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Development of a portable gas chromatograph–mass spectrometer embedded with a low-temperature adsorption thermal desorption module for enhanced detection of volatile organic compounds

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A portable gas chromatograph–mass spectrometer (GC-MS) is an effective instrument for rapid on-site detection of volatile organic compounds (VOCs). Current instruments typically adsorb samples at ambient temperature, challenging the detection of low-boiling VOCs. In this study, a low-temperature adsorption thermal desorption method is proposed for sample enrichment in a portable GC-MS. The refrigeration module adopts a thermoelectric cooler (TEC), and a heating wire directly heats the adsorption tube to reduce the heat capacity. The miniaturization and low-power design make this module integrable into portable GC-MS devices. This module can reduce the temperature to around 0 °C within ten minutes for sample enrichment, and the heating system can increase the temperature to 260 °C within 20 seconds to ensure rapid desorption and injection of samples. Due to the miniaturization design, the total weight of the portable GC-MS is 21.7 kg, and the volume is 48 cm × 38 cm × 17 cm. Within merely 10 minutes, it completely separated and detected 65 VOCs in the TO-15 standard substance, with a detection limit down to 0.12 μg L^{-1} for toluene. The detection performance for low-boiling substances could be enhanced by up to 17 times compared to ambient temperature adsorption thermal desorption, such as 1,3-butadiene. Moreover, the results demonstrated long-term stability (RSD < 10% for 98% of the substances, with recovery rates from 91.66% to 109.12%). This study provides a feasible strategy for the rapid and reliable detection of VOCs in the air, holding great potential in the field of environmental monitoring.

Introduction

Volatile organic compounds (VOCs) are important indicators for the assessment of ambient air pollution levels, which play vital roles in atmospheric pollution events.[1] Some VOCs such as propionaldehyde and benzene are known to be toxic[2–4] and their long-term exposure may pose health hazards, including the development of long-term illnesses in severe instances,[5] exacerbation of respiratory conditions such as asthma,[6–8] and an increased susceptibility to cancer.[9–12] VOCs have also been recognized as possible precursors of photochemical smog,[13–15] participating in the photochemical generation of ground-level ozone (O$_3$) and secondary organic aerosols (SOA).[16–19] These reactions are complex processes in atmospheric chemistry and are closely linked to atmospheric pollution and climate change. Taking into account all these considerations, it would be very useful to develop effective techniques to reduce the adverse effects of air quality degradation. In recent years, there has been an increased emphasis on the detection and assessment of VOCs due to their pivotal role in understanding and addressing environmental and public health concerns associated with air quality deterioration. The ongoing research and advancements in VOC detection technologies are vital for effective pollution control and mitigation strategies to safeguard human health and the environment.

The most commonly used methods for detecting VOCs include gas chromatography and gas chromatography–mass spectrometry.[20] Gas chromatography can effectively separate complex mixtures based on differences[21] in adsorption properties and reduce interference between compounds. The detection of speciated VOCs can be achieved by a range of instruments, such as a mass spectrometer (MS), flame ionization detector (FID)[22] and photoionization detector (PID). Compared to other detectors, a mass spectrometer offers high

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sensitivity and resolution. It provides information regarding the molecular structure of a compound, which is useful for identifying unknown compounds.[23] In recent years, breakthroughs have been achieved in miniaturization technology, leading to the development of portable gas chromatography and gas chromatography–mass spectrometry systems for on-site detection of VOCs. While these instruments offer the advantages of rapid analysis, ease of operation, and low power consumption, their performance and sensitivity are challenging to match with laboratory-grade instruments. Therefore, in practical use, sample preconcentration techniques are indispensable.

Sample preconcentration techniques are employed to increase the concentration of target analytes, facilitating the detection and quantification of trace or low-concentration compounds. Prominent methods employed for this purpose include solvent extraction,[24] headspace techniques,[25,26] adsorption on solid sorbents,[27] and the full evaporation technique. Adsorption on solid sorbents is a commonly used method, which includes ambient temperature adsorption sampling and low-temperature adsorption sampling. Currently, the commonly employed adsorption thermal desorption technology in portable gas chromatography–mass spectrometry instruments relies on ambient temperature adsorption sampling, followed by the heating of the adsorbent to release the adsorbed target compounds for analysis. This technology has now been widely applied. For instance, Liu *et al.* developed a novel method for detecting Huanglongbing (HLB),[28] which combines headspace solid-phase microextraction with a portable GC-MS for the *in situ* field detection of volatile metabolites in citrus leaves. Additionally, Wang *et al.* presented a method for rapid *in situ* detection of VOCs in soil gas and groundwater using a portable GC-MS coupled with solid-phase microextraction,[29] demonstrated through a case study of a trichloroethene-contaminated site in Australia. Although the application of a portable GC-MS using ambient temperature adsorption thermal desorption technology is currently extensive, it also has certain limitations. Sampling with adsorbents at ambient temperature requires an extended sampling duration, and it is prone to breakthrough[30–34] for less volatile substances, exhibiting limited capture efficiency. Low-temperature adsorption sampling is an effective means of pre-concentrating an ambient air sample collected from continuous flow for online measurements on adsorbent materials at a specific temperature significantly lower than the ambient temperature, a process also known as "cryofocusing",[35] which significantly enhances the adsorption efficiency.[36–38]

In traditional approaches, the low temperature in adsorption tubes is usually achieved by liquid nitrogen or a coolant.[38] Apel *et al.* developed a fast response GC-MS for onboard aircraft[39] to measure carbonyl compounds from C2 to C4 and methanol, using liquid nitrogen for cryofocusing. The coolant used to circulate the refrigeration provides excellent cooling. Wang *et al.* developed an automated GC-MS/FID system[22] that eliminates the need for liquid nitrogen, using a multi-component refrigerant blend to achieve ultra-low temperatures

through a cascade of refrigeration cycles for VOC enrichment. All these methods have achieved cryofocusing and are sensitive enough to detect low pptv levels of all target analytes. However, none of them can achieve miniaturization, and it is not suitable to integrate them into a portable GC-MS. Peltier coolers, commonly referred to as thermoelectric coolers,[40] exhibit a significant value in cooling technology by harnessing the Peltier effect for heat transfer. This technology generates a cooling effect through the application of an electric current across dissimilar conductive materials, thereby creating a temperature differential. Peltier coolers have the advantages of simple structure and miniaturization and are fully electrically driven.[40] They do not require refrigerants and do not involve any potentially dangerous working fluids (only helium), making them suitable for building miniaturized cryofocusing devices that meet the requirements of compact instruments. Although their cooling capacity and minimum temperature cannot compete with refrigerant-based systems, they can still provide effective cooling in applications that do not require extremely low temperatures. In particular, Peltier coolers can respond quickly, rapidly cooling from ambient temperature to the target temperature. This feature is of great significance for instruments that require rapid temperature changes or maintaining specific temperature ranges. Guan *et al.* have used a Peltier cooler as a cold modulator for 2D gas chromatography,[2,41] reducing cost and power consumption without affecting the performance of the device.

