EFEITO DA TAXA DE FLUXO DO GAS DE TRANSPORTE E DA TEMPERATURA DA COLUNA SOBRE OS PARÂMETROS DE ADEQUAÇÃO DO CG-DCE PARA A MEDIÇÃO DE SF_6

EFFECT OF CARRIER GAS FLOW RATE AND COLUMN TEMPERATURE ON THE SUITABILITY PARAMETERS OF GC-ECD FOR SF_6 MEASUREMENT

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RESUMO

O teste de adequação do sistema de um CG é essencial para verificar sua adequação para a aplicação pretendida. A CG sempre usa uma temperatura de gás carreador e coluna, o que pode afetar seus parâmetros de adequação. Este estudo tem como objetivo avaliar os efeitos da taxa de fluxo de gás carreador (FLRT) e da temperatura da coluna (CLTP) nos parâmetros de adequação do sistema (SSP) da CG-DCE para medição SF_6 como tempo de retenção / t_R, fator de resposta / RF, número de pratos teóricos / N, e fator assimétrico / As. A avaliação foi conduzida através da análise cuidadosa do cromatograma SF_6 e os dados obtidos foram utilizados para calcular os valores t_R, R, N e As. Verificou-se que o t_R aumenta linearmente (R^2 = 0,9978) aumentando o FLRT, mas diminui linearmente (R^2 = 0,9991) ao aumentar o CLTP. O RF diminui linearmente (R^2 = 0,9939) ao aumentar o FLRT. Curiosamente, o RF foi afetado pelo CLTP com 2ª tendência da ordem polinomial (R^2 = 0,9949). O N aumenta linearmente (R^2 = 0,9404) aumentando o FLRT, mas o N foi afetado pelo CLTP com 2ª tendência da ordem polinomial (R^2 = 0,9769). O As foi encontrado para aumentar ligeiramente com FLRT (R^2 = 0,1288), enquanto o A_s foi afetado pela TC com 2ª tendência da ordem polinomial (R^2 = 0,9778). Estes resultados estão em bom acordo com os estudos anteriores do SSP.

Palavras-chave: *Testes de adequação, cromatografia gasosa, detector de captura de elétrons, detector seletivo, hexafluoreto de enxofre.*

ABSTRACT

System suitability testing of a GC is essential to verify its suitability for intended application. The GC always uses a carrier gas and column temperature, which may impact on its suitability parameters. This study is aimed to evaluate the effects of carrier gas flow rate (FLRT) and column temperature (CLTP) on the system suitability parameters (SSP) of GC-ECD for SF_6 measurement such as retention time/t_R, response factor/*RF*, theoretical plate numbers/*N*, and asymmetric factor/A_s. The evaluation was conducted by carefully profiling the SF_6 chromatogram and the data obtained were used to calculate the t_R, *RF*, *N*, and A_s values. It was found that the t_R increases linearly (R^2 = 0.9978) by increasing the FLRT, but decreases linearly (R^2 = 0.9991) by increasing the CLTP. The *RF* decreases linearly (R^2=0.9939) by increasing the FLRT. Interestingly, the *RF* was affected by the CLTP with 2nd polynomial order trend (R^2=0.9949). The *N* increases linearly (R^2 = 0.9404) by increasing the FLRT but the *N* was affected by the CLTP with 2nd polynomial order trend (R^2 = 0.9769). The A_s was found to increase slightly with FLRT (R^2 = 0.1288), while the A_s was affected by the CT with 2nd polynomial order trend (R^2 = 0.9778). These results are in a good agreement with previous SSP studies.

