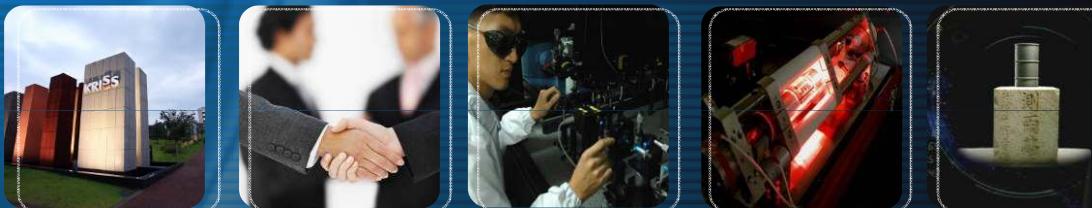


Gravimetric standard scales of SF₆ and N₂O at ambient level



Korea Research
Institute of
Standards and Science



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1

Development of SF₆/air calibration scale

2

Development of N₂O/air calibration scale

Towards Global Center of Excellence in Metrology

- Through close partnership with customers worldwide

Comparability vs. Compatibility

GAW report No. 206

Currently, some of the terms related to measurements as well as to Quality Assurance & Quality Control (QA/QC) in atmospheric science are used with different meanings and/or on the basis of different definitions. Since GAW is now a participant in the Bureau International des Poids et Mesures (BIPM, web site www.bipm.org) the use of accepted terminology within GAW has become even more important. It is possible that a number of terms and ISO recommendations might not be familiar to the GAW community. Some terms might even require a revision of current usage within GAW.

A special explanation can be helpful here in the context of the above-mentioned transition from "comparability" to "compatibility". "Comparability" means that results (of different labs) are comparable i.e. can be compared. In a metrological sense this simply means that results have to be on the same scale to be compared. By consistent use of the same scale for the same compound (in all steps such as measurements, determination of corrections etc), one will have comparability of results. "Compatibility", a property of a set of measurement results, means that results are compatible, within a specified numerical value. Metrologically this means (an oversimplification): the absolute value of the difference between any pair of measured values from two different measurement results is within a chosen value which does not have to be the same as the total combined uncertainty. For instance, the total combined uncertainty in two labs might be ± 0.1 permil (for example) and still results can be compatible within 0.01 permil.

Recommended compatibility goal of measurements

Component	Compatibility goal	range in the unpolluted troposphere
CO ₂	± 0.1 ppm (± 0.05 ppm in the southern hemisphere)	360 ... 430 ppm
$\delta^{13}\text{C-CO}_2$	± 0.01 ‰	-7.5 ... -9 ‰ vs. VPDB
$\delta^{18}\text{O-CO}_2$	± 0.05 ‰	-2 ... +2 ‰ vs. VPDB
$\delta^{13}\text{C - CH}_4$	± 0.02 ‰	-80 ... -20 ‰ vs. VPDB
$\delta\text{D - CH}_4$	± 1 ‰	-400 ... +0 ‰ vs. VSMOW
$\delta^{14}\text{C-CO}_2$	± 1 ‰	0 ... 70 ‰
O ₂ /N ₂	± 2 per meg	-250 ... -550 per meg (vs. SIO scale)
CH ₄	± 2 ppb	1700 ... 2100 ppb
CO	± 2 ppb	30 ... 300 ppb
N ₂ O	± 0.1 ppb	320 ... 335 ppb
H ₂	± 2 ppb	450 ... 600 ppb
SF ₆	± 0.02 ppt	6 ... 10 ppt

"The numbers in this table are the scientifically desirable value, **They may not be the currently achievable minimal measurement uncertainty (1 sigma)** for individual analyses of most species"

Measurement uncertainty

For instance,

1 point calibration

$$C_{\text{unknown}} = \left(\frac{R_{\text{unknown}}}{R_{\text{ref}}} \right) \cdot (C_{\text{ref}})$$

$$u(C_{\text{unknown}}) = \left(\frac{R_{\text{unknown}}}{R_{\text{ref}}} \right) \cdot (C_{\text{ref}}) \cdot \sqrt{\left(\frac{u(R_{\text{unknown}})}{R_{\text{unknown}}} \right)^2 + \left(\frac{u(R_{\text{ref}})}{R_{\text{ref}}} \right)^2 + \left(\frac{u(C_{\text{ref}})}{C_{\text{ref}}} \right)^2}$$

2 point calibration

$$C_{\text{unknown}} = \left(\frac{R_{\text{unknown}} - R_{\text{ref}1}}{R_{\text{ref}2} - R_{\text{ref}1}} \right) (C_{\text{ref}2} - C_{\text{ref}1}) + C_{\text{ref}1}$$

$$\begin{aligned} u(C_{\text{unknown}})^2 &= \left[\left| \left(\frac{R_{\text{unknown}} - R_{\text{ref}1}}{R_{\text{ref}2} - R_{\text{ref}1}} \right) \cdot (C_{\text{ref}2} - C_{\text{ref}1}) \right| \cdot \right. \\ &\quad \left. \sqrt{\left(\frac{u(R_{\text{unknown}} - R_{\text{ref}1})}{R_{\text{unknown}} - R_{\text{ref}1}} \right)^2 + \left(\frac{u(R_{\text{ref}2} - R_{\text{ref}1})}{R_{\text{ref}2} - R_{\text{ref}1}} \right)^2 + \left(\frac{u(C_{\text{ref}2} - C_{\text{ref}1})}{C_{\text{ref}2} - C_{\text{ref}1}} \right)^2} \right]^2 \\ &\quad + u(C_{\text{ref}1})^2 \end{aligned}$$

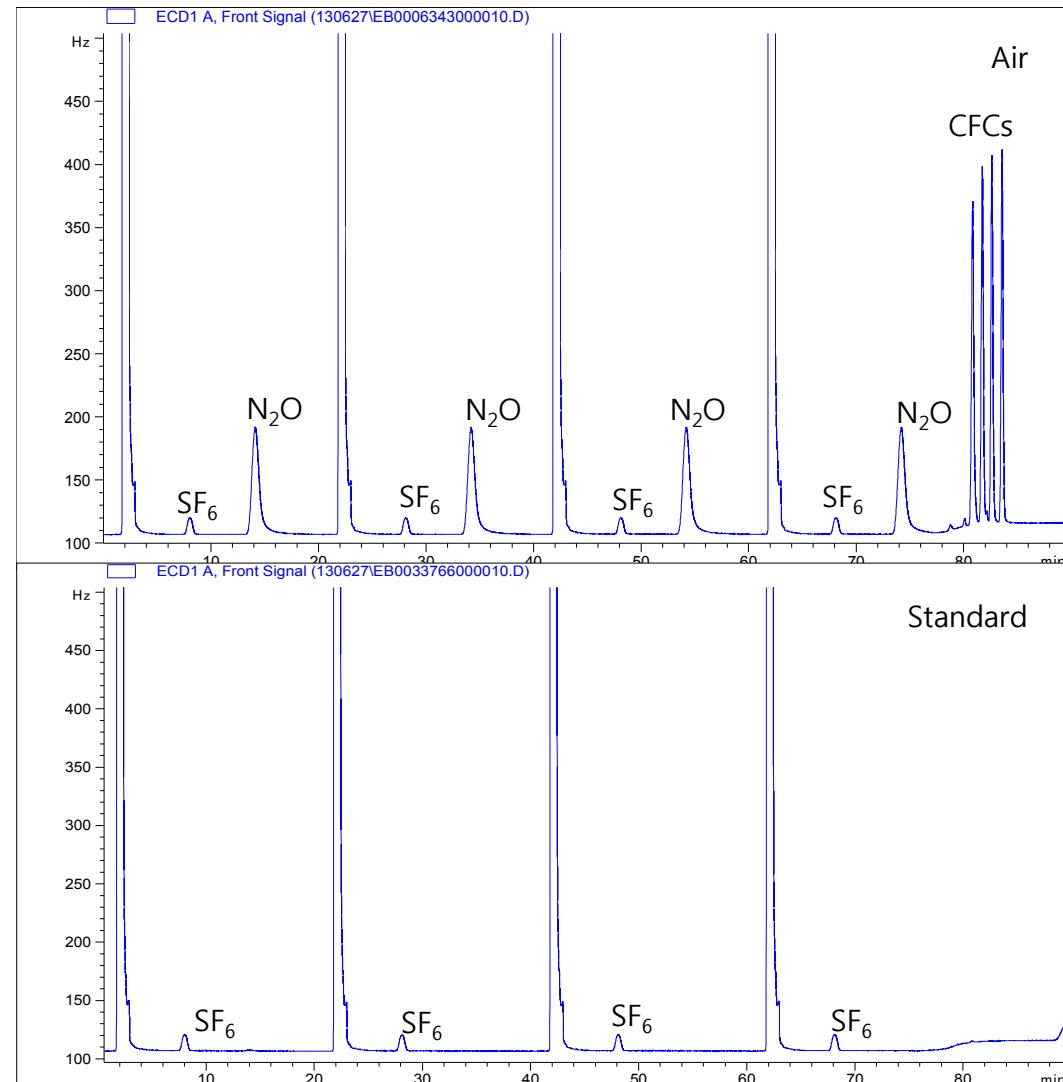
R: instrument response
C: mole fraction

Where, $u(R_i - R_j) = \sqrt{u(R_i)^2 + u(R_j)^2}$

Measurement sequence

<Analytical condition>

Specification	Condition
Detector	μ ECD
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