Based on the above content, it could be seen that cryofocusing is widely used in desktop GC-MSs, but there is little related research on portable GC-MSs. This study proposes an innovative idea of using the adsorption thermal desorption technology of 'low-temperature + adsorbent' in a portable GC-MS, and develops a miniaturized fast gas chromatograph–linear ion trap–mass spectrometer (GC-LIT-MS) for the detection of VOCs in the air. By embedding a low-temperature adsorption thermal desorption module in the existing portable GC-MS, the system completes the separation and detection of 65 VOCs in the air within 10 minutes, with a minimum detection limit of 0.12 $\mu g\ L^{-1}$ for toluene, and a maximum of 17 times increase in comparison with that of using ambient temperature adsorption thermal desorption in the peak area for the detection performance of low-boiling substances. In addition, the measurement results show long-term stability and reliability, providing a feasible strategy for the rapid and reliable detection of VOCs in the air that has great potential in the field of environmental monitoring.

Experimental section

Chemicals and materials

The TO-15 standard containing 65 VOCs at a concentration of 1 parts per million (ppm), and a mixture of five low-boiling substances, chloroethylene, 1,3-butadiene, monobromomethane, dichloromethane, and *n*-hexane, at a concentration of 1 ppm were used as the analytical sample, and a mixed stan-

dard of fluorobenzene, *p*-bromofluorobenzene and 1,4-dichlorobenzene at a concentration of 1 ppm was used as an internal standard. All analytes were purchased from ANPEL Laboratory Technologies (Shanghai, China) or Dikma Technologies (Beijing, China), and the TO-15 standard was produced by Dalian Daite Gases Co. The carrier gas used was helium. High-performance liquid chromatography (HPLC) grade methanol was purchased from Fisher Scientific (Fairlawn, NJ).

The Summa canisters were cleaned with a canister cleaner at elevated temperatures prior to use, and the canisters were evacuated (<50 mTorr) after cleaning and set aside for use. A high-precision static diluter was used to dilute the TO-15 standard with high-purity nitrogen to a mixture of standard gases at concentrations of 2, 10, 25, and 50 ppb for storage in the Summa canisters, with care taken to humidify the canisters to minimize adsorption of compounds into the canisters.

The low-temperature adsorption thermal desorption module

A preconcentration device operates in several stages:[42] (1) adsorption of gaseous molecules at a specific low temperature; (2) desorption of the molecules at a higher temperature and their injection into the GC column for separation and (3) cooling down to the specific low temperature before the next sampling and analysis.

The adsorption tube, filled with a solid phase adsorbent, is used to pre-concentrate the sample. Features to be considered include the size and internal volume, the mass and type of adsorbent used, and the temperature of operation. These properties can be tailored for optimum performance, depending on the analyte of interest and the amount of preconcentration required to bring that compound into the detection range of the detector. To prepare the adsorption tube, stainless steel tubing was cut into a 90 mm length, cleaned by repeated flushing with ethanol and acetone, and oven dried. Quartz wool was inserted into the tube and was secured by packing the end of the tube with compacted quartz wool. The tube is integrated into the gas circuit by securing polyetheretherketone (PEEK) end caps with internal threads. The sealing between the two is achieved through an O-shaped fluororubber ring. The heating wire and thermocouple are evenly wound on the surface of the stainless steel tube, achieving a heating rate up to 28 °C s^{-1} with precise and rapid temperature control.

Different types of adsorbents were used when trapping VOCs from the atmosphere,[43] including graphitized carbon materials such as Carbotrap and carbon-based molecular sieves (CMS). Tenax is a polytetrafluoroethylene (PTFE)-based adsorbent and one of the most widely used for the pre-desorption of VOCs. It is characterized by high thermal stability, oxidation resistance, and low adsorption for water, and good adsorption for most of the substances with medium and high boiling points, making it suitable for the enrichment of VOCs in the range of C6 to C26.

The thermoelectric cooling module comprises a Peltier cooler, a dissipator, and a fan, and is constructed as shown in Fig. 1. An alumina plate is utilized to secure and encase the tube. The cold junction of the Peltier cooler is coated with a thermally conductive resin and firmly attached to an aluminum oxide block. When current passes through, the cold side absorbs heat, while the hot side releases heat, in accordance with the Peltier effect. By integrating a thermoelectric cooling system with an adsorption tube, the tube is housed within a cavity structure for non-contact air cooling. This configuration ensures uniform cooling and reduced energy consumption. The temperature of the tube can be lowered from ambient temperature to zero degrees in six minutes.

The thermal behavior of the adsorption tube by experimental observation was studied. Fig. 2 shows the heating and cooling performance of the adsorption tube with a combination of natural convection cooling and forced convection cooling.
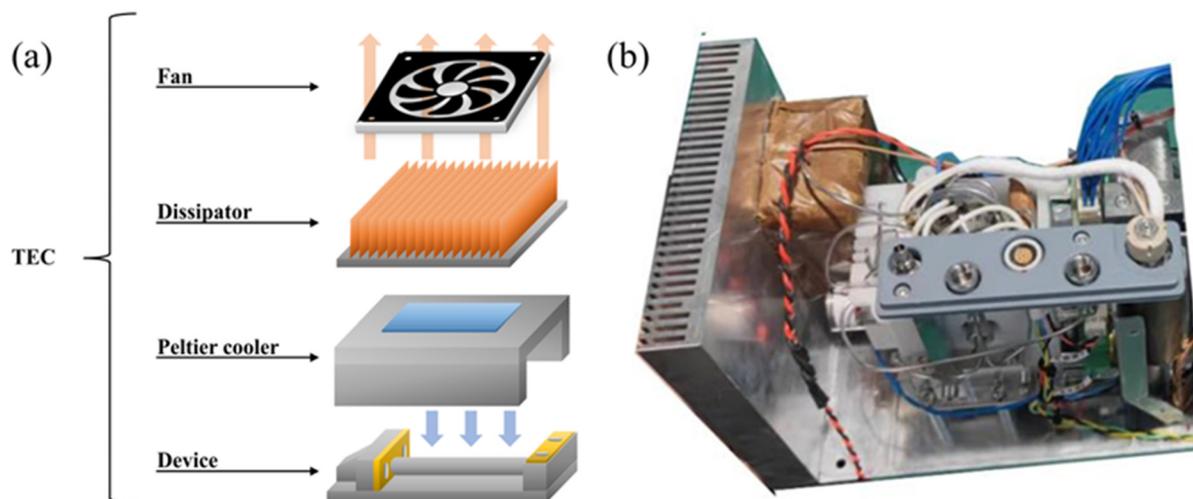

