



High-precision analysis of SF₆ at ambient level

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Abstract. This work reports on the development of a technique for the precise analysis of ambient SF₆. This technique, which involves a gas chromatograph/electron capture detector (GC-ECD) coupled with an Activated Alumina-F1 (AA-F1) column, performed well in the measurements, particularly in terms of accuracy, which complies with the World Meteorological Organization (WMO)-recommended compatibility of 0.02 ppt. Compared to the Porapak Q technique, we observed a sharper peak shape for the SF₆ stream, which substantiates the improvement in the analytical precision. The traceability to the WMO scale was tested by calibrating the GC-ECD/AA-F1 analyser using five SF₆ standards provided by the WMO/Global Atmosphere Watch (GAW) Central Calibration Laboratory (CCL) for SF₆ (NOAA, United States of America). After calibration by various methods, the GC-ECD/AA-F1 accurately estimated the mole fraction of SF₆ in the working standard prepared by the World Calibration Centre for SF₆ operated by the Korea Meteorological Administration (KMA)/Korea Research Institute of Standards and Science (KRISS). Among the calibration methods, the two-point calibration method emerged to be the most economical procedure in terms of the data quality and measurement time. It was found that the KRISS scale of SF₆/N₂ was biased by 0.13 ppt when compared to the WMO scale of SF₆/air; this bias is probably due to a different matrix.

into force in 2005, binds a number of countries with an obligation to reduce the human-activity-induced emissions of four greenhouse gases – CO₂, CH₄, N₂O, and SF₆ – and two groups of halocarbon gases, which include hydrofluorocarbons and perfluorocarbons. Consequently, most industrialised nations have devoted tremendous effort in reducing and even restricting the anthropogenic emissions of GHGs. In order to standardise the accuracy and compatibility of the measurements, the Bureau International des Poids et Mesures (BIPM; International Bureau of Weights and Measures) and the World Meteorological Organization (WMO) have carried out several international comparisons of the greenhouse gas standards (van der Veen et al., 2007; Wessel et al., 2008; Dlugokencky et al., 2005; Lee et al., 2011). WMO and BIPM signed a memorandum of understanding (MOU) to ensure better collaboration and authorisation of non-metrology institutions supporting the Quality Assurance system within the GAW Programme to take part in the BIPM coordinated key comparisons.

Among the greenhouse gases mentioned, SF₆, despite its low global mean mole fraction (5–10 ppt), has attracted a lot of attention due to its long lifetime of 600–3200 yr in the troposphere. Its high global warming potential – 22 800 times greater than that of CO₂ – makes it one of the most potent GHGs. The global mean of SF₆ was measured as 7.5 ppt in 2012 (HATS database, 2013) and its growth rate is evaluated to be up to ~0.28 ppt yr⁻¹ (GAW Report No. 186, 2009; Rigby et al., 2010; Hall et al., 2011).

Naturally, the observation of SF₆ has become a vigorous activity under the GAW (Global Atmosphere Watch) Programme, which is supported by 80 countries and up to 400 observatory sites worldwide. Among those, 37 sites for SF₆

1 Introduction

Greenhouse gases (GHGs) in the atmosphere, which absorb and emit solar thermal energy, are known to be the prime cause of global warming. The Kyoto Protocol, which entered

observation are located mostly on the European and American continents, according to the Global Atmosphere Watch Station Information System (GAWSIS). The Korea Meteorological Administration (KMA), with technical cooperation from the Korea Research Institute of Standards and Science (KRISS), recently agreed to host the World Calibration Centre (WCC) for SF₆ in order to contribute to the programs of the WMO and GAW on the global observations of SF₆. At present, the establishment of a high-quality measurement system with reliable compatibility between the observation sites is regarded as a task of highest priority, taking into consideration the complications associated with the analytical results generated by a gas chromatography-electron capture detector (GC-ECD) system, which is the typical tool for the analysis of SF₆.

