



Research Article

Effect of Conventional Water Pretreatment Devices on Polar Compound Analysis

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ABSTRACT In general, water vapor in the sample gas can cause adverse effect on analytical instruments. Therefore, the removal of water vapor from the sample gas is a pivotal issue when analyzing polar compounds. The effects of water pretreatment devices on polar compound analysis were investigated in this study. Nafion dryer and Cooler, which are the most widely used water pretreatment device in the world, were compared. Three types of Nafion dryers and two types of Coolers were used. The main target polar compounds were methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), isobutyl alcohol (i-BuAl) and butyl acetate (BuAc) which are designated as odorous compounds in Korea. In order to investigate the effect of the water pretreatment device on target compounds, the water vapor removal test and the recovery test were conducted. When the water vapor removal test was performed with 50% and 90% of RH, Nafion dryers (65.4%–96.6%) showed higher water removal efficiencies than those of Coolers (34.2%–67.2%). During a recovery test, Nafion dryers revealed lower recovery rate and lower reproducibility than Coolers. In particular, Nafion dryers showed very low recovery rate and low reproducibility with respect to MEK and i-BuAl which had high water solubility. It was found that Nafion dryers were not suitable for polar compounds of concern. In addition, Coolers had limitation in water vapor removal as well. Therefore, further research on water pretreatment devices that can overcome the problems is necessary.

KEY WORDS Water pretreatment device, Nafion dryer, Cooler, Water solubility, Polar compound

1. INTRODUCTION

Recently, more systematic regulations for air pollutants have been implemented in the world as interest in air pollution is increasing (Zhang *et al.*, 2016; Han, 2006; Jeon, 2006). Since air pollution policy has been tightened, more effective and accurate measurements are required. As interest in the precision analysis of air pollutants and VOCs increased, researches on factors affecting sampling and analysis such as water vapor, material of sampling container, and adsorbent have been frequently reported (Kistenev *et al.*, 2012; Ras *et al.*, 2009; Palluau *et al.*, 2007; U.S. EPA, 1998; Campbell *et al.*, 1982). Especially, water vapor contained in samples affects not only the analyte but also analytical instruments. Furthermore, deteriora-

tion of adsorption capacity, destabilization of baseline in chromatography, and damage to column could be occurred by water vapor (Haberhauer-Troyer *et al.*, 1999). Moreover, it might also clog the transfer line of the instrument (Sundin *et al.*, 1995), interfere with the identification and quantification of analyte, and result in response variability in mass spectrometer (MS) analysis (U.S. EPA, 1998).

The problems related with water vapor could be minimized by removing water vapor using a water pretreatment device which is a preliminary stage of the sampling system or analytical instrument. Therefore, U.S. EPA and Korean Ministry of Environment (MOE) recommended the use of Nafion dryer and Cooler as a water pretreatment device (Perma pure, 2019; MOE *et al.*, 2018; MOE, 2018; NIER, 2007; U.S. EPA, 1999).

A Nafion dryer, which is the most commonly used as a water pretreatment device, is composed of a copolymer of Teflon and sulfonic acid. Thus, it can be used for highly corrosive gases due to its excellent chemical durability (Perma pure, 2019). Water vapor removal of the Nafion dryer is achieved by adsorption and desorption of water vapor by the Nafion membrane (U.S. EPA, 1998; Yang *et al.*, 1996). On the other hand, Cooler used a Peltier to cool down temperature below a dew point to remove continuously water vapor. The water vapor contained in the sample gas would be condensed into liquid water when it passed through a low temperature impinger (Jahnke, 2000).

Accordingly, Nafion dryers and Coolers widely used in the world and removing water vapor in different manners were compared in this study. MEK (methyl ethyl ketone), MIBK (methyl isobutyl ketone), *i*-BuAl (isobutyl alcohol), and BuAc (butyl acetate) were selected as main target compounds among odorous compounds present in the ambient air. These target compounds have high solubility in water and require to be pretreated before analysis. In order to evaluate the performance of the water pretreatment devices, a water vapor removal test coupled with a recovery rate of the target compounds was carried out.

