Comparative Study of Various Methods for Trace SF₆ Measurement Using GC-μECD: Demonstration of Lab-Pressure-Based Drift Correction by Preconcentrator

JEONGSOON LEE,^{a,b,d} GAHAE KIM,^{a,d} HAEYOUNG LEE,^c DONGMIN MOON,^a
JIN-BOK LEE,^a AND JEONG SIK LIM^{a,b}

^a Center for Gas Analysis, Korea Research Institute of Standards and Science, Daejeon, South Korea

^b Department of Measurement Science, University of Science and Technology, Daejeon, South Korea

^c Environmental Meteorology Research Division, National Institute of Meteorological Sciences, Jeju-do, South Korea

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ABSTRACT

This study presents a high-precision method, using a preconcentrator–gas chromatograph with microelectron capture detector (GC-μECD), to measure SF₆ at ambient levels. Carboxen 1000 was used as an adsorbent for the preconcentrator and exhibited a high adsorption efficiency for N₂O and SF₆ and low adsorption efficiency for O₂. This enabled the selective removal of atmospheric O₂ from analytes and improved repeatability of the SF₆ peak that followed the O₂ peak, in a separation column of activated alumina F1. In addition, the increased sensitivity resulting from preconcentrated SF₆ improved the signal-to-noise ratio. This led to better analytical precision in comparison with other measurement methods including the conventional and forecut–backflush (FCBF) methods. The precision-to-drift ratios of the conventional, FCBF, and preconcentration methods were 0.11, 0.10, and 0.03, respectively. Analytical precision of the preconcentration method was 0.08% for 10 consecutive injections; this was the best among the three methods. The long-term drift of the SF₆ response was inversely proportional to the laboratory pressure. Based on this finding, room pressure can be used to correct for ECD signal drift, with an uncertainty of 0.14% over a 48-h period, using the preconcentration method. Another advantage of the preconcentration method was the excellent linearity of the SF₆ response to a wide range of concentrations, including its ambient concentration.

1. Introduction

Global anthropogenic emissions of SF₆ are much less than 1% of total global CO₂ emissions [49.3 Gt of CO₂ equivalent (CO₂-eq) emissions in 2016] (Olivier et al. 2017). However, SF₆ remains in the atmosphere for approximately 850 years, once released (Ray et al. 2017). If SF₆ is used at current levels for the next 100 years,

its global warming potential will increase by a factor of 10 (EPA 2013). Atmospheric measurements of SF₆ have been made by numerous laboratories since the 1980s (Maiss and Levin 1994; Maiss and Brenninkmeijer 1998; Levin et al. 2010). To date, multiple measurement methods have been developed that use gas chromatography with electron capture detector (GC-ECD) and mass spectrometer (GC-MS) to measure atmospheric SF₆ at around 10 pmol mol⁻¹ levels (Simmonds et al. 1972; Elkins 1980; Elkins et al. 1996; Hall et al. 2007, 2011; Lim et al. 2013, 2017; Maiss et al. 1996; Miller et al. 2008; O'Doherty et al. 1993). Measurements of SF₆ dissolved in seawater showed concentrations at sub pmol L⁻¹ levels per hundred milliliters (Wanninkhof et al. 1991; Koo et al. 2005). Maiss et al. (1996) applied Porapak-Q, cooled by a dry-ice/isopropanol bath at -70°C, as an absorber coupled to a GC-ECD with a molecular 5 Å (MS-5A) separation column. This study achieved an analytical precision of 0.5%. In Miller et al.'s work (2008), Haysep D was electrically cooled to -165°C. At this temperature, atmospheric permanent gases such

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^dJeongsoo Lee and Gahae Kim contributed equally to this article.

Corresponding author: Jeong Sik Lim, lim.jeongsik@kriss.re.kr

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as O₂, N₂, CO₂, Kr, and so on were physically adsorbed; therefore, a microtrap was required to concentrate the analytes. This was called the Medusa system and enabled enough halocarbons to be concentrated to allow analysis by GC-MS. The analytical precision for SF₆ was reported to be 0.5% with this method. In O'Doherty et al.'s study (1993), Carboxen 1000/1003 cooled at -50°C was used as an adsorbent. This preconcentration system was coupled to GC-MS.

