GC with FI and PDHID detection for trace impurity analysis in bulk gases: a comparative evaluation

Oman Zuas 1, Muhammad Rizky Mulyana and Harry Budiman
Gas Analysis Laboratory, Metrology in Chemistry Research Group, Research Centre for Metrology-Indonesian Institute of Sciences (Pusat Penelitian Metrologi – LIPI), Kawasan PUSPIPTEK, Building 456, Kelurahan Setu, 15314, Tangerang Selatan, Banten, INDONESIA

E-mail: zuas.oman@gmail.com

Abstract. Some experimental problems challenge the users when using a GC equipped with FID or PDHID detector in the context of trace level impurity analysis in ultra high purity bulk gases. In this study, a comparative evaluation of GC-FID and GC-PDHID is conducted based on both author’s experiment and literature review in terms of two technical aspects i.e., imitation and capability. Findings shows that both GC-FID and GC-PDHID reflect capability aspect through a pretty detection sensitivity and quantification at trace level of the impurity compounds. Regarding detectability range of compounds, the GC-FID has relatively lower than the GC-FID since the FID responds to only hydrocarbon-type impurity compound, while PDHID can detect almost any compound, except neon. In case of limitation aspect for these two instruments, detectable range of target compounds and operating cost are remarkable. In addition, in context of operating cost and maintenance, however, the FID is relatively inexpensive in comparison to that of PDHID. Besides aforementioned technical aspects, other capabilities and limitations of both FID and PDHID are also evaluated and compared.

1. Introduction
Analysis of trace level impurities in bulk gases is a crucial. Ultra-high purity of bulk gases are important to satisfy the needs of application in many areas such as medicine, agriculture, fuels, semiconductor, and other manufacturing industries. The quality of bulk gases may have a direct impact during gas application processes as well as the quality of end products [1-3]. Nowadays, numerous quantitative analytical instruments for the analysis of trace impurities in bulk gases are available. Among other instruments, gas chromatography (GC) attracts much attention and has been world widely used. In a practice, the GC is commonly equipped with a detection device to respond the analyte emitted from the column so called detector[4]. Since it was firstly invented, the detector has been continuously developed to increase its response capability for achieving an optimum performance. To date, many type of detectors are employed with their capabilities and limitation. In this context, among others, flame ionization detector (FID) and pulse discharge helium ionization detector (PDHID) have been successfully applied[5, 6]. However, choosing a GC equipped with a proper detector which suits users in their analysis purpose is always a continuous issue. In this paper, we report a comparative evaluation of FID and PDHID that are commonly employed in trace impurities in bulk gases.

1 To whom any correspondence should be addressed.
2. Experimental Methods

2.1. Materials and Instruments
In this study, one aluminum gas cylinder containing eight different gas components (CO, H₂, Ar, O₂, N₂, CH₄, and CO) in He balance was prepared in house by the gravimetric method in accordance with ISO 6142 [7]. The concentrations (in ppm) of CO, H₂, Ar, O₂, N₂, CH₄, and CO in the prepared cylinder are 8.61, 3.94, 3.89, 4.15, 9.10, 3.94, 8.66, and 9.73, respectively. For the analysis of those all gas components, the following two different GC instruments were used i.e., a GC (7890B series, Agilent Hewlett Packard, USA) equipped with flame ionization detector (FID)-methanizer, and a GC (7890B, Agilent Hewlett Packard, USA) equipped with Pulsed Discharge Helium Ionization Detector (PDHID)

2.2. GC analytical Procedure
The GC-FID-methanizer analyses of gas component were conducted by adopting our previous publication [2]. The gas sample was introduced into GC system a constant of the sample flow rate (100 ml/min) and injected into a 2 mL sample loop as an injection line. The gas components were separated using a stainless steel packed column (Porapak Q, 6 feet, 1/8” outer diameter, Agilent Technology). The column oven was programmed temperature (the initial temperature was 40 °C-hold for 3.5 min, followed by ramping up 80 °C/min to 140 °C-hold for 4.5 min). The temperature of detector and methanizer were set at 250 °C and 375 °C. An ultra-high purity of He (99.999%) was used as a carrier gas. The FID gases used were H₂ and air at flow rate of 50 and 400 ml/min, respectively. For the GC-PDHID method, the analyses were conducted by following a procedure adopted from literature[8]. In short, the gas samples (40 ml/min) were injected into the GC system through injection line (1 ml stainless steel loop) with split ratio of 1:1. The temperature of column oven was programmed (the initial temperature was 40 °C-hold for 6.5 min, followed by ramping #1 down 100 °C/min to 30°C-hold for 8.4 min), followed by ramping #2 up 6 °C/min to 75°C-hold for 0 min, and then by ramping #3 up 12 °C/min to 160°C-hold for 0 min. The Separation of the gas components from their mixture were performed using two stainless packed columns that were parallel installed (column 1: Pora PLOT Q, 50 m × 530 µm × 20 µm and column 2:Molsieve 5A, 50 m × 530 µm × 20 µm).

