Effects of adsorbent sampling variables on the accurate measurement of isoprene

In-Young Choi

force@konkuk.ac.kr

Konkuk University   https://orcid.org/0000-0002-8236-0047

Trieu-Vuong Dinh
Konkuk University

Ki-Joon Kim
Konkuk University

Seungae Lee
Konkuk University

Dong-Eun Kim
Konkuk University

Bong-Hyun Jun
Konkuk University

Young-Min Park
Konkuk University School of Medicine

Jo-Chun Kim
Konkuk University

Abstract

Volatile organic compounds (VOCs) are air pollutants that require accurate measurements and analysis. Isoprene is a VOC and an important indicator of photochemical smog. Isoprene originates from various sources, including natural substances, human respiration, and industrial activities such as semiconductor, rubber, and lumber manufacturing. However, despite the availability of multiple methods for measuring VOCs, there are currently no clear guidelines for their analysis. This study aims to improve the accuracy of isoprene sampling and analysis. This was achieved by varying the adsorbent and sampling conditions, followed by gas chromatography and thermal desorption. Various sampling temperatures and flow rates were used to determine the recovery rate of isoprene using different adsorbents. Single-bed Carbosieve S and double-bed Tenax TA/Carbosieve S and Tenax TA/Carbotrap were used as adsorbents. It was found that Carbotrap revealed a higher isoprene recovery rate, although Carbotrap had a weaker adsorption capacity than Carbosieve S. Moreover, the recovery rate of isoprene increased significantly as the sampling temperature and flow rate decreased.

1. Introduction

Isoprene is one of the volatile organic compounds (VOCs) that is an essential indicator of environmental pollution and health in modern society [1−3]. VOCs contribute to the generation and transformation of numerous pollutants from various emission sources, such as industrial activities, vehicles, and natural sources, to widely distributed emission regions, including urban areas, rural areas, and the ocean, depending on the characteristics of their locations [4−9]. Globally, VOC emissions are much higher from natural sources. VOCs, including isoprene, are major atmospheric chemicals that are commonly emitted from natural sources [5, 8, 10, 11] 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 [8, 12]. 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]. Natural sources account for a more significant fraction of VOC emissions than artificial sources. However, artificial VOC emissions are increasing owing to human activities, and require more attention [13, 14]. Even it has been confirmed that isoprene is generated in human breath, and research on this is being conducted in various fields[15−17]. 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 [18, 19].

Isoprene is a colorless volatile liquid that is 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 repeating structure of ($-C_5H_9O_2-$) [9]. The above reactions 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 for immediate results, gas chromatography (GC)-based analyses, and photoionization detector measurements. However, GC/mass spectrometry (GC/MS) based on GC is the main method. Sampling is important for analyzing isoprene using GC, and solid adsorbents are commonly used to concentrate isoprene for analysis [20–23]. The sampling and analysis methods typically follow the procedures outlined by US EPA. However, there is a lack of information on the application methods of the solid adsorbents and sampling conditions [24–27].

In this study, a solid adsorbent based on black graphitized carbon, including Carbosieve S (SUPELCO, USA) and Carbotrap (SUPELCO, USA), which is commonly used and suggested by the US EPA, was used to investigate its adsorption performance for isoprene.

GC/MS analysis experiments were conducted to confirm the isoprene adsorption and recovery rates according to various sampling conditions.

Table 1
Properties of isoprene

Property	Value
Chemical formula	C_5H_8
Molar mass, g mol^{-1}	68.12
Density, g cm^{-3}	0.681
Melting point, °C (K)	-143.95 (129.20)
Boiling point, °C (K)	34.067 (307.217)
Autoignition, °C (K)	220 (493.15)
*Standard state at 25 °C and 100 kPa	

2. Method And Materials

2.1. 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 the accurate measurement of the substance necessary [28, 29]. 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. An 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 [26]. 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[30–32]. 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, namely Carbosieve S (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 [33–35]. Therefore, Tenax TA has long been used as a guard adsorbent for a multiple adsorption bed or trap. The adsorption agents selected for comparison were Carbosieve S and Carbotrap. The experiments were performed using Tenax TA in a dual bed.

Experimental variables were adsorption temperature, flow rate, and desorption temperature. The recovery rate test was conducted to determine optimal trap sampling conditions. The detailed experimental conditions are listed in Table 2.

Table 2
Experimental conditions

Conditions	Values
Adsorbent type	Carbosieve S
	Tenax TA/Carbosieve S
	Tenax TA/Carbotrap
Adsorbent mass (mg)	Carbosieve S : 180, 300
	Tenax TA/Carbosieve S : 110/60
	Tenax TA/Carbotrap: 110/100
Desorption temperature (℃)	250, 280
Adsorption temperature (℃)	25, 35, 40
Adsorption flowrate (ml min^{-1})	50, 100, 200
Carrier gas	He (99.999%, Rigas, Korea)

2.2. Sampling methods

Isoprene samples were adsorbed into a sample trap mixed with Tenax TA and Carbotrap or with Tenax TA and Carbosieve S . The mixing ratio of the two adsorbents were one-to-one, and the sampling flow rate of the sorbent trap was 150 ml.min^{-1}. The sampling time was ranged as 20–120 min, depending on the

concentrations of isoprene released under each condition [23–27]. The experimental procedure is shown in Fig. 1.

