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Effects of adsorbent sampling variables on the accurate measurement of isoprene

In-Young Choi*, Trieu-Vuong Dinh*, Ki-Joon Kim*, Dong-Eun Kim, Bong-Hyun Jun**,
Seungae Lee***, Young-Min Park****, and Jo-Chun Kim*,†**

*Department of Civil and Environmental Engineering, Konkuk University, 120 Neungdong-ro, Gwangjin-gu, Seoul 05029, Korea
**Department of Bioscience and Biotechnology, Konkuk University, 120 Neungdong-ro, Gwangjin-gu, Seoul 05029, Korea
***Department of Chemical Engineering, Konkuk University, 120 Neungdong-ro, Gwangjin-gu, Seoul 05029, Korea
****Department of Immunology, KU Open Innovation Center, School of Medicine, Konkuk University, Chungju 27376, Korea

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Abstract−Isoprene is an important volatile organic compound causing photochemical smog in the atmosphere; thus, accurate analysis of isoprene is essential. In this study, the effect of sampling conditions, including adsorbent types, sampling temperatures, and flow rates on the recovery of isoprene, was investigated. Common adsorption traps of isoprene, including Tenax TA/Carbosieve SIII, Tenax TA/Carbotrap, were used as adsorbents. Sampling temperatures varied from 25 °C to 40 °C. Sampling flow rates were 50, 100, and 200 mL min^{-1}. It was found that the Tenax/Carbotrap trap revealed the highest isoprene recovery rate; however, the Tenax/Carbosieve SIII trap depicted more significant loss of isoprene than the other one. As for sampling variables, the lower the temperatures and flow rates concerned were, the higher the isoprene recovery was. It was concluded that sampling temperatures and flow rates should be ≤35 °C and ≤50 mL min^{-1} during a sampling process, respectively. In addition, Carbosieve SIII should not be used for isoprene sampling due to its poor recovery rate.

Keywords: Isoprene, Adsorbent, Sampling Conditions, Gas Chromatography, Thermal Desorption

INTRODUCTION

Isoprene is one of the volatile organic compounds (VOCs) that is an essential indicator of environmental pollution and health in modern society [1-4]. VOCs contribute to the generation and transformation of numerous pollutants from various emission sources, such as industrial activity, vehicles, and natural sources, to widely distributed emission regions, including urban areas, rural areas, and the ocean, depending on the characteristics of their locations [5-10]. Globally, VOC emissions are much higher from natural sources. VOCs, including isoprene, are major atmospheric chemicals that are commonly emitted from natural sources [6,9,11,12] when they react with nitrogen oxides. They contribute to the formation of ozone and particulate matter in the atmosphere, which is monitored and analyzed to manage air quality [9,13]. Ozone and particulate matter contribute to air pollution and negatively affect human health. In particular, the ozone concentration in the atmosphere is an important indicator of an increase in the concentration of VOC emissions [2,14]. Natural sources account for a more significant fraction of VOC emissions than artificial sources. However, artificial VOC emissions are increasing owing to human activity, and require more attention [15,16]. It has even been confirmed that isoprene is generated in human breath, and research on this is being conducted in various fields [17-19]. In particular, the semiconductor and rubber manufacturing industries, which are undergoing rapid development in Korea and have contributed significantly to the economic growth of the country, have become a major source of isoprene emissions [20-22].

Isoprene is a colorless volatile compound soluble in most hydrocarbons and practically soluble in water. It is highly reactive and undergoes a reaction similar to that of butadiene. Isoprene units are abundant in nature. Isoprene reacts rapidly with oxygen in the air, and 1% conversion of isoprene occurs in approximately 3 h at 50 °C. The resulting product is a cyclic compound of oxygen and isoprene with a repeated structure of (-C5H9O2-) [10]. The reactions above give isoprene a dominant role in atmospheric chemistry, and its properties are shown in Table 1. Various methods can be used to analyze isoprene, such as chemiluminescence, gas chromatography (GC)-based, and photoionization detector measurements. Among them, GC-based analysis is a standard method for VOC analysis used in US EPA Method TO-17. This one presents a standard method for sampling VOCs using solid sorbents and for analyzing them using GC. Sampling conditions such as adsorbent type, temperature, and flow rate are presented here. Solid sorbents are commonly used to concentrate isoprene, and sorbents commonly used are graphitized carbon black-based ones such as Carbotrap, Tenax GR, Tenax TA, Carbosieve S3, Carboxen 569 [23-27]. Although this method is a standard VOC sampling and analysis method, it lacks specific sampling information on the highly reactive isoprene. To sample isoprene according to the TO-17 method, the selection of solid adsorbents and sampling conditions should be presented. However, when selecting a solid adsorbent, the user should consider the suitable combination by presenting information such as the carbon number of the target material, boiling point range, limit temperature for desorption, and surface area. In the case of the sampling flow rate, the range of 5 to 200 mL min^{-1} is sug-

