Trace impurities measurement in ultra-high purity gases and their uncertainties: case study on permanent gas impurities in pure nitrogen

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Abstract. Trace measurement for gas impurities plays an important role in the quality determination of pure-gases. High purity gases will certainly have a higher economic value than gases with lower purity, especially for the ultra-high purity gases used in the preparation of standard gas mixtures. These types of gases shall have a maximum limit for their impurities, which should be verified by a validated method. In this study, an experiment was conducted to determine the impurities in three cylinders of ultra-high purity nitrogen (UHP N2) gases using a validated gas chromatography equipped with pulse discharge helium ionization detector (GC-PDHID) method. The impurities detected by the GC-PDHID in the aforementioned UHP N2 samples consist of argon (Ar), oxygen (O2), methane (CH4), and carbon monoxide (CO). Meanwhile, hydrogen (H2) and carbon dioxide (CO2) cannot be seen on the chromatogram, then assumed to be lower than the PDHID’s detection limit. Concentrations of the impurities, along with their uncertainties, were found to be 0.987 ± 0.104; 5.818 ± 0.807; 3.163 ± 0.449; and 1.289 ± 0.158 µmol/mol for Ar, O2, CH4, and CO, respectively for the first N2 cylinder. H2 and CO2 were estimated to be half of the limit of detection, and H2O component was quoted from the UHP N2 manufacturer’s certificate of analysis. The other two N2 cylinders showed almost similar amounts of impurities. Based on the results, the actual purity for each of the three N2 gases can be estimated as 99.9987% mol/mol; 99.9987% mol/mol; and 99.9988% mol/mol. It is expected that the results of this study could useful as reference for both pure-gas manufacturers and consumers to properly determine the quality of their products.

1. Introduction

Pure-gases industries have substantial markets, related to many kinds of applications, such as electronical, medical, food processing, research activities, etc [1]. Such applications typically require certain gases with specific purity criteria in the process. Price and quality of gas products is purity-dependent. Therefore, manufacturers of the pure-gases are obliged to properly determine the purity of their gas products.

One of the most important applications of pure-gases is in the preparation process of standard gas mixtures (SGM). The SGMs can be used as the reference materials for the calibration of gas measurement process, in order to comply with ISO/IEC 17025 [2]. The SGMs are a mixture of two or more parent gases, typically with ultra-high purity grade, in one cylinder with certified value of composition [3]. Previous experiment has reported that the purity of the pure-gases has a significant effect to the composition of the SGMs [4], implying that proper purity determination of the pure-gases is of great importance.
Furthermore, the SGMs as mentioned above were often composed of low concentration target components mixed in a balance gas. Ultra-high purity nitrogen (UHP N$_2$) is one of the most common gases that have been used as balance gas. For instance, N$_2$ has been used as a balance for preparation of SGM for vehicle emission measurement, or for preparation of artificial air by combining with oxygen. In addition, some international laboratory comparison reports have shown the utilization of UHP N$_2$ as the balance gas for preparation of other SGMs [5-6]. Thus, purity determination of UHP N$_2$ is of great importance for obtaining an accurate composition of the SGMs.

Purity of UHP N$_2$ can be estimated by measuring its trace impurities [7]. In their production plant, UHP N$_2$ gases are usually produced from the air [8]. Therefore, characteristic of trace impurity components in UHP N$_2$ gases should be typically similar to air components, such as argon (Ar), oxygen (O$_2$), hydrogen (H$_2$), carbon dioxide (CO$_2$), carbon monoxide (CO), moisture (H$_2$O), and methane (CH$_4$) in trace concentration level [9-10].

Currently, some methods have been developed to measure the aforementioned gas components in N$_2$. Gas chromatography - thermal conductivity detector (GC-TCD) method that has been recognized for its ability as a universal detector to identify high concentration level of gas component [11]. While gas chromatography - flame ionization detector (GC-FID) with methanizer is known for its sensitivity for detecting trace level gas components. However, the FID with methanizer can only be used for flammable components i.e., hydrocarbon containing compounds such as CO, CH$_4$ and CO$_2$ [12-13]. In addition, gas chromatography – pulsed discharged helium ionization detector (GC-PDHID) is known as an emerging GC method. PDHID is an universal-type detector for gas components at low concentrations [14]. Therefore, in this study, the measurement of trace impurities in UHP N$_2$ gas using GC-PDHID was carried out and discussed. Uncertainty estimation of the measurement result was also described in detail. It is expected that the results can be useful as a reference for the industry, especially the ultra-high purity gas manufacturers, in order to properly determine the purity of their gas products along with the uncertainty.

