

Simultaneous Analysis of Greenhouse Gases by Gas Chromatography

Chunxiao Wang

Senior Applications Chemist
Agilent Shanghai



Background

CO₂, CH₄, N₂O are considered the main greenhouse gases in the Earth's atmosphere.

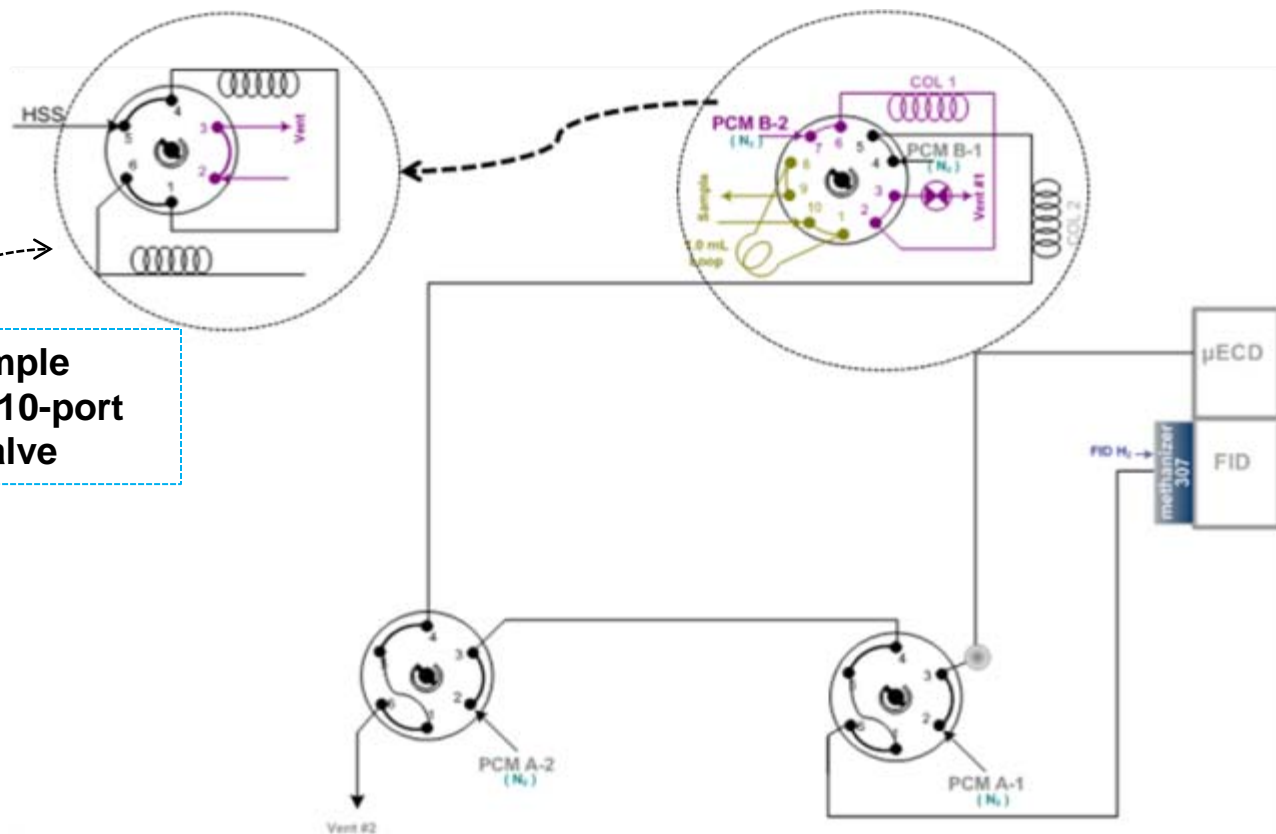
Continuous measurement of these gases provides meaningful information to track greenhouse gases emission trend and help in the fight against climate change.

Two Agilent 7890GC systems **SP1-7890-0468** and **SP1-7890-0467** meet the different requirements for simultaneous analysis of greenhouse gases including CH₄, CO₂, and N₂O in real samples



SP1-7890-0468

--Single Channel with Dual Detectors for N₂O, CO₂, CH₄



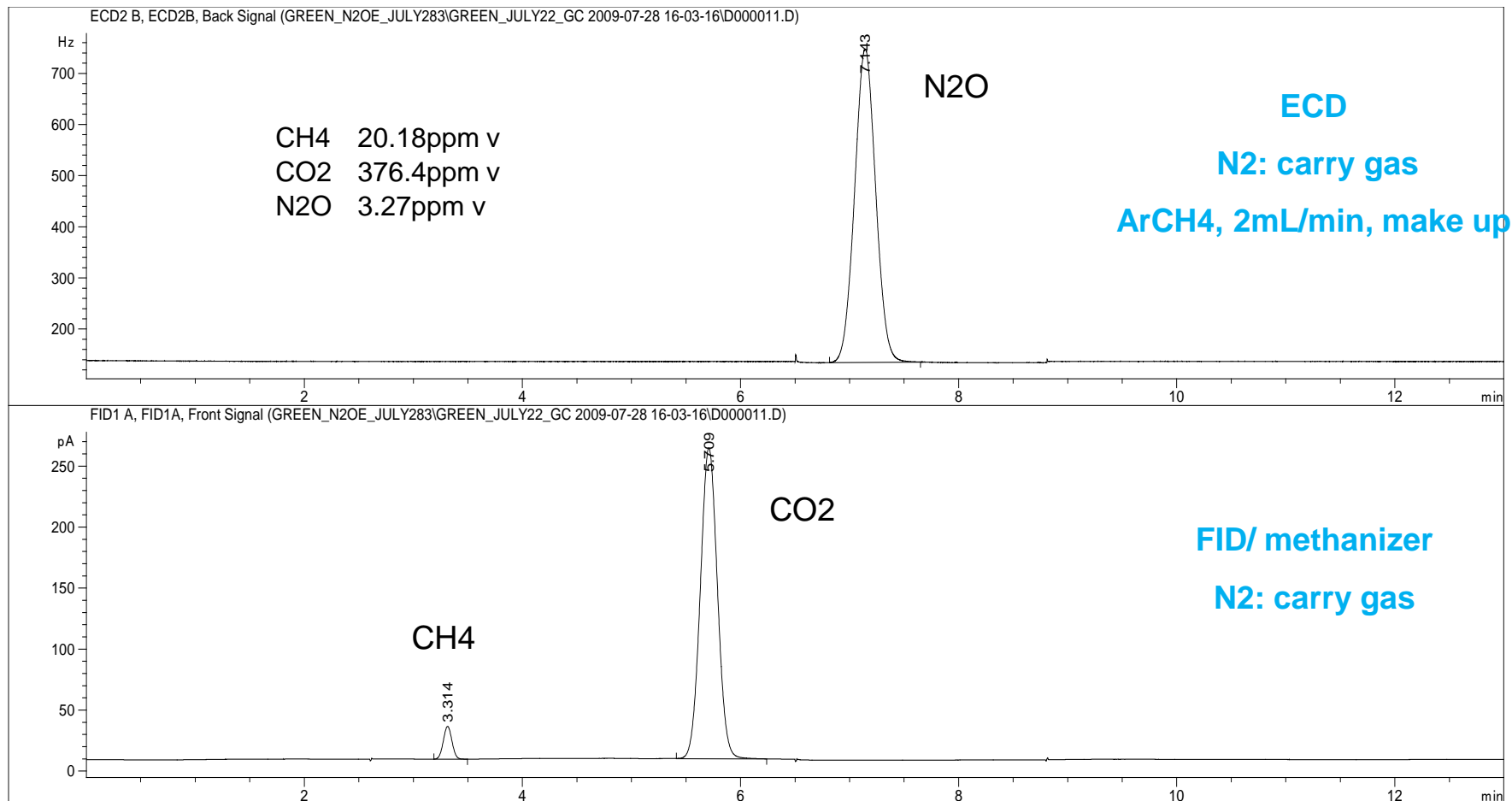
If HSS is required for sample injection, using option a 10-port valve instead of 6-port valve

