MEASUREMENT OF NITROUS OXIDE IN A NITROGEN MATRIX USING GAS CHROMATOGRAPHY WITH MICROELECTRON CAPTURE DETECTION: VALIDATION OF ANALYTICAL METHOD

O. ZUAS¹, M. R. MULYANA¹, N. HAMIM², H. BUDIMAN¹

¹Gas Analysis Laboratory, Metrology in Chemistry Research Group, Research Centre for Metrology, Indonesian Institute of Sciences (RCM-LIPI)

²Electrochemistry Laboratory, Metrology in Chemistry Research Group, Research Centre for Metrology, Indonesian Institute of Sciences (RCM-LIPI)

E-mail: oman.zuas@lipi.go.id

ABSTRACT: Atmospheric nitrous oxide (N_2O) as one of the most potent greenhouse gases significantly contributes to the global warming effect. Therefore, an accurate and valid measurement method for monitoring its environmental release is of great importance. In this study, an analytical method for the measurement of N_2O in a nitrogen (N_2) matrix using gas chromatography and microelectron capture detection (GC- μ ECD) has been validated. The analytical method was validated in terms of some performance parameters such as system suitability, precision (repeatability and reproducibility), linearity, limit of detection (LoD) and limit of quantitation (LoQ), accuracy and method robustness. The results show that the GC system was found to be suitable for the measurement of N_2O in the N_2 matrix. The repeatability and reproducibility of the method were found to have %RSD of 1.42 and 0.71, respectively, indicating that the method is repeatable and reproducible for N_2O measurement. The linearity of the method was excellent, having the R^2 value of 0.9998. The LoD and LoQ of the method were found to be 0.10 and 0.34 $\mu\text{mol mol}^{-1}$, respectively. Evaluation of method accuracy showed that the method is also accurate for the measurement of N_2O in the N_2 matrix. The method's roughness indicated that the method was quite stable and unaffected by slight changes in the experimental conditions. From this study, it can be concluded that the validated method can be used in testing laboratory for internal quality assurance programs purposes related to the measurement of N_2O in N_2 matrix.

KEYWORDS: Nitrous oxide; Method validation; Gas chromatography; Electronic capture detector.

1. INTRODUCTION

The concentration of nitrous oxide (N_2O) in atmosphere has reached to about 398.55 nmolmol^{-1} (equivalent to part per billion) in 2014 and tend to increase, where 40% of that amount was originated from anthropogenic activities such as agriculture, transportation, and industries (Anderson et al., 2010). The N_2O is one of the most potent greenhouse gases and its

atmospheric lifetime is about 150 years (de Miranda et al., 2015). The N_2O has very high global warming potentials (GWPs) at about 298 times relative to CO_2 and significantly contribute to the earth's climate (Ermolaev, 2015; Komiya et al., 2010). In this regards, accurate data obtained by a valid measurement method for monitoring the environmental release of the N_2O to decrease its forcing on global warming effect is of great importance.

For the measurement of N_2O , a number of analytical technique having reliable procedure have been reported such as those based on chromatographic (with electron capture, thermal conductivity, atomic emission, and mass selective detections) and spectroscopic (infra-red, laser absorption, and cavity ring-down) (Akdeniz et al., 2009; Teodoru et al., 2015; Vardag et al., 2014; Wang, 2012; Zhang et al., 2013). Among others, gas chromatography equipped with micro-electron capture detector (GC- μ ECD) is an obvious method and widely used, employing a range of detectability. Besides, the GC- μ ECD has low operational cost compared to other methods.

Regardless its tremendous capacity over other methods, a practical application of the GC- μ ECD to provide accurate and reliable results for the N_2O measurement has created a need to re-assess the measurement practice of testing laboratories. Owing to the fact that a good laboratory practice for the testing laboratories as the basis for accreditation assessment complying with ISO/IEC 17025 is important. According to ISO/IEC 17025, a reliable and accurate result can only be obtained by using a validated method (BSN, 2008). Method validation is a part of quality assurances to declare that a high quality of analytical result is provided (Budiman and Zuas, 2015). In general, method validation refers to a documented procedure used by a laboratory to ensure that the method performance for the determination of particular analyte meets the required criteria (EURACHEM, 2014).