2. MATERIALS AND METHODS

2.1 Materials

Ketones, alcohols, and acetates among VOCs are difficult to measure and analyze due to their high solubility in

water. The solubility of MEK, MIBK, *i*-BuAl, and BuAc was 275 g/L, 95 g/L, 19.1 g/L, and 6.8 g/L, respectively (MOE, 2008). Styrene, on the other hand, had solubility in water of 0.3 g/L and was simply used as a comparative compound (MOE, 2008). In this study, a mixed standard gas (5 compounds mixed, Rigas, Korea) containing 10.3 $\mu\text{mol/mol}$ of MEK, 10.4 $\mu\text{mol/mol}$ of *i*-BuAl, MIBK, BuAc and styrene was used.

2.2 Water Pretreatment Device

The water pretreatment devices used in this study were Nafion dryer and Cooler which are used widely in the world. A short length (25.4 cm) Nafion dryer of mono tube (N-Mono) (MD-110-12F-4, Perma Pure products, USA), a long length (360 cm) Nafion dryer of mono tube (N-Roll) (SWG-A01-36/KF, Sensep, Japan), and a short length (30 cm) Nafion dryer of poly tube (50 tubes) (N-Poly) (PD-50T-12MPS, Perma Pure products, USA) were used in this study. Cooler-G (TC-Standard 6122, Buhler technologies, Germany) and Cooler-K (Electric cooler SEC-2001B, Saehan hi-tech., Ltd., Korea) were also employed. The purge gas of Nafion dryers was N_2 gas (99.99%, Rigas, Korea), and the Coolers were set at 4°C of the optimal temperature as recommended by manufacturers.

2.3 Analytical System

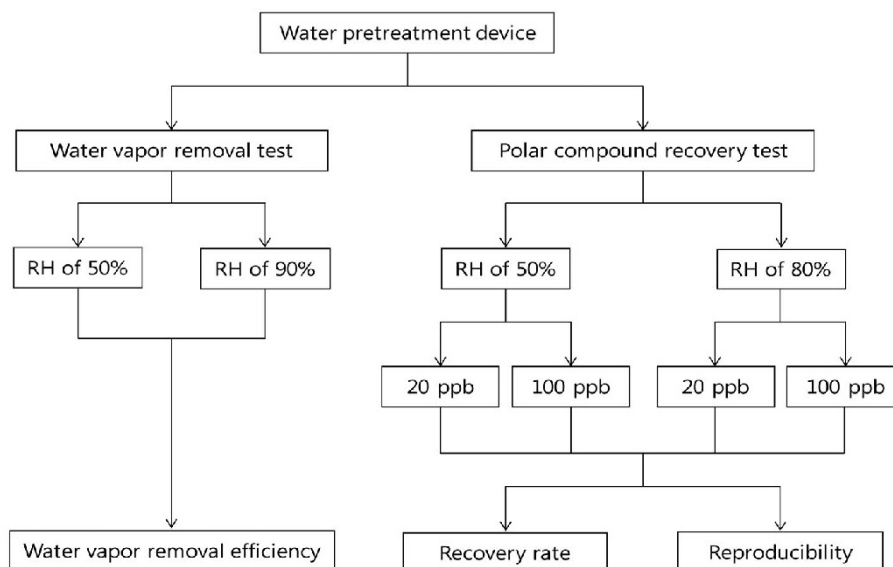
This study was carried out based on the measurement method of target compounds (ISO 16000-6, ISO 16017-1, ISO 16017-2, ES 09307.a) (MOE, 2018; U.S. EPA, 2004, 2003, 2000). A thermal desorber (TD) (Unity 2, Markes international, UK) was used for concentrating target compounds. Gas chromatography (GC) (6890, Agilent technologies, USA)/ Mass spectrometer (MS) (5975, Agilent technologies, USA) was used as an analytical instrument. Capillary column DB-624 (60 m \times 0.320 mm \times 1.80 μm) which was suitable for VOC measurement was used. The cold trap of TD was U-T9TNX-2S (Markes international, UK), and the adsorption tube for sampling was C1-AXXX-5003 (Markes international, UK). The operating conditions of the analytical instruments are summarized in Table 1.

2.4 Experimental Method

In order to evaluate the performance of water pretreatment devices, the experimental procedure is depicted in Fig. 1. To investigate the water vapor removal efficiency, the relative humidity (RH) of samples was varied at RH

Table 1. Analytical setup of TD and GC/MS.