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[†] To whom correspondence should be addressed.
E-mail: jckim@konkuk.ac.kr

Table 1. Gas chromatography/mass spectrometry analytical methods

Gas chromatography/mass spectrometry system			
GC Oven	Initial temperature	40	°C
	Hold time	5	min
	Ramping rate (1st)	2	°C min^{-1}
	Next temperature	120	°C
	Hold time	1	min
	Ramping rate	10	°C min^{-1}
	Final temperature	240	°C
	Hold time	2	min
	Total running time	60	min
MS Detector	Ionization mode	EI (70 eV)	
	Ion source temperature	250	°C
	Interface temperature	250	°C
	TIC scan range	29-280	m/z
	Threshold	150	°C
Thermal desorber			
Sampling-tube desorption temperature		280	°C
Sampling-tube holding time		10	min
Minimum cold-trap temperature		−10	°C
Maximum cold-trap temperature		320	°C
Cold-trap hold time		5	min
Transfer-line temperature		120	°C
Heated-valve temperature		120	°C

gested based on the suction tube with the outer diameter of 1/4-inch, and a flow rate of higher than 200 mL min^{-1} is not recommended. In the case of sampling temperature, normal atmospheric conditions are presumed, and it is recommended to achieve equilibrium with ambient temperature. In addition, the temperature at the time of sampling is limited to suggesting a method to minimize the effect on moisture by setting the temperature below 30 degrees when the humidity is low and above 30 degrees when the humidity is high based on a relative humidity of 65% [27]. This method of sampling and analyzing VOCs is still in use today without being reformed [28-30]. If the wrong adsorbent is used, the loss of isoprene due to on-sorbent reaction or artifact formations can occur. Therefore, it is necessary to investigate the effect of adsorbents and sampling variables on the sampling isoprene.

The aim of this study was to determine the best sampling conditions for isoprene using an adsorption tube. Common adsorbents for VOCs, including Carbosieve SIII, Carbotrap, and Tenax - TA, were used to investigate the isoprene recovery rates associated with various temperatures and flow rates. Through this study, optimal adsorbent, sampling temperature, and flow rate would be suggested.