2.3. Analytical methods

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 x 0.32 mm, 1.8 μm, Agilent, USA). Table 2 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 ºC for 5 min for the analysis of isoprene. The temperature was increased at a rate of 2 ºC min^{-1} to 120 ºC and then at 10 ºC min^{-1} to 240 ºC. Finally, the temperature was maintained at 240 ºC for 2 min [36].

Table 3
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		250, 280, 300	°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

2.4. 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 ppm. Volumes of 1, 10, 100, 500, 1000, and 2000 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. 2). 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, OriginLab, USA) was used for statistical processing of experimental data.

3. Results And Discussion

3.1. Effect of desorption temperature on the recovery of isoprene

Carbosieve S is a porous carbon material that has been widely studied for its potential use in gas separation and purification applications. The main characteristics of Carbosieve S 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 S 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 [37]. However, the adsorption capacity of Carbosieve S decreases with increasing relative humidity. Therefore, the effect of relative humidity must be carefully considered when using Carbosieve S to measure VOCs in humid environments [34, 38].

The effectiveness of Carbosieve S was evaluated through a series of experiments focused on a single substance's adsorption. To assess the isoprene adsorption performance, we compared the results from two sampling traps employing Tenax TA mixed with Carbosieve S and only Carbosieve S. Previous studies have reported that a recovery rate of 40% can be achieved using 60 mg of Carbosieve S [39]. To increase the isoprene adsorption rate, the amount of Carbosieve S used was increased from 180 mg to 300 mg.

The isoprene recovery rate of Carbosieve S was evaluated based on two different desorption temperatures. In this study, the sampling flow rate and sampling temperature were 100 ml/min and 20 °C, respectively. The commonly used desorption temperature in the VOC measurements, namely 250 °C, was compared with 280 °C desorption temperature. The experimental results showed that the recovery rate of isoprene was not strongly affected by the desorption temperature of the adsorbent (Fig. 3). A sufficient amount of adsorbent was added, considering the breakthrough point. However, a recovery rate of about 30% was achieved, regardless of the amount of adsorbent. Besides, when the desorption temperature was increased from 250 to 300 °C, the recovery rate was slightly higher. When another extra work with 300 mg/350 °C was separately conducted, the recovery rate was improved up to 38%. Since

the recovery rate was still low, other variables except desorption temperature and the amount of the adsorbent, might directly affect the recovery rate of isoprene. Despite comparison by a rule of thumb on the difference of recoveries, it was found that the effect of the amount of adsorbent and desorption temperature on the recovery rate of isoprene was significant ($p = 0.00983$ at the significance level of 0.05). On the other hand, a study using a Carbosieve S Ⅲ (60 mg) trap coupled with Tenax TA (110 mg) followed by this experiment exhibited a recovery rate of 70%, indicating that Tenax TA could improve the recovery rate of isoprene.

In a previous study, it was assumed that losses of 1,3-butadiene and isoprene were caused by both fast reactions on adsorbent surface and irreversible adsorption. 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 demonstrated 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 S Ⅲ) resulted in a significant underestimation of these compounds. The losses increased with increasing storage time. The most remarkable effects were observed for Carbosieve S Ⅲ. In contrast, no considerable analyte losses were observed using the graphitized carbon black Carbotrap X [39]. is the graphitized carbon black seemed more effective in the enrichment of isoprene than the carbon molecular sieve.

Carbotrap is also a porous carbon material as Carbosieve S Ⅲ. 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 [40–42]. 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 [41, 42]. The experiment's results using Carbotrap are shown in Fig. 4. The experiment was conducted using a trap composed of Tenax TA and Carbotrap (Table 2). The sampling flow rate and sampling temperature were the same as in the above Carbosieve S Ⅲ study. Even at a temperature of 250 °C, which is lower than the recommended temperature of 280 °C, a recovery rate of 93.8% was achieved. At 280 and 300 °C, the recovery rates were improved to 99.4% and 99.7%, respectively. It was found that desorption temperatures significantly affected the recovery rate of isoprene ($p = 0.03072$ at the significance level of 0.05). After this experiment, all other ones were carried out based on 280 °C of desorption temperature for the long-term stability of adsorbents. The amount of adsorbents are depicted in Table 2 for the rest of experiments.

3.2. Effect of sampling temperatures on the recovery of isoprene

VOC sampling, including isoprene, is influenced by the temperature and flow rate [43]. 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 recovery rates of the Tenax TA/Carbosieve S and Tenax TA/Carbotrap traps were 63.50% and 87.97%, respectively (Fig. 5). Among sampling temperatures of concern, the first change in adsorption performance was observed at 35 °C and, 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 had a significant effect on the performance of adsorbents (Tenax TA/Carbosieve S and Tenax TA/Carbotrap, p = 6.5643E^{-6}, 1.9632E^{-6} at the significance level of 0.05).

3.3. Effect of flow rates on the recovery of isoprene

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}, which were based on the recommended range of 50−200 ml min^{-1} of adsorbent flow rates, and the sampling temperature was 25°C [44].

