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Rapid Greenhouse Gas Analysis by Gas Chromatography

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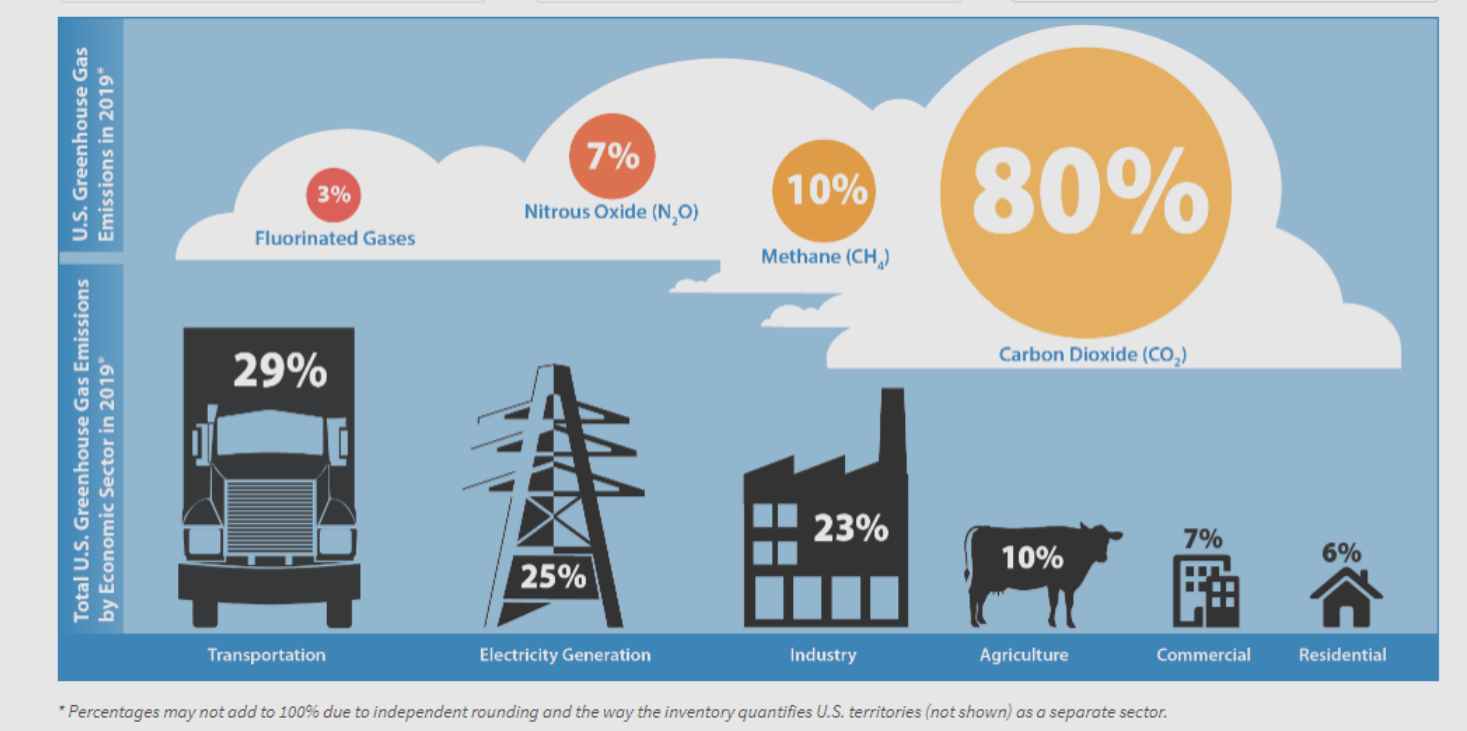
Shimadzu Scientific Instruments
NEMC 2022

