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Research Article

Effect of Nafion Dryer and Cooler on Ambient Air Pollutant (O_3, SO_2, CO) Measurement

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ABSTRACT Water vapor causes many problems in ambient air measurement by absorbing target compounds concerned. In accordance with Korean national standards and international organization for standardization (ISO), water removal devices (WRDs) such as Nafion dryer and Cooler have been applied to analyzers to mitigate or remove the effect of water vapor on the measurement of ambient air pollutants. However, it is not clearly defined which WRDs are suitable for the measurement. Thus, Roll type Nafion dryer (RN), Mono type Nafion dryer (MN), and Cooler (CL) were investigated to figure out their water removal efficiencies and their effect on target compounds. Ozone (O_3), sulfur dioxide (SO_2), and carbon monoxide (CO) were used as target compounds in this study. Concentrations of O_3, SO_2, and CO were 100 ppb, 150 ppb, and 25 ppm, respectively. All experiments were conducted at 25°C and 1 atm. Water vapor was varied as 0, 30, 50, and 80% of relative humidity (RH). In general, 10% decrements of O_3 and SO_2 with respect to relative humidity were clearly observed. In terms of a recovery, all WRDs revealed significant effect on O_3 and SO_2 recovery. Additionally, water removal of RN was the highest followed by MN and Cooler. Consequently, it was suggested that WRDs should be taken into account according to the chemical and physical specifications of ambient air pollutants of concern.

KEY WORDS Nafion dryer, Cooler, Ozone, Sulfur dioxide, Ambient air pollutant

1. INTRODUCTION

Generally, air pollutants are difficult to analyze because they are present relatively in low quantity in ambient air. Meanwhile, water is one of the common substances existing with vapor phase in ambient air, and it can be a main obstacle to analyze air pollutants due to its high concentrations in the air (ISO, 1998). According to air pollutant analysis methods, water vapor can absorb and react with target air pollutants. In addition, water vapor can affect the baseline signal of an analyzer, corrode analyzer's inner parts, and deteriorate filter efficiency (Williams *et al.*, 2006; Wilson and Birks, 2006; Campbell *et al.*, 1982). On the basis of Korean national standards and ISO, the water removal device should be employed for SO_2 and CO analysis. On the other hand, for O_3 analysis, the influence of water vapor should be corrected with respect to the humidity (Welp *et al.*, 2013; ISO, 2010; Palluau *et al.*, 2007; US EPA, 1998; Dunder and Leighty, 1997; McClenny *et al.*, 1991). However, water removal method is not clearly defined in ambient air pollutant analysis standards. Furthermore, Nafion^{TM} dryer and Cooler, which are commonly used for water removal, showed low water removal and low recovery (Kim *et al.*, 2019; US EPA, 2016, 1998; ISO, 2010, 1996, 1992; Haberhauer-Troyer *et al.*, 1999; Namieśnik and Wardencki, 1999; McClenny *et al.*, 1991). The 60–70% loss of ethylene and acetylene has been reported when Nafion^{TM} dryer was used as WRD, and the loss of 60–70% of Methyl ethyl ketone has been also reported with Cooler (Lee *et al.*, 2019a, b; Palluau *et al.*, 2007; US EPA, 1998; Dunder and Leighty, 1997). Analytes with large dipole moments and high solubility could be affected by high quantity of water vapor (Lide, 2011; Dunder and Leighty, 1997). Consequently, it is important to select an appropriated WRD according to the analytes to be measured. Thus, in this study, we compared the performance of WRDs and evaluated suitable water removal method for O_3, SO_2, and CO.

2. MATERIALS AND METHODS

O_3 analyzer (ANA 4, Winstech Co., Ltd., Republic of Korea), SO_2 analyzer (43i, Thermo Fisher Scientific INC., USA), CO analyzer (Serinus 30, Ecotech Pty Ltd., Australia) were used for air pollutant analysis. The specifications of each analyzer were described in Table 1.

SO_2 and CO analyzers were calibrated with SO_2 (10 ppm, Rigas Co., Ltd., Republic of Korea) and CO (100 ppm, Rigas CO., Ltd., Republic of Korea) standard gases, respectively. O_3 analyzer was accomplished with another approved analyzer (Korea Research Institute of Standards and Science, Daejeon, Republic of Korea). Zero air (99.99%, DongA Ltd., Anseoung, Republic of Korea) was used to dilute standard gases and to generate humid air. The O_3 standard was produced by an O_3 generator (DA-6200 Ozone Generator, DongAn Information Industrial CO., Ltd., Republic of Korea). SO_2 (10 ppm, Rigas Co., Ltd., Republic of Korea) and CO (100 ppm, Rigas CO., Ltd., Republic of Korea) standard gases were also used for measurement.