METHOD AND MATERIALS

1. Target Compound and Adsorbents

The emission of isoprene significantly impacts the oxidizing potential of air. This impact accounts for a large proportion of the air environment, making accurate measurement of the substance necessary [31,32]. Therefore, this experiment was carried out to determine suitable adsorbents and sampling conditions for isoprene sampling using solid adsorbents based on GC and thermal desorption. The isoprene standard (GC grade, purity 99.5%, Sigma Aldrich, USA) was handled using a brown 2 mL vial for isoprene generation and measurement according to the procedures described in US EPA Method 8260D [33]. The standard was used without further purification and converted into a gas material using a static dilution bottle (SUPELCO, USA), which is a simple method for preparing, storing, and using VOC standard materials [34-36]. A static dilution bottle was used to convert the solution into a gaseous material. Subsequently, 1 mL of the isoprene standard material was injected into a 2 liter static dilution bottle and evaporated to prepare the standard gas. The concentration of the prepared standard gas was sampled using a syringe for the adsorption experiment and was determined to be approximately 220 ppmv. Experiments were conducted using two adsorbents, Carbosieve SIII (60/80 mesh, SUPELCO, USA) and Carbotrap (20/40 mesh, SUPELCO, USA), coupled with Tenax TA (60/80 mesh, SUPELCO, USA). Tenax TA is a single-type polymer with applications ranging from C_6-C_{30}. It is a solid sorbent material commonly used to analyze semi-volatile organic compounds because of its inert characteristics, high porosity, high surface area, and low non-specific adsorption. In addition, it helps to prevent water-related analysis problems that are often encountered in multibed or carbon-based materials [37-39]. Therefore, Tenax TA has long been used as a guard adsorbent for a multiple adsorption bed or trap. Carbosieve SIII is a porous carbon material that has been widely studied for its potential in gas separation and purification applications. The main characteristics of Carbosieve SIII include its high surface area, narrow pore-size distribution, and high mechanical stability. Its surface area (900 m^2 g^{-1}) and pore volume (0.65 cm^3 g^{-1}) provide a large surface area for gas adsorption, which is important for efficient gas adsorption. The 3 Å-pore size of Carbosieve SIII makes it ideal for adsorbing small gas molecules. Its high surface area, narrow pore-size distribution, and good chemical stability make it suitable for industrial processes requiring efficient and selective gas adsorption [40]. However, the adsorption capacity of Carbosieve SIII decreases with increasing relative humidity. Therefore, the effect of relative humidity must be carefully considered when using Carbosieve SIII to measure VOCs in humid environments [38,41]. Carbotrap is also a porous carbon material as Carbosieve SIII. The adsorption coverage of Carbotrap ranges from C_4 to C_{14}, and it exhibits a wide range of application conditions. Carbotrap targets a wide range of VOCs, such as aliphatic hydrocarbon compounds, ketones, and aldehydes. It is advantageous for capturing strong volatile substances [42-44]. The main characteristics of Carbotrap include a high surface area, narrow pore-size distribution, and good mechanical stability. Their surface area (600 m^2 g^{-1}) and pore volume (0.35 cm^3 g^{-1}) provide a large surface area for gas adsorption, which is important for efficient gas adsorption. The 10 Å pore size of Carbotrap makes itself ideal for adsorbing small gas molecules [43,44]. Accordingly, Tenax-TA/Carbotrap trap (1/4-inch O.D. tube, Tenax TA/Carbotrap trap=110 mg/100 mg) was used to compare with Tenax-TA/Carbosieve SIII trap (1/4-inch O.D. tube, Tenax TA/Carbosieve SIII=110 mg/60 mg).

2. Isoprene Analytical Methods

2-1. Analytical Instrument

Isoprene was analyzed using a system that included a thermal desorber (Model Unity, Markes, UK), GC (HP Model 6890, Agilent, USA), and MS (HP Model 5973, Agilent, USA). The compounds were analyzed using a DP-624 column (60 m×0.32 mm, 1.8 μm, Agilent, USA). Table 1 shows the operating conditions of the thermal desorber and GC/MS. The sorbent was desorbed for 10 min in the thermal desorption pre-treatment system under various temperature conditions. The isoprene samples were then introduced into the GC/MS system after desorption from the adsorbent. Individual compound was separated on the column to allow adequate separation within the GC. Isoprene has a low molecular weight, which is classified as C5, and a boiling point of 34.067 °C, making it highly volatile. The GC oven program was set initially at 40 °C for 5 min for the analysis of isoprene. The temperature was increased at a rate of 2 °C min^{-1} to 120 °C and then at 10 °C min^{-1} to 240 °C. Finally, the temperature was maintained at 240 °C for 2 min [45].

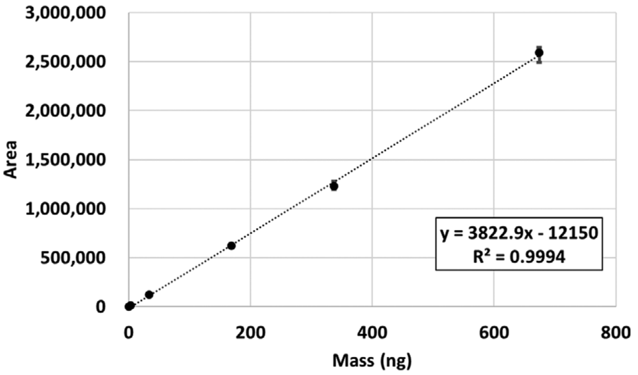

Fig. 1. Isoprene calibration curve.