In this paper, the study results from validation of analytical method of GC- μ ECD for the measurement of N_2O in N_2 matrix were evaluated. The evaluation was emphasized based on the following validation parameters such as method suitability, precision (repeatability and reproducibility), linearity, limit of detection (LoD) and quantification (LoQ), accuracy, and roughness. Specifically, the study is designed to provide a practical example to personals in testing laboratories in implementation of validation method for their existing internal quality assurance programs in the field of gas measurement.

2. MATERIALS AND METHODS

2.1. Materials

Two standard gas mixtures of N_2O in N_2 matrix were used in this study. The two standard gas mixtures were in-house prepared gravimetrically at our laboratory in accordance with ISO Guide 6142: Gas analysis - Preparation of calibration gas mixtures - Part 1: Gravimetric method for Class I mixtures (ISO Guide, 2015). The final concentrations of the two N_2O standard are $3.25 \mu\text{mol mol}^{-1}$ (labeled as NN-A standard) and $0.37 \mu\text{mol mol}^{-1}$ (labeled as NN-B standard). The $\mu\text{mol mol}^{-1}$ is equal to part per million. The NN-A standard was used in all experiment runs, while the NN-B standard was only used as a reference standard on the evaluation of method accuracy.

2.2. Instrumentation

An Agilent 7890B GC system equipped with a micro electron capture detector (μ ECD, Agilent Technologies, Santa Clara, CA) was used. In a typical work, separation of N_2O 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). The carrier gas was purified before entering the column using hydrocarbon filter (activated charcoal, Agilent Technology, USA).

2.3. Procedure

Measurement of N_2O

A certain volume of gas sample from standard cylinder was injected to the GC system through a mass flow controller (MFC, Brooks Instrument, USA). The MFC was used to maintain the consistency of gas flow rate. The MFC was installed between sample cylinder and a 1 mL sample loop (Agilent Technologies, USA) on the GC system. The detection of the N_2O was conducted by using a μ ECD under optimized analytical conditions 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, Hewlett-Packard Company). The measurement data was estimated by automated integration of the area under the resolved chromatographic profile.

Validation of Analytical Methods

The analytical method was firstly developed by investigating the suitability of the GC- μ ECD system. System suitability was conducted by injecting the NN-A standard into the GC- μ ECD under the same operating condition (Table 1) and the profile of generated chromatogram of the N_2O was then evaluated in term of its retention time, peak area, and peak height. The acceptance criterion of each parameter is set to maximum 2.5% of relative standard deviation (%RSD). After that, the developed method was validated. In the practical experiment, the validation process was carried out by assessing the measured data for each following validation parameters such precision (repeatability and reproducibility), linearity, limit of detection (LoD) and quantification (LoQ), accuracy, and roughness. The assessment procedure used for the calculation of the validation parameters were adopted from literatures (EURACHEM, 2014; Zuas and Budiman, 2016). Repeatability of the method was established by examining the response of the NN-A standard and expressed as percentage relative standard deviation (%RSD) from seven replications injections under the same operating condition and over a short time interval. The method reproducibility was determined by a similar procedure to that of repeatability except the time of 2 days interval was used instead of the same day. In addition, the method reproducibility was also assessed by using graphical technique so called control limit chart (Hovind et al., 2001; Masson, 2007). The linearity of the method was carried out by the evaluation of N_2O calibration curve. The calibration curve was constructed by plotting peak area of some N_2O standard as a function of their concentration. The N_2O standards used in constructing the calibration curve were obtained by

diluting the NN-A standard ($3.25 \mu\text{mol mol}^{-1}$) using dynamic dilution method. The LoD and LoQ of the method was determined at a signal-to-noise ratio (S/N) of 3 and 10, respectively, of the N_2O chromatogram at the lowest concentration used. The accuracy of the method was evaluated by comparing the concentration of NN-A standard against another independent gas standard (NN-B standard). Robustness of the method was determined by investigating the effect of small changes of the GC- μECD operating parameters (oven temperature, flow rate of carrier gas, and detector temperature) on the N_2O measurement results.

