JPPIPA 6(2) (2020)

Jurnal Penelitian Pendidikan IPA

Journal of Research in Science Education

http://jppipa.unram.ac.id/index.php/jppipa/index

Implementation of ISO 6142- *Gas Analysis - Preparation of Calibration Gas Mixtures - Gravimetric Method*: Composition Determination and Uncertainty Estimation of Gas Reference Material

Muhammad Rizky Mulyana[1], Harry Budiman[1], Oman Zuas[1*]

[1]Center for Research and Human Resources Development, National Standardization Agency of Indonesia, Kawasan PUSPIPTEK Gedung 420, Setu, Tangerang Selatan, Banten 15314, Indonesia

DOI: 10.29303/jppipa.v6i2.444

Article Info
Received : May 26th, 2020
Revised : June 30th, 2020
Accepted: July 10th, 2020

Abstract: Reference material plays an important role in determining the validity of measurement results based on SNI ISO/IEC 17025: 2017. In order to obtain a valid and accurate composition, the standard procedure for making gas reference material has been regulated in ISO 6142. Thus, this article will discuss in detail about the determination of the reference material composition along with its uncertainty based on ISO 6142. Starting with the results of a precise weighing, the concentration of each component of the gas reference material is determined gravimetrically and verified by analytical methods, one of which is gas chromatography (GC). The concentration uncertainty of each component is a combination of the contribution from repeatability of the weighing results, the uncertainty of the composition of the gas raw material, the molecular mass of the gas component, and the total uncertainty of the reference material verification. It is hoped that the detailed discussion in this article can improve the competence of stakeholders in the field of gas measurement in determining the composition of gas reference material concentrations and estimating uncertainty.

Keywords: Gas reference material; uncertainty evaluation; ISO 6142.

Citation: Mulyana, M.R., Budiman, H., & Zuas, O. (2020). Implementation of ISO 6142- *Gas Analysis - Preparation of Calibration Gas Mixtures - Gravimetric Method*: Composition Determination and Uncertainty Estimation of Gas Reference Material. *Jurnal Penelitian Pendidikan IPA (JPPIPA)*. 6(2). 221-226. doi. https://doi.org/10.29303/jppipa.v6i2.444

Introduction

Reference Material (RM), is a material made and verified by certain procedures resulting in a valid and traceable composition. Through a series of certification processes by an accredited institution or company, the reference material can be referred to as a Certified Reference Material (CRM). It plays an important role in determining the quality of measurement or testing results based on SNI ISO/IEC 17025: 2017 - "General Requirements for Competence of Testing Laboratories and Calibration Laboratories". Any kind of measurement method must be validated and calibrated using traceable reference material prior to utilization in routine testing (Badan Standardisasi Nasional, 2017).

This rule applies to all kinds of measurements, including those related to gases such as air quality, greenhouse gases, vehicle emissions, and many others, in which the validity is determined by the quality of the gas CRM used. It became of great importance to various local testing laboratories related to gas measurement, both government or privately owned, in order to meet the accreditation requirements of SNI ISO/IEC 17025: 2017. A number of local companies have gained the capability to produce their own gas CRMs, although with a relatively limited number of

Email: oman@bsn.go.id

components and concentration levels. Therefore, in order to fulfill the domestic requisite for gas CRMs in Indonesia, the gas metrology laboratory at National Standardization Body (BSN), formerly a sub-division under the Indonesian Institute of Sciences (LIPI), has begun to develop the primary gas RM. It requires international recognition which could be gained through inter-laboratory comparisons between countries (Zuas et al., 2019).

In order to obtain a valid and accurate composition value, the procedure of gas RM production has been described in ISO 6142 - "Gas Analysis - Preparation of Calibration Gas Mixtures - Gravimetric Method". It begins from the selection and testing of cylinders as a container of the gas RM up to the determination of the composition value and its uncertainty. It also stated that the cylinder must be made of a material that will not be involved in any kind of chemical reaction with the gas components inside. Any chemical reaction should also not occur between each component in the mixture of gas RM. This requirement must be fulfilled in order to obtain an accurate concentration value of the gas RM (International Organization for Standardization, 2002a).