2-2. Calibration Curves, Quality Assurance, and Quality Control

The standard gas was prepared by injecting 1 mL of the isoprene standard material into a 2 liter static dilution bottle. The static dilution bottle was used to create a continuous isoprene calibration line. A standard was used to calculate the isoprene concentration. The prepared standard gas has a concentration of approximately 220 ppmv. Volumes of 1, 10, 100, 500, 1,000, and 2,000 μL were directly injected into the GC/MS system using a syringe. The injected isoprene masses were 0.34, 3.37, 33.71, 168.55, 337.1, and 674.19 ng. Isoprene was analyzed using a GC/MS system in the SIM mode. The isoprene calibration curve showed a high linearity (R^2>0.9994) (Fig. 1). The quality assurance and control of the analytical system were performed by analyzing the same standard concentration three times to calculate the relative standard deviation and evaluate the analytical precision. In addition, OriginPro 2022 (9.9.0.220,

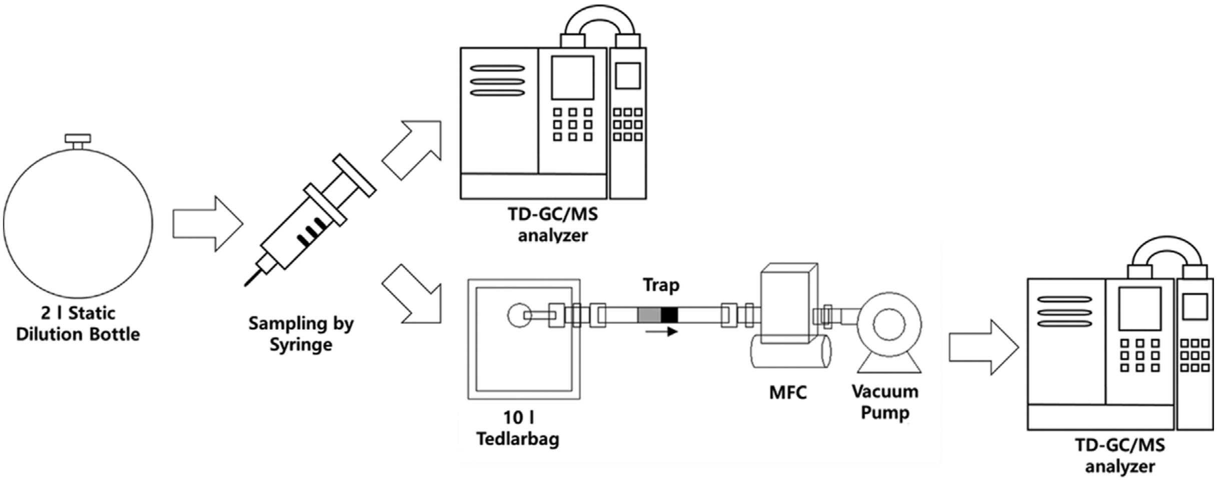

Fig. 2. Schematic diagram for isoprene sampling and analyzing.

Table 2. Experimental conditions

Conditions	Values
Adsorbent trap	Tenax TA/Carbosieve SIII Tenax TA/Carbotrap
Sampling temperature (°C)	25, 35, 40
Sampling flowrate (mL min^{-1})	50, 100, 200

OriginLab, USA) was used for statistical processing of experimental data.

3. Experimental Procedure

The effects of sampling temperatures and flow rates on the loss of isoprene during sampling were investigated. The experimental set-up is shown in Fig. 2. Experimental conditions were based on the US EPA standard method TO-17 for the collection and analysis of VOCs in ambient air. As recommended in the method, sampling flow rates should be from 5 to 200 mL min^{-1}. Therefore, the sampling flow rate in this study varied as 50, 100, and 200 mL min^{-1}. In terms of sampling temperature, ambient temperature is recommended based on the US EPA standard method TO-17. However, the ambient temperature may reach 40 °C. Therefore, the sampling temperatures were selected as 25, 35, and 40 °C. The experimental conditions are summarized in Table 2.

RESULTS AND DISCUSSION

1. Effect of Sampling Temperatures on the Recovery of Isoprene Using Tenax TA/Carbosieve SIII and Tenax TA/Carbotrap Traps

VOC sampling, including isoprene, is influenced by the temperature and flow rate [46]. Isoprene is highly volatile and can potentially evaporate at lukewarm (boiling point: 34.067 °C) conditions. Thus, the sampling temperature should be carefully considered. In this experiment, the effect of the sampling temperature on the recovery rate of isoprene was studied based on the laboratory temperature. The sampling temperature was 25, 35, and 45 °C, and the experiment was conducted based on these temperature conditions and a sampling flow rate of 100 mL min^{-1}. The experimental results are shown in Fig. 3.

