



Toward improving precision of SF₆ measurement: comparison between various analytical methods using GC-μECD

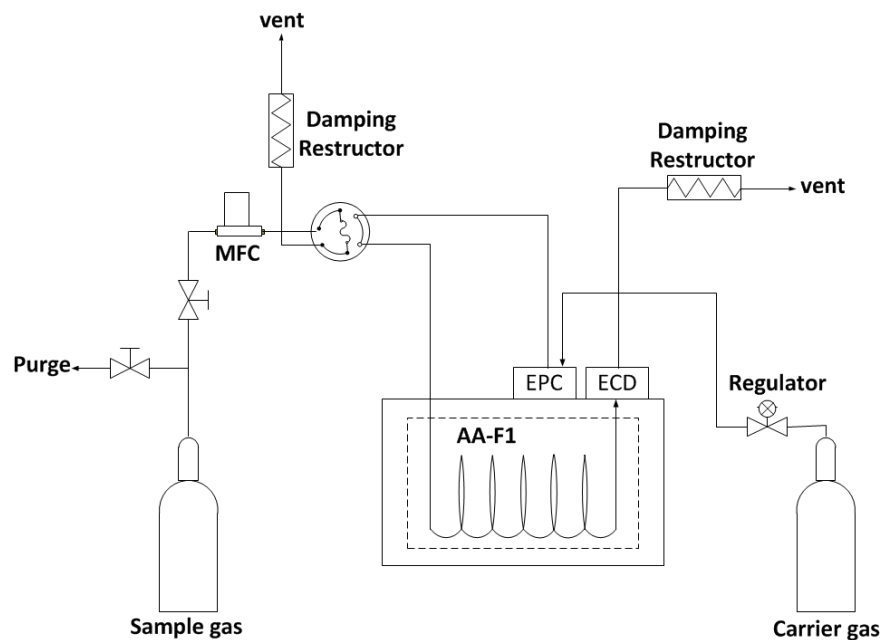
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Center for gas analysis

Recommended compatibility of measurements

Component	Compatibility goal	Extended compatibility goal	Range in unpolluted troposphere	Range covered by the WMO scale
CO ₂	± 0.1 ppm (Northern hemisphere) ± 0.05 ppm (South. hemisphere)	± 0.2 ppm	360 - 450 ppm	250 – 520 ppm
CH ₄	± 2 ppb	± 5 ppb	1700 – 2100 ppb	300 – 2600 ppb
CO	± 2 ppb	± 5 ppb	30 – 300 ppb	20 -500 ppb
N ₂ O	± 0.1 ppb	± 0.3 ppb	320 – 335 ppb	260 – 370 ppb
SF ₆	± 0.02 ppt	± 0.05 ppt	6 – 10 ppt	1.1 – 9.8 ppt
H ₂	± 2 ppb	± 5 ppb	450 – 600 ppb	140 – 1200 ppb
δ ¹³ C-CO ₂	± 0.01‰	± 0.1‰	-7.5 to -9‰ vs. VPDB	
δ ¹⁸ O-CO ₂	± 0.05‰	± 0.1‰	-2 to +2‰ vs. VPDB	
Δ ¹⁴ C-CO ₂	± 0.5‰	± 3‰	0-70‰	
Δ ¹⁴ C-CH ₄	± 0.5‰		50-350‰	
Δ ¹⁴ C-CO	± 2 molecules cm ⁻³		0-25 molecules cm ⁻³	
δ ¹³ C-CH ₄	± 0.02‰	± 0.2‰		
δD-CH ₄	± 1‰	± 5‰		
O ₂ /N ₂	± 2 per meg	± 10 per meg	-250 to -800 per meg (vs. SIO scale)	

GC-ECD system for SF₆ analysis



Low dead volume

- gauge less regulator
- Short gas tubes

Damping restrictor



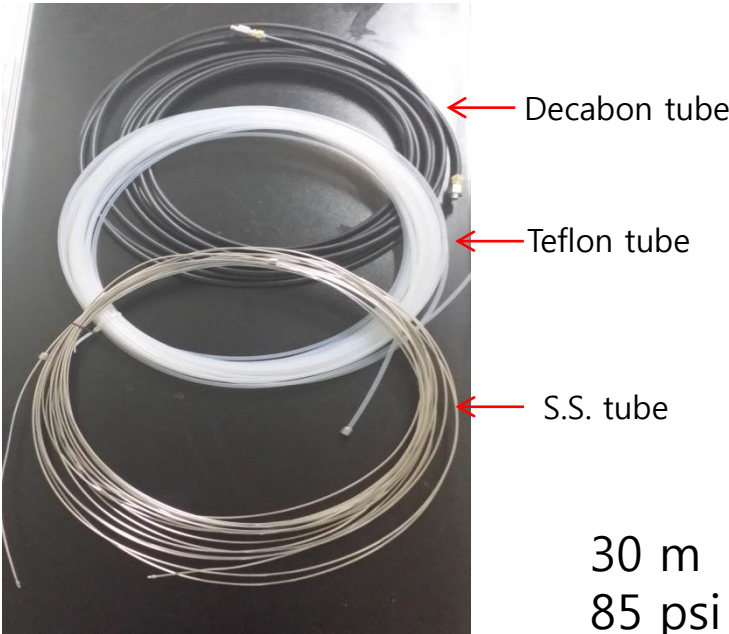
Agilent 6890A

Microcell electron capture detector

Tube material dependance

Stainless steel, Teflon, Decabon

Analytical Condition	
Detector	μECD
Detector temperature	350 °C
Carrier gas	P-5 gas, 90 psi
Oven Temperature	50 °C, 14 min 30 °C/min 190 °C 4 min
Column	RESTEK Activated Alumina F- 1 80/100 18 ft * 1/8 inch SS
Sample flow	100 mL/min
sample loop size	5 mL
Valve time	0.1 On/1.2 Off



		Sensitivity	Analytical repeatability (<i>k</i> =2)	%difference (with S.S tube)
S.S tube	SF ₆	126.75	0.17	-
	N ₂ O	38.54	0.14	-
Decarbon tube	SF ₆	127.55	0.16	+0.01
	N ₂ O	38.66	0.60	+0.30
Teflon tube	SF ₆	126.37	0.80	+0.02
	N ₂ O	36.70	3.5	-4.77

Regulator material dependence

Stainless steel, Brass



Gauge-less stainless steel regulator



brass regulator

	Sensitivity	Analytical repeatability (<i>k</i> =2)	%difference (with S.S)
S.S regulator	126.75	0.17	-
Brass regulator	126.32	0.20	0.34