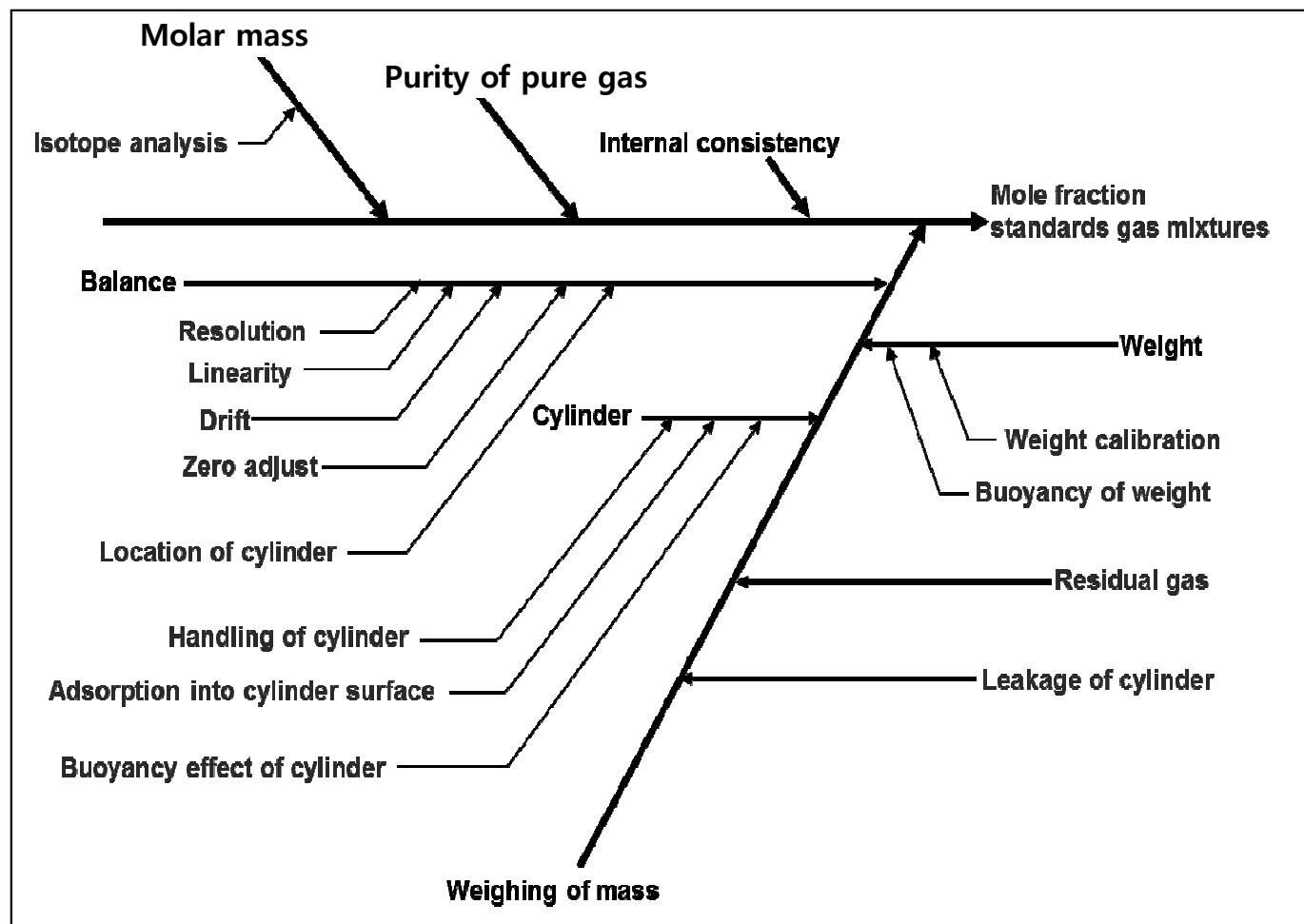
Measurement capability

For SF₆

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%)		

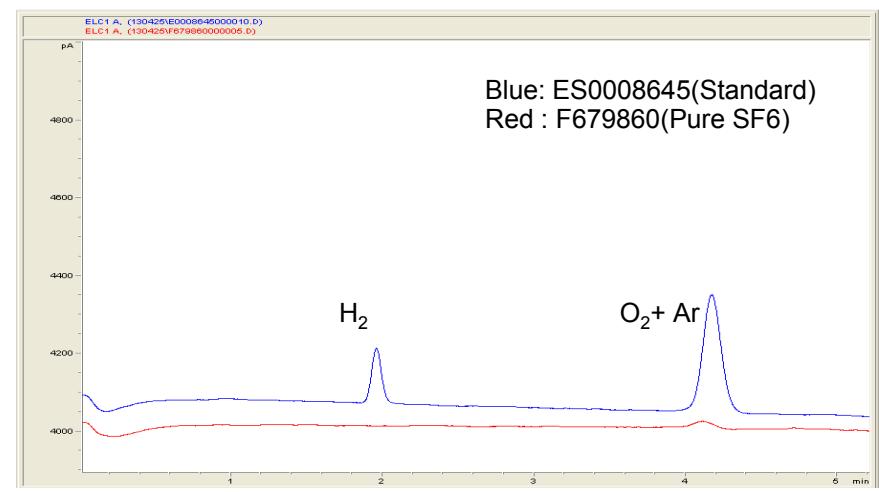
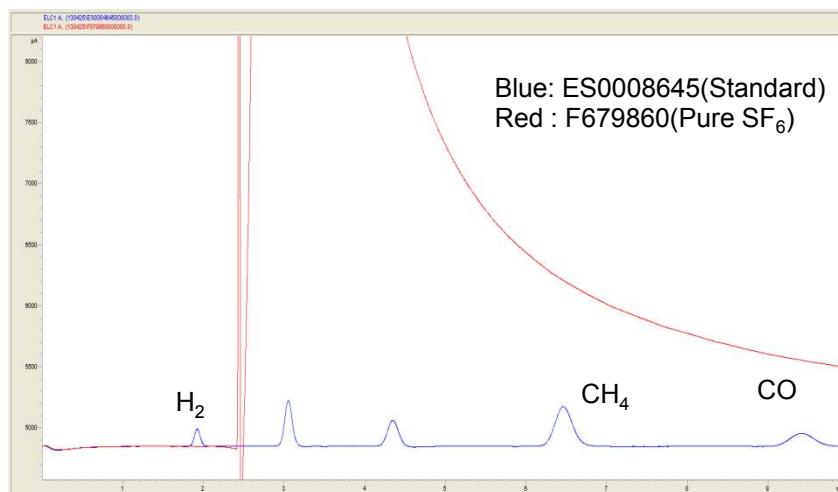
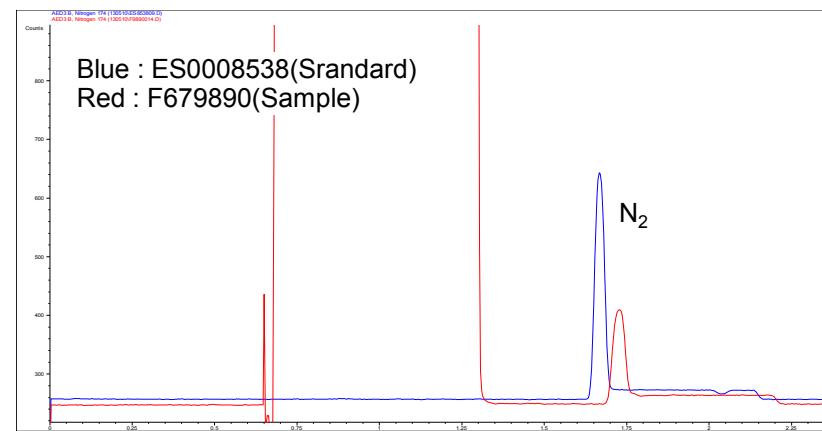
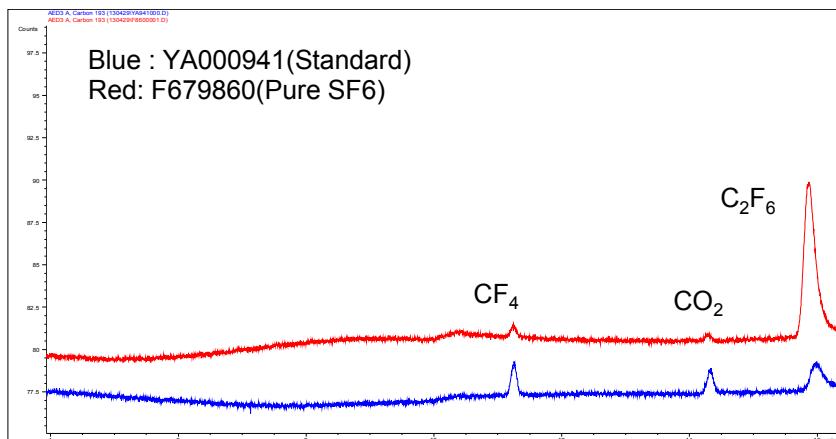
* 3 injection per a measurement

