

Calibration Methods of GC- μ ECD for Atmospheric SF₆ Measurements

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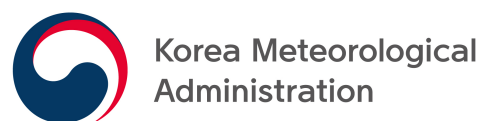
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1. INTRODUCTION

SF₆ is a substance which originates only from anthropogenic sources used primarily in the electricity and electronics supply industries, e.g. the semiconductor industry, where it is used as an electronic insulator due to its inertness. SF₆ is a trace gas that exists in small quantities at the level of ppt (parts-per-trillion, 1/10¹²) in the atmosphere, but its global warming potential is 23,500 times greater than that of CO₂ when compared over a 100-year period^[1]. In particular, SF₆ has an atmospheric lifetime of 3,200 years upon emission, and will eventually exacerbate the man-made greenhouse effect in the long term due to its higher radiative forcing, with greater significance in the future rather than in the present. Therefore, the measurement data of SF₆ will carry significant importance as basic materials for future discussions on climate change.

Since SF₆ is a greenhouse gas that exists in trace quantities at 5-15 ppt in the atmosphere, measurement of the gas requires a very precise procedure. This document provides guidelines on how to produce more accurate and precise values in continuous atmospheric SF₆ measurements, as well as the discrete sample analysis after collecting the air, preparation of standard gases for laboratory applications, and intercomparison experiments. These guidelines are also helpful to prepare the working standards, which have traceability to laboratory standards considering the scale propagation errors.

In this guideline document, WMO scale (NOAA-X2014) is used for the calibrations. The instrument setup and analysis methods refer to WMO (2015)^[2].

2. DEFINITIONS

The definitions are described as targeting on mainly SF₆ in World Meteorological Organization (WMO) Global Atmosphere Watch (GAW) network with a reference to WMO (2016)^[3]. For more detailed information, see references [3] and [4].

Central Calibration Laboratory (CCL)

Within the WMO/GAW network, laboratory responsible for maintaining the standard scale for the species under consideration.

World Calibration Centre (WCC)

Part of the WMO/GAW network, responsible for quality assurance measures for one or more components, by way of audits and intercomparisons. For each component under consideration, the WCC refers to the calibration scale maintained by the Central Calibration Laboratory designated by WMO/GAW.

Mole

The mole is a unit of measurement in chemistry. It expresses the quantity of a chemical substance. According to its atomic weight, the number of atoms contained in 12 grams of ¹²C, which is the isotope of carbon with a mass number of 12, is defined as 1 mole and is equal to Avogadro's number (6.02214129(27) × 10²³). A mole is a basic unit in the international system of units, and it is expressed as mol. For example, the mass of 1 mole of hydrogen (H₂) gas is 2.01588(14) g.

Mole fraction

Relative number of moles of the target species per mole of the sample mixture (possible units are nmol/mol, μ mol/mol, pmol/mol etc.). A specification whether it refers to dry or moist air is required.

Measurand

The quantity intended to be measured.

Composition

The composition is one of the chemical properties of a given gas mixture containing the types and concentrations of matrices and components of interest, and is expressed in mole fraction.

Matrix

This is defined as a gas that occupies the highest proportion of the composition of a gas mixture. This is used for the preparation of standard gases.

Ex SF₆ in N₂ (matrix = N₂)

Component of interest

This is defined as a specific ingredient with a certified mole fraction in the composition of a gas mixture. In this guideline this is SF₆.

Ex CO₂ and CH₄ in N₂ (components of interest are CO₂ and CH₄)

Response

This is defined as the magnitude of signals indicated by an analytic instrument such as peak heights or peak areas in the chromatogram when using gas chromatography. If peak heights are used, the peaks should be perfectly symmetrical in shape. Normally peak area is used for the measurement and this guideline also uses a peak area as a response value.

Carrier gas

This is defined as an inert gas that provides the current for an unknown gas sample to pass through a column. The selected gas should not affect the interaction between the unknown sample and the packing material in the column, or the sensitivity of a detector.

Makeup gas

This is defined as a gas that activates the operational status of an Electron Capture Detector (μ ECD).

Precision

This is the closeness of agreement between indications or measured quantity values obtained by replicate measurements on the same or similar objects under specified conditions. Measurement precision is usually expressed numerically by measures of imprecision, such as standard deviation, variance, or coefficient of variation under the specified conditions of measurement. For GAW this depends only on the distribution of random errors and does not relate to the "true" value or to the specified value.

Repeatability and repeatability condition

Repeatability is the measurement precision under a set of repeatability condition of measurement. Repeatability conditions include: the same measurement procedure; the same observer; the same measuring instrument, used under the same conditions; the same location; repetition over a short period of time.

Reproducibility and reproducibility condition

Reproducibility is the measurement precision under reproducibility conditions of measurement. Reproducibility conditions include: different locations; different operators; different measuring systems; replication made at significantly different times, e.g. Round Robin comparison Experiments in the GAW network

Sensitivity

This is defined as the change observed in the analysis equipment based on changes in the quantity of a sample, i.e. the minimum quantity or change that can be detected, or the magnitude of the response to constant pressure.

Calibration

Set of operations that establish, under specified conditions, the relationship between value of quantities (here, response) indicated by a measuring instrument or measuring system and the corresponding values realized by standards. The result of a calibration permits either the assignment of values of measurands to the indication (of measuring instrument) or the determination of corrections with respect to indications.

