

Abstract

According to the World Meteorological Organization (WMO) Global Atmosphere Watch (GAW) Strategic Plan: 2008–2015 (WMO, 2009a) WMO/GAW pays attention to systematical improvement of the quality of observations at global or regional monitoring sites. To ensure the comparability and compatibility of the measurements worldwide it is essential to maintain a traceability chain to the primary standard in the different laboratories around the world as well as to establish a quality control system.

Sulfur hexafluoride (SF_6), is reported to be very rare in the atmosphere at the global averaged annual mole fraction of about 7 ppt, it is one of the greenhouse gases regulated by Kyoto protocol and is increasing at a rate of 0.22 ppt yr^{-1} . Development of a working (or transfer) standard with very low concentration of SF_6 requires expert technologies and several knowhow of gas metrology. In order to meet the Data Quality Objective (DQO), the KMA has cooperated with the Korea Research Institute of Standards and Science (KRISS), which is the National Metrology Institute in South Korea.

So long as the Central Calibration Laboratory (CCL) for SF_6 was established, the Korea Meteorological Administration (KMA) is now trying to take another step forward to systematically support GAW stations in improving their traceability and quality system for SF_6 , thereby making a contribution to the WMO/GAW. Through hosting the World Calibration Center for SF_6 , which is one of GAW facilities, KMA will contribute to harmonization of the global SF_6 observations in the long run.

This work performed to demonstrate some measurement results on SF_6 which complies with the DQOs and is traceable to the WMO mole fraction scale for SF_6 . In order to produce a working standard which is traceable to the WMO scale, we developed highly precise method of a Gas Chromatography/Electron Capture Detector (GC/ECD) calibrated against the five cylinders (from NOAA, 2011) of the WMO scale. For all analysis the measurement repeatability was $< 0.02 \text{ ppt}$ (standard deviation) and analyzer's stability was controlled within a drift of 0.02 ppt . Finally, a working standard which is

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consistent with WMO scale and satisfies the WMO DQOs of ± 0.02 ppt was successfully produced and is ready to be transferred to the GAW stations.

1 Introduction

Greenhouse gases (GHGs) have been known as substances causing the greenhouse effect. Most countries including the industrialized nations exert every effort to limit and reduce the greenhouse gas emissions since the Kyoto Protocol's entry into force 2005, which is an agreement to reduce emissions of six greenhouse gases. Accurate observation data of ambient GHGs are vital for the study of the relationship between the global warming and the climate change, but it is not easy to quantify their mixing ratios owing to their globally and temporally insignificant variation. World Meteorological Organization (WMO) GAW programme is operating an international network composed by 80 countries, and ~ 400 observatory sites to improve scientific knowledge of climate change.

SF₆ in the atmosphere, one of the greenhouse gases regulated by Kyoto protocol, is the rarest among known greenhouse gases. SF₆ can stay in the atmosphere for a long time due to its stability, from 600 yr to 3200 yr. It has higher global warming potential than other greenhouse gases. Recently, the amount of SF₆ mole fraction is reported to be around 7 ppt and being increasing at a rate of 0.22 ppt yr⁻¹ (WMO, 2009b). Therefore, SF₆ observation becomes one of the important activities of the GAW Programme in support of climate change research. According to Global Atmospheric Watch Station Information System (GAWSIS), 37 stations have been observing SF₆. Most of the stations are located in European and American regions.

The KMA has observed greenhouse gases since 1998 and contributed the GAW programme as a regional GAW station. Currently, we are monitoring CO₂, CH₄, N₂O, SF₆, and three types of CFCs, namely CFC-11, CFC-12, CFC-113 on a regular basis. This data are being reported to the World Data Center for Greenhouse Gases (WD-CGG) in Japan. In order to meet the GAW Data Quality Objective (DQO), the KMA

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has cooperated with the Korea Research Institute of Standards and Science (KRISS), which is the National Metrology Institute in South Korea and with the Japan Meteorological Administration (JMA), which is the World Calibration Center for CH₄. Recently, the KMA and KRISS participated in the WMO Round Robin Exercise or Test (RRT) for five greenhouse species. So long as the Central Calibration Laboratory (CCL) for SF₆ was established, the Korea Meteorological Administration (KMA) is now trying to take another step forward to systematically support GAW stations in improving their traceability and quality system for SF₆, thereby making a contribution to the WMO/GAW. The KMA proposed to take on the responsibility as World Calibration Center (WCC) for SF₆ within the GAW Programme.