Uncertainty budget of gravimetric preparation



Impurity analysis of pure SF₆ gas

- 고순도 SF₆ 순도분석



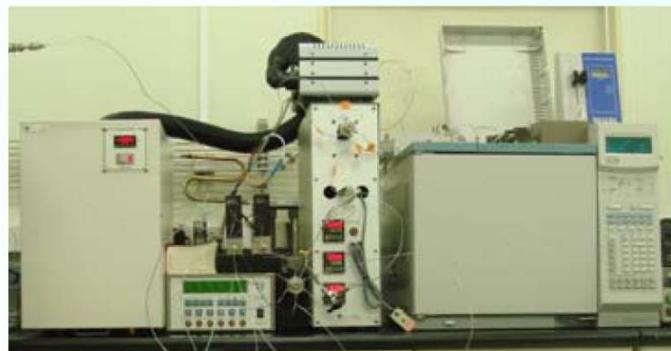
Impurity table

Component	Measured Conc. ($\mu\text{mol/mol}$)	Detector	Distribution	Applied Conc. ($\mu\text{mol/mol}$)	Standard Uncertainty ($\mu\text{mol/mol}$)
H ₂	<0.02	GC-PDD	rectangular	0.01	0.006
O ₂ +Ar	0.56	GC-PDD	normal	0.56	0.056
N ₂	55.19	GC-AED	normal	55.19	5.52
CH ₄	1.94	GC-PDD	normal	1.94	0.194
CO	<0.03	GC-PDD	rectangular	0.02	0.009
CO ₂	2.47	GC-AED	normal	2.47	0.25
THC	<1.00	GC-AED	rectangular	0.5	0.289
H ₂ O	13	Dew point meter	normal	13	1.3
CF ₄	1.94	GC-AED	normal	1.94	0.194
C ₂ F ₆	31.98	GC-AED	normal	31.98	3.198
C ₃ F ₈	<1.00	GC-AED	rectangular	0.5	0.29
SO ₂	<0.005	GC-AED	rectangular	0.003	0.001
S compounds	<0.005	GC-AED	rectangular	0.03	0.001
Impurities				108.11	6.533
SF₆ Purity {%(mole fraction)}				99.9892	0.0013 ($k=2$)

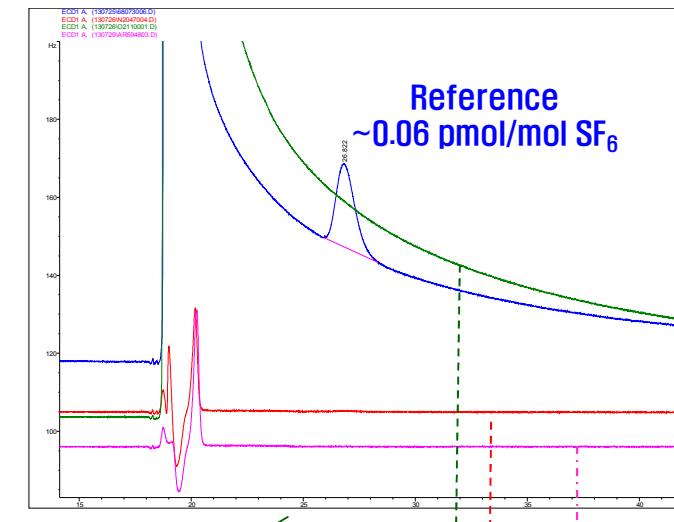
SF₆ impurity in pure gases (N₂, O₂, Ar)

<Analytical condition>

Specification	Condition
Detector	GC- μ ECD with cryogenic system
Detector temp.	250 °C
Oven temp.	60 °C
Column	AA-F1 80/100 24ft* 1/8 inch SUS
Run time	50 min
Carrier flow	P-5, 90psi
Sample flow	200 mL/min
Cryogenic time	10 min
Trap heating	5 min



