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MEASUREMENT OF SF_6 USING GC-ECD: A COMPARATIVE STUDY ON THE UTILIZATION OF CO_2-N_2 MIXTURE AND CH_4-Ar MIXTURE AS A MAKE-UP GAS

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Abstract. Comparison of 10% CO_2-N_2 and 5% CH_4-Ar gas mixture as a make-up of gas chromatography with electron capture detection (GC-ECD) for the measurement of sulfur hexafluoride (SF_6) was investigated. It was found that 10% CO_2-N_2 shows the make-up characteristic comparable to 5% CH_4-Ar. Thus, 10% CO_2-N_2 is considerable as an alternative to 5% CH_4-Ar.

Keywords: measurement, SF_6, greenhouse gases, GC-ECD, make-up gas.

1. Introduction

Sulfur hexafluoride (SF_6) is a long live greenhouse gas having atmospheric lifetimes of about 3200 years [1]. SF_6 has very high global warming potentials (GWPs) with 23,900 times higher than that of CO_2; thus, SF_6 plays important role in climate forcing [2]. SF_6 rises the temperature of earth because of its ability to trap the heat in atmosphere by which the other greenhouse gas (such as CH_4, CO_2, N_2O) can do so. In general, the presence of greenhouse gases in the atmosphere will affect the earth's climate.

Unlike other greenhouse gases, atmospheric SF_6 is predominantly of anthropogenic origin [3], making SF_6 does not naturally exist in significant concentrations in the atmosphere [4]. The important anthropogenic source of SF_6 emission, in particular, is the use of SF_6 as dielectric and insulating in electric power industry [5]. Besides, SF_6 is also used as a cover gas to protect molten magnesium in magnesium metal production and casting industry [6].

Since the industrial revolution (1750 AD), the atmospheric level of SF_6 has increased from near zero to about 6.8 pmol·mol^{-1} in 2009 [7]. Taking into account the anthropogenic nature of SF_6, the release of SF_6 into atmosphere is probably at low concentration but its contribution to the earth's climate is significant. Because of this, importance has been placed on raising awareness to continue measurement of atmospheric SF_6, by which the measurement data obtained can give meaningful information to track its emission trends and help in the fight against climate change [8].

In the area of SF_6 measurement, several analytical techniques with reliable procedure have been exploited such as those based on gas chromatography (GC) with an electron capture [9], thermal conductivity [10], mass selective detections [4], and atomic emission [10]. Besides spectroscopic technique equipped with infrared detection has also been reported [11]. Up-to-date, however, among all of those quantitative techniques for the measurement of SF_6 in atmospheric sample, the GC equipped with electron capture detector (GC-ECD) stand out and is in worldwide use, employing a low range of detectability [7]. A pretty detectability property of GC-ECD of SF_6 is due to its high molecular electronegativity, allowing an exceptional detection sensitivity and quantification at trace level [4].

In modern chromatography, it is an acceptable idea that a detector development is designated for achieving an optimum performance. In this regards, additional make-up gas before effluent entering the chromatography detector has been widely proven as one of remarkable processes. Nowadays, especially GC-ECD technique, ultra high purity N_2 and 5% CH_4-Ar gas mixture are the two typical gases that are suitable and sufficient to be used as make-up gases in GC equipped with ECD [12]. However, the concentration of target analyte expected is the main factor to be considered in choosing between those two make-up gases. For example, Ussiri *et al.* [13] measured

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anthropogenic N_2O from wetlands sample using GC-ECD. They found N_2 to be a crucial disadvantage for ECD in practice, which restricts its application where ECD could not detect low concentration of N_2O. On the other hand, a possible N_2O detection at the low atmospheric concentration could be achieved by replacing N_2 with 5% CH_4-Ar mixture. As in the most common cases, the addition of a make-up gas is essential to GC operation by adding it into a carrier gas to produce optimum detector response and stability.

In the last decade, study on the development of accurate GC-ECD measurement in term of the use of a new type of make-up gas has been reported by Wang *et al.* [14]. Their results indicated that CO_2-N_2 mixture, as a new type of GC-ECD make-up gas, was comparable to that of 5% CH_4-Ar mixture for N_2O measurement. Recently, Zhang *et al.* [15] reported that the use of CO_2-N_2 mixture as an ECD make-up gas could significantly improve the N_2O signal by 4-fold higher than that of high purity grade of N_2 make-up gas. Regardless improving the accuracy of GC-ECD for N_2O measurement, the use of CO_2-N_2 mixture is tremendous potential as safer and more economical make-up gas than that of 5% CH_4-Ar mixture.

Although CO_2-N_2 mixture has already been used in studies to achieve highly sensitive and accurate GC-ECD make-up gas for N_2O measurement [14, 15], the application of CO_2-N_2 mixture as the make-up gas for the measurement of SF_6 using GC-ECD has not yet been studied. On the other hand, nowadays, GC-ECD has been used to measure SF_6 but it has only limited application on the use of 5% CH_4-Ar mixture as the make-up gas [9]. This paper investigates the potential use of the CO_2-N_2 mixture as an alternative make-up gas to 5% CH_4-Ar mixture for the SF_6 measurement using GC-ECD. The investigations were conducted by comparing those two make-up gases in term of their contribution in affecting the system suitability, precision, accuracy, and linearity as well as limit of detection and quantification (LoD and LoQ) of the GC-ECD analytical method for the measurement of SF_6 at $nmol{\cdot}mol^{-1}$ (equal to part per billion) level.