Moreover, ISO 6142 regulates the determination of gas RM concentration value. In this case, there are three main factors affecting the concentration value of the gas component, which are: the weighed mass of each gas components in gas RM mixture, the concentration of each gas components in their parent gases used as raw materials, and the molecular mass of each gas components. Thus, the total uncertainty of the gas RM composition is a combination of uncertainty contributions from all of these factors (Mulyana, Budiman, Zuas, & Darmayanti, 2018).

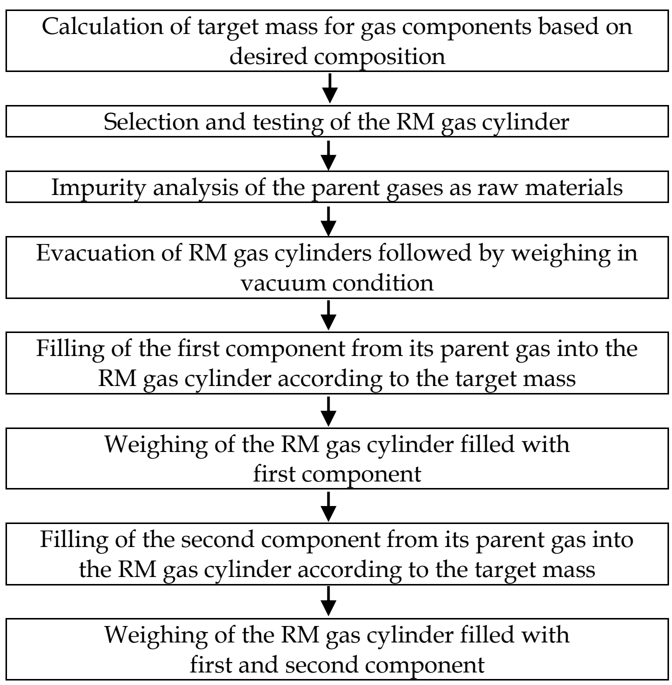
Uncertainty from weighed mass of the gas component, which was obtained from a series of repetitive weighing processes, can be estimated as a source of Type A uncertainty. Another source of Type A uncertainty is parent gas impurities data which can be analyzed at the laboratory. If there is no applicable impusity analysis in the laboratory, the composition of each gas component in the parent gases and their uncertainties can be cited from the provider's certificate. It can be considered as a Type B source of uncertainty (Mulyana et al., 2018). Lastly, the molecular mass of each gas components and their uncertainties can be cited from certain literatures, one of the main examples is the International Union of Pure and Applied Chemistry (IUPAC) database. By this way, it can be considered as a source of Type B uncertainty (Wieser et al., 2010).

For the next step, the calculated composition of the gas RM must be verified using the procedure described in ISO 6143 - "Gas analysis - Comparison methods for determining and checking the composition of calibration gas mixtures" (International Organization for Standardization, 2002b). This process should be considered as another additional contribution to the uncertainty of the gas RM composition. It must be estimated and included in the total combined uncertainty. As a side note, CRMs can only be produced and certified by institutions or companies accredited with SNI ISO 17034: 2016 - "General Requirements for Competence of Reference Material Producers" (Badan Standardisasi Nasional, 2016). The CRMs can be used as a tool of quality control in the testing laboratory in order to comply with SNI ISO/IEC 17025: 2017, if all of the standard requirements have been fulfilled.

In summary, the accurate concentration composition and its uncertainty based on ISO 6142 is a determining factor for the quality of a gas RMs. It will be discussed by detail in this article, which is expected to improve the stakeholders' competence in determining the gas RM composition and estimating its uncertainty. Therefore, domestic needs related to gas measurement can be fulfilled as more government and private agencies are becoming competent in producing their own gas RMs.

Method

In general, the steps of a gas RM production can be seen in Figure 1. At the gas metrology laboratory, each of these steps, from the selection and testing of the cylinder up to the determination of the composition and its uncertainty, has been carried out in accordance with standard procedure that refers to ISO 6142.