3. RESULTS AND DISCUSSION

3.1. System suitability

In a GC experiment, a system suitability test is an essential part with the purpose to verify that the GC system is adequate enough for an intended measurement. The suitability test of the GC system has been accepted in wide application because reliable measurement results obtained are based on a specific suitability parameters. In this regards, the suitability test was conducted by injecting seven replicates of N_2O ($0.99 \mu\text{mol mol}^{-1}$) under the same operating conditions (Table 1). The obtained chromatograms was carried out by observing its suitability criteria including retention time, peak area, and peak height. Figure 1 displays a representative of the GC- μECD chromatogram of N_2O in N_2 matrix. The suitability properties of the chromatogram are listed in Table 2. From Table 2, it can be seen that the GC- μECD used in this study is extremely suitable for measurement of N_2O in N_2 matrix because all evaluated parameters have %RSD values less than 2.5, indicating that the measurements of N_2O in N_2 matrix under the suitable condition were very consistence from run to run.

Table 1. Optimized operating condition of the GC- μECD for the measurement of N_2O in N_2 matrix

Parameter	Operating condition
Sample	
Flow rate (via MFC)	150 mL/min
Volume loop	1 mL, stainless steel
Valve Box heater	100°C, On
Oven temperature	90°C (isothermal)
Carrier gas	N_2 , 60 psi
Make-up gas	P5 (5% CH_4 in Ar), 2 mL/min
Detector	
Detection system	μECD
Temperature	350°C
Electrometer	On

Figure 1-Representative chromatogram of N₂O (0.99 μmol mol⁻¹) in N₂ Matrix.

Table 2. Suitability data of the GC-μECD system for the measurement of N₂O in N₂ matrix.

Parameter	Average value ($n = 7$)	%RSD
Retention time	1.05	0.39
Peak area	71.08	1.85
Peak height	14.00	1.29

3.2. Precision

Repeatability (intra-day precision) was conducted to assess the closeness between measured values from a number of measurements over a short period (EURACHEM, 2014; Zuas et al., 2016). Seven-injection replications of N₂O standard (2.87 μmol mol⁻¹) were performed and the repeatability of the method was predicted by comparing the relative standard deviation (%RSD) of the measurements against the calculated value obtained by means of Horwitz function (Eq. 1) (Jichem et al., 2001).

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

where c is the concentration of target analyte in decimal fraction. The results of the method repeatability evaluation are depicted in Table 3. As it can be seen in Table 3, the %RSD of the method repeatability was found to be 1.42, which is lower than 8.93 (0.67 x CV-Horwitz). This finding implies that the analytical method is categorized as an repeatable for the measurement of N₂O in N₂ matrix (Jichem et al., 2001).

The reproducibility (inter-day precision) is an analytical parameter indicating a variability of repeated measurement results that are obtained by using the same test method under different measurement day (Budiman and Zuas, 2015; EURACHEM, 2014). Seven repeated injection measurements at different days (day 1 and day 2) for the evaluation of method reproducibility were conducted and the results are listed in Table 3. It can be found that the %RSD value obtained (0.71 in Table 3) from the N₂O measurement are less than its corresponding CV Horwitz, implying that the analytical method is reproducible.

Table 3. Evaluation results for the precision of analytical method.

Parameters	Precision	
	Repeatability	Reproducibility
Average	2.99 ^a	2.87 ^b
SD	3.04	1.40
%RSD	1.42	0.71
CV-Horwitz	13.40	13.40
0.67 x CV-Horwitz	8.93	8.93

^aNumber of injection (n) = 7 replications; ^b Average value from day 1 (n = 7) and day 2 (n = 7).