Establishment and application of a standard scale requires expert technologies and several knowhow of gas metrology. As a member of Consultative Committee for Amount of Substance (CCQM) Gas Analysis Working Group (GAWG), KRISS has participated in several international comparison programs since the last 10 yr. In the international comparison CCQM-P41, which was carried out in 2004, the mole fraction scales for carbon dioxide (CO₂) were well agreed between WMO and NMIs (van der Veen et al., 2007; Wessel et al., 2008). In the case of methane (CH₄), the WMO scale was 1.4 % lower than the NMIs' scale. As the result, WMO changed their official scale to 1.3 % higher against gravimetric scale (Dlugokencky et al., 2005). Recent international comparison of CCQM-K68 had been performed to compare the mole fraction scales for nitrous oxide (N₂O). The NMIs' average scale was well agreed to WMO scale for N₂O (Lee et al., 2011). Based on the experience of standard and science, KRISS, NMI of Korea, would like to contribute to the GAW programme by maintaining and distributing the WMO scale of SF₆ to support SF₆ quality.

2 Scope

Activities of the WCC will involve maintenance of laboratory standards which are traceable to the WMO SF₆ mole fraction scale and audits of GAW sites to ensure the

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observations traceability to the WMO mole fraction scale for SF₆. According to the strategic plan of the WMO/GAW, in order to implement the GAW QA system WCC is required to conduct regular assessments of stations and apply standard operating procedures. Regular assessments consist of a system audit and a performance audit. The former is to check whether a station complies with the GAW QA system. It involves an assessment of station siting, infrastructures, organizations, operation, etc. The latter is to assess whether the measurement of SF₆ is being carried out in accordance with the GAW DQOs and to check the observation traceability toward the WMO mole fraction scales. The WCC, as one of GAW facilities undertakes the activities for their implementation by cooperating with other GAW facilities and contributes to harmonization of the measurement scale globally and spatially in the long run.

3 WCC and the WMO SF₆ mole fraction scale

Traditionally, SF₆ mole fraction scales are being provided by three laboratories, National Oceanic and Atmospheric Administration (NOAA), University of Heidelberg and Scripps Institution of Oceanography (SIO). The comparability between these three scales is known as generally good (WMO, 2009b). A need to compare among the SF₆ observation data produced from various GAW stations required one official scale. The scale was developed by NOAA in 2000 and has been prepared by a static gravimetric dilution method from 2006 and maintained up to now. Since 2009, NOAA plays a key role as a SF₆ Central Calibration Laboratory (CCL).

3.1 WCC tasks

The WCC's tasks are described in “a WCC in Box 7 of the GAW report no. 172” and implemented by shaping the terms of reference in detail as follows;

1. Assist Members operating GAW stations to link their observations to the GAW primary standard.

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The KMA shall provide appropriate assistance for GAW stations under the WMO so that they can produce SF₆ observation results which have traceability to the WMO mole fraction scale which is kept by the CCL, the NOAA/ESRL (Earth System Research Laboratory). Accordingly the KMA shall possess a set of the WMO SF₆ mole fraction scale to ensure their linkage to CCL, to distribute the WMO SF₆ mole fraction scale to the GAW stations, and to perform sites audits. For the purpose of the linkage, the KMA obtained from NOAA the WMO mole fraction scale for SF₆, such as cylinders in the range of 4–15 pmol mol⁻¹ in November 2010.

2. Develop quality control procedures following the recommendations by the scientific advisory groups (SAGs), support the QA of specific measurements and ensure the traceability of these measurements to the corresponding primary standard.

The KMA shall develop procedures to control the quality as recommended by the SAG to support the QA of measurements for SF₆ and ensure the traceability of these measurements within a year after being designated as WCC. Finally, the KMA is willing to cooperate with the NOAA in future for implementation of GAW quality system in measurement of SF₆.