Keywords: *Suitability tests, gas chromatography, electron capture detector, selective detector, sulfur hexafluoride.*

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INTRODUCTION

Ever since its discovery in early 1900s (Balaban, 2011), gas chromatography (GC) technique has made significant contribution in the field of chemical analysis. High sensitivity, good selectivity, and prominent detectability of the target analyte in a complex sample are predominantly reasons for choosing the GC among other related analytical techniques (Pfannkoch, *et al*., 2005, Wu, *et al*., 2014). In a practical GC experiment, the detection of target analyte in the mixture eluted from the column is conducted by device so called detector. Based on its detectability characteristic, the GC detector is grouped into two main categories i.e., universal and selective detector (Colon and Baird, 2004). The universal detector defines to any detector that able to response a wide range of analytes (chemical compounds), while a selective detector defines to any detector that has an ability to response analytes with specific elemental, molecular, or physical properties (Yuwono and Indrayanto, 2005). The former detector category may include flame ionization detector/FID (universal to carbon-containing analytes) and thermal conductivity detector/TCD (universal to any analytes having difference in thermal conductivity relative to carrier gas) (Deng, Yang et al. 2005, Haskin and Edwards 2013). The later category may include nitrogen phosphorus detector/NPD (detector which selective to nitrogen or phosphorus-containing analytes), flame photometric detector/FPD (selective to certain analytes containing phosphorus or sulfur element), and electron capture detector/ECD (selective to any analytes containing electronegative groups) (Yuwono and Indrayanto. 2005; Basuri *et al*., 2016, Bordagaray *et al*., 2016).

Among the aforementioned detectors, the ECD might be one of the most common used GC's detector and it can be found easily in both government and private laboratories worldwide. The ECD is known very sensitive for the detection of electron-absorbing molecules (with high electronegativity property) such as halogenated analytes, with detection sensitivity near one part per billion (ppb) level (Jin *et al*., 2012; Jong *et al*., 2014). Nowadays, the applications of the GC-ECD for the detection of halogenated-containing analytes have been reported by numerous analytical laboratory practitioners, by which the types of the analyzed sample are originated from diverse areas such as agricultural, soil, water, air and industrial products (Fattahi *et al*., 2007; Banghui *et al*., 2009; HunterJr *et al*., 2010; Yu *et al*.; 2012).

In the last two decades, increasing the GHGs levels in atmospheric is a worldwide concern. The GHGs could possibly increase the global warning effect because its ability to trap the heat in atmosphere lead to increase the climate change phenomenon (Blasing, 2016). Among the GHG species listed in Kyoto Protocol, the SF_6 is probably the longest lifetimes species in atmosphere (ca. 3200 years) with very high global warming potentials (GWPs) at about 23,900 times stronger than CO_2 species and thus plays important role in climate forcing (Fang, Hu et al. 2013, Blasing T.J. 2016). Naturally, atmospheric SF_6 exists in very low concentration (ca. sub-ppb level), owing to its anthropogenic origin (Santella *et al*., 2012; Jong *et al*., 2015). Therefore, the use of a very sensitive detection instrument, such as the GC-ECD, for the detection of the atmospheric SF_6 has been widely applied.

For the GC equipped with any type of detector, its running process is involving the use of both carrier gas and column as mobile phase and stationary phase, respectively. The carrier gas allows for passing through and separating the target analyte molecule on the column. Soundly, therefore, both carrier gas and column conditions may become two distinct factors affecting the separation process. With regards to the effect of carrier gas and column conditions on the GC analytical parameters, some studies have been reported previously. Sevcik (1976) reported that a flow rate difference of the carrier gas induces detector sensitivity on the GC measurement. Scott (1996) and Bebbrecht (1997) identified that the peak height of the GC is highly dependent of the change of column temperature. The effects of general operating conditions of the GC on the measurement parameters has been weel-summarized by Barwick (1999). However, study related to the effect of the operating conditions on the suitability parameter of the GC for a specific target analyte(s) is still promising to be directed.

This paper reports an investigation result on the study regarding the effect of flow rate of carrier gas and column temperature on the suitability parameters of GC-ECD for SF_6 measurement. Four suitability parameters were assessed including retention time (t_R), response factor (RF), theoretical plate numbers (N), and asymmetric factor (A_S). The data obtained may useful for understanding such effect; hence, some actions to reduce the uncertainty of the measurement can be taken for assuring the reliability of the analytical results.

THEORITICAL

2.1. Retention time (t_R)

The chromatography's retention time (t_R), as schematically shown in Fig. 1, is referred to the time required for a molecule of a target analyte to pass through the chromatography column (USP29, 2016). The retention time of the same target analyte may vary from time to time during measurement process due to a number of reasons such as poor column temperature repeatability, poor injection technique, and instability of the carrier gas flow rate (Barwick, 1999).