Regression analysis

This is a field of inductive statistics analysing relationships between two or more variables, i.e. causal relationships between variables. Regression analysis infers an interrelation by using a mathematical linear functional formula that represents the relationship between the change of specific variables and the change of other variables. The resulting functional formula is referred to as a regression equation. This equation is used to analyse how the change of specific variables (independent variables or explanatory variables) relates to the change of other variables (dependent variables), and to determine the causal relationship in such a case that one exists. This regression analysis is different from correlation analysis, which only examines the intimacy of relationships between simple variables, as opposed to causal relationships. This term is the same to the calibration curve analysis.

Certified reference materials (CRM)

Reference material, accompanied by documentation issued by an authoritative body and providing one or more specified property values with the associated uncertainty and traceability, using valid procedures. In this guideline document, CRMs are issued by CCL and link to WMO-X2014 scale.

These are used to calibrate measuring equipment, evaluate measuring methods, and determine the values of components in the atmosphere. They consist of homogeneous materials or substances with one or more sufficiently determined and certified properties, such as the ingredient names and state when stored in the storage container (i.e. gas, liquid, solid), accompanied by a certificate validating the specified property values (i.e. mole fraction, steam pressure). The uncertainty of the materials at a determined confidence level is also attached and denoted for each certified value.

Gravimetry

This is the general term for quantitative analysis methods using a gravity field. The method calculates the amount fraction of a substance by measuring the weight of analyte.

Reference gas mixture

This is defined as a gas mixture with a well-established composition that is used as the standard for comparison. In this guideline document, certified reference materials are used as references for comparison analysis.

Measurement uncertainty

Non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand. It includes components arising from systematic effects, such as components associated with corrections and the assigned quantity values of measurement standards, as well as the definitional uncertainty. Sometimes estimated systematic effects are not corrected for but, instead, associated measurement uncertainty components are incorporated. The parameter may be, for example, a standard deviation called standard measurement uncertainty (or a specified multiple of it), or the half width of an interval, having a stated coverage probability. Measurement uncertainty comprises, in general, many components. Some of these may be evaluated by Type A evaluation of measurement uncertainty from the statistical distribution of the quantity value from series of measurements and can be characterized by standard deviations. The other components, which may be evaluated by Type B evaluation of measurement uncertainty, can also be characterized by standard deviations, evaluated from probability density functions based on experience or other information.

Standard

In metrology, standards refer to units of measurement for physical or chemical quantities and the objects, systems, or experiments that demonstrate a correlation with the said quantities. In the WMO GAW Programme, there are many cases where certified reference materials of the WMO/GAW CCL and their direct by-products are all referred to as "standards." As a result, WMO "standards" are mainly used as comparison measurement reference values for certifying and calibrating the mole fraction or for maintaining the traceability of components of interest.

Scale (conventional reference scale)

The scale is the aggregation of certified reference materials whose calibrated or certified mole fractions are established at similar intervals to components of interest. The scale is based upon a number of primary measurement standards and a measurement procedure to interpolate other values. Within WMO/GAW, the conventional reference scale refers in particular to the calibration scale used within the WMO/GAW network. In the case of SF₆, this scale is implemented as a family of gas cylinders maintained at the CCL established in the Earth System Research Laboratory, National Oceanic and Atmospheric Administration. For the other scales accepted in the WMO/GAW Programme, consult the GAW Implementation Plan on the GAW website (<http://www.wmo.int/gaw>).

Traceability

Property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty. To minimize the accumulation of measurement uncertainty, institutes and monitoring stations maintain as direct as possible a path between their laboratory standards and CCL.

Figure 1 shows the traceability chain of WMO standards and it can be divided into the following steps: (1) The primary standard is prepared by gravimetry or equivalent method at the CCL; (2) the secondary standard is the measurement standard established through calibration with respect to a primary measurement standard for a quantity of the same kind^[1]. For trace gas measurements within WMO/GAW, this refers to a standard (natural air or synthetic gas mixture) with mole fractions for target species that are obtained from comparisons made by the CCL with primary standards kept at its laboratory; (3) Tertiary standard is the standard calibrated by comparison with secondary standards. For trace gases, it is used as a laboratory standard by the WCC, GAW stations and participating laboratories; and (4) Other standards are travelling and working standards, which are mostly used after correcting the atmospheric mole fraction of SF₆ to the dry air mole fraction. The terms of these standards are defined and explained below. Finally, among these standards a

travelling standard gas is used when WCC conducts a performance audit and when an international round-robin experiment is carried out in the WMO/GAW network.