In this study, we describe the analysis of SF₆ using a GC-ECD analyser coupled with an Activated Alumina-F1 (AA-F1) column; we also compared the performance of our method with that of the Porapak Q (PP-Q) technique. The working standards, prepared as dry air standards in aluminium cylinders, were analysed using the GC-ECD/AA-F1 calibrated against the WMO SF₆ scale. Using these results, the SF₆ mole fraction of the working standards with associated analytical uncertainty was assigned by various calibration methods. In addition, a comparison between the WMO and KRISS standards is discussed.

2 Experimental methods

2.1 Analyser preparation and measurement capability

Gas chromatography (GC) was used for the high-precision analysis of SF₆ gas mixtures in this study. Analytes were fed into the GC at a constant flow rate, which was regulated by a well-calibrated mass flow controller (M3030V, Line Tech., Korea). A P-5 (5% CH₄ in Ar, 45 psi) gas was used to carry the analytes through the gas lines and an Activated Alumina-F1 column (4 m, ID 2.0 mm, OD 1/8", 80–100 mesh, Restek) (Fig. 1). A clean and constant condition of the gas lines and the column was maintained to ensure good repeatability of measurement results. The Activated Alumina-F1 (AA-F1) column was baked at 180 °C between measurement cycles for 5 min to wash out potential contaminants, which may cause long-term reduction of the response and separating power. The well-known “backflush” method used in the presence of pre-column, which prevents the late-eluting compounds from reaching the main column (Hall et al., 2011), is a more gentle treatment method than the baking method, but it was not tried in this study. Gas lines configured to have a low dead volume were continuously rinsed. Using the regulator without a gauge, we expected to reduce the unwanted contribution of gases moored in the dead volume. Furthermore, restrictors at the ends of vent lines kept the pressure constant along the sample injection line, column, and

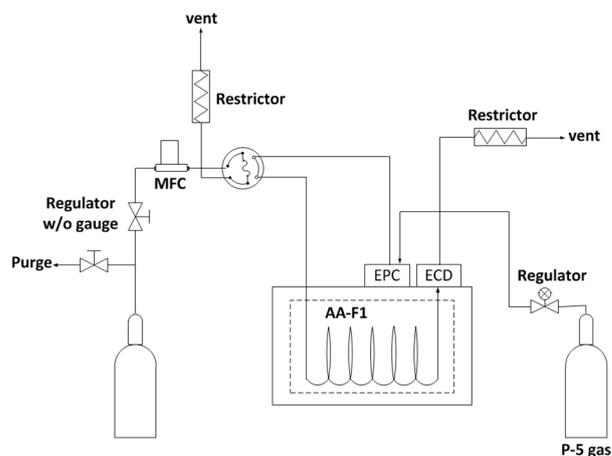


Fig. 1. Schematic diagram of the experimental setup. Using the regulator without a gauge, the unwanted contribution of gases moored in the dead volume was expected to be reduced. Two restrictors virtually isolated the instrument from variation in the ambient conditions of the lab and, therefore, lead to reasonable repeatability of the measurement results. EPC and ECD stand for the electronic pressure controller and electron capture detector, respectively. A series of measurements were performed while manually switching the left cylinder between sample and standard.

detector, regardless of ambient pressure (Fig. 1). This configuration helped to get a reasonably steady response factor. Chromatograms were then recorded, using the signal intensity of an electron capture detector (μ ECD, Agilent 6890N), as a function of the retention time of analytes in the column.