It was found that the recovery rates of the Tenax TA/Carbosieve SIII and Tenax TA/Carbotrap traps were 63.50% and 87.97%, respectively (Fig. 3). Among sampling temperatures of concern, the first change in adsorption performance was observed at 35 °C, which is near the boiling point of isoprene (34 °C). The result at 40 °C revealed that the recovery rate was significantly lower than that at 35 °C. However, no significant loss of isoprene was observed at 25 °C condition as expected. This result indicates that isoprene is not smoothly adsorbed when the temperature exceeds 35 °C during sampling. It was found that sampling temperatures have a significant effect on the performance of adsorbents (Tenax TA/Carbosieve SIII and Tenax TA/Carbotrap, $p=6.5643\times10^{-6}$, 1.9632×10^{-6} at the significance level of 0.05).

2. Effect of Flow Rates on the Recovery of Isoprene Using Tenax TA/Carbosieve SIII and Tenax TA/Carbotrap Traps

In this work, the influence of variations in flow rates on the recovery rate of isoprene was studied. Sampling flow rates were 50, 100, and 200 mL min^{-1} and the sampling temperature was maintained at 25 °C. The experimental results are presented in Fig. 4.

As shown in Fig. 4, the recovery rates of the Tenax TA/Carbosieve SIII and Tenax TA/Carbotrap traps were 72.37% and 94.70%, respectively. The sampling flow rate was expected to influence the adsorption performance, and the recovery rate of isoprene tended to decrease as the flow rate increased. It was found that the sampling flow rate had a significant effect on the recovery rate of isoprene (Tenax TA/Carbosieve SIII and Tenax TA/Carbotrap, $p=1.5050\times10^{-4}$, 8.5377×10^{-4} at the significance level of 0.05).

In both experiments above, the isoprene recovery of Tenax TA/Carbosieve SIII trap was lower than that of Tenax TA/Carbotrap trap. Tenax TA exists on both traps. Therefore, the loss of isoprene might be due to Carbosieve SIII. Therefore, an extra experiment with only Carbosieve SIII was conducted to demonstrate its effect on isoprene. 180 mg and 300 mg of Carbosieve SIII, which are much greater than initial 60 mg, were used to investigate the isoprene recovery rate. The experiment was conducted at 25 °C of sampling temperature and 100 mL/min of sampling flow rate. Since this adsorbent trap contained only Carbosieve SIII, the desorption temperature of 300 °C was used as the recommended temperature for Carbosieve SIII. The experimental results are depicted in Fig. 5. As shown, the isoprene recovery rates were less than 40%. This indicated that Carbosieve SIII itself affected the loss of isoprene.

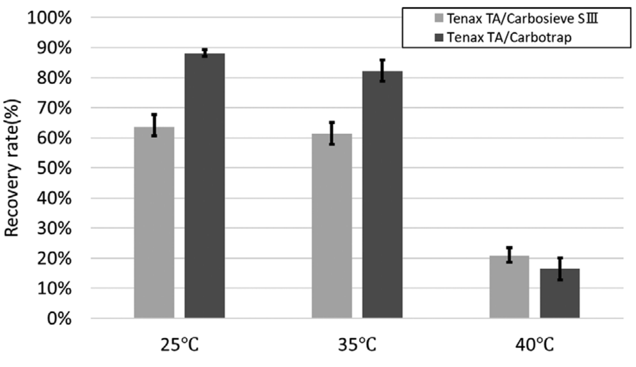

Fig. 3. Isoprene recovery rate based on the sampling temperature for Tenax TA/Carbosieve SIII and Tenax TA/Carbotrap tube traps.