A dynamic blending system is used to prepare the low level calibration standards using N₂ as diluents.

Typical GC Conditions

Valve temperature	100 °C
Oven temperature	60 °C
Mathanizer Temperature	370°C
Sample loop	1mL
Column 1,2 flow (N2)	21 mL/min (at 60C),, constant pressure
	Temperature : 250°C
FID	H2 flow: 48 mL/min
	Air flow: 500 mL/min
	Make up (N2): 2mL/min
ECD	Temperature : 350°C
	Make up, Ar-CH4(5%): 2mL/min

Chromatogram for Greenhouse Gases Standards



Quantitative precision

Repeatability for Greenhouse Gases Standards (n=21, exclude the first run)

Name	Average (Area)	STD DEV	RSD%
CH4	149.26	0.29	0.20
CO2	2779.04	17.16	0.62
N2O	8253.96	11.06	0.13

Greenhouse gases standards concentration, ppm V
CH4: 20.18, CO2: 376.4, N2O:3.27

... **Excellent quantitative precision**

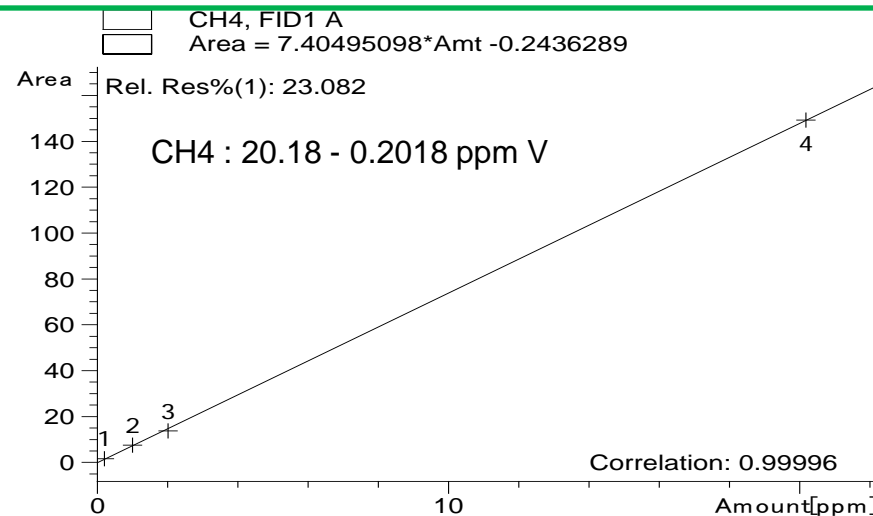
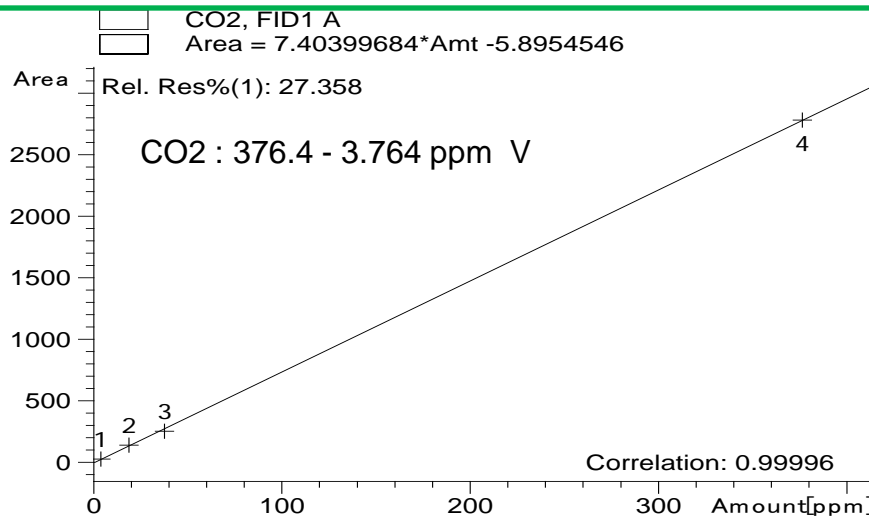
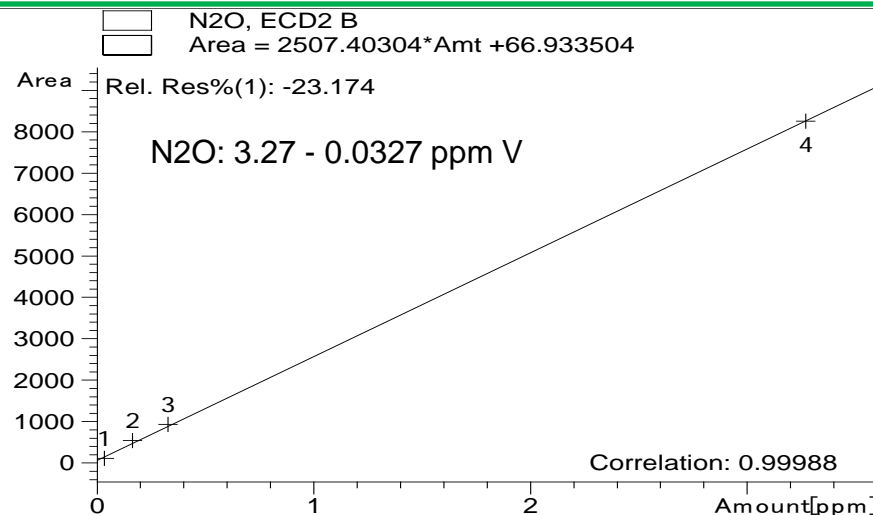
Multi-level Calibration for Greenhouse Gases Standards Using Dynamic Blending System

