Analytical Methods for Atmospheric SF₆ Using GC-µECD

WMO/GAW Report No. 222

World Calibration Centre for SF₆

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Weather · Climate · Water

GLOBAL ATMOSPHERE WATCH

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1. Application scope

This technical note seeks to precisely measure the concentration of SF_6 in the atmosphere. The procedure to determine SF_6 concentrations in the atmosphere with various methods using Gas Chromatography with micro Electron Capture Detector (GC-μECD) is described. It was based on securing traceability to the World Meteorological Organization(WMO) scale.

2. Definition of terms

Reference material

Material or substance, one or more of whose property values is sufficiently homogeneous and well established to be used for the calibration of an apparatus, for the assessment of a measuring method, or for assigning values to materials. In this note, the reference material is a standard from which SF_6 concentration in air (or artificial air) is certified by the Central Calibration Laboratory (CCL) for SF_6 or the World Calibration Centre (WCC) for SF_6 under the WMO Global Atmosphere Watch (GAW) Programme.

Standard

Objects, systems, or experiments that determine the units of measurement for physical or chemical quantities and the interrelations between them. In the GAW Programme, there are many cases where well-defined certified-reference materials and their direct by-products are all called standards. The standards are mainly used for certifying a mole fraction of gaseous components of interest, namely SF_6 in air.

Traceability

Property of the result of a measurement or the value attributed to a standard whereby it can be related to stated references (national or international standards), through a solid link of comparison of which all have a stated uncertainty. The traceability hierarchy within the WMO GAW network can be divided into the following steps: 1) the primary standard which is manufactured by gravimetry at CCL, 2) a secondary standard which is established at CCL that is manufactured typically by collecting an atmospheric sample and modulating its composition of which is calibrated by using the primary standard, 3) a laboratory standard and transfer/traveling standard which are calibrated at WCC/RCC against the secondary standard from CCL, 4) a laboratory standard or a working standard at other GAW stations which are calibrated against the secondary standard supplied by the CCL or the transfer standard supplied by the WCC/RCC, and 5) the working standard at GAW stations that could be calibrated using such a laboratory standard. The

traveling standard is used for an instrument performance and when the WCC conducts an audit, and as an unknown sample when a round robin test is carried out in the GAW network. The working standard is used routinely to calibrate or check material measures, measuring instruments, or reference materials. The laboratory, transfer, traveling, and working standards are all classified as tertiary standards.
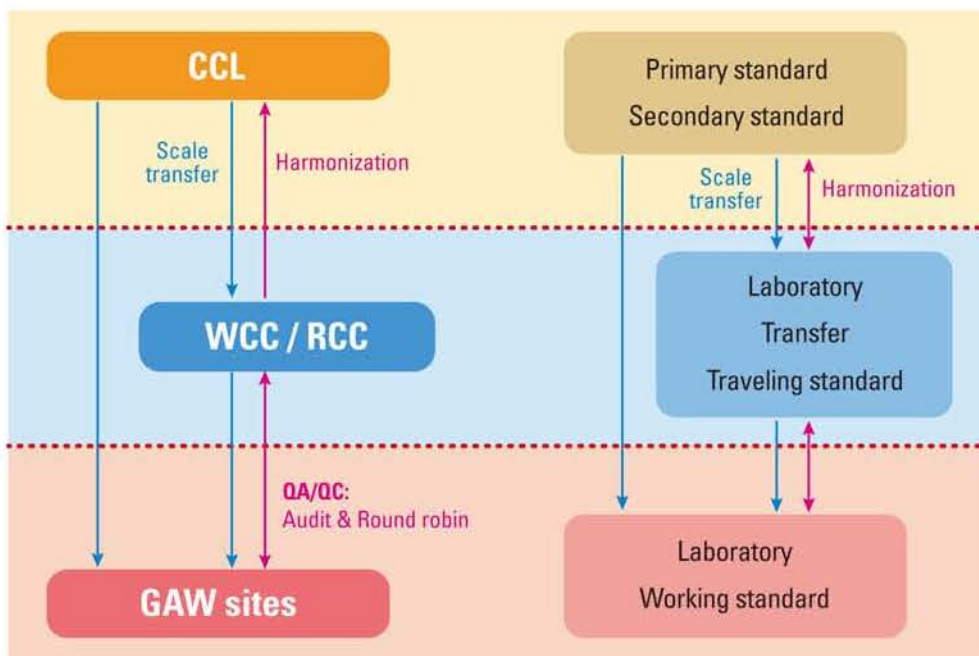
Figure 1. WMO traceability hierarchy.

Scale

The aggregation of standards whose mole fractions are certified with respect to the components of interest.

Composition

Characteristic of a gas mixture given by the content and kind of each specified mixture component (analyte) and the composition of the complementary gas (matrix).

Matrix

Gas that accounts for the highest composition fraction in a gas mixture.

For example. SF_6 in N_2 (matrix = N_2)

Component of interest

Specific ingredient with a certified mole fraction composition in a gas mixture.

For example. CO_2 and CH_4 in N_2 (component of interest = CO_2, CH_4)

Analyte

Substance or chemical constituent that is of interest in an analytical procedure. For instance, SF_6 is the analyte and the concentration of SF_6 is the measurable property of the analyte.

Calibration

Series of analytic operations that establish a relationship between quantitative values, represented with a measuring system, measure of material or comparison materials, and standards.

Uncertainty of measurement

Parameter associated with the result of a measurement that characterizes the dispersion of the values being attributed to a measurement quantity.

Signal to noise ratio (SNR)

Ratio of desired signal to background noise level. In gas chromatography, it is defined as the ratio of peak height to noise in root mean square.

Repeatability

Degree of change in a measurement obtained using a single analyst or instrument. It is often expressed as precision. The analytical conditions should be identical.

Reproducibility

Conformity or the degree of conformity between respective measured values when measuring the subject by an identical method under conditions where all or one of the measurements, measuring equipment, place of measurement, and time of measurement differ(s) from the other.

Gravimetry

General term for quantitative analysis methods using a gravity field. The method calculates the quantity of the analysis subject by measuring the weights of analysis samples or materials.

Mole fraction

Ratio of the number of moles of a component X to the total number of moles in the sample.

Sensitivity

Minimum quantity or change that can be detected by the measuring instrument.

Response

Magnitude of signals that an analytical instrument indicates. In gas chromatography, it is regarded as the integrated area under peak corresponding to interesting component of gases.

Carrier gas

Inert gas that provides a flow for an unknown gas sample to pass through a column. The selected gas does not interact with the gas sample and stationary phase packed in the separation column, and affect the sensitivity of a detector.

Make-up gas

Gas that activates the operation state of an Electron Capture Detector.

Compatibility

While the results of measurements obtained from different environments and analytic conditions do not exactly conform, the results from two laboratories are compatible if they are within a specified numerical value.

3. Test contents

Analytical species is SF_6 at a background atmospheric level, i. e., 5–15 ppt (pmol/mol).

The principle of measurement consists of two measurement equipments.

Gas Chromatography (GC)

In gas chromatography, a gas is carried through the column by a gas moving phase referred to as the carrier gas. After the gas sample is injected through the sample injection device, it is pushed into the column and the separated solutes pass the detector. The record of responses with time is a chromatogram.

Electron Capture Detector (ECD)

ECD is a GC detector based on a chemical phenomenon where neutral gas molecules with appropriate electro negativity react with thermal electrons to form negative ions. Activation gas (so-called make-up gas), mostly helium or argon, and beta particles (electrons with high kinetic energy released from radioactive isotopes) go through the collisional ionization process to form

thermal electrons with a high reactivity. Because typical make-up gas exhibits a low excitation energy, i.e., it is easy to emit free electron by the electron emitted from the ECD, resulting in emission of many more electrons, high sensitivity can be achieved by the presence of the make-up gas. The attenuation of the flow of those thermal electrons by the analysis material, i.e., the change in the electron current, is measured to quantify the analyte. Thus, ECD is very useful for the analysis of chemical species with high electron affinity (mostly halogenated compounds).