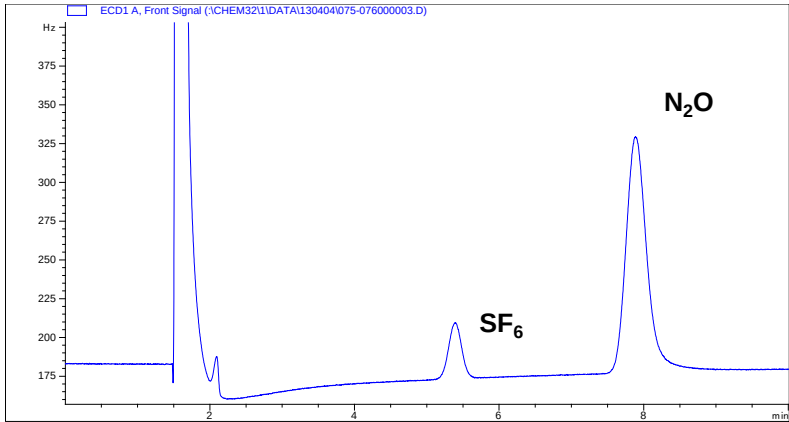
Detector Type	Detection level	Available regulator	Features	Target	
FID	All level > 50 ppm	High purity brass regulator	* S.S. diaphragm	CH ₄ , CO ₂	
TCD			* Nickel plated		
PID			brass barstock		
ECD			bodies		
ECD	< 50 ppm	High purity stainless steel regulator	* tied S.S.	SF ₆ , N ₂ O, CFC, HFCs	
MSD	All level		*S.S. barstock		
AED			bodies		

Comparison between separation column

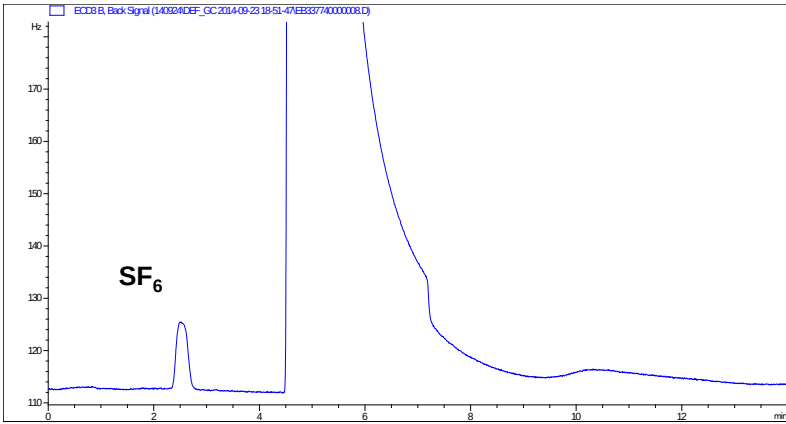
Molecular Sieve 5A, Porapak-Q and Activated Alumina-F1

Specification	Condition
Detector	GC- μ ECD
Detector temp.	380 °C
Makeup gas	15 mL/min
Oven temp.	50 °C
Carrier flow	P-5, 45 psi
Sample loop	2 cc
Sample flow	200 mL/min

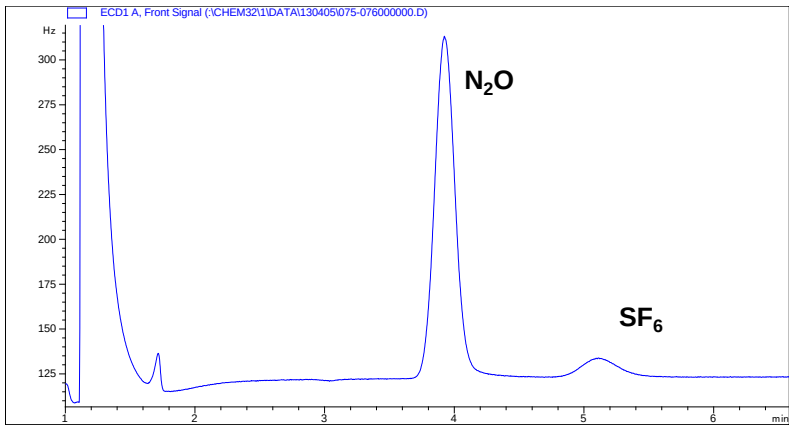
<AA-F1>



<MS-5A>



<PP-Q>

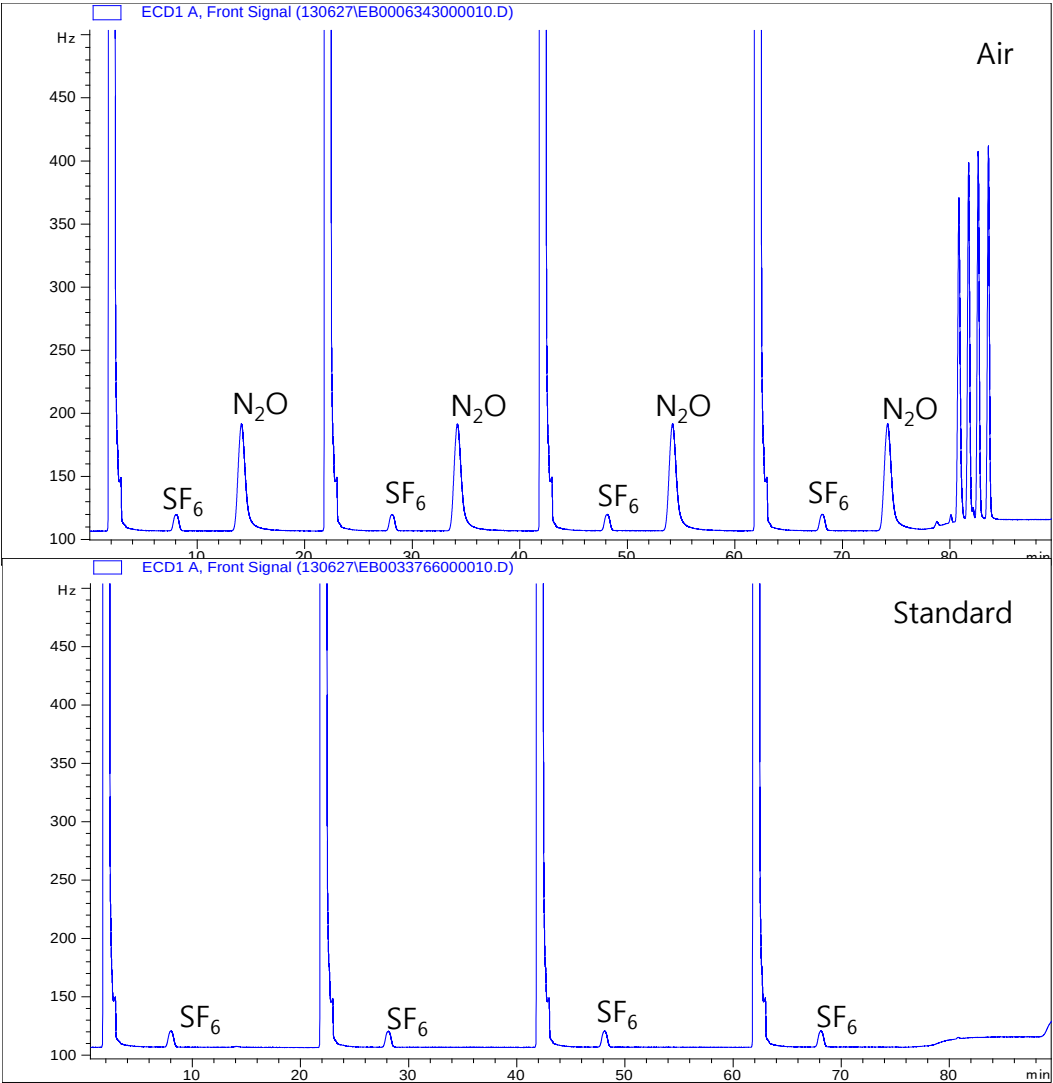


	SF_6 detection	SF_6 peak shape	N_2O detection	N_2O peak shape	O_2 Peak appearance
AA-F1	5	gaussian	8	asymmetric	At injection
PP-Q	5	Broadened	4	gaussian	At injection
MS-5A	2.5	Gaussian	Poorly defined		After SF_6