TD (Unity 2, Markes international, UK)		GC (6890, Agilent technologies, USA) MS (5975, Agilent technologies, USA)	
Cold trap	Tenax TA	Column	DB-624 (60 m × 0.320 mm × 1.80 μm)
Sample tube desorption	300°C (10 min)	Initial temp.	40°C
Cold trap low temp.	-10°C	Initial hold time	5 min
Cold trap high temp.	300°C	Temp. programing	10°C/min → 240°C (5 min)
Cold trap hold time	5 min		
Carrier gas (He gas)	1.5 mL/min		

**Fig. 1.** Experimental scheme for performance evaluation of water pretreatment device.

of 50% and 90% for medium and high humidity. In terms of the recovery rate, RHs of 50% and 80% were selected. In this test, a Tedlar bag was used to store a gas sample comprising of humid air and target compounds. The RH value was 80% to prevent the condensation of water in the Tedlar bag. Odor concentrations were selected based on the Korea national emission permission standard.

2.4.1 Analysis and Quality Management

Validation of the analytical method was performed through quality assessment and quality control evaluation. According to a test method, calibration curves were prepared to check the linearity. The limit of detection (LOD), limit of quantification (LOQ), and precision were also evaluated.

The calibration curve was prepared in the concentration range of 10–100 ppb according to the test method. In order to prepare five concentration samples (10 ppb,

20 ppb, 40 ppb, 80 ppb and 100 ppb), 10 mL, 20 mL, 40 mL, 80 mL, and 100 mL of the standard gas were injected into a 10 L Tedlar bag (SKC, USA), respectively, which is filled with N₂ (99.999%, Rigas, Korea). The sample was introduced into an adsorption tube for 5 minutes at a flow rate of 100 mL/min using a suction pump with a flow meter. Based on the test method, the coefficient of determination (R^2) for the linearity of the calibration curve should be at least 0.98.

The LOD was repeated 7 times with samples at a detectable concentration (0.5 ppb). The LOD was calculated as method detection limit (MDL) by multiplying the standard deviation (SD) for each result by 3.14. The LOQ was also calculated by multiplying the SD by 10. Based on the test method, the calculated MDL should be 10 ppb or less for MEK, i-BuAl, MIBK and BuAc, and 1 ppb or less for styrene.

Precision was evaluated by calculating the SD accord-

ing to the test method. A sample of 80 ppb in the range of the calibration curve was prepared. The SD was calculated by repeating the measurements 3 times. Based on the test method, the calculated precision should be less than 10%.

2.4.2 Removal of Water Vapor

To verify the water vapor removal performance of the water pretreatment device, a humidity generator based on bubble method was made and used. The humidity generator consisted of a bubble bottle, mass flow controllers, a mixing chamber, heaters for the bottle and the chamber. The humidity generator was connected directly to the water pretreatment device and generated humid air with 50% and 90% RH at a flow rate of about 2 L/min. Humidity was measured using humidity sensors (Testo 645, Testo, Germany) at the front and rear of water pretreatment device. The flow rate of humid air through the water pretreatment device was set at 100 mL/min, in this study based on a certified test method (MOE, 2018; U.S. EPA, 2004, 2003, 2000). All experiments were repeated three times.

2.4.3 Recovery Test

Four samples were prepared by mixing humid air and standard gas in a 10 L Tedlar bag. 20 mL and 100 mL of standard gases were injected into two Tedlar bags, respectively. The rest of volumes were filled with humid air generated at RH of 50% from humidity generator (Sample 1: 50% RH, 20 ppb; Sample 2: 50% RH, 100 ppb). In the same way, 20 mL and 100 mL of standard gases were injected into two Tedlar bags, respectively, and 9,980 mL and 9,900 mL of humid air with 80% RH were filled in the bag (Sample 3: RH of 80%, 20 ppb; Sample 4: RH of 80%, 100 ppb). In a recovery test, Tedlar bag was used to mix humid air and target compounds, so RH was set to 80% to prevent condensing the humid air on the wall of Tedlar bags.

In order to check concentration levels before target compounds passed water pretreatment devices, prepared samples were adsorbed into adsorption trap tubes at a flow rate of 100 mL/min for 5 minutes using a suction pump with a flow meter. In order to check the concentration of compounds recovered after water vapor was removed; the adsorption tube was also connected to the outlet of the device to adsorb samples. The recovery experiment was repeated three times.