Simmonds et al. measured SF₆ by applying an MS-5A column to a GC-ECD (Simmonds et al. 1972). The SF₆ peak avoided interference with the O₂ peak that appeared later and had long tails. Hall et al. (2007, 2011) suggested methods involving chromatographic separation with a Porapak-Q (PP-Q) column and P5 (5% CH₄ in Ar) or CO₂-doped nitrogen carrier gas. In these methods, SF₆ elutes after N₂O and the measurement precision was reported to be ~1%. They then employed a MS-5A column to reverse the order of elution (SF₆ before N₂O), which improved precision to <0.5%. Here, we used an AA-F1 column with a GC- μ ECD system (Lim et al. 2013). With the AA-F1 column, the appearance order of the elution corresponded to O₂ first followed by SF₆, and N₂O. Although a certain extent of chromatographical interference was observed between the long tail of the atmospheric oxygen and the SF₆ peak, 0.2% precision was reported by bracketing the drift correction and multipoint calibration. Recently, a trace SF₆ measurement technique based on a preconcentrator-GC- μ ECD equipped with a Carboxen 1000 adsorbent was introduced with the result that the atmospheric level of oxygen was hardly adsorbed (Lim et al. 2017). The response linearity, limit of detection (LOD), and repeatability of measurements with the preconcentration method were evaluated. Additionally, the precision and drift characteristics of the preconcentration method were compared with the temperature programming method, by using an AA-F1 separator based on μ ECD (conventional method) and forecut-backflush (FCBF) method, using a PP-Q separator similar to that of the method developed by Hall et al. (2011), but based on μ ECD.

a. Analytical methods

To conduct a comparative study of the conventional, FCBF, and preconcentration methods, three independent GC- μ ECD systems were ran at the same laboratory. The conventional method for the measurement of trace SF₆ in air was performed with an AA-F1 separation column. The FCBF method was performed with PP-Q for the precolumn and the main column. The MS-5A was the postcolumn. For the preconcentration method, the trap was equipped with Carboxen 1000. In

each method, 5% CH₄/Ar (P5 gas) was used as the carrier gas. This is a main difference between Hall et al.'s (2011) FCBF method and the method proposed in this study. A summary of the analytical conditions for each three methods are shown in Table S1 in the online supplemental material.

b. Conventional method

The conventional oven-temperature programming method uses an activated alumina F1 (AA-F1; 80/100 mesh and 7.3 m $\times$ 3.2 mm; Restek) separation column. To bake out late-appearing eluents such as chlorofluorocarbons (CFCs), the oven temperature was ramped to 200°C after the SF₆ and N₂O peaks appeared at 50°C. This method required a long run time because of the need to cool the oven from 200° to 50°C. This step corresponded to 50% of the total run time. The injection valve and sampling loop (10 mL) were placed in a second oven that was independently operated at 50°C, to minimize the temperature tolerance induced by oven temperature programming. This treatment prevented a mismatch between the thermal expansion of loaded gas and the loop size, thereby leading to improved precision in the amount of sample loaded. The P5 carrier gas was passed through an electronic pneumatic control (EPC) placed in the GC body (7890A; Agilent) and fed into a micro electron capture detector (G2397A; Agilent). The mass flow controller (MFC; Brooks) was used to control the flow rate of the sample gases. A flow restrictor (Frit filter; Valco) attached to the sample loop vent could pressurize the loaded amount of the sample (Fig. S1 in the online supplemental material). By using the restrictor at the end of the sample loop, pressure variations inside the loop were minimized during loading. This was affected by short-term fluctuations in room temperature. Therefore, pressurizing the sample loop with the flow restrictor (thereby increasing sample size), might lead to an improved signal-to-noise ratio (SNR), as well as repeatability of consecutive measurements, in comparison to no restrictor.