2.3. Comparison Method
The comparative evaluation between GC-FID-methanizer and GC-PDHID were conducted based on both author’s experiment and literature review in terms of two technical aspects i.e., limitation and capability of those two GC methods. The limitation aspect of those two GC was evaluated based on detectability range of impurities and their operating cost. Moreover, for their capability aspect, the evaluations were emphasized on the ability of the GC methods to quantify based on the following parameters such as GC system suitability, repeatability, limit of detection (LoD), limit of quantification (LoQ), and linearity. All those parameters were determined by adopting procedure in our previous works [2, 4, 9].

3. Results and Discussion

3.1. Limitation Aspect
In the analysis of chemical compound using GC-FID and GC-PDHID, detectable range and operating cost are very common limitation aspect. Figure 1(a) and Figure 1(b) show chromatogram separation of gas components from their mixture obtained by using GC-FID-methanizer, and GC-PDHID, respectively. From Figure 1(a), it can be seen that detectability range of GC-FID is relatively lower than the GC-PDHID. From seven components in the gas mixture, the GC-FID was only able to detect three component (CO, CO₂, and CH₄), as shown in Figure 1(a). Lower detectability range of GC-FID than the GC-PDHID is reasonable because FID is a specific detector which responds to only hydrocarbon-type impurity compound[2]. In contrary to GC-FID, from Figure 1(b), it can be observed that the GC-PDHID...
was able to detect all seven compounds in gas mixture. It has been well recognized that PDHID as a general type of detector can detect any compound, except neon [10]. The PDHID is a general type GC detector utilizing a low powered and stable pulse discharge in helium as an ionization source [11]. In context of operating cost and maintenance, however, the FID is relatively inexpensive in comparison to that of PDHID. Both GC-FID and GC-PDHID use helium as carrier gas with low helium consumption (less than 30 ml/min). However, GC-PDHID requires ultra high purity of helium (99.9995% purity or higher) to give optimum performance for analysis, while GC-FID only requires lower purity of helium (99.999% purity). A high purity requirement of helium lead to increase cost, where the cost of helium with 99.9995% purity can be three folds of helium with 99.999% purity. The PDHID also experiences to spend higher cost maintenance than GC-FID because GC-PDHID requires more frequently in replacing expensive filter of carrier gas.

3.2. Capability Aspect

In general, an integral part of any GC analysis is system suitability test. The system suitability test is conducted to verify the whole GC system so that the GC is adequate for a specific analysis [12]. This system suitability test has been applied many any previous GC analysis and accepted as a reliable method due to its ability to provide consistent analysis results [2, 4, 9]. The GC system suitability test was conducted by evaluating chromatogram of the injected gas sample using confirmation identity parameter. For GC which is equipped with different detector for detecting trace components may produce significant different of analytical data. The FID and PDHID are two different GC detector, meaning that they are also probably possess different characteristic. From Figure 1, it was clearly observed that the identity of chromatogram was significantly affected by the type of detector used. As can be seen in both chromatograms, the baseline of GC-FID, as shown in Figure 1(a) was found much lower than the baseline of GC-PDHID, as shown in Figure 1(b). The lower baseline (closer to zero) make easier to identify a target component, mainly for GC system used to determine of trace components. Target component at trace level cannot usually be identified due to covered by a high baseline. Thus, by comparison, Figure 1 confirms that the GC-FID was found to be more suitable than that of GC-PDHID for the analysis of the gas components under this study, especially for CO, CO\(_2\), and CH\(_4\). Table 1 shows the data of evaluation parameters such as repeatability, limit of detection (LoD), limit of quantification (LoQ), and linearity for comparing the capability between GC-FID and GC-PDHID. One can be noticed in the capability evaluation under this study, the evaluation is only conducted for three gas components (CO, CO\(_2\) and CH\(_4\)) because these three gas component are able to be detected by both GC used. While
the remain four gas component (H₂, Ar, O₂, and N₂) were not used for comparison evaluation because they were only detected by GC-PDHID.

**Table 1.** Parameter (repeatability, LoD, LoQ, and linearity) for the capability evaluation of GC-FID and PDHID.

| Gas component | Repeatability* | LoDb | LoQc | Linearity (R²) |
|---------------|----------------|------|------|----------------|
|               | FID  | PDHID | FID  | PDHID | FID  | PDHID | FID  | PDHID |
| CO            | 0.36 | 1.24  | 0.15 | 0.12  | 0.458| 0.78  | 0.999| 0.996 |
| CO₂           | 0.81 | 0.93  | 0.45 | 0.04  | 1.463| 0.14  | 0.999| 0.994 |
| CH₄           | 0.54 | 0.69  | 0.12 | 0.09  | 0.377| 0.35  | 0.998| 0.997 |