2. Experimental

2.1. Preparation of Compressed Gases

2.1.1. Make-up gases

The make-up gases for this comparison study were 10% $mol{\cdot}mol^{-1}$ CO_2 in nitrogen (herein after referred to as "CON") and 5% $mol{\cdot}mol^{-1}$ CH_4 in argon (herein after referred to as "CAR"). The compressed CON make-up gas (698 kPa) was in house laboratory prepared by a gravimetric method [16]. CON was prepared in a 10 l of clean and well-evacuated aluminum cylinder with a brass valve. In a typical procedure, the evacuated cylinder was first weighed on an analytical balances (Mettler Toledo, 0.1 g readability) and then with the added of 128 g of an ultra-high purity CO_2 (99.999 %, Air Liquid Indonesia). Following the addition of CO_2, 725 g of ultra-high purity N_2 (99.999 %, Air Liquid Indonesia) was added into the cylinder, giving a final compressed CON having concentration of 10% CO_2 in N_2. The compressed make-up gas CAR was customary purchased from a specialty gases company (Air Liquid Indonesia).

2.1.2. Gas standards

A secondary standard of SF_6 (10 $\mu mol{\cdot}mol^{-1}$) in He was purchased from a specialty gases company (Sarana Indotim Imex, Indonesia). Secondary gas standard is referred to a gas standard that is related to primary standard through analysis. This SF_6 secondary gas standard was used as parent standard to prepare sub-$\mu mol{\cdot}mol^{-1}$ level of SF_6 standard by a gravimetric method [16], giving a final value of 999.46 $nmol{\cdot}mol^{-1}$.

2.1.3. Gas mixture sample

In this study, the gas mixture sample is referred to a compressed gas mixture in a 2.5 aluminum cylinder that was prepared from ultra-high purity gases target by a gravimetric method [16]. The cylinder of gas mixture sample contains not only SF_6 (88.49 $nmol{\cdot}mol^{-1}$) but also contains relatively high concentration ($\mu mol{\cdot}mol^{-1}$level) of other gases including CO (1931.69 $\mu mol{\cdot}mol^{-1}$), CO_2 (2057.28 $\mu mol{\cdot}mol^{-1}$), CH_4 (1727.06 $\mu mol{\cdot}mol^{-1}$), O_2 (227.05 $\mu mol{\cdot}mol^{-1}$), and N_2 (85689.05 $\mu mol{\cdot}mol^{-1}$) with He as a gas balance.

2.2. Instrumentation and Operating Conditions

2.2.1. GC-ECD

The measurement of SF_6 was conducted on an Agilent 7890B GC system equipped with an electron capture detector (ECD, Agilent Technologies, Santa Clara, CA) under operating conditions as listed in Table 1. Separation of SF_6 was achieved using Hayesep Q packed columns (HQ 1.2 m, 3.2 mm OD, UM, Agilent Technology G3591-82519, pre-column) and a Hayesep R packed column (HR 1.8 m, 3.2 mm OD, Agilent Technology, G3591-82102, main column). The carrier gas was purified before entering the column using a hydrocarbon filter (activated charcoal, Agilent Technology, USA).

2.2.2. GC-TCD

The measurement of gas component in their mixture sample was performed using an Agilent 7890B GC system equipped with a single stage dual-packed column for separating the target gas component (CO, CO_2, CH_4, O_2 and N_2) from their mixture. In such dual-packed column, a packed J&W porapack Q column (1.8 m x 3.2 mm o.d. x 2 mm, 80–100 mesh particle size) was connected in series to a packed J&W molsieve 5A column (2.7 m x 3.2 mm o.d. x 2 mm, 80–100 mesh particle size. The detection of gas component was performed by using thermal conductivity detector (TCD). The GC-TCD operating conditions under study were tabulated in Table 1.

2.3. Procedures

2.3.1. GC-ECD measurement

For introducing both gas standard and gas mixture sample from aluminum cylinder into the GC system, a Brooks 5890E mass flow controller (Brooks Instrument, Hatfield, USA) was used in order to maintain the gas rate at constant flow (100 ml·min^{-1}). The mass flow controller system was installed just before the injection system consisted of a stainless steel tubing having 1/16 inch in diameters up to the loop inlet, a 1 ml stainless steel loop (Agilent, CA, USA). The measurement process was conducted under GC parameter as listed in Table 1. The output signal was monitored using installed software (OpenLAB CDS Chemstation Edition Rev. C.01.0727, Agilent Technology, USA), on a HP personal computer (HP ProDesk 490 G2 MT, Hewlett-Packard Company). The measurement data was estimated by automated integration of the area under the resolved chromatographic profile.

2.3.2. GC-TCD measurement

The gas mixture sample was introduced into GC using a similar procedure as in above GC-ECD measurement. The measurement was carried out under operating parameters as tabulated in Table 1. The output signal was monitored by HP personal computer (HP Pavilion Slimline 400 PC series, Hewlett-Packard Company) using an installed software (OpenLAB CDS Chemstation version A.2.3.57). An automated integration of the area under the resolved chromatographic profile was used to estimate the measurement data.

2.3.3. Comparison procedure

In the comparison process, the work was conducted by evaluating the influence of both make-up gases (CON and CAR) on the measurement method parameters including a system suitability, precision, accuracy, and linearity as well as limit of detection and quantification (LoD and LoQ). All data obtained from the SF_6 measurement by using each type of make-up gas were evaluated and the results were compared.

System suitability was evaluated by injecting five replications of the SF_6 standard into the GC-ECD. Profile of generated chromatogram of SF_6 was then evaluated based on the system suitability criteria including retention time (t_R), peak area, peak height, response factor (RF) and peak asymmetric factor (A_s).

Precision of the measurement method was evaluated in term of repeatability (intra-day precision) and reproducibility (inter-day or intermediate precision) [17]. Repeatability of the method was established by measuring the response of the SF_6 gas standard and expressed as a percentage relative standard deviation (%RSD) from five measurement replications. The %RSD is calculated by means of the following expression Eq. (1) [18]:

$$\%RSD = \frac{100}{\bar{y}}\sqrt{\Sigma\frac{(y_i-\bar{y})^2}{(n-1)}} \qquad (1)$$

where y_i is an individual measurement datum expressed as a peak area, $\bar{y}$ is the mean of the peak area value of five repeated injections, and n is the number of injection replication.