Standards sample information

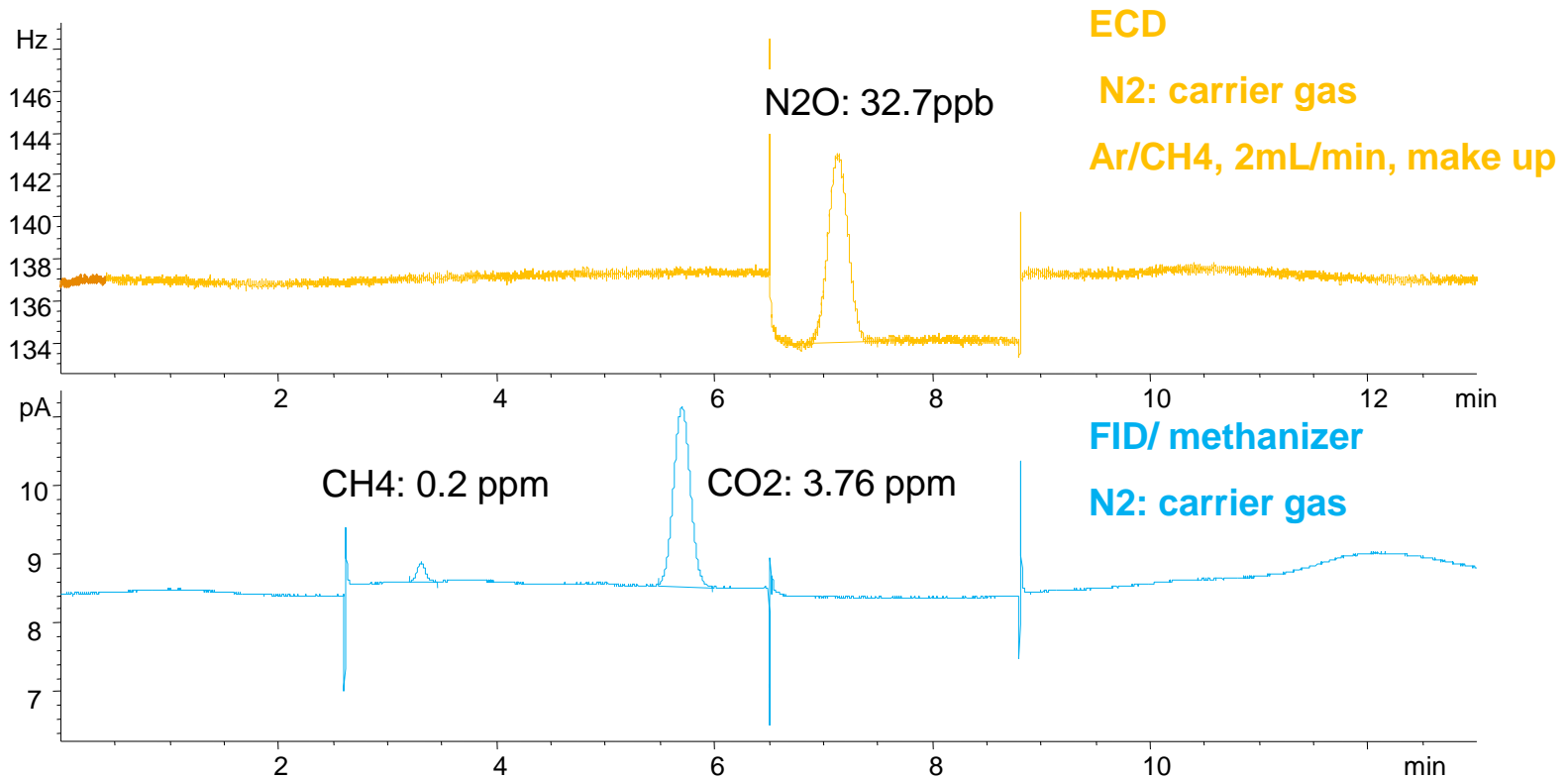
Greenhouse gases standards are diluted for multi-level calibration by dynamic blending

Concentration, ppm V

	Original	10 X diluting	20 X diluting	100X diluting
CH4	20.18	2.018	1.009	0.2018
CO2	376.4	37.64	18.82	3.764
N2O	3.27	0.327	0.1635	0.0327