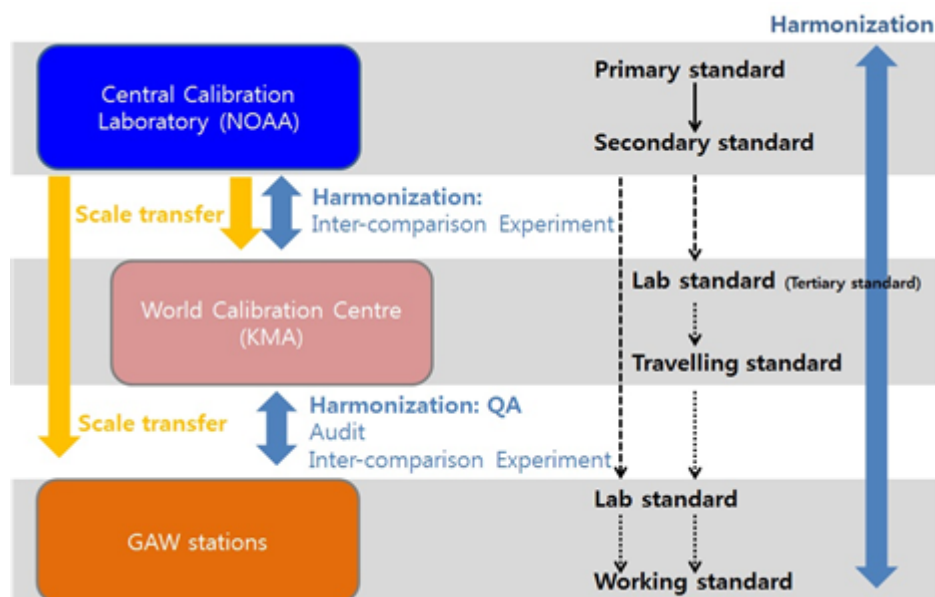


Figure 1. SF₆ traceability chain in WMO/GAW

Laboratory standard

In the WMO traceability chain, laboratory standards consist of the samples at WCC, RCC, and GAW stations that are calibrated against secondary standards of the CCL. This type of standard is the highest rank at an individual laboratory or station traceable to the WMO/GAW standard scale.

Working standard

This is used routinely to calibrate or verify measuring instruments or measuring system. A working standard is usually calibrated with respect to a reference measurement standard.

In WMO/GAW for stable gases, any gas (natural air or synthetic gas mixture) with assigned mole fractions of one or more trace species obtained from comparisons with the laboratory standards of an individual laboratory or station, or from comparisons with transfer standards provided by another laboratory, such as the WCC. For measurement of stable trace gases, usually gas cylinders denoted as working standards are employed as calibration cylinders for routine measurements.

Travelling standard

This is the measurement standard, sometimes of special construction, intended for transport between different locations. For measurements of stable trace gases within WMO/GAW, this refers in particular to compressed gas cylinders (natural air or synthetic gas mixture) for use at different locations with an assigned mole fraction of one or more trace species resulting from calibration(s) by the CCL or from comparisons with laboratory standards by an approved laboratory, such as the WCC.

Target cylinder (target gas)

Cylinder containing natural air or a synthetic gas mixture with assigned trace gas mole fraction that is treated as an (unknown) sample in a sequence of an analysis. In GAW the target cylinder, or target

gas, is used for quality control measures. In the hierarchy of standards the target gas is usually on the same level as a working standard.

Compatibility

Property of a set of measurement results for a specified measurand, such that the absolute value of the difference of any pair of measured quantity values from two different measurement results is smaller than some chosen multiple of the standard measurement uncertainty of that difference. Within the GAW network, this refers to the dispersion of measurements of the same standard performed by different laboratories within the network. Compatibility goals are motivated from the perspective of the required data quality and compatibility for interpretation of global or continental scale atmospheric data, obtained from different laboratories, and for joint use in atmospheric transport model inversion studies. This compatibility goal should be reached in the respective specified mole fraction ranges observed in the global background troposphere^[4].

Comparison measurement

The measured quantity is defined as a quantity subject to measurement, and the measured value is defined as the numerical value obtained from measurement. The comparison of the measurement is a method of measuring quantities that were previously measured, by directly comparing them to standard quantities. This is sometimes referred to interchangeably as analysis when measuring chemical properties.

Ex

The quantitative analysis of the mole fraction of an ingredient in an unknown sample is conducted when the mole fraction is determined by measuring the response of the corresponding equipment, and the response is compared with that from a certified reference material. The mole fraction can then be referred to as having been quantified because the quantity of the composition (in this case, mole fraction) was obtained through comparison measurement.

Intercomparison experiment or round-robin experiment

In experimental methodology, a round-robin experiment is a test (measurement, analysis, or experiment) performed independently by multiple laboratories or participants over several occasions. In a WMO/GAW round robin, each participating laboratory analyses values using its own independent method, using travelling standards supplied by the CCL, and compares the resulting values with those of other laboratories. An intercomparison experiment is an analysis of the same sample by two or multiple laboratories in a method similar to a round robin test. Intercomparison experiments are performed regularly by the WCCs for the GAW community.

3. TEST OVERVIEW

3.1 Component of interest

SF₆ at a background atmospheric level, i.e. 5-15 ppt (pmol/mol). The recommended compatibility goal of SF₆ is ± 0.02 ppt at a background atmospheric level and ± 0.05 ppt at other higher atmospheric levels^[4].

3.2 Measurement principle of GC- μ ECD

To analyse SF₆, GC-ECD (gas chromatography with electron capture detector) is the typical tool for the analysis that it described in this guideline document.

3.2.1 Gas Chromatography (GC)

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

3.2.2 Electron Capture Detector (ECD)

An ECD is a GC detector designed based on a chemical phenomenon where neutral gas molecules with the appropriate electronegativity react with thermal electrons to form negative ions. Activated gases, mostly helium or argon, and beta particles (electrons or antielectrons with high kinetic energy released from radioactive isotopes) undergo the collision ionization process to form thermal electrons with high reactivity and low energy. The attenuation of the flow of thermal electrons by the analysis material, i.e. the change in the current, is measured to determine the quantity of the analysis material. Thus, the ECD is highly useful for the analysis of chemical species with high electron affinity (mostly gases, including halogens).

4. PREPARATIONS

4.1 Preparations before testing

4.1.1 Certified reference material

For a reference material for comparison analysis, it is recommended to use certified reference materials, traceable to the WMO/GAW scale for SF₆ (WMO-X2014 scale) and with uncertainties specified. The materials are stored in cylinders made of aluminium, which is known to be stable against SF₆, and it is recommended that the residual pressure of the cylinders is higher than 100 psi to guarantee analysis consistency and convenience. The use of expired materials is prohibited.