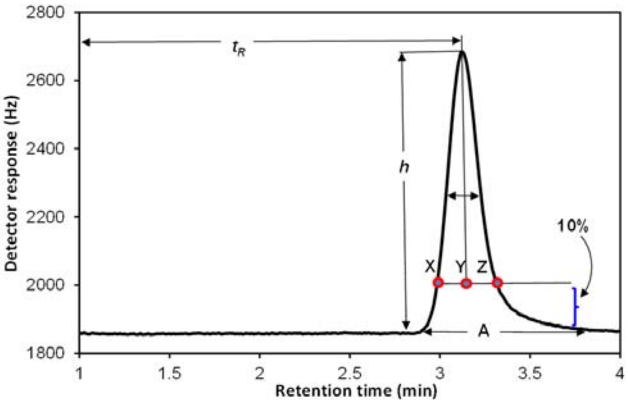

Figure 1. A schematic diagram of a typical GC chromatogram (t_R = retention time, h = peak height, and A = peak area).

2.2. Response factor (RF)

Response factor of the chromatography is a measure of the relative response of target analyte being analyzed compared to its detector response (Dettmer-Wilde and Engewald, 2014). The response of the detector is displayed as a peak. The most common formula to quantify the response factor of a target analyte is expressed as in Eq. 1.

$$\text{Response factor } (RF) = \frac{A}{C} \qquad \text{(Eq. 1)}$$

where A is peak area of the target analyte and C is concentration of analyte being analyzed. In chromatography study, peak area (A) is referred to the area enclosed between the peak and the baseline (Dettmer-Wilde and Engewald, 2014). Experimentally, the target analyte passed through from the column to a detector is measured. The measured analyte in the form of signal is integrated over time. In a modern chromatography system, quantitation is performed by feeding the detector signal into a digital recorder. The recorder produces a typical chromatogram (plot of signal versus time) (Gordon, 2013). The peak area of a target analyte may be determined by integrating manually or automatically, with the beginning and ending points of the peaks are indicated. The peak area (A) of the target analyte (Fig. 1) is calculated by using Eq. 2.

$$\text{Peak area } (A) = h_{max} x W_{0.5} \qquad \text{(Eq. 2)}$$

where h is peak height maxima and W is peak width (See Fig. 1).

2.3. Theoretical Plate Numbers (N)

Chromatography instruments measure the column performance and efficiency in terms of the number of theoretical plates (N)) and it is calculated by using Eq. 3) (McNair and Miller, 2011).

Theoretical plate numbers

$$(N) = 16\left(\frac{t_R}{W}\right)^{0.5} \qquad \text{(Eq. 3)}$$

where t_R is retention time of the target analyte (See Fig. 1). From the formula, it can be estimated that narrower peak widths at longer retention times may result a higher plate numbers.

2.4. Asymmetric Factor (A_S)

Peak asymmetry characteristic of a target analyte being analyzed is highly depended on several factors such as properties of the column, the sample matrix, and the analyte itself. Asymmetry factor (A_S) is defined as the distance from the center line of the peak to the back slope (YZ) divided by the distance from the center line of the peak to the front slope ($XY_{10\%}$), with all measurements made at 10% of the maximum peak height (Fig. 1). The equation for the calculation of A_S is given in Eq. 4 (McNair and Miller, 2011).

$$\text{Asymmetric factor } (A_s) = \frac{YZ}{XY_{10\%}} \qquad \text{(Eq. 4)}$$

where *YZ* is back slope and *XY* is front slope of the analyte peak (See Fig. 1).

MATERIALS AND METHODS

3.1. Preparation of Gas Standard

A secondary standard of SF_6 (158.92 ppb) in Helium (He) as a matrix was prepared from a parent standard SF_6 (10 ppm) purchased from Sarana Indotim Imex Indonesia. The preparation was conducted by the dilution technique in accordance with the ISO Guide: 6142-preparation of gas mixture-gravimetric method (ISO, 2015). Secondary gas standard is referred to a gas standard that is related to primary standard through analysis.