Measurement sequence

<Analytical condition>

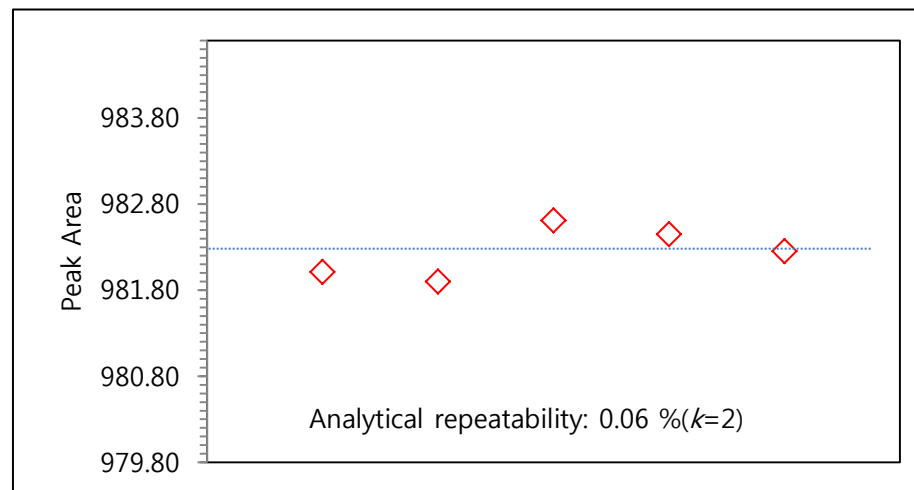
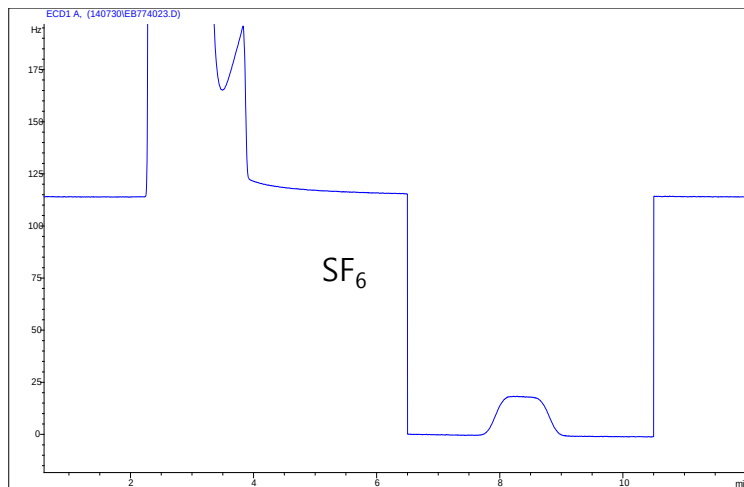
Specification	Condition
Detector	μECD
Detector temp.	350 °C
Reference flow	15 mL/min
Oven temp.	35 °C, 75 min 30 °C/min 170 °C 10min
Column	AA-F1 80/100 12ft* 1/8 inch SUS
Sample loop	10 mL
Carrier flow	P-5, 95psi
Sample flow	100 mL/min



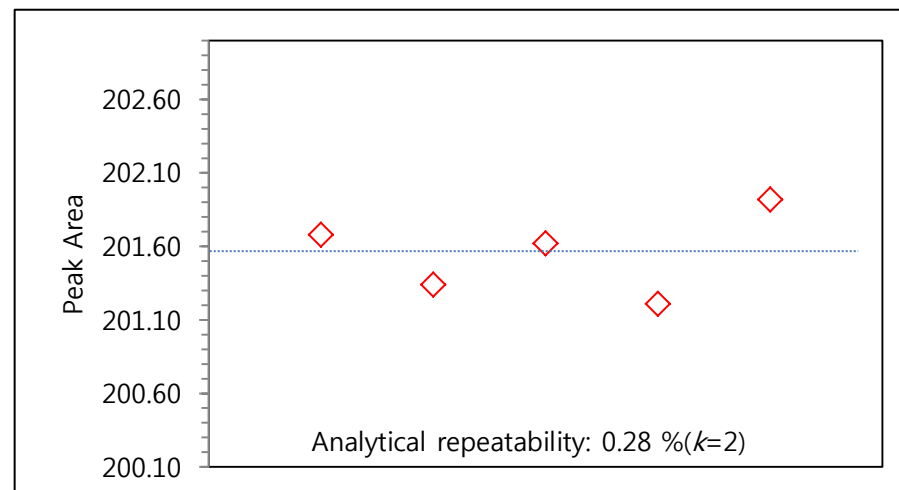
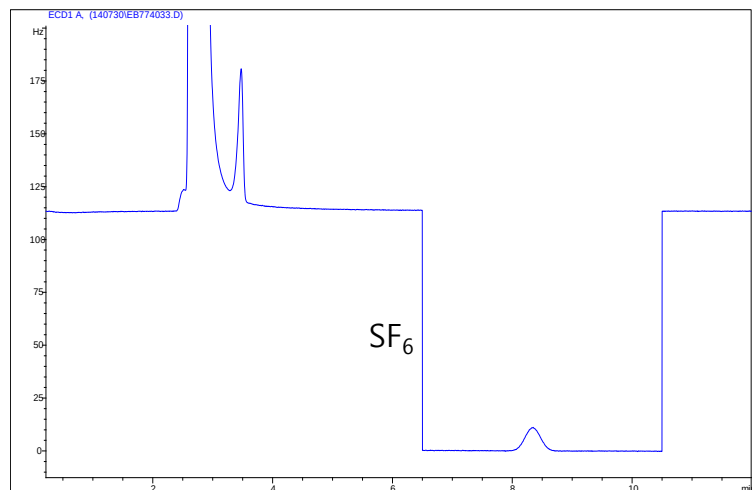
Instrument isolation