The recovery rates of the Tenax TA/Carbosieve S and Tenax TA/Carbotrap traps were 72.37% and 94.70%, respectively (Fig. 6). 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.

In the case of Carbosieve S , the results of the current and previous experiments [21] confirmed that the adsorption capacity for isoprene was lower than that of Carbotrap. Considering the adsorbent performance alone, Carbosieve S is known to have a larger specific surface area and stronger adsorption than Carbotrap [45]. However, the isoprene-adsorption performance results indicate that the performance of Carbosieve S was inferior to that of Carbotrap. Therefore, the tendency of the adsorption capacity deteriorated with increasing flow rate was greater in Carbosieve S than in Carbotrap. It was found that the sampling flow rate had a significant effect on the recovery rate of isoprene (Tenax TA/Carbosieve S and Tenax TA/Carbotrap, p = 1.5050×10^{-4}, 8.5377×10^{-4} at the significance level of 0.05).

In previous studies, a multi-bed trap, including Carbosieve S , was used to use the strong adsorption capacity possessed by Carbosieve S [46−48]. However, due to the strong adsorption capacity of Carbosieve S , the low flow rate of sampling was not possible in the humid air [49]. For the above reasons, this study has been initiated, and the recovery work on isoprene was carried out. Furthermore, recovery rate experiments were conducted using a double-layer trap (Tenax TA/Carbosieve S and Tenax TA/Carbotrap) with respect to isoprene sampling temperatures and sampling flow rates. As a result, the recovery rates of two different types of traps (Tenax TA/Carbosieve S , Tenax TA/Carbotrap) for isoprene

were confirmed to be 70% and 90% or more, respectively, and the trap using Tenax TA/Carbotrap showed the better recovery rate than the other.

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 [46]. 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 S trap. In conclusion, optimizing sampling temperatures and flow rates is critical in ensuring high recovery rates of isoprene. It was also proved that Carbosieve S was unsuitable for the sorbent of isoprene.

4. Conclusions

Because of the sensitive physical properties of isoprene, the isoprene recoveries varied 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 be decomposed during the adsorption process at high flow rates. A desorption temperature of 300 °C or 350 °C is recommended for Carbosieve S only, while a desorption temperature of 280 °C is recommended for the adsorbent coupled with Tenax TA, as it provides long-term stability for the sorbents.

In conclusion, the reasonable sampling and desorption variables for isoprene, when Carbotrap coupled with Tenax TA is used, are a sampling temperature of 35 °C or less, a sampling flow rate of 50 ml min^{-1}, and a desorption temperature of 280 °C. This study suggests that Carbosieve S is not suitable for isoprene sampling since it is one of the carbon molecular sieves, but Carbotrap is suitable for it because the sorbent belongs to one of the graphitized carbon black materials.

Declarations

References

1. C. Y. Hsu, H. C. Chiang, R. H. Shie, C. H. Ku, T. Y. Lin, M. J. Chen, N. T. Chen, and Y. C. Chen, Environmental Pollution 240, 95 (2018).
2. J. W. Ahn, T. V. Dinh, S. Y. Park, I. Y. Choi, C. R. Park, and Y. S. Son, Atmos Pollut Res 13, 101470 (2022).

3. K. Rumchev, H. Brown, and J. Spickett, *Volatile Organic Compounds: Do They Present a Risk to Our Health?* (2007).

4. P. A. Dominutti, J. R. Hopkins, M. Shaw, G. P. Mills, H. A. Le, D. H. Huy, G. L. Forster, S. Keita, T. T. Hien, and D. E. Oram, Environmental Pollution 120927 (2022).

5. G. A. Novak and T. H. Bertram, Acc Chem Res 53, 1014 (2020).

6. K. Na, Y. P. Kim, I. Moon, and K. C. Moon, Chemosphere 55, 585 (2004).

7. Q. Liang, X. Bao, Q. Sun, Q. Zhang, X. Zou, C. Huang, C. Shen, and Y. Chu, Environmental Pollution 265, (2020).

8. A. Kiendler-Scharr, J. Wildt, M. D. Maso, T. Hohaus, E. Kleist, T. F. Mentel, R. Tillmann, R. Uerlings, U. Schurr, and A. Wahner, Nature 461, 381 (2009).

9. H. M. Lybarger and U. by Staff, in *Kirk-Othmer Encyclopedia of Chemical Technology* (John Wiley & Sons, Inc., Hoboken, NJ, USA, 2014), pp. 1–19.

10. J. F. Lamarque, T. C. Bond, V. Eyring, C. Granier, A. Heil, Z. Klimont, D. Lee, C. Liousse, A. Mieville, B. Owen, M. G. Schultz, D. Shindell, S. J. Smith, E. Stehfest, J. van Aardenne, O. R. Cooper, M. Kainuma, N. Mahowald, J. R. McConnell, V. Naik, K. Riahi, and D. P. van Vuuren, Atmos Chem Phys 10, 7017 (2010).

11. A. Guenther, ! C Nicholas Hewitt, D. Erickson, R. Fall, C. Geron, T. Graedel, P. Harley, L. Klinger, M. Lerdau, W. A. Mckay, T. Pierce, B. Scholes, R. Steinbrecher, R. Tallamraju, J. Taylor, and P. Zimmerman, A Global Model of Natural Volatile Organic Compound Emissions (1995).