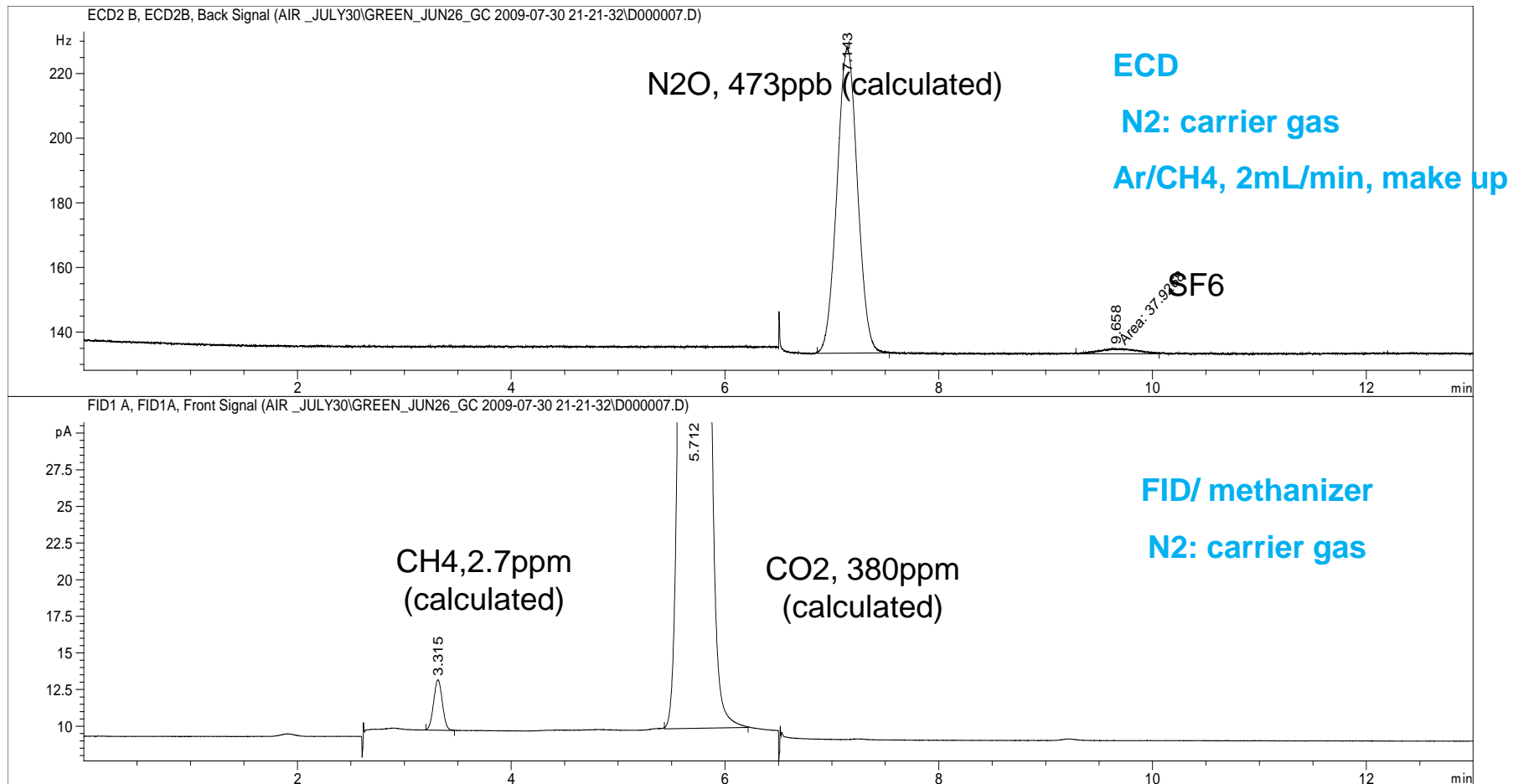


Chromatogram for CH₄, CO₂ and N₂O Standards with a 100-fold Dilution

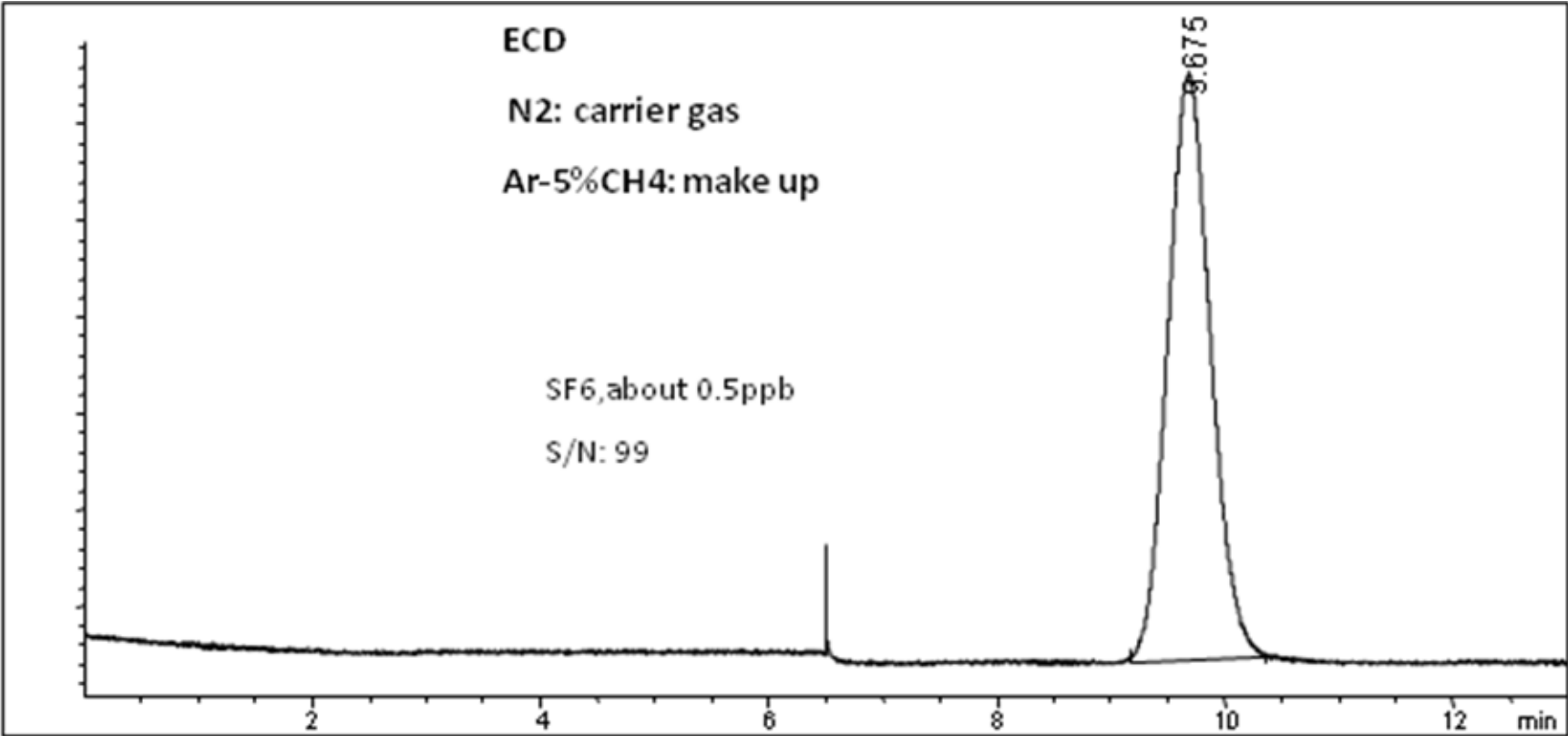


... Excellent Sensitivity

Chromatogram of Real Sample (Laboratory Air)