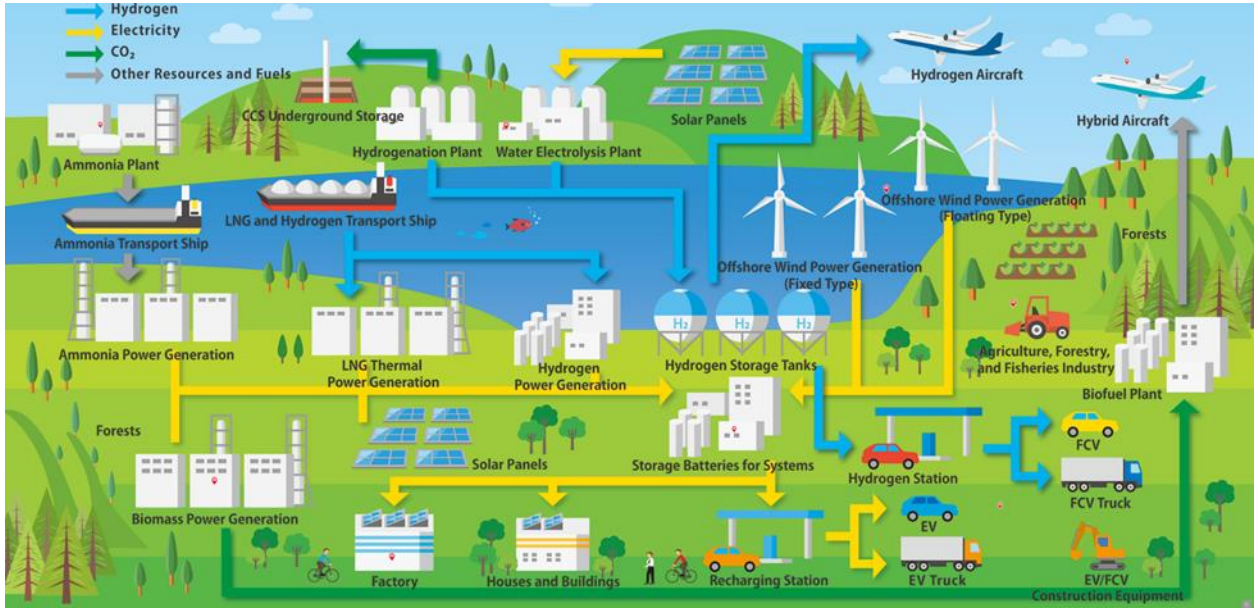
Green House Gas Emissions in US



https://cfpub.epa.gov/ghgdata/inventoryexplorer/

GHG Reduction Programs & Strategies

- Energy Efficiency
- Renewable Energy
- Supply Chain
- Waste Reduction and Diversion Strategies
- Reduce Methane Emissions
- Increase Fuel Efficiency in Transportation and Logistics



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Research & Innovation on going in multiple sectors and academia to implement suitable industrial processes, based on green chemistry.

GHG Reduction Programs & Strategies

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Key to the success of these efforts:
Proper and timely monitoring of GHG generated

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Analytical Techniques

- **Gas Monitors**
  - Good for continuous monitoring of flowing systems
  - Require LARGE amounts of sample (100 mL/min minimum flow rate)

- **Gas Chromatography**
  - Quantitative results
  - Run times depend upon system design
  - Sample required can be 1 mL or less, depending on setup
  - Different sample introduction techniques can be used

Gas Chromatography Drivers

- **Why not GCMS?**
  - GCMS is great for universal detection, but it is not suitable for air components that are found in the background.
  - The sensitivity is not as great as specialty detectors like the ECD.
- **What about water?**
  - Any moisture in the samples would be in vapor phase (since only gas is injected). The columns selected in this application are rugged with regards to water.
  - The system can be baked out at the end of each day at 120 C to remove any residual water in the system.
- **Why not use a universal detector instead of multiple specialty detectors?**
  - Universal detectors like a TCD or BID can be used, but a universal detector will detect all sample components (including the matrix). The signal from the different components may interfere with the signal of the targets of interest, and even hide it.
  - There isn't a good universal column for these analytes.
- **What if my sample is in Exetainer Vials and my standard is in a cylinder?**
  - Variety of sample introduction techniques can be used with Gas Chromatographs.