Moreover, based on the concept of fit for purpose for establishing the reproducibility of a GC measurement, controlling the quality of the measurement results is required. To achieve the purpose of such quality control, the process is carried out by constructing a common control program so called a control limit chart (warning and action limit) (Hovind et al., 2001). The control limit chart consists of five lines including one average line (AL), two warning limit (WL) lines, and two control limit (CL) lines. The AL represents the mean of the control values. The values of the two WL lines are the AL line $\pm$ two times standard deviation ($AL \pm 2SD$), while the two CL lines are the AL line $\pm$ three times standard deviation ($AL \pm 3SD$) (Masson, 2007). Figure 2 represents the control limit chart for the measurement of the N₂O in N₂ matrix. The results indicate that all control data values lie within or inside the warning limit, meaning that no occurrence error can be found for the measurement reproducibility. In a word, the analytical method for the measurement of N₂O in N₂ matrix is reproducible, which is in agreement with the above finding related to the %RSD and CV-Horwitz evaluation. However, if the control data values fall outside the limit, therefore, a remedial action is required to identify and remove the source of error (Zuas and Budiman, 2016).

Figure 2-The chart of control limit for the measurement of N₂O in N₂ matrix.

3.3. Linearity

In every method validation process, evaluation of the method linearity is extremely crucial to be performed because the linearity shows the method ability (within the given range) to obtain test result that are directly proportional to the concentration of the target analyte in the sample (EURACHEM, 2014). The linearity of the method was determined by analysing seven replicate injections of N₂O standard at nine concentration levels ranging from 0.19 to 3.25 μmol mol⁻¹. These concentration levels were obtained by diluting the NN-A standard (3.25 μmol mol⁻¹) by using dynamic dilution method. The obtained peak area of each N₂O standards were plotted against their concentration to obtain a calibration curve and the result is shown in Figure 3a. The linearity of the method was statistically evaluated and the results are tabulated in Table 4. From the Table 4, it can be seen that the correlation coefficient (R^2) of the method linearity for nine concentration point was found to be 0.9998, indicating that the analytical method for N₂O measurement in N₂ matrix is fitted to the linear model.

Moreover, the calibration curve was graphically evaluated by using a response factor model. This graphical model is used to evaluate the linearity data obtained from a calibration curve model, where the graph was obtained by plotting the response factor (peak area divided by their respective concentration) against corresponding concentration. The response factor against analyte concentration in a linear range should be relatively constant, with a minimum limit of 95% and a maximum of 105 % of the constant response. Figure 4 displays a graphical evaluation of the linearity of the analytical method for N₂O measurement. From Figure 4, it can be seen that response factor from three concentration points (0.19, 0.29 and 0.39 μmol mol⁻¹) exceeds the maximum limit (105% constant response). Thus, these three outlier points were excluded and the six remains points (0.59, 0.79, 0.99, 2.28, 2.86, and 3.25 μmol mol⁻¹) were used in constructing a new calibration curve and the result is displayed in Figure 3b. It can be seen from Figure 3b, the new calibration curve has $R^2 = 0.9998$, which is

very similar to the R^2 of the previous calibration curve (Figure 3a), implying that they have same level in linearity. However, from linearity data as shown in Table 4, it can be observed that new calibration curve (six concentration points as in Figure 3b) has greater slope (65.15) than previous one (nine concentration points as shown in Figure 3a). The greater slope of the new calibration curve indicates that its sensitivity is better than previous calibration curve. In addition, the intercept of the new calibration curve (i.e., 0.057) was found to be lower than previous calibration curve (1.275). For a linear equation, the intercept represents the constant systematic error or constant bias and the value of the intercept should be as close to zero as possible (Jhang et al., 2004). This implies that the constant systematic errors/constant bias of the new calibration curve (six concentration points) much smaller than the previous calibration curve (nine concentration points). In conclusion, the linearity of the analytical method from the new calibration curve for the measurement of the N_2O in N_2 matrix is more favorable than previous one.