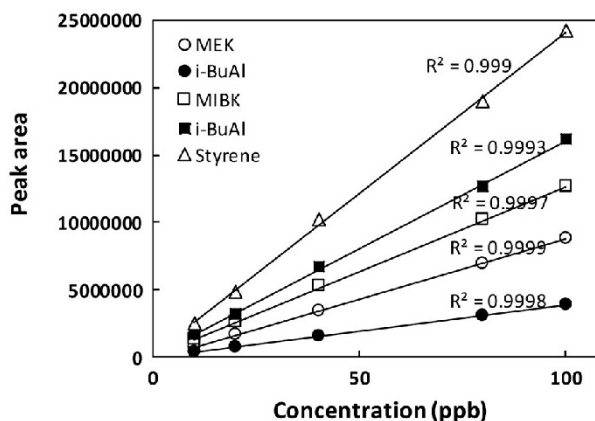


Fig. 2. Calibration curves of target compounds by TD-GC/MS.

3. RESULTS AND DISCUSSION

3.1 Quality Assurance

To evaluate the analytical method, a calibration curve was prepared as shown in Fig. 2. The correlation coefficients of the calibration curve of MEK, MIBK, i-BuAl, BuAc and styrene were in the range of 0.999 to 0.9999. In addition, MDL of MEK, MIBK, i-BuAl, BuAc and styrene obtained from multiplying the SD by 3.14 was 0.17 ppb, 0.12 ppb, 0.39 ppb, 0.09 ppb and 0.06 ppb, respectively (Lee *et al.*, 2019). On the other hand, the LOQ of MEK, MIBK, i-BuAl, BuAc and styrene obtained from multiplying the SD by 10 was 0.55 ppb, 0.38 ppb, 1.23 ppb, 0.30 ppb, 0.20 ppb, respectively (Lee *et al.*, 2019). Precision was evaluated as a SD by measuring concentrated samples three times at 80 ppb, and the precision of MEK, MIBK, i-BuAl, BuAc, and styrene were evaluated as 1.82%, 5.03%, 2.55%, 4.76%, and 9.84%, respectively (Lee *et al.*, 2019).

3.2 Removal of Water Vapor

In order to compare the water vapor removal performance of the water pretreatment devices, a water vapor removal test was performed with humid air at 50% and 90% RH.

At 50% RH, the water vapor removal efficiencies of N-Mono, N-Roll, N-Poly, Cooler-G and Cooler-K were $82.3 \pm 0.6\%$, $84.9 \pm 0.2\%$, $92.9 \pm 0.2\%$, $53.9 \pm 0.3\%$ and $34.2 \pm 0.9\%$, respectively. Under 90% RH condition, the water vapor removal efficiencies of N-Mono, N-Roll, N-Poly, Cooler-G and Cooler-K were $65.4 \pm 2.8\%$, $92.4 \pm 0.2\%$, $96.6 \pm 0.1\%$, $67.2 \pm 0.1\%$ and $62.4 \pm 0.1\%$, respectively. All water pretreatment devices except for

N-Mono showed higher water removal efficiencies at 90% RH than at 50%. In addition, it was confirmed that water removal efficiency for the Nafion dryers was higher than that of Coolers except N-Mono with 90% RH. Since N-Mono had the shortest length and the smallest area of membrane, it could not remove well water vapor contained in the sample at high humidity.

Son *et al.* (2013) reported that water vapor removal efficiencies were 81.3%–94.5% when a Nafion dryer was used to remove water vapor at 50% and 100% RH. In addition, it was confirmed that the water removal efficiency increased in proportion to the increment of RH from 50% to 100%. Haberhauer-Troyer *et al.* (1999) also found that the water removal efficiency increased (62% to 90%) as RH increased to 16%, 50% and 85% when water vapor was removed by the Nafion dryer.

The water removal effect of the Nafion dryer is strongly influenced by the length and diameter of tubes, the surface area of membrane, gas flow rate and operation temperature (U.S. EPA, 1998; Leckrone *et al.*, 1997). The Nafion dryers used in this study also showed that water removal efficiencies were different depending on the surface area of Nafion membrane. Surface area obtained

from the outside diameter and the length of the Nafion membrane of N-Mono, N-Roll, and N-Poly were 21.88 cm², 33.91 cm², and 358.57 cm², respectively (Permapure, 2019; Sunsep, 2019). As the surface area of Nafion dryer became wider, the water removal efficiency also increased.