Gas Chromatography Sample Introduction

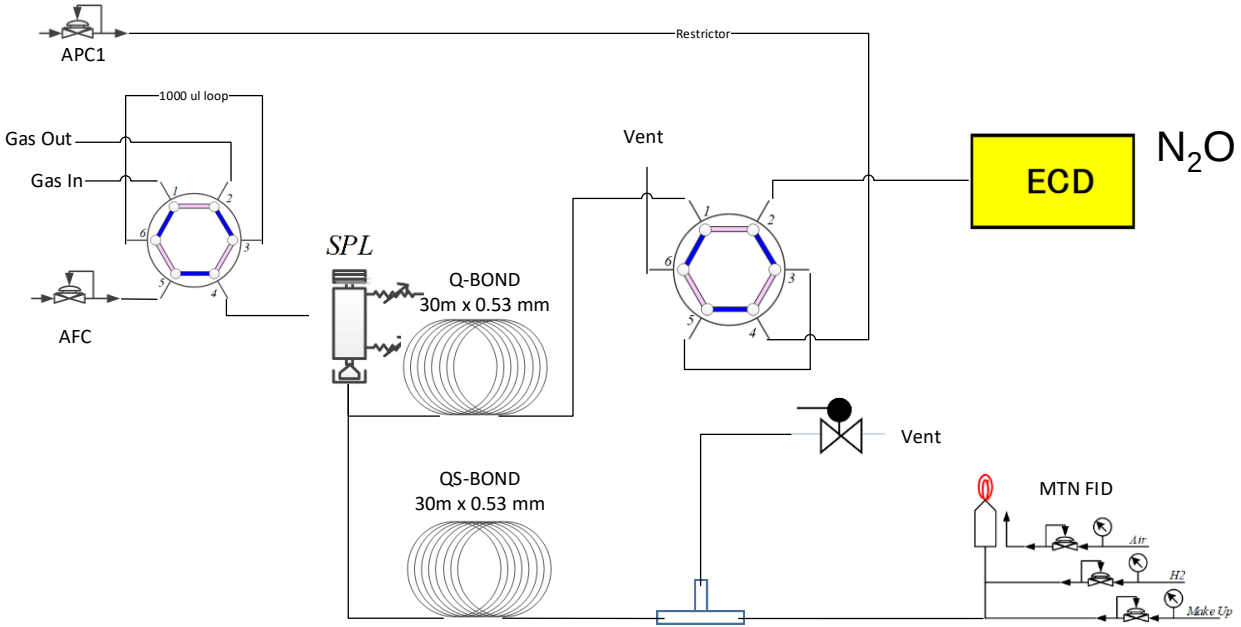
Multiple Sample Introduction Techniques

- Gas sampling valve flush on GC Top Deck for AOC-6000
- Specialty trays for Exetainer Vials for easy sampling
- Single Inlet for manual gas tight syringe injection
- External bulkheads for gas sample valve injection
  - Tedlar bags, Summa Cannisters, Standards
  - Reactor systems with sufficient headspace