Figure 3-Calibration curve of: (a) nine concentration points, and (b) six concentration points.

Figure 4-A graphical of control limit chart for the measurement of N_2O at nine concentration points.

3.4. LoD and LoQ

In every analytical measurement, the LoD and LoQ are also essential to be conducted. The LoD is defined as the lowest concentration of an analyte in a sample that can be detected, but not necessarily quantified as an exact value. The concentration of analyte at the LoD level can only be determined qualitatively. In other hands, a quantitative analysis is also possible to be performed at the LoD level; however, it may lead produce an inaccurate result since the uncertainty contribution is larger than the measurement result itself (EURACHEM, 2014). The LoQ is defined as the lowest concentration of an analyte in a sample that can be quantified with appropriate precision and accuracy, meaning that the minimum concentration of analyte in the sample can be reliably determined by conducting the LoQ evaluation). The LoD and LoQ of the N₂O were determined using a signal to noise (S/N) ratio method. Based on this S/N method the ratio values of LoD and LoQ are 3:1 and 10:1, respectively (EURACHEM, 2014; Zuas et al., 2016). The LoD and LoQ were determined from 0.59 $\mu\text{mol mol}^{-1}$ (as the lowest N₂O standard used in the linearity evaluation at six point concentrations range) and the results are tabulated in Table 4. From Table 4, it was found that the LoD and LoQ of the analytical method were 0.10 and 0.34 $\mu\text{mol mol}^{-1}$, respectively.

Table 4. Data indicating linearity of the method for N₂O in N₂ matrix and their LoD and LoQ values.

Calibration curve	Slope	Intercept	Linear range ($\mu\text{mol mol}^{-1}$)	R^2	LoD ^a ($\mu\text{mol mol}^{-1}$)	LoQ ^a ($\mu\text{mol mol}^{-1}$)
Nine points ^b	64.67	1.28	0.19 - 3.25	0.9998	0.09	0.29
Six points ^c	65.15	0.06	0.59 - 3.25	0.9998	0.10	0.34

^aAverage value from seven injection replications.

^bN₂O standards were 0.19; 0.29; 0.39; 0.59; 0.79; 0.99; 2.28; 2.86; and 3.25 $\mu\text{mol mol}^{-1}$. ^cN₂O standards were 0.59; 0.79; 0.99; 2.28; 2.86; and 3.25 $\mu\text{mol mol}^{-1}$.

3.5. Accuracy

Accuracy of an analytical method is defined as the closeness or the agreement between the measured and an accepted/true value (Taverniers et al., 2004; EURACHEM, 2014). Experimentally, the accuracy is a combination of the bias and precision of the analytical procedure; the bias of method ($\overline{CA}$) is the difference between the measured value and the value from certificate of reference standard, which was calculated using an expression below (Eq. 2) (EURACHEM, 2014).

$$\overline{CA} = \overline{X} - Y \quad (2)$$

where $\overline{X}$ is the average of measured value of reference standard, and Y is value from certificate of reference standard. For assessing the method accuracy, the values of

repeatability (S_w^2), reproducibility (S_b^2), and uncertainty value (μ_{RM}^2) from certificate of reference standard are included. A combination those three components results in σ value by using the following expression (Eq. 3) (EURACHEM, 2014):

$$\sigma = \sqrt{S_b^2 + \frac{S_w^2}{n} + \mu_{RM}^2} \quad (3)$$

where S_b is standard deviation from reproducibility (inter day precision). S_w is the standard deviation from repeatability (intra day precision), n is number of replications and μ_{RM} is the uncertainty of NN-B standard. The ISO Guide 33:2015 “Reference materials - Good practice in using reference materials” (ISO Guide, 2015) defines the acceptance criteria, where no bias is found if the σ value falls within $\pm 2\sigma$ at confidence level 95% (Eq. 4).

$$-2\sigma < X - Y < 2\sigma \quad (4)$$

From the Table 5, it can be evaluated that the measured value of the N₂O falls within $\pm 2\sigma$, implying that no evidence of bias can be found in the analytical method for the measurement of N₂O in N₂ matrix. In a word, the analytical method for the measurement of N₂O in N₂ matrix is accurate.