Table 1

Operating parameters of GC under study

Operating parameter	GC-µECD	GC-TCD
Aimed gas component	SF_6	CO, CO_2, CH_4, O_2, N_2
Carrier gas flow rate	N_2 at 21.5 ml·min^{-1}	He at 28.0 ml.min^{-1}
Injector temperature	523 K	373 K
Loop	SS tube, 1 ml	SS tube, 0.1 ml
Oven temperature	Isothermal, 345 K	Programmed, 313 K (10 min), 60 K/min, 433 K (8.5 min)
Detector temperature	573 K	523 K
Reference flow rate	–	He at 20 ml·min^{-1}
Make-up gas flow rate	2 ml·min^{-1}	He at 7.0 ml·min^{-1}
Injection mode	Splitless	–
Signal source / data rate / minimum peak width	µECD/5 Hz/0.04 min	TCD / 5 Hz / 0.04 min

The repeatability of the method is categorized acceptable if the %RSD value is less than 0.67 of the coefficient of variability Horwitz (CV-Horwitz) [19]. The CV-Horwitz is a predicted RSD value and it was obtained by using the following Horwitz function Eq. (2) [20]. The lower %RSD value is ascribable to the better measurement repeatability.

$$CV - Horwitz\,(\%) = 2^{(1-0.5\log c)} \tag{2}$$

where c is the concentration of SF_6 standard in a decimal fraction.

Moreover, the measurement precision in term of reproducibility was determined by a similar procedure to that of repeatability except the time interval 60 days was used instead of the same day. The acceptance criteria were set up where the %RSD value is below the CV-Horwitz value. In addition, the assessment of reproducibility was also conducted by setting up a control limit chart. Generally, the chart of control limit chart has five lines which is consisting of one average line (AL), two warning limit (WL) lines, and two control limit (CL) lines. AL represents the mean of the control values. Two WL lines are located at a distance of ± two times the standard deviation (SD) from the AL line (AL ± 2SD), while two CL lines are located at a distance of ± three times SD from AL (AL ± 3SD) [21].

In analytical measurement, accuracy values are dependent on two factors including bias and precision [19]. Measurement bias refers to the difference between the measured value and the value from standard certificate. The bias (Δ) of the GC-ECD method was calculated using Eq. (3).

$$\Delta = \bar{A} - B \tag{3}$$

where $\bar{A}$ and B are the average of measured value and the value from the certificate of SF_6 being measured, respectively.

Moreover, for the assessment of the method precision (σ), the values of repeatability, reproducibility, and uncertainty value from the certificate of reference standard are included. Thus, the value of σ is obtained by combining those three components, giving the following expression Eq. (4) [22].

$$s = \sqrt{SD_b^2 + \frac{SD_w^2}{n} + m_{RM}^2} \tag{4}$$

where SD_b^2 is the standard deviation (SD) from reproducibility; SD_w^2 is SD from repeatability precision, and μ_{RM}^2 is the uncertainty of the SF_6 standard stated in the certificate.

The acceptance criteria are set according to the ISO Guide 33:2000 "Uses of certified reference materials" [23], where no bias of the method is found if the observed bias of the method falls within $\pm 2\sigma$ at 95% confidence level (Eq. (5)).

$$-2s < \Delta < +2s \tag{5}$$

Linearity of the measurement method was assessed by using a calibration curve of a series concentration range of expected analyte [24]. In this study, nine different SF_6 gas standards with known concentration, ranging from 6.65 to 284.79 nmol·mol^{-1} were used. These nine different SF_6 gas standards were prepared from 999.46 µmol·mol^{-1} of SF_6 as a parent standard by a dynamic dilution method using a calibration dilution system (Model CMK, MCZ GmbH, Germany). The calibration curve was constructed by plotting peak area of the SF_6 gas standard as a function of their corresponding concentration. The equations of the calibration lines were calculated by linear regression and the corresponding equation is given by $y = bx + c$, where y is the peak areas values of SF_6, x is the concentration of SF_6, b is the slope and c is the intercept. LoD and LoQ were established at a signal-to-noise ratio (S/N) of 3 and 10, respectively [25, 26]. Response factor (RF) was obtained experimentally by dividing the area of spectral peaks of measured SF_6 with its corresponding concentration [27].

3. Results and Discussion

In this study, effectiveness in the use of CON as a make-up gas alternative to CAR was assessed based on their contribution in affecting the system suitability, precision, accuracy, linearity, and limit of detection and quantification (LoD and LoQ) of the analytical method for the measurement of SF_6 at sub-µmol·mol^{-1} level.

3.1. System Suitability

A system suitability test is an integral part in any measurement study using a gas chromatography method with the purpose to verify that the gas chromatographic system is adequate for the intended measurement. The system suitability tests are extremely valuable and have been accepted in wide application of gas chromatography method because reliable obtained results are based on a wide range of specific parameters [28]. In this study, the GC system suitability was conducted by injecting five replicates of the SF_6 standard (159.2 nmol·mol^{-1}) under the same operating condition except for the type of make-up gas (CON and CAR make-up gas were used). The obtained chromatograms were evaluated using the following criteria including confirmation identity, retention time, peak area, peak height, response factor and peak asymmetry factor. In general, for detecting trace gases using GC, the characteristics of the carrier gas used for the separation and the gas used for detection may be significantly affect the result of measurement. Because the SF_6 standard was measured using different make-up gases, therefore, the ability of those make-up gases to influence the system suitability test parameters were evaluated and the results were compared.