Fig. 1 The structure of the thermoelectric cooling module with the TEC system: (a) schematic view of the device; (b) picture of the device embedded in a portable GC-MS.
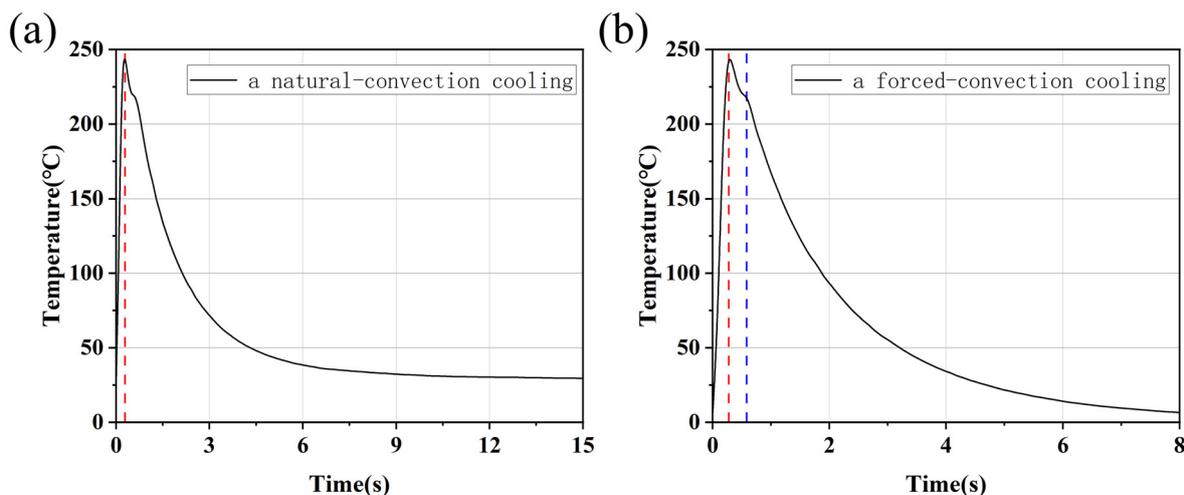
Fig. 2 Heating and cooling performance of a miniature pre-concentrator combined with (a) natural convection cooling and (b) forced convection cooling. The red dashed line represents the switching-off of the resistances, while the blue dashed line represents the switching-on of the fans.

It could be observed that the adsorption tube reaches a temperature of 240 °C within 15 seconds, which is sufficient for complete desorption. Once the fan is activated, the temperature of the adsorption tube cools down to the set temperature of 2 °C within approximately 10 minutes. It is worth noting that in the absence of the cooling device, the temperature of the adsorption tube only slowly decreases to ambient temperature over a period of 10 minutes.

The portable gas chromatograph–mass spectrometer (GC-MS)

The portable GC-LIT-MS system used in this study was developed based on the original instrument of our laboratory,[44] which consists of an adsorption tube, a low thermal mass GC, an electron ionization (EI) source, a linear ion trap, and a detector. It is equipped with a built-in carrier gas supply and a separate power supply, making it easy to transport. The instru-

ment developed in this study added a cooling device to achieve low-temperature adsorption thermal desorption sample enrichment, and optimized the chromatography and mass spectrometry modules. The internal layout design of the system follows the principles of maximizing space utilization and modular design, minimizing the volume and footprint (Fig. 3). The total weight is 21.7 kg, and the volume is 48 cm × 38 cm × 17 cm.

The EI method adopted by the instrument is suitable for thermally stable and volatile compounds and is compatible with chromatographic techniques. The outlet of the chromatographic column is inserted into the ion source through a heated sleeve for correct alignment and connection. The gas flow rate is adjusted to 0.2 ml min^{-1} to adapt to the vacuum conditions of the MS section. For the EI source and linear ion trap, the operating vacuum degree is required to be between
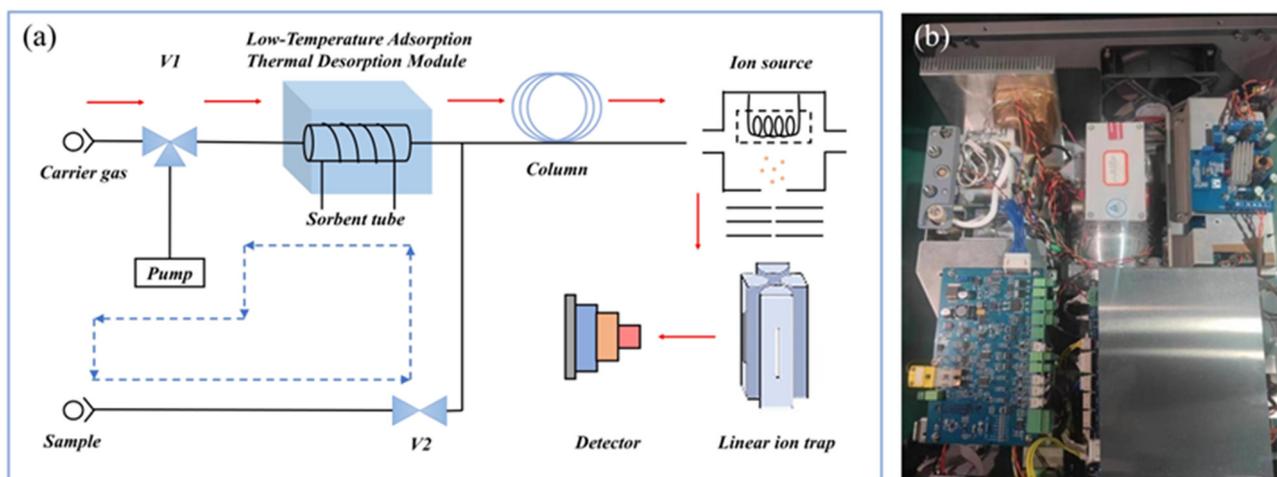

Fig. 3 (a) Schematic of the portable GC-LIT-MS system embedded with the low-temperature adsorption thermal desorption module. The blue dashed arrows represent sampling paths, while the red solid arrows represent analysis paths. (b) Picture of the entire system.

10^{-4} Torr and 10^{-5} Torr. Different from the original instrument, this instrument selects the turbomolecular pump (HiPace 80Neo, Pfeiffer Vacuum Technology Inc., Germany) as the vacuum pump. This pump has the advantages of small size, light weight, and anti-aging, and is suitable for integration into miniaturized and portable devices. Moreover, its pumping speed for nitrogen can reach up to 67 L s^{-1}, achieving a vacuum degree that is one order of magnitude higher than that of the original instrument.

Considering the wide boiling point range and complex composition of VOCs, this study used a DB-5 chromatographic column (size 30 m × 0.25 mm × 0.25 μm) produced by Agilent Technologies (USA) to separate the compounds in the TO-15 standard substance. Compared with the column used in the original instrument, the column capacity of the new column is increased, thus better fulfilling the requirements of the increased pumping speed of the vacuum pump on the system carrier gas flow rate. Meanwhile, the novel chromatographic column exhibits an enhanced column performance, which enhances the separation effect of the sample, thereby improving the sensitivity of the instrument detection.