3.2. GC Instrumentation and Operating Conditions

The measurement of SF_6 was conducted by using an Agilent 7890B GS system equipped with an electron capture detector (ECD, Agilent Technologies, Santa Clara, CA) was used. In a typical work, separation of SF_6 was achieved using Hayesep Q packed columns (HQ 1,2 m, 1/8 inch OD, UM, Agilent Technology G3591-82519, precolumn) and a Hayesep R packed column (HR 1.8 m, 1/8 inch OD, Agilent Technology, G3591-82102, main column). Table 1 lists the operating conditions of the GC-ECD under this study. The carrier gas was purified before entering the column using hydrocarbon filter (activated charcoal, Agilent Technology, USA).

Table 1. *Operating conditions of the GC-ECD*

Parameter	GC-μECD
Target analyte	SF_6
Carrier gas flow rate	N_2 at 21.5 ml/min
Injector temperature	250°C
Loop	SS tube, 1 ml
Column temperature	Isothermal, 72°C
Detector temperature	350°C
Reference flow rate	-
Make-up gas flow rate	5% CH_4-95% Ar (2 ml/min)
Injection mode	Splitless
Signal source / data rate / minimum peak width	μECD / 5 Hz / 0.04 min

3.3. System Suitability Test Procedures

For introducing the SF_6 secondary gas standard from aluminum cylinder into the GC system and to maintenance the gas rate at constant flow (100 ml/min), a Brooks 5890E mass flow controller (Brooks Instrument, Hatfield, USA) was used. 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.01.07, Agilent Technology, USA), on a HP personal computer (HP ProDesk 490 G2 MT, Hawlett-Packard Company). The measurement data was estimated by automated integration of the area under the resolved chromatographic profile.

3.4. Evaluation of System Suitability

The data for the system suitability evaluation was obtained by injecting at least five replications of the SF_6 secondary gas standard into the GC-ECD with percentage relative standard deviation (%RSD) was set to 0.5 as a maximum value. Profile of generated chromatogram of the SF_6 from every injection was carefully examined to investigate the effect of both carrier gas and column temperature on the system suitability of GC-ECD. The data obtained were then used to calculate the suitability parameters including retention time (t_R), response factor (*RF*), numbers of theoretical plate (*N*), and asymmetric factor (A_s).

RESULTS AND DISCUSSION

In SF_6 measurement principle, strong electronegative SF_6 molecules in the GC effluent passing through the column and then the SF_6 molecules capture free electrons resulted from a collision between electron emitter (radionuclide ^{63}Ni) and carrier gas molecules. The capturing of the electron reduces the current and it is recorded as a positive peak (AP, 2016). In practice, checking the GC system is extremely importance before conducting a measurement of analyte in samples so that effectiveness of the final operating system can be assured (USP29, 2016).

In this study, checking the system suitability was conducted by examining the effect of operating of the GC-ECD for the measurement of SF_6. For this purpose, the SF_6 standard (158.92 ppb) was chromatographed on Hayesep R packed column. The first experiment was performed by examining the effect of flow rate of carrier gas, followed by the second experiment on investigation the effect of column temperature on the aforementioned suitability parameters. The effects of carrier gas and column temperature on the system suitability parameters investigated are graphically presented and discussed.

4.1. Retention Time (t_R)

Figure 2a and 2b display the dependency of the retention time (hereinafter denoted as t_R) of SF_6 on the flow rate of carrier gas and column temperature, respectively. In the field of GC technique, the flow rate of carrier gas (mobile phase) can be used to indicate how fast the carrier gas is carrying the target analyte through the column, meaning that the lower flow rate of carrier gas will have the longer t_R and vice versa (Dettmer-Wilde and Engewald, 2014). Interestingly, from Fig. 2a it can be clearly observed that the t_R of SF_6 increases linearly (R^2 = 0.9978) by increasing the rate of carrier gas flow, indicating that increased the flow rate would not decrease the t_R of the SF_6. This phenomenon was not found in agreement with previous reports (El-Naggar, 2013; Zuas and Budiman, 2016), where the t_R of carbon-based compounds decreased with increasing the rate of carrier gas flow because a faster flow rate of the carrier gas may decrease the time of vaporized molecules spend in the column. Under experimental condition of this study for the SF_6 measurement, it may attributable to the strong interaction between SF_6 (non-polar molecule) target component and the stationary phase (column), leading to increase the t_R by increasing the flow rate of carrier gas. Nevertheless, in general, the t_R in a GC separation process is controllable, meaning that a suitable t_R for the target analyte can be possibly attained by adjusting the flow rate of carrier gas (Zuas and Budiman, 2016).