The matrix gas of the materials prepared by gravimetry, a so-called "primary method," is a synthesized gas consisting of oxygen, nitrogen, and argon (a gas mixture of pure oxygen, nitrogen, and argon gases based on the composition of atmospheric air) or a background atmospheric gas without SF₆, and the mole fraction of the SF₆ manufactured is at 5-15 ppt.

In these guidelines, the materials that can be used as the reference are: (1) the tertiary standard calibrated using the secondary standard supplied by the CCL; and (2) the working and travelling standard calibrated by WCC or using the tertiary standard supplied by the CCL.

4.1.2 Analysis sample

Analysis samples can consist of samples of the ambient dry air collected in accordance with the laboratory's chosen approach^[5], traveling standards for round-robin tests, or ambient air samples. The use of cylinders with a minimum storage pressure higher than 100 psi is recommended to ensure the consistency and convenience of the analysis.

4.1.3 Preparation of GC- μ ECD

In order to cleanse pollutants from the gas line, column, and detectors, the baseline of the equipment is checked by injecting a flow of P5 gas (5% CH₄ in argon) at a minimum rate of 30 mL/min. Based on the premise that the required environmental conditions can be maintained, the baseline of detector chromatogram is a state which is kept constant for at least 30 minutes. In this state, the gas lines and columns are clean, and the flow rate of the activated gas (P5) to drive the μ ECD is appropriately selected and maintained.

4.2 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 is maintained in the range of 40-60%.

4.3 Required measures before testing

Connecting parts must be inspected with a leakage detection solution in order to prevent gas leaks.

5. SPECIFICATIONS AND DIAGNOSTIC PROCEDURES OF THE ANALYSIS SYSTEM

5.1 An example of equipment specifications

It should be noted that the specifications of required equipment as presented below are general recommendations. In the case of SF₆ gas chromatography analysis, the surrounding environment (temperature and pressure) and the degree of sample contamination (in particular, the mixing of oxygen, which reacts sensitively to ECD, and other gases derived from fluorine) may affect the separation ability between peaks and signal-to-noise ratio. Thus, the final analyst should establish a condition that optimizes the ground state of the equipment and degree of SF₆ separation as appropriate.

- (1) Certified reference materials: Refer to Section 4.1.1 for further details.
- (2) Sample for analysis: Refer to Section 4.1.2 for further details.
- (3) GC oven: According to the degree of SF₆ separation in the chromatogram, fixed temperatures as outlined below can be used interchangeably with the temperature programme (refer to the examples below). The criterion for judgment is whether there is an overlap with the peak of a material that has a similar retention time to that of SF₆.
 - Ex 1** If using a isothermal temperature: 35-60°C for the analysis
 - Ex 2** If using a gradient temperature:
57°C for 16.5 minutes, at a rate of 35°C/min to 165°C for 7.7 minutes, or at the rate of 35°C/min to 170°C for 16.5 minutes.
- (4) Sample loop and mass flow controller (MFC):
 - Ex** Sample loop: 7 mL, flow rate: 30-200 mL/min.
- (5) Carrier gas: P5 (5% CH₄ in argon) at 55 psi or higher (28 mL/min or higher).
- (6) Detector: μ ECD is set at an appropriate temperature (approximately 375°C).

- (7) Column: Restek activated alumina F-1, 12 ft * 2 each, 1/8 inch stainless steel (SS) (spare replacements recommended) in this experiment.

Ex Porapak-Q, Heysep-Q, and other relevant columns can be used.

- (8) Thermo-hygrometer and pressure gauge.

5.2 An example of analysis

- (1) Set up the column, oven temperature, carrier gas flow rate, and temperature of the detector in reference to the example presented in Section 5.1.
- (2) Check the stability of the baselines.
- (3) Inject a sample into the sample loop through the mass flow controller and continue the flow of a reference gas or an analysis sample to ensure analytical repeatability.

NOTE

If the sample quantity is insufficient, decrease the flow rate to 5 ml/min after injecting the sample and revert to the original flow rate 2-3 minutes before the next injection.

- (4) Ensure that the repeatability of the reference material analysis is within 0.2% in accordance with the "diagnostic procedures of the analysis system to secure test conditions" presented in reference [2].
- (5) Inject the reference gas and measure at least three times.
- (6) Inject the sample to be measured and measure at least three times.
- (7) Inject the reference gas again and measure at least three times.
- (8) Conduct a qualitative analysis by comparing the retention time of the chromatogram of the sample ingredients with that of the reference gas material.
- (9) Conduct a quantitative analysis by comparing the response of the equipment to the sample with that of the reference material in accordance with the analysis method presented in this technical note.

5.3 Diagnostic procedures of the analysis system to secure test conditions

The method of self-diagnosis to secure test analysis conditions and other various methods to improve the separation ability of the peaks were described in Chapter 5 and Annex 1 of reference [2].