↓

Filling of the third component (or more, if applicable) from its parent gas into the RM gas cylinder

↓

Weighing of the RM gas cylinder filled with first, second, and third component (or more, if applicable)

↓

Homogenization of the gas RM mixture in the cylinder followed by calculation of its composition

↓

Verification of the gas RM composition using a validated method

↓

Short-term stability testing

↓

Estimation of the combined uncertainty

Figure 1. The steps of gas RM production (Mulyana & Zuas, 2017)

For the first step, ISO 6142 has stated that the surface of the cylinder used to contain the gas RM should not react with the components inside (International Organization for Standardization, 2002a). Polished aluminum cylinders can be used for gas RM composed of inert components. However, a suitability test must be done in order to ensure that there is no reaction between the inner wall of the cylinder and the components of the gas RM, or between one gas component and another in the mixture (Mulyana, Zuas, & Budiman, 2017).

In addition, the pure parent gases which will be used as raw material for the gas RM should also be tested for its purity. The composition of relevant impurities inside the parent gases should be measured as well. For this purpose, instruments such as gas chromatography equipped with a pulsed discharged helium ionization detector (GC-PDHID) can be used in inert pure gases testing (Mulyana, Budiman, Zuas, & Hindayani, 2019).

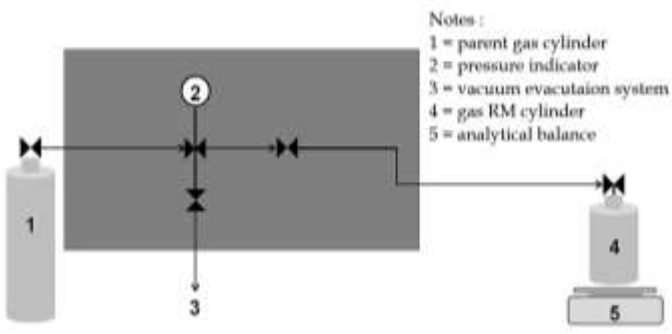


Figure 2. Schematic of gas RM filling system in BSN (Mulyana et al., 2018)

For the filling of the gas component from the parent gases into the gas RM cylinder, the filling system shown in Figure 2 has been used at the gas metrology laboratory. Stainless steel tubing with inner surface mirrors was selected in order to prevent contamination in the system. Moreover, tube flushing and evacuation must be done to ensure that there is no gas component left in the system.

The mass of the gas components filled into the RM cylinder has to be weighed accurately. At gas metrology laboratory, it can be done using a mass comparator with high precision. Determination of the gas RM concentration composition can be done using these weighing results of each gas component, which is known as the gravimetric method (International Organization for Standardization, 2002a; Mulyana & Zuas, 2017).

The gas RM composition which was calculated by the gravimetric method should be verified using a validated analytical method. In this case, gas chromatography with a thermal conductivity detector (GC-TCD) and a flame ionization detector equipped with a methanizer (GC-FID-methanizer) has been used at gas metrology laboratory (Zuas et al., 2019). The short-term stability of the gas RM should also be tested using similar analytical method. As the final step, all uncertainty factors that contribute to the value of the composition of the gas RM must be identified and estimated as a combined uncertainty.

Result and Discussion

As previously mentioned, there are three main factors in determining the gas RM composition and its uncertainty. These three factors are the main variables in Eq. 1, which has been accepted globally in the form of ISO 6142, to calculate the concentration of a gas component i in a gas reference material.

$$x_i = \frac{\sum_{A=1}^{P} \left(\frac{x_{i,A} \cdot m_A}{\sum_{i=1}^{n} x_{i,A} \cdot M_i} \right)}{\sum_{A=1}^{P} \left(\frac{m_A}{\sum_{i=1}^{n} x_{i,A} \cdot M_i} \right)} \tag{1}$$

In Eq. 1 above, x_i represents the concentration of component $_i$, and P for the amount of parent gases used. Meanwhile, n is the number of components in the gas RM mixture, m_A is the mass of parent gas $_A$ which has been transferred into the gas RM cylinder, M_i is the molecular mass of component $_i$, and $x_{i,A}$ is the

concentration of component $_i$ in parent gas $_A$ (International Organization for Standardization, 2002a; Mulyana et al., 2018). The three main factors in Eq.1 discussed in this study are:
- mass of gas component transferred into the cylinder, m_A
- the concentration of the gas component in the pure gas raw material, $x_{i,A}$
- the molecular mass of each gas component, M_i.