The adsorption tube was cooled down to approximately 0 °C for sample enrichment. In the injection process, the sampling time was set to 3 min, the spiking time was 0.15 min, the pre-desorption time was 0.2 min, and the desorption time was 0.7 min. In the separation process, the initial temperature (50 °C) was held for 2 min, then increased to 120 °C at a rate of 25 °C min^{-1}, and finally raised to a final temperature of 260 °C at a rate of 30 °C min^{-1}, with a hold time of 1 min. The whole process lasted for 10.47 min.

This instrument utilizes resistance heating for the chromatographic column. The chromatographic column, heating wire, and temperature sensor are arranged in a circular configuration to maximize the heat exchange area while minimizing component exposure. A sealing tape is applied around the ring surface to ensure airtightness and facilitate uniform heat conduction, thereby maintaining a stable column temperature.

Using K-type thermocouples to measure temperature, the thermoelectric potential signal generated by the temperature gradient is amplified and converted into a digital signal. According to the PID control principle, the collected signal is compared with the set value. By integrating the parameters of proportional, integral, and derivative, automatic temperature control is achieved.

Results and discussion

Adsorption efficiency

Preconcentration is a critical step in gas chromatography–mass spectrometry. The low-temperature adsorption thermal desorption method employed in this experiment can improve the sensitivity and detection limits of VOCs. The efficiency of adsorption depends on temperature, with lower temperatures facilitating the adsorption of low-boiling VOCs more efficiently as mentioned above.

Temperature also significantly affects the desorption process, with higher temperatures promoting desorption of adsorbed VOCs. Therefore, the desorption temperature should be optimized to ensure complete desorption without thermal decomposition or degradation. Temperature control is also critical in preventing breakthrough phenomena, where high temperatures may cause the permeation of compounds through the adsorbent, reducing trapping efficiency.

Understanding the influence of temperature on adsorption and desorption is crucial for the successful application of low-temperature preconcentration techniques in a portable GC-MS to achieve accurate and sensitive VOC analysis. Experimental optimization of temperature parameters enables efficient adsorption and desorption, thereby improving the performance and capabilities of the instrument for environmental monitoring and analytical applications.

To evaluate the adsorption efficiency of the low-temperature preconcentration device, TO-15 standard samples with a concentration of 50 ppb were analyzed at adsorption temperatures of 0 °C and 35 °C, as shown in the total ion chromatograms in Fig. 4. It can be observed from the figure that, under the influence of the low-temperature preconcentration device, the overall peak intensity of VOCs is significantly enhanced, particularly for low-boiling VOCs with retention times of less than 2 minutes and 30 seconds, which exhibited a five-fold or greater increase in peak intensity. As the temperature increases, the adsorption efficiency of the adsorbent for VOCs decreases, and breakthrough phenomena become more pronounced. Therefore, the low-temperature device effectively prevents the permeation of low-boiling substances during the adsorption process, leading to increased peak intensities. For high-boiling substances, the concentration effect of the low-temperature preconcentration device noticeably diminishes, resulting in only a slight increase in peak intensity.

To further investigate the device's detection performance for low-concentration samples, TO-15 standard samples with a concentration of 10 ppb were analyzed at 0 °C and 35 °C, and
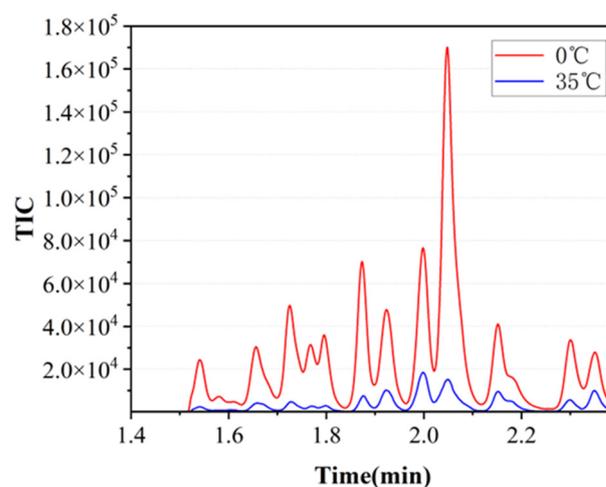

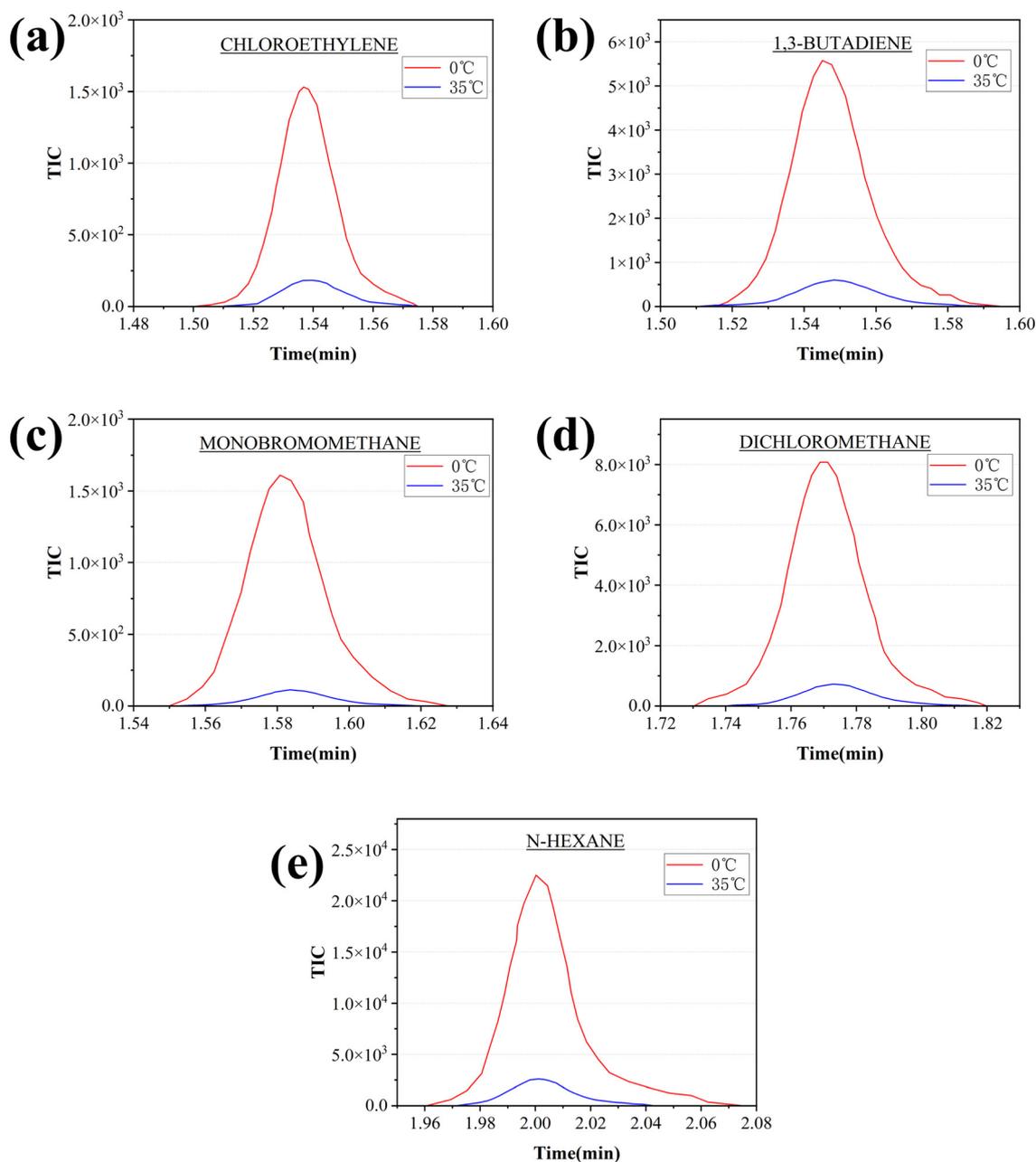Fig. 4 Total ion chromatogram of VOCs at ambient and low temperatures.