Damping restrictor effect

w/ Restrictor



w/o Restrictor



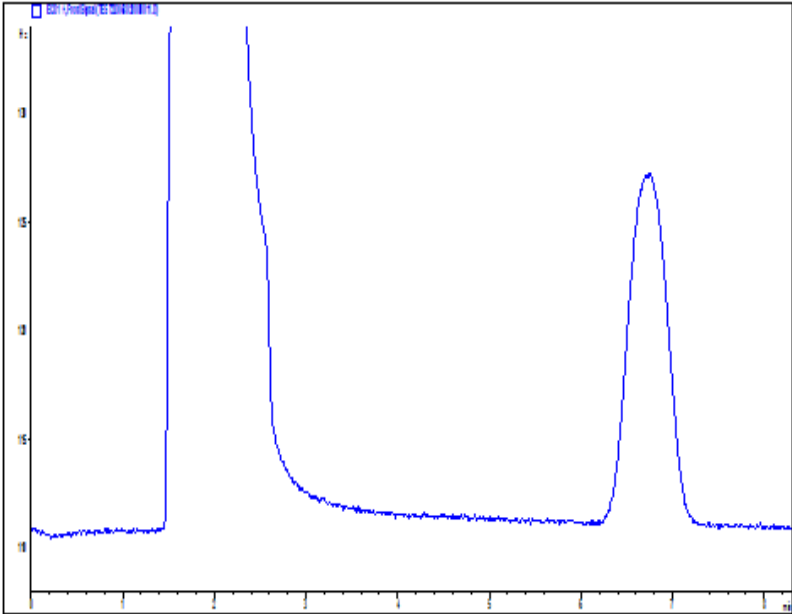
Drift correction

Number of measurements*	Peak area	Ratio Value $S_i \cdot 2 / (R_i + R_{i+1})$	Deviation [%]	Instrumental drift [%]
R1	473.04			
S1	541.89	1.1454	0.00	
R2	473.17			+ 0.03
S2	541.80	1.1439	-0.13	
R3	474.10			- 0.20
S3	541.31	1.1427	-0.23	
R4	473.29			-0.20
S4	541.72	1.1465	0.10	
R5	471.70			-0.33
S5	541.99	1.1483	0.26	
R6	472.27			+0.12
Average		1.1454		
Standard deviation		0.0022 (0.19%)		

* 3 injection per a measurement

Best precision of Activated Alumina F1 column

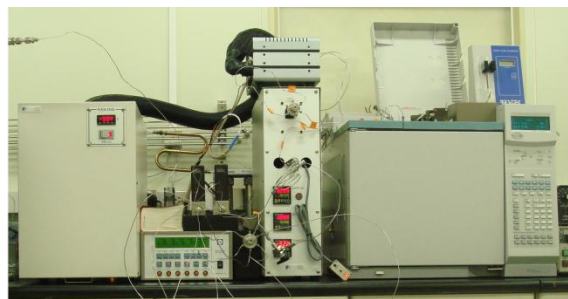
Analytical Condition	
Detector	μECD
Detector temperature	375 °C
Make up gas	P-5 gas, 30 mL/min
Carrier gas	P-5 gas, 45 psi
Oven Temperature	35 °C, 7 min
Column	RESTEK Activated Alumina F-1 80/100 12 ft * 1/8 inch SS
Sample flow	50 mL/min
sample loop size	7 mL
Valve time	0.1 On/1.1 Off
restrictor	Less pressurized



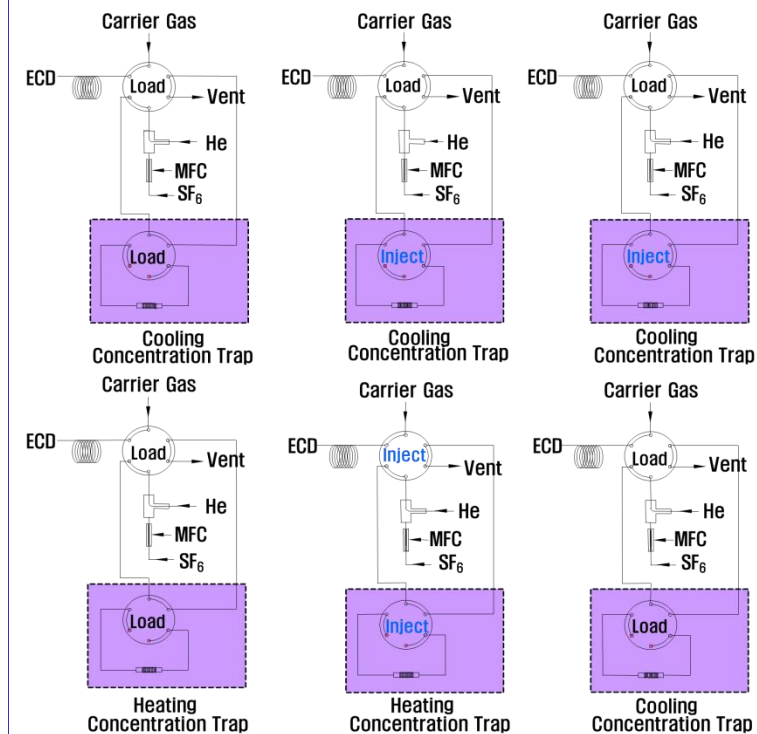
Cyl.No.	Conc. [pmol/mol]	1	2	3	Ave.	RSD [%]	SD [pmol/mol]
D068020	11.948	469.8	469.0	469.9	469.6	0.11	0.013

Coupled with LN₂ preconcentrator

Valve diagram and examples



Pre-concentration system

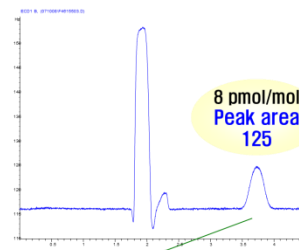


감응치 및 S/N ratio 증가

Normal condition

Detector : uECD
 Heater temp. : 350 °C
 Oven temp. : 40 °C, isothermal
 Column : Restek PorataqQ
 4m, 1/8", SUS
 Carrier gas : ArCH₄
 Carrier flow : 29 mL/min (60 psi)

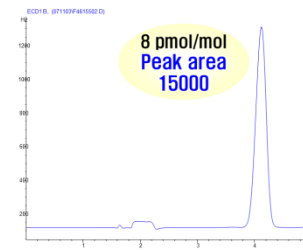
Sample flow : 200 mL/min
 Sample loop vol. : 5 mL



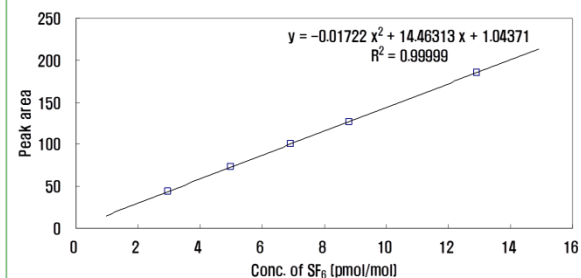
Concentrative condition

Detector : uECD
 Heater temp. : 375 °C
 Oven temp. : 90 °C, isothermal
 Column : Restek PorataqQ
 4m, 1/8", SUS
 Carrier gas : ArCH₄
 Carrier flow : 29 mL/min (60 psi)

Absorption temp. : -65 °C
 Sampling time : 5 min
 Sample flow : 100 mL/min
 He purge time : 0.5 min
 Desorption time : 3 min