On the other hand, it is reported that the water vapor removal effect of a Cooler depended on material, surface area, length of impinger, gas flow rate, and temperature of cooling parts (Jahnke, 2000). In addition, Lee *et al.* (2019) also confirmed that difference in water removal efficiency depended on the internal shape of an impinger and the inner part where water vapor is removed. The impinger having a spiral shape on the wall has a larger contact area than the other impinger, showed higher water vapor removal.

3.3 Recovery Rate of Water Pretreatment Device

Recovery rates of target compounds with respect to different pretreatment devices were illustrated in Fig. 3.

When the N-Mono was used to remove water vapor, the average recovery rates for each compound were 43.8%, 6.21%, 54.2%, 53.6%, and 99.6% under all RH

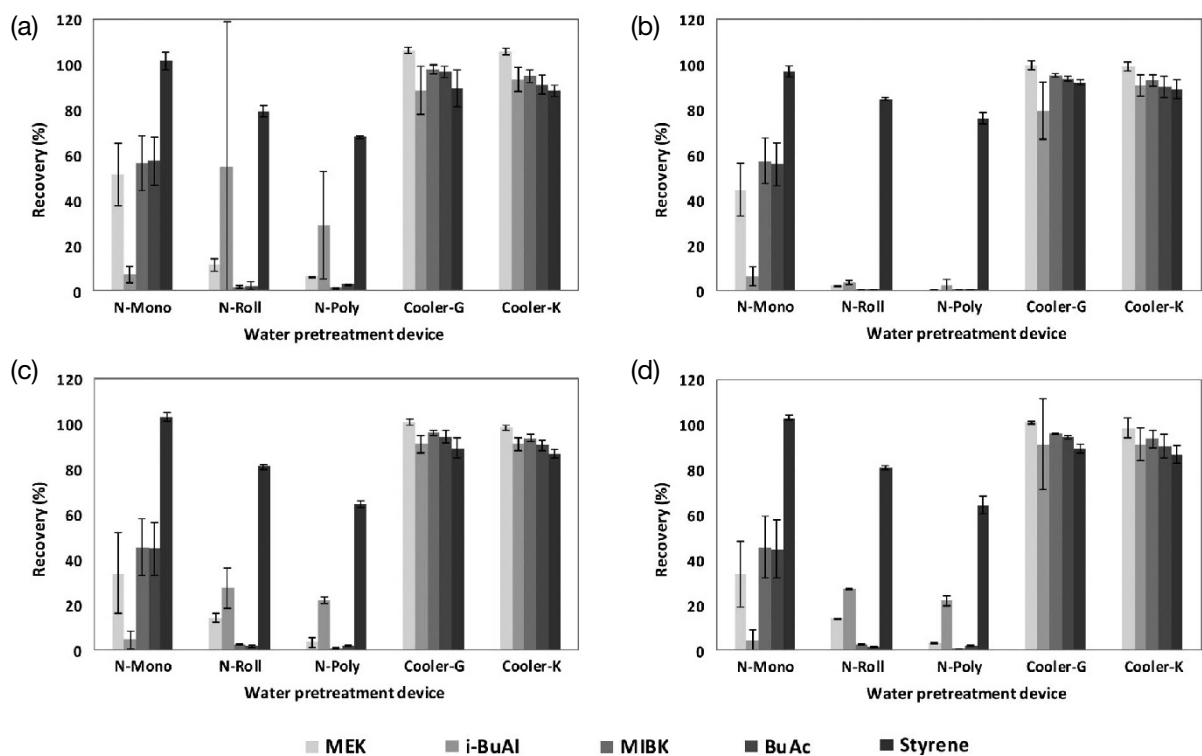


Fig. 3. Recovery rates of water pretreatment devices in this study: (a) 50% RH, 20 ppb; (b) 50% RH, 100 ppb; (c) 80% RH, 20 ppb; (d) 80% RH, 100 ppb (adapted from Lee *et al.*, 2019, appl. Sci.).

and initial concentration conditions of MEK, i-BuAl, MIBK, BuAc, and styrene. For the N-Roll, the average recovery rates were 7.50%, 21.4%, 1.47%, 1.50%, and 82.8%, respectively, under all conditions of MEK, i-BuAl, MIBK, BuAc, and styrene. When the N-Poly was used, the average recovery rates were 2.70%, 14.1%, 0.75%, 1.59%, and 70.7% under all conditions of MEK, i-BuAl, MIBK, BuAc, and styrene, respectively.