4. Preparations

4.1 Response drift due to laboratory conditions and their improvement

Laboratory conditions have a considerable impact on analytical results. In particular, temperature and pressure in the laboratory exert the greatest influence. The left panel in Figure 2 represents the experimental results obtained under drifts in laboratory temperature and pressure. It is clear that a temperature change (up to ~3 ℃) leads to a response drift (less than 1 %). This might affect the total precision of the analytical replica. The right panel in Figure 2 shows experimental results obtained under tight temperature tolerance (less than 1.0 ℃) and constant pressure (1.0 atm) during experiments. Total analytical precision is 0.13%, suggesting that laboratory conditions have a significant impact on analytical repeatability.
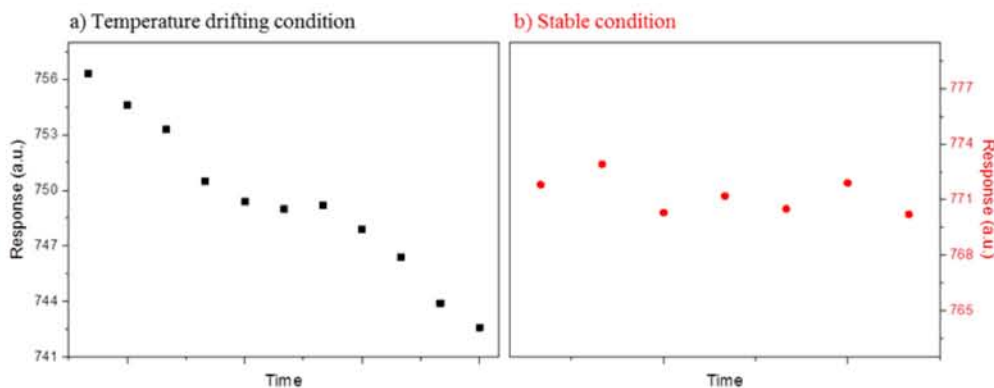

Figure 2. Experimental results obtained under a) temperature drifting condition and b) stable condition. Data have been taken every 40 mins.

Analytical repeatability can only be achieved by maintaining a constant temperature and pressure. Errors arising from fluctuating laboratory conditions can be minimized by mounting a restrictor at the end of the sample line and the detector vent, thus ensuring the maximum possible independence of the temperature and pressure around the analyzer from those of the surrounding

environment. For detailed effects by installing the restrictor, refer to Annex 1. The results obtained with and without the use of the restrictor are displayed in the left panel and right panel of Figures 3, respectively. It is shown that the analytical repeatability increased from 0.28% ($k = 2$) to 0.06% ($k = 2$) with the help of the restrictor.
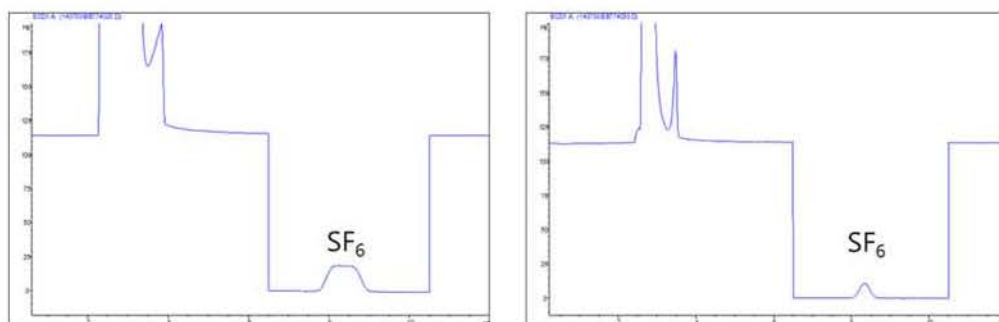

Figure 3. Chromatograms with a restrictor on the tip of the sample line (left) and without the restrictor (right).

4.2 Preparations before testing

Reference material

It is recommended to use certified reference materials traceable to the WMO scale. The materials were stored in cylinders made of aluminum, which is known to be stable against SF_6, and it is recommended that the residual pressure of the cylinders be higher than 100 psi to guarantee a stable mixing ratio of SF_6. The use of expired materials is prohibited. The reference materials under the GAW umbrella that can be used as the standard are: 1) The primary or secondary standard supplied by CCL, 2) the tertiary laboratory standard, transfer standard, traveling standard, and working standard calibrated by WCC using a secondary standard of CCL and 3) the reference gas mixture, manufactured by using gravimetry according to ISO 6142, that secures the traceability to the WMO scale.

Analyte

Dehumidified air contained at high pressure gas cylinder, flask, and canister can be analyzed. Also, The secondary and tertiary standard corresponding to the laboratory, transfer/traveling standard, and working standard also can be set to the analyte for the certification of their SF_6 concentration. The use of cylinders with a minimum storage pressure higher than 100 psi is recommended to secure the consistency of the analysis

Preparations for GC-μECD

To flush residual gases and pollutants in the gas sampling tubes and separation column and

detector, the ground state of the equipment is checked by flowing P5 gas (5 % CH_4 in argon) at a minimum rate of 30 ml/min. On the premise that the required environmental conditions are kept, the ground state of a detector is where the base line of a chromatogram is kept constant for at least 30 minutes. In this state the gas tubes and columns are clear, and the flow rate of the make-up gas (P5) to drive the ECD is appropriately selected and maintained. It is also required that a leak test of the connecting parts including fittings and regulators should be performed before commencing the main experiments.

Required environmental conditions

The room temperature is kept in the range of 15–28°C, with a tolerance of ±0.5°C. Changes in pressure are kept within 10 Torr and the humidity are maintained in the range of 40–60 %.

5. Conventional GC-µECD method

5.1 Equipment specifications

It should be noted that the specifications of the equipment presented in the below items, (1) – (6), are general recommendations. In the case of SF_6 gas chromatography analysis, the surrounding environment (temperature and pressure) and contaminated samples (in particular, the mixing of oxygen, carbon dioxide, and the other gases derived from fluorine) may affect the separation capability and SNR. Based on the decision of an analyst, a condition that optimizes the ground state of the equipment should be set up before starting as described in the previous section.

(1) GC oven

The static temperature (35~60°C) can be applied in order for optimum separation ability among analytes. Whether there is overlap with a similar retention time of another analyte is a one criterion. Or, in case of air samples, programmed temperature variation (a combination of ramping and seizing the oven temperature) can be applied for rapid elution (baking out) of uninteresting halocarbons of which retention times are longer than SF_6 (typically after 10 min in Porapak-Q and Activated Alumina F1 columns, adapted in this note). For instance the temperature is initially programmed to 57°C for 16.5 minutes, and then raised to 170°C at the rate of 35 °C/min and kept for 16.5 minutes. The ramping rate and duration should depend on the retention times of other uninteresting gases and desired time for a single injection.

(2) Sample loop and mass flow controller (MFC)

The volume of the sample loop is 7 ml. The flow rate can be set between 30 and 200

ml/min, depending on the desired precision of analysis. Because high flow rate yields high precision but consumes a large amount of reference material and sample, care should be taken. MFC should be well calibrated against flow meter.

(3) Carrier gas

P5 (5 % CH_4 in argon) fed at <55 psi, corresponding to ~ 30 ml/min, through an electronic pneumatic control (EPC) installed in GC body or external MFC.

(4) Detector

ECD is set up at an appropriate temperature (approximately 375°C)

(5) Column

Activated Alumina F1 evenly packed in stainless steel tube of 12 ft long, 1/8 inch diameter. Securing an extra column for replacement is recommended.

(6) Regulator and pressure gauge

Stainless steel regulator should be equipped on high pressure gas cylinder for safety and quality of analysis. Detailed discussion of the material dependence in precision will be discussed in Annex 2.

5.2 Test procedure

(1) Set up the column, oven temperature, carrier gas flow rate, and temperature of the detector in reference to the specifications of the equipment presented in Section 6.1.

(2) Check the stability of the base lines. When baseline of chromatogram is wavy, flushing by a carrier gas is needed until it turns flat.

(3) Put a sample into the sample loop through the mass flow controller and continue the flow of a reference sample or an unknown sample into it to secure repeatability condition for a sufficient period of time at least 2–3 minutes.

(4) Check the repeatability of the reference material, and ensure it is within the desired standard deviation in accordance with the "diagnostic procedure of the analysis system to secure test conditions" presented in Annex 1.

(5) The reference is injected and analyzed at least 3 times.

(6) The sample is injected and analyzed at least 3 times.

(7) The reference is injected and analyzed at least 3 times to complete the "bracketing sequence" of Reference-Sample-Reference (R-S-R).

(8) For ensuring the identities of the analytes, compare the retention times in the chromatograms of the sample and the reference.

(9) For assigning the concentration of SF_6, compare the responses of the reference and the sample.