Preconcentrator/GC-ECD

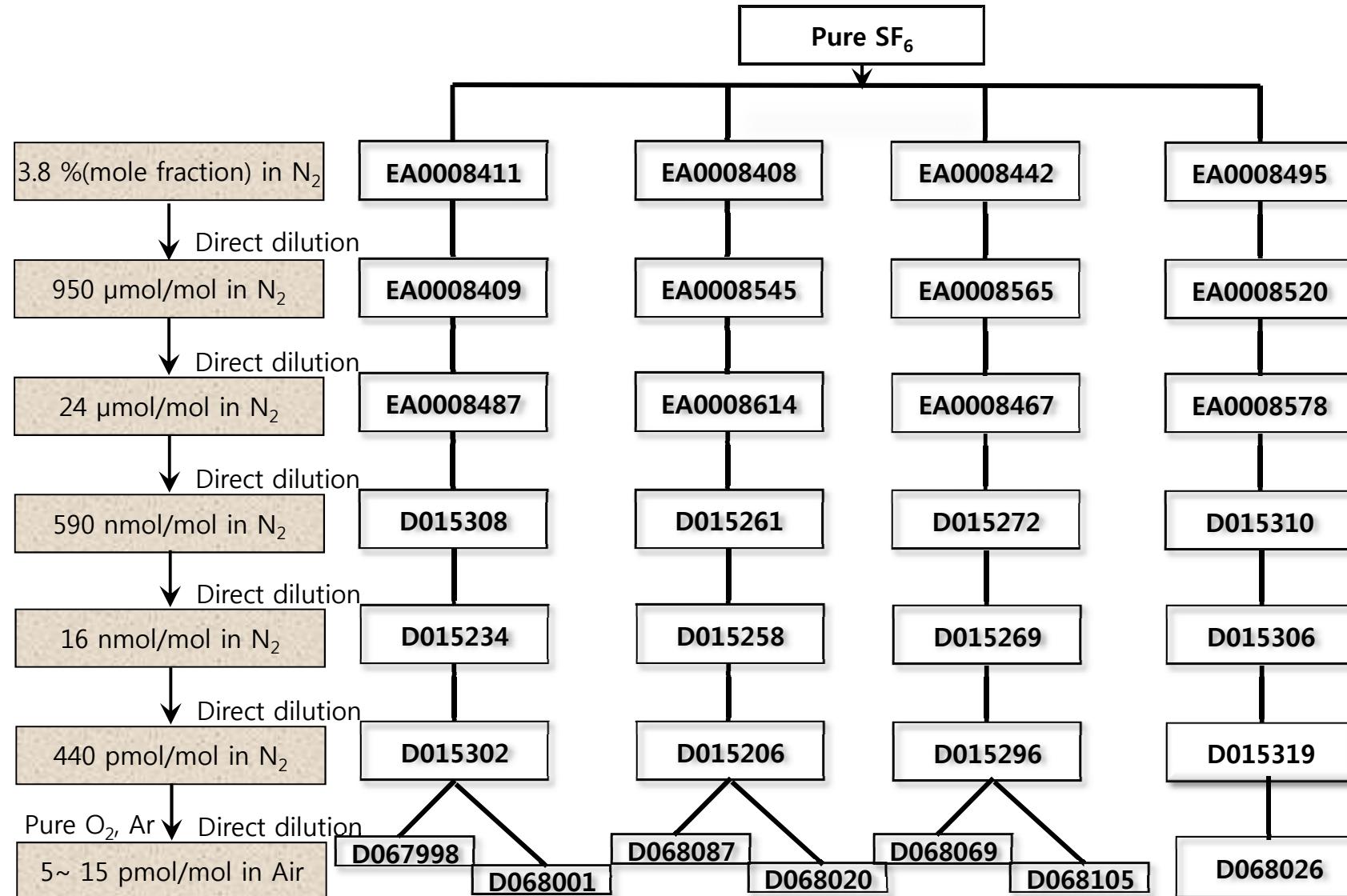


SF₆ in O₂ <0.002 pmol/mol

SF₆ in N₂ <0.002 pmol/mol

SF₆ in Ar <0.002 pmol/mol

Preparation of Reference Gas Mixture



Schematic diagram of preparation for SF₆ gases

Automatic weighing



A	B	C	D	E	F	G	H	I	J	K	L	M
from SF6 440 ppt/N2 D015302(6-1)												
6	empty											Tare(D799816)
7	Date1	Time1	Temp1	Humidity1	Pressure1	Weight1	Date2	Time2	Temp2	Humidity	Pressure	Weight2
8	130616	171859	24.4	71	994.98	13617.422	130616	172050	24.4	70.9	995	13643.184
9	130616	171904	24.4	71	994.97	13617.422	130616	172055	24.4	70.9	995	13643.185
10	130616	171909	24.4	71	994.97	13617.422	130616	172100	24.4	70.9	995	13643.185
11	130616	171914	24.4	71	994.96	13617.422	130616	172105	24.4	70.9	995	13643.185
12	130616	171919	24.4	71	994.96	13617.422	130616	172110	24.4	70.9	995	13643.185
13	130616	171924	24.4	71	994.95	13617.423	130616	172115	24.4	70.9	995	13643.185
14	130616	171929	24.4	71	994.95	13617.423	130616	172120	24.4	70.9	995	13643.185
15	130616	171934	24.4	71	994.96	13617.423	130616	172125	24.4	70.9	995	13643.186
16	130616	171939	24.4	71	994.96	13617.424	130616	172130	24.4	70.9	995	13643.186
17	130616	171944	24.4	71	994.96	13617.425	130616	172135	24.4	70.9	995	13643.186
18						13617.424						13643.186
19						-25.762						
20												
21												
22	Date1	Time1	Temp1	Humidity1	Pressure1	Weight1	Date2	Time2	Temp2	Humidity	Pressure	Weight2
23	130616	172448	24.4	70.9	994.95	13617.425	130616	172639	24.5	70.8	994.9	13643.190
24	130616	172453	24.4	70.9	994.95	13617.426	130616	172644	24.5	70.8	994.9	13643.190
25	130616	172458	24.4	70.9	994.95	13617.426	130616	172649	24.5	70.8	994.9	13643.190
26	130616	172503	24.4	70.9	994.95	13617.426	130616	172654	24.5	70.8	994.9	13643.190
27	130616	172508	24.4	70.9	994.94	13617.426	130616	172659	24.5	70.8	994.9	13643.190
28	130616	172513	24.4	70.9	994.95	13617.427	130616	172704	24.5	70.8	994.9	13643.190
29	130616	172518	24.4	70.9	994.95	13617.427	130616	172709	24.5	70.8	994.9	13643.190
30	130616	172523	24.4	70.9	994.94	13617.427	130616	172714	24.5	70.8	994.9	13643.191
31	130616	172528	24.4	70.9	994.94	13617.428	130616	172719	24.5	70.8	994.9	13643.191
32	130616	172533	24.4	70.9	994.95	13617.428	130616	172724	24.5	70.8	994.9	13643.191
33						13617.428						13643.191
34						-25.763						
35												
36												
37	Date1	Time1	Temp1	Humidity1	Pressure1	Weight1	Date2	Time2	Temp2	Humidity	Pressure	Weight2
38	130616	173035	24.5	70.8	994.95	13617.431	130616	173224	24.5	70.8	995	13643.193
39	130616	173040	24.5	70.8	994.95	13617.431	130616	173230	24.5	70.8	995	13643.193
40	130616	173045	24.5	70.8	994.95	13617.431	130616	173235	24.5	70.8	995	13643.193
41	130616	173050	24.5	70.8	994.95	13617.431	130616	173240	24.5	70.8	995	13643.193
42	130616	173055	24.5	70.8	994.95	13617.432	130616	173245	24.5	70.8	995	13643.193
43	130616	173100	24.5	70.8	994.95	13617.432	130616	173250	24.5	70.7	995	13643.194
44	130616	173105	24.5	70.8	994.95	13617.432	130616	173255	24.5	70.7	995	13643.194
45	130616	173111	24.5	70.8	994.95	13617.432	130616	173300	24.5	70.7	995	13643.195
46	130616	173116	24.5	70.8	994.95	13617.432	130616	173305	24.5	70.7	995	13643.195
47	130616	173121	24.5	70.8	994.95	13617.433	130616	173310	24.5	70.7	995	13643.195
48						13617.432						13643.195
49						-25.762						
50						평균						
51						-25.763						
						표준편차						0.001

<Gravimetric method excel sheet>

Gravimetric preparation value and associated uncertainties

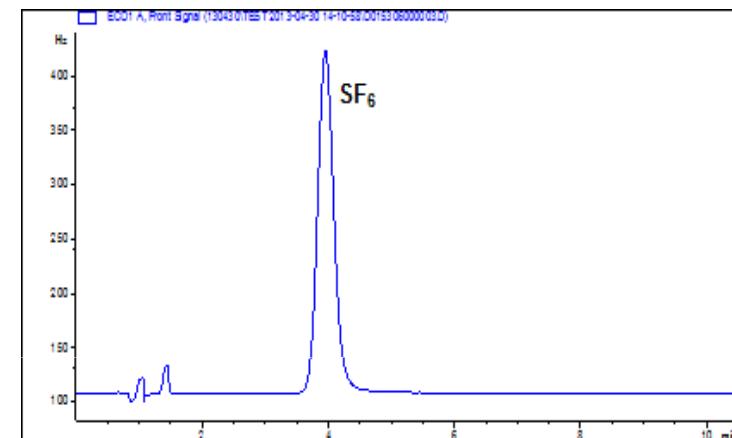
Cylinder no	Concentration (ppt)	Expanded uncertainty (ppt)	Rel $U(k=2)$ uncertainty(%)	Balance gas
D067998	5.510	0.0029	0.052	Air
D068001	15.038	0.0072	0.048	Air
D068087	7.003	0.0031	0.044	Air
D068020	11.948	0.0050	0.043	Air
D068105	8.144	0.0036	0.044	Air
D068069	8.164	0.0035	0.043	Air
D068026	9.021	0.0039	0.043	Air

Consistency check of gravimetric dilution

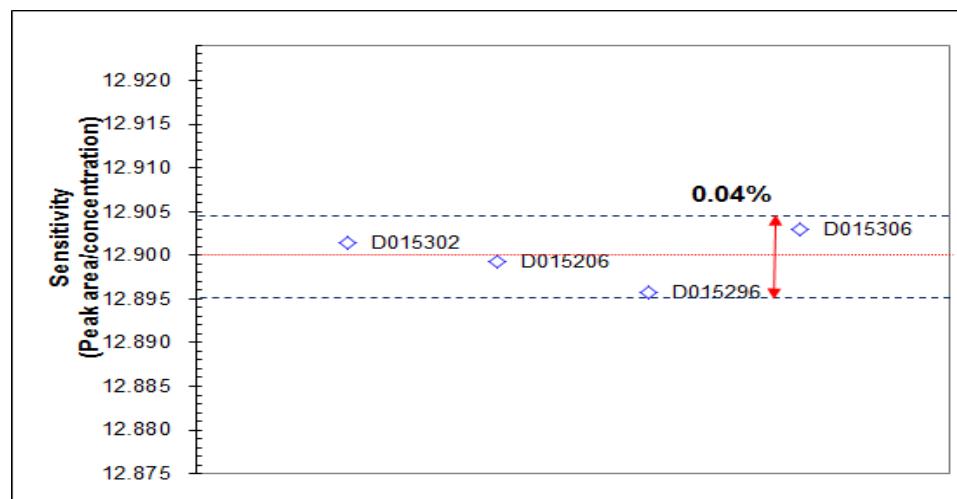
- 6th step

<Analytical condition>

Specification	Condition
Detector	μ ECD
Detector temp.	350 °C
Reference flow	20 mL/min
Oven temp.	65 °C
Column	PP-Q 80/100 13ft* 1/8 inch SUS
Sample loop	5 mL
Carrier flow	P-5, 50psi
Sample flow	150 mL/min