c. Forecut-backflush method

In the conventional method, an O₂ peak with a long tail interferes with SF₆ (when AA-F1 is used) or N₂O (when PP-Q is used) peaks, and this interference reduces the measurement precision of the analyte. In addition, there is a concern that the control precision of the oven temperature in the static section may be reduced due to the repetitive increase and decrease in the oven temperature, for reducing the elution time of the CFCs during measurement of the atmospheric sample. The forecut-backflush technique for ambient SF₆ and N₂O

measurement can be used to overcome the disadvantages (Hall et al. 2011). As depicted in the previous study, the fastest eluent, O_2 , was forecut (heart cut) before it reached the μ ECD, where it remains for a long period and interferes in the ionization of the SF_6 analyte. With this method, the total run time was shortened by approximately 30 min, in comparison with that of the conventional method (50 min), as GC oven baking was no longer required. The GC- μ ECD system for the FCBF method consists of a 10-port valve and a 4-port valve, as shown in Fig. S2 of the online supplemental information. A PP-Q (80/100 mesh and $1.8\text{ m} \times 3.2\text{ mm}$; Restek) was used as the precolumn, a PP-Q (80/100 mesh and $3.7\text{ m} \times 3.2\text{ mm}$; Restek) was used as the main column, and an MS-5A ($1.8\text{ m} \times 3.2\text{ mm}$, Restek) was used as the postcolumn. The differences between this setup and that used by Hall et al. (2011) (the “NOAA FCBF” method), are summarized in supplemental Table S1. Both setups were identically designed, except for the types of columns and multiposition valves used. In contrast to the conventional method, the makeup gas flow rate was decreased by as much as 5 mL min^{-1} , but the methods were still very similar to each other. Considering that a detector’s sensitivity can be enhanced by lowering the makeup gas flow rate, the μ ECD for the FCBF method might appear to show a higher sensitivity and SNR in comparison with the conventional method, as shown by a twofold increase in the response of the FCBF method, in comparison to the conventional method (Table S1). Nevertheless, because detector sensitivity depends on the individual instrument, a decreased makeup gas flow rate could not be the sole reason for the increased sensitivity. A flow restrictor installed at the vent of the μ ECD detector might be another factor enhancing the detector sensitivity, by pressurizing eluent analytes within the μ ECD cavity, even though the sample loop size was 5 times smaller with the FCBF method. Nevertheless, the GC- μ ECD system (7890A/G2397A) for the FCBF method showed better SNR, despite the small sample loop size (Table S1). The gas line configuration of the FCBF method was essentially designed to match the concept presented in the previous study from Hall et al. (2011), although each column was longer and the oven temperature was higher by about $25^\circ\text{--}30^\circ\text{C}$. Another difference with this study is that a P5 carrier gas was used with the μ ECD instead of a CO_2 doped N_2 carrier gas that was used with the ECD. Other details of the analytical conditions are tabulated in supplemental Table S1, in conjunction with those used in the previous study. The run time of the proposed method is a more than a factor of 2 longer than that described by Hall et al. (2011). (Fig. 1d) Decreases in the column length and increases in the flow rate of the carrier gas in the study of Hall et al. (2011), can shorten the elution times of N_2O and

FIG. 1. Representative chromatograms of working gases obtained by the (a) conventional method, (b) FCBF method, (c) preconcentration method, and (d) NOAA FCBF method. The baseline of each chromatogram was expanded from the shaded part in the inset. The magnification factor is given below the magnified image. An SNR for each method is given in Table S1 of the online supplemental material. The chromatogram of the NOAA FCBF method was taken at 9.9 ppt SF_6 and 331.9 ppb N_2O . In the case of the FCBF method, oxygen peaks were not detected because of forecutting. The right inset in (c) shows chromatograms obtained by the preconcentration method in which desorption temperatures were set to 200° (blue), 150° (red), and 100°C (green). The tailing effect was observed at lower desorption temperature because of significant interaction between adsorbent (Carboxen 1000) and both absorbers (SF_6 and N_2O) at lower temperature. Because of the chemical selectivity of Carboxen 1000, an oxygen peak in the preconcentration method was hardly observable in comparison with the conventional method. The SNR of each method corresponded to 220, 280, and 3480, respectively.

SF_6 . Valve configuration and working mechanisms are further detailed in Fig. S2.