Roll type Nafion^{TM} dryer (SWG-A01-36/KF, Sunsep, Japan), Mono type Nafion^{TM} dryer (MD-070-12F-4, Perma Pure, USA), and Cooler (SEC-2001B, Seahan hitech, Republic of Korea) were used as WRDs. Such WRDs were selected because they have been already predominantly used in the real field. Nafion dryer and Cooler were recommended as WRDs to remove water (Namieśnik and Wardencki, 1999). RN and MN were selected to compare performance with respect to surface area of the Nafion^{TM} membrane. The surface areas of RN and MN were 638.1 cm^2 and 54.1 cm^2, respectively. Humidity sensors (Testo-648, Testo Ltd., Germany) were used for the measurement of relative humidity (RH) during this experiment campaign. The experimental procedure used in this study was presented in Fig. 1.

O_3 and SO_2 which could be affected by water vapor were selected as target gases. CO gas was tested as a reference gas because of its stability. Temperature was set in the range of 25°C ± 1°C, humidity level was also set with RH 30%, 50%, and 80% to simulate atmospheric environmental conditions in Korea. The sampling flow was set to 1 L/min with respect to analyzers. Therefore, the flow rate of WRDs was also maintained as 1 L/min. To keep the same flow rate, the excess flow was vent by split in front of WRDs. Purging procedure was conducted for 30 minutes between each experiment. Each experiment was triplicated (i.e., n = 3).

The concentrations of target O_3, SO_2, and CO gas were 100 ppb, 150 ppb, and 25 ppm, respectively, which are the maximum level of Korean National ambient air criteria. The result of each experiment was compared

Table 1. Specifications of each target gas analyzer.

	ANA 4 O_3 analyzer	43i SO_2 analyzer	Serinus 30 CO analyzer
Target gas	Ozone	Sulfur dioxide	Carbon monoxide
Range	0–500 ppb	0–10,000 ppb	0–200 ppm
Lower detection limit	0.5 ppb	1 ppb	0.05 ppm
Linearity	± 1% of span gas concentration	± 1% of full scale	± 1% of full scale
Zero drift	< 1 ppb	< 1 ppb	< 0.1 ppm
Span drift	± 1% of full scale per day	± 1% of full scale per week	0.5% of reading per day

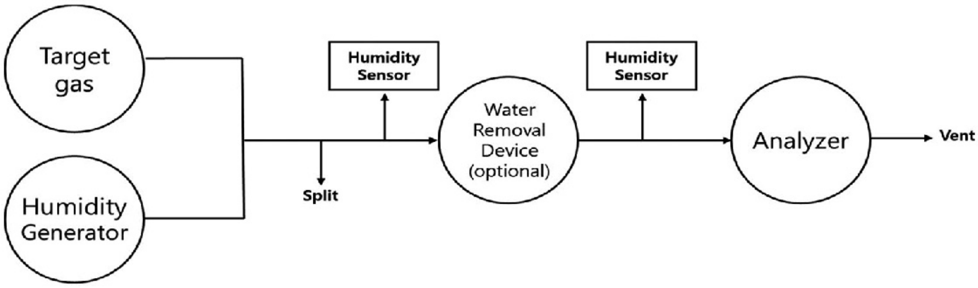

Fig. 1. Diagram for water removal and target gas recovery experiments.

