



Article Development of a Moisture Pretreatment Device for the Accurate Quantitation of Water-Soluble Volatile Organic Compounds in Air

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Abstract: In air pollutant monitoring using sensors, moisture can adversely affect the analytical accuracy of volatile organic compounds (VOCs). Therefore, a new moisture pretreatment device (KPASS–Odor) for analyzing VOCs in the air was developed, based on frost and created by a desublimation process inside a cold tube. The performance of KPASS–Odor was compared with conventional devices (i.e., a NafionTM dryer and a cooler) through the measurements of low watersoluble VOCs (i.e., benzene, toluene, ethyl benzene, p-xylene, and styrene) and relatively high ones (i.e., methyl-ethyl ketone, methyl isobutyl ketone, butyl acetate, and isobutyl alcohol) using gas chromatography (GC) and sensor methods. Regarding the GC method, the recovery rates for KPASS–Odor and the cooler were >95% and >80%, respectively, at a flow rate of 500 mL/min for all compounds. For the NafionTM dryer, the recovery rates differed between low and high water-soluble compounds, which exhibited the rates \geq 88% and \leq 86%, respectively. In terms of the sensor method, the VOC recovery rates of KPASS–Odor and the NafionTM dryer were found to be >90% and <50%, respectively. Therefore, KPASS–Odor was determined to be the most suitable moisture pretreatment device for highly soluble VOCs of concern in this study.

Keywords: VOCs; moisture removal; cooler; Nafion; KPASS; PID sensor

1. Introduction

Most volatile organic compounds (VOCs) are known to be toxic odors that adversely affect human health through carcinogenicity and mutation [1,2]. VOCs are classified as being generated by nature and artificially emitted from human activities. Artificially emitted VOCs are generated and emitted from various industrial processes, such as petrochemical facilities and laundry [3]. Korea's Ministry of Environment currently manages odorous VOCs in real time through the continuous monitoring of stationary emission sources [4]. Real-time VOC monitoring methods have been widely developed and used [5–7]. The most popular method is direct air sampling-mass spectrometry (MS), in which air samples are directly introduced into an MS without a gas chromatography (GC) system or a thermo-desorption instrument [5]. Another popular method is a portable GC system, which is smaller than a conventional GC system, coupled with a photoionization detector (PID), a flame ionization detector (FID), or an MS [5,6]. Gas sensors have an essential role in industry, agriculture, life detection, and other fields, and recently, VOC semiconductor sensors have been well known [7–12]. Although these abovementioned methods apply different principles for the continuous monitoring of VOCs, they have the same problem of moisture effects [6,7,10,13]. Generally, in ambient air, when the sample contains an excessive amount of moisture during the collection and analysis of odor samples, the interference and loss of target compounds to be analyzed can occur [14]. Moisture collected with the samples can lower the adsorbent retention capacity, penetrate the device (when analyzing the compounds with the device),



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). and destabilize the baseline chromatography, causing damage to the column and changing the time during which the analyte is in the analytical instrument, thereby interfering with detection [15]. In addition, moisture may also extinguish the flame of an FID, reducing the vacuum of an MS detector [16]. Humidity interference is also an important variable in the design of gas sensors. Although many studies have made great progress in compensating for the effect of humidity on gas detection performance, gas sensors are generally affected by temperature and humidity [11,12]. Therefore, the National Odor Process Test Act and the United States Environmental Protection Agency (USEPA) recommend using a pretreatment device that removes moisture at the initial stage of air pollutant analysis [17–21]. However, the moisture pretreatment devices currently in use have been reported to have various problems, such as the reduction in or deformation of the analytes to be analyzed [22–24]. Some polar compounds were removed, and benzene, heptane, and other compounds were reported to be adsorbed inside the NafionTM [22,23,25–29]. The USEPA [30] reported that the recovery rate of all non-methane organic compounds decreased by 20-30% owing to the loss of certain polar VOCs when NafionTM dryers were used. The USEPA furthermore [20,30] reported that the careful selection of moisture pretreatment devices is necessary because polar VOCs could be eliminated by pretreatment devices that contain NafionTM dryers. Recently, a humidity compensation algorithm has been developed to improve the accuracy of a sensor [11,12]. However, this method still has a limitation in use. Therefore, a moisture pretreatment device is still required to remove moisture without sample interference for accurate measurement and analysis.

For moisture pretreatment devices, a NafionTM dryer is usually recommended for samples collected in a low-moisture-content atmosphere [17-20,31]. In addition, a NafionTM dryer (or cooler) is recommended for chimneys and discharge sources with a high moisture content [18,31]. The NafionTM dryer is the most common moisture pretreatment device. Owing to its high chemical durability, it has been applied to corrosive gas analysis [18]. It can remove moisture through the adsorption/desorption of moisture through a Nafion TM membrane [32]. The cooler is a moisture pretreatment device that uses a Peltier thermoelectric device to remove water vapor by lowering the temperature of the extracted gas to the dew point temperature. The moisture in the sample gas is condensed and removed as a liquid when passing through a low-temperature impinger. The moisture removal effect of the cooler may vary depending on the surface area, length, gas flow rate and impinger material [33]. However, it was found that some target analytes were lost significantly. SO_2 was found to be lost at rates of 19.3%, 29.3%, and 61.5% under a relative humidity of 30%, 50%, and 80%, respectively, when a cooler was used to remove the moisture [34]. Lee et al. [35] reported that the loss of isobutyl alcohol, methyl isobutyl ketone, butyl acetate, and styrene was approximately 19%, 4%, 5%, and 10%, respectively, in association with 80% relative humidity. For the NafionTM dryer, the loss of the target analyte was also reported. When a NafionTM dryer coupled with an O_3 analyzer was used to measure 330 ppbv of O_3 , a 2 ppbv measurement error was found [36]. The NafionTM dryer was found to cause the loss of H_2S (i.e., 23 ppbv) by up to 7% at 100% RH [37]. The loss rate of dimethyl sulfide at 13 ppbv and 100% RH was 10% [37], and that at 4.9 ppbv and 90% RH was approximately 2% [15]. In particular, isobutanethiol was found to be lost by up to 29% at 1.6 ppbv and 92% RH [15].

The moisture pretreatment device plays an important role in removing moisture before collecting and analyzing samples so that accurate measurements can be made, especially for real-time continuous measurements. Moisture pretreatment devices for environmental atmospheres are attached to the front of the analysis device, often used for analyzing trace amounts. Therefore, the potential loss of analytes caused by the moisture pretreatment device is an important research task worldwide. This study involves fundamental development research on a moisture pretreatment device that does not interfere with VOC analytes. This study also aims to compare and investigate the recovery rates of odorous VOCs with respect to the flow rates of the air passing through the new and conventional moisture pretreatment devices. The VOCs used in this study are classified into two categories:

those with relatively high water-soluble compounds (methyl ethyl ketone, methyl isobutyl ketone, butyl acetate, and isobutyl alcohol) and those with low water-soluble compounds (benzene, toluene, ethylbenzene, p-xylene, and styrene). Additionally, the study includes a comparison of the effect of the new and traditional devices on the performance of a VOC sensor.