On the other hand, when the experiment was performed using Cooler-G, the average recovery rates of each compound were 101%, 81%, 96.3%, 94.6%, and 90.9% under all conditions of MEK, i-BuAl, MIBK, BuAc, and styrene. When water vapor was removed using Cooler-K, the average recovery rates for MEK, i-BuAl, MIBK, BuAc, and styrene under all conditions were 100%, 91.7%, 94.4%, 90.8%, and 88.6%, respectively (Lee *et al.*, 2019).

When water vapor was removed by Nafion dryers the lower overall recovery performance of target compounds was observed clearly. In particular, the N-Roll and the N-Poly showed that the recovery of target compounds was significantly lower than that of N-Mono. Since N-Roll and N-Poly had a larger surface area of Nafion membrane than that of N-Mono, it was presumed that polar compounds were simultaneously removed when water vapor was removed by adsorption-desorption reaction on Nafion membrane. Im *et al.* (2007) confirmed that the recovery rate was less than 20% when Nafion dryer was used for the analysis of four compounds except styrene.

When analyzing some polar compounds with a Nafion dryer as a water pretreatment device, the analyte was simultaneously removed while water vapor was removed (Zielinska *et al.*, 1996; Hsu *et al.*, 1991; McGlenny *et al.*, 1991). Nafion dryers also led to the rearrangement of some monoterpenes and removed important oxygen compounds (Burns *et al.*, 1983). When water vapor was treated with a Nafion dryer in order to analyze benzene or low molecular VOCs, artificial formation and contamination might be occurred (Seo *et al.*, 2011; Son *et al.*, 2009). Zielinska *et al.* (1996) reported that all polar compounds were lost when a Nafion dryer was used, and that the concentration of total non-methane hydrocarbons were also reduced to 10–20% as the concentration of some paraffins, olefins, and aromatics decreased. In addition, U.S. EPA (1998) reported that a specific polar VOC was lost when using a Nafion dryer, resulting in a 20%–30% reduction in recovery of total non-methane

organic compounds. The U.S. EPA (1998, 1999) also reported that careful selection of a water pretreatment device is needed because polar VOCs could be removed by the pretreatment device including the Nafion dryer.

On the other hand, the Coolers showed higher recovery rate than the Nafion dryers. In particular, the Cooler-G showed slightly higher recovery than the Cooler-K for all compounds except i-BuAl. This difference might be occurred by the material of an impinger. Impinger materials for the Cooler-G and the Cooler-K were Teflon and Glass, respectively. According to Deming *et al.* (2019), the effect of different materials on gaseous compounds was tested using tubes of various materials, and it was confirmed that Teflon material did not affect gaseous compounds rather than glass.

In addition, Lee *et al.* (2019) reported that i-BuAl had a lower recovery than other compounds due to the high water solubility and low vapor pressure of i-BuAl. MEK which has the highest solubility in water was dissolved rapidly in condensed water in the Cooler's impinger. However, due to its high vapor pressure (78 mmHg, at 20°C), it evaporated quickly to maintain equilibrium. On the other hand, i-BuAl has high solubility in water and dissolves rapidly in condensed water. However, due to its low vapor pressure (9 mmHg, at 20°C), the time to equilibrium is delayed, resulting in low recovery.

For condensation dryers such as Coolers, Dunder *et al.* (1997) warned that the use of condensation dryers could remove compounds that are intended to be analyzed by the interaction of condensed water with water-soluble air pollutants. Kim (2018) confirmed that O₃ and SO₂ recovered 61.1%–88.0% and 38.6%–80.7% after removing water vapor by using a Cooler. Therefore, if a Nafion dryer and a Cooler are used for the analysis of polar and reactive compounds, it might affect compounds to be analyzed.

The reproducibility of polar compounds concerned after water vapor removal was evaluated as relative standard deviation (RSD).