Fig. 5 Comparison of the peak area of the samples at 0 °C and 35 °C: (a) chloroethylene; (b) 1,3-butadiene; (c) monobromomethane; (d) dichloromethane; and (e) n-hexane.

the peak areas of some of the low-boiling compounds were compiled to observe the trapping of five specific low-boiling compounds (chloroethylene, 1,3-butadiene, monobromomethane, dichloromethane, and *n*-hexane), as shown in Fig. 5. The results indicate that under low-temperature adsorption conditions, the five substances exhibited increases in the peak area of 15.88-fold, 17.45-fold, 14.82-fold, 11.57-fold, and 13.91-fold, respectively (see Table 1). This suggests that for lower-concentration low-boiling samples, the effect of the low-temperature device becomes more pronounced, with enhancements of up to 11–17-fold. When the sample concentration is below

Table 1 Peak area of the samples at 0 °C and 35 °C

Compound	Retention time	Peak area (0 °C)	Peak area (35 °C)
Chloroethylene	1.539	2208	139
1,3-Butadiene	1.545	8638	495
Monobromomethane	1.582	2564	173
Dichloromethane	1.768	2303	199
n-Hexane	1.999	39 071	2808

10 ppb, certain substances cannot be detected at ambient temperature, but only at low temperatures.

Linearity

Linearity refers to the ability of the detector of an analytical instrument to respond proportionally to the concentration of the analyte in the sample, and it is an important indicator for evaluating the performance of the instrument or the analytical method. Four standard concentrations of TO-15 standard compounds and five low-boiling VOCs (1,1,2,2-tetrafluoro-1,2-dichloroethane, chloroethylene, 1,3-butadiene, trichlorofluoromethane (Freon 11), and dichloromethane) were selected for observation. By conducting linearity experiments on these substances, we can systematically study the performance of low-boiling substances with different chemical structures and polarities during the detection process, gain a deeper understanding of the mechanism of low-boiling substance detection, and provide scientific basis and guidance for improving detec-
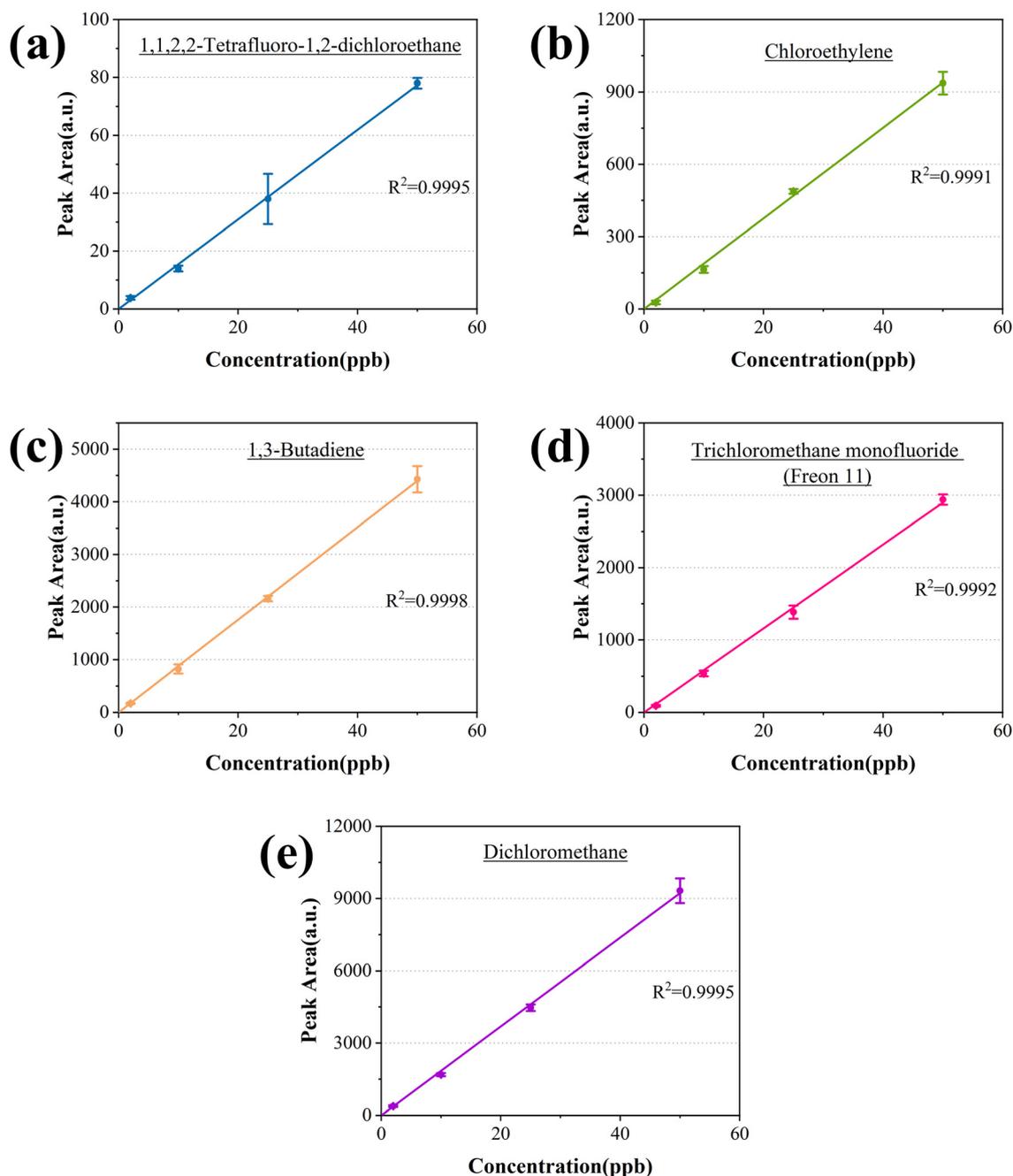

Fig. 6 Average peak area *versus* injected sample concentration in the adsorption tube. Sampling flow rate = 5 N mL min^{-1}, desorption temperature = 220 °C, injection time = 90 s. (a) 1,1,2,2-Tetrafluoro-1,2-dichloroethane, (b) chloroethylene, (c) 1,3-butadiene, (d) trichloromethane monofluoride (Freon 11), and (e) dichloromethane.