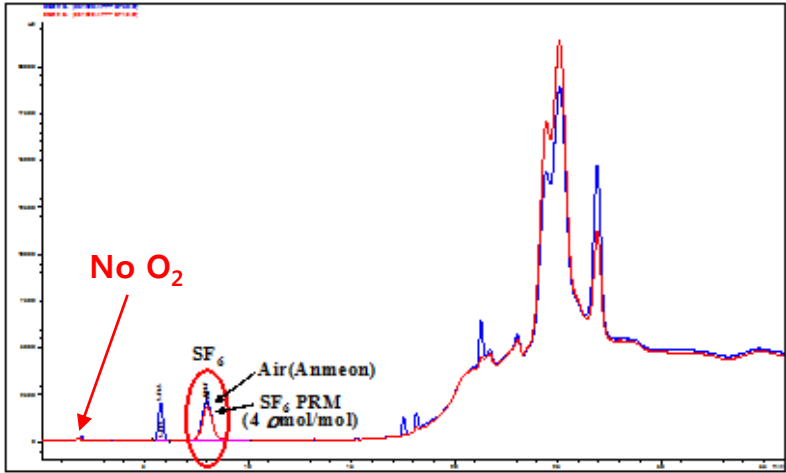
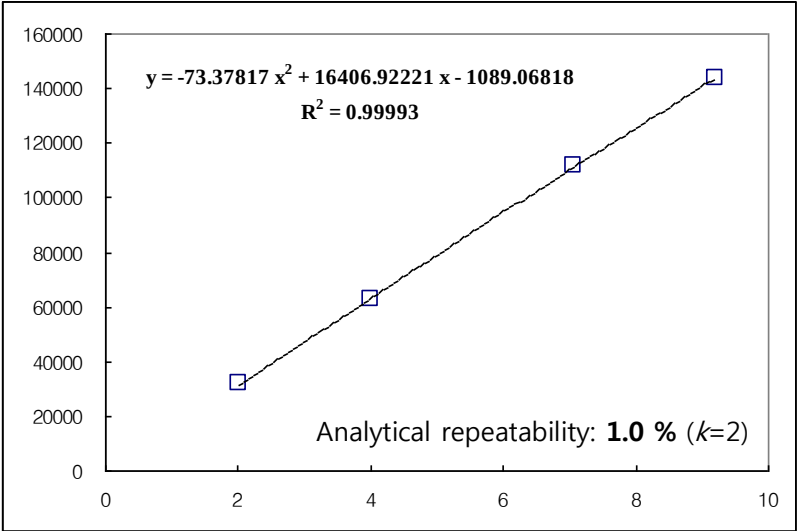
Calibration curve in normal condition



Example chromatogram

Specification		condition
Detector	μ ECD (Electron Capture Detector)	
Column	Restek PorapakQ Packed, 80/100, 1/8 " , 4m	
Oven temp.	35 °C, 10 min 20 °C/min, 235 °C, 16 min	
Carrier gas	ArCH ₄	
Carrier flow	28 mL/min	
Sample flow	50 mL/min	
Concentrator	Sampling temp.	-80 °C
	Sampling time	2 min
	Desorption temp.	170 °C
	Desorption time	3 min
	Purge gas	He (18 mL/min)

- 1. Increased S/N ratio
- 2. No oxygen interference
- 3. Column baking is needed
- 4. Total precision very depends on the precision of preconcentration



<Chromatogram of SF₆ in Air>

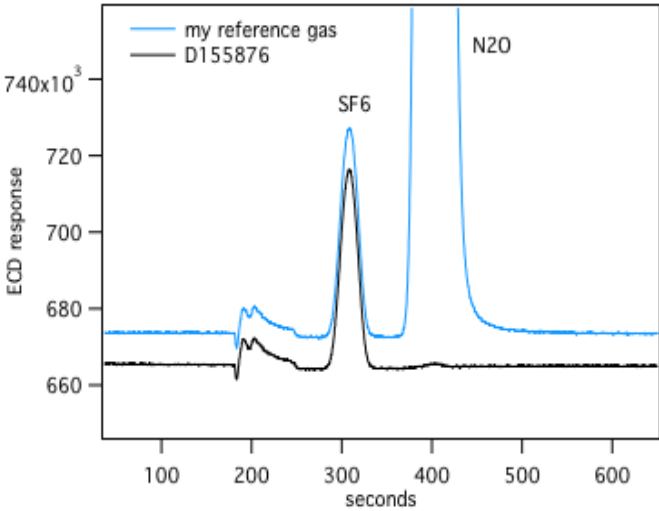
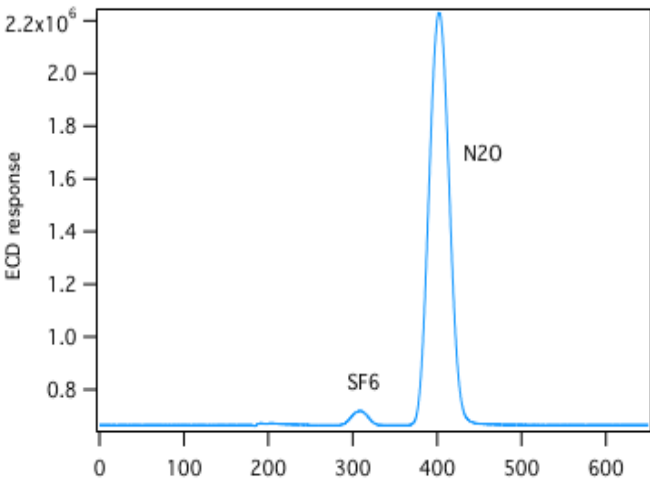
Heart cutting – Back flush method

NOAA result

- GC-ECD//PP-Q/MS-5A//back-flush

Specification	Condition
Detector	ECD, Agilent
Detector temp.	370 °C
Oven temp.	90 °C(porapak Q), 180 °C(MS 5A)
Column	Porapak Q and molecular sieve 5A
Carrier gas	Nitrogen doped with CO2