Fig. 1 shows the comparative chromatograms of SF_6 obtained by measuring using GC-ECD with the same operating conditions but different in make-up gas used. From Fig. 1, it was clearly seen that the type of make-up can influence the identity of the chromatogram, especially in term of the chromatogram baseline. The lowest baseline of the GC response was obtained when CAR was used as the make-up gas (b), while CON make-up significantly increased the baseline of the GC response (a). The chromatogram of the SF_6 standard obtained without make-up gas is also included in the inset of Fig. 1 for comparison only, showing its highest baseline of the GC response with the SF_6 chromatogram having a great peak tailing (uppermost line in the inset of Fig. 1). The result implies that the addition make-up gas is essential to the GC operation leading to effect the detector response [13, 29].

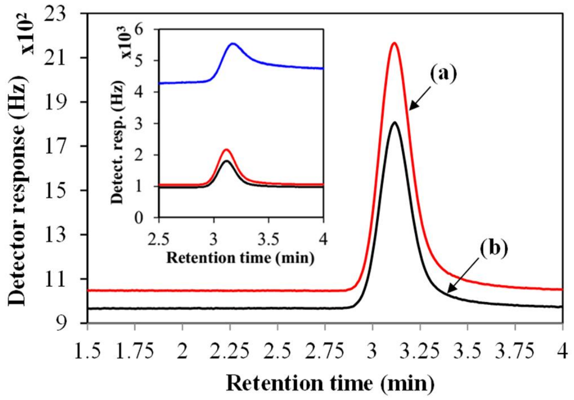

Fig. 1. Typical chromatograms of SF_6 standard (159.82 nmol·mol^{-1}) obtained with CON (a) and CAR (b) make-up gas. The chromatogram of SF_6 standard obtained without make-up gas (uppermost line in inset) is also included for comparison only

Table 2 tabulates other GC parameters for a system suitability test. Data in Table 2 display that the system suitability used in this study is great because all evaluated parameters have the RSD values less than 1.0 %. The retention time of the SF_6 standard was very consistence from run to run (RSD = 0.02 %, *n* = 5) for both CON and CAR are equivalent. Consistency of the retention time obtained indicates that the GC system was free from some factors affecting the measurement such as a column temperature, carrier gas flow rate, and column contamination [29, 30]. Good consistency in term of the peak area obtained under both make-up gases was also attained which are characterized by low RSD values for the SF_6 standard measurement. Although a slightly lower consistency of the obtained peak area using CON make-up gas (RSD = 0.34 %, *n* = 5) than CAR make-up (RSD = 0.15 %, *n* = 5) is observed (Table 2). This good peak area consistency from injection to injection was probably due to a good stability of the GC operating condition during analysis. On the other hand, instability of GC operating parameters (such as oven temperature, flow rate of carrier gas and detector temperature) may cause higher %RSD due to the inconsistency of the obtained peak area [29, 31].

In addition, an optimal consistency was obtained for the peak height of the SF_6 standard (Table 2), giving %RSD values of 0.19 % (*n* = 5) and 0.15 % (*n* = 5) for CON and CAR make-up gas, respectively. Good repeatability of the sample injection could be the reason of this phenomenon [29]. However, the influence of the make-up gas type was clearly found and differs between the two make-up gases where the peak height of SF_6 from CON was higher than that of CAR make-up gas, indicating that the ECD detector was more responsive to CON than CAR make-up gas. Likewise, the calculated response factor from CON (RSD = 0.28 %, *n* = 5) make-up gas was greater than the corresponding response factor from CAR (RSD = 0.19 %, *n* = 5). Theoretically, a response factor is the ratio between the concentration of an analyte being analyzed and the detector response to that analyte [32], meaning that the increase in the peak area of SF_6 would increase its response factor. As it can be seen in Table 2, at the same concentration of SF_6, the obtained peak area of SF_6 using CON (13714.34) is higher than that of CAR make-up gas (9984.72). The higher of obtained peak area using CON would give a higher response factor (85.81) in comparison to that of CAR make-up gas (62.48) and *vice versa.*

Table 2

GC parameter for suitability tests of the method for the SF_6 measurement using different make-up gases

GC Parameter	Make-up gases	
	CON	CAR
Retention time (t_R)	3.11 (*n* = 5, %RSD = 0.02)	3.12 (*n* = 5, %RSD = 0.02)
Peak area	13714.34 (*n* = 5, %RSD = 0.34)	9984.72 (*n* = 5, %RSD = 0.15)
Peak height	1105.12 (*n* = 5, %RSD = 0.19)	824.41 (*n* = 5, %RSD = 0.15)
Response factor (RF)	85.81 (*n* = 5, %RSD = 0.28)	62.48 (*n* = 5, %RSD = 0.19)
Peak asymmetry factor (T)	1.26 (*n* = 5, %RSD = 0.54)	1.18 (*n* = 5, %RSD = 0.37)

Moreover, peak asymmetry factors of the obtained chromatogram for both make-up gases were found identical from injection to injection, giving low %RSD values (Table 2). The peak asymmetry factor of SF_6 chromatogram under CON make-up gas was found to be 1.26 (RSD = 0.54 %, n = 5), that is higher than that of under CAR make-up gas with the obtained value of 1.18 (RSD = 0.37 %, n = 5). From this system suitability study, one can be noticed that the characteristics of the make-up gas used for detection significantly influence the profile of the SF_6 chromatogram profiles (system suitability).

3.2. Precision

For the GC method the measurement precision is one of the critical important parameters to be determined. The precision is the measure of closeness of analyte concentrations to each other when the measurements are conducted under identical conditions (the same method, same sample, same laboratory condition, and the same operator) over a certain period of time [33-35]. In the area of GC measurement for any kind of matrix (liquid and gas), the measurement precision is commonly evaluated in term of repeatability (intra-day precision) and reproducibility (inter-day or intermediate precision) [30, 35].