Table 2 Retention time, relative standard deviation, limit of detection and recovery for all substances

No.	Compounds	Retention time	RSD	LOD	Recovery
1	Propylene	1.317	3.44%	0.26	101.28%
2	1,1,2,2-Tetrafluoro-1,2-dichloroethane	1.352	9.16%	0.55	91.88%
3	Dichlorodifluoromethane	1.364	9.52%	0.58	97.14%
4	Chloroethylene	1.384	6.96%	0.46	100.96%
5	1,3-Butadiene	1.404	9.97%	0.58	92.27%
6	Monochloromethane	1.404	7.14%	0.46	102.33%
7	Ethyl chloride	1.421	9.73%	0.13	98.67%
8	Monobromomethane	1.436	8.33%	0.58	108.53%
9	Ethanol	1.488	9.72%	0.59	94.91%
10	Trichloromethane monofluoride (Freon 11)	1.500	5.91%	0.38	101.87%
11	Acrolein	1.508	2.12%	0.16	100.16%
12	Acetone	1.524	6.44%	0.40	98.82%
13	Isopropyl alcohol	1.548	3.10%	0.19	100.50%
14	1,1-Dichloroethylene	1.564	9.99%	0.65	103.24%
15	1,2,2-Trifluoro-1,1,2-trichloroethane (Freon 113)	1.572	5.22%	0.24	100.41%
16	Dichloromethane	1.608	9.34%	0.60	102.99%
17	Carbon disulfide	1.628	8.04%	0.56	97.07%
18	*trans*-1,2-Dichloroethylene	1.697	3.57%	0.24	107.77%
19	Methyl *tert*-butyl methyl ether	1.701	9.83%	0.55	91.66%
20	Vinyl acetate	1.741	8.75%	0.56	102.20%
21	1,1-Dichloroethane	1.745	3.89%	0.29	100.02%
22	*n*-Hexane	1.805	3.21%	0.20	100.02%
23	2-Butanone	1.817	8.51%	0.51	99.08%
24	*cis*-1,2-Dichloroethylene	1.857	6.70%	0.43	101.01%
25	Ethyl acetate	1.886	4.22%	0.26	98.37%
26	Chloroform	1.946	7.82%	0.57	97.32%
27	Tetrahydrofuran	2.002	6.52%	0.40	98.61%
28	1,1,1-Trichloroethane	2.086	3.80%	0.25	104.20%
29	1,2-Dichloroethane	2.135	2.07%	0.13	99.05%
30	Benzene	2.195	7.75%	0.56	99.25%
31	Carbon tetrachloride	2.203	8.17%	0.56	109.12%
32	Cyclohexane	2.207	7.71%	0.43	103.54%
33	*n*-Heptane	2.469	11.23%	0.80	98.19%
34	Trichloroethylene	2.497	7.71%	0.50	102.58%
35	1,2-Dichloropropane	2.529	8.76%	0.70	97.63%
36	Methyl methacrylate	2.594	4.70%	0.29	99.76%
37	Monobromodichloromethane	2.622	9.90%	0.76	97.22%
38	1,4-Dioxane	2.638	9.84%	0.60	96.98%
39	*cis*-1,3-Dichloropropene	2.879	3.44%	0.23	107.90%
40	4-Methyl-2-pentanone (methyl isobutyl ketone)	2.891	4.99%	0.61	97.93%
41	*trans*-1,3-Dichloropropene	3.156	5.48%	0.36	104.89%
42	Toluene	3.160	1.73%	0.12	106.15%
43	1,1,2-Trichloroethane	3.272	3.26%	0.22	102.22%
44	2-Hexanone	3.397	8.77%	0.59	106.10%
45	Dibromochloromethane	3.546	5.96%	0.35	93.93%
46	Tetrachloroethylene	3.571	5.93%	0.36	96.85%
47	1,2-Dichloroethane	3.648	8.07%	0.54	107.18%
48	Chlorobenzene	4.033	5.99%	0.40	107.34%
49	Ethylbenzene	4.180	7.04%	0.49	100.60%
50	*m*-Xylene	4.288	7.63%	1.03	204.43%
51	Styrene	4.521	8.60%	0.56	102.91%
52	*o*-Xylene	4.525	7.37%	0.50	107.00%
53	Bromoform	4.545	7.60%	0.38	94.54%
54	1,1,2,2-Tetrachloroethane	4.825	4.32%	0.29	106.02%
55,56	*m/p*-Ethyltoluene	5.255	9.46%	0.55	92.89%
57	1,3,5-Trimethylbenzene	5.303	8.85%	0.55	98.25%
58	1,2,4-Trimethylbenzene	5.538	9.26%	0.55	94.01%
59	*m*-Dichlorobenzene	5.657	8.18%	0.48	92.61%
60	Benzyl chloride	5.725	9.30%	0.58	99.94%
61	*p*-Dichlorobenzene	5.741	8.84%	0.43	96.88%
62	*o*-Dichlorobenzene	5.902	7.53%	0.37	98.39%
63	1,2,4-Trichlorobenzene	7.011	6.09%	0.19	100.51%
64	Naphthalene	7.099	6.45%	1.08	95.47%
65	Hexachloro-1,3-butadiene	7.215	6.46%	0.88	97.68%

tion performance. Each sample underwent three injections. The average peak area of the analyzed samples was correlated with the injection concentration, and a calibration curve (Fig. 6) was plotted to assess the linearity of the instrument. For all compounds, the peak area linearly increased with the injection concentration. As shown in the figure, each cali-

bration curve successfully fitted a linear relationship, and the determination coefficient (R^2) exceeded 0.999, enabling a wide range of linear responses even at extremely low concentrations.

In a series of experiments with varying sample concentrations, after each analysis, a blank was performed immediately after desorption to evaluate any carryover in the adsorbent within the adsorption tube.

Repeatability, LOD and recovery

Repeatability refers to the consistency of the results obtained by measuring the same sample multiple times using the same instrument and method under the same or similar conditions. Therefore, similar to all analytical instruments, evaluating the repeatability of this experiment is crucial for ensuring the long-term consistency and reliability of the instrument results. To assess repeatability, uniform parameters were employed, including a desorption temperature set at 220 °C, an injection time of 90 seconds, and consistency maintained throughout the entire testing period. Seven 2 ppb concentration TO-15 samples were prepared and tested multiple times, with a blank injection run between each test to eliminate sample residue. The results of seven experiments were recorded, and relative standard deviation was calculated to evaluate the repeatability of this experiment. At the same time, the detection limits and recoveries of all substances were calculated for assay method evaluation (see Table 2).

