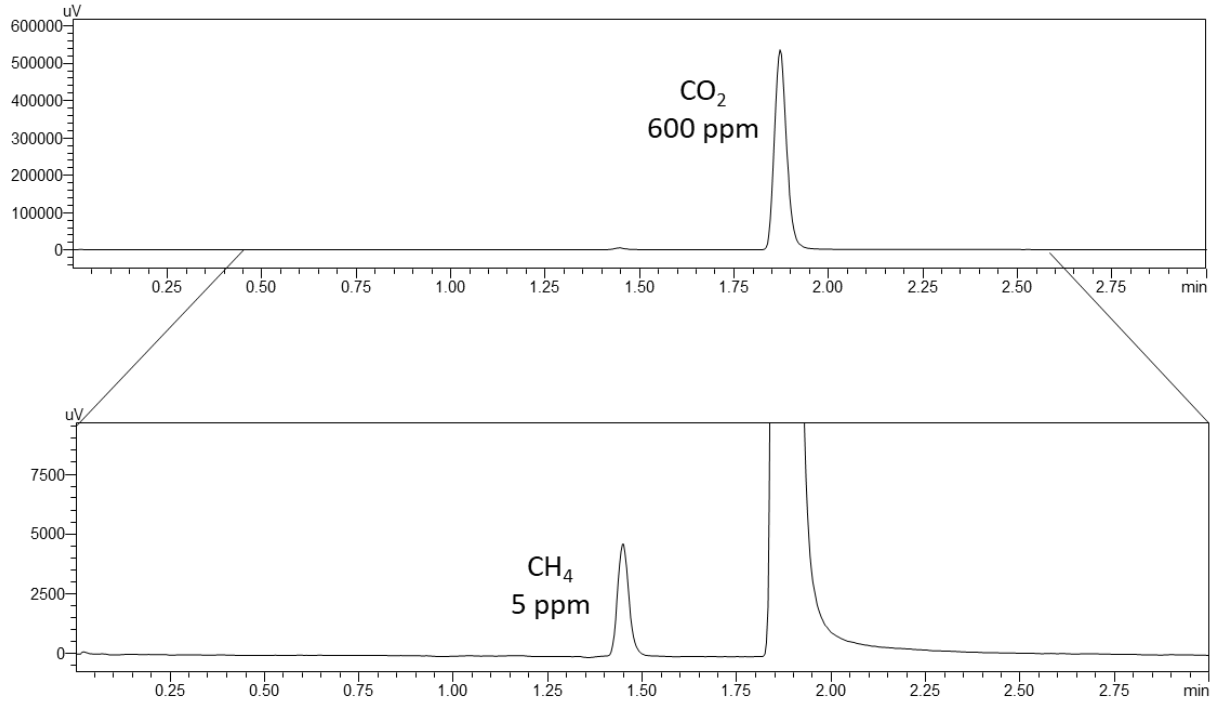

Figure 2: Representative chromatograms for Standard 1 on Jetanizer™-FID

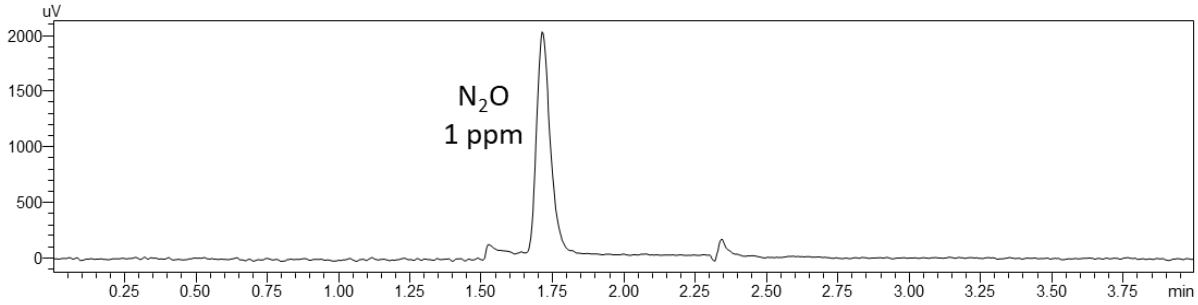

Figure 3: Representative chromatograms for Standard 1 on ECD

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	CALCULATE D LOQ (PPM)	CALCULATED LOD (PPM)
NITROUS OXIDE	ECD	1.72	6,597	0.18	32.50	0.31 (±0.02)	0.10 (±0.006)
METHANE	Jetanizer™-FID	1.46	9,914	0.72	46.37	1.11 (±0.2)	0.37 (±0.08)
CARBON DIOXIDE	Jetanizer™-FID	1.88	1,227,780	0.31	5267.50	1.18 (±0.2)	0.39 (±0.08)

The system displayed repeatability with under 1% relative standard deviation for all analytes. Calculated limits of detection for methane and carbon dioxide are below 0.4 ppm for both analytes with a limit of quantitation around 1 ppm. Nitrous oxide displayed a calculated limit of detection of around 0.1 ppm with a limit of quantitation of just above 0.3 ppm.

This analyzer can be expanded to other analytes including light hydrocarbons. To demonstrate the performance of this system for additional analytes, Standard 2, which contains light hydrocarbons, was injected in triplicate. Additionally, to demonstrate heart-cutting capabilities, acetylene, a known coking agent on methanizer catalyst materials, was selected to heart cut to vent. A representative chromatogram is shown in Figure 4.