5.3 Comparison of elution characteristics of various separation columns

For SF_6 analysis, an Activated Alumina F-1 (AA-F1) column, Porapak Q (PP-Q) and Molecular sieve 5A (MS-5A) show sufficient separation ability. As in Figures 4, 5, and 6, the chromatograms represent the results obtained using each of these columns. Table 1 outlines the separation characteristics of each column. The results indicate that the Activated Alumina F-1 is the most suitable column for analyzing SF_6 due to its rapid retention time and considerably good resolution.
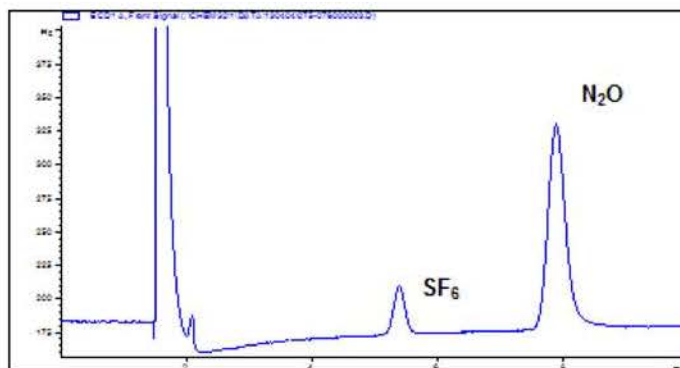

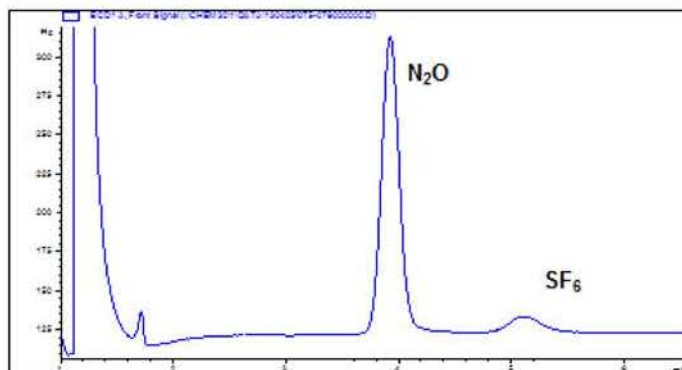**Figure 4.** Chromatogram obtained using Activated Alumina F-1 column.

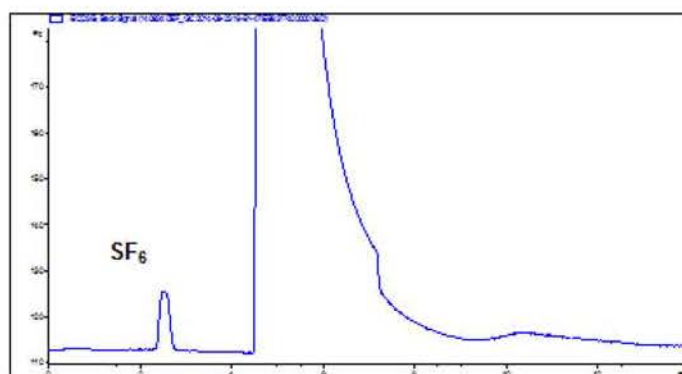**Figure 5.** Chromatogram obtained using Porapak Q column.

Figure 6. Chromatogram obtained using Molecular sieve 5A column.

Table 1. Separation characteristics according to column type.

Column	SF_6 Detection Time (mins)	SF_6 Peak Shape	N_2O Detection Time (mins)	N_2O Peak Shape	O_2 Peak Location
AA-F1	5	Gaussian	8	Asymmetric	before SF_6 Peak
PP-Q	5	Broadened	4	Gaussian	before SF_6 Peak
MS-5A	2.5	Gaussian	trace	Very wide-	after SF_6 Peak

5.4 Analysis characteristics according to sample loop volume

The sample loop volume affects the analytical precision according to the magnitude of the response. The results obtained using loops having 5 ml and 2 ml are illustrated in Figures 7 and 8, respectively. The results show that a smaller sample loop volume leads to lower sensitivity and

analytical repeatability. The chromatograph shows that the use of a large-capacity sample loop increases the SF_6 and O_2 peaks concurrently, thus it may affect the separation ability in cases where a higher volume is applied. This result suggests that excessively large or small sample loop capacities should be avoided during analysis.
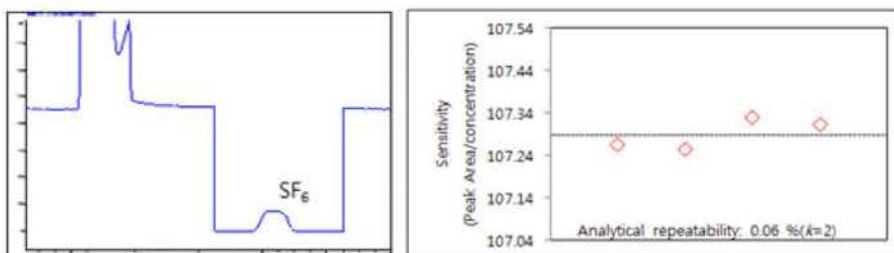

Figure 7. Chromatogram obtained when 5 ml sample loop was used.
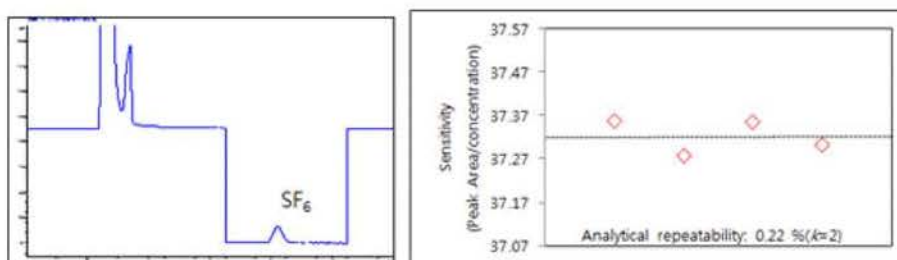

Figure 8. Chromatogram obtained when 2 ml sample loop was used.

5.5 Typical analytical conditions and chromatogram

The chromatogram representing the analysis results after setting up the analytical conditions in Table 2 is shown in Figure 9.

Table 2. Typical analytical conditions for SF_6 in air by using GC-µECD.

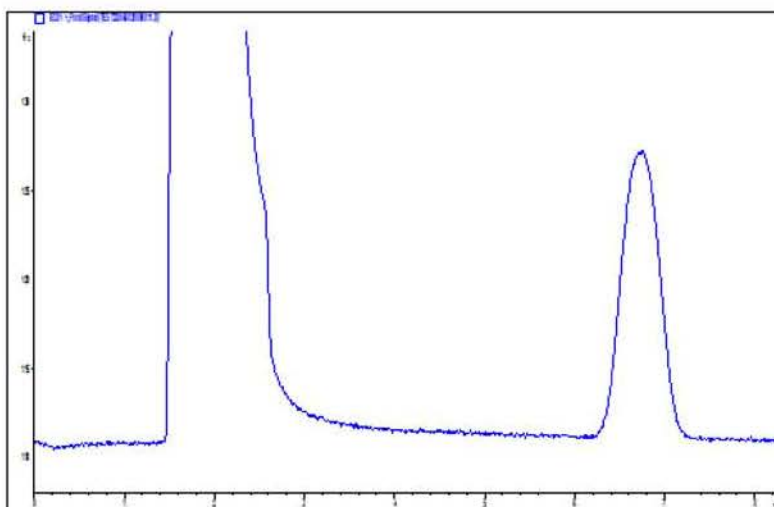| Instrumentation	Analytical conditions
Detector	µECD
Temperature of detector	375°C
Make-up gas	p5 gas, ~30 ml/min
Carrier gas	p5 gas, 20 ml/min
Oven temperature	35°C, 7 mins
Separator tube	Activated Alumina F-1 80/100 12 ft * 1/8 inch SS
Sample flow rate	50 ml/min
Sample loop	7 ml
Valve time setting	0.1 on/2.0 off

Figure 9. Chromatogram obtained for the analytical conditions in Table 2.

6. Measurement with a pre-concentrator

6.1 Equipment specifications

For the required equipment specifications, refer to section 5.1.