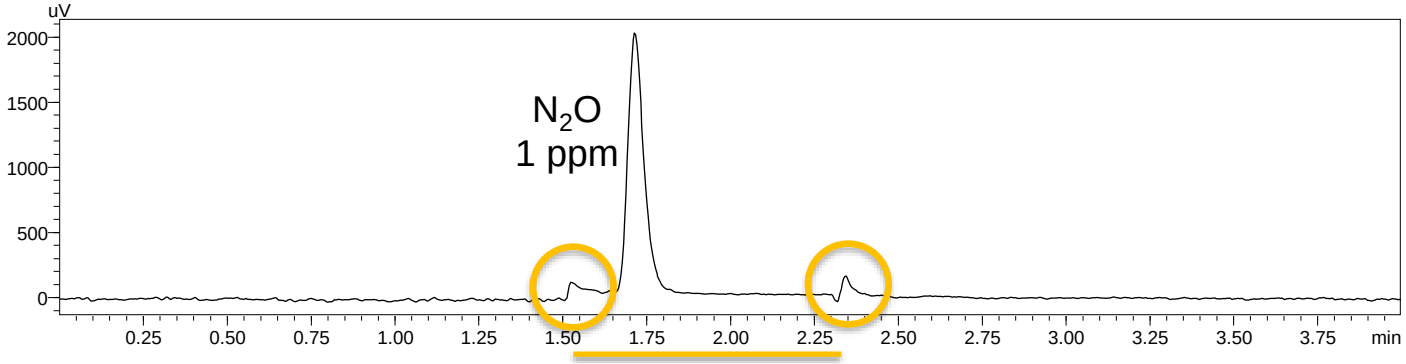
Gas Chromatography Setup

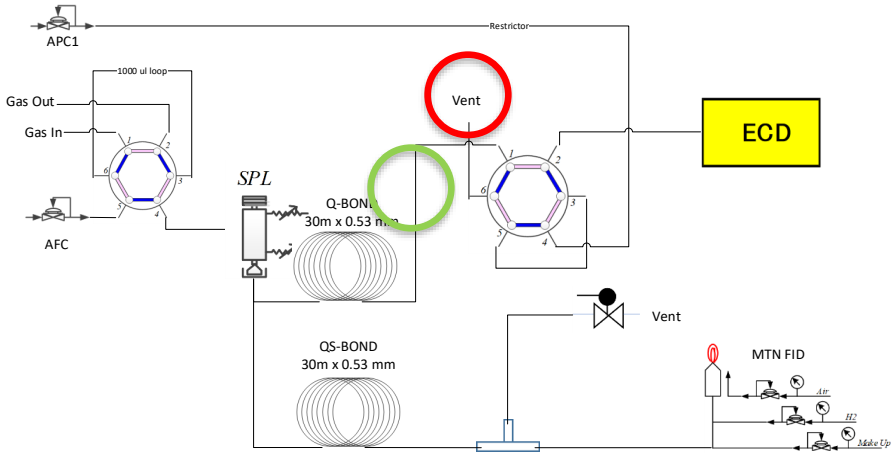
- **GC-2030**
  - Small Footprint
- **3.5 minute run time**
  - Capillary Optimized
  - CH_4, CO, CO_2, N_2O
  - If present, C_2H_4, C_2H_6, C_2H_2 are analyzed
- **Isothermal Run**
  - GC run time = GC cycle time
- **Gas Sample Valve with 1 mL loop**
- **Nitrogen carrier**

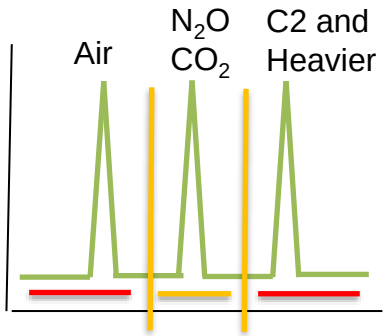
GC Flowpath


APC1
Restrictor
1000 ul loop
Gas Out
Gas In
AFC
SPL
Q-BOND
30m x 0.53 mm
Vent
ECD
N_2O
Vent
QS-BOND
30m x 0.53 mm
MTN FID
Air
H2
Make Up
CO, CH_4, CO_2