In order to show the resolving power of the GC-ECD/AA-F1, chromatograms taken by Activated Alumina-F1 and Porapak Q (4 m, ID 2.0 mm, OD 1/8", 80–100 mesh, Restek) were compared. Both Porapak Q (PP-Q) and activated alumina-F1 (AA-F1) columns can separate SF₆ from the background matrix under identical measurement conditions (4 m of column length, oven temperature of 35 °C, detector temperature of 380 °C, and carrier gas flow of 28 mL min⁻¹). As depicted in Fig. 2, it is clearly shown that tighter elution of SF₆ stream strongly imply excellent ability of the AA-F1 for SF₆ analysis, compare to the PP-Q. As an additional benefit of using AA-F1, potential signal interference between N₂O (260–360 ppb at ambient level) and SF₆ (5–10 ppt at ambient level), which appears later and gains lower sensitivity with PP-Q, can be avoided by virtue of the longer separation. It should be noted that a combination of PP-Q and molecular sieve 5A (Hall et al., 2011) also results in similar separation and analytical precision of SF₆, but this combination requires two column ovens operating at different temperatures; this disadvantage increases maintenance effort.

In order to correct the instrument drift, we performed a series of measurements while switching analytes from sample to reference (Table 1). These consecutive measurements yielded a converging ratio value as follows:

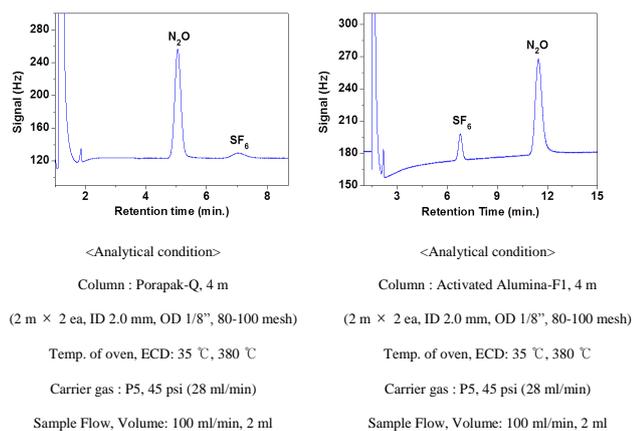


Fig. 2. Chromatograms taken using the GC-ECD coupled with two different types of columns installed in the GC.

$$S_i \cdot 2 / (R_i + R_{i+1}), \quad (1)$$

where S_i is the peak area of the i th sample and R_i is that of the i th reference. Through this method, a short-term drift of the instrument ($< 0.3\%$ relative) was considerably reduced with the help of the term in denominator, $(R_i + R_{i+1})/2$, which tracks the variation of the detection sensitivity. The standard deviation (1σ) of five ratios was 0.19% , which satisfies the compatibility goal recommended by the WMO for the measurement of SF₆ (± 0.02 ppt). It is worthwhile to mention here that the N₂O at ambient levels can be measured to within ~ 0.5 ppb of an analytical uncertainty by means of the AA-F1 technique. For testing the ECD response, the peak areas corresponding to SF₆ were determined using five NOAA gas cylinders with mole fractions of 3.946, 5.920, 7.972, 9.595, and 11.887 ppt (Fig. 3, Table 2). Eventually, the response values obtained from the calibrated analyser gets to be traceable to the WMO scale.

2.2 Preparation of working standard

Traditionally, SF₆ mole fraction scales have been provided by three laboratories, at the National Oceanic and Atmospheric Administration (NOAA), the University of Heidelberg, and the Scripps Institution of Oceanography (SIO). The compatibility between these three scales is generally known to be good (GAW Report No. 186, 2009). Nevertheless, because of the necessity for reliable comparison among SF₆ observation stations, the requirement for a unified scale has arisen. Accordingly, WMO/GAW has adopted the NOAA SF₆ scale as the WMO reference scale, which will be maintained by NOAA in their role as the Central Calibration Laboratory (CCL). In addition, CCL as a central facility supplies well-calibrated air to GAW analytic laboratories as needed for conducting inter-comparisons in collaboration with WCC

Table 1. Repeated measurement of reference and sample in order to compensate for instrumental drift between measurement cycles; every area data point is a result of three successive analyses.

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		

* R_i stands for i th reference measurements and S_i does i th sample measurement.