12. C. M. da Silva, E. C. C. A. Souza, L. L. da Silva, R. L. Oliveira, S. M. Corrêa, and G. Arbilla, Bull Environ Contam Toxicol 97, 653 (2016).

13. K. Kim, J. Kim, and J. Lim, J. of the Korean Society for Environmental Analysis 8, 132 ~ 136 (2005).

14. J.-C. Kim, J. Kosae 22, (2006).

15. N. Nath, A. Kumar, S. Chakroborty, S. Soren, A. Barik, K. Pal, and F. G. de Souza, ACS Omega (2023).

16. T. Karl, P. Prazeller, D. Mayr, A. Jordan, J. Rieder, R. Fall, and W. Lindinger, *Human Breath Isoprene and Its Relation to Blood Cholesterol Levels: New Measurements and Modeling* (2001).

17. J. King, P. Mochalski, K. Unterkofler, G. Teschl, M. Klieber, M. Stein, A. Amann, and M. Baumann, Biochem Biophys Res Commun 423, 526 (2012).

18. H. M. Chein and T. M. Chen, J Air Waste Manage Assoc 53, 1029 (2003).

19. H. M. Chein, T. Ming Chen, S. G. Aggarwal, C. J. Tsai, and C. C. Huang, J Air Waste Manage Assoc 54, 218 (2004).

20. T. RD, Toxicology 113, 242 (1996).

21. D. Kotzias, Fresenius Environ Bull 3, 220 (1994).

22. H. F. Linskens and J.. F. Jackson, *Modern Methods of Plant Analysis* (1997).

23. H. F. Linskens and J.. F. Jackson, *Modern Methods of Plant Analysis* (1992).

24. U. Epa, *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* (1999).

25. U. Epa, *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* (1999).

26. Aswir and H. Misbah, *METHOD 8260D VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY* (USA, 2018), pp. 1–13.

27. Oliver and Karen, *Method TO-15A Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially Prepared Canisters and Analyzed by Gas Chromatography-Mass Spectrometry (GC-MS)* (2019).

28. S. J. Snow, J. D. Krug, J. M. Turlington, J. E. Richards, M. C. Schladweiler, A. D. Ledbetter, T. Krantz, C. King, M. I. Gilmour, S. H. Gavett, U. P. Kodavanti, A. K. Farraj, and M. S. Hazari, Atmos Environ 295, 119525 (2023).

29. A. Guion, S. Turquety, A. Cholakian, J. Polcher, A. Ehret, S. Université, P. S. L. Université, and É. Polytechnique, 1043 (2023).

30. D. Biagini, T. Lomonaco, S. Ghimenti, M. Onor, F. G. Bellagambi, P. Salvo, F. di Francesco, and R. Fuoco, Talanta 200, 145 (2019).

31. P. v. Doskey and W. Gao, Journal of Geophysical Research Atmospheres 104, 21263 (1999).

32. W. J. Broadgate, P. S. Liss, and S. A. Penkett, Geophys Res Lett 24, 2675 (1997).

33. Y. H. Kim and K. H. Kim, Anal Chem 85, 7818 (2013).

34. D. Helmig and L. Vierling, Anal Chem 67, 4380 (1995).

35. Y. H. Kim, K. H. Kim, J. E. Szulejko, and D. Parker, Anal Chem 86, 6640 (2014).

36. J. H. Ahn, K. H. Kim, J. E. Szulejko, E. E. Kwon, and A. Deep, Microchemical Journal 125, 142 (2016).

37. T. D. G. and A. J. F. F Innocenti, R A Robionson, *DIFFERENTIAL ABSORPTION LIDAR (DIAL) QUANTIFICATION OF VOC FUGITIVE EMISSIONS FROM SMALL SOURCES IN LOS ANGELES AREA, USA, OCTOBER 2015* (Middlesex, 2017).

38. O. Monje, J. Catechis, and J. C. Sager, SAE Technical Papers (2007).

39. K. Dettmer, T. Knobloch, and W. Engewald, Fresenius J Anal Chem 366, 70 (2000).

40. V. Camel and M. Caude, J Chromatogr A 710, 3 (1995).

41. A. Poormohammadi, A. Bahrami, A. Ghiasvand, F. G. Shahna, and M. Farhadian, J Environ Health Sci Eng 17, 1045 (2019).

42. P. Foley, N. Gonzalez-Flesca, I. Zdanevitch, and J. Corish, Environ Sci Technol 35, 1671 (2001).

43. Ö. O. Kuntasal, D. Karman, D. Wang, S. G. Tuncel, and G. Tuncel, J Chromatogr A 1099, 43 (2005).

44. A. Kumar and I. Víden, Environ Monit Assess 131, 301 (2007).

45. M. Richter, E. Juritsch, and O. Jann, J Chromatogr A 1626, 461389 (2020).

46. C. Geron, A. Guenther, J. Greenberg, H. W. Loescher, D. Clark, and B. Baker, *Biogenic Volatile Organic Compound Emissions from a Lowland Tropical Wet Forest in Costa Rica* (2002).