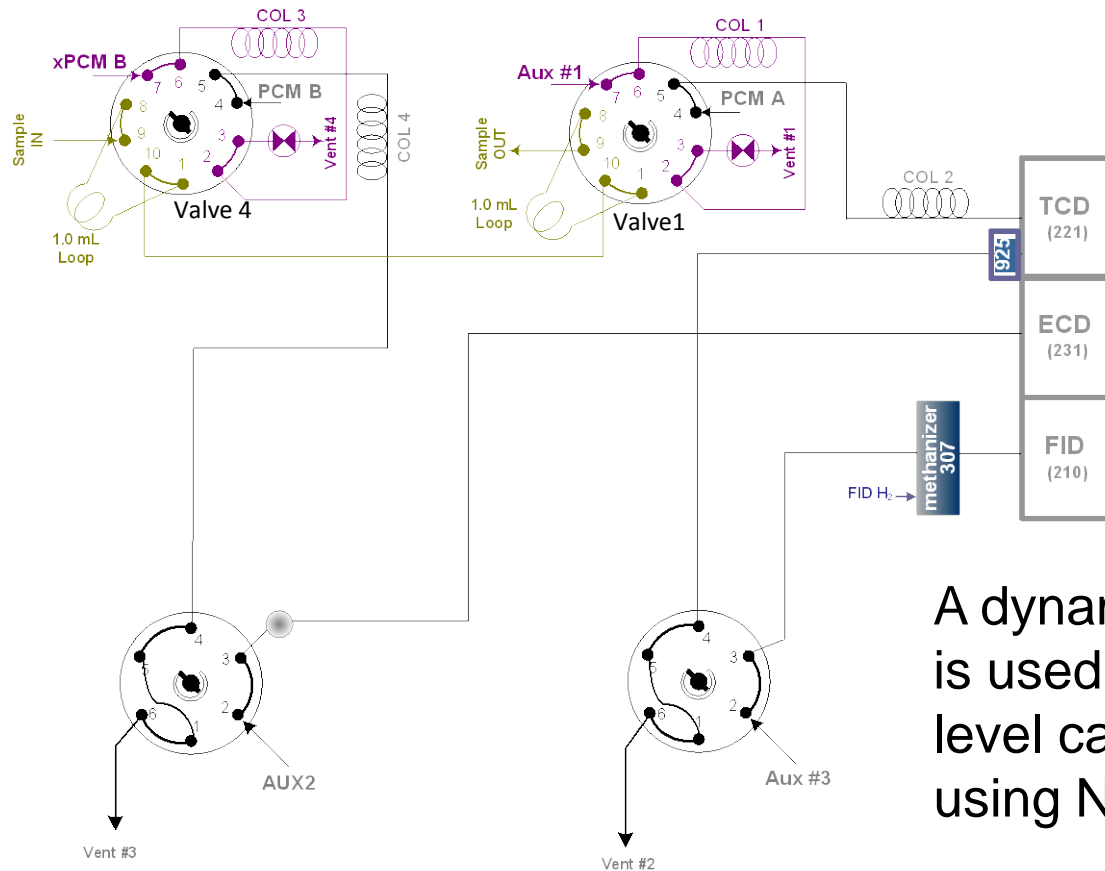


Chromatogram of SF6 Standard at Approximately 0.5 ppb



SP1-7890-0467

- Separate channels for N₂O and CO₂/CH₄
- CO₂ can be analyzed at wide concentration levels

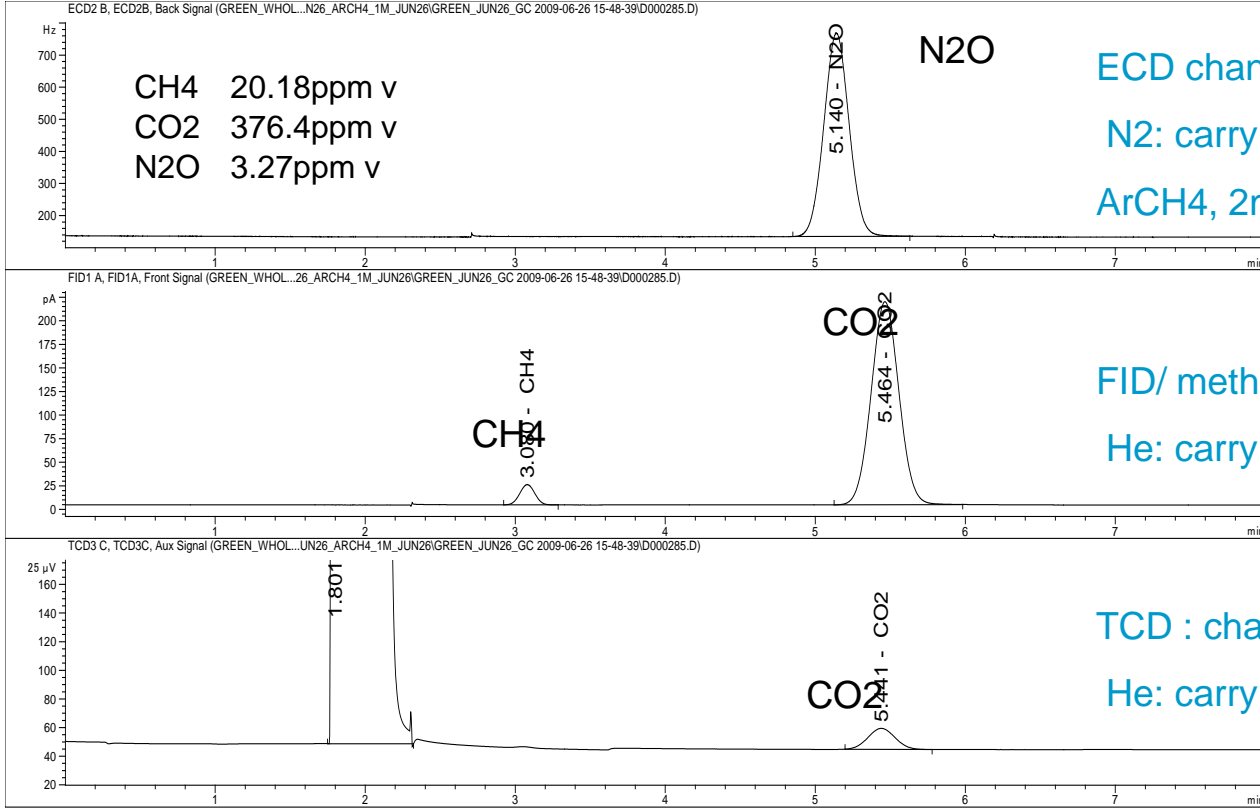


A dynamic blending system is used to prepare the low level calibration standards using N₂ as diluents.