2. Experimental Methods
The measurement of trace impurities in this study was carried out using the validated GC-PDHID method that has been proven suitable in previous experiments [15]. The PDHID temperature was set to 220 °C while the oven temperature was programmed as follows:

1. initially 40 °C and hold for 6.5 min,
2. ramp down by 100 °C/min to 30 °C and then hold for 8.4 min,
3. ramp up by 6 °C/min to 75 °C and then hold for 0 min,
4. ramp up by 12 °C/min to 160 °C.

Flow rate of the samples was set at constant 40 ml/min. Meanwhile, flow rate of the carrier gas was programmed as follows:

1. initially 10 ml/min and hold for 11.5 min,
2. ramp down 60 ml/min by each minute to 5 ml/min and then hold for 3.4 min, ramp up 60 ml/min by each minute to 10 ml/min.

2. 1 Materials
Three individual cylinders (50 liters in volume of each) of ultra-high purity (UHP) N$_2$ gases (99.9995% purity, 200 barr) were used in this study. For the experiment, from each cylinders, a small volume was injected into the GC-PDHID. All of N$_2$ cylinders were attached with a company certificate of analysis. Compositions of impurities stated in the certificate are listed in Table 1.
Table 1. Impurities composition of the UHP N\textsubscript{2} samples

| Components            | Specification |
|-----------------------|---------------|
| O\textsubscript{2}    | ≤ 2 µmol/mol  |
| Total Hydrocarbon (as CH\textsubscript{4}) | ≤ 0.1 µmol/mol |
| CO\textsubscript{2}   | ≤ 0.5 µmol/mol |
| CO                    | ≤ 0.5 µmol/mol |
| CH\textsubscript{4}   | ≤ 1 µmol/mol  |
| C\textsubscript{3}H\textsubscript{8} | ≤ 1 µmol/mol |
| H\textsubscript{2}    | ≤ 1 µmol/mol  |
| H\textsubscript{2}O   | ≤ 3 µmol/mol  |
| N\textsubscript{2}    | balance       |

Calibration of the PDHID response to the gas components in the UHP N\textsubscript{2} samples was done using SGMs traceable to NIST and NIM China. The SGMs’ composition can be seen at the Table 2.

Table 2. Composition of the components in SGMs

| Components | Concentration (µmol/mol) |
|------------|--------------------------|
|            | SGM AH06015 | SGM AH06001 | SGM AH06014 | SGM AH06013 |
| CO\textsubscript{2} | 2.36         | 4.26         | 6.69         | 8.63         |
| H\textsubscript{2}  | 1.16         | 2.28         | 4.00         | 3.88         |
| Ar           | 1.14         | 2.25         | 3.95         | 3.83         |
| O\textsubscript{2} | 1.22         | 2.40         | 4.20         | 4.08         |
| N\textsubscript{2} | 2.49         | 4.52         | 7.19         | 9.10         |
| CH\textsubscript{4} | 1.16         | 2.28         | 4.00         | 3.88         |
| CO           | 2.36         | 4.26         | 6.72         | 8.68         |

Uncertainty 5% for all components (k=2)

2.2 Instruments

The main instrument used in this study was the GC Agilent 7890B Series (Agilent Technologies, USA). It was equipped with a PDHID for detection of the gas components, and two capillary columns for components separation. The first column was PoraPLOT Q (50m x 530µm x 20µm) to separate heavy gas components of the impurities which was CO\textsubscript{2}. The second column was MolSieve 5A that was used to separate light gas components such as argon (Ar), oxygen (O\textsubscript{2}), hydrogen (H\textsubscript{2}), carbon monoxide (CO), and methane (CH\textsubscript{4}).