Mass of the transferred gas component in gas RM cylinder can be calculated using the results of the weighing. One set of weighing repetition must be carried out each time one gas component is transferred from its parent gases to the gas RM mixture, as listed in the steps in Figure 1. The weighing is done by comparing the sample cylinder to the reference cylinder with similar material and dimensions. In this regard, the mass of transferred gases are equal to the weight difference before and after the filling of each gas component into the cylinder, after subtracted by the weight of the reference cylinder. The gas metrology laboratory at the National Institute of Metrology China (NIM China) has developed an equation that can be used to calculate the mass of the transferred gas components as shown in Eq. 2 below:

$$m_A = e(\Delta w_A - \Delta w_{A-1}) + K\Delta P\rho_{air} + \delta V\rho_{air} + \Delta L \quad (2)$$

In Eq. 2, m_A is the mass of the gas component $_A$ in the cylinder, e is the calibration factor or linearity of the mass balance, Δw_A is the mass difference between sample cylinder and the reference cylinder after the filling of component $_A$ into the cylinder, while Δw_{A-1} is the mass difference of the reference material cylinder and cylinder reference before the filling of component $_A$ into the cylinder (Wang, Zhou, & Zhao, 2008). As for the other factors such as ΔP which is the pressure change in the cylinder, K which is the cylinder volume expansion coefficient, δV which is the volume variation caused by the temperature difference, and ΔL as the lost or added mass due to dust, exfoliation, and many other random factors can be mitigated by taking extra care to the environment and the cylinder condition (Mulyana et al., 2018).

Another significant factor in determining the gas RM composition is the concentration of each gas component in their respective parent gases. This can be obtained as the results of parent gas impurity testing, also shown as a step in Figure 1. If the gas RM is a single-component mixture, for example, carbon dioxide (CO_2) in the nitrogen (N_2) matrix, thus the concentration of CO_2 and N_2 in both CO_2 parent gas and N_2 parent gas become the two relevant impurities that must be taken into account. If the gas RM consists of two target components in a matrix, each of the three relevant impurities in three-parent gases must be taken into account, and so on. Alternatively, the concentration of relevant impurities in the pure gases stated in the certificate given by the provider or a competent testing laboratory can be used if impurity analysis could not be carried out due to the laboratory limitations (Mulyana et al., 2018).

As for the molecular mass of the gas component, which is also a major factor in determining the gas RM composition, the value can be obtained from acceptable literatures. In this case, a database from the International Union of Pure and Applied Chemistry (IUPAC) can be used as a valid source to find out the molecular mass of each gas component.

At the final step, uncertainty of the gas RM composition has to be estimated as a combination of all the contributing factors from each source of uncertainty. Therefore, it is necessary to identify the sources of uncertainty which could affect the concentration of gas components.