Table 5. Accuracy data of the GC- μ ECD for the measurement of N₂O in N₂ matrix

Bias, $C\Delta = X - Y$	σ	2σ	$-2\sigma < C\Delta < 2\sigma$
($\mu\text{mol mol}^{-1}$)	($\mu\text{mol mol}^{-1}$)	($\mu\text{mol mol}^{-1}$)	($\mu\text{mol mol}^{-1}$)
- 0.258	0.173	0.346	$-0.346 < - 0.258 < 0.346$

3.6. Robustness

Robustness is a part of analytical method validation to evaluate the effect a number of analytical method parameters (factors) on the results of a measurement. The method robustness defines the capacity to generate some results, which remains unaffected by minor changes of the experimental conditions during analysis (EURACHEM, 2014). In this study, the robustness of the method was assessed by investigating the effect of small changes of the GC- μ ECD parameters (such as oven temperature, flow rate of the carrier gas, and detector temperature) on the measured concentration of the N₂O in N₂ matrix. For the robustness study, a standard containing 2.99 $\mu\text{mol mol}^{-1}$ N₂O was used and the results of the robustness study are tabulated in Table 6. It can be seen in Table 6, small changes of the GC- μ ECD parameters have no significant effects on the measured concentration of N₂O in N₂ matrix implying that the analytical method used is robust.

Table 6. Statistical analysis of three-parameter variation effect using one-way ANOVA

Parameter	Mean Values	<i>p</i> -values
Oven Temperature		
- 92 °C	- 3.010	0.999
- 90 °C	- 2.991	
- 88 °C	- 3.045	
Detector temperature		
- 352 °C	- 2.797	0.999
- 350 °C	- 2.991	
- 342 °C	- 2.625	
Carrier Gas Flow rate		
- 62 psi	- 3.139	0.998
- 60 psi	- 2.991	
- 58 psi	- 2.891	

4. CONCLUSION

For a routine work, validation of an analytical method used is crucial important. Evaluation results for each validation parameter indicated that the validated method offers a sufficient proof concerning the reliability of the GC- μ ECD method for the measurement of N₂O in N₂ matrix with further keeping the degree of user confidence regarding their analytical data. In addition, the developed and validated method could also be used as a good reference for local and international in the validation of the measurement method for other target gas components.

5. ACKNOWLEDGEMENT

The authors gratefully acknowledged the Indonesian Government for financially supporting this study within the scope of project “Strengthening Chemical Metrology Competency and Infrastructure” and Ministry of Research, Technology and Higher Education of Indonesia through Supporting Program Batch II No. 1883.1/D/KPT/2016. The authors also would like to extend our appreciation to K. D. Purnama from Diponegoro University for helping in data collection.

