Development of Sulfur Hexafluoride (SF_6) Certified Reference Materials at Ambient Level

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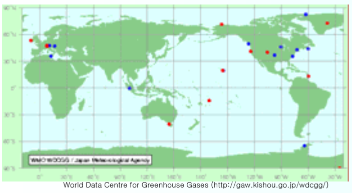
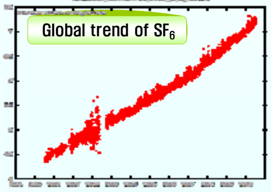
Introduction

Global mean concentration of SF_6 in 2009 was 6.5 pmol/mol which is much lower than other major greenhouse gases. Nevertheless, the global warming potential of SF_6 is much higher than other greenhouse gases due to its long lifetime in atmosphere, which is approximately 3200 years (IPCC, 2007). At present, semiconductor and display TV industries are expanded dramatically in Korea, and these IT industries use SF_6 in etching and cleaning processes. From 2007, the Korea Global Atmosphere Watch Center (KGAWC) has monitored SF_6 at Anmyeon island. SF_6 concentration in Anmyeon island showed a little higher than global mean value, which is about 7.5 pmol/mol in 2009 (KMA, 2010).

In this study, we developed SF_6 certified reference materials at ambient level.

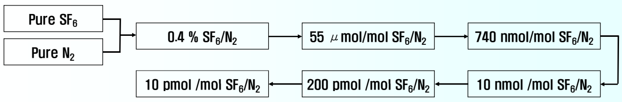


World Data Centre for Greenhouse Gases (http://gaw.kishou.go.jp/wdcgg/)



Preparation of Reference Gas Mixtures

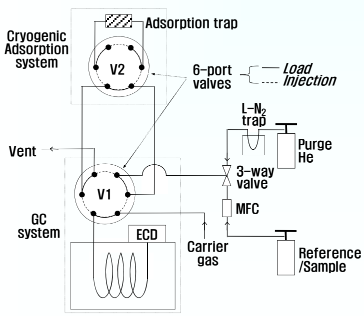
SF_6 gas mixtures were prepared by means of subsitutional gravimetric method. In order to prepare gas mixtures with low concentration SF_6, pure SF_6 gas (99.9 %, Matheson Trigas, USA) was 6 times diluted with pure nitrogen gas (99.9999 %, Deokyang Energen Co., Korea), consecutively, in 6.4 L aluminum cylinders which has polish treated on the inner surface (Luxfer, Australia).



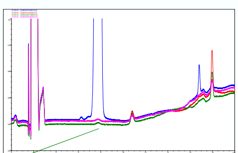
SF_6 Impurity in Pure Nitrogen

Impurity analysis in pure nitrogen as dilution gas is one of the important factor on preparation of accurate reference materials. Thus, the amount of SF_6 in nitrogen gas largely affects to the concentration of SF_6 standard gas mixture particularly in low concentration. Therefore we measured SF_6 in pure nitrogen using a cryogenic pre-concentration system attached to the GC/ECD and confirmed that only less than 0.01 pmol/mol of SF_6 existed in pure nitrogen gases.

Cryogenic Pre-concentration system



Procedure	3-way valve	V1	V2
Stand by	He	Load	Load
Absorption	R/S	Load	Injection
He purge	He	Load	Injection
Desorption	He	Load	Load
Introduction	He	Injection	Injection



SF_6 chromatogram in pure N_2
(LOD of system = 0.005 pmol/mol)

Uncertainty Evaluation for Preparation

During gravimetric preparation process, several factors affected to the SF_6 concentration, like balance itself, weighing procedure and purity of source gases, weighing (ISO, 1993). We estimated the uncertainty of reference materials using GUM program (Workbench Version 2.3), that are described the uncertainty budget of one gas mixture. We found that largest uncertainty contributor for the uncertainty of gas mixture was impurities in source nitrogen gases.

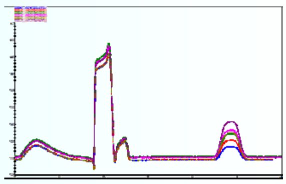
Quantity	Estimate / X_i	X_i unit	Evaluation type (A or B)	Distribution	Standard uncertainty / $u(x_i)$	Sensitivity coefficient / c_i	Uncertainty contribution / pmol mol⁻¹
Purity of SF_6 gas	0.99910	mol/mol	B	Normal	0.000115	6	0.00069
Purity of N_2 gas	0.9999977	mol/mol	B	Normal	0.0000007	−6	−0.000004
SF_6 impurity in source N_2	10×10^{-15}	mol/mol	B	Rectangular	2.5×10^{-15}	1.0×10^{12}	0.0025
Other impurities In source N_2	0.0000023	mol/mol	B	Rectangular	0.68×10^{-12}	−9300	−0.0063
Weight of empty cylinder	−0.011652	g	A	Normal	0.0000017	−380	−0.00064
Weight of cylinder after charging SF_6	0.0037362	g	A	Normal	0.0000023	390	0.0009
Weight of cylinder after charging N_2	0.7048196	g	A	Normal	0.0000010	−8.3	−0.0000085
Uncertainty from weighing	0.0	g	B	Normal	0.0000024	750	0.0018
SF_6 concentration	**5.9727**	**pmol mol⁻¹**			**0.0071 0.12**	**pmol mol⁻¹ %**	

Internal Consistency between Reference Materials

After preparation, reference gas mixtures were compared to each other to ensure the internal consistency. The analytical condition and chromatogram for the gas mixtures are shown in below. We measured 5 times for each gas mixtures and employed A-B-A method to correct the instrumental drift. The calibration curve among 6 gas mixtures appeared as a second order polynomial regressions curve, in which the peak area is depending on the concentration of gas mixtures.

Analytical Condition

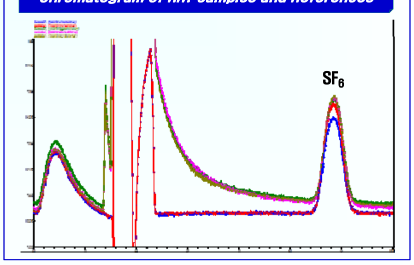
Detector : μECD
Detector Heating temp. : 385 ℃
Oven temp. : 35 ℃, isothermal
Column : Restek Alumina-F1 80/100
4 m, 2.0 mmID, 1/8 inOD, SUS
Carrier gas : P5 gas (CH_4 5 % in Ar)
Carrier flow : 30 mL/min
Sample flow : 100 mL/min
Sample loop vol. : 5 mL



Conclusion

As a result of this study, we developed a set of ambient level SF_6 reference gas mixtures with standard uncertainty of 0.5 %, which taken from verification and gravimetric preparation uncertainties. KRISS and KGAWC used these SF_6 standard gas mixtures as references for analysis of sample cylinders, which were provided by WMO as Round Robin Test (RRT).

Chromatogram of RRT samples and References



References

- WMO (2007), GAW Report No. 186. 14th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques.
- KMA (2010), Report of Global Atmosphere Watch 2009.
- ISO (1993), Guide to the Expression of Uncertainty in Measurement. Geneva, Switzerland

KRISS