Figure 2b depicts the effect of column temperature on the t_R of SF_6. It can be seen from Fig. 2b that the t_R of the SF_6 decreases by increasing the column temperature (R^2 = 0.9991), showing that higher temperature of the column lead to shorter t_R of SF_6. This finding implies that the ability of target analyte to interact with the stationary phase at higher column temperature is lower (Bruner, 1993).

In general, if the compound does not interact with the stationary phase, the t_R will decrease making the component stay in the gas phase but this can result in a poor separation (especially for sample containing multi components). On the other hand, the components should interact with the stationary phase for better separation by which the application of higher column temperature is sometime preferred. Conversely, a low column temperature will cause the entire amount of target analyte to be condensed resulting in poor separation of the target analyte due to a low interaction with the stationary phase (Clark, 2007).

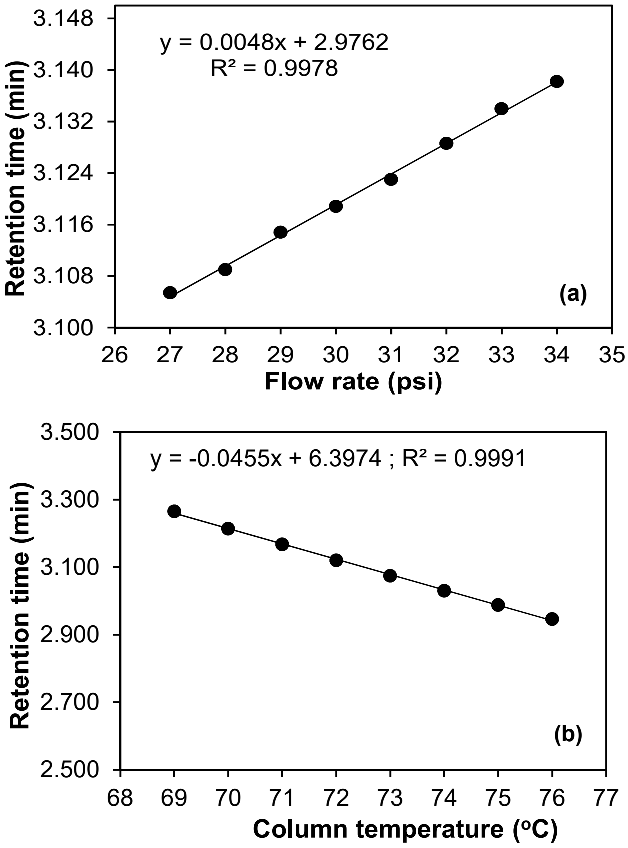

Figure 2. *Graphical dependencies of the t_R on: (a) flow rate of carrier gas, and (b) column temperature for the measurement of SF_6 using GC-ECD.*

4.2. Response Factor (R_F)

Some detector respond to any compound eluting from the column while others respond only compound with category or class of compounds having specific structure, functional groups or atom (Yuwono and Indrayanto, 2005; Basuri *et al.*, 2016). Detectors that exhibit response to specific or class of compounds are called selective detector (Yuwono and Indrayanto, 2005). One is interested in the ability of the selective detector to detect the characteristics of the target compound while reject everything else. For example, electron capture detector (ECD) can be very selective to halogen-containing compound (Jin *et a*l., 2012). Likely, the response of the gas components that reach the ECD in the GC instrument is similar to other detector types, which is proportional to their size of a spectral peak. Besides the detector response is dependent on the individual target gas component (Dettmer-Wilde and Engewald, 2014). Thus, determination of the response of a gas component in term of its response factor (hereinafter denoted as *RF*) for a specific detector is highly recommended.

In the GC technique, the *RF* is defined the ratio between the concentration of an component being analyzed and the response of the detector to that component (Botana, 2015).