REFERENCES

- AKDENIZ, N.; JACOBSON, L. D.; HETCHLER, B. P.; VENTEREA, R. T.; SPOKAS, K. A. **Measurement of nitrous oxide concentrations from Wisconsin dairy barns**. In: ASABE ANNUAL INTERNATIONAL MEETING, 2009, Reno-Nevada. Paper no.: 096595, p. 2–7. June 2009.
- ANDERSON, B.; BARTLETT, K.; FROLKING, S.; HAYHOE, K.; JENKINS, J.; SALAS, W. **Methane and nitrous oxide emissions from natural sources**. Office of Atmospheric Programs, US EPA, EPA 430-R-10-001, Washington DC. Available in: <http://scholars.unh.edu/earthsci_facpub/484/>. Accessed on: 17 Aug. 2016.
- BSN (BADAN STANDARDISASI NASIONAL). **Persyaratan umum kompetensi laboratorium pengujian dan laboratorium kalibrasi** (In Indonesian). Jakarta: 2008. Available in: <http://sisni.bsn.go.id/index.php/sni_main/sni/detail_sni/9509>. Accessed on: 25 July 2016.
- BUDIMAN, H.; ZUAS, O. Validation of analytical method for determination of high level carbon dioxide (CO₂) in nitrogen aas (N₂) matrix using gas chromatography thermal conductivity detector. **Periódico Tchê Química**, v.12, p. 7-16, 2015.
- de MIRANDA, M. S.; FONSECA, M. L.; LIMA, A.; DE MORAES, T. F.; RODRIGUES, F. A. Environmental Impacts of Rice Cultivation. **American Journal of Plant Sciences**. v. 6, p. 2009-2018, 2015.
- ERMOLAEV, E. **Greenhouse gas emissions from food and garden waste composting**. 2015. Doctoral Thesis, Swedish University of Agricultural Sciences. Uppsala. Sweden. 2015.
- EURACHEM. **The fitness for purpose of analytical methods a laboratory guide to method validation and related topics**. 2nd Edition. 2014. Available in: <<https://www.eurachem.org>>. Accessed on: 5 Aug. 2016).
- HOVIND, H.; MAGNUSSON, B.; KRYSELL, M.; LUND, U.; MÄKINEN, I. Internal quality control-handbook for chemical laboratories, **Nordtest Report Tr 569 (NT TR 569 - English - Edition 4)**, Nordic Innovation, Stensberggata, Oslo, 2011. Available in: <<http://www.nordtest.info/>>. Accessed on: 12 Aug. 2016.
- ISO GUIDE. **Guide 33:2015(En)-Reference materials-good practice in using reference materials**. International Organization for Standardization. 2015. Geneva, Switzerland. Available in: <<https://www.iso.org/o>>. Accessed on: 25 Aug. 2016.
- ISO GUIDE. **Guide 6142:2015(En) - Gas analysis -preparation of calibration gas mixtures-part 1: Gravimetric method for class I mixtures**. 2015. Geneva, Switzerland. Available in: <<https://www.iso.org/o>>. Accessed on: 13 Aug. 2016.

- JHANG, J. S.; CHANG, C. C.; FINK, D. J.; KROLL, M. H. Evaluation of Linearity in the Clinical Laboratory. **Archives of Pathology & Laboratory Medicine**.v. 128, p. 44-48, 2004.
- JICHEM, L.; ENGMAN, J.;SCHRODER, T. Evaluation of Results Derived from the Analysis of certified reference materials: A user-friendly approach based on simplicity. **Fresenius Analytical Chemistry**. v. 370, p. 178-182, 2001.
- KOMIYA, S.; SHOJI, Y.; NOBORIO, K.; YAZAKI, T.; TOOJINDA, T.; SIANGLIW, M. **Climatic impacts on greenhouse gas emissions in rice paddy fields, Soil Solution**. in: WORLD CONGRESS OF SOIL SCIENCES. 2010. Brisbane,17–19.Availablein: <http://iuss.org/19th%20WCSS/Symposium/>. Accessed on 2 Aug.2016
- MASSON, P. Quality control techniques for routine analysis with liquid chromatography in laboratories. **Journal of Chromatography A**. v. 1158, p. 168-173, 2007.
- TAVERNIERS, I.; LOOSE, M. D.; BOCKSTAELE, E. V. Trends in quality in the analytical laboratory: Analytical method validation and quality assurance. **Trac-Trend in Analytical Chemistry**. v. 23, p. 535-552, 2004.
- TEODORU, C. R.; NYONI, F. C.; BORGES, A. V.; DARCHAMBEAU, F.; NYAMBE, I.; BOUILLON, S.Dynamics of greenhouse gases (CO₂, CH₄, N₂O) along the Zambezi river and major Tributaries, and their importance in the Riverine carbon budget. *Biogeosciences*. v. 12, no. 8, p. 2431-2453, 2005.
- VARDAG, S. N.; HAMMER, S.; O'DOHERTY, S.; SPAIN, T. G.; WASTINE, B.; JORDAN, A.; LEVIN, I. Comparisons of continuous atmospheric CH₄, CO₂ and N₂Omeasurements - Results from a travelling instrument campaign at Mace Head. **Atmospheric Chemistry Physic**, v.14, no. 16, p. 8403-8418, 2014.
- WANG, C. Simultaneous analysis of greenhouse gases by gas chromatography. **Agilent Technology**, v. 4, no. 14. p.1-8, 2012.
- ZHANG, Y.; Mu, Y.; Fang, S.; Liu, J. An improved GC-ECD method for measuring atmospheric N₂O. **Journal of Environtal Sciences (China)**.v. 25, no. 3, p. 547-553, 2013.
- ZUAS, O.; BUDIMAN, H. Estimating precision and accuracy of GC-TCD method for carbon dioxide, propane and carbon monoxide determination at different flow Rate of carrier gas. **Hemijaska Industrija**. v. 70. no. 4, p. 451-459, 2016.
- ZUAS, O.; BUDIMAN, H.; MULYANA, M. R. Temperature effect on thermal conductivity detector in gases (carbon dioxide, propane, carbon monoxide) analysis: A gas chromatography experimental study. **Journal of Basic and Applied Research International**. v. 13, no. 4, 232-238, 2016