(1) Pre-concentration system

With a pre-concentrator, SF_6 is pre-concentrated prior to analysis in order to enhance the sensitivity of GC-µECD. A concentration trap, in which the gas can be adsorbed and, therefore, concentrated as a function of loading time, is the key of this system. In this technical note, a carboxen 1000 80/100 mesh is used as an adsorbent. High-purity He (> 99.999 %) gas should be prepared to purge and flush the trap, in addition to P5 gas that is used as a carrier gas. The gas line of the pre-concentration system consists of a so-called sample injection valve and pre-concentrator valve (Figure 10). The process of concentration is divided into the following six steps: 1) The high-purity He constantly flows in the trap with the two valves turned off, and the temperature of the pre-concentrator is set to about -65℃ or less; 2) with the pre-concentrator valve and sample injection valve turned on, the sample is adsorbed in the trap; 3) with the sample injection valve turned off, high-purity He flows to purge the non-adsorbed O_2 and the other gases on the line; 4) with the pre-concentrator valve turned off, the temperature of the pre-concentrator is raised to 100°C or higher to desorb the sample; 5) with the valves turned on, the carrier gas enters the detector with the gas loaded in the trap so that SF_6, N_2O and CFCs can be detected; 6) during the measurement, the pre-concentrator is returned to the initial state for the next pre-concentration cycle.
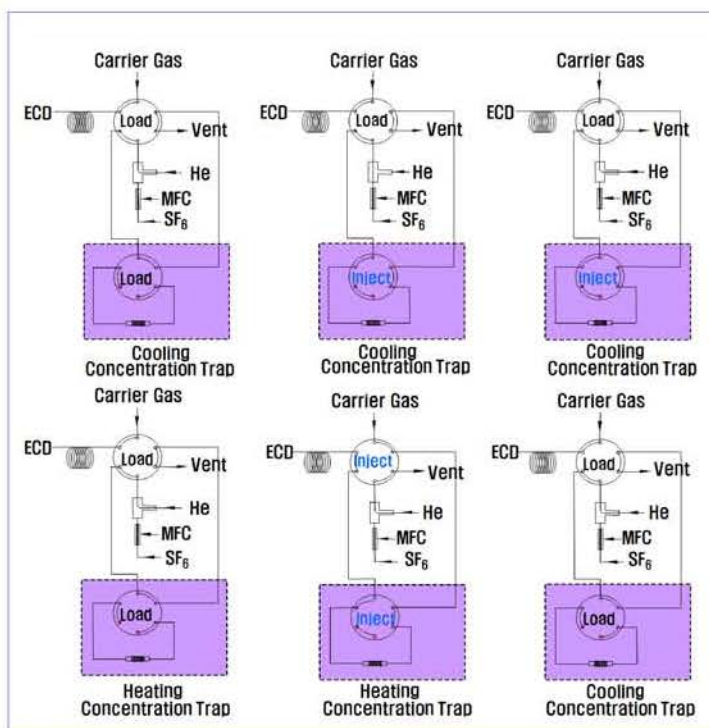

Figure 10. Pre-concentration system on GC-µECD.

6.2 Test procedure

(1) Check whether the temperature of the pre-concentration system can be suitably controlled between -80°C and 170°C.

(2) Check whether the pressure of the high-purity He gas entering the pre-concentration system is sufficiently high, depending on the recommended flow rate of the system used.

(3) Check that times for turning the pre-concentrator valves on and off are precisely scheduled.

(4) Set the column, oven temperature, carrier gas flow rate, and temperature of the detector according to the required instrument specifications presented in Section 6.

(5) Check the status of the base line.

(6) Inject samples or reference into the pre-concentrator through the mass flow controller. To ensure stable analytical repeatability, a reference or unknown sample is consistently injected.

(7) Check the repeatability of the reference material, and ensure it is within desired standard deviation. WMO recommends 0.05 ppt as Data Quality Objective (DQO) for atmospheric SF_6 measurement. Total analytical repeatability should include the repeatability of the pre-concentration process but exclude the interference by O_2 peak. Therefore, the standard deviation of final results is expected more or less than that of the conventional system, i.e., without the pre-concentrator, depending on the competition between the two systems.

(8) Inject and analyze the reference at least 3 times.

(9) Inject and analyze the sample at least 3 times.

(10) Inject, and analyze the reference at least 3 times to complete the "bracketing sequence" of R-S-R.

(11) For ensuring the identities of analytes, compare the retention times between the sample and the reference chromatograms.

(12) For assigning the concentration of SF_6, compare the response of the reference and sample.

6.3 Typical analytical conditions and chromatogram

Table 3 and Figure 11 show the analytical conditions using the pre-concentrator in accordance with the above-described procedure and the resulting chromatograms.

Table 3. Analytical conditions for SF_6 measurement using the pre-concentrator/GC-µECD.

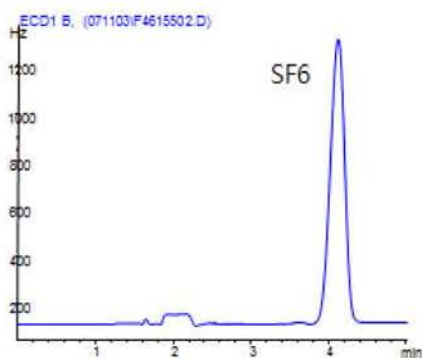| Instrumentation		Analytical Conditions
	Detector	µECD
	Detector temperature	360℃
	Column	PorapakQ 80/100 12ft * 1/8 inch SS
	Carrier gas	P-5 gas, 28 ml/min
	Oven temperature	35℃, 10 mins 20℃/min, 235℃ 16mins
	Sample flow rate	50 ml/min
Pre-concentrator	Absorption temp.	- 80℃
	Sampling time	2 mins
	Desorption temp	170℃
	Desorption time	3 mins
	Purge gas	He 18 ml/min

Figure 11. Chromatogram obtained using the pre-concentrator-GC-ECD.

7. Fore-cutting/back-flush method

7.1 Equipment specifications refer to section 5.1.

The fore-cutting and back-flush method is well known as a candidate method to avoid those problems in the analysis of atmospheric SF_6. In the conventional method, an interference of O_2 peak to SF_6 peak is one of main factors to reduce the analytical repeatability. Additionally, CFCs, which are very sensitive to ECD, show long retention times, and this can be time-consuming. The valve system should be set up with multi-position valves. It is recommended to have two types of frequently used columns (12ft and 6ft each), namely the RESTEK Activated Alumina 1/8 inch SS and RESTEK PorapakQ 1/8 inch SS as pre- and main column, including replacement. In this note, the Molecular sieve 5A column as a post-column requires an extra temperature control to manipulate the retention time of analytes. As illustrated in Figure 12, the valve system consists of a 10-port valve and a 4-port valve. The on-off state of the valves is configured as follows: 1) initially, the two valves are in the off-state; 2) with the 10-port valve turned on, the sample in the sample loop passes through the pre-column and main-column, and the 4-port valve is turned on so that O_2 contained in the sample can be vented; 3) after O_2 is vented, with the 4-port valve still on, SF_6 and N_2O are detected; 4) the 10-port valve is turned off and CFCs remaining in the pre-column are vented.

7.2 Test procedure

Pre-column + main column
(1) The system described here is set up with an Activated Alumina 1/8 inch SS, 6ft and 12ft as the pre-column and main column, respectively. The post column trap is not installed.

(2). Based on the required instrument specifications described in 6.1, properly configure all columns in the GC oven, oven temperature, flow rate of carrier gas, and detector temperature.

(3) Check the stability of the base line.

(4) Inject samples into the sample loop through a mass flow controller. To ensure a stable analytical repeatability, the standard reference or unknown sample is consistently injected.

(5) To set up the on-off timers of the two valves, the sample is injected while the valves are turned on (from step 1 to 3, leaving out step 2 in Figure 12). Check the retention times of the O_2, SF_6, and N_2O peaks.

(6) After confirming the each peak retention times, turn off the 10-port valve and raise the oven temperature to about 90℃. (If the CFCs peak appears, raise the oven temperature or control flow rate of the carrier gas in the pre-column to make the CFCs remain in the pre-column so that they can be vented instead of reaching the detector.) –The phase on "back-flush."
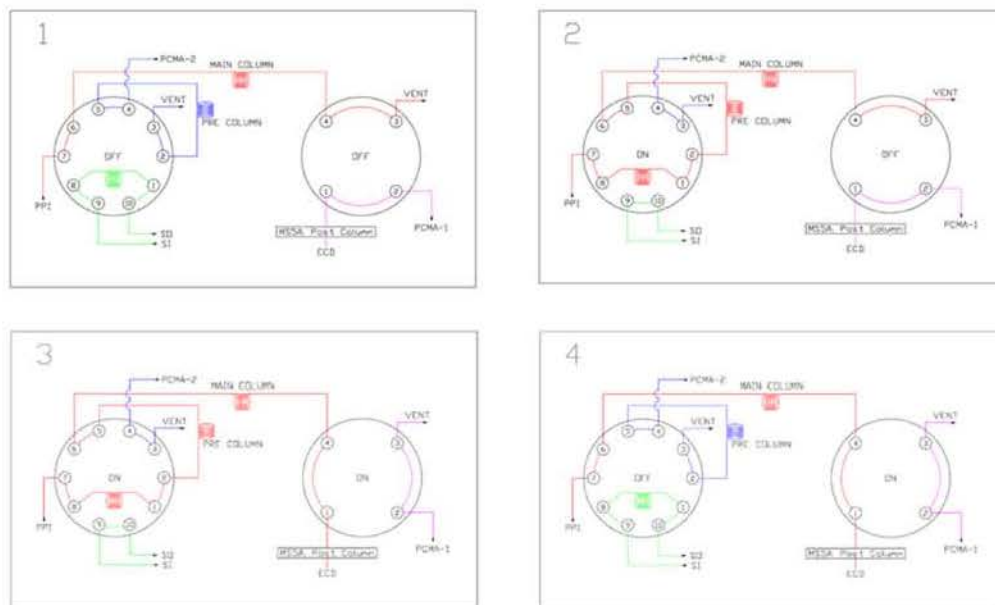

Figure 12. Fore-cutting/back-flush valve system on GC-µECD.