2. Materials and Methods

2.1. Apparatus

2.1.1. Principle of Operation of the KPASS–Odor System

A new moisture removal device, called KPASS (Key Compound PASSer)-Odor, was developed in this study to minimize the interference effect of moisture during the analytical process of odorous compounds. The operation principle of KPASS–Odor is based on a frost filter inside a cold tube. The frost filter was produced based on a desublimation process, in which water vapor directly changes from the gas phase to the solid phase, and hydrogen bonding took place among water molecules below the triple point of water. In addition, the Mpemba effect also plays an important role in the operation of KPASS-Odor. The Mpemba effect is a phenomenon in which water in a high-temperature state freezes faster than moisture in a low-temperature state in a specific situation. This phenomenon is related to intermolecular interactions and hydrogen bonds [38]. Hydrogen bonds between water molecules at low temperatures induce molecular attraction; therefore, the covalent bonds between oxygen and hydrogen atoms within water molecules accumulate energy as they lengthen. Water molecules in high-temperature conditions have a wider gap. The attraction of hydrogen bonds weakens and the covalent bond length between oxygen and hydrogen atoms shortens, thereby releasing energy [39]. High temperatures result in the breaking of weak hydrogen bonds within water molecules and increase the number of clusters with strong hydrogen bonds. Clusters accelerate nucleation, leading to the formation of hexagonal grids of ice during the process of cooling water, subsequently resulting in faster cooling than natural freezing [40]. Accordingly, the inlet gas is heated up and then suddenly cooled to -15 °C by a cold tube such that water changes from the gas phase to frost and gets attached onto the inner tube. Compared to water, these analytes lose energy at a lower temperature slower than water because of the Mpemba effect, remain in the gas phase, and can easily penetrate the cold tube. A prototype of KPASS–Odor was made by Nara Control Inc. (Seoul, Republic of Korea) for investigating its performance, and the schematic is shown in Figure 1.



Figure 1. Schematic of KPASS-Odor.

As shown in Figure 1, when the gas containing high moisture enters the equipment through the gas inlet port, moisture is removed at the cold trap. Then, the relatively low-moisture sample gas is introduced into an analytical device. The removed moisture in the form of frost is discharged to the outside through a purging stage. Two three-way solenoid valves are used to control the flow direction of the sampling and purging stages.

2.1.2. Conventional Moisture Pretreatment Devices

Two conventional moisture pretreatment devices, including a cooler (TC-Standard 6122, Buchlert technologies, Ratingen, Germany) and a Polytube NafionTM dryer (SWG-

A01-36/KF (3 m), AGC, Tokyo, Japan), were used to compare with KPASS-Odor. A moisture pretreatment device shall be used according to the environment in which samples are taken. The NafionTM dryer is usually recommended for samples from an environmental atmosphere with a low moisture content. It is also recommended to use a NafionTM dryer or Cooler for stacks and discharge sources with a high moisture content in the samples [21,30]. Coolers and NafionTM dryers have different principles, and they are widely used moisture pretreatment devices. The cooler uses a Peltier thermoelectric element to lower the temperature of moisture gas to a dew point and condenses gaseous moisture into liquid water to remove moisture. Even if there is a change in the ambient temperature and sample gas temperature, the dew point is stably maintained [13,41,42]. The NafionTM dryer removes moisture by adsorption and desorption reactions to the moisture of the NafionTM membrane inside the tube. When the moisture-containing sample gas passes through the inside of the NafionTM membrane, the water molecules are adsorbed by the hygroscopic membrane. The adsorbed water molecules are desorbed through the purge gas flowing outside through the membrane. Moisture removal continues until the humidity becomes the same by the humidity gradient of the purge gas and the wet sample gas [13,41,42].

2.1.3. VOC Analytical Instruments

The sampling and analysis of the target compounds were conducted according to ISO 16000-6, ISO 16017-1, ISO 16017-2, and ES 09307.a. The samples were collected in cleaned adsorbent traps, which were desorbed using a thermal desorber (Unity 2, Markes International, Bridgend, UK) and analyzed quantitatively using a GC/MSD (Model 6890/5973, Agilent Technologies, Inc., Santa Clara, CA, USA). Table 1 provides detailed information about the analytical system. A capillary column DB-624 (60 m × 0.320 mm × 1.80 μ m) was used as the analysis column. A concentration tube (U-T9TNX-2S, Markes International, Bridgend, UK) filled with Tenax TA was used as a cold trap. The operating conditions of the analytical equipment are depicted in Table 1.

	TD (Unity 2, M	larkes International,	Bridgend, UK)			
Pre-Desorption	Prepu	rge time	1 min			
Sample tube	Tube hold		10 min			
	Oven ter	nperature	320	320 °C		
	Split		1.3:1			
Cold trap	Pre-trap fire purge/min		1 min			
	Trap low		−10 °C			
	Trap high		320 °C			
Description	Trap hold		10 min			
	Split		2.3:1			
GC (6890, Agilent Technologies, Santa Clara, CA, USA)						
Column	DB-624 (60 m \times 0.32 mm \times 1.8 μ m, Agilent, USA)					
		Rate	Temp	Hold		
	Initial		40 °Ĉ	4 min		
Oven Condition	ramp 1	10 °C/min	250 °C	5 min		
	Run Time		30 min			
Carrier	1.5 mL/min for He gas					
	MSD (5975 Agiler	nt technologies, Santa	a Clara, CA, USA)			
Source	100 °C					
Temperature	190 C					
Mass range	35~350 amu					

Table 1. The program parameters of GC/MSD/TD.

A Photo Ionization Detector (PID) sensor (AMOS-1000, ACEN Co., Ltd., Suwon, Republic of Korea) was used to investigate the performance of moisture pretreatment devices as an application case. The lower detection limit of the sensor was 5 ppb of the total volatile organic compound (TVOC).

2.2. Materials

Among various indicators indicating the physical properties of VOCs, the n-octanol/ water partition coefficient (K_{ow} , log K_{ow}) is used as an index to indicate the hydrophilicity and hydrophobicity of VOCs [43,44], and a value may be obtained by the following Equation (1) [44,45]. Generally, a higher log K_{ow} value increases the hydrophobicity of VOC, and, thus, the solubility in water decreases.

$$\log K_{ow} = \log P = \log \left(\frac{[VOC \ concentration]octanol}{[VOC \ concentration]water} \right)$$
(1)

where [VOC concentration]octanol is the VOC concentration in octanol and [VOC concentration]water is the VOC concentration in water.

In addition, the constant value (Henry's constant, Henry's constant, *H*) of the Henry law is also used as an indicator of the physical properties of VOCs [44,46,47]. Henry's law states that the amount of gas that can be dissolved in the same amount of liquid at the same temperature is directly proportional to the partial pressure of the gas. Thus, VOCs can be classified into hydrophilic and hydrophobic VOCs based on the Henry constant obtained under the condition of the liquid being water [44,47]. VOCs with an H value of less than 0.1 at 25 °C are generally classified as hydrophilic, and VOCs with an H value of 0.1 or higher are classified as hydrophobic [44,47].

$$H = \left(\frac{[VOC \ concentration]gas}{[VOC \ concentration]liquid}\right)$$
(2)

where [VOC concentration]gas is the VOC concentration in the gas phase and [VOC concentration]liquid is the VOC concentration in the liquid phase.

Table 2 shows the physical characteristics of the odorous VOCs used in this study. Among the VOCs in the atmosphere, benzene, toluene, ethylbenzene, p-xylene, and styrene are the materials with a low water solubility, and methyl ethyl ketone, methyl isobutyl ketone, butyl acetate, and isobutyl alcohol have a high water solubility. Solid adsorption tubes (Tenax TA (35/60), Markes International, Bridgend, UK) were used to measure nine materials simultaneously. These included the melting and boiling points, the solubility, Henry's constant, and the Chemical Abstracts Service (CAS) number.

2.3. Experimental Procedure

2.3.1. Selection of Optimal Purging Conditions for KPASS–Odor

To efficiently remove the moisture contained in the sample gas without causing any analyte loss, the optimal purging conditions of KPASS–Odor are important because water droplets remaining after purging can absorb analytes. An experiment was conducted to identify the stable operating conditions with a moisture gas at 90% relative humidity at the maximum flow rate of 500 mL/min to determine the optimal purging conditions. The purging temperature, purging time, and purging flow rate were taken into account as purging variables. The purging temperatures were varied as 5, 20, and 50 °C. The purging flow rates were varied from 0.5 to 12 L/min based on the pump's specification. In terms of purging time, one and five minutes were selected. During the experiment, the cooling temperature of the moisture pretreatment device was kept constant, as in our previous study [37]. To know the moisture removal efficiency is an essential part to be verified, along with the stable operation of the equipment. Therefore, after running the purging variables proposed, the moisture removal efficiency system was checked to confirm the moisture removal efficiency for each purging condition.