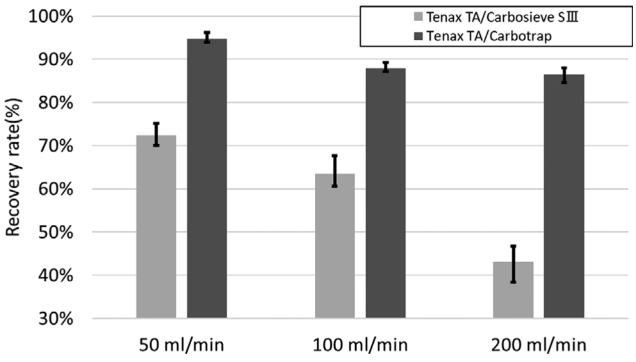

Fig. 4. Isoprene recovery rate based on the flow rate for Tenax TA/Carbosieve SIII and Tenax TA/Carbotrap tube traps.

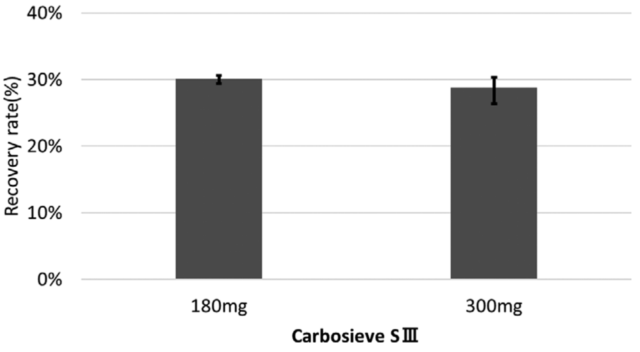

Fig. 5. Isoprene recovery rate based on the Carbosieve SIII amount (mg)/desorption temperature (°C).

In the case of Carbosieve SIII, the results of the current and previous experiments [24] confirmed that the adsorption capacity for isoprene was lower than that of Carbotrap. Considering the adsorbent performance alone, Carbosieve SIII is known to have a larger specific surface area and stronger adsorption than Carbotrap [47]. However, the isoprene-adsorption performance results indicate that the performance of Carbosieve SIII is inferior to that of Carbotrap. Therefore, the tendency of the adsorption capacity deteriorating with increasing flow rate was greater in Carbosieve SIII than in Carbotrap. In previous studies, a multi-bed trap, including Carbosieve SIII, was used to use the strong adsorption capacity of Carbosieve SIII [48-50]. However, due to this strong adsorption capacity, the low flow rate of sampling was not possible in the humid air [51]. On the other hand, it was assumed that losses of 1,3-butadiene and isoprene were caused by both fast reactions on adsorbent surface and irreversible adsorption [52]. After a storage duration of seven days, only 20% of 1,3-butadiene and 26% of isoprene were recovered. The results presented in this paper demonstrate that the adsorptive enrichment of reactive light hydrocarbons such as 1,3-butadiene and isoprene using the carbon molecular sieves (Carboxen 569, Carboxen 1003, and Carbosieve SIII) results in a significant underestimation of these compounds. The losses increased with increasing storage time. The most remarkable effects were observed for Carbosieve SIII. In contrast, no considerable analyte losses were observed using the graphitized carbon black Carbotrap X [52].

In general, the recovery rate of isoprene varied according to sampling temperatures and flow rates, especially when the sampling temperature increased. A previous study explains that there could be a loss during sampling at a temperature beyond the boiling point of isoprene, and this study also proved that it was true [48]. In the case of the sampling flow rate, it was found that the recovery rate was low due to the fast flow rate, and this tendency was evident especially in Tenax TA/Carbosieve SIII trap. Consequently, optimizing sampling temperatures and flow rates is critical in ensuring high recovery rates of isoprene. It was also proved that Carbosieve SIII was unsuitable for the sorbent of isoprene.

CONCLUSIONS

Due to the sensitive physical properties of isoprene, isoprene recovery varies considerably with respect to various sampling conditions. Sampling methods should be reasonably selected based on sampling temperatures and flow rates. Sampling temperature is the main variable to consider while sampling. A sampling temperature higher than 35 °C reduced the recovery rate of isoprene significantly since the boiling point of the analyte is 34 °C. Furthermore, a reasonably low flow rate should also be maintained, as isoprene might decompose during the adsorption process at high flow rates.

In conclusion, reasonable sampling conditions for isoprene, when Carbotrap coupled with Tenax TA is used, were found to be a sampling temperature of ≤35 °C, a sampling flow rate of ≤50 mL min^{-1}. It is suggested that Carbosieve SIII should not be used for isoprene sampling since it belongs to carbon molecular sieves.

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