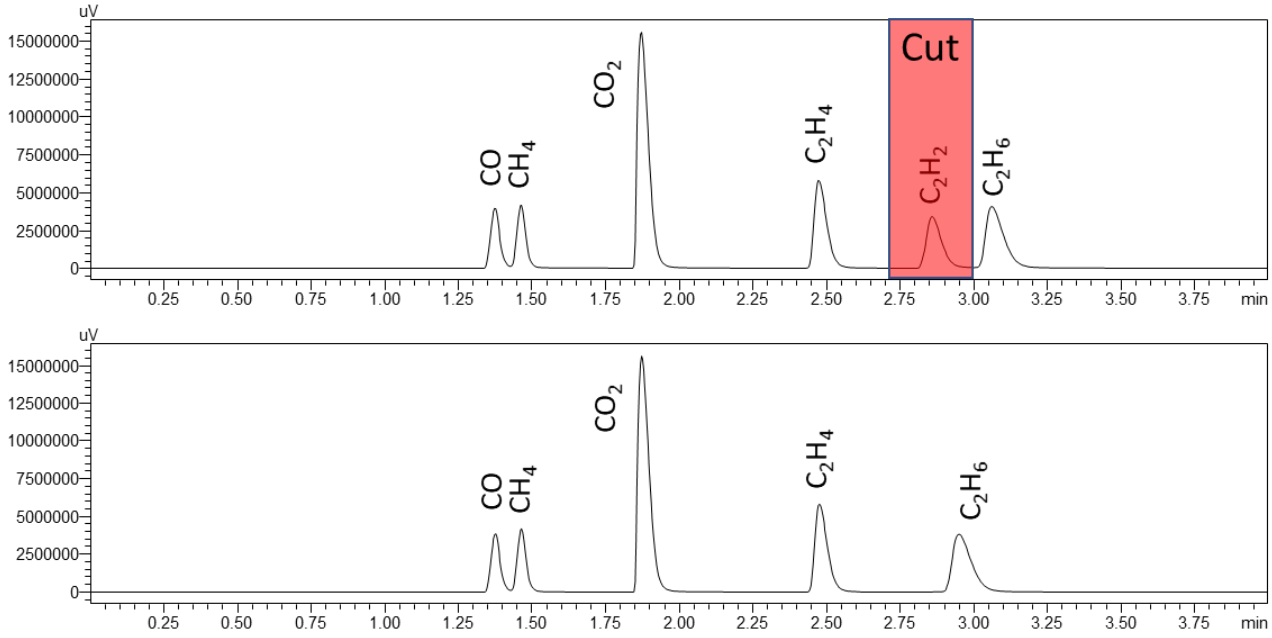

Figure 4: Representative chromatograms of Standard 2 with heart cutting acetylene to vent.

With Standard 2, separation of permanent gas/carbon monoxide composite peak, methane, carbon dioxide, ethylene, acetylene and ethane were completed in under 3.5 minutes. Oxygen, which normally causes significant baseline disturbances on traditional methanizers, causes no major deflections on the baseline with the Jetanizer™. As a result, carbon monoxide is detected by the Jetanizer™-FID with no interference from the coeluting permanent gas components.

The resulting data from Standard 2 is shown in Table 4. The peak areas were calculated normalized to methane to account for discrepancies in injection technique between data sets.

Standard 2 was injected in triplicate with the heart-cut valve timed to remove acetylene. The resulting data of Standard 2 is shown in Table 5. The heart-cut valve displayed no major disturbances to the baseline and caused only a minor change in retention time in the peak eluting after the heart cut. Peak areas normalized to methane indicate that the heart cut did not affect the peak areas of neighboring peaks.

With acetylene vented, the repeatability improved significantly with percent relative standard deviation dropping from 1 % to less than 0.3 %. Previous studies have shown some absorption of acetylene, which can have adverse effects on repeatability. This heart-cut technique can be applied to other high-concentration analytes or potentially harmful analytes to the methanizer catalyst material.

Table 4: Relative standard deviation for Standard 2

ANALYTE	DETECTOR	RETENTION TIME (MIN)	AVERAGE PEAK AREA	RSD% (N=3)	PEAK AREA NORMALIZED TO METHANE
CARBON MONOXIDE	Jetanizer™-FID	1.39	8601785	1.00	0.96
METHANE	Jetanizer™-FID	1.48	8910063	0.67	1.00
CARBON DIOXIDE	Jetanizer™-FID	1.90	39994197	0.17	4.60
ETHYLENE	Jetanizer™-FID	2.51	16664855	0.11	1.92
ACETYLENE	Jetanizer™-FID	2.90	11355536	1.01	1.39
ETHANE	Jetanizer™-FID	3.10	17121040	0.06	1.97

Table 5: Relative standard deviation for Standard 2 with heart cutting acetylene

ANALYTE	DETECTOR	RETENTION TIME (MIN)	AVERAGE PEAK AREA	RSD% (N=3)	PEAK AREA NORMALIZED TO METHANE
CARBON MONOXIDE	Jetanizer™-FID	1.39	7844457	0.27	0.93
METHANE	Jetanizer™-FID	1.48	8370707	0.25	1.00
CARBON DIOXIDE	Jetanizer™-FID	1.89	39239009	0.20	4.66
ETHYLENE	Jetanizer™-FID	2.50	16478246	0.29	1.94
ETHANE	Jetanizer™-FID	2.99	16389142	0.14	1.97

■ Conclusion

The capillary greenhouse gas design has been shown to be a highly repeatable and rapid analysis. With an analysis for nitrous oxide, methane, and carbon dioxide in under 2.5 minutes and calculated detection limits below 0.5 ppm for all analytes, high throughput and sensitivity can be achieved. The design is highly expandable with both the ability to quantify additional analytes and the ability 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, and robust.

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