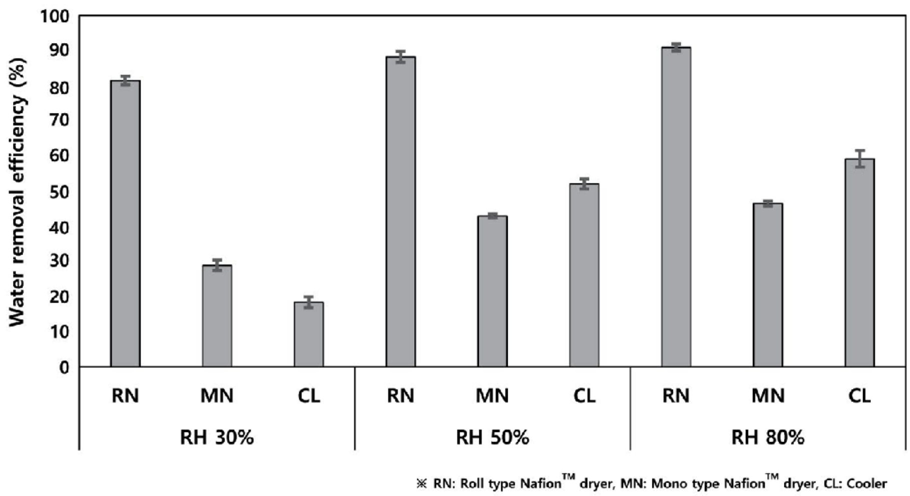

Fig. 2. Water removal efficiency with respect to each WRD.

with initial concentration under dry condition using Predictive Analytics Software (PASW 18, SPSS Inc, Hong Kong).

3. RESULTS

3. 1 Water Removal

The water removal performance of each WRD is exhibited in Fig. 2.

The lowest water removal was observed under 30% RH condition and the highest one was obtained at 80% RH. The water removal efficiency in all WRDs increased in proportion to the increment of humidity.

The CL revealed the water removal up to 59.2% under the RH condition of 80%. The largest relative standard deviation (RSD) in all WRDs was observed at RH of 30% owing to the lack of water to remove. The RN showed the best performance among the WRDs in this work. MN showed lower water removal than that of RN. The lengths of RN and MN were varied as 3.6 m and 0.3 m, respectively. Water removal performance of Nafion™ dryer depends on membrane surface area. The surface areas of RN and MN were 638.9 cm^2 and 54.1 cm^2 respectively. This different water removal could be explained by the conspicuous difference in length (Boylan *et al.*, 2014; Ye and LeVan, 2003) reported that the water removal efficiency of Nafion™ dryer depended on operating conditions of the dryer, increasing with dryer length and drying flow rate. Additionally, water removal was non-linear (Boylan *et al.*, 2014). In this study, operating conditions and flow rates were the same and only the length was different. To improve water removal performance, surface area of the Nafion™ dryer should be maximized. However, there are problems such as clogging, contamination, and adsorption on membrane, an appropriate diameter and a surface area ratio are required.

3.2 Ozone (O_3)

The O_3 experiment was carried out at 100 ppb based on Korean national ambient air criteria. The O_3 recovery results are presented in Fig. 3.

As shown in Fig. 3, the average O_3 concentrations without WRD at the RH of 30%, 50%, and 80% were 98.7 ppb, 95.9 ppb, and 89.6 ppb, respectively. The influence of O_3 measurement by water vapor was observed clearly. This O_3 reduction by water vapor has been also reported elsewhere (Boylan *et al.*, 2014; Wilson and Birks, 2005; ISO, 1998).

When the results were compared by t-test with dry and RH conditions, the assumption that all concentrations would be the same was not met. The paired t-test was conducted between the concentration at humid conditions and the initial concentration. It was found that it was not considered to be statistically significant except Nafion^{TM} dryer at RH of 30%. Since the water was not completely removed after the water removal device, it could influence the measurement. In addition, it could affect the base concentration of O_3 by the adsorption and reaction on the surface of the Nafion^{TM} dryer and the contact with water droplets in the inner tube of the CL (US EPA, 2016, 1998; Boylan *et al.*, 2014; ISO, 2010, 1998).

3.3 Sulfur Dioxide (SO_2)

Based on the national ambient air criteria, SO_2 experiment was conducted at 150 ppb. The SO_2 recovery results are depicted in Fig. 4.

As shown in Fig. 4, average concentrations of SO_2 without WRDs in the humid samples were 148.1 ppb, 144.9 ppb, and 141.5 ppb with respect to 30% RH, 50% RH, and 80% RH, respectively. Paired t-test results denoted that the initial concentration of SO_2 in dry conditions was significantly different with SO_2 concentrations without WRD application. The p-value less than 0.05 showed its similarity in all humidity ranges. Hence, the effect of SO_2 measurement by water vapor was clearly observed. Mohn and Emmenegger (2014) reported on the SO_2 measurement by water. When RN, MN and CL were employed to remove water vapor at RH of 30%, the SO_2 recoveries were 97.4%, 97.9%, and 81.0%, respectively. In case of 50% RH, SO_2 recovery of each WRD was 98.1%, 97.3%, and 72.7%, respectively. The SO_2 recoveries under the RH condition of 80% were 95.3%, 94.2%, and 39.4%, respectively.