For repeatability (intra-day precision), the investigation was conducted to assess the closeness between measured values of a number of measurements for a short time period (the same day) [36]. The repeatability for measurement method was verified by injecting the five replicate injections of the SF_6 standard for each concentration level. The repeatability was then predicted by using the %RSD that is theoretically calculated using Horwitz function (Eq. 2) and the results are displayed in Fig. 2. As it can be seen in Fig. 2, the %RSD of the repeatability for both CON (a) and CAR (b) shows an overall gradual decrease as the SF_6 concentration increased. This finding indicates that repeatability performance of the method for measuring the sample would be higher as the concentration of SF_6 standards increased. In a word, the repeatability of measurement for high sample concentration is errorless than another low sample concentration. However, one can be clearly noticed under this study that the repeatability of the method obtained using CON (a) and CAR (b) make-up gas were found to be lower than 0.67 of CV-Horwitz (c), implying that the repeatability of the method is categorized acceptable and precise sufficiently [18, 30, 31]. Thus, conducting a set of measurement to obtain a lower %RSD was not needed because the repeatability of the method is sufficient enough [37]. The reproducibility (inter-day precision) refers to the variability results of a repeated measurement that are obtained with the same test method at different and longer periods [36]. In the reproducibility study to evaluate the effect of make-up gas used, the procedure was similar to that of repeatability except the measurement period where a longer period was conducted instead of the same day. In this study, five repeated measurements at different days (1 and 60 days) were conducted and the results are listed in Table 3. From Table 3, it can be seen that the %RSD values obtained from the measurement using CON and CAR are less than their corresponding CV Horwitz, implying that the reproducibility met the required criterion [18]. However, the %RSD values of the two make-up gases were found to be different, illustrating that the reproducibility performance (%RSD) of the GC-ECD method is obviously affected by the characteristic of the make-up gas used. Moreover, even though the reproducibility method for CON and CAR (Table 3) are acceptable, it was observed that CON make-up gas showed its exceptional reproducibility having the lower %RSD values than the CAR make-up gas. This finding implies that the measurement using CON make-up gas is more reproducible than that of CAR make-up gas. In addition, it is also important to have in mind a concept of fit for the purpose to establish the reproducibility of a GC measurement [30]. Within this concept, controlling the quality of the measurement results is required. Consequently, setting up a control program by using a chart so called the control program chart is important, which remains the most common control program in the area of GC measurement [30, 37].

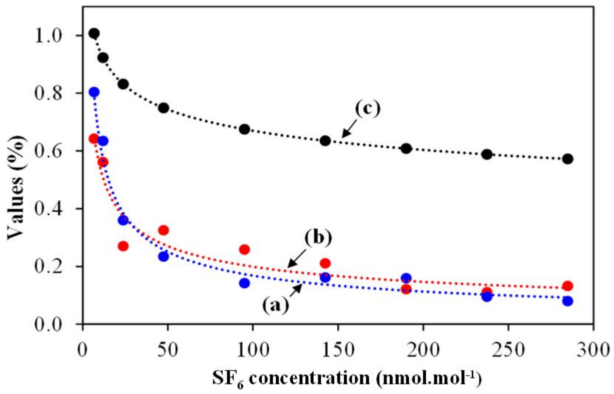

Fig. 2. The %RSD for repeatability of SF_6 standard at difference concentration level obtained using CON (a), CAR (b) as make-up gas, and their corresponding 0.67 of CV-Horwitz (c)

For the evaluation of the control program, the SF_6 concentration used was of 11.87 nmol·mol^{-1}. Fig. 3 displays the chart of control program for the measurement obtained at different days using CON (a) and CAR make-up gas (b). As it can be seen in both figures, the control data values (blue circles) in all periods lie within or inside both the warning limit (dot red line) and control limit (dot blue line). This finding implies that the reproducibility of the measurement method is acceptable. On the other hand, once the control data values fall outside the limit a remedial action must be taken so the source of error can be identified and removed [37].

3.3. Accuracy

Accuracy of a measurement method refers to the closeness or the agreement between the measured and an accepted/true value [33,35]. Practically, the accuracy is a combination of the bias and precision of an analytical procedure [18]. In this SF_6 measurement, the accuracy means the closeness of measured values (known value) of SF_6 in an independent standard cylinder (here in after called SF_6-independent standard) to SF_6 in a series reference standard cylinders (here in after called SF_6-reference standards). Taking into account the repeatability results of precision studies of SF_6-reference standards as discussed above, the accuracy was evaluated against SF_6-independent standard having the concentration of 159.82 nmol·mol^{-1}. For the accuracy assessment, the work was conducted by measuring five repeated injection replication of SF_6-independent standard followed by calculating the bias and precision and the results are tabulated in Table 4. From the Table 4, it can be observed that all bias values of SF_6 from the measurement using CON and CAR as the make-up gas fall within $-2\sigma < \Delta < 2\sigma$. This result indicates that the GC-ECD method using both make-up gas for the SF_6 measurement is accurate because of the given criteria [23]. In a word, no evidence of bias could be found in the method used for the SF_6 measurement, implying that the characteristic of make-up gases had no effect on the method accuracy during the GC-ECD measurement.