6. LINEARITY CHECK OF INSTRUMENTAL RESPONSE AND SELECTION OF CALIBRATION METHODS

The calibration of test results is based on the premise that responses to a μ ECD are linear in relation to the mole fraction of SF₆, or to reiterate, the sensitivities are the same within the range of mole fractions of interest. Responses from the analysis equipment are checked for linearity during a one-year period in case of real-time observation. However, when participating in an intercomparison experiment or analysing flask samplings while operating a central laboratory, a multi-point calibration must be performed before analysing mole fractions of interest. The responses at each mole fraction are calculated using the one-point calibration presented in Section 7 and the two-point calibration in Section 8. Multi-point calibration uses five or six reference materials, including a range

of mole fractions of SF₆ in the atmosphere, while the remaining four or five cylinders using the representative cylinder as reference are analysed repeatedly. Table 1 is an example that illustrates such a process.

**Table 1. An example of analysis for drawing a calibration curve.
Each CRM was injected 3 times.**

Name	CRM(T) ₁ ¹⁾	CRM(1)	CRM(T) ₂	CRM(2)	CRM(T) ₃	CRM(3)
Certified mole fraction (ppt)	9.102	9.026	9.102	8.144	9.102	...
Response 1	496.38	493.38	497.04	447.35	497.26	...
Response 2	496.14	493.56	497.08	447.70	497.63	...
Response 3	496.18	493.30	497.03	447.37	497.58	...
Mean response	496.23	493.41	497.05	447.47	497.49	...
Standard deviation	0.13	0.13	0.03	0.20	0.20	...
Relative standard deviation (%)	0.03	0.03	0.01	0.04	0.04	...
Sensitivity	54.52	54.67	54.61	54.94	54.66	...
DCSIR ²⁾		54.56		54.63		...
Corrected sensitivity		54.61		54.92		
Corrected response		493.01		447.28		
Drift (%)		-	0.16		0.09	...

¹⁾ CRM: Certified Reference Material, CRM(T): Certified Reference Material with a function of target cylinder

²⁾ DCSIR: Drift Corrected Sensitivity of Imaginary Reference. See formula (2) and (3)

CRM(T)_i in Table 1 is a standard with _i connoting the order. When the responses of certified reference materials are recalculated in consideration of equipment drift using the CRM(T), the procedures below are followed in order. Theoretically, the sensitivities of CRM(i) are recalculated in consideration of changes in the sensitivities of CRM(T)_i as reference and the responses of CRM_i are recalculated in accordance with the ratio of differences in sensitivity (corrected responses). The formula is as follows:

$$\text{Sensitivity} = \text{Mean response} / \text{Certified mole fraction} \quad (1)$$

$$\text{DCSIR}(\text{CRM}(i)) = (\text{Sensitivity}(\text{CRM}(T)_i) + \text{Sensitivity}(\text{CRM}(T)_{i+1})) / 2 \quad (2)$$

$$\text{DCSIR}(\text{CRM}(T)) = \text{Sensitivity}(\text{CRM}(T)_1) \quad (3)$$

$$\text{Corrected sensitivity}(\text{CRM}_i) = \text{Sensitivity}(\text{CRM}_i) \times (\text{DCSIR}(\text{CRM}_{i-1}) / \text{DCSIR}(\text{CRM}_i)) \quad (4)$$

$$\text{Corrected response (CRM}_i\text{)} = \frac{\text{Corrected sensitivity (CRM}_i\text{)} \times \text{Certified mole fraction (CRM}_i\text{)}}{\text{Corrected sensitivity (CRM}_i\text{)}} \quad (5)$$

If the response values for all certified reference materials are not obtained continuously within the given analysis period, corrected responses obtained through repeated analysis under similar conditions may be used as well. The corrected responses obtained through continuous analysis as outlined above are drawn in a diagram to demonstrate their correlation to the certified mole fractions, after which a calibration curve is replicated followed by a linear analysis as illustrated below.

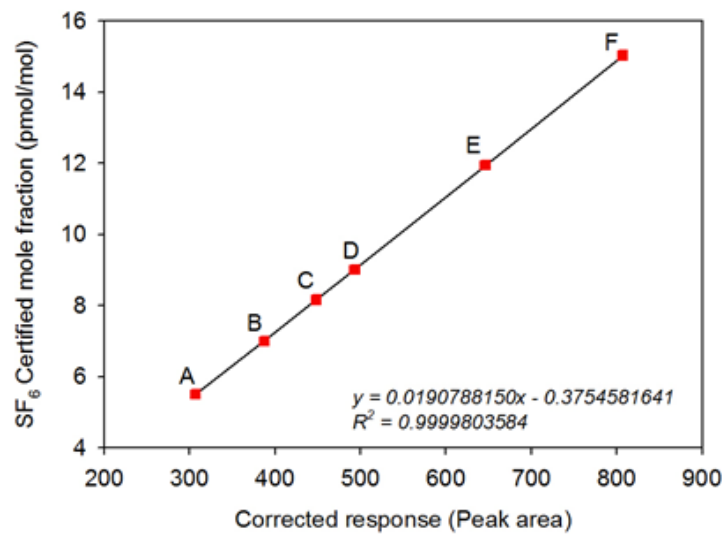


Figure 2. A curve of equipment responses to the certified mole fractions of the certified reference material of SF₆. Typical measurement repeatability is 0.3%.

Table 2. Comparison between analysed responses and associated theoretical values using a calibration curve

Cylinder number	Certified mole fraction (pmol/mol)	Corrected response	Theoretical value (pmol/mol)	Residual (pmol/mol)
A	5.510	307.21	5.486	0.024
B	7.003	387.08	7.010	-0.007
C	8.164	448.07	8.173	-0.009
D	9.021	493.41	9.038	-0.017
E	11.948	646.14	11.952	-0.004
F	15.038	807.21	15.025	0.013

The response linearity can be assessed by replicating a linear diagram illustrating the relationship between the gravimetric concentrations of the certified reference materials (using more than four reference materials) to the responses shown in Figure 2 or by replicating a regression line obtained from a secondary polynomial.