Compound		Chemical	Molecular Weight	Мр	Вр	Solubility	Henry's Constant (H) at 23 °C [44,46,47]	CAS
Full Name	Abbreviation	Formula	(g/g mole)	(°C)	(°C)	(g/100 mL)	(Air–Water Partition, Dimension- less)	No.
Benzene	В	C ₆ H ₆	78.11	6	80	0.18	0.22	71-43-2
Toluene	Т	C ₆ H ₅ CH ₃	92.14	-95	111	none	0.24	108-88-3
Ethylbenzene	Е	$C_6H_5C_2H_5$	106.16	-95	136	0.015	0.28	100-41-4
Xylene	Х	$C_6H_4(CH_3)_2$	106.16	-25	144	none	0.18	106-42-3
Styrene	S	C ₆ H ₅ CHCH ₂	104.15	-30.6	145	0.03	0.10	100-42-5
Methyl ethyl ketone	MEK	CH ₃ COCH ₂ CH ₃	72.11	-86	80	29	$2.0 imes 10^{-3}$	78-93-3
Methyl isobutyl ketone	MIBK	CH ₃ COCH ₂ CH(CH ₃) ₂	100.16	-84.7	117–118	1.91	$8.5 imes 10^{-3}$	108-10-1
Butyl acetate	BuAc	CH ₃ COO(CH ₂) ₃ CH ₃	116.16	-78	126	0.7	$1.0 imes10^{-2}$	128-86-4
Isobutyl alcohol	I-BuAl	(CH ₃) ₂ CHCH ₂ OH	74.12	-108	108	8.7	$3.1 imes 10^{-4}$	78-83-1

Table 2. Information of target VOCs in this study.

2.3.2. Investigation of Moisture Removal Efficiencies by Three Moisture Pretreatment Devices

Three moisture pretreatment devices, including KPASS–Odor, a cooler, and a NafionTM dryer, were used to investigate their moisture removal efficiencies. Nitrogen (99.99%, Rigas, Daejeon, Republic of Korea) gas was injected into the humidity generator at a flow rate of 2 L/min to create a moist gas environment with a relative humidity (RH) of \geq 90%. The humidity of the generated moisture gas was checked using temperature and humidity sensors (Testo 645, Testo Inc., Lenzkirch, Germany) installed at the front and rear ends of the moisture pretreatment device. The moisture removal rate was determined by comparing the humidity data at the front and rear ends of the pretreatment device. The gas flow rates passing through the pretreatment device were set at 200 and 500 mL/min. Figure 2 shows a schematic diagram of a system for researching the moisture removal efficiency and target analyte recovery rate of the moisture pretreatment device.



Figure 2. Sampling train for comparing gas recovery rates associated with a moisture pretreatment system.

2.3.3. Investigation of VOC Recovery Rates by Three Moisture Pretreatment Devices Using GC/MSD/TD

To accurately compare the VOC recovery rates through different pretreatment devices, VOC samples were analyzed by the GC/MSD/TD system. Two standard gases were

used to prepare calibration curves. The first was made up of benzene 20.4 μ mol/mol, toluene 20.4 μ mol/mol, ethyl benzene 20.2 μ mol/mol, p-xylene 20.2 μ mol/mol, and styrene 20.5 μ mol/mol (five-odor mixture, Rigas, Daejeon, Republic of Korea), and the second was made up of Methyl ethyl ketone 10.3 μ mol/mol, butyl acetate 10.3 μ mol/mol, isobutyl alcohol 10.3 μ mol/mol, and Methyl isobutyl ketone 10.4 μ mol/mol (four-odor mixture, Rigas, Daejeon, Republic of Korea). The adsorption tube was thermally cleaned at 300 °C for 2 h before use [31,48]. To prepare various levels of samples for calibration curves, nitrogen (99.99%, Rigas, Daejeon, Republic of Korea) and prepared mixed standard gases (5 Odor Mixture, 4 Odor Mixture, Rigas, Daejeon, Republic of Korea) were injected into a 10 L Tedlar bag (SKC Inc, Covington, GA, USA). Tedlar bags have been widely used for VOC sampling and analysis because they show negligible VOC losses [49,50]. The sample adsorbed on the adsorption tube was then analyzed using GC/MSD/TD. Five concentrations were prepared for calibration curves. According to the standard sample, the amount collected in the adsorption tube was converted into mass (ng), and a calibration curve for the peak area was prepared.

A humidity generator was used to inject a moisture-containing gas into a pretreatment device. Subsequently, the amount of moisture removed after passing through the moisture pretreatment device was determined. The gas flow rate injected into the humidity generator was adjusted using a gas volume flow meter (Defender 520-M, Mesalabs, Lakewood, CO, USA) and a needle valve. The gas volume flow meter was calibrated using an area flow meter (RMA-26-SSV, Dwyer, Michigan City, IN, USA).

To determine the recovery rate of odorous VOCs in the moisture pretreatment devices (KPASS–Odor, Cooler, and NafionTM dryer), the concentrations of the target gases before and after passing through the devices were compared. The standard gases were diluted 100 times with the moisture-containing gas and then passed through the pretreatment device at a constant flow rate. The samples were collected from the front and rear ends of the moisture pretreatment devices using Tenax TA adsorption tubes (Markes International, Bridgend, UK), and the measurement results were compared. Samples at the front and rear of the devices were taken three times. In order to obtain the accuracy and precision of the analysis results, three repeated experiments were performed under the same conditions. The results were expressed as the mean, standard deviation, and relative standard deviation. The stabilization time was secured by allowing moisture and VOC gases to flow for 2 h before sampling. Samples were collected three times at 5 min intervals at the front and rear ends of the moisture pretreatment device. The results of each experiment were calculated using the following equations.

$$Average(x) = \frac{1}{n} \sum_{i=1}^{n} Xi$$
(3)

Standard deviation(s) =
$$\sqrt{\frac{\sum_{i=1}^{n} (xi-x)^2}{n-1}}$$
 (4)

Relative satandard deviation(RSD%) =
$$\frac{s}{r} \times 100$$
 (5)

2.3.4. Comparison of the Effect of KPASS–Odor and the NafionTM Dryer on the Performance of a PID Sensor

An experiment was conducted to investigate the effect of KPASS–Odor and the NafionTM dryer on the performance of a VOC sensor. A PID sensor (AMOS-1000, ACEN Co., Ltd., Suwon, Republic of Korea) was used in this study. First, the effect of moisture on the sensor was investigated. A sample under the dry condition was prepared by diluting VOC-mixed gases (five-odor mixture, four-odor mixture, Rigas, Daejeon, Republic of Korea) with N₂ (99.99%, Rigas, Daejeon, Republic of Korea) in a 10 L Tedlar bag (SKC Inc, Covington, GA, USA). On the other hand, a sample under the wet condition was made using moist N₂ (i.e., 85% RH) and VOC-mixed gases at the same concentration as the one

under the dry condition. Each sample was introduced into the PID sensor at a flow rate of 200 mL/min for 30 min, respectively, and the two results were compared in the end (Figure 3). Second, the effect of moisture pretreatment devices on the performance of the sensor was considered. Samples under Dry and Wet conditions were also produced as explained above. Each sample was passed through the moisture pretreatment device at a flow rate of 200 mL/min and introduced into the PID sensor for 10 min (Figure 3). Each experiment was conducted three times. Since the sensor could not measure the individual VOC as the GC/MSD, the TVOC was concerned, and the recovery rate of VOCs was evaluated based on TVOC concentrations.