d. Preconcentration method

The home-built preconcentrator-GC- μ ECD system consisted of two 6-port multiposition valves, two solenoid

valves, a three-way valve, and an adsorption trap filled with Carboxen 1000 (80/100 mesh and 140 mg; Supleco) mounted on the refrigerator. As shown in Fig. 2, the preconcentration system is divided into a flushing/injection part and a trapping part. Figure 2a shows the valve configuration in the preparation step. The line was flushed with high-purity helium (50 mL min^{-1} ; $>99.999\%$), and the trap was maintained at a designated temperature. Figure 2b shows the ready step in which all gas lines and traps were purged with He. All valves were set to the “off” position. Figure 2c shows the preconcentration step in which the trap valve and injection valve were opened and the sample was adsorbed to the trap at a constant flow rate (50 mL min^{-1}). The SF_6 sampling volume of the trap was preserved because O_2 and N_2 hardly adsorbed in the Carboxen 1000, as shown in Fig. 1c. Figure 2d shows the flushing step in which residual O_2 and N_2 in the trap were flushed out by helium. Figure 2e shows the desorption step in which the trap was closed and heated to 200°C to desorb the preconcentrated analyte. Figure 2f shows the injection step in which the two valves were opened, and the desorbed sample was carried by P5 gas, followed by separation of the mixed analytes from the column and injection into the detector. Trap temperature was maintained at 200°C to be baked and then started to cool down. Before proceeding to the next step, all analytes were injected into the GC- μECD . Figure 2g shows the purge step, in which trap valves were kept turned on while the trap cooled down with the injection valve turned off. All gas lines were flushed with He. The preconcentrator was then set to prepare for the next measurement. During GC measurement, samples for the next measurement were preconcentrated, to save running time. For this method, the GC body corresponded to Agilent 6890A, and the μECD corresponded to Agilent G2397A. The precolumn and main column were separated for the backflushing of CFCs. The precolumn corresponded to AA-F1 (80/100 mesh and $1.8 \text{ m} \times 3.2 \text{ mm}$; Restek) and the main column corresponded to AA-F1 (80/100 mesh and $3.7 \text{ m} \times 3.2 \text{ mm}$; Restek). The optimization of the analytical condition is discussed in a later section. The three methodologies were performed by independent GC- μECD systems. The trap temperature for adsorption was set at -30°C . Considering that the measurement precision of the adsorption temperatures between -50° and -20°C were equivalent (Fig. 3c), -30°C was chosen to achieve adequate adsorption power within a short cooling time of 7.5 min. The desorption temperature was set at 200°C and maintained for 5 min. The desorption speed used was appropriate, as shown by clear resolution of SF_6 and N_2O peaks (inset of Fig. 1c). As the separation column is responsible for

chromatographic separation, the broadening of the peak observed at lower temperatures was caused by slowly desorbed analytes. It can be assumed that adequate desorption speed ensured scant carry-over in the trap. The optimized operating conditions for the preconcentrator method are shown in supplemental Table S1.

2. Results and discussion

a. Response of the preconcentrator-GC- μECD system

The response of the preconcentrator-GC- μECD system was tested as a function of sampling volume. The flow rates of the working standard ($11.93 \text{ pmol mol}^{-1} \text{ SF}_6$ in air; D442234) were varied and included 20, 40, 60, and 80 mL min^{-1} (Fig. 3a). A linear regression analysis exhibited a high correlation to the sample flow rates, with $R^2 > 0.9999$, meaning that the recovery rate of the preconcentration system was linear up to about $48 \text{ pmol mol}^{-1} \text{ SF}_6$. The ECD measurements with an N_2 carrier gas (with CO_2 doping) and the μECD with P5 gas showed nonlinear responses at ambient levels (Hall et al. 2011; Lim et al. 2013). This study showed the potential of the preconcentration method to serve as a linearly responding measurement technique. The nonlinearity of the μECD , which strongly depends on the instrument used, can be tuned by adjusting the detector temperature and flow rate of the carrier (or makeup) gas (Fig. S3 in the online supplemental material). Therefore, the linearity condition should be optimized by individual laboratories. Given that a calibration strategy is complicated by a nonlinearly responding instrument with a range of analyte concentrations, the linear-behaving characteristics of the preconcentration method proposed in this study enable a simplified calibration strategy, as well as a drift correction scheme. Though it is expected that the SNR would increase with sample size, we selected a sample flow rate of 40 mL min^{-1} and a preconcentration time of 5 min. A strong correlation ($R^2 > 0.9999$) between response and preconcentration time was shown in a linear regression, confirming that the linear behavior of the preconcentration method was demonstrated in this study.

b. Limits of detection

The LODs were determined using a gravimetrically prepared working gas of $5.47 \text{ pmol mol}^{-1} \text{ SF}_6$ in air. Measurements of lower concentrations were performed with a dynamically diluted mix of the working gas and high-purity N_2 ($>99.9999\%$). The resulting concentration was in the subpicomole per mole range. The dilution ratio was defined as the ratio of flow rates of each

FIG. 2. (a) Gas-plumbing configuration of the preconcentration method. The working mechanism of the preconcentrator is depicted at each step of (b) ready, (c) preconcentration, (d) flushing, (e) desorption, (f) injection, and (g) purge. Note that only the preconcentration compartments are represented in (b)–(g). Refer to the main text for details about the working mechanism.