Because currently the KMA is observing SF₆ with GC/ECD (Gas Chromatograph/Electron Capture Detector), the KMA has an expertise of SF₆ measurement. The analyzing system has been calibrated by the primary standards provided by the KRISS in the past and will be changed into WMO scale from now on. For precise calibration of SF₆ analyzing system, the primary standards with at least 5 different concentration levels are required due to the non-linear characteristics of ECD.

3. Maintain laboratory and transfer standard that are traceable to the primary standard.

In order to maintain laboratory and transfer standards with the traceability to the WMO SF₆ mole fraction scale, the KMA shall establish a system to produce the

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laboratory standards based on the WMO SF₆ mole fraction scale of the CCL, such as an analysis system as well as a system to collect and compress dry air. The laboratory standards will be used to calibrate an analysis system, to measure SF₆ in the atmosphere and to produce the transfer or other laboratory standards of various amounts of SF₆ mole fraction which are to be prepared by sampling naturally (or filling artificially) SF₆ sparser or denser air. The laboratory and transfer standard are maintained by calibration against the WMO SF₆ mole fraction scale on a regular basis.

Meantime, compression equipment for dry air, a large number of 30 l and 6 l aluminum cylinders are also necessary. To produce the laboratory standards, the KWA set up a vacuum system with the heating apparatus and a turbo-pump that is able to lower the inside pressure of the cylinder down to less than 10⁻³ mbar. To produce a better laboratory standard KMA will technically cooperate with CCL.

4. Perform regular calibration and performance audits at GAW sites using transfer standards.

The KMA shall carry out basically calibration and audits every 3 yr using SF₆ transfer standards. To do so, RRT and corrective actions will be conducted. Intervals and methods of the performance audits of the stations could be changed if there is any request from the SAG.

5. Provide, in co-operation with the QA/SACs, training and long-term technical help for stations.

The KMA shall establish systems and facilities to provide stations with long-term training and technical support regarding QA/QC and measurement in cooperation with the QA/SAC. In particular, the KMA will set up GC/ECD for SF₆ to use it for training within 3 yr after being designated as WCC.

3.2 Analysis method

A highly repeatable GC method for comparing gas mixtures of SF₆ in air was developed for this study. The comparison analysis is carried out by gas chromatography equipped with μ ECD (an Agilent 6890N) using an activated alumina-F1 column (2 m \times 2 ea, ID 2.0 mm, 80–100 mesh) and a 7 ml volume loop. P-5 (CH₄ 5% in Ar) gas is used as a carrier gas. The carrier gas was introduced with a flow of \sim 28 ml min⁻¹ depending on the analyzer condition. Samples passes through a Multi Position Valve (MPV) directly connected to each cylinder, then through a mass flow controller (6890N GC/ECD, Agilent, USA) to be finally introduced in the sample loop. A sample flow is optimized to be introduced at a rate of 200 ml min⁻¹ into a loop volume of 7 ml.

Generally two columns, such as propak Q column and Alumina F-1, can separate SF₆. For this study in order to select an adequate column two different columns were tested. Figure 2 shows two chromatograms by two different columns. In Fig. 2 it is shown that Activated Alumina F-1 column (Restek, USA) separates more effectively SF₆ from oxygen (O₂), nitrous oxide (N₂O) and other gases. It is found that the SF₆ peak from an Alumina F-1 column can be distinguished from others. A propak Q column looks suitable for analyzing N₂O in air. Therefore for the separation of SF₆ peaks from any others, alumina-F1 column was selected. When we used total 4 m of column, oven temperature 35° and carrier gas flow 28 ml min⁻¹, we separated SF₆ clearly from other components in air under the analytical condition even though matrix of the WMO scale was compressed air.