Figure 3. Experimental set-up for the VOCs recovery rate using a PID sensor.

3. Results and Discussion

3.1. Selection of Optimal Purging Conditions for KPASS–Odor

Table 3 shows the experimental results for the optimal purging flow conditions of KPASS–Odor. The experiment was conducted by dividing flow rates into seven stages. When the tube inside KPASS–Odor is saturated with frost, it should be cleaned by purging with air. The optimal purging flow should remove all water droplets in the device as fast as possible. Due to the complicated structure with many unions and valves, removing all water droplets usually takes a long time. As shown in Table 3, the flow rate at 12 L/min showed the shortest purging time. Thus, it was selected as the optimal purging flow.

	Air Flow	Elapsed Time to Fully Clean
Order	(L/min)	(min)
1	0.5	>20:00
2	1	>20:00
3	2	>20:00
4	5	~10
5	8	~8
6	10	~7
7	12	~5

Table 3. Effect of purging flow on the performance of KPASS–Odor.

When the pressure in the tube of the device increases due to saturated frost, it automatically moves to the purging stage and cleans the tube. Figure 4 shows the pressure change in the equipment according to the purging time condition. When the purging time was 60 s, it was confirmed that the purging process due to the pressure change in the equipment is automatically performed at intervals of 5 h, as short as 30 min. Unlike the previous experimental results, the purging time of 300 s was confirmed to have no clogginess during continuous operation for 24 h. These results demonstrated that the presented purging time of 5 min was a stable one. Table 4 presents the results of the moisture removal efficiency experiment with respect to various purging times. It was confirmed that the high moisture removal efficiency was 87.1% under 5 min of purging, when no clogging phenomenon occurred, and the measured humidity value was constantly maintained, as seen in Table 4.



Figure 4. Comparison of VOC recovery rates according to various moisture pretreatment devices: (a) purging time: 60 s; (b) purging time: 300 s. (Note: lines indicate normal pressure and dots indicate abnormal pressure).

	60 s			300 s		
Purging Time	Inlet (RH%)	Outlet (RH%)	Removal Efficiency (%)	Inlet (RH%)	Outlet (RH%)	Removal Efficiency (%)
Average	90.6	15	83.4	89.6	11.6	87.1
SD N	4.08 720	2.95 720	2.92 720	2.6 720	1.78 720	1.92 720

Table 4. Effect of KPASS-Odor purging time on outlet humidity.

Note: SD is the standard deviation.

In terms of purging temperature, the temperatures were set at 5, 20, and 50 °C by controlling the Peltier. The experimental results are shown in Table 5. It was found that the humidity of the gas that passed through the moisture pretreatment was stably formed at a purging temperature of 5 °C. The moisture removal efficiency was 90.1%. Under the purging temperature of 20 °C, the average humidity passing through the moisture pretreatment device increased to 15.3%, and the moisture removal efficiency decreased to 82.3%. As for 50 °C, the average humidity passing through the moisture pretreatment device increased to 24.4%, and the moisture removal efficiency decreased to 71.7%. As a result, it was confirmed that the purging temperature of 5 °C was the most suitable temperature for moisture removal efficiency. In the purging stage, the frost that accumulated in the tube of the Peltier is removed to prevent pressure from occurring in the tube. If the purging temperature is high, the frost accumulated in the tube can be quickly removed, but it takes a long time to return to the operating temperature of -15 °C. The frost can be efficiently removed at a purging temperature of 5 °C to prevent pressure from being generated. This

Purging 5 °C 20 °C 50 °C Temperature Removal Removal Removal Inlet Outlet Inlet Outlet Inlet Outlet Efficiency Efficiency Category Efficiency (RH%) (RH%) (RH%) (RH%) (RH%) (RH%) (%) (%) (%) 90.1 82.3 71.7 Average 98.1 9.69 86.0 15.3 86.2 24.4SD 0.23 0.27 1.67 0.53 1.53 0.40 1.61 2.940.70 N 800 800 800 800 800 800 800 800 800

temperature condition showed the highest moisture removal efficiency because it took a short time to return to an operating temperature of -15 °C.

Table 5. Effect of KPASS–Odor purging temperature on outlet humidity.

Note: SD is the standard deviation.

Focusing on the fact that the operating conditions can be changed, a study was conducted to find the optimal purging conditions for KPASS–Odor. If moisture in the equipment is accumulated, internal pressure is generated and significantly affects the moisture pretreatment process. The purging cycle changes according to the amount of moisture contained in the analytical sample. Accordingly, the cycle affects the moisture removal efficiency, which is expected to have a significant impact on the analysis of odorous VOCs. The continuous odor monitoring system is an automatic one that collects and analyzes odors in the environmental atmosphere in real time. Meanwhile, the amount of moisture in the sample changes from time to time according to various humidity and weather conditions. Therefore, the moisture pretreatment device should remove moisture very efficiently, sending samples to the analytical device for the next stage of analysis. Based on the above experimental results, the moisture removal efficiency was 90.1% by adjusting the purging temperature, purging time, and operating time. Thus, these optimal purging conditions were applied to other experiments.

3.2. Moisture Removal Efficiency for Three Moisture Pretreatment Devices

Figure 5 shows a comparison of the moisture removal efficiency of the moisture pretreatment devices concerning two different flow rates. At a flow rate of 200 mL/min, the moisture removal efficiencies of KPASS–Odor, the cooler, and the NafionTM dryer were 88.8%, 73.6%, and 95.9%, respectively. In the NafionTM dryer, the relative humidity of the sample gas after moisture removal was maintained at an average of 3.8%, and the relative standard deviation (RSD) was 3.7%, indicating stable moisture removal. KPASS–Odor showed that the relative humidity of the sample gas passing through the water pretreatment device was approximately 10%. However, the cooler showed that the moisture in the sample after moisture removal was \geq 20% of the RH.

Under 500 mL/min flow rate conditions, the results showed moisture removal efficiencies for KPASS–Odor, the cooler, and the NafionTM dryer of 89.1%, 71.4%, and 94.5%, respectively. The low flow rates showed similar moisture removal efficiencies. The NafionTM dryer showed the lowest RH out of the moisture-removed devices, with an average of 5.22%, and the RSD was 5.6%, confirming stable moisture removal. The average RH was approximately 10% for KPASS–Odor. However, the cooler showed a higher RH after moisture removal than that of the low flow conditions. Similar to the experiment under low flow conditions, the NafionTM dryer showed the highest moisture removal efficiency, even at high flow rates, and the moisture was stably removed.

Lee et al. [13] studied the moisture removal efficiency under 50% and 90% RH conditions. The results showed RHs of 92.9% and 96.6% for the NafionTM dryer, 53.9% and 67.2% for the cooler, and 85.3% and 91.6% for the desolvator, respectively. Compared to the 50% RH conditions, it was confirmed that a 90% RH showed a higher moisture removal efficiency. Additionally, Son et al. [37] confirmed the moisture removal efficiency using a NafionTM dryer and desolvator to be 81.3% to 94.5% and 94.6% to 96. 1% under the same

100 80 60 40 20 KPASS-Odor Cooler Nafion dryer 200mL/min = 500mL/min

RH conditions, respectively. The results of this study, which varied the flow conditions, showed a similar trend compared to those of previous studies [13,37].