FIG. 3. (a) SF_6 response (peak area) of $11.9 \text{ pmol mol}^{-1}$ SF_6 in air working gas (D442234) as a function of the sample flow rate for preconcentration. (b) SF_6 response as a function of preconcentration time at 40 mL min^{-1} of flow rate. Preconcentration volume is also given below each of the indicated preconcentration times. Both tests showed very good linearity in SF_6 responses in a wide range of preconcentrating volumes, suggesting a linear response in atmospheric level. (c) SF_6 response as a function of trap temperature. No significantly improved measurement repeatability was found among data points. The error bar representing repeatability cannot be seen because of its small scale. Overall repeatability is better than 0.1%.

gas that are controlled by two well-calibrated MFCs. A regression analysis of the instrumental response as a function of the SF_6 concentration resulted in a slope and an associated standard deviation. The LOD is determined as follows:

$$\text{LOD} = 3(S_y/m),$$

where S_y denotes the standard deviation of the slope and m denotes the slope determined by regression analysis. With respect to the conventional method, there were various ratios of flow rates between two mass flow controllers for the standard gas mixture and high purity N_2 , with dilution ratios of 1:4, 1:3, 1:2, 2:3, and 1:1. The LOD estimated by the slope of the regression line and the standard deviation was $0.03 \text{ pmol mol}^{-1}$. For the FCBF method, the dilution ratios were set to 1:20, 1:10, 1:8, 1:4, 1:2, and 1:1, and the LOD was $0.02 \text{ pmol mol}^{-1}$ (Fig. 4b).

Although the sample loop sizes of the conventional method were 5 times that of the FCBF method, the LODs of the two methods were close to each other. This might be because SF_6 elution from the FCBF method was earlier, compared to the conventional method, with the SF_6 peak being narrower and higher. In general, high peaks can improve SNR. In addition, the restrictor on the μECD outlet reduces detector noise by dampening room-pressure fluctuations. The dilution ratios for the LOD test using the preconcentration method corresponded to 1:40, 1:20, 3:40, 1:10, and 1:8, and the LOD was determined to be $0.008 \text{ pmol mol}^{-1}$ (Fig. 4c). The atmospheric level of SF_6 , 10 ppt, was way above the limit of qualification LOQ ($\text{LOQ} \sim 3.3 \times \text{LOD}$), 0.026 ppt. As expected, the LOD of the preconcentration method was improved by enhancements in the amount of SF_6 injected. The trend of the LODs for each method followed the SNR, which were 220, 280, and 3480 for the

FIG. 4. Evaluation of the LOD of the (a) conventional method, (b) FCBF method, and (c) preconcentration method. Dynamic dilution by the adjustment of ratios of flow rates of the working gas ($5.47 \text{ pmol mol}^{-1}$ SF_6 in air) and dilution gas ($\text{N}_2 > 99.999\%$) extends the concentration of diluted gas to the subpicomole per mole level. The calibration slope is 32.268 for (a), (98.586 for (b), and 10 550.999 for (c). the standard deviation of the calibration curve slope is 0.3262 for (a), 0.5910 for (b), and 27.81 for (c), yielding LODs of 0.03, 0.02, and $0.008 \text{ pmol mol}^{-1}$, respectively.

conventional method, the FCBF method, and the preconcentration method, respectively. Because detector operating conditions (detector temperature and makeup gas flow rate) were identical for both the FCBF method and the preconcentration method, the enhanced SNR and LOD of the preconcentration method is solely determined by the analytical method of preconcentration.