47. B. Tolnai, J. Hlavay, D. Moller, H.-J. Prumke, H. Becker, M. Dostler, and H. Hungary´´, *Combination of Canister and Solid Adsorbent Sampling Techniques for Determination of Volatile Organic Hydrocarbons ´´¨¨¨* (2000).

48. G. Barrefors and G. Petersson, *VOLATILE HYDROCARBONS FROM DOMESTIC WOOD BURNING* (1995).

49. G. Barrefors and G. Petersson, *Assessment of Ambient Volatile Hydrocarbons from Tobacco Smoke and from Vehicle Emissions* (1993).

Figures
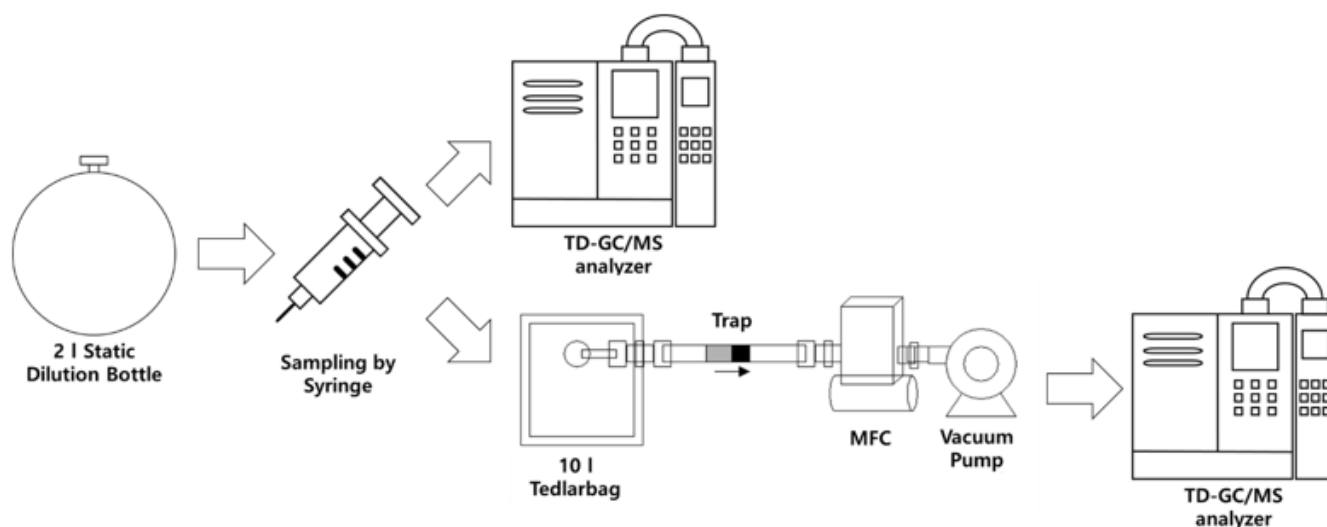
Figure 1

Schematic diagram for isoprene sampling and analyzing.
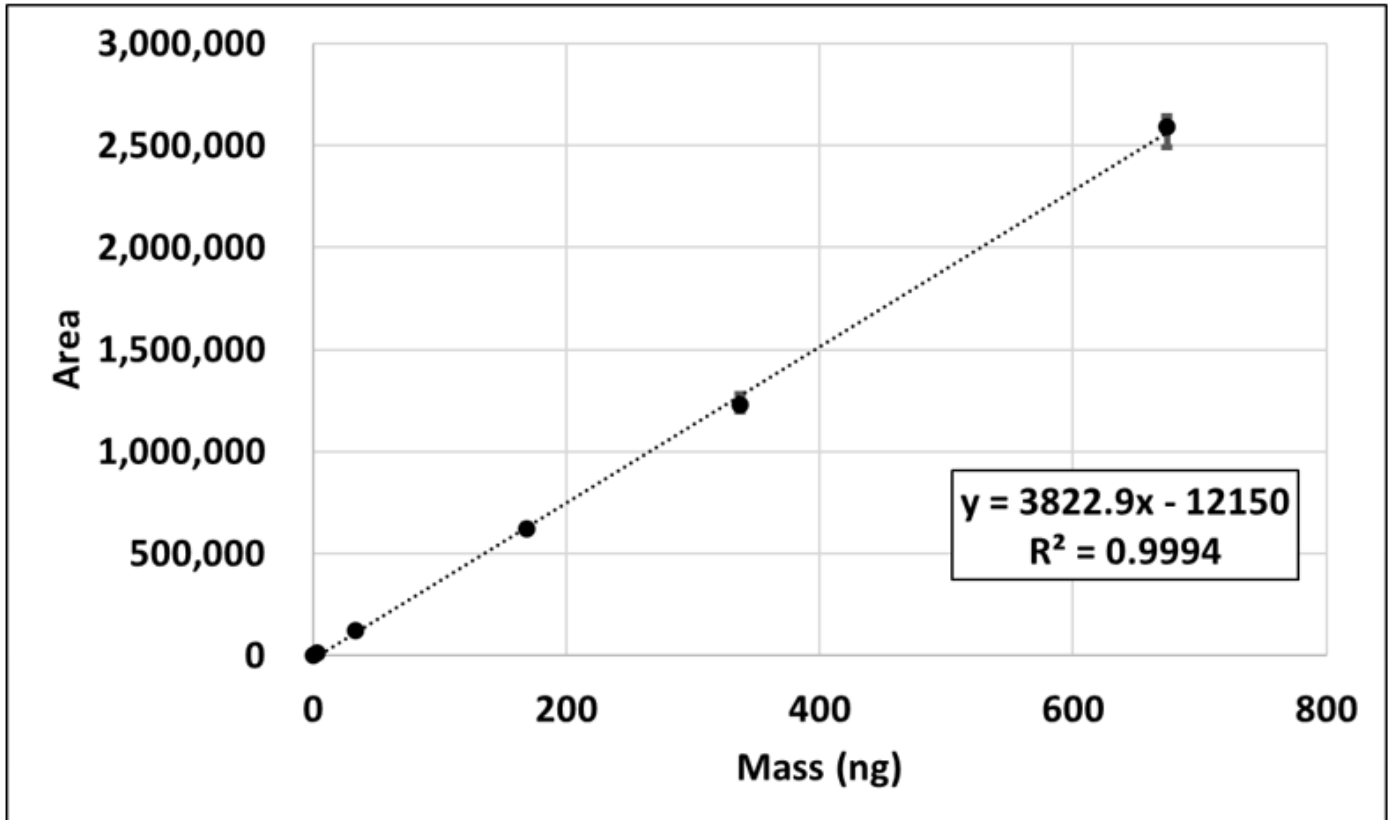
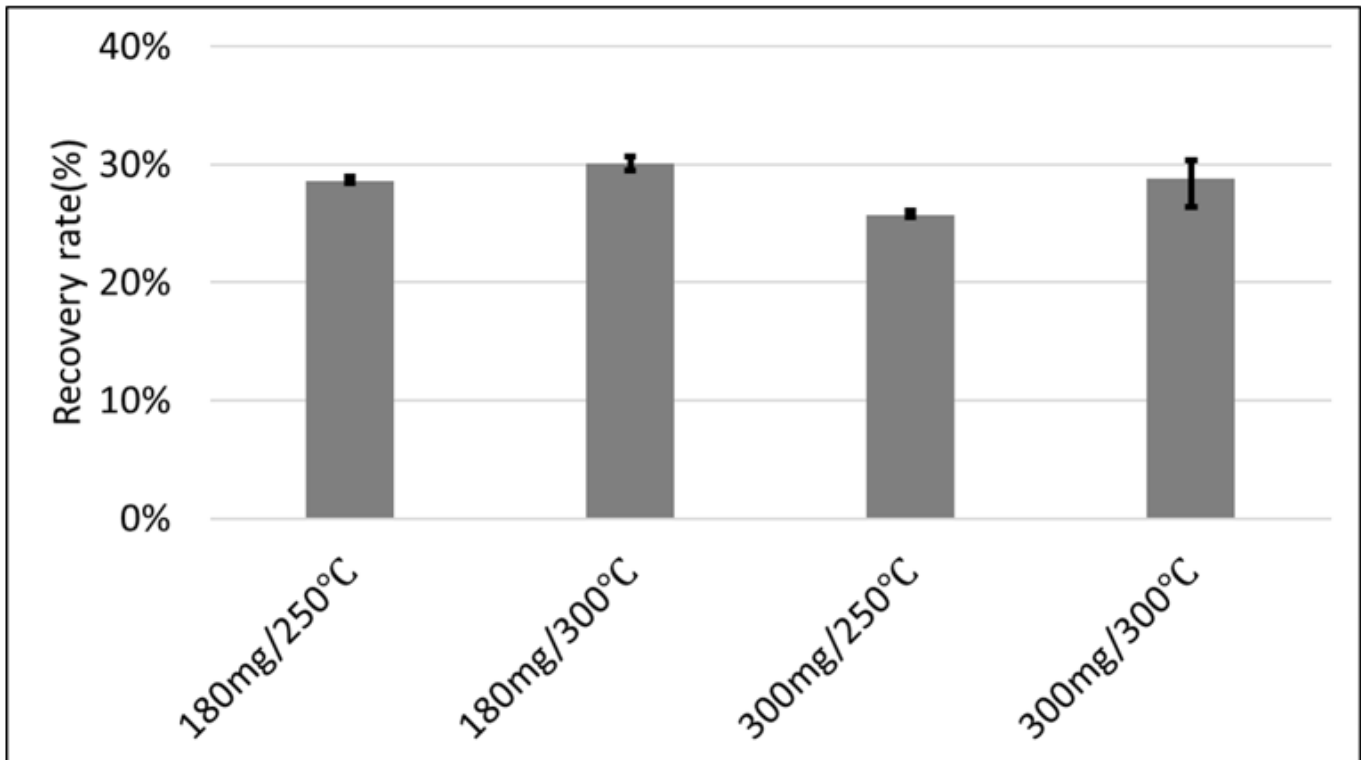**Figure 2**

Isoprene calibration curve.