The peak areas of different samples exhibited moderate variations, while the variations in retention times of different samples were negligible. The peak areas of 98% of the compounds had relative standard deviations (% RSD) of less than 10%, indicating that the portable GC-MS analysis using an integrated thermoelectric cooler is repeatable.

Conclusions

In this study, a miniaturized low-temperature adsorption thermal desorption GC-LIT-MS was proposed for the rapid measurement of various VOCs in the air. Based on the thermoelectric cooling technical approach, a miniaturized low-temperature adsorption thermal desorption module was fabricated to achieve cryofocusing and rapid desorption and injection of samples, which was also the first time that thermoelectric cooling technology was integrated into a portable GC-MS. The total weight of the portable GC-MS is 21.7 kg, and the volume is 48 cm × 38 cm × 17 cm. The separation and detection of the TO-15 standard substance containing 65 VOCs could be completed in just 10 minutes. The experimental conditions were optimized, including studying the effect of adsorption temperature on the peak area of low-boiling VOCs. The results showed that the instrument could detect toluene with a detection limit down to 0.12 μg L^{-1}, and the detection performance for low-boiling substances was improved by 11–17 times compared to ambient-temperature adsorption thermal desorption, indicating that the low-temperature device effectively prevented the permeation of low-boiling VOCs during the adsorption process, thereby increasing the peak intensity and improving the detection sensitivity of the instrument. Five low-

boiling VOCs showed excellent linear responses ($R^2 > 0.999$) at extremely low concentrations. In addition, the repeatability and recovery were evaluated, and the RSD percentages of the seven groups of samples were generally less than 10%, and the recovery range was 91.66% to 109.12%, indicating that the measurement results were stable and highly reproducible.

Nevertheless, further testing is necessary to assess potential interferences and other performance-related issues. Future research will focus on field testing, instrument validation, and the utilisation of integrated sampling and pre-processing techniques for the *in situ* detection of actual polluted exhaust gases in diverse environments.

Author contributions

Yulin Chen contributed to writing – original draft, validation, investigation, formal analysis, data curation, and conceptualization. Junwei Qiu contributed to writing – review & editing, writing – original draft, methodology, formal analysis, and visualization. Kai Xu contributed to software and writing – review & editing. Huijun Zhu contributed to resources and data curation. Xinxin Lu and Shuo Zhang contributed to validation, investigation, and project administration. Xiaoxu Li contributed to conceptualization, supervision, and funding acquisition.

Data availability

Data used in this publication are contained within the paper. Raw data supporting the results can be obtained upon reasonable request to the corresponding author.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

References

1 X. Guan, Z. Zhao, S. Cai, S. Wang and H. Lu, Analysis of volatile organic compounds using cryogen-free thermal modulation based comprehensive two-dimensional gas chromatography coupled with quadrupole mass spectrometry, *J. Chromatogr. A*, 2019, **1587**, 227–238.

2 R. Li, A. Xu, Y. Zhao, H. Chang, X. Li and G. Lin, Genetic algorithm (GA)-Artificial neural network (ANN) modeling for the emission rates of toxic volatile organic compounds (VOCs) emitted from landfill working surface, *J. Environ. Manage.*, 2022, **305**, 114433.

3 E. Durmusoglu, F. Taspinar and A. Karademir, Health risk assessment of BTEX emissions in the landfill environment, *J. Hazard. Mater.*, 2010, **176**, 870–877.

4 J. C. Lerner, E. Y. Sanchez, J. E. Sambeth and A. A. Porta, Characterization and health risk assessment of VOCs in occupational environments in Buenos Aires, Argentina, *Atmos. Environ.*, 2012, **55**, 440–447.

5 B. Szulczyński, T. Dymerski, J. Gębicki and J. Namieśnik, Instrumental measurement of odour nuisance in city agglomeration using electronic nose, E3S Web of Conferences, 2018, vol. 28, p. 01012.

6 L. Trasande and G. D. Thurston, The role of air pollution in asthma and other pediatric morbidities, *J. Allergy Clin. Immunol.*, 2005, **115**, 689–699.

7 S. Mentese, N. A. Mirici, T. Elbir, E. Palaz, D. T. Mumcuoğlu, O. Cotuker, C. Bakar, S. Oymak and M. T. Otkun, A long-term multi-parametric monitoring study: Indoor air quality (IAQ) and the sources of the pollutants, prevalence of sick building syndrome (SBS) symptoms, and respiratory health indicators, *Atmos. Pollut. Res.*, 2020, **11**, 2270–2281.

8 M. Szyszkowicz, T. Kousha, J. Castner and R. Dales, Air pollution and emergency department visits for respiratory diseases: a multi-city case crossover study, *Environ. Res.*, 2018, **163**, 263–269.

9 I. Cheng, C. Tseng, J. Wu, J. Yang, S. M. Conroy, S. Shariff-Marco, L. Li, A. Hertz, S. L. Gomez and L. Le Marchand, Association between ambient air pollution and breast cancer risk: the multiethnic cohort study, *Int. J. Cancer*, 2020, **146**, 699–711.

10 S. P. Eckel, M. Cockburn, Y.-H. Shu, H. Deng, F. W. Lurmann, L. Liu and F. D. Gilliland, Air pollution affects lung cancer survival, *Thorax*, 2016, **71**, 891–898.

11 S. De Vito, E. Massera, M. Piga, L. Martinotto and G. Di Francia, On field calibration of an electronic nose for benzene estimation in an urban pollution monitoring scenario, *Sens. Actuators, B*, 2008, **129**, 750–757.

12 A. G. Ribeiro, G. S. Downward, C. U. de Freitas, F. C. Neto, M. R. A. Cardoso, M. d. R. D. de Oliveira, P. Hystad, R. Vermeulen and A. C. Nardocci, Incidence and mortality for respiratory cancer and traffic-related air pollution in São Paulo, Brazil, *Environ. Res.*, 2019, **170**, 243–251.

13 D. Pérez-Rial, P. López-Mahía and R. Tauler, Investigation of the source composition and temporal distribution of volatile organic compounds (VOCs) in a suburban area of the northwest of Spain using chemometric methods, *Atmos. Environ.*, 2010, **44**, 5122–5132.

14 M. Mahilang, M. K. Deb and S. Pervez, Biogenic secondary organic aerosols: A review on formation mechanism, analytical challenges and environmental impacts, *Chemosphere*, 2021, **262**, 127771.

15 S. Chen, Z. Xu, P. Liu, Y. Zhuang, M. Jiang, X. Zhang, Z. Han, Y. Liu and X. Chen, Assessment of volatile organic compound emissions from pesticides in China and their contribution to ozone formation potential, *Environ. Monit. Assess.*, 2022, **194**, 737.