Table 3

The %RSD for reproducibility using different make-up gases and their corresponding CV-Horwitz

Day	Make-up gases			
	CON		CAR	
	RSD, %	CV-Horwitz, %	RSD, %	CV-Horwitz, %
1	0.635	1.378	0.562	1.378
60	0.637	1.378	0.638	1.378

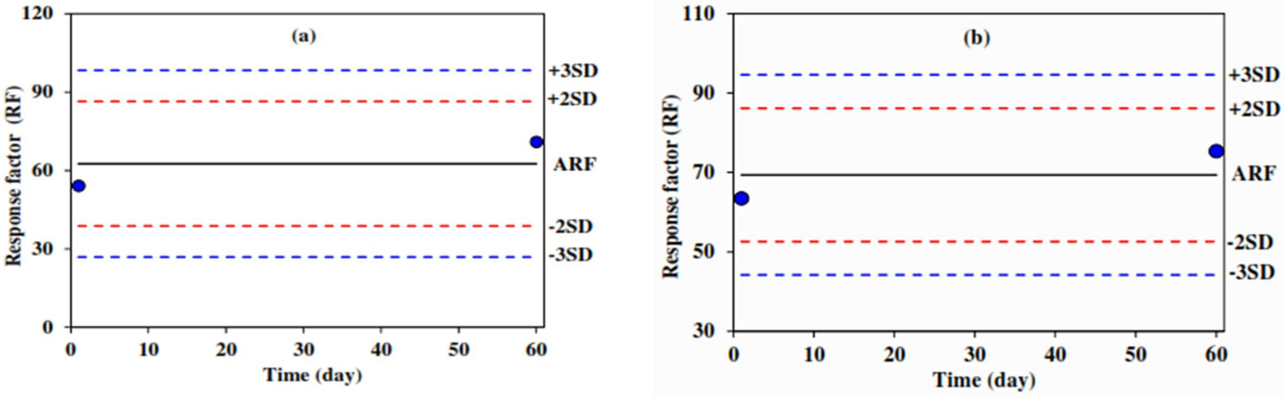

Fig. 3. The chart of control limit for the measurement of SF_6 standard at concentration of 11.87 nmol·mol^{-1} using CON (a) and CAR (b) make-up gas. For interpretation of the references to color in the figure, the reader is referred to the web version of the article

Table 4

Accuracy of GC-ECD using CON and CAR as the make up gas for the measurement of SF_6 and their corresponding sigma values

Parameter	Make-up gases	
	CON	CAR
Bias (Δ, nmol·mol^{-1})[a]	7.76	–7.53
Precision of method (σ, nmol·mol^{-1})	9.38	9.37
$\pm 2\sigma$ (nmol·mol^{-1})	18.75	18.75

Note: [a] All the bias values fall within the acceptance criteria: $-2\sigma < \text{Bias} < +2\sigma$.

3.4. Linearity

Linearity of a method refers to the ability of the method to demonstrate that the test results are proportional to the concentration of analyte being measured [35]. The linearity of the method at different make-up gases was determined by analyzing five replicates of the SF_6 standard at nine concentration levels ranging from 6.65 to 284.79 nmol·mol^{-1}. The peak area of each SF_6 standards was then plotted against the concentration of SF_6 to obtain the calibration curve and the result is displayed in Fig. 4.

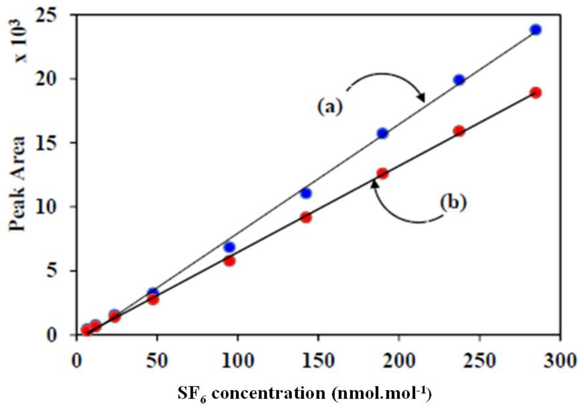

Fig. 4. Linear response of nine SF_6 standards ranging from 6.65 to 284.79 nmol·mol^{-1} for CON (a) and CAR (b) make-up gas

The statistical evaluation results for the method linearity for both CON and for CAR make-up gases are listed in Table 5. From Table 5, it can be found that the correlation coefficient (R^2) for CON make-up gas (R^2 = 0.9940) is slightly lower than that of CAR (R^2 = 0.9994). These results indicate that the linear relationship between the concentration of SF_6 and detector response for GC-ECD measurement using CON as the make-up gas is lower than CAR to some extent.

3.5. Detection and Quantitation Limits (LoD and LoQ)

In every analytical measurement, determination of limit of LoD and LoQ is essential to be conducted because usefulness of a measurement may depend on the appropriate determination for both. LoD is referred to the lowest concentration of an analyte in a sample that can be detected, but not necessarily quantified as an exact value under the stated measurement conditions [35]. The concentration of analyte at LoD is only possible to be determined qualitatively. On the other hand, a quantitative analysis is also possible to be performed at the LoD level; however, it may produce an inaccurate result since the uncertainty contribution is larger than the measurement result itself [18]. Moreover, LoQ is referred to the lowest concentration of an analyte in a sample that can be quantified with appropriate precision and accuracy under the stated measurement conditions, meaning that the minimum concentration of analyte in the sample can be reliably determined by conducting the LoQ evaluation [34, 35]. However, a possible high uncertainty associated with the measurement quantification can be obtained when the values obtained is below the LoQ level, resulting an unreliable results of a measurement. LoD and LoQ of SF_6 were determined using a signal to noise (S/N) ratio method [25]. Based on this S/N method the ratio values of LoD and LoQ are 3:1 and 10:1, respectively. LoD and LoQ were determined from 6.65 nmol·mol^{-1} of the SF_6 standard (as the lowest concentration level among the SF_6 standards used in this study). The calculated LoD and LoQ for the SF_6 measurement using CON as the make-up gas were found to be 0.741 nmol·mol^{-1} (n = 5, %RSD = 0.149) and 2.470 nmol·mol^{-1} (n = 5, %RSD = 0.149). While the calculated LoD and LoQ for the SF_6 measurement using CAR as the make-up gas are 0.514 nmol·mol^{-1} (n = 5, %RSD = 0.155) and 1.714 nmol·mol^{-1} (n = 5, %RSD = 0.155), respectively. By comparison, the calculated LoD and LoQ using CON are higher than those using CAR make-up gas.