c. Test for short-term precision and long-term drift

The standard gas mixture of $11.93 \text{ pmol mol}^{-1} \text{ SF}_6$ in air (D442234) was measured 10 times consecutively, to evaluate the repeatability of measurements using each of the three methods. For the conventional method, the average SF_6 response (peak area) was 858, with a relative standard deviation (RSD) of 0.17% at 1σ . For the FCBF method, the average SF_6 response was 1926, with an RSD of 0.14% at 1σ . The repeatability of the FCBF method was slightly better than that of the conventional method, which can be attributed to higher SNR. A lack of oxygen interference from forecut might be another reason for better measurement repeatability. The conventional method requires additional time to cool down the oven, yielding a total run time of 50 min, which is twice the run time of the FCBF method. The average SF_6 response from the preconcentration method was 15 241, which was approximately 10 times higher than that of the other two methods. Improved measurement repeatability, to a precision of 0.08% (from 10 consecutive measurements) for $11.93 \text{ pmol mol}^{-1} \text{ SF}_6$ in air (D442234) was due to a high SNR. This implies a beneficial result from the preconcentration process when conducted under similar detector operating conditions. This result is better than the “Medusa” preconcentrator for GC-MS, which showed a 0.5% annual mean of the standard deviation (Miller et al. 2008). In the case of a preconcentrator, the packed adsorbent Carboxen 1000 effectively dampened pressure fluctuation, as did the flow restrictor installed at the sample loop. This enabled a more consistent sample volume load. In addition, the preconcentration lacked O_2 due to the chemical selectivity of the Carboxen 1000. (Fig. 1 c) The absence of oxygen in the μECD detector might contribute to the improved precision of the SF_6 measurement (Simmonds et al. 1972).

To assess the long-term instrumental drift, each system was simultaneously tested under same laboratory conditions. The evaluation was performed in the same laboratory for 48 h. During the evaluation, the temperature and pressure were recorded at intervals of 30 min. Gravimetrically prepared gas mixtures (SF_6 in air) of 13.29 (D232832), 11.93 (D442241), and 11.93 (D442234) pmol mol^{-1} were used as the working standards for the conventional method, the FCBF method, and the preconcentration method, respectively. In the

conventional method, each measurement was conducted at intervals of 43 min, and 99 valid measurement data points were obtained. For the FCBF method, 140 valid measurement data points were obtained every 30 min. For the preconcentration method, measurements were obtained every 30 min, and 138 valid measurement data points were collected. As shown in Fig. 5, the normalized sensitivity for the three methods is plotted in dotted lines over time. The black lines in Figs. 5a, 5c, and 5e denote the generalized moving average, obtained by using the “LOWESS” algorithm. The moving average of the normalized sensitivity of each method was considered by slowly varying responses corresponding to the long-term asymptote. Therefore, slow drift was separated from randomly scattered values in a short-term time frame, which corresponded to the measurement precision. Therefore, in Figs. 5b, 5d, and 5f, the residuals of each measurement value from the moving average implied measurement precision. Thus, long-term drift and short-term precision were sufficiently decoupled to suppress covariance. The short-term precision exhibited normal distribution, thereby confirming the random effect that governs measurement precision. The corresponding standard deviations (1σ) for each method were 0.22%, 0.20%, and 0.05%, respectively, which were equivalent to the repeatability test by the 10 consecutive measurements described earlier in this section. In all three methods, the normalized sensitivities of each measurement tended to be inversely proportional to the laboratory pressure. The maximum drifts of each method were 2.15%, 1.88%, and 1.82%, where μECDs coupled with the restrictor (for FCBF and preconcentration methods) might have shown a similar extent of drift. Conversely, a less significant correlation with the laboratory temperature was observed. Direct comparison cannot be made because independent detectors were used with each method. Instead, the ratio between the drift rate represented by the maximum deviation of the normalized sensitivity and standard deviation of residuals, called precision-to-drift ratio (PNR), was used as an indicator for comparing methods. Consequently, PNRs of respective methods were 0.10, 0.11, and 0.03 for the conventional, FCBF, and preconcentration methods, respectively, implying that the preconcentration method offers comparative advantage, in terms of the PNR, over other methods. The results indicate that the preconcentration method can be an effective alternative for the standard-free drift correction method, for continuous measurement of atmospheric levels of SF_6 by GC- μECD . Drift correction was performed using laboratory-pressure measurements (Fig. 6). The standard

FIG. 5. Normalized sensitivity as a function of time for the (a) conventional method (open triangles), (c) FCBF method (open squares), and (e) preconcentration method (open circles). (b),(d),(f) the corresponding residuals from the moving averages (the red line) in (a), (c), and (e). Standard deviations of residuals (1σ) are 0.22%, 0.20%, and 0.05%, respectively, which are given as the histograms in the side panels. Laboratory (g) pressure and (h) temperature are also shown. Gravimetric gas mixtures (SF_6 in air) of 13.29 (D232832), 11.93 (D442241), and 11.93 (D442234) pmol mol^{-1} were used as the working standard for the conventional method, FCBF method, and preconcentration method, respectively.