Nafion dryers showed very unstable reproducibility with respect to MEK and i-BuAl which had high solubility, as presented in Fig. 4. In particular, the N-Roll showed the worst reproducibility with maximum RSD of 117% and 60.3% for i-BuAl and BuAc at all conditions. In addition, the N-Poly showed very unstable reproducibility with maximum RSD of 74% and 100% for MEK and i-BuAl. These results may be caused by adsorption and desorption phenomenon in the Nafion membrane

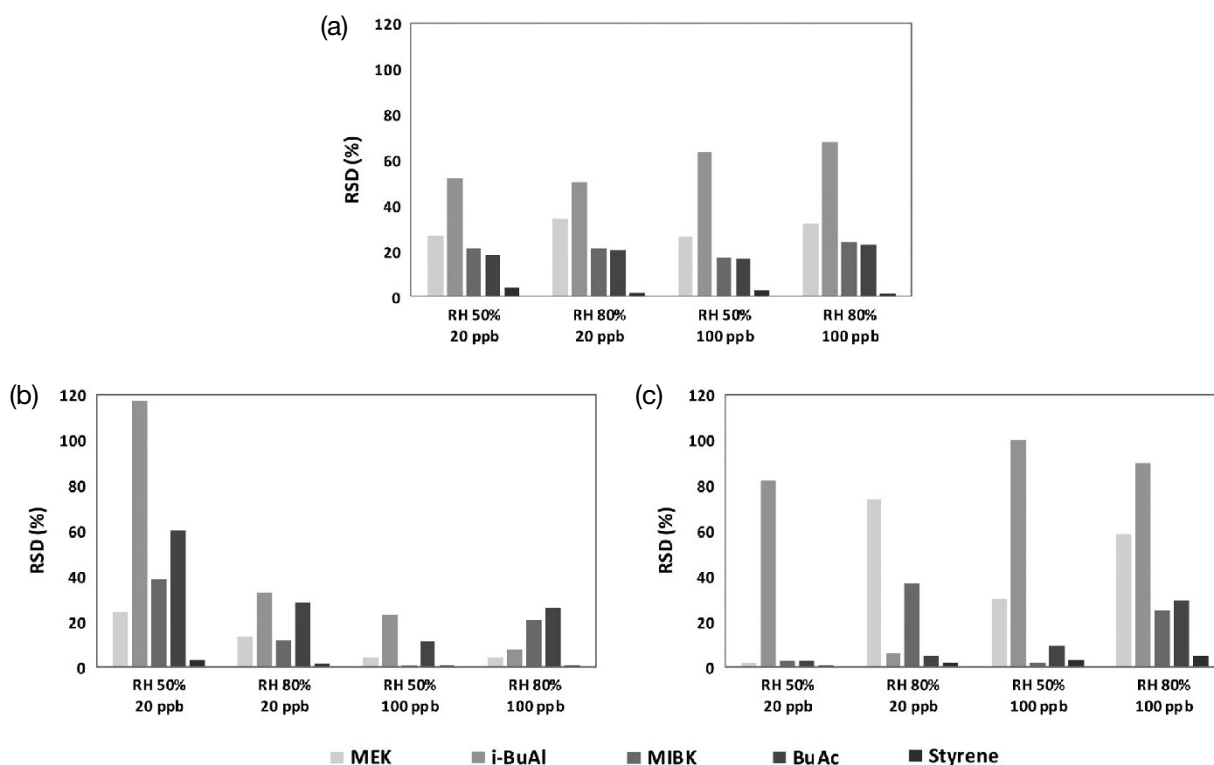


Fig. 4. Reproducibility of target compounds using Nafion dryers: (a) N-mono; (b) N-Roll; (c) N-Poly.