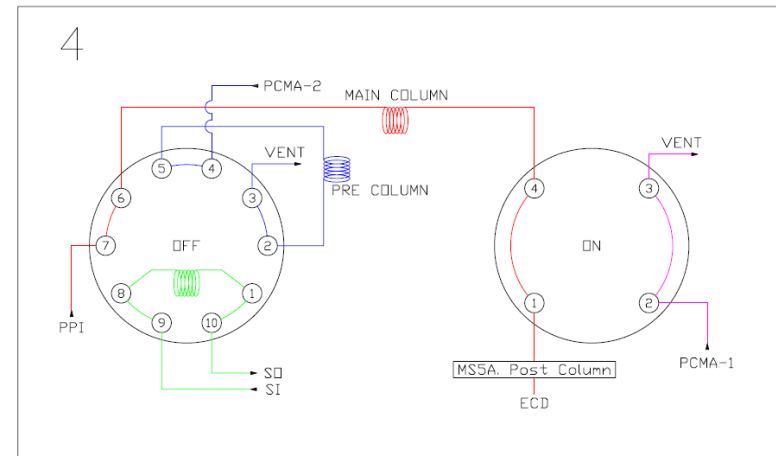
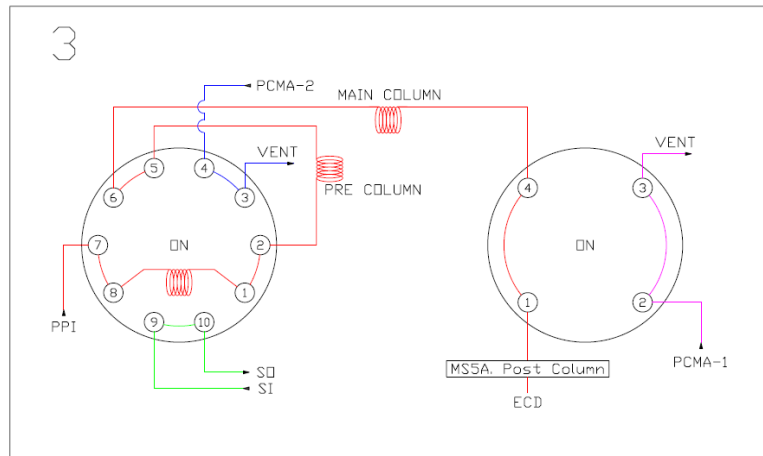
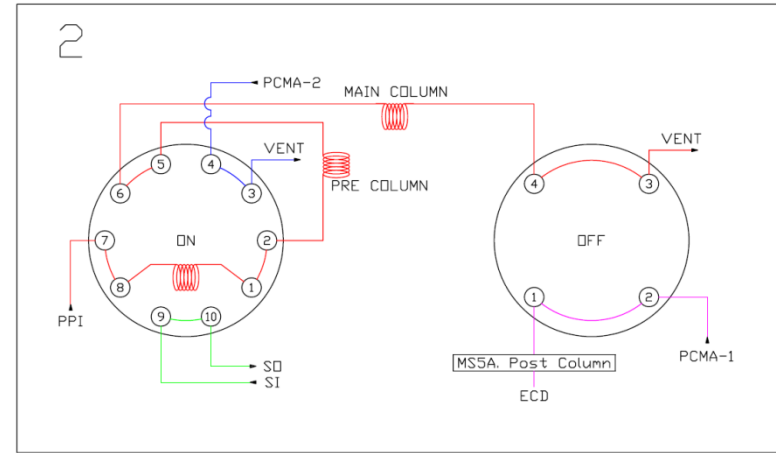
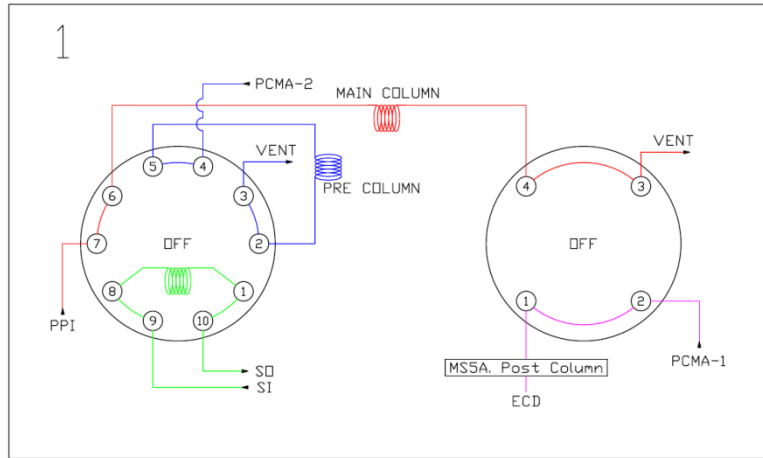
- Sequence: A B A B A ...
A=reference gas, natural air
B=sample
- Calibration method: Linear based on peak height



* generated by Brad Hall

Heart cutting – Back flush method

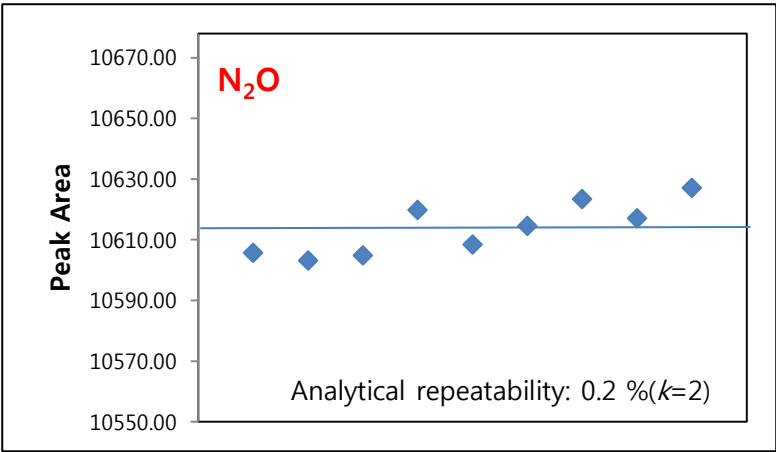
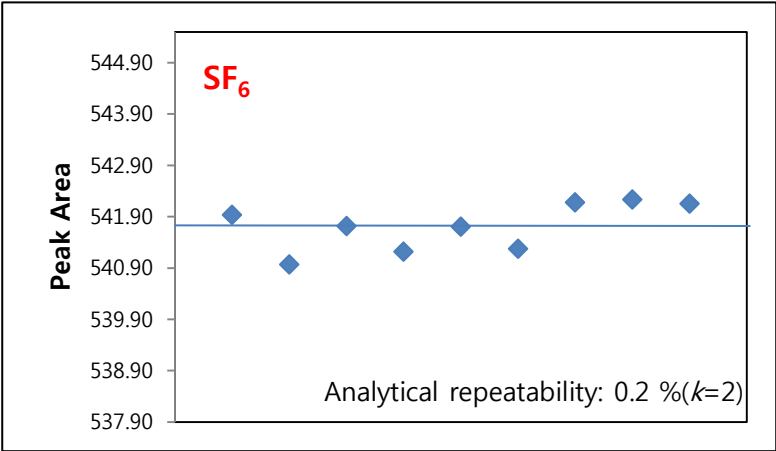
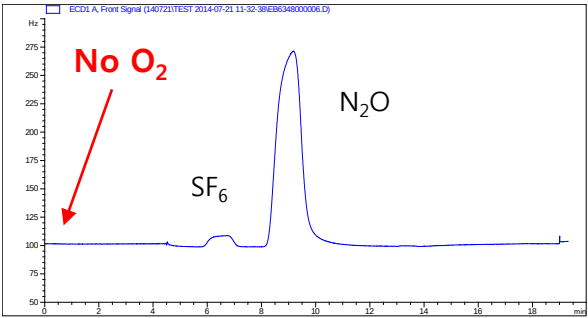
Valve diagram