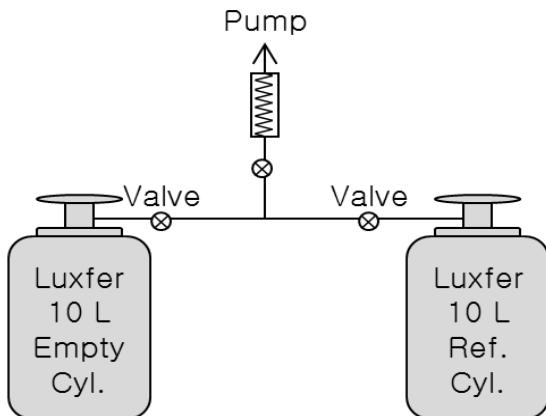


<Chromatogram of 6step SF₆ mother gas>



Stability test

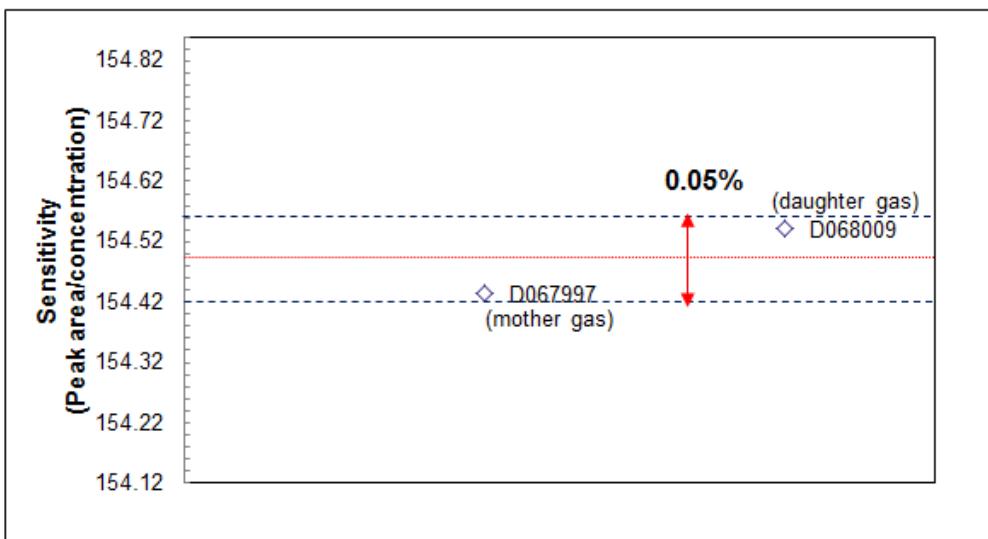
- Short-term stability



<Equal division Method>

<Analytical condition>

Specification	Condition
Detector	μ ECD
Detector temp.	390 °C
Reference flow	20 mL/min
Oven temp.	75 °C
Column	AA-F1 80/100 24ft* 1/8 inch SUS
Sample loop	10 mL
Carrier flow	P-5, 85psi
Sample flow	150 mL/min



Stable longer than 6 month!

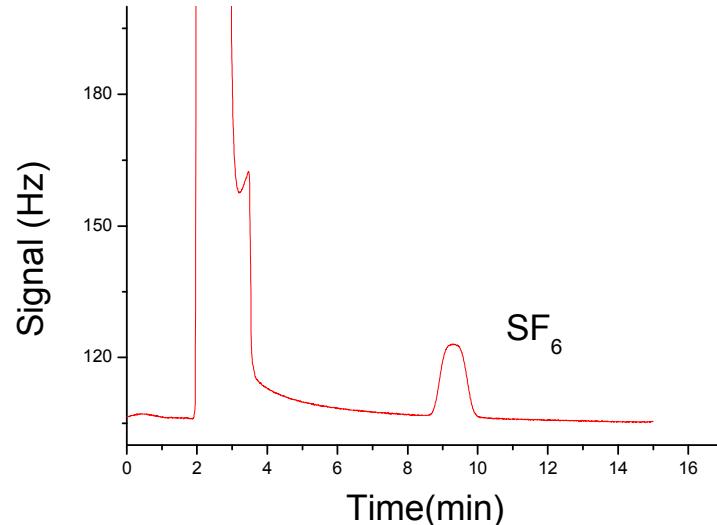
Combined uncertainties of the certified values

Cylinder	Mole fraction (pmol/mol)	% Uncertainty of Gravimetry ($k=1$)	% Uncertainty of stability ($k=1$)	% Uncertainty of verification ($k=1$)	% Uncertainty ($k=2$)	Uncertainty ($k=2$) (pmol/mol)
D068001	15.038	0.024	0.1	0.2	0.45	0.07
D068105	8.144	0.022	0.1	0.2	0.45	0.04
D068026	9.021	0.021	0.1	0.2	0.45	0.04
D067998	5.510	0.026	0.1	0.2	0.45	0.02
D068087	7.003	0.022	0.1	0.2	0.45	0.03
D068069	8.164	0.021	0.1	0.2	0.45	0.04
D068020	11.948	0.021	0.1	0.2	0.45	0.05