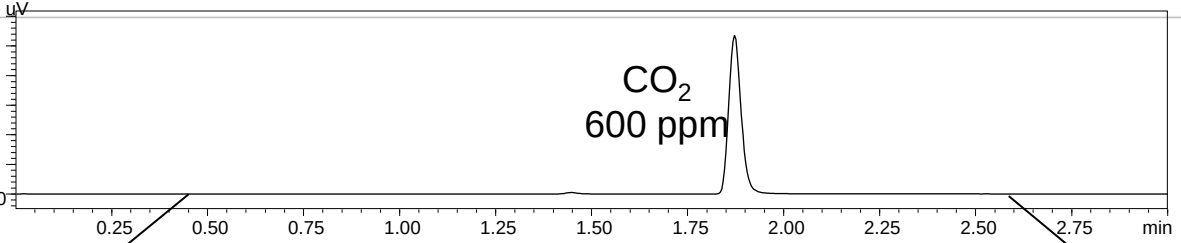
GC Chromatograms - ECD

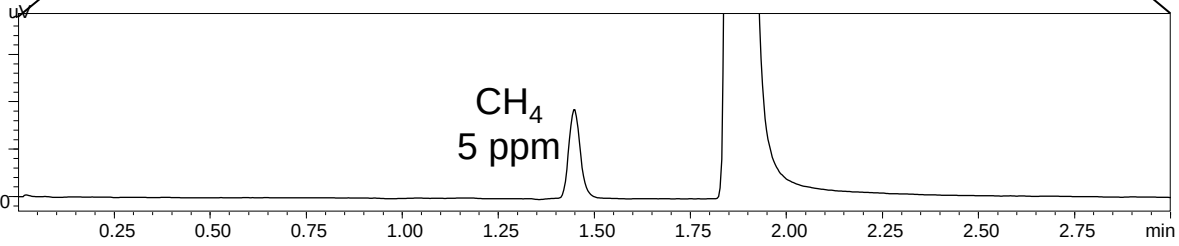


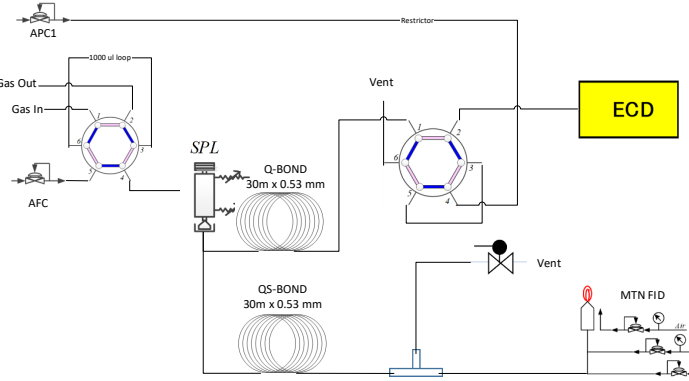




GC Chromatograms – Jetanizer FID







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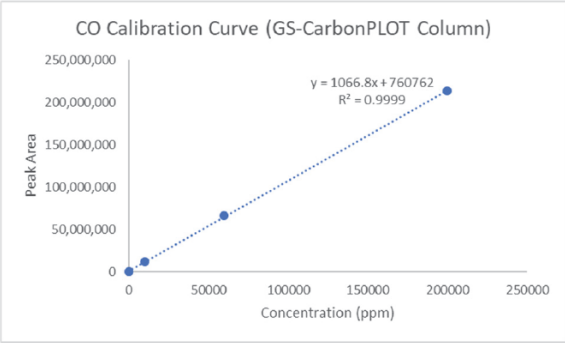
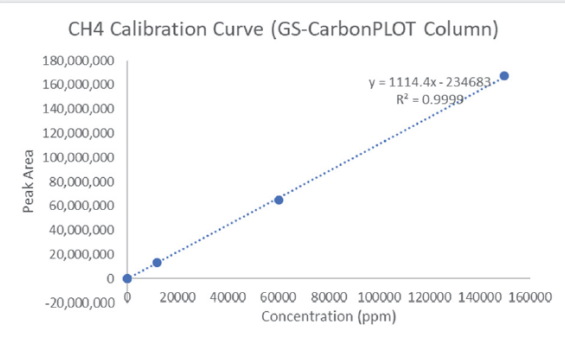
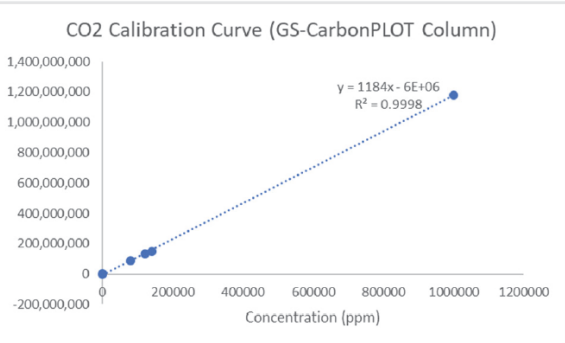
Linearity– Jetanizer FID