A study [13] was conducted in triplicate for 20 min each to investigate the moisture removal efficiency of a moisture pretreatment device. A pretreatment device should stably remove moisture over an extended period to reduce moisture inflow into the analytical instrument and stably remove moisture from the sample gas to reduce interference with the study material as well as to improve the recovery rate. Therefore, in this study, it was determined that the sample should be continuously measured for 180 min. A constant amount of moisture was steadily injected into the moisture pretreatment device for 180 min (3 h), and the moisture exiting through the moisture pretreatment device was measured. Kim et al. [41] compared the moisture removal efficiencies of three moisture pretreatment devices by varying the moisture concentration conditions. Relative humidities of 30%, 50%, and 80% were compared. The results showed that the three moisture pretreatment devices had the highest moisture removal efficiency under a relative humidity of 80%. Therefore, this study determined that the higher the initial moisture, the greater the amount of moisture the pretreatment device could remove. Accordingly, in this study, it was decided to use a 90% RH as the moisture concentration condition. In a previous study [41], the moisture removal efficiencies were 93.6%, 59.2%, and 90.5%, for the desolvator, cooler, and NafionTM dryer, respectively, under 80% RH. In this study, 89.1%, 71.4%, and 94.5% moisture removal efficiencies were observed for KPASS–Odor, the cooler, and the NafionTM dryer, respectively, at an RH of \geq 90% and a flow rate of 500 mL/min.

3.3. Investigation of VOC Recovery Rates by Three Moisture Pretreatment Devices Using GC/MSD/TD

A calibration curve was prepared with a standard gas to confirm the linearity of the GC/MSD and to determine the recovery rate. The coefficient of determination (r^2) of the calibration curve was \geq 0.999 for all target components. Specifically, the concentrations of benzene, toluene, ethyl benzene, p-xylene, styrene, methyl-ethyl ketone, isobutyl alcohol, methyl isobutyl ketone, and butyl acetate were 0.9995, 0.9995, 0.9993, 0.995, 0.9991, 0.9993, 0.995, 0.9987, and 0.9991, respectively. The relative standard deviation for replicate sampling at the front end of the pretreatment device was \leq 4% for the nine compounds, demonstrating good analysis reliability.

3.3.1. Reproducibility of the VOC Recovery Rate by Three Moisture Pretreatment Devices

To determine the recovery rate of odorous VOCs from the pretreatment device, the recovery rates of the compounds were compared with regard to three different moisture removal conditions. The reproducibility of the odorous VOCs was confirmed by adsorbing the moisture-removed sample gas, replicating the sampling, and analyzing it three times with GC/MSD/TD.

The sample gas with an RH of \geq 90% was passed through KPASS–Odor at a flow rate of 200 mL/min. The gas after the moisture removal was collected and analyzed. It was determined that the RSD of the triplicate experiments was less than 3%, indicating a highly reproducible experiment. When a higher flow rate (500 mL/min) was used, the RSD was <2%, indicating high reproducibility.

Reproducibility using the cooler was confirmed by collecting and analyzing the sample gas that passed through the cooler under a flow rate of 200 mL/min. Eight of the sample compounds showed RSD values of <6%. However, the RSD of I-BuAl was 7.66%, which was relatively higher than those of the other components. Reproducibility was confirmed by collecting and analyzing the sample gas under a flow rate of 500 mL/min. The RSD was within 4% for all compounds, indicating a higher reproducibility than the 200 mL/min flow rate.

The triplicate collection and analysis of the sample gas, which passed through the NafionTM dryer at a flow rate of 200 mL/min, showed that the reproducibility of the analysis was very low compared to the other two pretreatment devices. The RSD results were: BuAc (38.5%), I-BuAl (32.3%), MIBK (20.2%), ethyl benzene (16.6%), styrene (13.7%), toluene (13.6%), MEK (13.3%), p-xylene (13.3%), and benzene (8.48%). The RSD results from the higher flow rate (500 mL/min) were all within 10%, except for I-BuAl, which was 33%.

Based on the reproducibility results of the two flow conditions, it was confirmed that the reproducibility was higher for the higher flow rates (i.e., the sample gas spent less time inside the NafionTM dryer). The amount of the sample lost to the membrane film of the NafionTM dryer was reduced, resulting in a more stable sample collection.

Lee et al. [13] reported that a cooler showed <5.66% reproducibility for the compounds, barring I-BuAl, which showed a reproducibility of 2.92 to 8.14%. Lee et al. [35] reported that a NafionTM dryer showed very unstable reproducibility for MEK and I-BuAl, with >60% reproducibility. This result indicates that some target compounds were also removed while removing moisture from the membrane inside the NafionTM dryer. The difference in reproducibility results also appears in the difference in the sampling processes between this study and Lee et al.'s [13]. Lee et al. [13] combined gas containing moisture with a sample gas in a Tedlar sampling bag and passed it through a moisture pretreatment device to collect samples in an adsorption trap. However, in this study, we attempted to reduce interference with external substances by mixing moist gas and sample gas through a continuous gas flow line without using a Tedlar bag.

3.3.2. Effect of Moisture Pretreatment Devices on the VOC Recovery Rates

Figure 6 shows the results of the VOC recovery rate using three types of pretreatment devices. The experiment determined that the recovery rate of KPASS–Odor was the highest (\geq 95%). However, the NafionTM dryer had a low VOC recovery rate with high water solubility, and the recovery rate deviation among different compounds was large.

At a flow rate of 200 mL/min, the recovery rate of KPASS–Odor was >95% for all compounds. At a flow rate of 500 mL/min, the recovery rate was >96% for all components. The recovery rate of the cooler was 96% for benzene and 95% for toluene. For the other components, the recovery rates were determined to be 91%, 91%, 88%, 87%, 87%, 86%, and 80% for MEK, MIBK, p-xylene, styrene, BuAc, ethyl benzene, and I-BuAl. The recovery rate at 500 mL/min was 97% for benzene, toluene, and ethyl benzene. The rates for the other target compounds were 96% for p-xylene, 95% for styrene, 93% for MEK, MIBK, and BuAc, and 86% for I-BuAl. It was determined that the recovery rate of the NafionTM dryer

differed significantly for each compound. At a flow rate of 200 mL/min, the recovery rates for benzene, ethylbenzene, and p-xylene were >95%, and they were 91%, 44%, 34%, 29%, and 2% for styrene, MIBK, MEK, BuAc, and I-BuAl, respectively. At a flow rate of 500 mL/min, the rates were 98%, 97%, 97%, 94%, 88%, 86%, 76%, 65%, and 13% for benzene, ethyl benzene, p-xylene, styrene, toluene, MIBK, MEK, BuAc, and I-BuAl, respectively.



Figure 6. Comparison of VOC recovery rates according to various moisture pretreatment devices: (a) KPASS–Odor; (b) Cooler; (c) NafionTM dryer.

A comparative graph is presented in Figure 7 to assess variations in the recovery rates for each type of pretreatment device according to the flow rate. The recovery rate for KPASS–Odor was slightly higher for the higher flow rate, but it was insignificant. The recovery rate using the cooler was higher for all nine compounds under the high flow rate than under the low one. Specifically, the recovery rates of ethylbenzene, p-xylene, and styrene (low water-soluble compounds) increased to \geq 95%. The recovery rates using the NafionTM dryer showed an increase in four of the five low water-soluble compounds (excluding toluene). The highly water-soluble compounds of MEK, MIBK, and BuAc showed significantly higher recovery rates under the high flow conditions than those under the low ones. The recovery rate of I-BuAl increased by 11% to 13% when a higher flow rate was applied, but a significant amount the compound was lost. The moisture removal efficiency was not affected by changes in the flow rates. However, the recovery rate of VOCs was affected by their residence time in the moisture pretreatment device. As the residence time decreased, the recovery rate increased.