(7) After finishing the back-flush phase, inject carrier gas to vent the O₂ peak and then turn on the 10-port valve. After the retention time of O₂, turn on the 4-port valve. (When the main carrier gas of the 10-port valve and that of the 4-port valve have different flow rates, the base line can be temporarily fluctuated while the 4-port valve is turned on. If this happens, the flow rates should be regulated to similar levels to keep the base line stable.) – The phase on "fore-cutting"

(8) Check the repeatability of the reference material, and ensure it is within desired standard deviation. To improve the repeatability, perform the "self-diagnosis procedure" properly.

(9) Inject and analyze the reference at least 3 times.

(10) Inject and analyze the sample at least 3 times.

(11) Inject and analyze the reference at least 3 times to complete the "bracketing sequence" of R-S-R.

(12) For ensuring the identities of analytes, compare the retention times in chromatograms of the sample and the reference.

(13) For assigning the concentration of SF_6, compare the responses of the reference and sample.

Pre-column + main column + post-column

(1) The system described here is installed with an Activated Alumina 1/8 inch SS, 6ft and 12ft as the pre- and main column, respectively. Porapak-Q columns with same dimension can also be used. Additionally, a trap containing a Molecular sieve 5A as a post-column is set up between the 4-port valve and the detector.

(2) Based on the required instrument specifications listed under the section 6.1, the columns, properly configure oven temperature, flow rate of carrier gas, and detector temperature.

(3) Check the stability of the base line.

(4) Inject samples into the sample loop through the mass flow controller. To ensure a stable analytical repeatability, the reference or unknown sample is consistently injected.

(5) To set up the on-off timer of the two valves, inject the sample while the valves are turned on (from step 1 to 3, leaving out step 2 in Figure 12). Check the retention times of the O_2, SF_6, and N_2O peaks.

(6) Verify back-flush timing: After verifying the peak retention times, turn off the 10-port valve and raise the oven temperature to about 90℃. (If the CFCs peak appears, raise the oven temperature or control flow rate of the carrier gas in the pre-column to make the CFCs remain in the pre-column so that they can be vented instead of reaching the detector.)

(7) Verify fore-cutting timing: inject carrier gas to vent the O_2 peak and then turn on the 10-port valve. After the retention time of O_2 peak, turn on the 4-port valve. (If the temperature of the post-column is too high, the pressure can increase, leading the base line to fluctuate temporarily when the 4-port valve is turned on. In that case, the trap temperature should be regulated to keep the base line stable.)

(8) Check the repeatability of the reference material, and ensure it is within desired standard deviation. To improve the repeatability, perform the "self-diagnosis procedure" properly.

(9) Inject and analyze the reference at least 3 times.

(10) Inject and analyze the sample at least 3 times.

(11) Inject and analyze the reference at least 3 times to complete the "bracketing sequence" of R-S-R.

(12) For ensuring the identities of analytes, compare the retention times between the sample and the reference chromatograms.

(13) For assigning the concentration of SF_6, compare between the responses of the reference and sample.

7.3 Analytical conditions and chromatograms

Pre-column + main column

Table 4 and Figure 13 show the analytical condition and chromatogram for fore-cutting/ back-flush method. The AA-F1 is adapted for the pre- and main columns. In this section, it is intended to describe how to improve the analytical condition rather than to give optimal results since the plumbing configuration and dimensions for fore-cutting and back-flush setup are flexible depending on the analyst(s).

Table 4. Analytical conditions for the fore-cutting/back-flush method equipped with pre- and main columns of AA-F1.

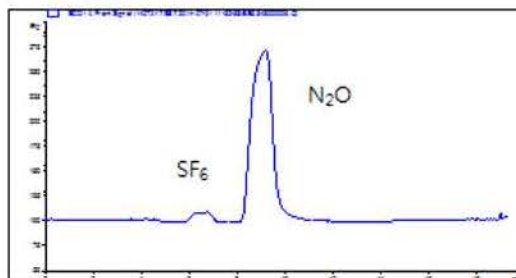| Instrumentation	Analytical Conditions
Detector	μECD
Detector temperature	360℃
Make-up gas	P-5 gas, 5 ml/min
Main carrier gas	P-5 gas, 40 ml/min
4-port valve carrier gas	P-5 gas, 51 psi
Back-flush carrier gas	P-5 gas, 18 psi
Oven temperature	50℃, 13 mins 30 ℃/min, 90℃ 5 mins
Pre column	AA-F1 80/100 6 ft * 1/8 inch SS
Main column	AA-F1 80/100 12 ft * 1/8 inch SS
Sample flow rate	40 ml/min
Sample injection tube	10 ml
10-port valve time setup	0.1 On/13 Off
4-port valve time setup	4.5 On/19 Off

Figure 13. Chromatogram taken by the fore-cutting/back-flush method of which analytical condition is presented at Table 4.

Pre-column + main column + post column (I)

Table 5 and Figure 14 show the analytical conditions initially configured in accordance with the test procedure described in 8.2.2 and the chromatograms taken under this analytical condition. Pre- and main columns are the AA- F1 column and post column is the MS-5A. It should be noted that the on/off time of the multi-position valves should depend on the dead volumes, i.e., the tube length along the sampling line excluding columns.

Table 5. The initially configured analytical conditions of the measurements using the fore-cutting/back-flush method.

| Instrumentation	Analytical Conditions
Detector	μECD
Detector temperature	360℃
Make up gas	P-5 gas, 5 ml/min
Main carrier gas	P-5 gas, 40 ml/min
4-port valve carrier gas	P-5 gas, 47 psi
Back-flush carrier gas	P-5 gas, 18 psi
Oven temperature	55℃, 14 mins 30℃/min, 90℃ 4 mins
Pre column	AA-F1 80/100 6ft * 1/8 inch SS
Main column	AA-F1 80/100 12ft * 1/8 inch SS
Post column	MS-5A
Post-column temperature	185℃
Sample flow rate	40 ml/min
Sample injection tube	10 ml
10-port valve time setup	0.1 On/14 Off
4-port valve time setup	4.5 On/19 Off
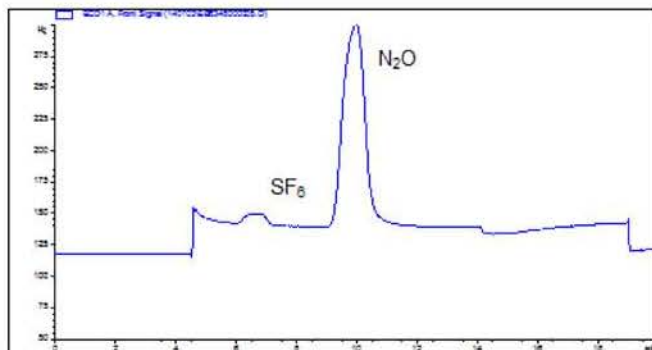
Figure 14. Chromatogram taken by the fore-cutting/back-flush method of which analytical condition is presented at Table 5.

Figure 14 is a chromatogram representing the result of the measurements of the dry air. Main and pre-columns are commercially available AA-F1, and post-column is homemade with MS-5A. For the preparation of the post column, the MS-5A grains are evenly packed into 30cm long stainless steel tubes by using a vibrator equipped with rotary pump. The first peak is the SF_6 and the second peak corresponds to N_2O. O_2 and CFCs existing in dry air are clearly vented and thus not detected. While the SF_6 and N_2O peaks are clearly distinguishable, the base line becomes unstable when the 4-port is turned on. Therefore, the temperature of the post-column controlled by an external device is decreased from 185℃ to 165℃ to address this problem. This is because the packing density seems to be higher than that of pre- and main columns. Therefore one can adjust the packing density of post-column material in order to avoid the steps and fluctuation in the baseline, instead of adjusting the post-column temperature. Nevertheless, adjusting the temperature is recommended for this purpose due to the simplicity and convenience. In those ways, the pressure in post-column can be down-adjusted to drag down the response of ECD even for the appearance of inert gas to the detector such as carrier gases of P5. Additionally, the oven temperature where the pre- and main columns sit was decreased from 55℃ to 40℃ to enhance the separation ability between the SF_6 and N_2O peaks (Table 6). As a result, the peaks were more clearly distinguishable with stable baseline (Figure 15).