The coefficient of determination, shown as R^2 , can be used as the basis to assess linearity. If R^2 is greater than 0.9999 (four decimal point) upon fitting the straight regression line according to $y = a \times x$, where a denotes the slope of the calibration curve, i.e. the ratio y/x , and the residual values are less than compatibility goal (Table 2), the response of the detector is judged to be linear and one-point calibration can be used (refer to Section 7).

However, if R^2 is greater than 0.9999 with a straight line calibration function with a non-zero intercept approximating the true calibration function within a specific range gases according to $y = a \times x + b$, where a denotes the slope of the calibration curve and b the intercept of the analysis function. When the residual values are less than compatibility goal (Table 2), two point calibration is recommended (refer to Section 8). Example is presented in Figure 2.

If R^2 is greater than 0.9999 with a secondary polynomial regression line and is judged on whether R^2 is improved (strong non-linearity is indicated if R^2 approaches 1 when fitting the regression line to a secondary polynomial), equipment response would be non-linear. The multi-point calibration method is recommended with the example given in Table 1 presented in Section 6. However, for continuous measurements at in situ stations this multi-point calibration cannot be applied frequently and two-point calibration method presented in Section 8 is recommended. In this case the reference materials should be close to and bracket an expected sample value. Sections 7 and 8 also refer to [5] and [6].

7. DETERMINATION OF MOLE FRACTION AND ANALYSIS UNCERTAINTY WITH ONE-POINT CALIBRATION

7.1 Determination of mole fraction with one-point calibration

In the case where equipment response is confirmed to be linearly proportional to the mole fraction of the analysis sample after checking the linearity of the equipment through the multi-point calibration illustrated in Section 6, the mole fraction of an unknown sample is determined by the one-point calibration method. When this method is used for the analysis, the value of CRM should be similar to the one of the sample to exclude other possible error. The analysis is carried out with a certified reference material, followed by a sample, then another certified reference material (CRM-sample-CRM), and uses the following formula for determination of the mole fraction. However, at this point, it is important to use a certified reference material which has the closest mole fraction to that of the unknown sample.

$$C_{\text{sample}} = R_{\text{sample}} / R_{\text{CRM}} \times C_{\text{CRM}} \times f_{\text{drift}} \quad (6)$$

- R_{sample} : Response value of the sample
- R_{CRM} : Response value of the certified reference material
- C_{CRM} : Certified mole fraction of the certified reference material
- f_{drift} : Equipment drift

Assuming that the equipment drift is linear with time, f_{drift} can be obtained as follows:

$$f_{\text{drift}} = (2 \times R_{\text{CRM}'}) / (R_{\text{CRM}'} + R_{\text{CRM}''}) \quad (7)$$

Herein, $R_{\text{CRM}'}$ is the average of the responses from the first set of repeated measurements (at least three times) of the certified reference material, while $R_{\text{CRM}''}$ is the average of the responses of the second set of repeated measurements (performed three times) of the certified reference material. Thus, the response of an unknown sample whose drift has been corrected, $R_{\text{corr.}}$ ($=R_{\text{corrected}}$), is as follows:

$$R_{\text{corr.}} = f_{\text{drift}} \times R_{\text{sample}}$$

$$\text{thus, } C_{\text{sample}} = R_{\text{corr.}} / R_{\text{CRM}} \times C_{\text{CRM}} \quad (8)$$

If the drift value defined as follows is at a lower level than the analysis repeatability represented by Relative Standard Deviation (RSD), f_{drift} is 1.

$$\text{drift}(\%) = (R_{\text{CRM}''} - R_{\text{CRM}'}) / R_{\text{CRM}''} \times 100 \quad (9)$$

Even when equipment operation conditions are set up in accordance with the specifications of the equipment, it is not the case that analysis repeatability is immediately secured. Thus, analytical conditions should be optimized until analysis repeatability reaches 0.2% after injecting the sample three or four times in accordance with the procedure for self-diagnosis as illustrated in Annex 1 of reference [2].

7.2 An example of one-point calibration

Table 3 shows the analysis procedure as outlined in Section 5. Each measurement was repeated three times and the relative standard deviation in the first CRM analysis was determined to be 0.08%. The relative standard deviation in the second CRM analysis is 0.16%, but the equipment drift is 0.41%, thereby requiring a correction against the drift. Thus, the mole fraction is determined as follows:

$$\begin{aligned} C_{\text{sample}} &= R_{\text{sample}} / R_{\text{CRM}} \times C_{\text{CRM}} \times f_{\text{drift}} = R_{\text{corr.}} / R_{\text{CRM}} \times C_{\text{CRM}} \\ &= 2086.6 / 1962.7 \times 6.432 \\ &= 6.838 \text{ (ppt)} \end{aligned}$$

Table 3. An example of the initial data organization for comparison analysis

<i>Name</i>	<i>CRM¹⁾</i>	<i>Sample</i>	<i>CRM¹⁾</i>
Certified mole fraction (ppt)	6.432		6.432
Response 1	1962.6	2089.2	1972.8
Response 2	1964.4	2092.5	1972.2
Response 3	1961.2	2090.8	1967.1
Mean response	1962.7	2090.8	1970.7
Standard deviation	1.60	1.65	3.13
RSD ²⁾ (%)	0.08	0.08	0.16
f_{drift}		0.998	
$R_{\text{corrected}}$ ³⁾		2086.6	
Drift (%)		-	0.41