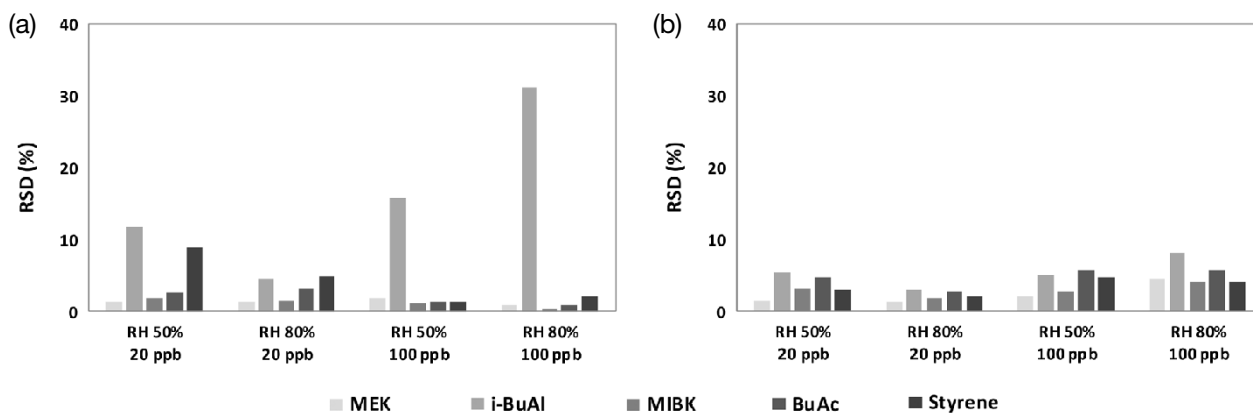


Fig. 5. Reproducibility of target compounds using Coolers: (a) Cooler-G; (b) Cooler-K (adapted from Lee *et al.*, 2019, appl. Sci.).

through the process of simultaneous removal of water vapor and polar compounds as mentioned in 3.2 and 3.3.

The Coolers showed higher reproducibility than the Nafion dryers as depicted in Fig. 5. However, it was found that there was a lower recovery for i-BuAl. The Cooler-G showed unstable reproducibility with the maximum RSD of 31.2% for i-BuAl. The Cooler-K also revealed the unstable reproducibility of RSD 2.92–8.14%

for i-BuAl. This might be related to the internal spiral shape of the impinger and the low vapor pressure of i-BuAl as mentioned in 3.2 and 3.3.

As presented in Fig. 3, Cooler-G showed slightly higher recovery than Cooler-K for all materials except i-BuAl. However, this difference seemed to be little statistically significant. On the other hand, the reproducibility of the Cooler-K was better than that of the Cooler-G as Fig. 5.

Consequently, Cooler-K could be more applicable to a real field than Cooler-G as the water pretreatment device for all target compounds concerned in this study.

The water pretreatment devices should be capable of selectively removing only water vapor without interfering with target analytes. The results of this study and other studies suggested that Nafion dryers and Coolers, which are used most in the world, be inadequate as water pretreatment devices for some peculiar compounds. In particular, since analytes often are present in small quantities in the ambient air, the selection of a suitable water pretreatment device for the analytes is very important.

4. CONCLUSIONS

This study compared both Nafion dryers and Coolers in terms of sampling and analysis performance, which have been widely used as water pretreatment devices for polar compounds. The water vapor removal efficiency of Nafion dryers was generally higher than that of Coolers, except for the N-Mono at RH of 90%. Since the surface area of the N-Roll and the N-Poly were wider than that of the N-Mono, their water vapor removal efficiency was somewhat higher. It is suggested that the N-Mono or the Coolers be not suitable for use as water pretreatment devices when the sample humidity is high.

The recovery test revealed that the Nafion dryers had a significantly lower recovery rate than the Coolers. In particular, the N-Roll and the N-Poly were found to remove large amounts of target compounds except for styrene. For a reproducibility evaluation, Nafion dryers showed particularly low reproducibility for MEK and i-BuAl which have high solubility in water. The low recovery and reproducibility of Nafion dryers for target compounds might be due to the surface area of Nafion membrane. The Cooler-G and the Cooler-K also revealed slightly different recovery and reproducibility because the internal spiral shape and material (e.g., Teflon or glass) of the impinger were different.

Although Coolers showed a higher recovery and stable reproducibility than Nafion dryers, their water vapor removal efficiency was lower than that of Nafion dryers. It was also found that the Nafion dryer had very low recovery and reproducibility for the target compounds in this study. It was consequently considered that Nafion dryers and Coolers were inappropriate as a water pretreatment device for analyzing target compounds of con-

cern.

Suitable water pretreatment device according to the sample environment and the characteristics of the analyte is very important for accurate and reliable analysis. Hence, further research is needed for different water pretreatment devices to find out the appropriate devices with reference to various analytes.

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