To have a good analytical precision, response of gas chromatogram was examined. Table 1 shows a series of 11 measurement results of two different cylinders of a sample (*S*) and a reference (*R*) alternately. For production of one data point from a cylinder at least three injections were carried out and total 30 min analysis run elapsed. One data point comprised of the three repeats has a standard deviation (1 σ) of \sim 0.20% (relative). Each response ratio was obtained by dividing sample's peak area by average of both references (before and after sample analysis) to compensate any analyzer

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drift during analysis. The drift of the analyzer was within 0.3 % (relative) whose contribution was included in the value of response ratio. The results of the comparison analysis (ISO, 2001b) of sample and reference cylinders are shown in Table 1. The standard deviation of the mean of the results of the 5 ratios (each of which consists of 5 independent comparisons) is 0.22 % (relative) with the maximum deviation of 0.26 %, which comply with the WMO/GAW recommendation on SF₆. On the basis of this data set and many other similar sets we estimate the standard uncertainty of SF₆ analysis to be 0.3 % (relative).

3.3 Calibration to the WMO scale

We received the WMO scale (5 cylinders) from the CCL for SF₆ (NOAA), and analyzed them to calibrate a GC/ECD. The SF₆ measurement results are shown in Table 2 and Fig. 4. The calibration curve obtained from NOAA cylinders fit well with secondary polynomial function of $R^2 \sim 0.99998$. Measured mole fractions agree with NOAA's reported values within the standard deviation of each cylinder, which indicates that the analytical ability by KRISS satisfies with WMO recommendation level, ± 0.02 ppt.

In Table 2 the differences between the WMO scale and the calibrated value are within ~ 0.02 ppt of the repeatability uncertainty. Finally, the analyzer calibrated against the cylinders from CCL, because the calibrated results were consistent within DQOs. During the analysis the standard deviation of one data point obtained from 3 or 4 repeats were within 0.02 ppt.

3.4 Preparation of working standard – traceable to the WMO scale

In order to maintain laboratory and transfer standards with the traceability to the WMO SF₆ mole fraction scale, the WCC should produce a laboratory standards based on the WMO SF₆ mole fraction scale.

Both systems for analyzing SF₆ (ISO, 2001b) and for sampling a compressed dry air are required to produce a laboratory standard. As an example, of standard production

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3.5 Comparison of the scales between WMO and KRISS

We analyzed three NOAA cylinders together with two KRISS cylinders. KRISS cylinders were prepared by gravimetric method (ISO, 2001a) in nitrogen balance. Because the cylinders were prepared with gravimetric method a possible existence of SF₆ in the nitrogen, because it is the main balance gas, is very critical. So a pure nitrogen gas (Deokyang Energen Inc., Korea) was analyzed to check whether SF₆ as an impurity exist. As a measurement result, the amount of SF₆ in pure nitrogen is to be less than 0.01 ppt, when compared to the 6 ppt SF₆ mixture which is prepared in KRISS. In the chromatogram of Fig. 6, blue line is SF₆ of 6 ppt prepared in KRISS and green, pink, and red lines are nitrogen gases used.

As shown in Table 4 and Fig. 6, KRISS scale agreed with the WMO scale within 1.5%. To reduce the analytical error caused by different matrices (KRISS standard is SF₆ in nitrogen balance and the WMO scale is in air), we put a lot of effort to inject same amount of sample gas into GC/ECD by controlling an injection flow and vent. As reported in 2009 (Min et al., 2009) gas flow rate can be changed when gases with different matrices pass through one thermal mass flow controller, which influences measurement value. We are in preparation of this work.

After all, we found that there is some deviation between two scales which is more than their analysis uncertainties. Therefore we prepare gravimetrically (ISO, 2001a) gas standard mixtures with the almost same balance composition with air such as, 0.78 mol mol⁻¹ N₂, 0.21 mol mol⁻¹ O₂ and 0.01 mol mol⁻¹ Ar, for more precise and accurate comparison with the WMO scale.

4 Conclusions

This paper describes the task of the proposed World Calibration Center for SF₆ to implement quality assurance system for SF₆ observations at ambient level which are traceable to WMO scale and satisfies WMO DQO. For the analysis a Gas

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Chromatography/Electron Capture Detector (GC/ECD) was used and calibrated against the WMO scales (five cylinders from the CCL, NOAA, 2011), and consequently a working cylinder which is traceable to the WMO scale was produced. As a result of analysis their uncertainties were < 0.02 ppt for measurement repeatability standard deviation and < 0.02 ppt for analyzer drift. Finally the working standard was consistent with WMO scale within the combined uncertainty of repeatability and drift.