The disadvantage of NafionTM dryers was also reported elsewhere. Lim et al. [51] and Lee et al. [13] used the highly soluble compounds of MEK, I-BuAl, MIBK, and BuAc to determine the removal rate of the compounds using a NafionTM dryer. Lim et al. [51] confirmed that more than 80% of the material studied was removed after passing through the NafionTM dryer. Lee et al. [13] determined that I-BuAl decreased by more than 90%, and the other three compounds decreased by less than 60%. These results showed a similar tendency to the results of the experiment under the 200 mL/min flow condition of this study. It was reported that the larger the surface area of the membrane of the NafionTM dryer, the higher the number of adsorbed compounds and the lower the recovery rate. The NafionTM dryer has been shown to have a considerable influence on the analysis of analytes with high water solubility [13]. When using this moisture pretreatment device, some polar compounds were removed simultaneously [23,25–27]. It was also reported that benzene, heptane, and other compounds were adsorbed inside the NafionTM dryer [22,28,29]. In addition, a problem was identified where artifact formation is generated when benzene is passed through the NafionTM dryer [24]. The cooler showed a higher recovery rate than the NafionTM dryer for compounds with high moisture solubility. According to Deming et al. [52], who tested the effect of different materials on gas compounds using tubes of various materials, it was determined that Teflon materials did not affect gas compounds, unlike glass.



Figure 7. Variations in recovery rates by moisture pretreatment devices with respect to flow rates: (a) 200 mL/min, high solubility; (b) 500 mL/min, high solubility; (c) 200 mL/min, low solubility; (d) 500 mL/min, low solubility.

Between the cooler and KPASS–Odor, there is no significant difference in the recovery rates of BTEXS because they are hydrophobic compounds, which are not easy to dissolve in water in the cooler, based on Henry's constant H (Table 1). However, there is a difference in the recovery rates of MBK, MIBK, BuAc and I-BuAl. These compounds are hydrophilic VOCs that can easily absorb by water, but the cooler removes moisture under the liquid phase. In contrast, the removed moisture in KPASS-Odor is in the solid phase. Therefore, the cooler can cause the loss of hydrophilic VOC. Lee et al. [53] reported that the recovery rate of I-BuAl was lower than that of other compounds because of its high water solubility and low vapor pressure. MEK, which has the highest water solubility, dissolved rapidly in the condensed water within the impinger of the cooler. However, owing to its high vapor pressure (78 mmHg at 20 °C), it evaporated quickly and maintained equilibrium. In contrast, I-BuAl rapidly dissolved in condensed water owing to its high water solubility. In addition, it has been reported that the recovery rate is low because of the delay in the time taken to reach equilibrium due to the low vapor pressure (9 mmHg at 20 °C). Dunder et al. [54] warned that the use of a cooler (a condensation dryer) could remove compounds by the interaction of water-soluble air pollutants with the condensate. Kim et al. [41] demonstrated that O₃ and SO₂ showed recovery rates of 61.1-88.0% and 38.6-80.7%, respectively, after removing water vapor using a cooler. Therefore, if the NafionTM dryer or cooler is used for the analysis of polar and reactive compounds, care should be taken because the compounds under analysis may have an effect on the rate of recovery.

This study and other previous studies have shown that the most commonly used NafionTM dryers and coolers could be unsuitable for some specific VOCs, as mentioned before. In particular, because a small number of VOCs are often present in the atmosphere,

it is important to select a moisture pretreatment device suitable for them. Based on the recovery rate tests under high moisture conditions, the KPASS–Odor device was, in general, found to have the highest recovery rate for all VOCs concerned, with high and low moisture solubility.

3.4. Comparison of the Effect of KPASS–Odor and the NafionTM Dryer on the Performance of a PID Sensor

The effect of moisture on the performance of the PID sensor was investigated and shown in Figure 8. A sample under dry conditions and a sample under wet conditions, prepared at the same VOC concentration, were introduced into the sensor for 30 min at a flow rate of 200 mL/min. The average concentration of the samples under dry conditions was 185 ± 3.8 ppb, and the average concentration of the samples under wet conditions was 261 ± 5.1 ppb. This result indicated that there was an effect of moisture on the performance of the PID sensor, and the error rate was approximately 40%. The effect of humidity on the PID sensor was well reported elsewhere [55–57]. Pyo et al. [55] declared that the ambient humidity could affect the generated current of a PID sensor. Furthermore, it was reported that the response of a PID sensor to toluene was reduced to 78% at 90% RH [57]. Xu et al. [56] found that the long-term high humidity affected TVOC, as observed by a PID sensor, and recommended that the moisture should be removed to maintain the good performance of the PID sensor when long-term high RH occurs.



Figure 8. Moisture interference effect for a PID sensor.

Figure 9 shows the results of the TVOC recovery rate of the PID sensor with respect to different moisture conditions (i.e., 0 and 85% of RH) and pretreatment devices (i.e., NafionTM dryer and KPASS–Odor). Samples under dry conditions showed TVOC recovery rates of 79% and 101%, respectively, after passing through the NafionTM dryer and KPASS–Odor. This pattern was similar to the above results because the loss of some VOCs was caused by the Nafion membrane. Under wet conditions, it was found that the TVOC recovery rates for the NafionTM dryer and KPASS–Odor were 48% and 93%, respectively. This indicated that KPASS–Odor helped improve the PID sensor's performance by removing moisture content in the sample gas. Thus, a PID sensor coupled with KPASS–Odor is recommended for monitoring VOCs in the high-humidity air.



Figure 9. VOCs response of a PID sensor with respect to various moisture pretreatment devices and humidity conditions.

4. Conclusions

This study investigated the effect of different moisture pretreatment devices, including conventional devices such as a NafionTM dryer, a cooler, and the recently developed KPASS–Odor device, on the recovery rate of VOCs. Five non-polar VOCs with low water solubility (benzene, toluene, ethylbenzene, p-xylene, and styrene) and four relatively high soluble compounds (MEK, I-BuAl, MIBK, and BuAc) were considered. The cooler condenses moisture and removes it under a liquid phase. The NafionTM dryer is a moisture pretreatment device that adsorbs moisture through the NafionTM membrane and removes it using purging gas. KPASS–Odor is a new type of water vapor pretreatment device that removes moisture by changing it into the form of frost.

KPASS–Odor showed an >85% moisture removal efficiency and a 95% recovery rate for all components under low (200 mL/min) and high (500 mL/min) flow conditions, as well as stable reproducibility within 3%. The cooler maintained a moisture removal efficiency of 70% under both flow conditions. The recovery rate was \geq 80% for all compounds under low flow conditions, a high recovery rate of 90% (except for I-BuAl) was made under high flow conditions, and stable reproducibility within 6% was revealed. The NafionTM dryer showed the highest water removal efficiency of \geq 94% under both flow conditions and a recovery rate of \geq 90% for materials with low water solubility. However, its reproducibility was unstable compared to that of the other devices. For highly soluble compounds, the recovery rate of the four compounds was \leq 50% under low flow conditions; however, except for I-BuAl, all compounds showed a significant increase in the recovery rate under high flow conditions.

Appropriate moisture pretreatment devices are crucial for obtaining accurate and reliable measurements. This is particularly important when measuring trace polar and hydrophilic compounds so that the device can selectively remove moisture without interfering with target analytes.

The VOCs recovery rate experiment using a PID sensor demonstrated that TVOC concentrations were affected by moisture, which can cause approximately 40% error at 85% RH. In addition, the recovery rate of VOCs was confirmed by passing through the NafionTM dryer and KPASS–Odor at a flow rate of 200 mL/min under the same concentration of dry and wet conditions. The recovery rates under the two conditions (i.e., dry and wet conditions) exhibited different results for the NafionTM dryer (79%/48%) and KPASS–Odor (101%/93%). It was found that KPASS–Odor exhibited a better performance than the NafionTM dryer, helping to reduce the error rate of the PID sensor to approximately 7%.

In this study, KPASS–Odor showed a high moisture removal efficiency, a relatively high recovery rate for the nine compounds, and a high recovery rate under both flow rate conditions. It also showed high reproducibility in the outlet VOCs concentration. Therefore, KPASS–Odor could also be one alternative method to be used during sampling and in analyzing odorous VOCs. KPASS–Odor is a novel approach, so the literature on it is relatively scarce. More research on other VOCs under various field conditions is required in the future. The accurate measurement and analysis of VOCs emitted from various residential areas and industrial facilities that produce harmful substances will be needed as well.