The GC-PDHID system was also equipped with a helium getter (Valco Instruments, USA) and a mass flow controller Brooks 0254 (Brooks Instruments, USA). The helium getter was used for purifying the helium carrier gas, while the mass flow controller was used to maintain the sample flow at a constant rate.

2.3 Procedure

The GC-PDHID system was calibrated by injecting four SGMs as listed in Table 2. Detector’s response of each component in SGMs, in the form of peak area, was averaged from seven replications. Following the calibration, three UHP N\textsubscript{2} samples were injected into the GC-PDHID system with similar procedure and operating conditions. Average peak area of each component in sample (A\textsubscript{sample}) was then compared with the peak area of each corresponding components in SGMs (A\textsubscript{SGMs}). This method can be considered as a single-point calibration, since the peak area from each component in the samples was compared only to the corresponding peak area of the SGM with the closest concentration value. Concentration of impurities component in UHP N\textsubscript{2} samples was quantified using Equation 1 [16], in which the C\textsubscript{sample} corresponds to the concentration of component in the sample while C\textsubscript{SGMs} corresponds to concentration of components in SGMs.
\[ C_{\text{sample}} = \left( \frac{A_{\text{sample}}}{A_{\text{SGMs}}} \right) \times C_{\text{SGMs}} \]  

(1)

Standard deviation of peak area of samples divided by peak area of SGMs can be considered as an uncertainty source of the measurement result \((u(A_{\text{sample}}/A_{\text{SGMs}}))\). Another uncertainty source is the SGMs certificate. In this case, the uncertainty of each component’s in the SGMs \((u(C_{\text{SGMs}}))\) was 2.5%. This value came from the 5% uncertainty stated in Table 2, divided by its coverage factor \((k=2)\). These uncertainties were then combined to estimate the measurement uncertainty of impurities component of UHP N\(_2\) samples \((u(C_{\text{sample}}))\) by using Equation 2 below[16]. The combined uncertainty of concentrations for sample component was then multiplied by the coverage factor \((k)\) of 2 in order to fulfill 98% confidence level.

\[
\left( \frac{u(C_{\text{sample}})}{C_{\text{sample}}} \right)^2 = \left( \frac{u(A_{\text{sample}}/A_{\text{SGMs}})}{A_{\text{sample}}/A_{\text{SGMs}}} \right)^2 + \left( \frac{u(C_{\text{SGMs}})}{C_{\text{SGMs}}} \right)^2
\]  

(2)

3. Results and Discussion

Each UHP N\(_2\) samples has been injected to the GC-PDHID system using the procedure described above. The chromatogram of injected sample is shown in Figure 1, in which all impurities component of UHP N\(_2\) samples can be clearly distinguished without interference. Ar and O\(_2\) peaks are quite close to each other, but they can still be integrated properly without any significant issue. Typical atmospheric air components can be found in the chromatogram except H\(_2\)O, CO\(_2\) and H\(_2\). However, H\(_2\)O was undetectable using method used in this study. In addition, both CO\(_2\) and H\(_2\) may presence in UHP N\(_2\) samples, but their concentration were below the detection limit of the PDHID. In this study, the detection limit of CO\(_2\) and H\(_2\) were 0.044 and 0.530 µmol/mol, respectively [15].

![Figure 1. Typical PDHID chromatogram of UHP N\(_2\)](image)

Averaged peak areas of Ar, O\(_2\), CH\(_4\), and CO in both SGMs and UHP N\(_2\) samples are listed in Table 3. The averaged peak area of all of three UHP N\(_2\) samples were found to similar one to another. The peak area of Ar and CO in the samples are close to corresponding peak area from SGM AH06015, while O\(_2\) peak area of the samples are close to corresponding peak area from SGM AH06014. N\(_2\) peak areas of the samples are close to corresponding peak area from SGM AH06001, except for UHP N\(_2\) sample 1 which is close to SGM AH06013. These results were considered as a basis for quantification of each component concentration in UHP N\(_2\) samples.
Table 3. Average peak area for both UHP N\textsubscript{2} samples and SGMs