In addition, we found that there is some deviation between two scales of KRISS and WMO. When measured with the same amount injection technique, the WMO scale was 1.5 % higher than that of KRISS. It is regarded that the difference is mainly from different matrix of two mixtures. Accordingly we prepare gravimetrically gas mixtures of the almost same balance composition with air for more precise and accurate comparison with the WMO scale. The results of a production of standard mixture in artificial air will be reported in future paper.

Acknowledgements. This work was supported by Korea Research Council of Fundamental Science and Technology (KRCF) through National Agenda Project of “Development of measurement technology solving climate change” and by KMA through the project of “Establishment of foundation research to meet WMO WCC-SF₆”. The authors thank KRISS and KMA colleagues for continuing cooperation and discussion.

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Table 1. Comparison data from GC analyzer; one area is from 3 successive analysis.

| Number of measurement | Area | Ratio value $S_i \cdot 2 / (R_i + R_{i+1})$ | Deviation [%] | 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 | | |
| Std. dev. | | 0.0022 | | |

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Table 2. Analytical result for SF₆ CRMs from NOAA and KRISS.

| Scale | Cyl. No. | $C_{\text{WMO-scale}}$ [ppt] | Standard deviation ^a (u) [ppt] | Peak area | $C_{\text{calibrated}}$ [ppt] | Difference ^b | |
|--------------------|----------|---------------------------------|---|--------------|----------------------------------|-------------------------|-------|
| | | | | | | [ppt] | [%] |
| WMO scale scale | FB03441 | 3.946 | 0.015 | 174.12 | 3.937 | −0.009 | −0.23 |
| | FB03443 | 5.920 | 0.017 | 260.51 | 5.941 | +0.021 | +0.36 |
| | FB03444 | 7.972 | 0.023 | 346.38 | 7.964 | −0.008 | −0.10 |
| | FB03447 | 9.595 | 0.018 | 414.28 | 9.585 | −0.010 | −0.10 |
| | FB03450 | 11.887 | 0.020 | 509.43 | 11.893 | +0.006 | +0.05 |

^a Standard deviation as a value reported by NOAA.

^b Difference = $C_{\text{calibrated}} - C_{\text{WMO-scale}}$.

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Table 3. Total uncertainty budget of the working standard (CC315007) of C_{unknown} .

| Uncertainty factor (from Eq. 1) | Measured value | Standard deviation (u) | Measured value | Note |
|------------------------------------|------------------------------------|-------------------------------|--------------------------------|-------------------------|
| R_{unknown} | 327.65 | $u(R_{\text{unknown}})$ | 1.01 | for 3 repeats |
| R_{ref1} | 260.51 | $u(R_{\text{ref1}})$ | 0.19 | for 3 repeats |
| R_{ref2} | 346.38 | $u(R_{\text{ref2}})$ | 1.49 | for 3 repeats |
| C_{ref1} | 5.920 ppt | $u(C_{\text{ref1}})$ | 0.017 | reported |
| C_{ref2} | 7.970 ppt | $u(C_{\text{ref2}})$ | 0.023 | reported |
| C_{unknown} (CC315007) | 7.524 ppt (obtained from Eq. 1) | $u(C_{\text{unknown}})$ | 0.047 (obtained from Eq. 2) | Combined uncertainty |

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Table 4. Measurement result between two scales.