Heart cutting – Back flush method

Pre: AA-F1, main: AA-F1

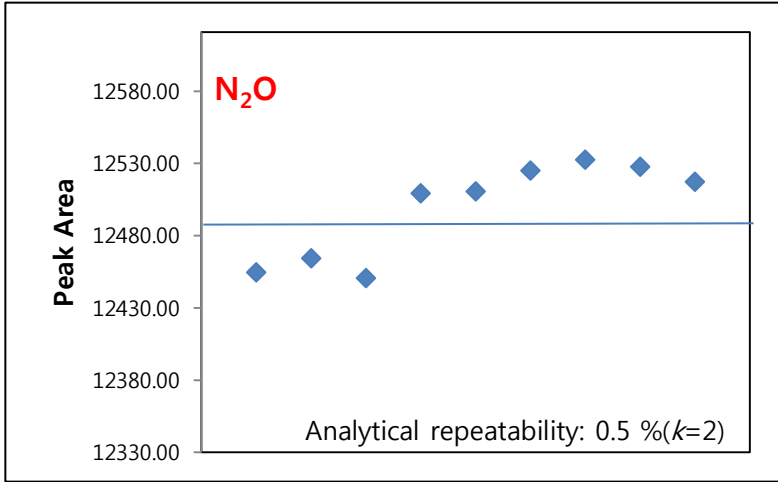
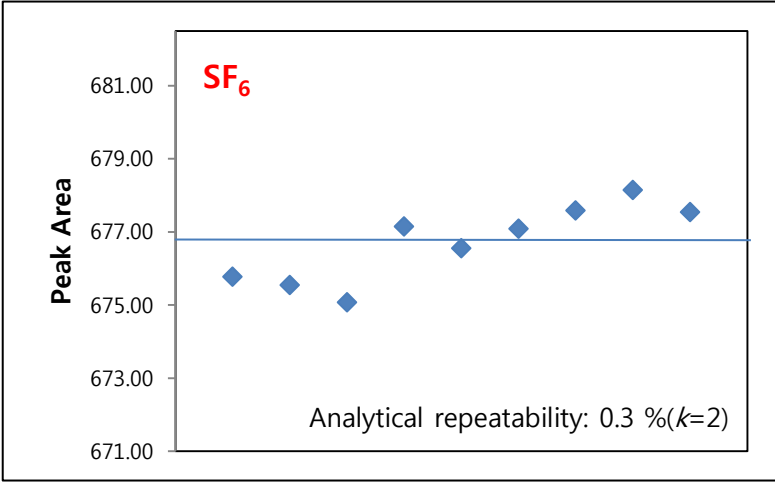
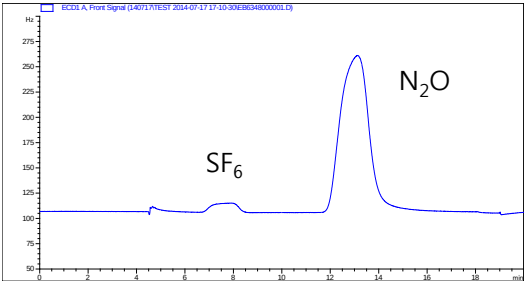
Specification	Condition
Detector	GC- μ ECD
Detector temp.	360 °C
Oven temp.	50 °C 13 min 30 °C/min 90 °C 5 min
Pre-Column	AI-F1 80/100 6ft* 1/8 inch SUS
Main-Column	AI-F1 80/100 12ft* 1/8 inch SUS
Carrier flow	P-5, 40 mL/min
PCM A-1	47 psi
PCM A-2	18 psi
Sample loop	10 cc
Sample flow	40 mL/min
V1 load time	0.1 ~ 13 min
V2 load time	4.5 ~ 19 min



Heart cutting – Back flush method

Pre: AA-F1, Main: AA-F1, Post: MS-5A

Specification	Condition
Detector	GC- μ ECD
Detector temp.	360 °C
Oven temp.	40 °C 18 min 30 °C/min 90 °C 5 min
Pre-Column	AI-F1 80/100 6ft* 1/8 inch SUS
Main-Column	AI-F1 80/100 12ft* 1/8 inch SUS
Post-Column	MS-5A(165 °C)
Carrier flow	P-5, 45 mL/min
PCM A-1	47 psi
PCM A-2	18 psi
Sample loop	10 cc
Sample flow	80 mL/min
V1 load time	0.1 ~ 18 min
V2 load time	4.5 ~ 23 min