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References

- 1. Kim, P.-H. A Study on Trimethylamine Control Characteristics Using Advanced Oxidizing Technique. Master's Thesis, Konkuk University, Seoul, Republic of Korea, 2010.
- 2. United States Environmental Protection Agency. Technical Overview of Volatile Organic Compounds. Available online: https://www.epa.gov/indoor-air-quality-iaq/technical-overview-volatile-organic-compounds (accessed on 22 February 2023).
- 3. Park, H.-M.; Lee, G.-B.; Ryu, J.-C.; Agustin, M.R.; Park, I.-Y.; Im, B.-J. Monitoring on Residual Volatile Organic Compounds Remaining in Industrial Waste Water. *J. Korean Soc. Environ. Anal.* **2003**, *6*, 169–177.
- 4. The Korea Ministry of Environment. Status of Designation of Odor Management Area. Available online: https://www.me. go.kr/home/web/policy_data/read.do?pagerOffset=0&maxPageItems=10&maxIndexPages=10&searchKey=&searchValue= &menuId=10262&orgCd=&condition.orderSeqId=6918&condition.rnSeq=870&condition.deleteYn=N&seq=6919 (accessed on 2 December 2022).
- Badjagbo, K.; Sauvé, S.; Moore, S. Real-Time Continuous Monitoring Methods for Airborne VOCs. *TrAC Trends Anal. Chem.* 2007, 26, 931–940. [CrossRef]
- 6. You, D.-W.; Seon, Y.-S.; Jang, Y.; Bang, J.; Oh, J.-S.; Jung, K.-W. A Portable Gas Chromatograph for Real-Time Monitoring of Aromatic Volatile Organic Compounds in Air Samples. *J. Chromatogr. A* 2020, *1625*, 461267. [CrossRef]
- Hori, H.; Ishimatsu, S.; Fueta, Y.; Ishidao, T. Evaluation of a Real-Time Method for Monitoring Volatile Organic Compounds in Indoor Air in a Japanese University. *Environ. Health Prev. Med.* 2013, 18, 285–292. [CrossRef]
- 8. Schütze, A.; Baur, T.; Leidinger, M.; Reimringer, W.; Jung, R.; Conrad, T.; Sauerwald, T. Highly Sensitive and Selective VOC Sensor Systems Based on Semiconductor Gas Sensors: How To? *Environments* **2017**, *4*, 20. [CrossRef]
- Lin, T.; Lv, X.; Hu, Z.; Xu, A.; Feng, C. Semiconductor Metal Oxides as Chemoresistive Sensors for Detecting Volatile Organic Compounds. Sensors 2019, 19, 233. [CrossRef]
- Simonenko, N.P.; Glukhova, O.E.; Plugin, I.A.; Kolosov, D.A.; Nagornov, I.A.; Simonenko, T.L.; Varezhnikov, A.S.; Simonenko, E.P.; Sysoev, V.V.; Kuznetsov, N.T. The Ti0.2V1.8C MXene Ink-Prepared Chemiresistor: From Theory to Tests with Humidity versus VOCs. *Chemosensors* 2022, *11*, 7. [CrossRef]
- 11. Wang, Y.; Zhou, Y. Recent Progress on Anti-Humidity Strategies of Chemiresistive Gas Sensors. Materials 2022, 15, 8728. [CrossRef]
- Liu, C.; Duan, Z.; Zhang, B.; Zhao, Y.; Yuan, Z.; Zhang, Y.; Wu, Y.; Jiang, Y.; Tai, H. Local Gaussian Process Regression with Small Sample Data for Temperature and Humidity Compensation of Polyaniline-Cerium Dioxide NH3 Sensor. *Sens. Actuators B Chem.* 2023, 378, 133113. [CrossRef]
- Lee, J.-Y. The Effect of Different Water Pretreatment Systems on the Analysis of Odorous Compounds in Ambient Air. Master's Thesis, Konkuk University, Seoul, Republic of Korea, 2018.

- 14. Kistenev, Y.V.; Kuryak, A.N.; Makogon, M.M.; Ponomarev, Y.N. The System for Dehumidification of Samples in Laser Gas Analysis. *Atmos. Ocean. Opt.* 2012, 25, 92–95. [CrossRef]
- 15. Haberhauer-Troyer, C.; Rosenberg, E.; Grasserbauer, M. Investigation of Membrane Dryers and Evaluation of a New Ozone Scrubbing Material for the Sampling of Organosulphur Compounds in Air. *J. Chromatogr. A* **1999**, *852*, 589–595. [CrossRef]
- 16. Brown, J. Choosing the Right Adsorbent for Your Thermal Desorption Gas Chromatography Applications. Available online: https://www.sigmaaldrich.com/KR/ko/collections/webinars/w883186467 (accessed on 2 November 2022).
- 17. Lee, M.-D. Review of Odor Measurement and Analysis Method-Standard Method of Odor Compounds. J. Korean Soc. Environ. Eng. 2007, 29, 761–767.
- 18. Perma Pure. Available online: http://www.permapure.com (accessed on 2 December 2022).
- 19. The Korea National Institute of Environmental Research. *Air Pollution Monitoring Network Installation and Operation Guidelines* (2021); The Korea National Institute of Environmental Research: Seoul, Republic of Korea, 2021.
- U.S. Environmental Protection Agency. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air Second Edition. Compendium Method TO-17 Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes; Center for Environmental Research: Cincinnati, OH, USA, 1999.
- The Korea Ministry of Environment. VOCs—Cold Trap—GC Method—On-Line Monitoring Method; The Korea National Institute of Environmental Research: Incheon, Republic of Korea, 2018.
- Gong, Q.; Demerjian, K.L. Hydrocarbon Losses on a Regenerated Nation[®] Dryer. J. Air Waste Manag. AsSoc. 1995, 45, 490–493. [CrossRef]
- 23. Hsu, J.P.; Miller, G.; Moran, V. Analytical Method for Determination of Trace Organics in Gas Samples Collected by Canister. J. *Chromatogr. Sci.* **1991**, *29*, 83–88. [CrossRef]
- 24. Son, E.-S.; Seo, Y.-K.; Lee, D.-H.; Lee, M.-D.; Han, J.-S.; Baek, S.-O. A Study on the Performance Optimization of a Continuous Monitoring Method for Hazardous VOCs in the Ambient Atmosphere. *J. Korean Soc. Atmos. Environ.* **2009**, 25, 523–538. [CrossRef]
- McGlenny, W.A.; Pleil, J.D.; Evans, G.F.; Oliver, K.D.; Holdren, M.W.; Winberry, W.T. Canister-Based Method for Monitoring Toxic VOCs in Ambient Air. J. Air Waste Manag. AsSoc. 1991, 41, 1308–1318. [CrossRef]
- Taurková, P.; Svoboda, M.; Musil, S.; Matoušek, T. Loss of Di- and Trimethylarsine on Nafion Membrane Dryers Following Hydride Generation. J. Anal. At. Spectrom. 2011, 26, 220–223. [CrossRef]
- 27. Zielinska, B.; Sagebiel, J.C.; Harshfield, G.; Gertler, A.W.; Pierson, W.R. Volatile Organic Compounds up to C20 Emitted from Motor Vehicles; Measurement Methods. *Atmos. Environ.* **1996**, *30*, 2269–2286. [CrossRef]
- Shaw, S.L. The Production of Non-Methane Hydrocarbons by Marine Plankton; Massachusetts Institute of Technology: Cambridge, MA, USA, 2001.
- 29. Baek, S.-O.; Moon, Y.-H. Evaluation of Adsorbent Sampling Methods for Volatile Organic Compounds in Indoor and Outdoor Air. *Anal. Sci. Technol.* **2004**, *17*, 496–513.
- 30. U.S. Environmental Protection Agency. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air Second Edition Compendium Method TO-14A Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Specially Prepared Canisters with Subsequent Analysis By Gas Chromatography; Center for Environmental Research: Cincinnati, OH, USA, 1999.
- The Korea Ministry of Environment. Toluene, Xylene, Methylethylketone, Methylisobutylketone, Butylacetate, Stylene and i-Butylalcohol— Cold Trap/Thermal Desorption—GC Method; The Korea National Institute of Environmental Research: Incheon, Republic of Korea, 2018.
- Yang, J.; Conver, T.S.; Koropchak, J.A.; Leighty, D.A. Use of a Multi-Tube Nafion[®] Membrane Dryer for Desolvation with Thermospray Sample Introduction to Inductively Coupled Plasma-Atomic Emission Spectrometry. *Spectrochim. Acta Part B Spectrosc.* 1996, *51*, 1491–1503. [CrossRef]
- 33. Jahnke, J.A. Continuous Emission Monitoring, 3rd ed.; John Wiley & Sons: Hoboken, NJ, USA, 2022; pp. 49-50.
- Kim, D.-J.; Dinh, T.-V.; Lee, J.-Y.; Choi, I.-Y.; Son, D.-J.; Kim, I.-Y.; Sunwoo, Y.; Kim, J.-C. Effects of Water Removal Devices on Ambient Inorganic Air Pollutant Measurements. Int. J. Environ. Res. Public Health 2019, 16, 3446. [CrossRef]
- Lee, J.-Y.; Dinh, T.-V.; Kim, D.-J.; Choi, I.-Y.; Ahn, J.-W.; Park, S.-Y.; Jung, Y.-J.; Kim, J.-C. Effect of Conventional Water Pretreatment Devices on Polar Compound Analysis. *Asian J. Atmos. Environ.* 2019, *13*, 249–258. [CrossRef]
- 36. Wilson, K.L. Water Vapor Interference in the UV Absorption Measurement of Atmospheric Ozone; University of Colorado Boulder: Boulder, CO, USA, 2005.
- Son, Y.-S.; Lee, G.; Kim, J.-C.; Han, J.-S. Development of a Pretreatment System for the Analysis of Atmospheric Reduced Sulfur Compounds. Anal. Chem. 2013, 85, 10134–10141. [CrossRef]
- 38. Tyrovolas, I.J. Explanation for the Mpemba Effect. J. Mod. Phys. 2017, 08, 2013–2020. [CrossRef]
- 39. Sun, C.Q. Mpemba Paradox: Hydrogen Bond Memory and Water-Skin Supersolidity. arXiv 2015, arXiv:1501.00765.
- Tao, Y.; Zou, W.; Jia, J.; Li, W.; Cremer, D. Different Ways of Hydrogen Bonding in Water—Why Does Warm Water Freeze Faster than Cold Water? J. Chem. Theory Comput. 2017, 13, 55–76. [CrossRef]
- Kim, D.-J. The Effect of Water Pretreatment Device on Environmental Air Pollutants (O₃, SO₂, CO) Measurements and Analysis. Master's Thesis, Konkuk University: Seoul, Republic of Korea, 2019.
- 42. Gil, H.-N.; Kim, J.-C. The Effect of Hybrid Water Pretreatment Device on the Recovery Rate of HCl from Its Emission Sources. Master's Thesis, Konkuk University, Seoul, Republic of Korea, 2021.