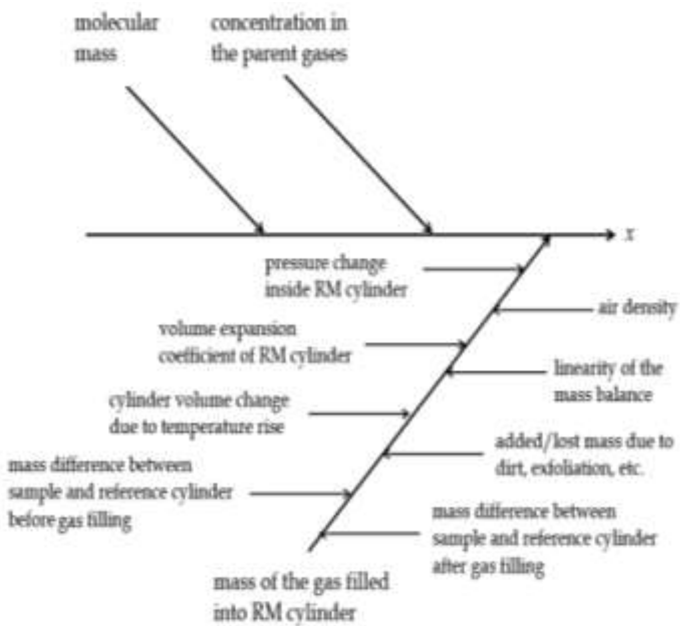


Figure 3. Fishbone diagram of gravimetric uncertainty sources (Mulyana et al., 2018)

Based on Equation 1 for the gravimetric method, uncertainty of gas component concentration x came from three determinant factors as shown in the fishbone diagram in Figure 3. The first one was the molecular mass of the gas component. In certain literatures, such as databases from IUPAC, the molecular mass of each gas component are listed along with their uncertainty values (Wieser et al., 2010). These can be quoted as a contribution to the combined uncertainty of gas component concentration x. In this regard, it can be classified as Type B uncertainty (Mulyana et al., 2018).

The next contribution of uncertainty came from the mole fraction, or concentration, of the gas component in the parent gases. As explained in the previous chapter, there are a number of relevant impurities that must be quantified in every single cylinder of parent gas. If the concentration of these relevant impurities were obtained from the results of own-laboratory analysis, then the uncertainty of the analytical method itself must be included as a Type A uncertainty contribution to the combined uncertainty. In the gas metrology laboratory, this is a combination of the repeatability of the parent gas sample analysis, the repeatability of the standard gas analysis used for calibration, and the uncertainty stated at the calibration standard gas certificate (Mulyana et al., 2019). It has also been described previously that the concentration of relevant impurities in parent gases and their uncertainties can be quoted from the provider or other testing agency through the certificate of analysis. In this regard, it can be classified as a Type B uncertainty source (Mulyana et al., 2018).

The last uncertainty contribution studied here came from the mass of the gas component which has been transferred into the cylinder. It arose from the weighing process, which involves several other uncertainty sources as shown in Figure 3. As described in previous chapter, some of these sources can be minimized by maintaining the filling environment conditions and gas weighing in a clean and constant state. Added or lost mass due to dirt and exfoliation can be minimized by keeping the cylinder of the reference material clean, using special gloves in handling it, and avoiding rough impact between the cylinder and other object. The linearity factor can be quoted from the calibration certificate of the mass balance as Type B uncertainty source, which is a constant value. Thus, there are two main factors left which contribute to the combined uncertainty of gas RM composition. These are the mass difference between sample cylinder and reference cylinder before the filling of gas component into the cylinder; and the one after the filling. Both of their uncertainty came from the weighing repeatability, which is a source of Type A uncertainty (Milton, Vargha, & Brown, 2011; Wang et al., 2008).

All of the various factors mentioned above must be taken into account in the determination of gas RM composition and its uncertainty. The three main factors affecting the composition of gas components, along with their sources and types of uncertainty, are summarized in Table 1.

Tabel 1. The main factors in the determination of gas RM composition and their uncertainty sources

Factor/variable	Significant uncertainty sources	Type of uncertainty sources
Mass of each gas components filled into the RM cylinder	Repeatability of the weighing process	Type A
Concentration of each gas components in the parent gases	Repeatability of the impurity analysis, or Certificate of analysis from the provider or accredited testing labs	Type A or Type B
Molecular mass of each gas components	Valid literature or database	Tepe B

Conclusion

By referring to ISO 6142, the calculation of the factors discussed in this article has been prescribed in the standard procedure for gas RMs production at the gas metrology laboratory in BSN. This procedure is based on previous studies and has been applied in international laboratory comparisons (Budiman, Mulyana, & Zuas, 2017). Surely this procedure is not an absolute method that is applicable for every gas RMs producer, due to the difference of environmental conditions between each laboratory. Therefore, it is suggested for stakeholders in the field of gas measurement to take different approaches in determining the composition of their gas RMs and estimating the uncertainties, by taking the factors discussed in this article into account.