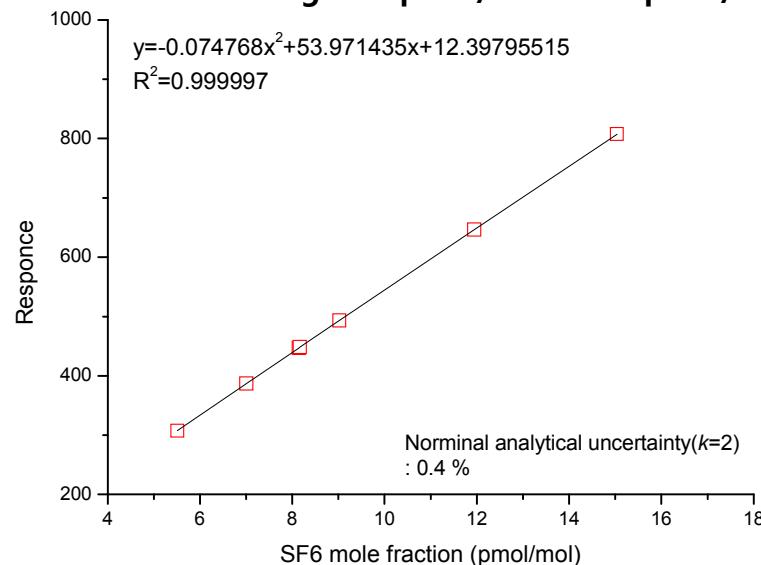
KRISS SF₆ scale

<Analytical condition>

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



<Concentration range : 5 pmol/mol ~ 15 pmol/mol>

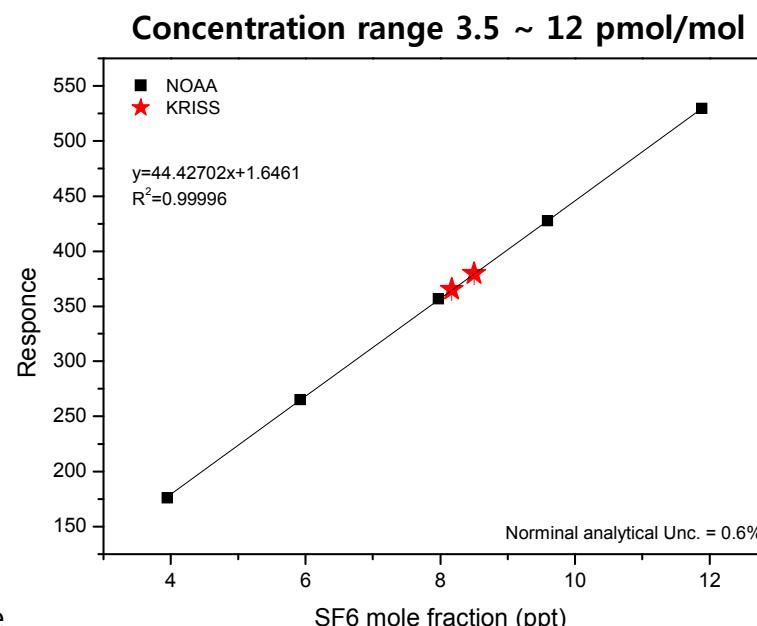
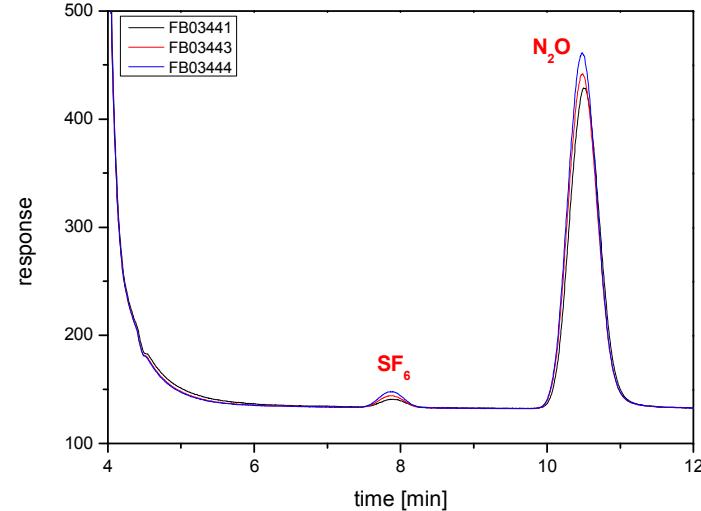


Cylinder	SF ₆ mole fraction (pmol/mol)		Residual (ppt)
	Gravimetry	Calibration	
D068001	15.038	15.042	0.004 [0.029%]
D068105	8.144	8.143	-0.001 [-0.013%]
D068026	9.021	9.026	0.005 [0.052%]
D067998	5.510	5.505	-0.005 [-0.097%]
D068087	7.003	7.011	0.008 [0.109%]
D068069	8.164	8.165	0.001 [0.012%]
D068020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

Comparison between NOAA and KRISS scales

Specification	Condition
Detector	μ ECD
Detector temp.	375 °C
Oven temp.	70 °C, 13 min 30 °C/min 190 °C 4 min
Column	AA-F1 80/100 12ft* 1/8 inch SUS
Sample loop	10 ml
Carrier flow	P-5, 25 ml/min
Sample flow	50 ml/min

Cyl. No.	Grav. conc. [pmol/mol]	Corr. Sens.	residual [%]
FB03441	3.946	44.648	0.440
FB03443	5.92	44.803	-0.221
FB03444	7.972	44.746	-0.253
FB03447	9.595	44.560	0.086
FB03450	11.887	44.537	0.065
KRISS 7-3	8.173	44.698	-0.156
KRISS 7-11	8.506	44.637	-0.036



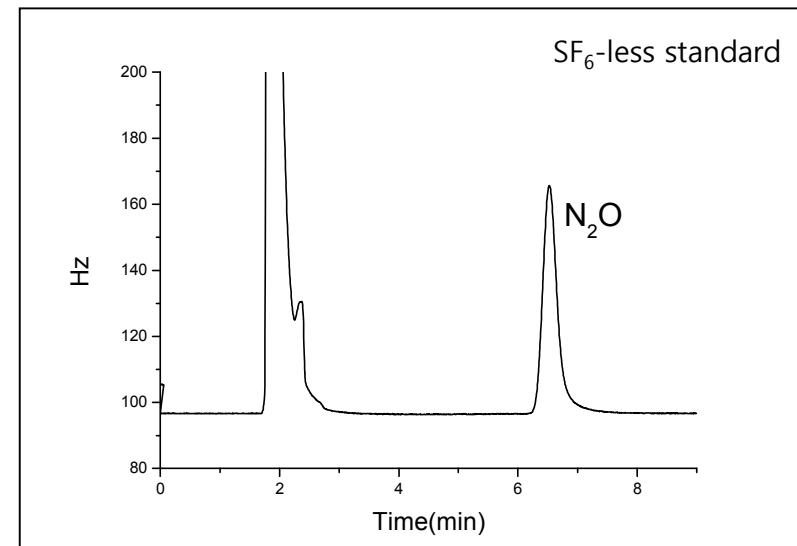
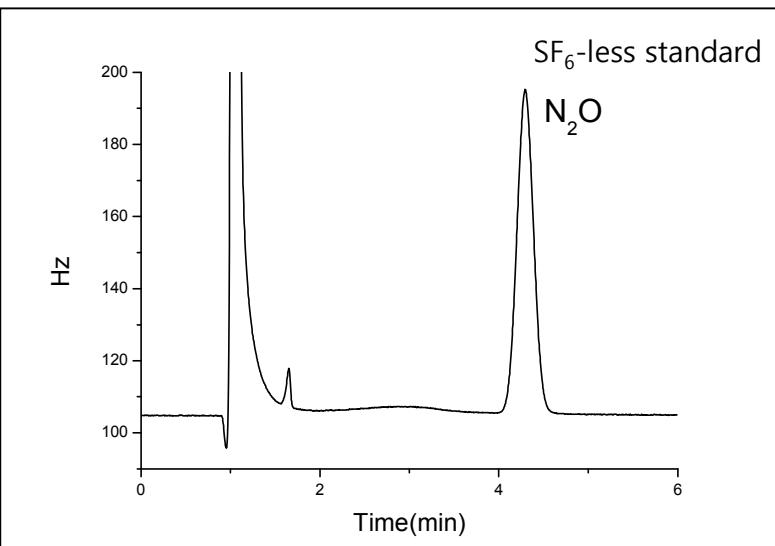
KRISS SF₆/N₂ standards were biased by 0.13 ppt from NOAA scale

N₂O in air scale

Analytical condition and chromatogram

Specification	Condition
Detector	μ ECD
Detector temp.	380 °C
Reference flow	20 mL/min
Oven temp.	45 °C
Column	PP-Q 80/100 13ft* 1/8 inch SUS
Sample loop	1 mL
Carrier flow	P-5(CH ₄ 5% / Ar), 45psi
Sample flow	140 mL/min

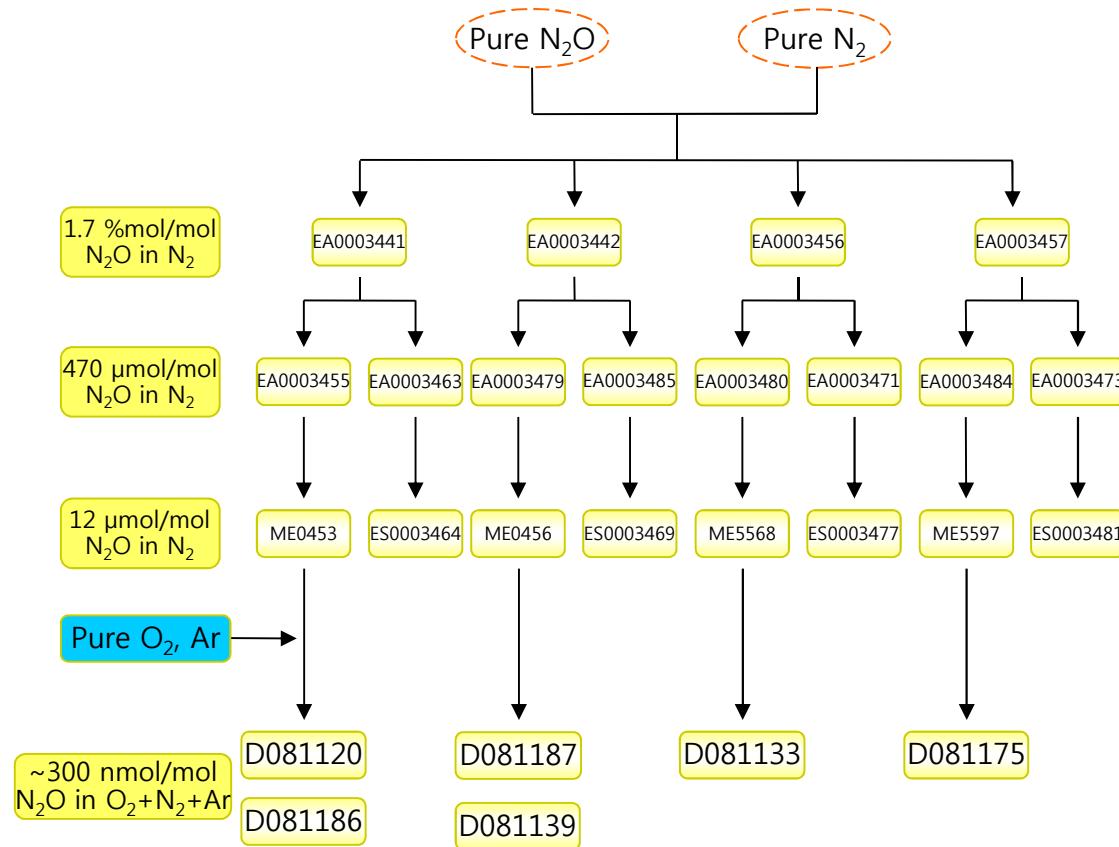
Specification	Condition
Detector	μ ECD
Detector temp.	350 °C
Reference flow	20 mL/min
Oven temp.	75 °C
Column	AA-F1 80/100 12ft* 1/8 inch SUS
Sample loop	2 mL
Carrier flow	P-5(CH ₄ 5% / Ar), 95psi
Sample flow	100 mL/min