Typical GC Conditions

Valve temperature	100 °C
Oven temperature	60 °C
Sample loop	1mL
Column 1,2 flow (He)	21 mL/min (at 60C),, constant pressure
Column 3, 4 flow (N2)	21 mL/min (at 60C),, constant pressure
	Temperature : 200°C
FID	H2 flow: 48 mL/min
	Air flow: 500 mL/min
	Make up (N2): 2mL/min
	Temperature: 200°C
TCD	Reference flow: 40 mL/min
	Make up: 2 mL/min
ECD	Temperature : 350°C
	Make up, Ar-CH4(5%): 2mL/min
Mathanizer	Temperature : 370°C

Chromatogram for Greenhouse Gases Standards Sample



ECD channel
 N2: carry gas
 ArCH4, 2ml/min, make up

FID/ methanizer channel
 He: carry gas

TCD : channel
 He: carry gas

Quantitative precision for Greenhouse Gases Standards(n=20, exclude the first run)

Name	Average (Area)	STDVE	RSD%
CH4	151.61	0.64	0.42
CO2(FID)	2788.51	14.72	0.53
N2O	7467.92	13.91	0.19
CO2(TCD)	186.00	0.80	0.43

Greenhouse gases standards concentration, ppm V

CH4: 20.18, CO2: 376.4, N2O:3.27

... Excellent Quantitative precision

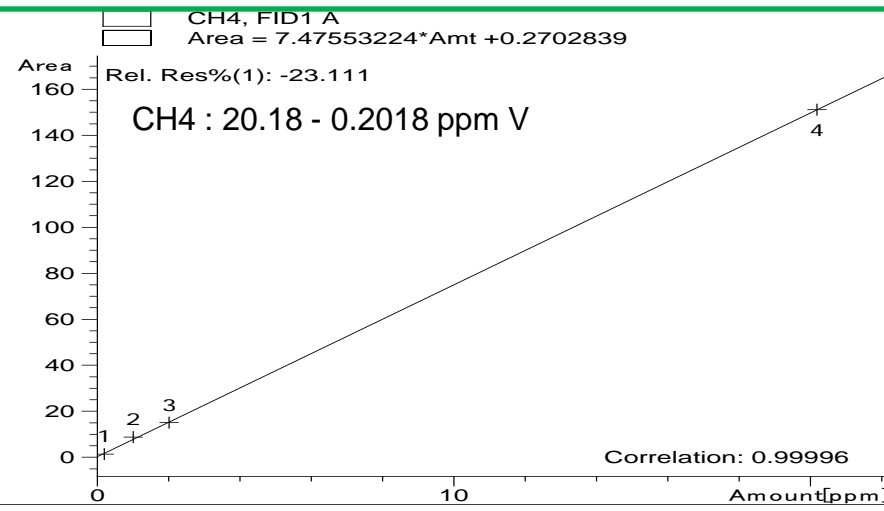
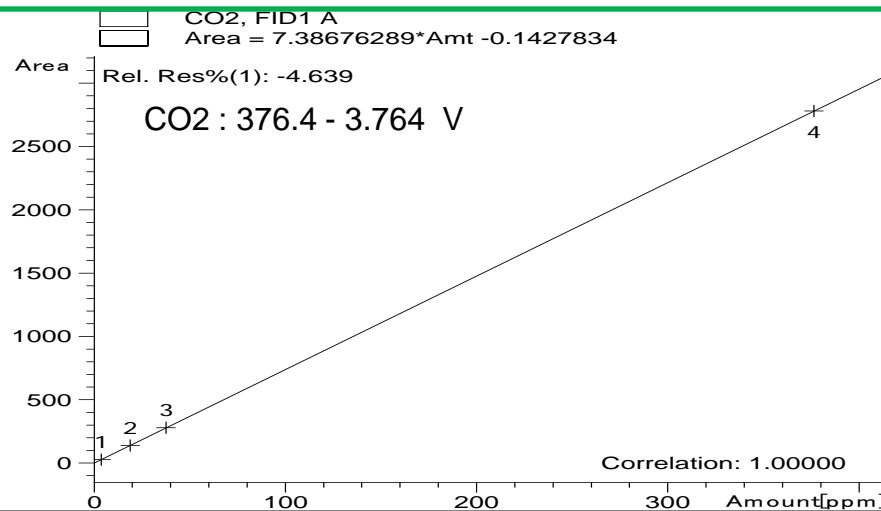
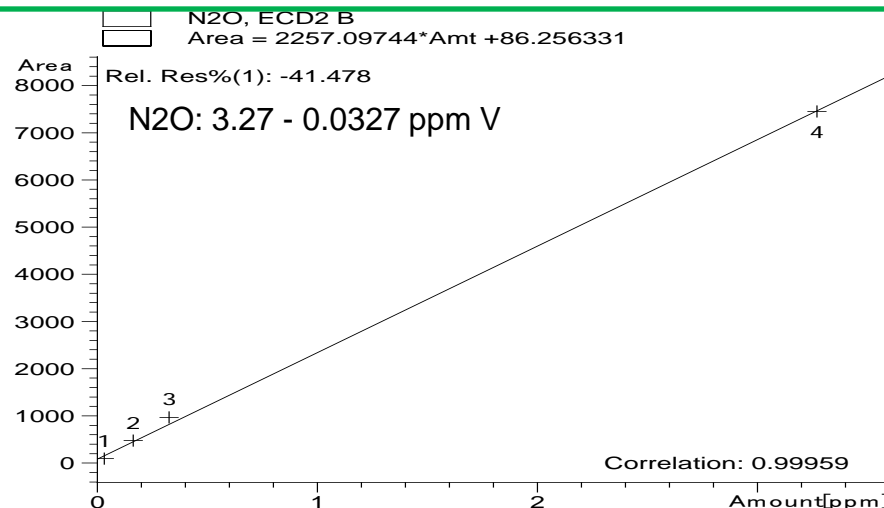
Multi-level Calibration for Greenhouse Gases Standards Using Dynamic Blending System