Reference

Badan Standardisasi Nasional. (2016). *SNI ISO 17034:2016 – "Persyaratan Umum Kompetensi Produsen Bahan Acuan."* Jakarta: Badan Standardisasi Nasional.

Badan Standardisasi Nasional. (2017). *SNI ISO/IEC 17025:2017 – "Persyaratan Umum Kompetensi Laboratorium Pengujian dan Laboratorium Kalibrasi."* Jakarta: Badan Standardisasi Nasional.

Budiman, H., Mulyana, M. R., & Zuas, O. (2017). Toward their uncertainty estimation Gravimetric Dilution of Calibration Gas Mixtures (CO 2 , CO , and CH 4 in He Balance): Toward Their Uncertainty Estimation, *020056*. https://doi.org/10.1063/1.4973183

International Organization for Standardization. (2002a). ISO 6142 - "Gas Analysis - Preparation of Calibration Gas Mixtures - Gravimetric Method." *International Organization for Standardization*. https://doi.org/10.1017/CBO9781107415324.004

International Organization for Standardization. (2002b). ISO 6143 - "Gas analysis - Comparison methods for determining and checking the compposition of calibration gas mixtures." *International Organization for Standardization*. https://doi.org/10.1017/CBO9781107415324.004

Milton, M. J. T., Vargha, G. M., & Brown, A. S. (2011). Gravimetric methods for the preparation of standard gas mixtures. *Metrologia*, *48*(5), R1–R9. https://doi.org/10.1088/0026-1394/48/5/R01

Mulyana, M. R., Budiman, H., Zuas, O., & Darmayanti, N. T. E. (2018). Ketidakpastian Pengukuran: Evaluasi, Sumber-Sumber dan Kontribusinya dalam Pembuatan Bahan Acuan Campuran Gas (N2O dalam Matriks N2) Secara Gravimetri. *Jurnal Standardisasi*, *20*(1), 19–32.

Mulyana, M. R., Budiman, H., Zuas, O., & Hindayani, A. (2019). Trace impurities measurement in ultra-high purity gases and their uncertainties: Case study on permanent gas impurities in pure nitrogen. *Journal of Physics: Conference Series*, *1153*(1). https://doi.org/10.1088/1742-6596/1153/1/012035

Mulyana, M. R., & Zuas, O. (2017). Penentuan Komposisi Gravimetrik Bahan Acuan Gas Biner dan Estimasi Ketidakpastiannya. *Buletin Metrologi Kimia Indonesia*, (1), 51–60.

Mulyana, M. R., Zuas, O., & Budiman, H. (2017). Studi Pengujian Kontainer Bahan Acuan Gas (Berbentuk Silinder): Kasus Gas CO2 dalam N2 Matriks. In *Pertemuan dan Presentasi Ilmiah Kalibrasi, Instrumentasi dan Metrologi (PPI KIM) ke-43* (pp. 104–114).

Wang, D., Zhou, Z., & Zhao, Y. (2008). Uncertainty Calculation of Gas Mixture Prepared by Gravimetric Method. In *6th Workshop of APMP/TCQM Gas Analysis Working Group*. Daejeon.

Wieser, M. E., Holden, N., Coplen, T. B., Böhlke, J. K., Berglund, M., Brand, W. A., … Zhu, X.-K. (2010). Atomic weights of the elements 2011 (IUPAC Technical Report). *Pure and Applied Chemistry*, *83*(2), 2012. https://doi.org/10.1351/PAC-REP-10-09-14

Zuas, O., Mulyana, M. R., Budiman, H., Hindayani, A., Styarini, D., Herwahyu Krismastuti, F. S., & Sirenden, B. H. (2019). Development of metrology for gas analysis at the Research Centre for Metrology-Indonesian Institutes of Sciences. In *IOP Conference Series: Materials Science and Engineering* (Vol. 536). https://doi.org/10.1088/1757-899X/536/1/012006