Impurity analysis

	Impurity	Measured concentration ($\mu\text{mol/mol}$)	Distribution	Applied concentration ($\mu\text{mol/mol}$)	Standard uncertainty ($\mu\text{mol/mol}$)
1	H ₂	<0.1	Rectangular	0.05	0.0289
2	O ₂	0.2	Normal	0.2	0.006
3	N ₂	0.3	Normal	0.3	0.009
4	CO ₂	0.52	Normal	0.52	0.010
5	CH ₄	<0.05	Rectangular	0.0025	0.0144
6	CO	<0.05	Rectangular	0.0025	0.0144
7	H ₂ O	0.3	Normal	0.3	0.15
8	THC	<0.01	Rectangular	0.005	0.0029
			N ₂ O	999998.6	0.156

Dilution tree



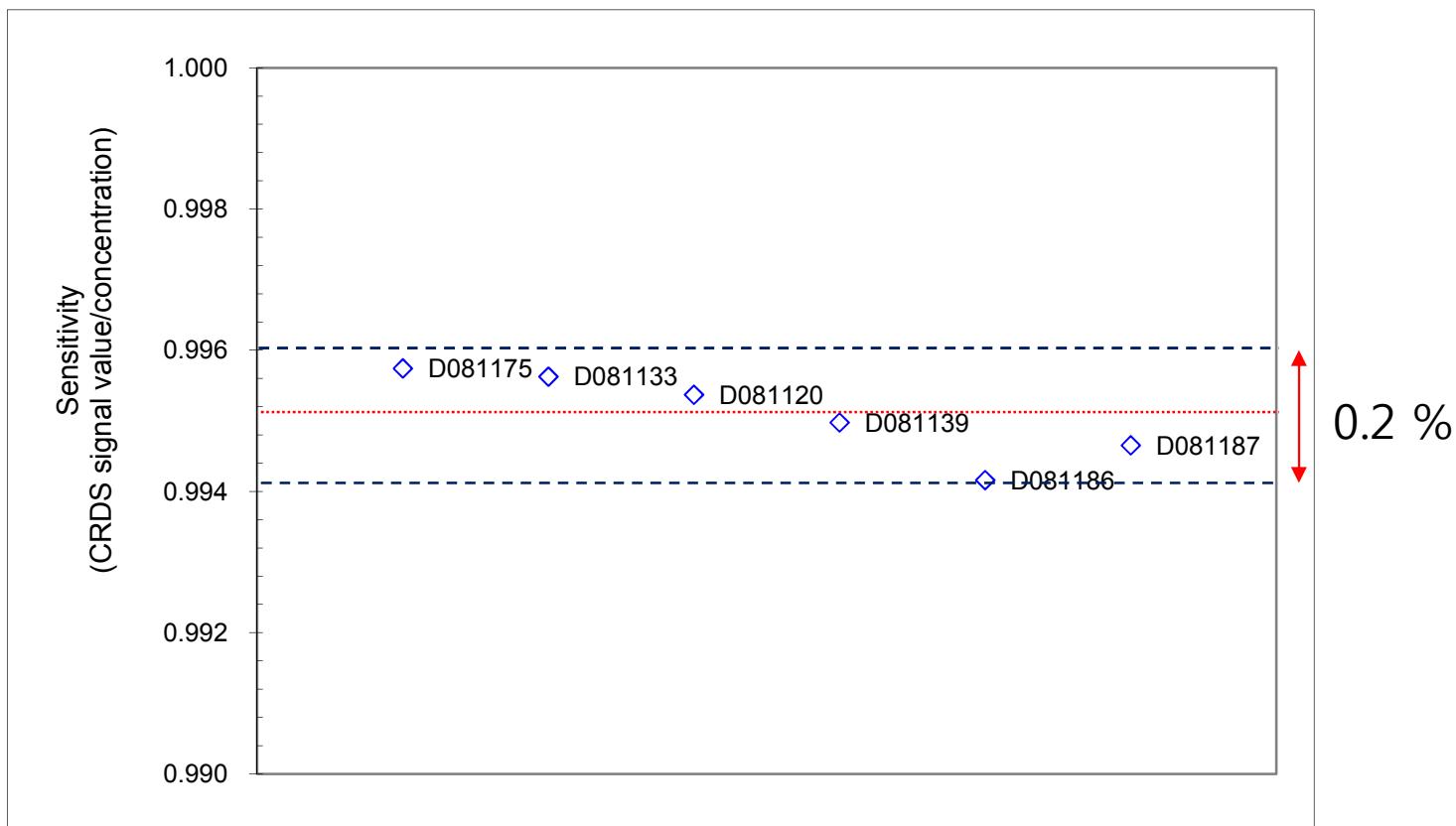
Schematic diagram of preparation for N_2O gases

Preparation of Reference Gas Mixture

- Gravimetric mole fraction and uncertainty

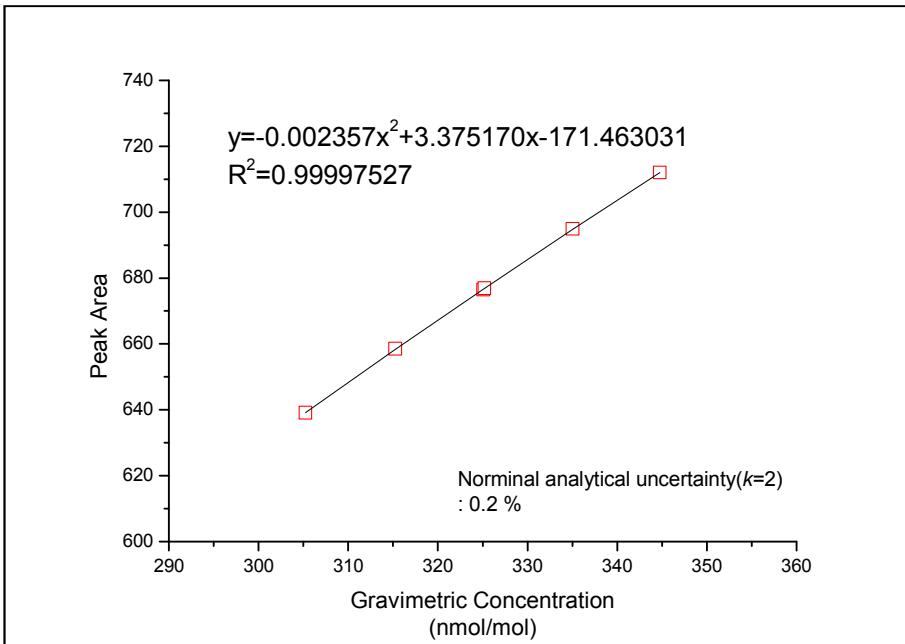
Cylinder	N ₂ O (nmol/mol) [%U, k=2]	O ₂ (%mol/mol) [%U, k=2]	N ₂ (%mol/mol) [%U, k=2]	Ar (%mol/mol) [%U, k=2]
D081175	305.22 [0.06]	20.8906 [0.002]	78.2021 [0.0005]	0.9073 [0.020]
D081133	315.27 [0.06]	20.9539 [0.002]	78.1381 [0.0005]	0.9079 [0.020]
D081120	325.07 [0.06]	20.6928 [0.002]	78.4050 [0.0005]	0.9021 [0.019]
D081139	325.20 [0.06]	20.9131 [0.002]	78.1533 [0.0005]	0.9336 [0.020]
D081187	335.05 [0.06]	20.8012 [0.002]	78.3128 [0.0005]	0.8860 [0.022]
D081186	344.78 [0.06]	19.5920 [0.002]	79.4622 [0.0005]	0.9458 [0.019]