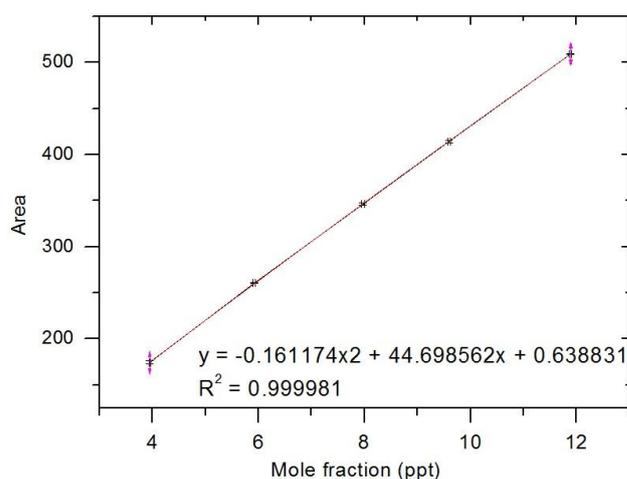


Fig. 3. Peak area plot as a function of the assigned mole fraction of the WMO standards. The response curve was approximated by a least square fit of a second-order polynomial with an agreement of $R^2 = 0.999981$. Residuals are listed in Table 2.

or RCC (Regional Calibration Center; GAW Report No. 172, 2009).

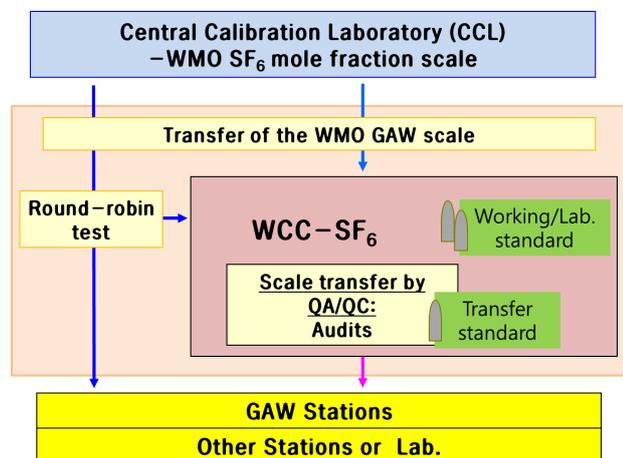
Dry air for sampling was captured into a 29.5 L aluminium Luxfer cylinder (UK, CC315007) that was evacuated to less than 10^{-3} mbar for a few hours. Then, an oil-free air compressor (SA-3E series, RIX Industries) pumped air into this prepared cylinder. To remove the air moisture during the sampling process, a chemical trap filled with granulated magnesium perchlorate ($Mg(ClO_4)_2$) was inserted into the air flow line. After sampling, the SF₆ mole fraction was assigned by the GC/ECD analyser calibrated by the WMO standards (Fig. 4).

Table 2. Analytical results of SF₆ standard gases from the NOAA.

Calibration scale	Cyl. No.	$C_{\text{assigned}}^{\text{a}}$ [ppt]	Standard deviation ^a		$C_{\text{calculated}}^{\text{b}}$ [ppt]	Difference ^c	
			[ppt]	Peak area		[ppt]	[%]
WMO 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 C_{assigned} and standard deviation is a preassigned value of NOAA standards. ^b $C_{\text{calculated}}$ is a value estimated from the approximated response curve at the corresponding peak area. The function of the approximated curve is given in Fig. 3.

^c Difference = $C_{\text{calculated}} - C_{\text{assigned}}$.