¹⁾ CRM: Certified Reference Material, refer to 4.1.1

²⁾ RSD (%): Relative standard deviation = Standard deviation/Mean response x 100, degree of precision

³⁾ $R_{\text{corrected}}$: Corrected mean response

7.3 Evaluation of analysis uncertainty for one-point calibration

7.3.1 If only considering the analysis repeatability

Measurement uncertainty can be expressed by measurement repeatability, assuming that measurement precision was sufficiently great. Repeated measurements are made according to the analysis procedure outlined in Section 7.2. The sample is analysed three times in the order of CRM, sample, CRM, sample, CRM, sample, and CRM. At least three injections are made in every stage of the analysis consisting of each CRM and sample. In the case where a higher (lower) level of analysis uncertainty is required, the number of repeated measurements is increased (or decreased).

Table 4. An example of the uncertainty calculation by analysis repeatability

<i>Measured value of sample (ppt)</i>			<i>Mean value (ppt)</i>	<i>Standard deviation (ppt)</i>
1	2	3		
6.886	6.858	6.873	6.872	0.014

7.3.2 If considering the error increase in the one-point calibration formula

If there are few repeated measurements, analysis uncertainty is evaluated in consideration of the error increase in the formula for mole fraction determination as presented in Section 7.2. The uncertainty of a single measurement by the error increase method is determined as follows. The sequence of the minimum single analysis is set as CRM'-sample-CRM''. Here, the second CRM analysis result (CRM'') is used for the correction of equipment drift, but is not considered as an error factor for the mole fraction determination.

$$u(C_{sample}) = \left(\frac{R_{corr.}}{R_{CRM}}\right) \times (C_{CRM}) \times \sqrt{\left(\frac{u(R_{sample})}{R_{sample}}\right)^2 + \left(\frac{u(R_{CRM})}{R_{CRM}}\right)^2 + \left(\frac{u(C_{CRM})}{C_{CRM}}\right)^2} \quad (10)$$

- $u(C_{CRM})$: Uncertainty of the certified reference material
- C_{CRM} : Mole fraction of certified reference material
- $u(R_{CRM})$: Standard deviation of the certified reference material
- R_{CRM} : Response value of the certified reference material
- $u(R_{sample})$: Standard deviation of the analysis of the unknown sample
- R_{sample} : Correction response value of the unknown sample ($R_{corrected}$)

Assuming that the uncertainty of the certified reference material is ± 0.013 ppt (0.2%), the analysis uncertainty using the values presented in Table 3 is:

$$u(C_{sample}) = \frac{2086.6}{1962.7} \times 6.432 \times \sqrt{0.0008^2 + 0.0008^2 + 0.002^2} = 0.016 \text{ (ppt)}$$

Thus, the analysis uncertainty of two-point calibration is 0.016 ppt ($\mu\text{mol/mol}$).

8. DETERMINATION OF MOLE FRACTION AND ANALYSIS UNCERTAINTY WITH TWO-POINT CALIBRATION

8.1 Determination of mole fraction with two-point calibration

The two-point calibration method is used under the assumption that the sensitivity of the analysis equipment after the multi-point calibration illustrated in Section 6 is not linear in response to changing mole fractions. The analysis is conducted in the following order: certified reference material 1, an unknown sample, certified reference material 2, and certified reference material 1 again (CRM1-sample-CRM2- CRM1). The procedure of repeated measurements and the method of determining mole fraction and analysis uncertainty are similar to those of the one-point calibration, and the differences are illustrated as follows.

When measured values can be predicted, an example of the selection of reference samples was suggested. If the responses of unknown samples can be predicted, the CRM is determined as the interval values and information on reference uncertainty (reference uncertainty is indicated in the CRM cylinder) is checked. For example, if the mole fraction of the unknown sample is expected to be 7 ppt ($\mu\text{mol/mol}$), the following CRMs are selected.

- CRM1: 6.432 ± 0.013 ppt (uncertainty: 0.20%, $k=1$)

- CRM2: 7.565 ± 0.019 ppt (uncertainty: 0.25%, $k=1$)

Based on the assumption that equipment responses show linearity in a given range of certified reference materials, the following concentration relation formula is used:

$$C_{sample} = C_{CRM1} + (C_{CRM2} - C_{CRM1}) \times \frac{R_{corr.} - R_{CRM1}}{R_{corr.CRM2} - R_{CRM1}} \quad (11)$$

Here, $R_{corr.CRM2}$ is the response of the equipment to certified reference material 2 (CRM2) with the drift corrected.

Assuming that equipment drift is linear with time, $f_{drift}(i)$ can be obtained as follows:

$$f_{drift}(i) = \left\{ \frac{(3 \times R_{CRM1'})}{3 R_{CRM1'} + (R_{CRM1''} - R_{CRM1'})i} \right\} \quad (12)$$

Here, $R_{CRM1'}$ is the average (mean value) of the responses of the certified reference material 1 (CRM1') from the first set of repeated measurements, and $R_{CRM1''}$ (CRM1'') is the average of the responses of the certified reference material 1 from the second set of repeated measurements. Thus, the response of the unknown sample with corrected drift, $R_{corr.}$ ($=R_{corrected}$), and the response of certified reference material 2, $R_{corr.CRM2}$, respectively, are as follows:

$$R_{corr.} = f_{drift}(i) \times R_{sample} \quad (13)$$

$$R_{corr.CRM2} = f_{drift}(i + 1) \times R_{CRM2} \quad (14)$$

If the drift value defined as follows is smaller than the RSD (%) of the subset of repeated measurements, f_{drift} is 1.