Consistency check



Verification Test of N₂O CRM-μECD

- Verification test <Concentration range : 305 nmol/mol ~ 345 nmol/mol>



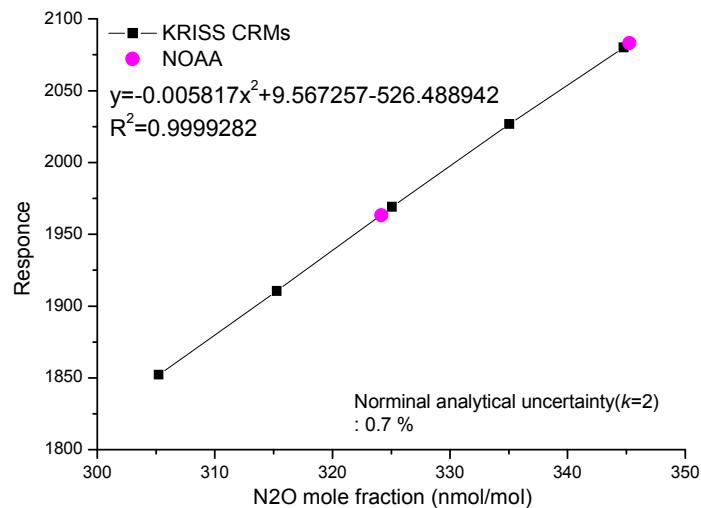
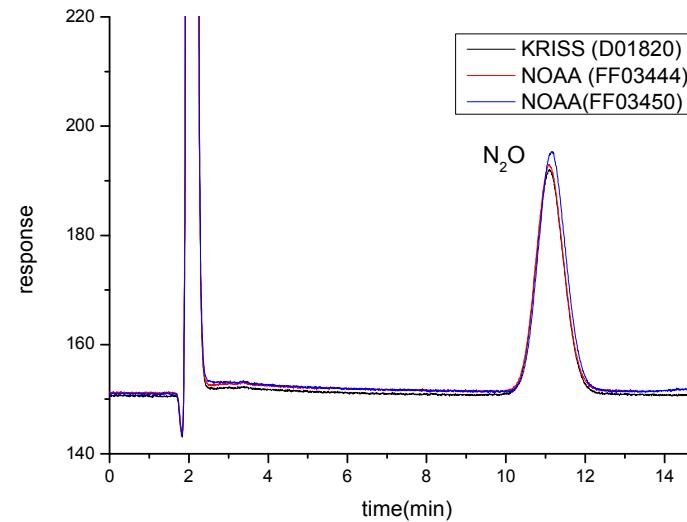
Cylinder	N ₂ O concentration(nmol/mol)		Residual[%]
	Gravimetry	Calibration	
D081175	305.22	305.19	-0.03[-0.009]
D081133	315.27	315.36	0.09[0.029]
D081120	325.07	324.97	-0.10[-0.031]
D081139	325.20	325.18	-0.02[-0.005]
D081187	335.05	335.11	0.06[0.017]
D081186	344.78	344.77	-0.01[-0.004]

Combined uncertainties of the certified values

Cylinder	Mole fraction (nmol/mol)	% Uncertainty of Gravimetry ($k=1$)	% Uncertainty of verification ($k=1$)	% Uncertainty of analysis ($k=1$)	Uncertainty ($k=2$) (%)	Uncertainty ($k=2$) (nmol/mol)
D081175	305.22	0.03	0.1	0.06	0.24	0.73
D081133	315.27	0.03	0.1	0.06	0.24	0.76
D081120	325.07	0.03	0.1	0.06	0.24	0.78
D081139	325.20	0.03	0.1	0.06	0.24	0.78
D081187	335.05	0.03	0.1	0.06	0.24	0.80
D081186	344.78	0.03	0.1	0.06	0.24	0.83

Comparison between NOAA and KRISS scales

Specification	Condition
Detector	μ ECD
Detector temp.	375 °C
Make up gas	40 mL/min
Oven temp.	32 °C
Column	PP-Q 80/100 12ft* 1/8 inch SS
Sample loop	0.75 ml
Carrier flow	P-5, 30 psi
Sample flow	100 ml/min



Cylinder	Concentration (nmol/mol)	Corr. Concentration (nmol/mol)	Difference [%]
D081175	305.22	305.28	0.02
D081133	315.27	315.05	-0.07
D081120	325.07	325.09	0.01
D081187	335.05	335.16	0.03
D081186	344.78	344.67	-0.03
FB03444	324.18	324.08	-0.03
FB03450	345.27	345.20	-0.02

→ NOAA

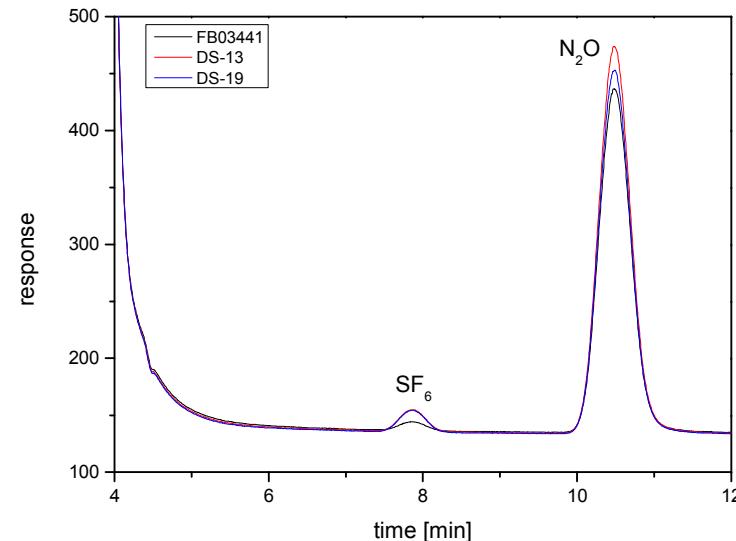
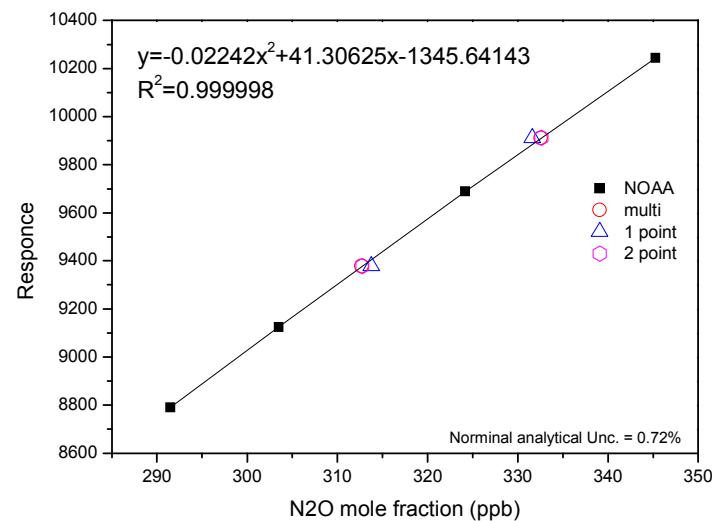


Thank you

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Measurement of working standards

Specification	Condition
Detector	μ ECD
Detector temp.	375 °C
Oven temp.	70 °C, 13 min 30 °C/min 190 °C 4 min
Column	AA-F1 80/100 12ft* 1/8 inch SUS
Sample loop	10 ml
Carrier flow	P-5, 25 ml/min
Sample flow	50 ml/min



Cyl. No.	Grav. conc. [nmol/mol]	Corr. Sens.	residual [%]
FB03441	291.51	30.156	-0.007
FB03443	303.5	30.066	0.010
FB03444	324.18	29.889	-0.009
FB03450	345.27	29.668	0.001

Cyl. No.	peak area	multi	1 point	2 point
DS-13	9911.297439	332.559	331.603	332.627
DS-19	9378.151347	312.682	313.765	312.775