Standards sample information

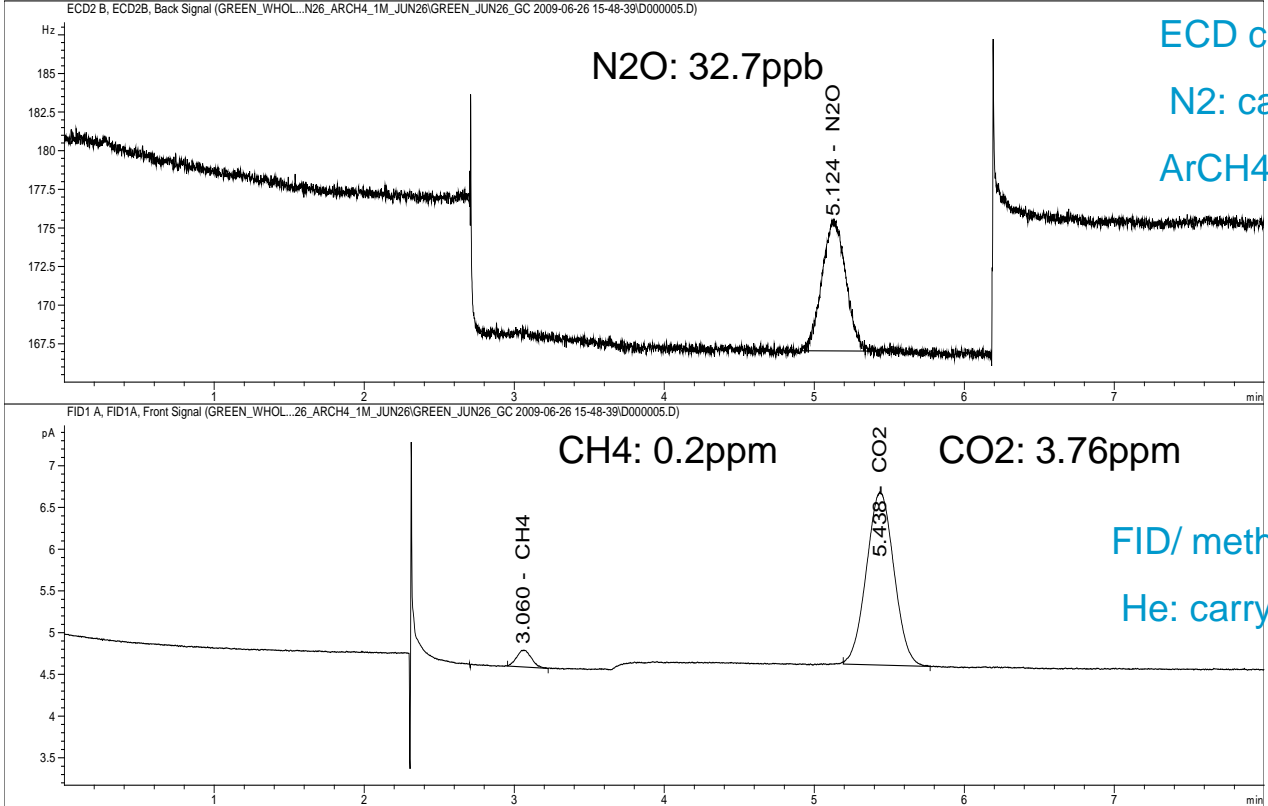
Greenhouse gases standards are diluted for multi-level calibration by dynamic blending

Concentration, ppm V

	Original	10 X diluting	20 X diluting	100X diluting
CH4	20.18	2.018	1.009	0.2018
CO2	376.4	37.64	18.82	3.764
N2O	3.27	0.327	0.1635	0.0327