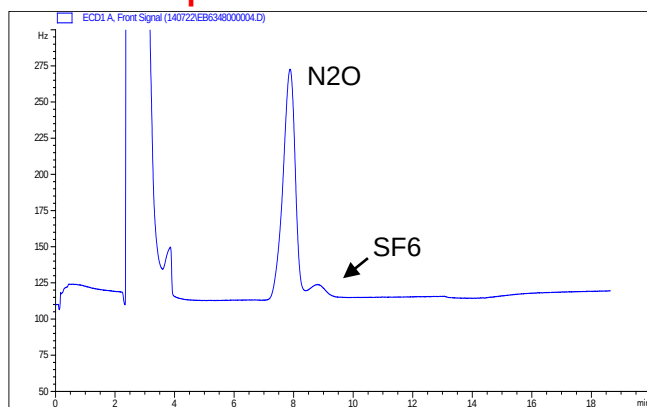


Heart cutting – Back flush method

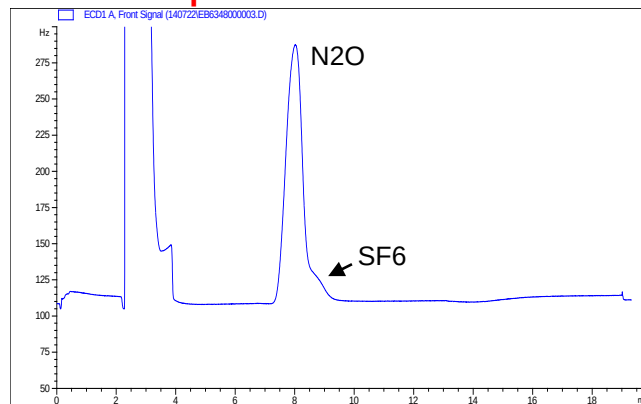
Pre: PP-Q Main: PP-Q Post: MS-5A

* Temperature dependence on MS-5A

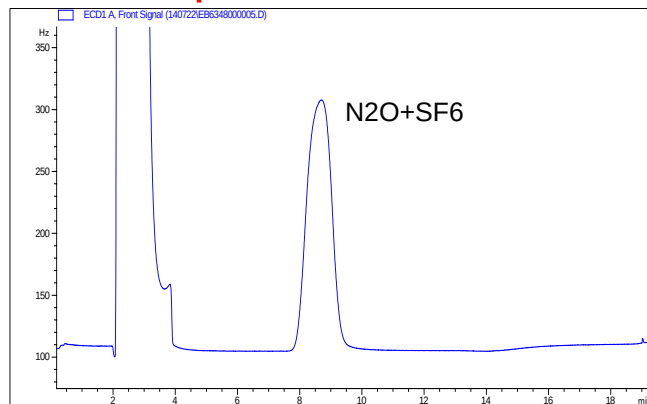
MS-5A temp.: 185 °C



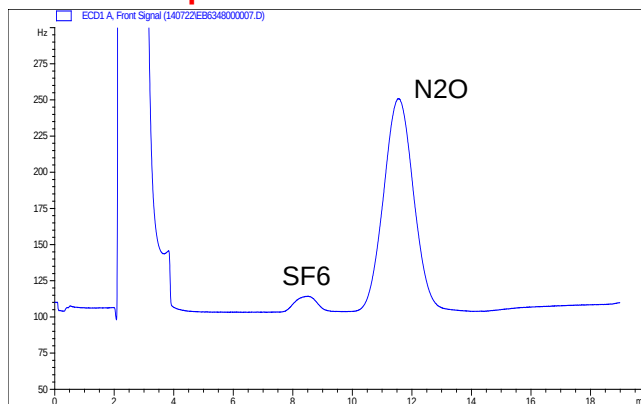
MS-5A temp.: 165 °C



MS-5A temp.: 140 °C



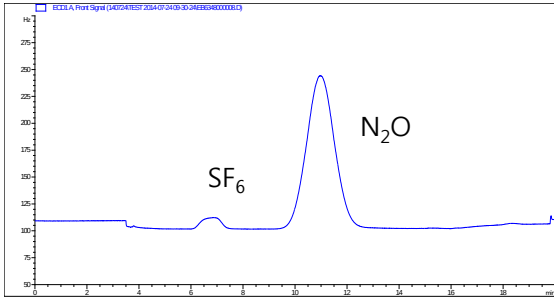
MS-5A temp.: 110 °C



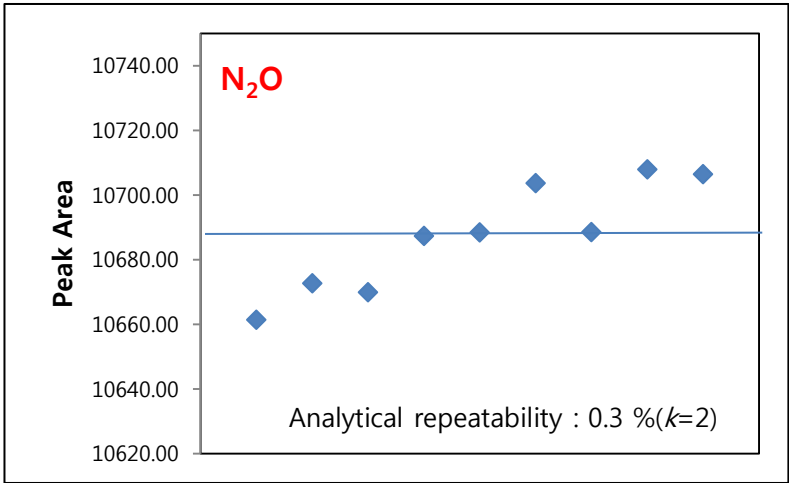
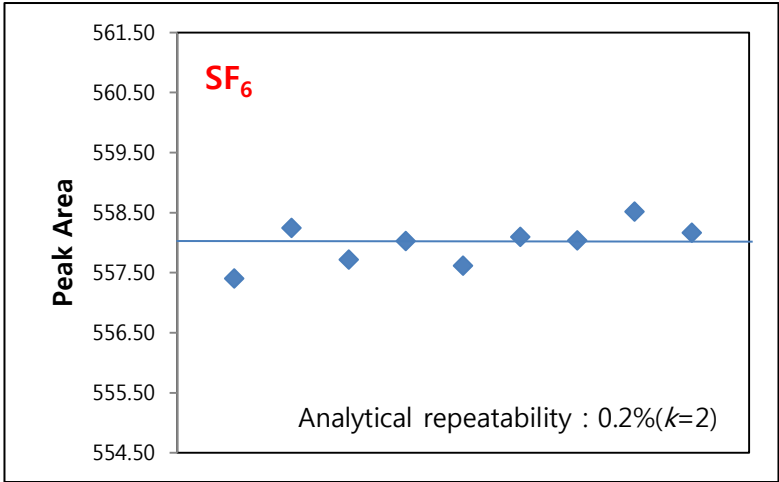
Heart cutting – Back flush method

Pre: PP-Q Main: PP-Q Post: MS-5A

Specification	Condition
Detector	GC- μ ECD
Detector temp.	360 °C
Oven temp.	60 °C 15 min 30 °C/min 90 °C 4 min
Pre-Column	PP-Q 80/100 6ft* 1/8 inch SUS
Main-Column	PP-Q 80/100 12ft* 1/8 inch SUS
Post-Column	MS-5A(105 °C)
Carrier flow	P-5, 40 mL/min
PCM A-1	51 psi
PCM A-2	18 psi
Sample loop	10 cc
Sample flow	40 mL/min
V1 load time	0.1 ~ 15 min
V2 load time	3.5 ~ 19.8 min



* Best results



Intercomparison of Heart cutting – Back flush methods

	Pre+Main Column (Alumina+Alumina)		Pre+Main+Post Column (Alumina+Alumina+MS5A)		Pre+Main+Post Column (PP-Q+PP-Q+MS5A)	
	SF ₆	N ₂ O	SF ₆	N ₂ O	SF ₆	N ₂ O
Peak Area	541.70	10613.77	676.71	12498.98	557.97	10687.32
Analytical repeatability(<i>k</i> =2)	0.2 %	0.2 %	0.3 %	0.5 %	0.2 %	0.3 %
Features			Asymmetric peak shape		Temp. control for Post column	

Summary

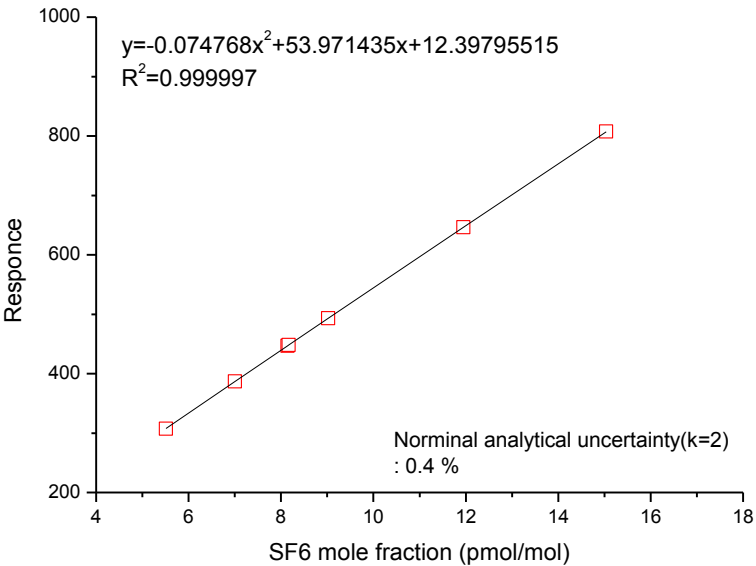
	Running time	O ₂ interference	SF ₆ peak shape	N ₂ O Peak shape	Best Analytical Precision	features
AA-F1	25 min	O	Guassian	Asymm	0.2 %	Column baking
preconcentrator	30 min	X	Gaussian	-	1.0 %	Final precision depends on the repeatability of preconcentrator
Heart cutting -back flush	18 min	X	Gaussian	Gaussian	0.2 %	



Thank you!

Detector response linearity

- calibration method



Cylinder	SF ₆ mole fraction (pmol/mol)		Residual (ppt)
	Gravimetry	Calibration	
D068001	15.038	15.042	0.004 [0.029%]
D068105	8.144	8.143	-0.001 [-0.013%]
D068026	9.021	9.026	0.005 [0.052%]
D067998	5.510	5.505	-0.005 [-0.097%]
D068087	7.003	7.011	0.008 [0.109%]
D068069	8.164	8.165	0.001 [0.012%]
D068020	11.948	11.941	-0.007 [-0.062%]

Calibration methods	Multi-point	Three-point		Two-point	One-point	
WMO scales	FB03441	FB03441	FB03443	FB03443	FB03443	FB03444
FB03443	FB03443	FB03444	FB03444			
FB03444	FB03444	FB03447				
FB03447						
FB03450						
Calculated value	7.520	7.516	7.524	7.524	7.446	7.541
Difference from multi-point calibration method		-0.004	+0.004	+0.004	-0.074	+0.021