Particularly, the recovery rate with CL decreased sharply as RH increased. Due to SO_2's large dipole moment and solubility, the compound was considered to be absorbed into water droplets which are condensed inside of the CL. According to paired t-test results, RN (RH 30%, 50%) and MN (RH 30%) did not show statistically significant difference with the initial condition. For the CL, there was a statistically significant difference by t-test results. The decrease of SO_2 recovery might be caused by its contact with water droplet which is condensed in CL impinger. (Kim *et al.*, 2019; Mohn and Emmenegger, 2014; ISO, 2013; Lide, 2011). It is considered that SO_2 could be more affected by water droplets due to its higher water solubility and dipole moment than those of O_3 and CO (US EPA, 2016; ISO,

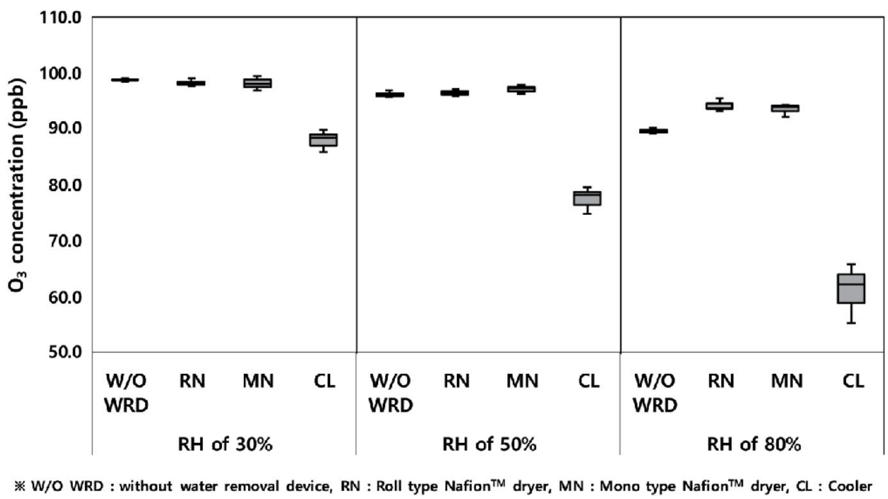

Fig. 3. Variations of O_3 concentration after WRDs deployment with different humidity conditions.

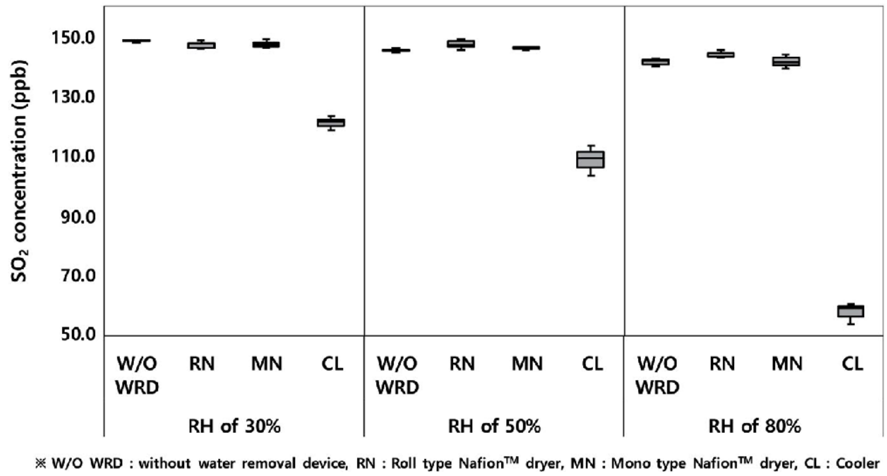

Fig. 4. Variations of SO_2 concentrations with respect to WRDs deployment with different humidity conditions.