| Scale | Cyl. No. | $C_{\text{WMO-scale}}$ [ppt] | Standard deviation (u) [ppt] | Peak area | $C_{\text{calibrated}}$ [ppt] | Difference ($C_{\text{calibrated}} - C_{\text{WMO-scale}}$) | |
|--------------------|----------|---------------------------------|--|--------------|----------------------------------|--|-------|
| | | | | | | [ppt] | [%] |
| The WMO scale | FB03443 | 5.920 | 0.017 | 221.92 | 5.917 | −0.003 | −0.04 |
| | FB03444 | 7.972 | 0.023 | 295.93 | 7.918 | +0.006 | +0.07 |
| | FB03447 | 9.595 | 0.018 | 353.90 | 9.592 | −0.003 | −0.03 |
| The KRISS scale | ME5591 | 7.237 | 0.02 | 272.81 | 7.334 | +0.097 | +1.34 |
| | ME5499 | 8.999 | 0.02 | 337.23 | 9.128 | +0.129 | +1.43 |

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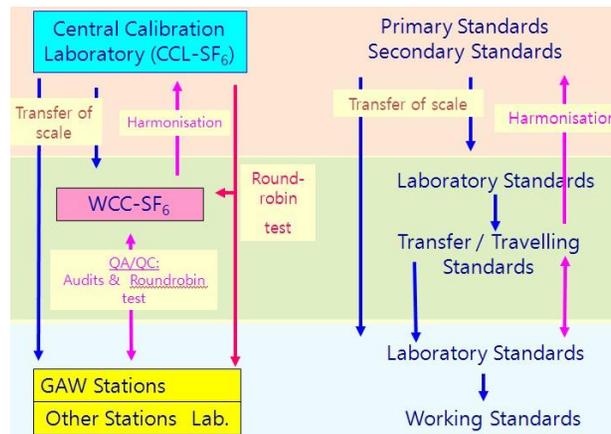
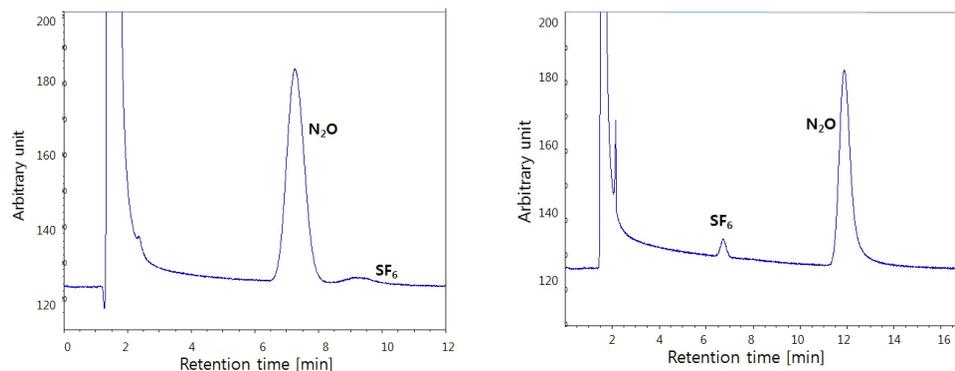


Fig. 1. Traceability of SF₆ from the CCL to GAW stations (modified from WCC-N₂O).

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Analytical condition

Detector: μ ECD
 Temp. of Oven, Heater: 35°C, 380°C
 Column: PP-Q 4 m
 Carrier gas: P5, 45 psi ($\sim 26 \text{ ml min}^{-1}$)
 Sample Flow, Volume: 100 ml min^{-1} , 1 ml

Analytical condition

Detector: μ ECD
 Temp. of Oven/Heater: 35°C, 375°C
 Column: Activated alumina-F1
 Carrier gas: P5, 45 psi ($\sim 26 \text{ ml min}^{-1}$)
 Sample Flow, Volume: 100 ml min^{-1} , 2 cc

Fig. 2. Chromatograms depending on column selection installed at the GC/ μ ECD (x-axis: retention time, minutes; y-axis: amount of response, arbitrary).

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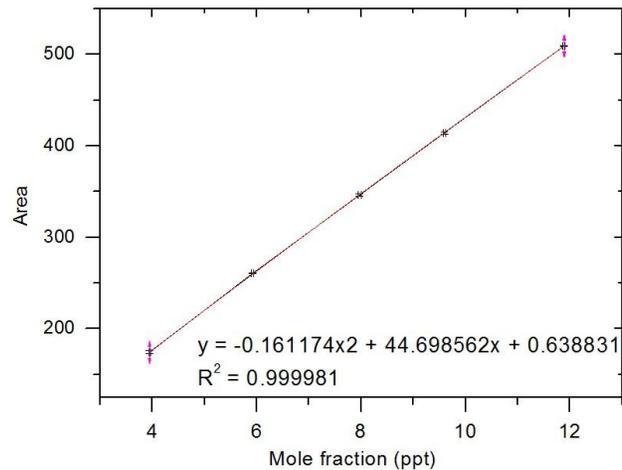



Fig. 3. Calibration curve for NOAA cylinders.