Figure 3

Isoprene recovery rate based on the Carbosieve S amount(mg)/desorption temperature (℃).
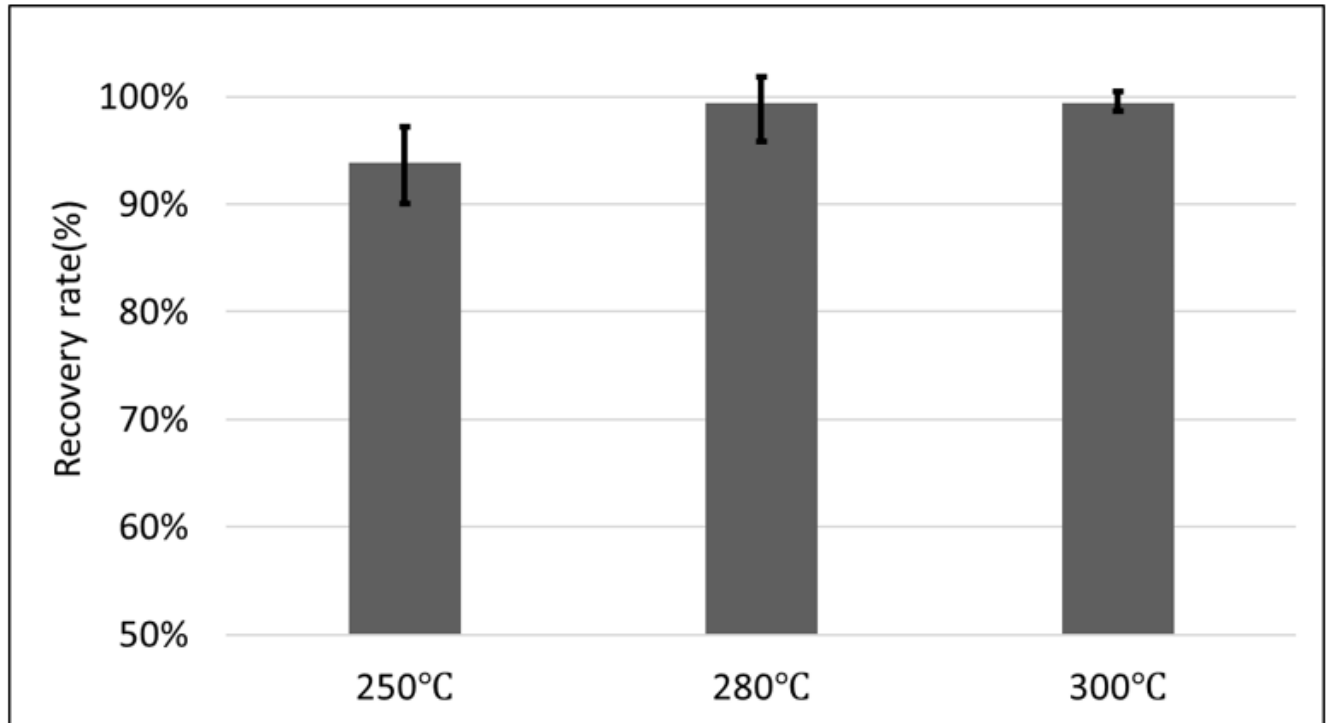

Figure 4

The recovery rate of isoprene with respect to the desorption temperature of Tenax TA (110 mg)/Carbotrap (100 mg).
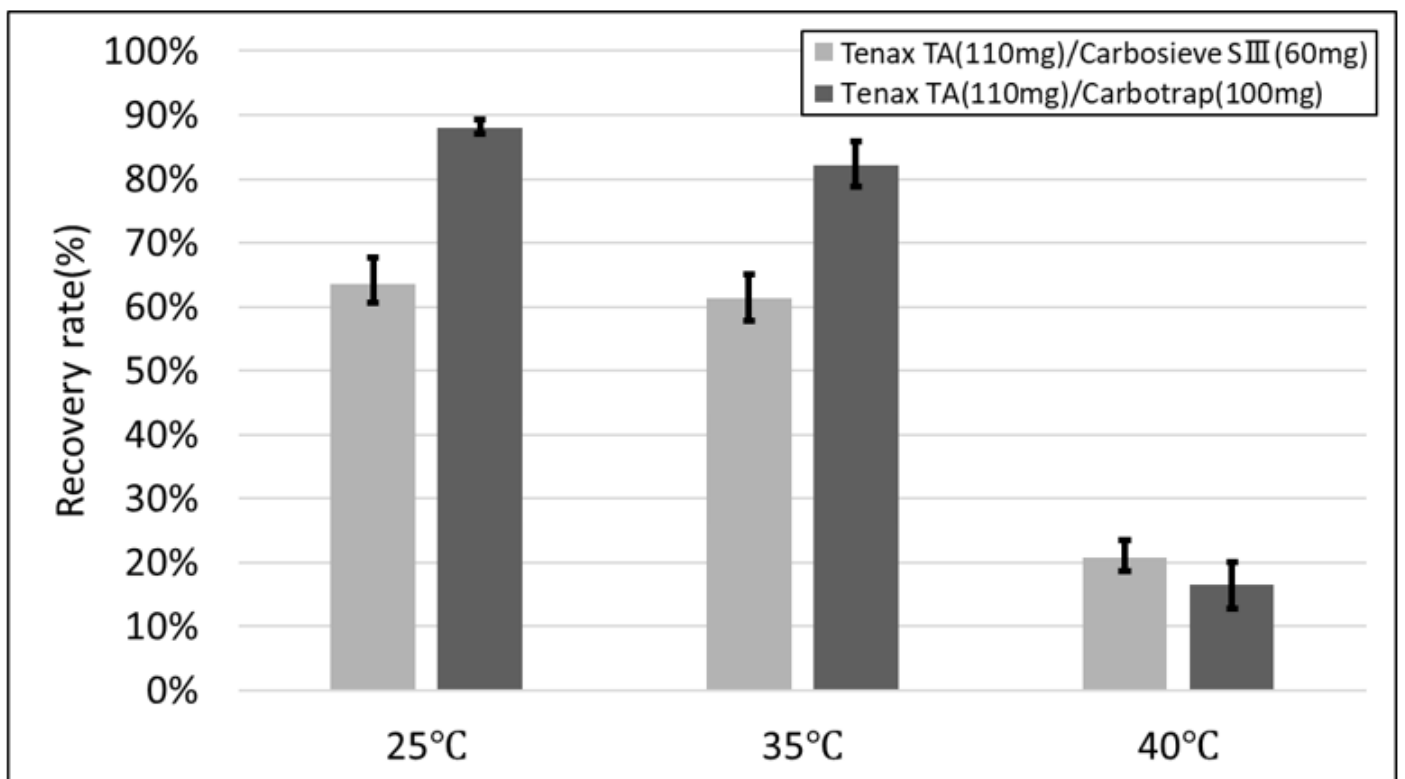
Figure 5