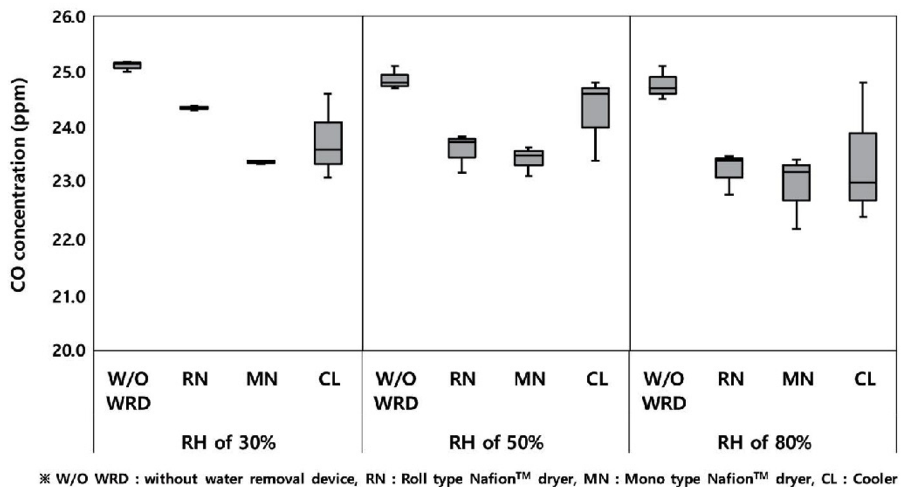

Fig. 5. Variations of CO concentration with respect to WRDs and humidity conditions.

2010, 2007).

3.4 CO

Since CO has very small dipole moment and low solubility in water, CO was used as a reference gas (Lide, 2011). The initial concentration of CO gas was 25 ppm which is the maximum value of the ambient air criteria. The CO recovery results are depicted in Fig. 5. In order to observe the effect of water on the CO measurement, the measured CO concentrations without WRDs were 25.1 ppm, 24.8 ppm and 24.7 ppm at 30%, 50%, and 80% RH, respectively. The paired t-tests between the initial concentration and results without WRDs showed a significant water effect (p-values $>$0.05). Therefore, it indicated that CO measurement was not influenced by water vapor.

When RN, MN and CL were employed to remove water vapor at 30% RH, CO recoveries were 97.4%, 93.6%, and 94.4%, respectively. In case of 50% RH, CO recovery of each WRD was 95.0%, 94.0%, and 98.4%, respectively. Likewise, CO recovery of each WRD with RH condition of 80% was 93.6%, 92.8%, and 92.0%, respectively. In case of 80% RH, the lowest recovery rate was obtained.

It was found that there was no statistical difference between initial CO and humid condition (p-value $>$0.05) except MN RH 80% case. In case of CO, the concentration of the ambient air standard was relatively high with ppm unit. Furthermore, the solubility and dipole moment were also relatively low. From these reasons, the effect of water vapor on CO measurement was low (Zellweger *et al.*, 2012; Lide, 2011; ISO, 2007; Gerbig *et al.*, 1999). Therefore, any type of WRDs can be used for CO measurement.

4. CONCLUSIONS

The effect of WRDs (RN, MN, CL) on the measurement of ambient air pollutants (O_3, SO_2, CO) were evaluated. Three types of WRDs were applied to evaluate the effect of water vapor on the measurement of ambient air pollutants. About 10% decrement of O_3 was observed at 80% RH condition. For SO_2, 7% decline was also observed at RH of 80%. However, no significant difference was observed with respect to CO. These results demonstrated that water vapor in ambient air could influence on O_3 and SO_2 measurement except CO. The highest water removal was accomplished with RN. In cases of MN and CL, water removal efficiencies were about 46.5% and 59.2%, respectively. These water removals are considered to be unsuitable as a WRD for measuring the ambient air pollutants of concern.

When the effect of WRDs on the measurement of O_3, SO_2 and CO was evaluated, it was revealed that the measurement of O_3 and SO_2 could be influenced by WRDs. In terms of CO, despite the slight decrement, CO concentration after WRDs treatment did not show any significant difference compared to its initial concentration. However, WRDs are considered to be still indispensable in order to protect analyzers from internal corrosion by water vapor. When Nafion^{TM} dryer was used, it was found that the recovery of O_3 and SO_2 was slightly higher than that of the case without WRD. However, it it is considered that its low water removal efficiency should be overcome for the measurement of ambient air pollutants.

In addition, even though two different Nafion^{TM} dryers were deployed in this work, there was a performance difference with respect to the length and the surface area of them. Therefore, it is necessary to take into account the appropriate specifications of the dryers.

CL showed higher instability due to the higher RSD than that of other WRDs. For these reasons, it is regarded that CL is not suitable WRD for ambient air measurement.

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