| Sample/SGM code       | Average Peak Area      | O\textsubscript{2} | CH\textsubscript{4} | CO   |
|------------------------|------------------------|---------------------|---------------------|------|
| UHP N\textsubscript{2} sample 1 | 265.793                | 1154.344            | 1513.136            | 256.671 |
| UHP N\textsubscript{2} sample 1 | 257.428                | 1177.440            | 1424.082            | 251.453 |
| UHP N\textsubscript{2} sample 3  | 246.300                | 1159.874            | 1359.137            | 262.828 |
| SGM AH06015           | 306.842                | 570.755             | 724.601             | 469.945 |
| SGM AH06001           | 505.363                | 669.878             | 1178.664            | 764.239 |
| SGM AH06014           | 777.477                | 833.289             | 1920.831            | 1280.392 |
| SGM AH06013           | 766.573                | 805.844             | 1856.045            | 1688.995 |

Concentrations of Ar, O\textsubscript{2}, CH\textsubscript{4}, and CO in UHP N\textsubscript{2} samples were quantified using Equation 1 as described in the “Procedure” section. For components that were considered under limit of detection, the concentration was quantified as half of their detection limit, while the uncertainty was estimated as \(\frac{1}{2}\sqrt{3}\) of their detection limit \(\text{[7]}\). A similar was applied for moisture (H\textsubscript{2}O component), which was quoted from the company certificate of analysis. The quantified concentration of all components, along with their expanded uncertainty at 98% confidence level \((k=2)\) are listed in Table 4.

Table 4. Purity table of the three UHP N\textsubscript{2} samples

| Component | Concentration ± Expanded Uncertainty (µmol/mol) | UHP N\textsubscript{2} sample 1 | UHP N\textsubscript{2} sample 2 | UHP N\textsubscript{2} sample 3 |
|-----------|-------------------------------------------------|---------------------------------|---------------------------------|---------------------------------|
| Ar        | 0.987 ± 0.104                                   | 0.956 ± 0.101                   | 0.915 ± 0.096                   |
| O\textsubscript{2} | 5.818 ± 0.807                                   | 5.935 ± 0.835                   | 5.846 ± 0.814                   |
| CH\textsubscript{4} | 3.163 ± 0.449                                   | 2.755 ± 0.382                   | 2.629 ± 0.362                   |
| CO        | 1.289 ± 0.158                                   | 1.263 ± 0.154                   | 1.320 ± 0.162                   |
| CO\textsubscript{2} | 0.022 + 0.012                                   | 0.022 ± 0.012                   | 0.022 ± 0.012                   |
| H\textsubscript{2}  | 0.265 ± 0.153                                   | 0.265 ± 0.153                   | 0.265 ± 0.153                   |
| H\textsubscript{2}O | 1.500 ± 0.866                                   | 1.500 ± 0.866                   | 1.500 ± 0.866                   |
| Total impurities concentration | 13.044 µmol/mol or 0.0013 %mol/mol | 12.696 µmol/mol or 0.0013 %mol/mol | 12.497 µmol/mol or 0.0012 %mol/mol |
| N\textsubscript{2} Purity (+100% mol/mol - total impurities concentration) | \(99.9987 ± 0.0001\)% | \(99.9987 ± 0.0001\)% | \(99.9988 ± 0.0001\)% |

*Uncertainty of the purity was estimated as square root of the sum of all impurities’ uncertainty

It can be seen that the purity of the N\textsubscript{2} gases shown in Table 4 was different from the specification stated in the products’ certificate, which was 99.9995% mol/mol. O\textsubscript{2}, CH\textsubscript{4}, and CO concentrations were found to be higher than the certified value from the company. Many factors might be taken into consideration as the cause of this difference, such as the gas transfer line in the production plant, the cylinders used as the gas container, transportation to the laboratory, etc \(\text{[17-18]}\). Based on these findings, it is very important for both pure-gas company and gas consumer to properly measure the pure-gases before routine usage, especially if the purity of the gases become crucial effect on the consumer’s applications.

4. Conclusion

In conclusion, The impurities concentration and the purity of three N\textsubscript{2} gas measured in this study were found to be different than the specified value at the company’s certificate of analysis. This may become an issue for any applications such as medical, electronical, or SGMs production that requires high purity gases with certain criteria. Therefore, proper measurement of trace impurities in pure gases
should be the highest priority for the company (gas manufacturers) and consumers involved in the aforementioned applications.

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