3.6. Method Application

The application of GC-ECD method is a subject of great concern in the atmospheric environment science, especially for quantitative measurement of greenhouse gases including SF_6 [9], N_2O [15], hydrofluorocarbons [38], and (HFCs), and perfluorocarbons (PFCs) [39]. These halogenated greenhouse gases have been listed in the Kyoto Protocol and their concentration in the atmosphere have been significantly increased over the past century. In this study, the application of the method was conducted to assess selectivity performance for the SF_6 measurement (88.49 nmol·mol^{-1}) in the presence of other gas components as interferers including CO, CO_2, CH_4, O_2 and N_2 in the gas sample mixture. Table 6 tabulates the concentration of each gas component in the gas mixture sample.

The gas mixture sample was injected (five replications) to the GC-ECD under the same operating condition using different make-up gases. Table 7 shows the measurement results for selectivity evaluation. As it can be observed that the measurement results obtained by the method using CON and those determined using CAR are excellent. This finding was expected from the good methodology comparison given by both CON and CAR obtained as previously discussed in Section System Suitability. Nonetheless, one can be clearly identified from this observation that the selectivity of the method for measurement of SF_6 in a gas mixture sample containing other gas components (Table 7) was found to be similar to that of suitability characteristics from the SF_6 standard (Table 2). Thus, it can be concluded that these measurement results indicated that method is highly suitable for quantitative measurement of SF_6 either in gas standard or gas mixture sample. In general, the measurement method is capable of detecting known and unknown concentration of SF_6 in gas samples and free from interference of other gas components.

Table 5

Linear regression fit data for the measurement of SF_6 using different make-up gases

Parameter	Make-up gases	
	CON	CAR
Linearity range, nmol·mol^{-1}	6.65–284.79	6.65–284.79
Slope (b)	85.073	67.45
Intercept (a)	562.55	287.14
Correlation coefficient (R^2)	0.9981	0,9994

Table 6

Concentration of each gas component in the gas mixture sample

Individual gas component in the gas mixture sample					
SF_6	CO	CO_2	CH_4	O_2	N_2
88.49 nmol·mol^{-1}	1931.69 µmol·mol^{-1}	2057.28 µmol·mol^{-1}	1727.06 µmol.mol^{-1}	227.05 µmol·mol^{-1}	85689.05 µmol·mol^{-1}

Note: All gas components were simultaneously measured by using GC-TCD except for SF_6 the GC-ECD was used

Table 7

Chromatographic parameter for selectivity of the method for measuring SF_6 in the gas mixture sample

GC Parameter	Make-up gases	
	CON	CAR
Retention time (t_R)	3.12 (*n* = 5, %RSD = 0.04)	3.11 (*n* = 5, %RSD = 0.04)
Peak area	6961.79 (*n* = 5, %RSD = 0.21)	5683.92 (*n* = 5, %RSD = 0.11)
Peak height	462.62 (*n* = 5, %RSD = 0.24)	415.44 (*n* = 5, %RSD = 0.18)
Response factor	78.71 (*n* = 5, %RSD = 0.21)	64.21 (*n* = 5, %RSD = 0.11)
Peak asymmetry (T)	1.29 (*n* = 5, %RSD = 0.42)	1.20 (*n* = 5, %RSD = 0.33)

4. Conclusions

For assessing the use of CON as a make-up gas for the SF_6 measurement using GC-ECD in comparison to that of CAR, the analytic method parameters such as system suitability, precision, accuracy, linearity, and limit of detection and quantification (LoD and LoQ) were considered. Measurement proved the CON make-up gas to be suitable for measurement of SF_6 that is comparable to that of CAR make-up gas. Measurement precision applying the two types of make-up gases (CON and CAR) demonstrated a good degree of repeatability and reproducibility. No bias of the method was found, implying that the GC-ECD method using both make-up gases for the SF_6 measurement are accurate. The CON make-up gas gave a good linearity in the SF_6 concentration ranging from 6.65 to 284.79 nmol·mol^{-1} and it was comparable to that of CAR make-up gas. Detection limits of SF_6 from CON and CAR were 0.741 and 0.544 nmol·mol^{-1}, respectively, at 6.65 nmol·mol^{-1} of the SF_6 standard. Application of CON and CAR for GC-ECD technique shows that those two types of make-up gases have been successfully applied to the measurement of SF_6 in gas sample without interference by other gas components in the sample mixture. Consequently, the assessment results presented under given criteria of this study and method application indicate that CON can be utilized as a make-up gas alternative to CAR for the GC-ECD measurement of SF_6 in a routine analysis.