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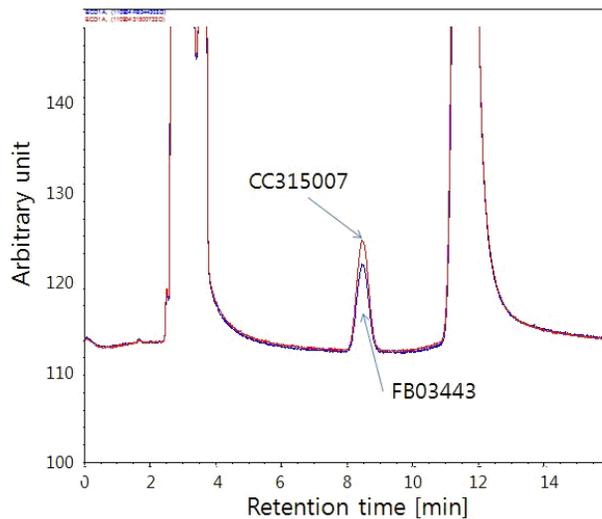


Fig. 4. Chromatogram of air sample cylinder (CC315007) for a working standard overlaid on the FB03443. (x-axis: retention time, minutes; y-axis: amount of response, arbitrary).

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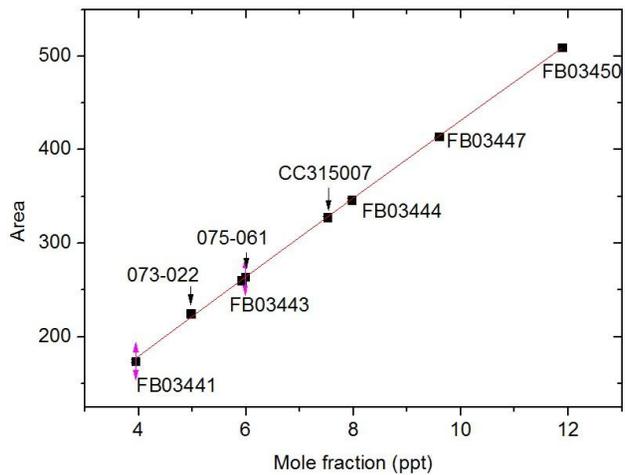


Fig. 5. Working standard (CC315007) on the Calibration curve with WMO scale.

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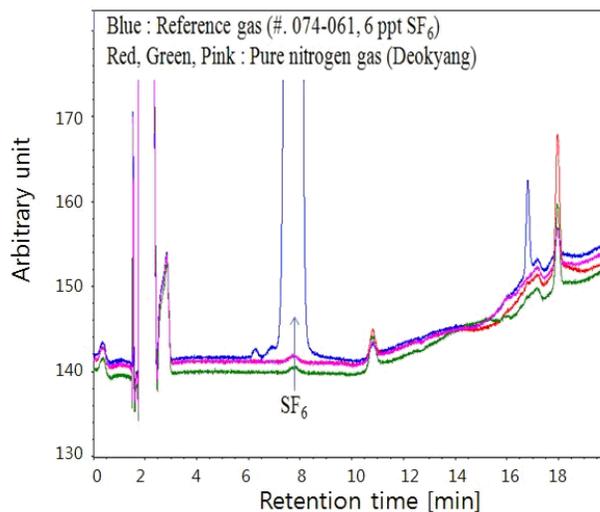


Fig. 6. Chromatograms of SF₆ in pure nitrogen gases and prepared SF₆ 6 ppt standard (x-axis: retention time, minutes; y-axis: amount of response, arbitrary).

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