**Fig. 4.** Traceability chain of SF₆ from the CCL and GAW stations.

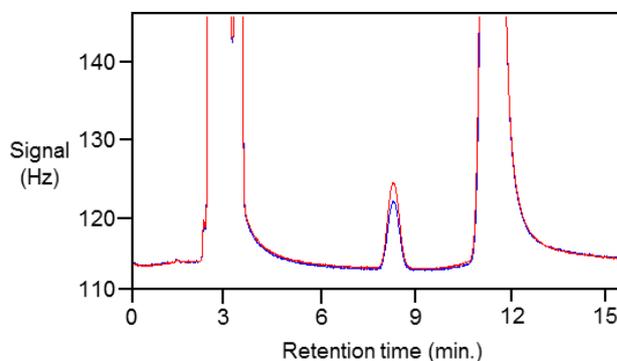
3 Results

3.1 High-precision analysis for SF₆

Figure 5 shows two overlaid chromatograms: one was a chromatogram of the working standard (CC315007, in air), and the other was that of the WMO cylinder (FB03443, in air). Due to the identity of the used matrix, a close proximity of the overall shapes was observed. Based on the assumption that the straight calibration curve is ensured in the mole-fraction interval of interest, a routine calibration such as single- and two-point methods can be carried out. In the single-point calibration, the mole fraction of the working standard was determined using following equation:

$$C_{\text{unknown}} = \left(\frac{R_{\text{unknown}}}{R_{\text{ref}}} \right) \cdot (C_{\text{ref}}), \quad (2)$$

where C is the mole fraction of SF₆, R is the response area, and the subscripts stand for the references and the unknown sample. Using the standard FB03443 (5.92 ppt) for one point calibration the working standard, which was assigned a value of 7.52 ppt from the multi-point calibration,

**Fig. 5.** Chromatogram of a working standard (CC315007, red) overlaid on one of the five WMO cylinders (FB03443, blue)

was found to be 7.45 ppt (0.07 ppt lower). While using the FB03444 (7.97 ppt) for one point calibration, the working standard was found to be 7.54 ppt (that is only 0.02 ppt higher). It is therefore suggested that the linearity of ECD response cannot be guaranteed outside the range of at least 0.45 ppt. The associated uncertainty was then determined using the following equation:

$$u(C_{\text{unknown}}) = \left(\frac{R_{\text{unknown}}}{R_{\text{ref}}} \right) \cdot (C_{\text{ref}}) \cdot \sqrt{\left(\frac{u(R_{\text{unknown}})}{R_{\text{unknown}}} \right)^2 + \left(\frac{u(R_{\text{ref}})}{R_{\text{ref}}} \right)^2 + \left(\frac{u(C_{\text{ref}})}{C_{\text{ref}}} \right)^2}, \quad (3)$$

where $u(R_i)$ is the measurement uncertainty considering the drift correction, and $u(C_{\text{ref}})$ is the standard deviation of the NOAA standard. The uncertainties were found to be 0.03 ppt for both FB03443 and FB03444 references.

To improve a degree of accuracy, the two-point calibration method was then considered. With the nearest bracketing by FB03443 and FB03444, the SF₆ mole fraction of the working standard was determined by the following equation:

$$C_{\text{unknown}} = \left(\frac{R_{\text{unknown}} - R_{\text{ref1}}}{R_{\text{ref2}} - R_{\text{ref1}}} \right) (C_{\text{ref2}} - C_{\text{ref1}}) + C_{\text{ref1}}. \quad (4)$$

Table 3. Calculated result of SF₆ in the working standard CC315007 depending on the calibration methods that are referred to the WMO scale. Unit is ppt.

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

Table 4. Total uncertainty budget of the working standard (CC315007).

Uncertainty factor	Standard uncertainty	Note
R _{unknown}	327.65	u(R _{unknown}) 0.61 for 3 repeats
R _{ref1}	260.51	u(R _{ref1}) 0.51 for 3 repeats
R _{ref2}	346.38	u(R _{ref2}) 0.65 for 3 repeats
C _{ref1}	5.920 ppt	u(C _{ref1}) 0.017 Preassigned
C _{ref2}	7.972 ppt	u(C _{ref2}) 0.023 Preassigned
C _{unknown}	7.524 ppt	u(C _{unknown}) 0.037 Two-point calibration