Table 6. Improved analytical conditions when using pre-, main and post columns of the 6 ftAA-F1, 12 ft AA-F1 and MS-5A, respectively.

| Instrumentation	Analytical Conditions
Detector	μECD
Detector temperature	360℃
Main carrier gas	P-5 gas, 40 ml/min
4-port valve carrier gas	P-5 gas, 47 psi
Back-flush carrier gas	P-5 gas, 18 psi
Oven temperature	40℃, 18 mins 30 ℃/min, 90℃ 4 mins
Pre-column	AA-F1 80/100 6ft * 1/8 inch SS
Main column	AA-F1 80/100 12ft * 1/8 inch SS
Post column	MS-5A 30 cm SS
Post-column temperature	165℃
Sample flow rate	80 ml/min
Sample injection tube	10 ml
10-port valve time setup	0.1 On/14 Off
4-port valve time setup	4.5 On/19 Off
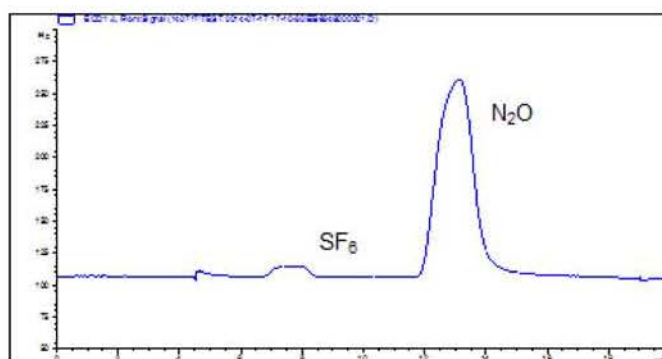
Figure 15. Chromatogram taken by the fore-cutting/back-flush method of which analytical condition is presented at Table 6.

Pre-column + main column + post column (II)

Table 7 outlines the initial analytical conditions for the configuration of the PP-Q columns as the pre- and main columns. Figure 16 shows the corresponding chromatogram. Since the peak shape of N_2O when using PP-Q can be expected to be better than AA-F1 in terms of tailing phenomenon, if both SF_6 and N_2O are interested, analytical conditions described in this section might be helpful to obtain a reasonable level of precision for N_2O. It is recommended that, in case of only SF_6 analysis, AA-F1 is better for saving analysis time due to the shorter retention time of SF_6 than PP-Q. Furthermore, an additional benefit of AA-F1 is that one might back-flush N_2O easily.

Table 7. The initially configured analytical conditions of the measurements using the fore-cutting/ back-flush method (columns: PP-Q and MS-5A).

Instrumentation	Analytical Conditions
Detector	μECD
Detector temperature	360℃
Make-up gas	P-5 gas, 5 ml/min
Main carrier gas	P-5 gas, 40 ml/min
4-port valve carrier gas	P-5 gas, 51 psi
Back-flush carrier gas	P-5 gas, 18 psi
Oven temperature	60℃, 13 mins 30℃/min, 90℃ 5 mins
Pre-column	PP-Q 80/100 6 ft * 1/8 inch SS
Main column	PP-Q 80/100 12 ft * 1/8 inch SS
Post-column	MS-5A 30 cm SS
Post-column temperature	165℃
Sample flow rate	40 ml/min
Sample injection tube	10 ml
10-port valve time setup	0.1 On/13 Off
4-port valve time setup	0.1 On/19 Off

Figure 16 is a chromatogram representing the results of the measurements of dry air at the analytical conditions tabulated in Table 7. The first peak corresponds to O_2, and the second is N_2O which is more sensitive to μECD than SF_6 at ambient levels. SF_6 appears as a rise beside the N_2O peak. O_2 was not subjected to fore-cutting to verify the retention time temporally in Figures 16 and 17. The post-column temperature was changed from the initial setting value of 165℃ to 185℃ in order to enhance the separation ability between the SF_6 and N_2O peaks which are overlapped. The resultant chromatogram is shown in the upper-left panel of Figure 17.
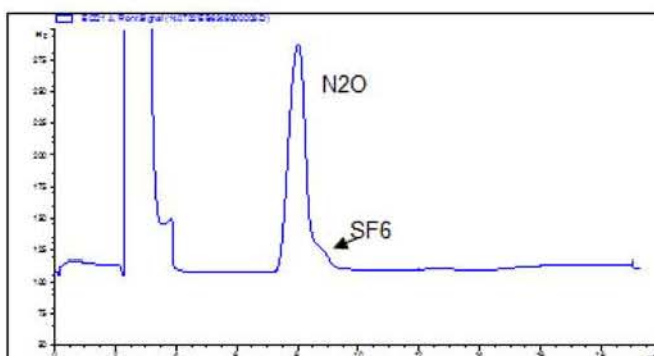

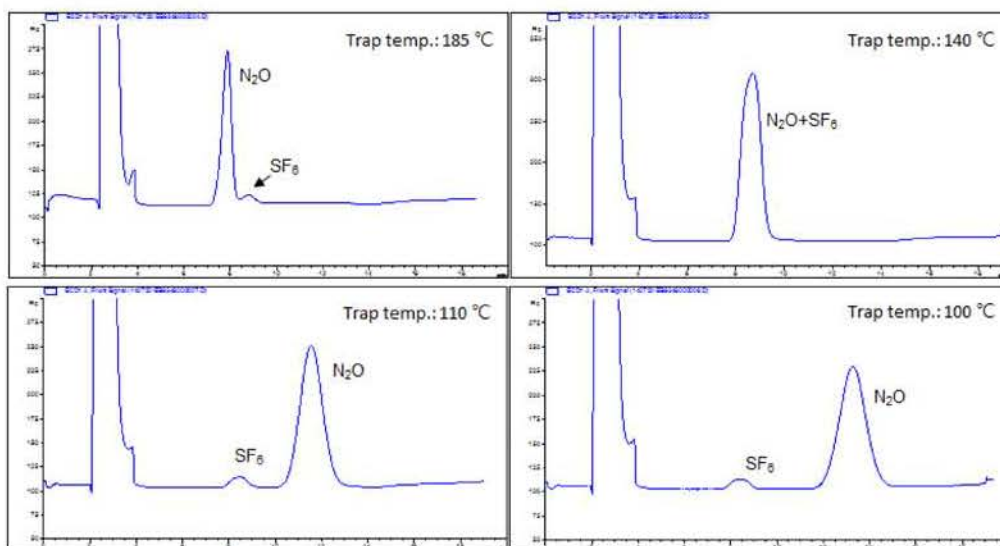**Figure 16.** Chromatogram at the post-column temperature of 165℃.

Figure 17. Changes in chromatograms as a function of the post-column temperature.

In Figure 17, it is shown that appearance order and peak shape are strongly affected by the post-column temperature. The N_2O retention time is manipulated as a function of the post-column temperature rather than the SF_6. Furthermore, the post-column temperature is proportional to the width of both peaks. Between 140℃ and 185℃, N_2O and SF_6 are hardly separable. As it was found, the SF_6 and N_2O peaks were too close to each other at 110℃ but too far apart at 100℃. It is concluded that the temperature was to be compromised at 105℃. Table 8 outlines the optimized analysis conditions, and Figure 18 shows the corresponding chromatogram. In Figure 18, fore-cutting for vanishing O_2 was performed. Therefore, only SF_6 and N_2O appeared.

Table 8. Analytical conditions of the measurements using the fore-cutting/back-flush and GC-ECD (columns: Porapak Q and Molecular sieve 5A).

| Instrumentation	Analytical Conditions
Detector	μECD
Detector temperature	360℃
Makeup gas	P-5 gas, 5 ml/min
Main carrier gas	P-5 gas, 40 ml/min
4-port valve carrier gas	P-5 gas, 51 psi
Back-flush carrier gas	P-5 gas, 18 psi
Oven temperature	60℃, 15 mins 30℃/min, 90℃ 4 mins
Pre-column	PP-Q 80/100 6 ft * 1/8 inch SS
Main column	PP-Q 80/100 12 ft * 1/8 inch SS
Post-column	MS-5A 30 cm SS
Post-column temperature	105℃
Sample flow rate	40 ml/min
Sample injection tube	10 ml
10-port valve time setup	0.1 On/15 Off
4-port valve time setup	3.5 On/19.8 Off
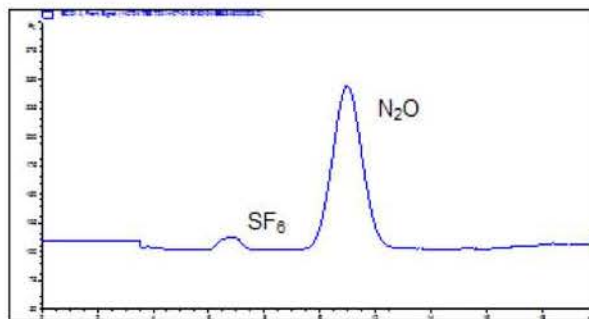
Figure 18. Chromatogram at the optimized condition when using PP-Q and MS-5A columns.