*in % relative standard deviation (%RSD) of seven sample injection

b in part per million (ppm)

c in part per million (ppm)

Repeatability of the GC measurement is refered to the closeness between measured value of number repeated measurements using same equipment, same condition and same operator in a short period[4]. Repeatability is a very common indicator to verify good performance of an analytical instrument, implying a good consistent analysis results. From Table 1, it can be seen that GD-FID has a lower %RSD in comparison to that of GC-PDHID, meaning that the GC-FID is more repeatable than GC-PDHID for measurement of CO, CO₂ and CH₄. Low repeatability of the GC-PDHID indicates its instability [6]. The LoD and LoQ are two very important parameter to evaluate the performance of an analytical instrument, which is indicate the abality of the instrument to low concentration of target component. The lower LoD and LoQ values, the better capability. The LoD is defined as the lowest concentration of a target component that can be detected by an instrumen [2, 4, 13], while the LoQ is defined as the lowest concentration of a target component in a sample that can be quantified by an analytical instrument under an optimum operating conditions[2, 4]. From Figure 1, it can be clearly observed that both LoD and LoQ of the GC-PDHID are lower than the GC-FID. Lower of LoD and LoQ of the GC-PDHID indicates that the GC-PDHID has a higher capability in detection of target component at trace level, meaning that the GC-PDHID is more sensitive than GC-FID [6]. Moreover, another parameter to evaluate the performance of an analytical instrument is linearity. The linearity of an analytical method is defined as the ability of an analytical instrument to demonstrate that the test results are proportional with the concentration of the component being measured[4, 13]. The linearity of both GC-FID and GC-PDHID were estimated by analysing seven replicates of the target gas component, and the results are shown in Table 1. From Table 1, it can be observed that the coefficient correlation (R²) for GC-FID is slightly higher than that of GC-PDHID. Lower R² values of the GC-PDHID than GC-FID indicates that the linear relationship between the concentration of target component and detector response for GC-PDHID is lower than GC-FID [2]. A similar phenomenon was found and reported in our previous work (4) for SF6 analysis using two different make-up gas [4].

**4. Conclusion**

In conclusion, characteristic of GC-FID only to respons hydrocarbon-type compound limits its capability while GC-PDHID is able to respond wide range of compounds. Although the PDHID requires high operating cost and maintenance. Moreover, evaluation results indicates that GC-FID is better than that of GC-PDHID for capability parameter under this study (repeatability, LoD, LoQ, and linearity). Although GC-PDHID is remarkable good in sensitivity, however, the GC-PDHID does not suite for routine work because of its instability and high operating cost.

**5. Acknowledgement**

The authors acknowledged the Government of the Republic of Indonesia for financially supporting this work through the National Priority Program of LIPI with SK Ka. P2 Metrologi-LIPI No.: B-056/A/JI.1/2018.
6. References

[1] Miricioiu M., Niculescu V, Zgavarogea R, Petrenau I., and Nechifor G 2015 15th International Multidisciplinary Scientific GeoConference SGEM 2015 126.

[2] Budiman H, and Zuas O 2017 Sci. Study & Res. Chem. & Chem. Eng., Biotechnol., Food Ind. 18 259.

[3] Kaminski M, Jastrze D, and Kaminski MM 2003 J. Chrom. A. 989 277.

[4] Zuas O, Budiman H, and Hamim N 2017 Chem. & Chem. Technol. 11 420.

[5] Wentworth W.E. Cai H. and Stearns S 1994 J. Chrom. A, 688 (1–2) 135.

[6] Roberge MT, Finley JW, Lukaski HC, and Borgerding AJ 2004 J. Chrom. A. 102719.

[7] GUIDE, I. Guide 6142:2015(En) - Gas analysis -preparation of calibration gas mixtures-part 1: Gravimetric method for class I mixtures. Geneva, Switzerland.

[8] Hindayani A, Zuas O, Mulyana MR, and Budiman H, Styarini D, Krismastuti FSH, Sirenden B H. Presented on Internation Conference on Physic and Its Aplication 9th (9th ICOPIA), Solo, Centre of Java, Indonesia, August 14. 2018.

[9] Zuas O, Mulyana MR, Hamim N, and Budiman H 2017 J. Eng. Exact Sci. 3 381.

[10] VICI 2003 Pulsed Discharge Detector Model D-4-I-VA38-R Instruction Manual, Valco Instruments Co. Inc. Source: https://www.vici.com/support/manuals/d4_var.pdf. Accessed on 01 July 2018.

[11] VICI, 2018, Pulsed Discharge Detector Models D-3-I-HP and D-3-I-7890 Instruction Manual. Source: https://www.vici.com/support/manuals/d3_hp.pdf. Accessed on 25 June 201.

[12] Kupiec T 2004. Int. J. Pharm. Comp. 8 305.

[13] ICH-Guidelines-Q2A, Validation of analytical methods: definition and terminology. (CPMP/ICH/381/95). International Council for Harmonization.