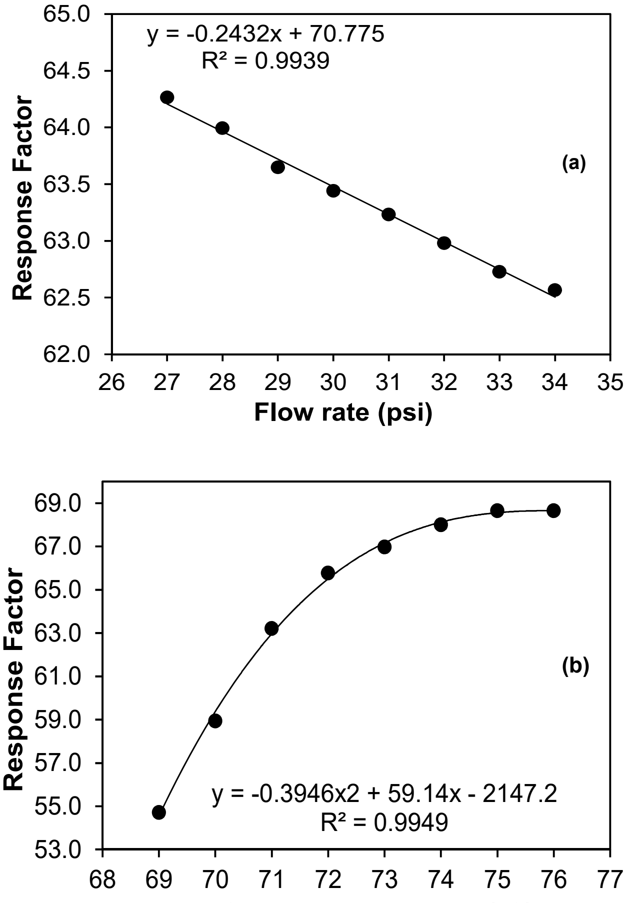

Figure 3. *Graphical dependencies of the RF on the flow rate of carrier gas (a) and column temperature (b) for the measurement of* SF_6 *using GC-ECD.*

The *RF* of GC technique can be obtained by measuring a known quantity of component and determining the relevant peak area. The *RF* of component being analyzed is dependent on the GC operating parameters such as flow rate of carrier gas and column temperature (Onuska and Karasek, 2012). These facts imply that the *RF* of individual component have to be firstly evaluated experimentally. Figure 3a and 3b present plot of *RF* of SF_6 as a function of the carrier gas flow rate and column temperature, respectively. From Fig. 3a, it can be observed that the *RF* of the SF_6 was found to be decrease linearly (R^2 = 0.9939) by increasing the flow rate of carrier gas. The response of GC detector is highly proportional to the concentration of component being analyzed, where increase the flow rate can dilute the target component (Cazes, 2005), which may further lower the *RF* and then decrease the response factor.

Moreover, plot of the *RF* of SF_6 as a function of column temperature is depicted in Fig. 3b. Figure 3b clearly confirms that increasing the column temperature up to 72°C leads to a significant increase in *RF* of the SF_6 component. However, when the column temperature was greater than 73°C, the *RF* of SF_6 increases slowly. The trend of the *RF of* SF_6 was found to be second order of polynomial (R^2 = 0.9949).