8. Summary

GC-ECD is a popular technique for the analysis of the atmospheric SF_6. In this report, technical details and test procedures of conventional, pre-concentration and fore-cutting and back-flush methods were given. In Table 9, detailed characteristics of introduced analytical methods are summarized. Total analysis time for one sample injection and typical peak shapes of SF_6 and N_2O are given. For repeatable integration of the peak area, to aim for a Gaussian shape is recommended. Because this report focuses more on the SF_6 analysis rather than N_2O, the analytical condition for SF_6 is the only subject to be optimized. If N_2O is interested, PP-Q column is possible replacement for the conventional and pre-concentrator methods. Because O_2 peak, appearing first in chromatogram, is large and therefore shows a long tail, it is worth noting whether O_2 appears or not in order to avoid the discouragement on securing repeatable condition. In case of the analysis of a dry air sample that contains CFCs, column baking by increasing oven temperature, namely rapid ejection of CFCs of which retention time is longer than SF_6 or N_2O at AA-F1 or PP-Q, is needed for saving analysis time. The analysis times of the conventional and pre-concentrator methods in Table 9 are based on the assumption that no baking is adapted. If only SF_6 and N_2O are contained in a target cylinder, no baking is required. It should be noted that the suggested analysis time also depends on the sampling valve configuration and optimized analytical conditions. By using the pre-concentrator, improved analytical precision seems to be expected due to high SNR (at least typically 100 times better than conventional method). But total analytical precision also depends on that of the pre-concentrator itself. In case of the fore-cutting/back-flush method, low dead volume and precise valve timing are additional factors to have high precision.

Table 9. Comparison of the three analysis techniques.

	Conventional GC-ECD (AA-F1)	Pre-concentrator/ GC-ECD (AA-F1)	Fore-cutting/ back-flush method (PP-Q and MS-5A)
Analysis time	25 mins	30 mins	18 mins
Interference of O_2 peak	O	X	X
Shape of SF_6 peak	Gaussian	Gaussian	Gaussian
Shape of N_2O peak	Asymmetric	Not tested	Gaussian
Remarks	Column backing required for air sample	Analysis repeatability influenced by the pre-concentrator repeatability	

Annex 1. The diagnostic procedure of the analysis system to secure test conditions

1. Flow chart for self-diagnosis

Self-diagnosis of the procedures could secure sufficient analytical conditions to measure atmospheric SF_6 by satisfying the evaluation conditions illustrated in the flowchart until the repeatability of repeated injections reaches 0.2%. This flow chart is designed for the conventional method with Activated Alumina F1 column and works only for daily basis readjustment based on the assumption that the analytical condition is very well established. It should be mentioned that, because a degree of response and separation capability strongly differ with individual detectors and columns, respectively, detailed analytical condition should be optimized before using this chart. Furthermore, criterion for the repeatability (or precision) depends on the laboratory.

2. Examples for improving precision

2.1 Measurement using GC-ECD

The chromatogram representing the analysis results after setting up the analytical conditions in Table A1 is shown in Figure A1.

Table A1. Tested analytical conditions.

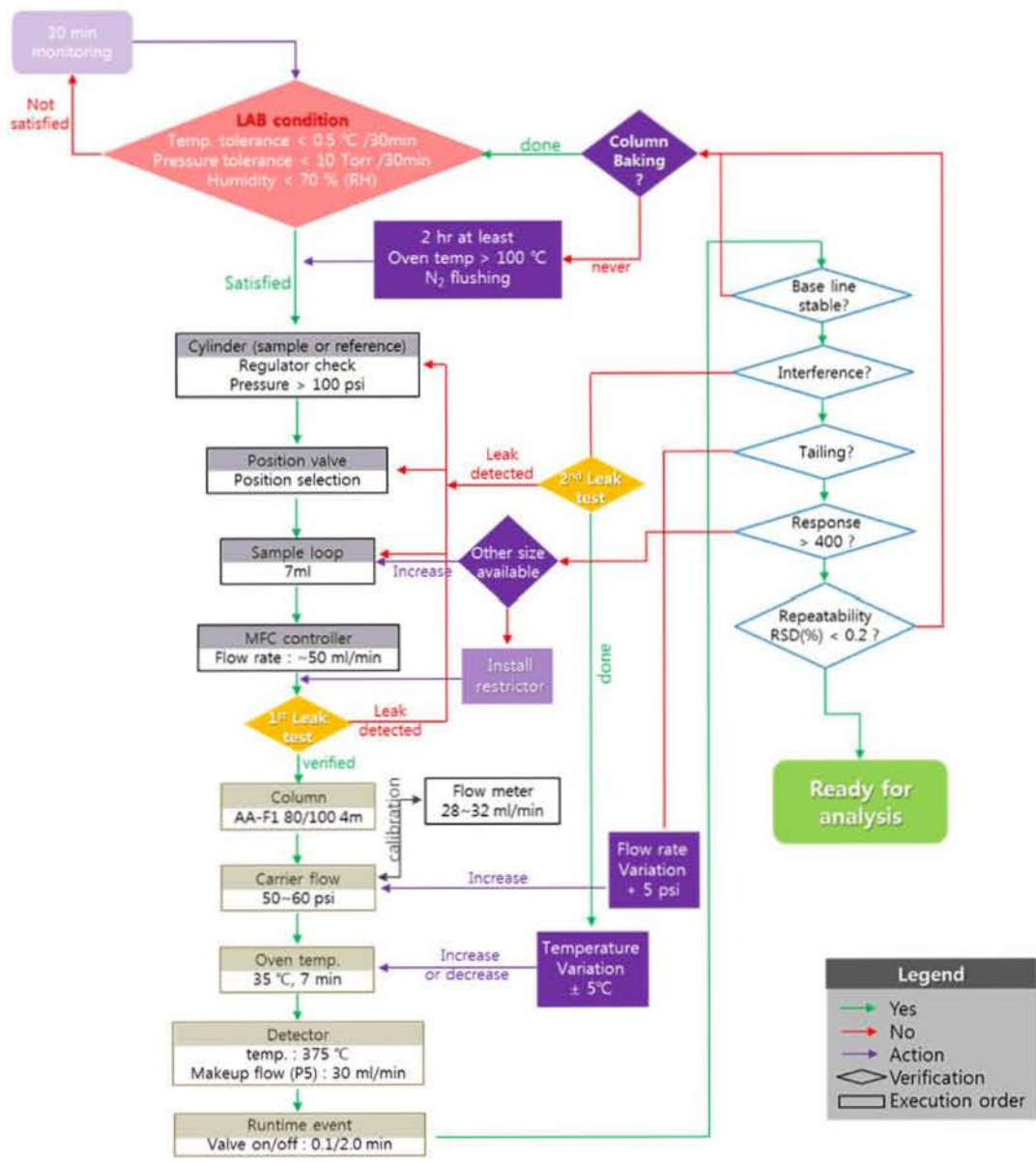| Instrumentation	Analytical conditions
Detector	μECD
Temperature of detector	375 °C
Make up gas	p5 gas, 30 ml/min
Carrier gas	p5 gas, 60 psi (20 ml/min)
Oven temperature	35 °C, 7 mins
Separator tube	AA-F1 80/100 12 ft * 1/8 inch SS
Sample flow rate	50 ml/min
Sample loop	7 ml
Valve time setting	0.1 On/ 2.0 Off

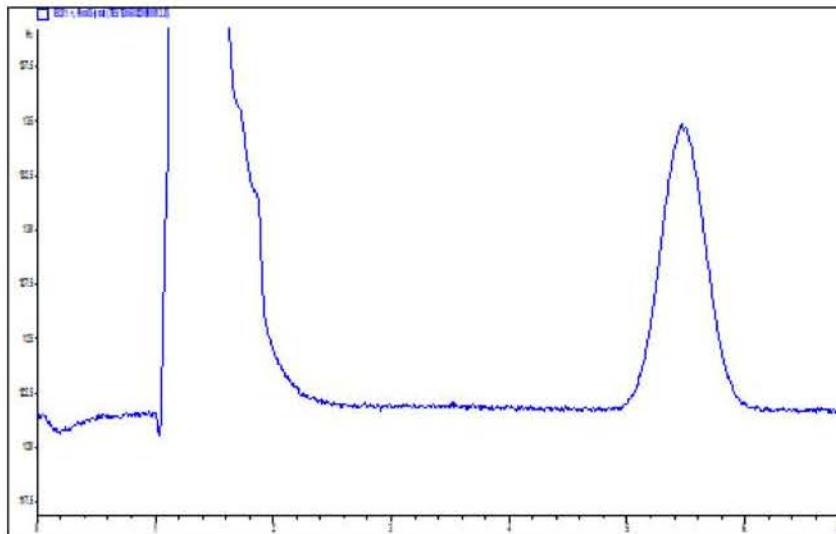**Figure A1.** Flowchart for the self-diagnosis of test conditions.

Figure A2. Chromatogram corresponding to the analytical condition tabulated in Table A1.

Table A2. The repeatability test corresponding to the analytical condition tabulated in Table A1.