Further, the associated uncertainty was propagated as follows:

$$u(C_{\text{unknown}})^2 = \left[\frac{\left| \left(\frac{R_{\text{unknown}} - R_{\text{ref1}}}{R_{\text{ref2}} - R_{\text{ref1}}} \right) \cdot (C_{\text{ref2}} - C_{\text{ref1}}) \right|}{\sqrt{\left(\frac{u(R_{\text{unknown}} - R_{\text{ref1}})}{R_{\text{unknown}} - R_{\text{ref1}}} \right)^2 + \left(\frac{u(R_{\text{ref2}} - R_{\text{ref1}})}{R_{\text{ref2}} - R_{\text{ref1}}} \right)^2 + \left(\frac{u(C_{\text{ref2}} - C_{\text{ref1}})}{C_{\text{ref2}} - C_{\text{ref1}}} \right)^2}} \right]^2 + u(C_{\text{ref1}})^2 \quad (5)$$

where $u(R_i - R_j)$ is equal to $\sqrt{u(R_i)^2 + u(R_j)^2}$. Final assignment of the mole fraction of the working standard is 7.52 ± 0.04 ppt. The elements of the uncertainty budget are tabulated in Table 4. To approximately compensate the quadratic response of the detector over atmospheric levels of SF₆, a bracketing calibration with the WMO scale can be applied.

Values calculated using the various calibration methods are compared in Table 3. Slight deviations among calibration methods can be considered as analytical imperfections. Nevertheless, the calculated mole fractions were still within the values of the recommended compatibility goal. A significant difference was seen only when the single-point method was employed. Thus, we suggest the two-point calibration method as a higher priority method for the certification of a working standard, considering the measurement time and reliability of the data.

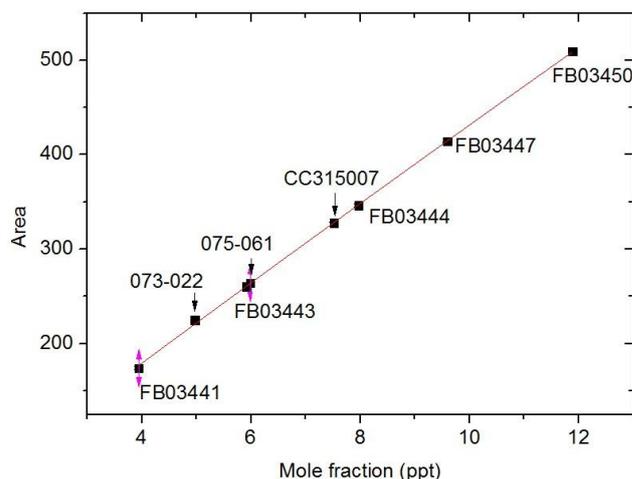


Fig. 6. Responses of working standard (CC315007, in air) prepared at WCC-SF₆ and KRISS gravimetric standards (073-022 and 075-061, both in nitrogen). KRISS standards are biased by 0.13 ppt from WMO scales due to the matrix effect.

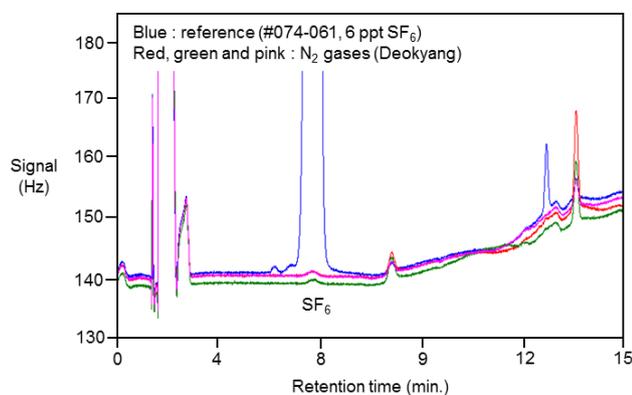
3.2 Comparison between the WMO standards and the KRISS standards