$$\text{drift} = \frac{(R_{CRM1''} - R_{CRM1'})}{R_{CRM1'}} \times 100 (\%) \quad (9)$$

8.2 An example of two-point calibration

Table 5. An example of the comparison analysis of two-point calibration of SF₆

Name	CRM1'	Sample	CRM2	CRM1''
Certified mole fraction (ppt)	6.432		7.565	6.432
Response 1	1962.6	2089.2	2307.9	1972.8
Response 2	1964.4	2092.5	2306.7	1972.2

Response 3	1961.2	2090.8	2310.7	1967.1
Mean response	1962.7	2090.8	2308.4	1970.7
Standard deviation	1.60	1.65	2.05	3.13
RSD (%)	0.08	0.08	0.09	0.16
f_{drift}		0.9986	0.9973	
$R_{\text{corrected}}$		2088.0	2302.2	
Drift (%)		-		0.41

Though overall analysis repeatability is 0.10%, equipment drift is 0.41%, thereby requiring a correction against the drift. Thus, the concentration is determined as follows:

$$\begin{aligned}
 C_{\text{sample}} &= C_{\text{CRM1}} + (C_{\text{CRM2}} - C_{\text{CRM1}}) \times \frac{R_{\text{corr.}} - R_{\text{CRM1}}}{R_{\text{corr.CRM2}} - R_{\text{CRM1}}} \\
 &= 6.432 + (7.565 - 6.432) \times \left(\frac{2088.0 - 1962.7}{2302.2 - 1962.7} \right) \\
 &= 6.432 + (1.133) \times \left(\frac{125.3}{339.5} \right) = 6.85 \text{ (ppt)}
 \end{aligned}$$

8.3 Evaluation of analysis uncertainty for two-point calibration

8.3.1 If only considering the analysis repeatability

Same as presented in Section 7.2.1.

8.3.2 If considering the error increase in the two-point calibration formula

If there are few repeated measurements, analysis of uncertainty is evaluated in consideration of the error increase in the formula for mole fraction determination as presented in Section 5. The uncertainty of a single measurement by the error increase method is determined as follows:

$$\begin{aligned}
 u(C_{\text{sample}})^2 &= \left[\left| \frac{R_{\text{corr.}} - R_{\text{CRM1}}}{R_{\text{corr.CRM2}} - R_{\text{CRM1}}} \times (C_{\text{CRM2}} - C_{\text{CRM1}}) \right| \right. \\
 &\quad \times \sqrt{\left(\frac{u(R_{\text{sample}} - R_{\text{CRM1}})}{R_{\text{sample}} - R_{\text{CRM1}}} \right)^2 + \left(\frac{u(R_{\text{CRM2}} - R_{\text{CRM1}})}{R_{\text{CRM2}} - R_{\text{CRM1}}} \right)^2 + \left(\frac{u(C_{\text{CRM2}} - C_{\text{CRM1}})}{C_{\text{CRM2}} - C_{\text{CRM1}}} \right)^2} \\
 &\quad \left. + u(C_{\text{CRM1}})^2 \right]
 \end{aligned}$$

$$\text{Here, } u(R_i - R_j) = \sqrt{u(R_i)^2 + u(R_j)^2} \quad (15)$$

Assuming that the uncertainty of certified reference material 1 (CRM1) is 0.013 ppt ($\mu\text{mol/mol}$, 0.2 %) and certified reference material 2 (CRM2) is 0.019 ppt ($\mu\text{mol/mol}$, 0.25%), the analysis uncertainty using the values presented in Table 1 is as follows:

$$\textcircled{1} \quad \frac{u(R_{\text{sample}} - R_{\text{CRM1}})}{R_{\text{sample}} - R_{\text{CRM1}}} = \frac{\sqrt{1.65^2 + 1.60^2}}{2088.0 - 1962.7} = \frac{2.3}{125.3} = 0.0184$$

$$\textcircled{2} \quad \frac{u(R_{\text{CRM2}} - R_{\text{CRM1}})}{R_{\text{CRM2}} - R_{\text{CRM1}}} = \frac{\sqrt{2.05^2 + 1.60^2}}{2302.2 - 1962.7} = \frac{2.6}{339.5} = 0.0077$$

$$\textcircled{3} \quad \frac{u(C_{\text{CRM2}} - C_{\text{CRM1}})}{C_{\text{CRM2}} - C_{\text{CRM1}}} = \frac{\sqrt{0.019^2 + 0.013^2}}{7.565 - 6.432} = \frac{0.023}{1.133} = 0.0203$$

$$\begin{aligned} \textcircled{4} \quad u(C_{\text{sample}}) &= \sqrt{\left\{ \left(\frac{125.3}{339.5} \times 1.133 \right) \times \sqrt{0.0184^2 + 0.0077^2 + 0.0203^2} \right\}^2 + 0.013^2} \\ &= \sqrt{(0.4182 \times \sqrt{0.00081})^2 + 0.013^2} = \sqrt{0.012^2 + 0.013^2} = 0.0177 \end{aligned}$$

Thus, the analysis uncertainty of two-point calibration is 0.0177 ppt ($\mu\text{mol/mol}$).

9. SUMMARY

These guidelines describe various calibration methods to measure and to analyse SF₆ using GC- μ ECD. In particular, details in Chapters 7 and 8 can be useful in calibrating measurements made not only by μ ECD but also utilizing other detectors for various trace gases.

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