DETERMINAÇÃO DO ÓXIDO NITROSO EM UMA MATRIZ DE NITROGÊNIO, USANDO CROMOTOGRAFIA EM FASE GASOSA COM DETECTOR DE CAPTURA ELETRÔNICA: VALIDAÇÃO DO MÉTODO ANALÍTICO

O. ZUAS¹, M. R. MULYANA¹, N. HAMIM², H. BUDIMAN¹

¹Gas Analysis Laboratory, Metrology in Chemistry Research Group, Research Centre for Metrology, Indonesian Institute of Sciences (RCM-LIPI)

²Electrochemistry Laboratory, Metrology in Chemistry Research Group, Research Centre for Metrology, Indonesian Institute of Sciences (RCM-LIPI)

E-mail: oman.zuas@lipi.go.id

RESUMO: A presença de óxido nitroso (N_2O), um dos gases de efeito de estufa mais potentes, contribui significativamente para o aquecimento global. Desta forma, é muito importante disponibilizar métodos de medição exatos e válidos para a monitorização da emissão deste gás para o ambiente. Neste estudo, foi validado um método analítico para a medição de N_2O numa matriz de azoto (N_2) usando cromatografia em fase gasosa com microdetector de captura eletrônica (GC- μ ECD). O método analítico foi validado em termos de alguns parâmetros de desempenho, como a adequação do sistema, precisão (repetibilidade e reprodutibilidade), linearidade, limite de detecção (LoD) e limite de quantificação (LoQ), exatidão e robustez do método. Os resultados mostram que o GC é adequado para a medição de N_2O numa matriz de N_2 . A repetibilidade e reprodutibilidade do método foi quantificada por desvios padrão relativos (RSD) de 1,42 % e 0,71 %, respectivamente, indicando que o método é adequado para medições de N_2O . A linearidade do método foi excelente, tendo-se observado um R^2 de 0,9998. O LoD e LoQ do método é 0,10 e 0,34 $\mu\text{mol mol}^{-1}$, respectivamente. A avaliação da exatidão do método demonstrou que este também é exato para medições de N_2O em matriz de N_2 . A robustez do método indica que o método é bastante estável e pouco afetado por alterações nas condições experimentais. Pode-se concluir deste estudo que o método validado pode ser usado em laboratórios de ensaio para programas internos de garantia da qualidade relacionados com medições de N_2O em matriz de N_2 .

PALAVRAS-CHAVE: Óxido nitroso, Validação de método, Cromatografia em fase gasosa, Detector de captura eletrônica.