FIG. 6. Correlation between sensitivities of the (a) conventional method, (b) FCBF method, (c) preconcentration method and “1 over laboratory pressure” (P^{-1}). Inversely proportional behavior between laboratory pressure and sensitivities is clearly observed. The Pearson’s R values for (a), (b), and (c) are 0.73, 0.88, and 0.94, respectively. Respective standard deviations (1σ) of relative regular residuals are (d) 0.40%, (e) 0.24%, and (f) 0.14%.

deviations (1σ) of relative regular residual representing uncertainty for drift correction by laboratory pressure were 0.40%, 0.24%, and 0.14% for the conventional, FCBF, and preconcentration methods, respectively. The sample size being controlled by the MFC could be affected by temperature variation, because an MFC that is also affected by the surrounding temperature cannot provide an absolute flow rate. Nevertheless, the result implied that temperature variation was less correlated to variations in sensitivity compared to variations in pressure. (Fig. 5h) Considering an atmospheric level of SF_6 (10 ppt), the uncertainty of the laboratory-pressure-based correction for the preconcentration method corresponds to 0.014 ppt. Imperfection in decoupling short-term scattering (precision) from the long-term moving average (drift) leads to increased uncertainty regarding laboratory-pressure-based drift correction. The laboratory-pressure-based drift correction for the preconcentration method suggested that this method showed potential as a new method for fulfilling the WMO compatibility goal of SF_6 detection, of 0.02 ppt. Considering that the preconcentrator-GC- μECD equipped with the Carboxen 1000 adsorbent showed perfect linearity to atmospheric levels of SF_6 , as shown in Fig. 3, the preconcentration method might not require multipoint calibration. The preconcentration method, combined with room-pressure drift

correction, could significantly reduce the need to run reference standards.

3. Conclusions

A comparative study of the preconcentration method, the conventional method, and the FCBF method was conducted. The conventional method was constructed using an AA-F1 separator and μECD (P-5 carrier gas), while the FCBF method was constructed using PP-Q and MS-5A separators and μECD (P-5 carrier gas). The preconcentration method was constructed using Carboxen 1000 adsorbent cooled at -30°C , an AA-F1 separator, and μECD (P-5 carrier gas). Long-term drift and short-term precision of the two nonpreconcentration methods were compared with the preconcentration method. Responses for periodic injections of control standards for 48 h were decomposed to short-term precision and long-term drift by using the LOWESS algorithm. This algorithm uses the moving average corresponding to the long-term drift. Short-term precision was represented by the residual of measured values from the moving average and were 0.22%, 0.20%, and 0.05% for the conventional method, the FCBF method, and the preconcentration method, respectively. The SF_6 responses deviated as much as 2.15%, 1.88%, and 1.82%, respectively. Inversely proportional relationships between laboratory pressure

and responses enabled drift correction by laboratory pressure. Uncertainties of the laboratory-pressure-based drift corrections were 0.40%, 0.24%, and 0.14%, respectively. The laboratory-pressure-based drift correction for the preconcentration method suggests that this method shows potential as a new method for fulfilling the WMO compatibility goal of SF₆, 0.02 ppt. Within the finding that the preconcentration method can respond linearly to the atmospheric level of SF₆, a multipoint calibration is not required. This suggests that once sensitivity is determined, a calibration standard is not required for a while. In this study, the analytical conditions for pressure drift correction were maintained for 48 h, with a correction uncertainty of 0.14%. Therefore, the preconcentration method might reduce the maintenance effort for continuous measurement and offer high frequency and reasonable quality data on atmospheric levels of SF₆. Further investigations regarding an efficient methodology for extending the period of linearly responding behavior by use of the preconcentrator-GC- μ ECD, and to conduct in situ measurement with the standard-free drift correction scheme, will be pursued in the near future.

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