Comparison analysis between the three selected WMO standards and the two KRISS standards was carried out. KRISS standards were prepared by gravimetric method (ISO 6142, 2001). Since the matrix was pure nitrogen, counterchecking to pick up traces of SF₆ in nitrogen (99.999 %, Doek-yang Energen, Korea) became a very critical process to obtain an accurate value of the SF₆ mole fraction. The GC/ECD chromatogram (Fig. 7) shows an SF₆ trace in a high-purity N₂ cylinder, suggesting the importance of impurity analysis. Here it should be noted that gas lines were rinsed clean using different N₂ cylinders between cycles of impurity analysis. Even though the amount of SF₆ impurity was found to be less than 0.01 ppt, it is negligible from the point of

Table 5. Measurement results of the comparison between the WMO and KRISS standards.

Calibration scale	Cyl. No.	C _{Assigned} [ppt]	Standard deviation [ppt]	Peak area	C _{calculated} [ppt]	Difference* [ppt] [%]	
WMO standards	FB03443	5.920	0.017	221.92	5.917	-0.003	-0.04
	FB03444	7.972	0.023	295.93	7.978	+0.006	+0.07
	FB03447	9.595	0.018	353.90	9.592	-0.003	-0.03
KRISS standards	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

* Difference = C_{calculated} - C_{assigned}.

**Fig. 7.** Chromatograms of trace SF₆ in pure nitrogen (red, green, and pink) and KRISS SF₆ standard (blue, 6 ppt in nitrogen).

view of excessive nitrogen, a 6-ppt SF₆ mixture should be biased by 0.17 %. Another potential deviation between the SF₆ mole fractions of the WMO standards and the KRISS standards can be caused by the different matrices used. Supposing that the different matrices induced an alteration of the gas flow rate at the thermal mass flow controller (MFC), different amounts of gas mixture might possibly be loaded in the sample loop of constant volume (Min et al., 2009). Considering similar molecular weight of nitrogen to air and higher flow rate (100 mL min⁻¹) compared to the sample size (2 mL), this effect seems to be very minor. Rather, the presence of oxygen in the WMO standards can temporarily affect the ECD response regardless of arrival time at the detector. Nevertheless, the KRISS standards listed in Table 5 seem to be in reasonable agreement with the WMO standards (agreement within 0.13 ppt). We believe that air-balanced standards should reduce a degree of the deviation between the WMO and the KRISS scales. In the near future, for equivalent comparison with the WMO scales, we will carry out a gravimetric preparation of an SF₆ standard with synthetic air comprising 0.78 mol/mol N₂, 0.21 mol/mol O₂, and 0.01 mol/mol Ar.

4 Summary and conclusion

A high-precision analysis of SF₆ at ambient conditions is presented. Instead of using the typical Porapak Q column, an Activated Alumina F1 column was coupled with a GC-ECD for measurement of SF₆. The accuracy of the measurement was improved by (1) optimised analytical conditions for the complete isolation of the SF₆ measurement, (2) meticulous care taken in the elimination of potential contaminants built up in the column and (3) correction of the short-term drift of the instrument. Namely, the optimized analytical conditions represented by the narrow SF₆ peak supported the precision tests attempted in this study. With the help of the short-term drift correction, the measurement uncertainty was restricted to less than 0.02 ppt, which satisfies the compatibility goal recommended by WMO for SF₆. Various calibration methods for calculating the SF₆ mole fraction of the working standard prepared at WCC-SF₆, operated by KMA/KRISS, were presented. The two-point calibration method emerged to be the most efficient in terms of measurement time and reliability of the data. It was found that the matrix effect caused a difference of 0.13 ppt in the mole fraction between the two scales prepared by KRISS and NOAA. We believe that mimicking the air composition for the main balance improves the gap between the KRISS and the WMO scales. The study of the gravimetric generation of an SF₆ standard mixture in artificial air will be reported in the near future.

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