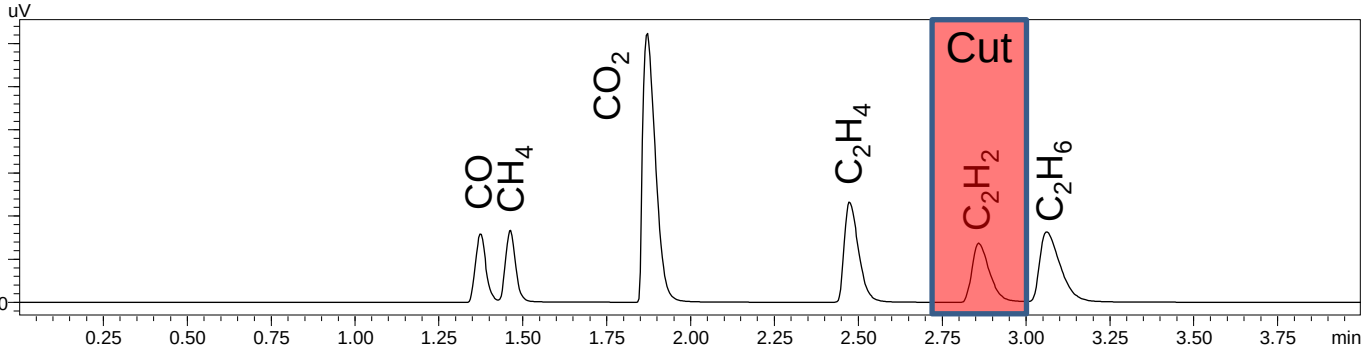
Concentration of Standards (ppm)						
Analytes	**Low TOGAS Standard 1**	**Low ppm Std Standard 2**	**12% CO_2 Standard 3**	**14% CO_2 Standard 4**	**8% CO_2 Standard 5**	**CO_2 Balance Standard 7**
Carbon Monoxide	100	0.96	59800	9900	199900	0
Methane	100	0.87	149900	60100	11900	53.5
Carbon Dioxide	400	2.55	120100	140100	78900	999935

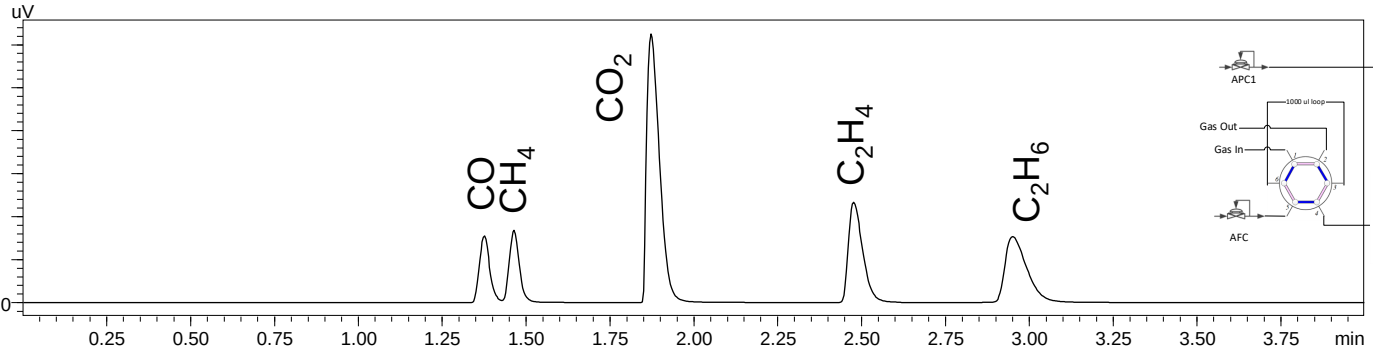


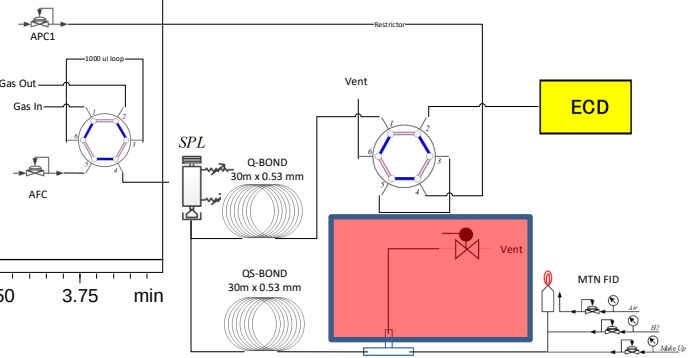




GC Chromatograms – Jetanizer FID







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Limits of Detection and Repeatability