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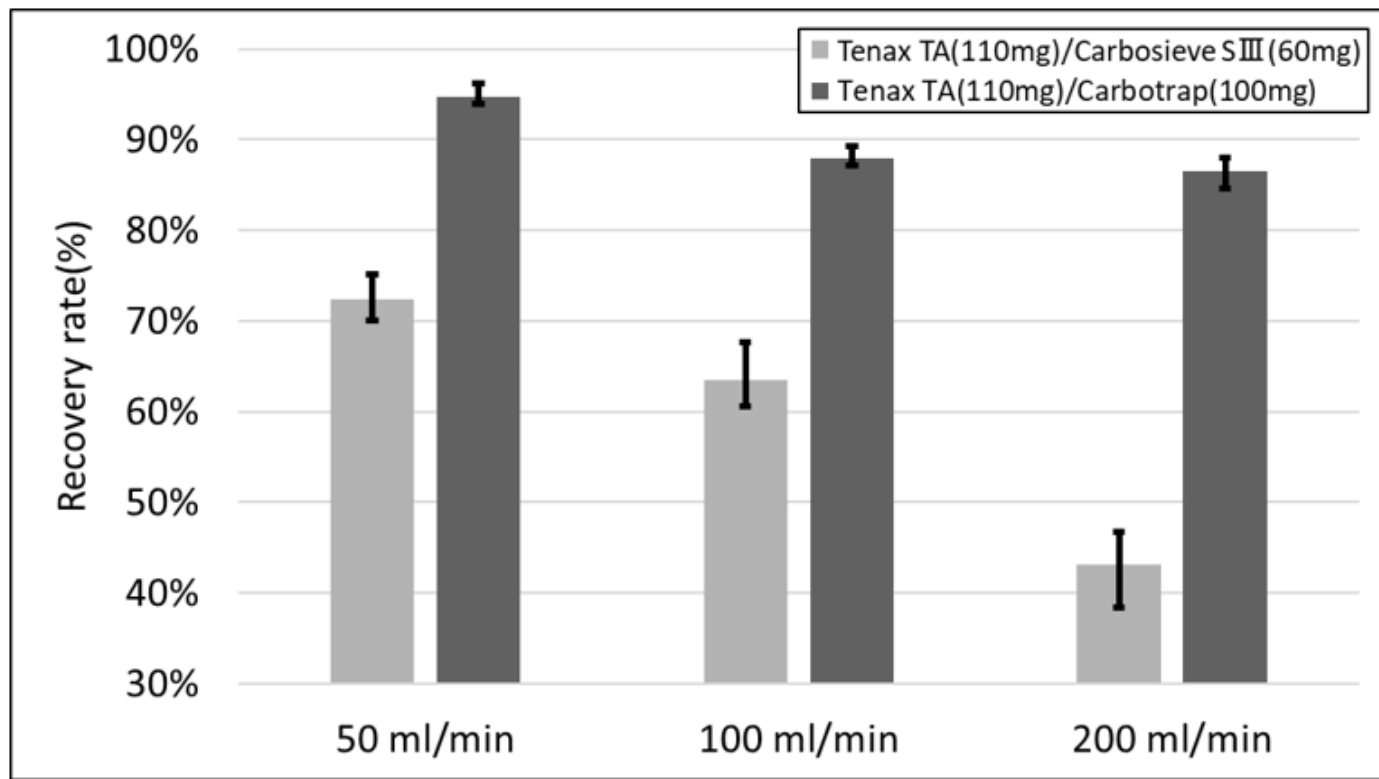

Figure 6

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