Mole fraction [pmol/mol]	1	2	3	4.	Average	Relative standard deviation [%]	Standard deviation [pmol/mol]
11.948	352.3	353.4	353.9	354.4	353.5	0.25	0.013

The first peak in Figure A2 is O_2 and the second peak is SF_6. One can see that the two peaks are clearly separated. The response averages obtained by four injections is 353.53, and the relative standard deviation (standard deviation/response) is 0.25% (Table A2). One can select a method to increase the sensitivity in order to improve the repeatability. For this purpose, it was considered to enlarge the volume of the sample loop or to install a restrictor at the end of the sample line. It is clearly seen that the peak width becomes wider under the same conditions as in Table A1. The response average is 890.13, the relative standard deviation is improved to 0.14% (Table A3), and the precision is improved.
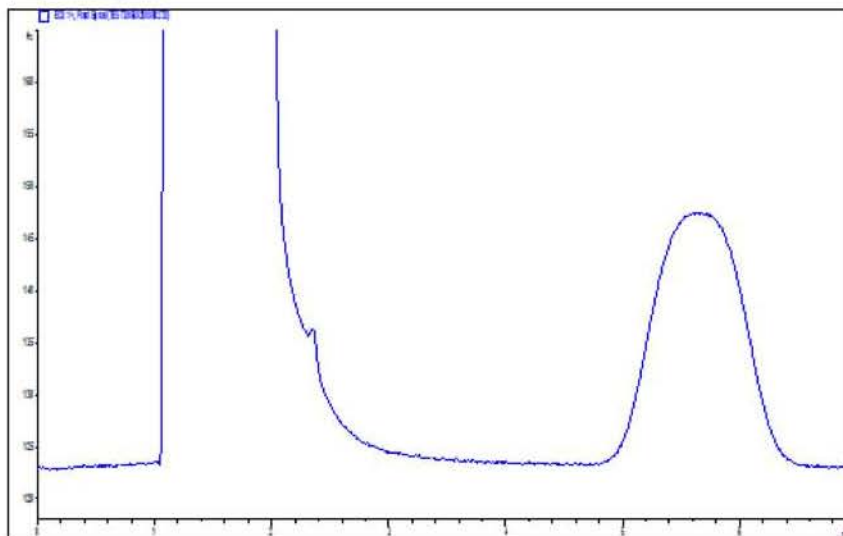
Figure A3. The chromatogram with a flow restrictor.

Table A3. The repeatability test with a restrictor.

Mole fraction [pmol/mol]	1	2	3	4.	Average	Relative standard deviation [%]	Standard deviation [pmol/mol]
11.948	891.1	890.5	890.5	888.4	890.1	0.14	0.016

However, as the width of the SF_6 peak becomes wider, the detection stability can be decreased to a cause less repeatable condition in response due to residual O_2 in the detector. To enhance the separation resolution, the gap between the two peaks can be widened by lowering the oven temperature or decreasing the flow rate. For this purpose, in the following test, the flow rate of the carrier gas is decreased to 45 psi. This led to the improvement in the separation resolution of the O_2 peak (Figure A4), and the average of the responses of three injections is 469.58 and the relative standard deviation is 0.11% (Table A4). Though the responses decrease, the analysis repeatability is improved.
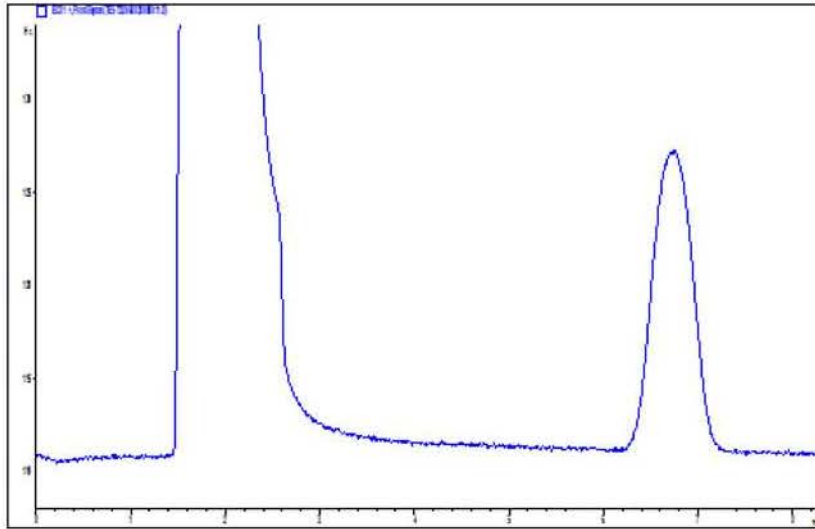
Figure A4. The chromatogram at decreased carrier gas flow rate.

Table A4. The repeatability test when the flow rate of the carrier gas is decreased.

More fraction [pmol/mol]	1	2	3	Average	Relative standard deviation [%]	Standard deviation [pmol/mol]
11.948	469.8	469.0	469.9	469.6	0.11	0.013

Annex 2. Comparison of the materials and different types of parts

1. Comparison of different flask materials in sampling and analysis

For comparison purposes, dry air was sampled in Anmyeondo (AMY, 36.539E, 126.330N, Korea) in a glass flask, stainless steel flask, and two canisters (SilcoCan canister and To-Can canister), as shown in Figures A5, A6 and A7.

The analysis result of the SilcoCan canister should be most accurate presumably owing to the chemically stable coating that eliminates adsorption effects. Furthermore, a canister takes advantages in sampling volume and gas-tight sealing. In other words, high sampling amount by pressurized sampling (up to 24 l) is sufficient for multiple injections, leading to a greater level of precision. Gas-tight sealing prevents potential leakage, which might cause the contamination or a change of the mixing ratio of interesting component. Therefore, it is a valid discussion to compare the accuracies against the Silcocan canister value as a reference. The to-Can canister also showed a reasonable agreement within an analytic uncertainty of 0.3 %. The glass flask is known for having a high chemical stability, but low-pressured sampling affects its repeatability with a large deviation.

Figure A5. Glass flasks. In order to block stray light, a scrap is wrapped.

Figure A6. Stainless steel flasks.

Figure A7. SilcoCan (left) & To-Can (right) canister.

2. Comparison of sampling tubes

    To compare the effects of different tube materials, analyses were performed after connecting the sample and GC with various tubes. Three types of tubes were compared: decarbon, Teflon, and stainless steel (SS) tubes (Figure A8).

Figure A8. Types of gas tubes.

The analytical results obtained by applying different types of the tubes showed that the SS tube and decarbon tube achieved similar levels of consistency for SF_6, while the Teflon tube was found to have a considerably lower analytical precision (Table A5). For N_2O, only the SS tube displayed a superior analytical repeatability.

Table A5. Comparison of sampling tubes according to the material.

Tube type	Component	Sensitivity	Analytical repeatability (k=2)	% difference (with SS tube)
SS tube	SF_6	126.75	0.17%	-
	N_2O	38.54	0.14%	-
Decarbon tube	SF_6	127.55	0.16%	+0.01
	N_2O	38.66	0.60%	+0.30
Teflon tube	SF_6	126.37	0.80%	+0.02
	N_2O	36.70	3.5%	-4.77

3. Recommendations for the section of regulator type and plumbing material

Among the various regulators, a gauge-less type is recommended for measuring greenhouse gases to reduce the dead volume. While performing an analysis, the consistent use of the same regulator is strongly recommended to eliminate contamination effects. Table A6 lists available regulators and materials according to the detectors. Stainless steel suits for GHGs analysis when using ECD.

Figure A9. Gauge-less high purity SS regulator.

Figure A10. High purity brass regulator.

Table A6. Detector and available regulators according to the detection limits.

Detector Type	Detection level	Available regulator	Characteristics	Applicability
FID				
TCD	All level	High purity brass regulator	*SS diaphram *Nickel plated brass barstock body	High-concentration; CH_4, CO_2 analysis
PID				
ECD	> 50ppm			
ECD	< 50ppm		*Tied SS diaphragm *SS barstock body	SF_6, N_2O, and CFC analysis
MSD		High purity SS regulator		
AED	All levels			

Quoted standards and references

ISO/IEC Guide 98-3:2008: Guide to the Uncertainty Measurement expression (GUM).

ISO/IEC 17025:2005: General requirements for evaluating testing and calibration laboratories.

ISO 6142: Gas analysis – Preparation of calibration gas mixtures – Gravimetric method.

ISO 6143: Gas analysis comparison methods for determining and checking the composition of calibration gas mixtures.

ASTM D 2685:2003: Standard gas chromatography test method for air and carbon tetrafluoride in sulfur hexafluoride.

GAW Report No. 206, 16th WMO/IAEA meeting on carbon dioxide, other greenhouse gases, and related measurement techniques (GGMT-2011).

Analytical Methods for
Atmospheric SF6 Using GC-µECD

WMO/GAW Report No. 222

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