4.3. Number of Theoretical Plate (N)

Theoretical plate numbers (hereinafter denoted as *N*) in gas chromatography is defined as a hypothetical zone in which two phases of a substance (the liquid and vapor phases) establish an equilibrium with each other (Bruner, 1993). Generally, the *N* in a column can be used to indicate how well the column to separate similar analytes; thus, the *N* is commonly used to index the columns performance or column efficiency (Gordon, 2013), and it can be calculated using the Eq. 3. The Eq. 3 explicitly implies that the *N* is highly correlated with the GC instrument resolution, meaning that changing in the *N* values may influence the instrument's resolution (Dettmer-Wilde and Engewald, 2014). Figure 4a presents a graphical dependency of the *N* on the flow rate of carrier gas. From this figure, it can be clearly seen that the *N* values increase slowly with increasing the flow rate of carrier gas. Taking into account the *N* definition as in the Eq. 3, it is noticeable that changes in the retention time and peak width may impact to the *N* values of the GC. Increase in the peak width of the target analyte at constant retention time would decrease the *N* values, while increase the retention time at a constant peak width lead to increase the *N* values. In accordance with the Fig. 4a, one can be expected that increasing the *N* values of the GC for the measurement of SF_6 might be probably due to increase the retention time (see Fig. 1a) rather than decrease in peak width of the SF_6. Because of the *N* value of the GC-ECD for measurement of SF_6 (Fig. 4a) increased with increasing the flow rate (R^2 = 0.9404); therefore, the efficiency of the column performance of the GC-ECD for SF_6 measurement is better at higher than lower flow rate of the carrier gas. In general, high column efficiency in a GC is beneficial to obtain a complete narrow peak which requires less peak separation (Sherma and Zweig, 2013). In practice, however, the column efficiency is highly dependent on many GC operating parameters such as column dimensions (diameter, length and film thickness), the type of carrier gas and its flow rate, as well the compound and its retention time (Bruner, 1993; Dettmer-Wilde and Engewald, 2014).

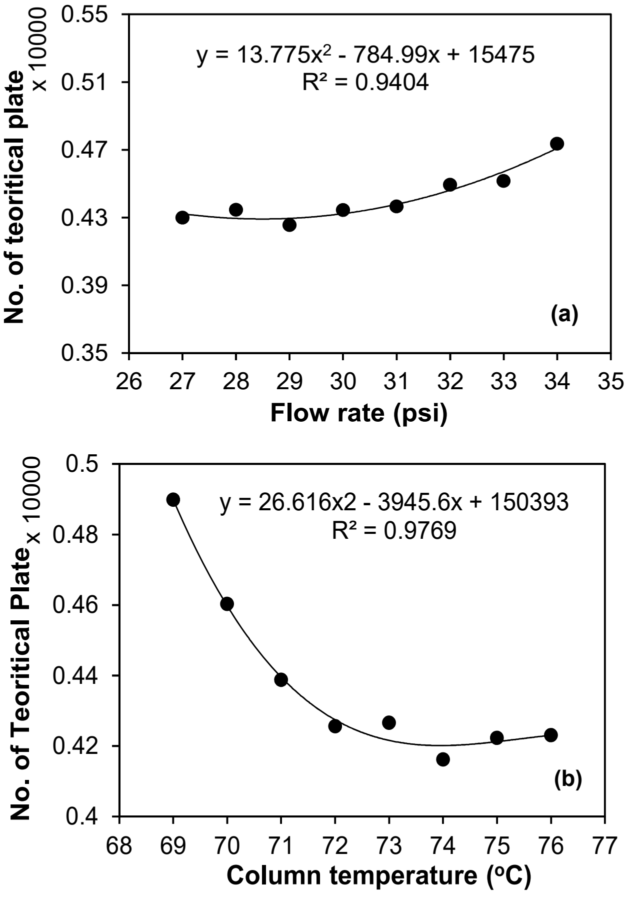

Figure 4. *Graphical dependencies of the N on the flow rate of carrier gas (a) and column temperature (b) for the measurement of SF_6 using GC-ECD.*

Figure 4b displays a graphical trend regarding the *N* values at different column temperature for the measurement of SF_6. As it can be seen for Fig. 4b the *N* value of the GC significantly decrease with increasing the column temperature up to 72°C and then decreasing slowly. This finding indicates that the effectiveness of the column for the SF_6 measurement decreases with increasing the column temperature because higher column temperature contributes to the faster elution (shorter retention time) of the SF_6. This phenomenon is in agreement with the Fig. 2b, where the SF_6 retention time decreased with increasing the column temperature. Decreasing the trend of the *N* values of the GC-ECD for the SF_6 measurement was found to be a second order of polynomial (R^2 = 0.9769). An isothermal temperature condition of GC column is required since the *N* value is only valid for a certain temperature point. On the other hands, changes in the temperature of GC column would result in highly inflated, leading to change the *N* value (Rood, 2007; Hubschmann, 2015).