- 43. Giaginis, C.; Tsantili-Kakoulidou, A. Alternative Measures of Lipophilicity: From Octanol–Water Partitioning to IAM Retention. J. Pharm. Sci. 2008, 97, 2984–3004. [CrossRef]
- 44. Yun, J.; Cho, K.-S. A Review on the Treatment of Volatile Organic Compounds Using Absorbents. J. Odor. Indoor Environ. 2018, 17, 95–121. [CrossRef]
- 45. Bruce, L.J.; Daugulis, A.J. Solvent Selection Strategies for Extractive Biocatalysis. Biotechnol. Prog. 1991, 7, 116–124. [CrossRef]
- 46. Vuong, M.-D.; Couvert, A.; Couriol, C.; Amrane, A.; Le Cloirec, P.; Renner, C. Determination of the Henry's Constant and the Mass Transfer Rate of VOCs in Solvents. *Chem. Eng. J.* **2009**, *150*, 426–430. [CrossRef]
- 47. Muñoz, R.; Daugulis, A.J.; Hernández, M.; Quijano, G. Recent Advances in Two-Phase Partitioning Bioreactors for the Treatment of Volatile Organic Compounds. *Biotechnol. Adv.* 2012, 30, 1707–1720. [CrossRef]
- 48. The Korea Ministry of Environment. *Methods for Determination of Hazardous and Volatile Organic Compounds in Ambient Air— Adsorbent Trap Method;* The Korea National Institute of Environmental Research: Incheon, Republic of Korea, 2021.
- 49. Ahn, J.-W.; Pandey, S.K.; Kim, K.-H. Comparison of GC-MS Calibration Properties of Volatile Organic Compounds and Relative Quantification Without Calibration Standards. *J. Chromatogr. Sci.* **2011**, *49*, 19–28. [CrossRef]
- 50. U.S. Environmental Protection Agency. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* Second Edition Compendium Method TO-15 Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/ Mass Spectrometry (GC/MS); Center for Environmental Research: Cincinnati, OH, USA, 1999.
- Im, M.; Ju, D.; Kim, H.; Song, K.; Park, K. A Study of Analytical Method for 4 Legally-Designated Compounds [MEK, MIBK, n-Butyl Acetate, i-Butyl Alcohol] in Ambient Air Using On-Line Thermal Desorber with GC/FID. J. Korean Soc. Dor. Res. Eng. 2007, 6, 145–153.
- 52. Deming, B.L.; Pagonis, D.; Liu, X.; Day, D.A.; Talukdar, R.; Krechmer, J.E.; de Gouw, J.A.; Jimenez, J.L.; Ziemann, P.J. Measurements of Delays of Gas-Phase Compounds in a Wide Variety of Tubing Materials Due to Gas–Wall Interactions. *Atmos. Meas. Tech.* **2019**, 12, 3453–3461. [CrossRef]
- 53. Lee, J.-Y.; Dinh, T.-V.; Kim, D.-J.; Choi, I.-Y.; Ahn, J.-W.; Park, S.-Y.; Jung, Y.-J.; Kim, J.-C. Comparison of Water Pretreatment Devices for the Measurement of Polar Odorous Compounds. *Appl. Sci.* **2019**, *9*, 4045. [CrossRef]
- 54. Dunder, T.A.; Leighty, D.A. Comparison of Thermoelectric and Permeation Dryers for Sulfur Dioxide Removal during Sample Conditioning of Wet Gas Streams; Air and Waste Management Association: Pittsburgh, PA, USA, 1997.
- 55. Pyo, S.; Lee, K.; Noh, T.; Jo, E.; Kim, J. Sensitivity Enhancement in Photoionization Detector Using Microelectrodes with Integrated 1D Nanostructures. *Sens. Actuators B Chem.* **2019**, *288*, 618–624. [CrossRef]
- 56. Xu, W.; Cai, Y.; Gao, S.; Hou, S.; Yang, Y.; Duan, Y.; Fu, Q.; Chen, F.; Wu, J. New Understanding of Miniaturized VOCs Monitoring Device: PID-Type Sensors Performance Evaluations in Ambient Air. *Sens. Actuators B Chem.* **2021**, *330*, 129285. [CrossRef]
- Khoshakhlagh, A.H.; Golbabaei, F.; Beygzadeh, M.; Carrasco-Marín, F.; Shahtaheri, S.J. Evaluation of Direct Reading Photoionization Detector Performance under Various Operational Parameters. *Environ. Health Eng. Manag.* 2021, *8*, 123–128. [CrossRef]

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