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References

[1] Blasing T.: Recent Greenhouse Gas Concentrations. Oak Ridge National Laboratory. United State Department of Energy. http://cdiac.ornl.gov/pns/current_ghg.html
[2] Fang X., Hu X., Janssens-Maenhout G. *et al*.: Environ. Sci. Technol., 2013, **47**, 3848. https://doi.org/10.1021/es304348x
[3] Santella N., Ho D., Schlosser P. *et al*.: Atmos. Environ., 2012, **47**, 533. https://doi.org/10.1016/j.atmosenv.2011.09.012
[4] Jong E., Macekm P., Perera I. *et al*.: J. Chromatog. Sci., 2015, **53**, 854. https://doi.org/10.1093/chromsci/bmu154
[5] Takase A., Kanoh H., Ohba T.: Sci. Rep., 2015, **5**, 11994. https://doi.org/10.1038/srep11994
[6] Gandara M.: Mater. Technol., 2011, **45**, 633.
[7] Asai K., Tsujimura M., Fantong W. *et al*.: Hydrol. Res. Lett., 2011, **5**, 42. https://doi.org/10.3178/hrl.5.42
[8] Fang X., Thompson R., Saito T. *et al*.: Atmos. Chem. Phys., 2014, **14**, 4779. https://doi.org/10.5194/acp-14-4779-2014
[9] Hall B., Dutton G., Mondeel D. *et al*.: Atmos. Meas. Tech., 2011, **4**, 2441. https://doi.org/10.5194/amt-4-2441-2011
[10] http://kcdb.bipm.org/appendixb/ appbresults/ccqm-k15/ccqm-k15_final_report.pdf
[11] Peng X., Wang X., Huang Y.: Spectrosc. Spect. Anal., 2012, **32**, 1535.
[12] Wells D., Hess P.: Method for Determination and Evaluation of Chlorinated Biphenyl (BPs) in Environmental Matrices. [in:] Barcelo D. (Ed.), Sample Handling and Trace Analysis of Pollutants: Techniques, Applications and Quality Assurance, 1st edn. Elsevier, Amsterdam 2000.
[13] Ussiri D., Lal R., Jarecki M.: Soil Till. Res., 2009, **104**, 247. https://doi.org/10.1016/j.still.2009.03.001
[14] Wang Yi., Wang Yu., Ling H.: Adv. Atmos. Sci., 2010, **27**, 1322. https://doi.org/10.1007/s00376-010-9212-2
[15] Zhang Y., Mu Y., Fang S. *et al*.: J. Environ. Sci. China, 2013, **25**, 547. https://doi.org/10.1016/S1001-0742(12)60090-4
[16] ISO Guide 6142: Gas analysis – preparation of calibration gas mixtures – gravimetric method, 2001.
[17] Basavaiah K., Anil kumar U., Tharpa K. *et al*.: Iran. J. Chem. Chem. Eng., 2009, **28**, 31.
[18] Budiman H., Zuas O.: Periodico Tche Quimica, 2015, **12**, 7.
[19] Taverniers I., Loose M., Bockstaele E.: TrAC-Trend Anal. Chem., 2004, **23**, 535.
[20] Linsinger T., Josephs R.: TrAC-Trend Anal. Chem., 2006, **25**, 1125.
[21] Masson P.: J. Chrom. A, 2007, **158**, 168. https://doi.org/10.1016/j.chroma.2007.03.003
[22] Walker R., Lumley I.: TrAC-Trend Anal. Chem., 1999, **18**, 594.
[23] ISO Guide 33: Uses of certified reference materials, 2000.
[24] Nahid N.: Iran. J. Chem. Chem. Eng., 2002, **21**, 80.
[25] Mcnair H., Miller J.: Basic Gas Chromatography. John Wiley & Sons, Inc, New York 1998.
[26] Shoeibi S., Iman M., Hossein R. *et al*.: Iran. J. Chem. Chem. Eng., 2013, **33**, 21.
[27] Patnaik P.: Analysis of Organic Pollutants by Gas Chromatography. Lewis Publishers, Washington D.C. 1997.
[28] Kupiec T.: Int. J. Pharm. Comp., 2004, **8**, 305.
[29] Barwick V.: J. Chrom. A, 1999, **849**, 13. https://doi.org/10.1016/S0021-9673(99)00537-3
[30] Zuas O., Budiman H.: Hem. Ind., 2016, **70**, 451. https://doi.org/10.2298/HEMIND150315051Z
[31] Zuas O., Budiman H.: Teknol. Indonesia, 2016, **39**, 59.
[32] Kushwah D., Patel H.., Sinha P. *et al*.: E-J. Chem., 2011, **8**, 1504. https://doi.org/10.1155/2011/462364
[33] AOAC. Guide 3: How to meet ISO 17025 requirements for method verification in the analytical laboratory accreditation criteria committee. Association of Official Analytical Chemists. http://www.aoac.org
[34] NATA. Guidelines for the validation and verification of quantitative and qualitative test methods. National Association of Testing Authorities. http://www.nata.com.au
[35] ICH-Guidelines-Q2A, Validation of analytical methods: definition and terminology. (CPMP/ICH/381/95). International Council for Harmonization. http://www.pharma.gally
[36] Budiman H., Hamim N., Zuas O.: Procedia Chem., 2015, **16**, 465. https://doi.org/10.1016/j.proche.2015.12.080
[37] Hovind H., Magnusson B., Krysell M. *et al*.: Internal Quality Control–Handbook for chemical laboratories, NORDTEST Report TR 569, Nordic Innovation Stensberggata, Oslo, 4th edn., Norway 2011.
[38] Sousa S., Bialkowski S.: Anal. Chim. Acta, 2013, **433**, 181. https://doi.org/10.1016/S0003-2670(01)00789-9
[39] Kim H., Yea S., Ro C. *et al*.: Bull. Korean Chem. Soc., 2002, **23**, 301. https://doi.org/10.5012/bkcs.2002.23.2.301

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ВИЗНАЧЕННЯ SF_6 З ВИКОРИСТАННЯМ ГАЗОВОЇ ХРОМАТОГРАФІЇ З ДЕТЕКТОРОМ ЗАХОПЛЕННЯ ЕЛЕКТРОНІВ: ПОРІВНЯННЯ СУМІШЕЙ CO_2-N_2 І CH_4-Ar ЯК ДОПОМІЖНОГО ГАЗУ

Анотація. *Для визначення гексафлюору сульфуру* (SF_6) *досліджено суміші 10%* CO_2-N_2 *і 5 %* CH_4-*Ar як допоміжного газу в газовій хроматографії з детектором захоплення електронів (ГХ-ДЕЗ). Встановлено, що 10%* CO_2-N_2 *можна порівняти з 5 %* CH_4-*Ar і така суміш може бути використана як альтернатива.*

Ключові слова: *вимірювання,* SF_6*, парникові гази, ГХ-ДЕЗ, допоміжний газ.*