Chromatogram for Greenhouse Gases Standard Sample Diluted 100x

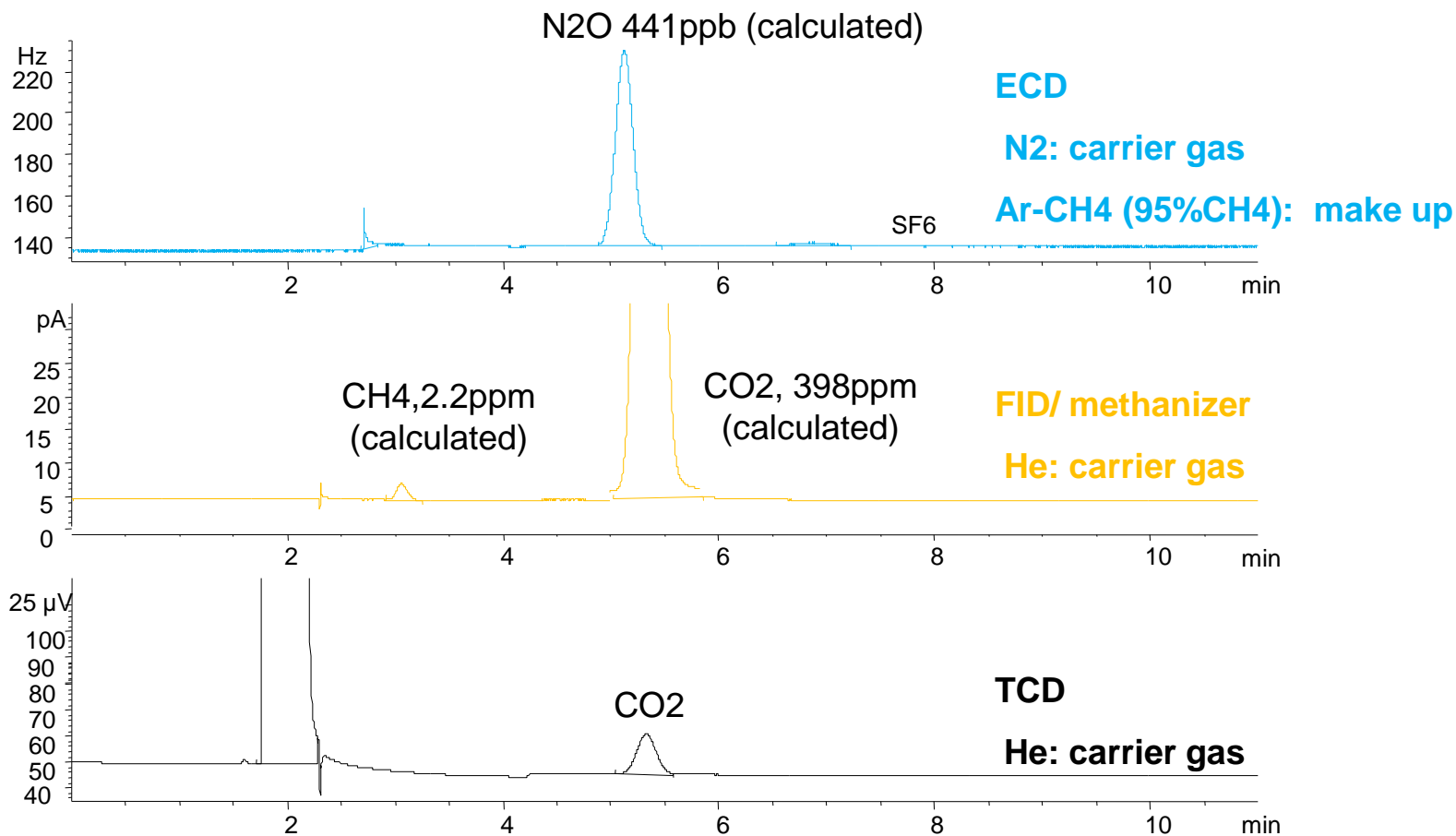


ECD channel
N2: carry gas
ArCH4, 2ml/min, make up

FID/ methanizer channel
He: carry gas

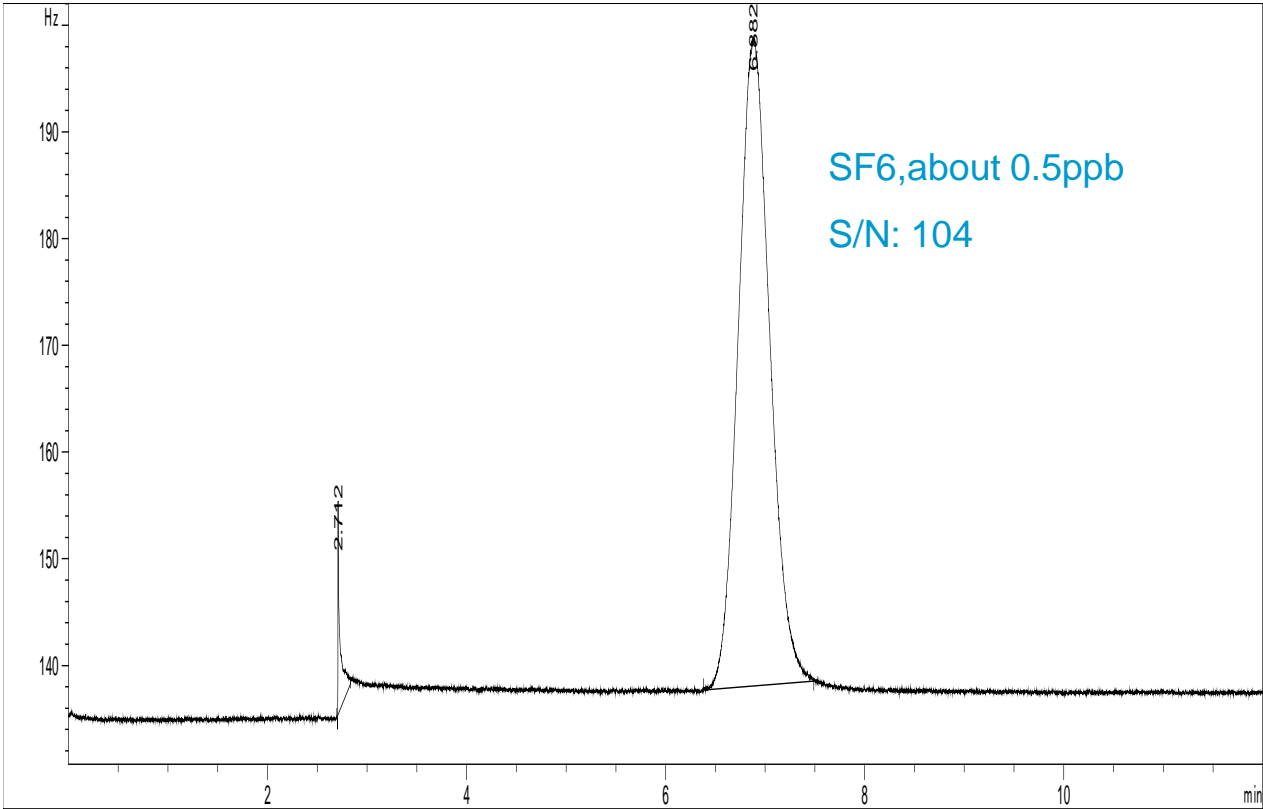
... Excellent Sensitivity

Chromatogram of Real Sample (Laboratory Air)



**Results obtained for greenhouse gases by
SP1-7890-0467 are equivalent to SP1-7890-0468**

Chromatogram for SF6 Standard (100ppb) Diluted 200x



Comparison between SP1 7890-0468 and SP1 7890-0467

		SP1 7890-0468	SP1 7890-0467)
Configuration	Channel	Single channel	Two separated channel
	Detector	FID, uECD	FID, uECD, TCD
	Valve/Column	3-Valve/2-Column	4-Valve/4-Column
	Methanizer	Yes	Yes
Possibility of auto-sampling by HSS		Yes	No
Fast analysis		No	Yes
Quantification ranges	N20 (Lowest quantification limit)	30ppb	30ppb
	CH4	0.2ppm -20%	0.2ppm -20%
	CO2	0.4 ppm- 0.2% by FID-methanizer	0.4 ppm – 0.2% by FID-methanizer 20 ppm - 20% by TCD

Summary

- ✓ 7890 A GC with multi-valve, ECD, methanizer-FID combination provides simultaneous analysis of greenhouse gas with one injection.
- ✓ The ECD's high sensitivity ensures the detection of N₂O at ppb level.
- ✓ An easy-to-use union based on Capillary Flow Technology is used to connect valves and μ ECD improving the chromatographic performance including the peak shape.
- ✓ The systems are easily expanded to include the determination of sulfur hexafluoride.
- ✓ Analyzer SP1 7890-0468 has single channels with a simpler valve configuration and It is possible to use a 6-port valve instead of a 10-port to allow auto-sampling by a Headspace sampler.
- ✓ Analyzer SP1 7890-0467 has 2 separate channels with three detectors achieve even faster results. The separate channels increase flexibility to make the valve switching time less critical and the method easier to set up. The use of the third TCD, also allows measure a wide concentration range of CO₂.
- ✓ Results obtained on both analyzers are the same for greenhouse gases (N₂O, CH₄, CO₂ and SF₆).