4.4. Asymmetry Factor (A_s)

Asymmetric factor (hereinafter denoted as A_s) or tailing factor is a measure of peak tailing of a target analyte being analyzed (McNair and Miller, 2011). In an ideal condition, any chromatographic peaks should be characterized by symmetric (or Gaussian peaks) shape. Experimentally, asymmetric (or tailing) of the GC peak may frequently found due to GC operating condition such as instrument dead-volume, adsorptive effects of the stationary phase, and the quality of the column packing (Rotzsche, 1991; Dettmer-Wilde and Engewald, 2014). Figure 5 shows the effect varying flow rate of carrier gas and column temperature on the A_s for the measurement of SF_6 by using GC-ECD.

As can be seen in Fig. 5a, any increase in the flow rate of carrier gas gave a small change on the A_s of SF_6 peaks (R^2 = 0.1288) in comparison to other suitability parameters as discussed above. The curve was tend to form a flat shape, indicating that the flow rate of carrier gas has very small effect on the A_s of SF_6 peaks. The values of A_s at all points of flow rate were found to be slightly higher than the acceptance value and gave asymmetric of SF_6 peaks. An acceptable value of A_s should be in the range of 0.9-1.2, meaning that the tailing factor would apparent if the A_s value exceeds 1.2 (Cazes, 2004; Dettmer-Wilde and Engewald, 2014).

Moreover, Figure 5b shows the effect of column temperature on the A_s of SF_6 peak measured using GC-ECD. The A_s of SF_6 peak was found to be increase slightly by increasing the column temperature up to the first 71°C, after that any increase in column temperature makes decrease in the A_s of the SF_6, giving a trend which follows a second order of polynomial (R^2 = 0.9778). This finding implies that the column temperature has an effect on the A_s value of SF_6, where the A_s value of SF_6 peak can be difference (decrease or increase) at any point of column temperature. This phenomenon might be correlated to the temperature dependency of the stationary phase to adsorb the SF_6, indicating that the value of A_s for SF_6 measurement can be obtained by altering the column temperature at a certain point.

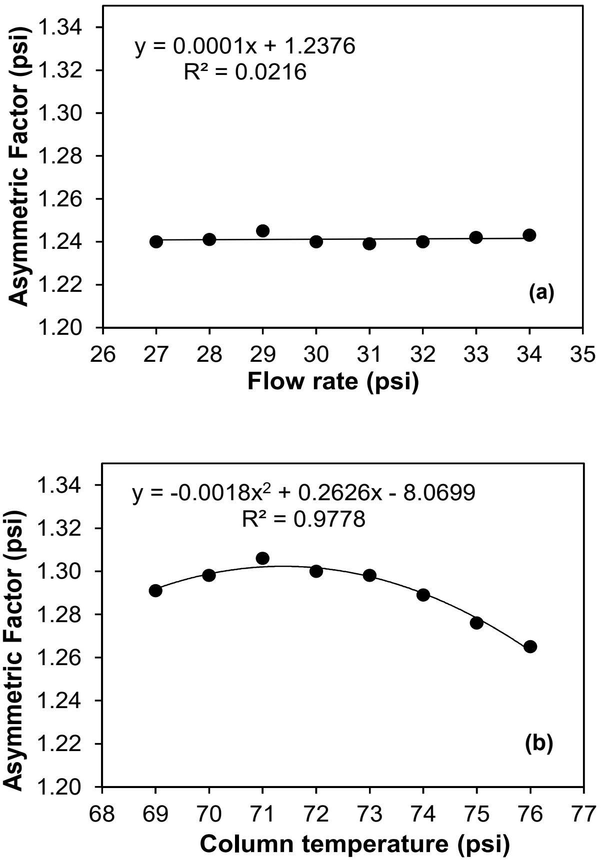

Figure 5. *Graphical dependencies of the A_s on the flow rate of carrier gas (a) and column temperature (b) for the measurement of SF_6 using GC-ECD.*

CONCLUSION

Study the effect of carrier gas flow rate and column temperature on the system suitability parameters of GC-ECD for the measurement of SF_6 has been successfully conducted. The effects of flow rate and column temperature on the parameters of the system suitability tests of the chromatography method might be characterized by the interaction properties between SF_6 as non polar compound and the stationary phase (column). An important conclusion from this study that investigation regarding the effect of operating condition on the system suitability tests of chromatography method is crucial as an initial step for any chromatographic method application.

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