ANALYTE	DETECTOR	RETENTION TIME (MIN)	AVERAGE PEAK AREA	RSD% (N=3)	S/N	CALCULATED 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)

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

% RSD up to 1% with acetylene eluting to Jetanizer FID

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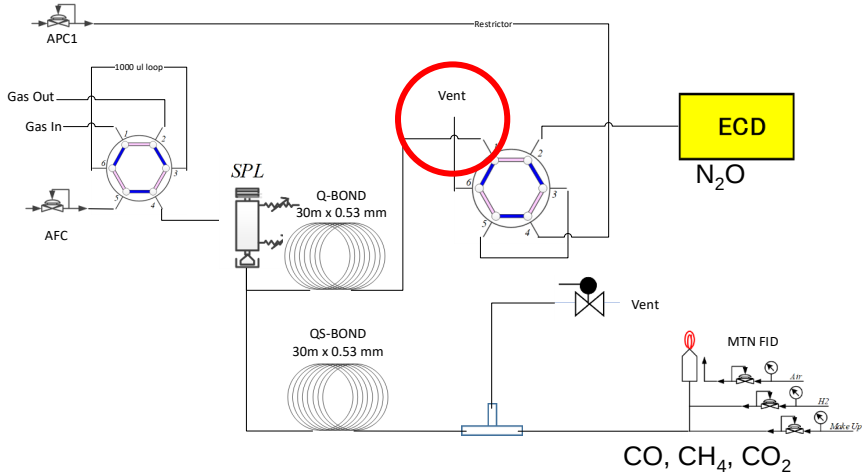
Limits of Detection and Repeatability

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

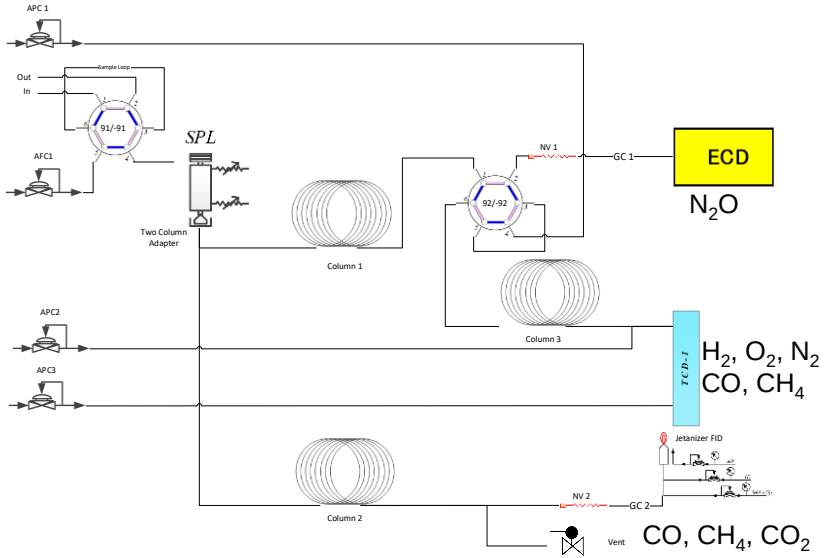
% RSD <0.3% with acetylene cut to vent

Analysis Expansion

- Addition of H_2, O_2, or N_2
- High concentrations of CO and CH_4



Nitrogen Carrier Gas



Argon Carrier Gas

Summary

- **Gas Chromatography offers a fast, user-friendly analysis of Greenhouse Gas**
- **Highly repeatable and sensitive analysis**
  - < 1 ppm LOD for all GHG analytes
  - < 1.01 % RSD
- **Small sample size required**
  - 1 mL of sample for each analysis
- **Flexible sample introduction for simple sample handling**
  - Exetainer vials, Tedlar Bags, Manual syringe injection, Headspace vials
- **Expandable to inorganic gas analysis**

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Questions?

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