16 J. Xu, J. Ma, X. Zhang, X. Xu, X. Xu, W. Lin, Y. Wang, W. Meng and Z. Ma, Measurements of ozone and its precursors in Beijing during summertime: impact of urban plumes on ozone pollution in downwind rural areas, *Atmos. Chem. Phys.*, 2011, **11**, 12241–12252.

17 L. Hildebrandt, N. M. Donahue and S. N. Pandis, High formation of secondary organic aerosol from the photo-oxidation of toluene, *Atmos. Chem. Phys.*, 2009, **9**, 2973–2986.

18 M. Shao, S. Lu, Y. Liu, X. Xie, C. Chang, S. Huang and Z. Chen, Volatile organic compounds measured in summer in Beijing and their role in ground-level ozone formation, *J. Geophys. Res.: Atmos.*, 2009, **114**(D2), DOI: 10.1029/2008JD010863.

19 P. Carpenter, P. Ciccioli, A. Goldstein, J. F. Hamilton, T. Hoffmann, A. C. Lewis, M. Mannozzi, S. O'Doherty, S. Reimann and J. Roberts, Volatile organic compounds in the atmosphere, Wiley Online Library, 2007.

20 Y. Li, Analytical methods for the analysis of volatile natural products, *Nat. Prod. Rep.*, 2023, **40**, 922–956.

21 P. E. Leary, B. W. Kammrath and J. A. Reffner, in *Field-Portable Gas Chromatography–Mass Spectrometry, Encyclopedia of Analytical Chemistry: Applications, Theory and Instrumentation*, 2006, pp. 1–23.

22 M. Wang, L. Zeng, S. Lu, M. Shao, X. Liu, X. Yu, W. Chen, B. Yuan, Q. Zhang, M. Hu and Z. Zhang, Development and validation of a cryogen-free automatic gas chromatograph system (GC-MS/FID) for online measurements of volatile organic compounds, *Anal. Methods*, 2014, **6**, 9424–9434.

23 Y. Zhai, Y. Feng, Y. Wei, Y. Wang and W. Xu, Development of a miniature mass spectrometer with continuous atmospheric pressure interface, *Analyst*, 2015, **140**, 3406–3414.

24 K. Demeestere, J. Dewulf, B. De Witte and H. Van Langenhove, Sample preparation for the analysis of volatile organic compounds in air and water matrices, *J. Chromatogr., A*, 2007, **1153**, 130–144.

25 V. Safarova, S. Sapelnikova, E. Djazhenko, G. Teplova, G. Shajdulina and F. K. Kudasheva, Gas chromatography–mass spectrometry with headspace for the analysis of volatile organic compounds in waste water, *J. Chromatogr. B: Biomed. Sci. Appl.*, 2004, **800**, 325–330.

26 A. C. Soria, M. J. García-Sarrió and M. L. Sanz, Volatile sampling by headspace techniques, *TrAC, Trends Anal. Chem.*, 2015, **71**, 85–99.

27 N. Turner, M. Jones, K. Grice, D. Dawson, M. Ioppolo-Armanios and S. J. Fisher, δ13C of volatile organic compounds (VOCS) in airborne samples by thermal desorption-gas chromatography-isotope ratio-mass spectrometry (TD-GC-IR-MS), *Atmos. Environ.*, 2006, **40**, 3381–3388.

28 X. Liu, M. Yi, W. Mo, Q. Huang, Z. Huang and B. Hu, Portable Mass spectrometry approach combined with machine learning for onsite field detection of Huanglongbing disease, *Anal. Chem.*, 2023, **95**, 10769–10776.

29 L. Wang, Y. Cheng, R. Naidu, S. Chadalavada, D. Bekele, P. Gell, M. Donaghey and M. Bowman, Application of portable gas chromatography–mass spectrometer for rapid field based determination of TCE in soil vapour and groundwater, *Environ. Technol. Innovation*, 2021, **21**, 101274.

30 Ö. O. Kuntasal, D. Karman, D. Wang, S. G. Tuncel and G. Tuncel, Determination of volatile organic compounds in different microenvironments by multibed adsorption and short-path thermal desorption followed by gas chromatographic–mass spectrometric analysis, *J. Chromatogr., A*, 2005, **1099**, 43–54.

31 Y.-C. Chiang, P.-C. Chiang and C.-P. Huang, Effects of pore structure and temperature on VOC adsorption on activated carbon, *Carbon*, 2001, **39**, 523–534.

32 X. Li, L. Zhang, Z. Yang, P. Wang, Y. Yan and J. Ran, Adsorption materials for volatile organic compounds (VOCs) and the key factors for VOCs adsorption process: A review, *Sep. Purif. Technol.*, 2020, **235**, 116213.

33 L. Zhu, D. Shen and K. H. Luo, A critical review on VOCs adsorption by different porous materials: Species, mechanisms and modification methods, *J. Hazard. Mater.*, 2020, **389**, 122102.

34 M. J. Lashaki, S. Kamravaei, Z. Hashisho, J. H. Phillips, D. Crompton, J. E. Anderson and M. Nichols, Adsorption and desorption of a mixture of volatile organic Compounds: Impact of activated carbon porosity, *Sep. Purif. Technol.*, 2023, **314**, 123530.

35 F. Obersteiner, H. Bönisch, T. Keber, S. O'Doherty and A. Engel, A versatile, refrigerant- and cryogen-free cryofocusing–thermodesorption unit for preconcentration of traces gases in air, *Atmos. Meas. Tech.*, 2016, **9**, 5265–5279.

36 T. J. Bruno, Simple, quantitative headspace analysis by cryoadsorption on a short alumina PLOT column, *J. Chromatogr. Sci.*, 2009, **47**(7), 569–574.

37 J. E. Nichols, M. E. Harries, T. M. Lovestead and T. J. Bruno, Analysis of arson fire debris by low temperature dynamic headspace adsorption porous layer open tubular columns, *J. Chromatogr. A*, 2014, **1334**, 126–138.

38 W. Wang, H. Chen, W. Zhu, Z. Gong, H. Yin, C. Gao, A. Zhu and D. Wang, A two-staged adsorption/thermal desorption GC/MS online system for monitoring volatile organic compounds, *Environ. Monit. Assess.*, 2023, **195**, 869.

39 E. Apel, A. Hills, R. Lueb, S. Zindel, S. Eisele and D. Riemer, A fast-GC/MS system to measure C2 to C4 carbonyls and methanol aboard aircraft, *J. Geophys. Res.: Atmos.*, 2003, **108**(D20), DOI: 10.1029/2002JD003199.

40 A. Martínez, D. Astrain and A. Rodríguez, Experimental and analytical study on thermoelectric self cooling of devices, *Energy*, 2011, **36**, 5250–5260.

41 J. Luong, X. Guan, S. Xu, R. Gras and R. A. Shellie, Thermal independent modulator for comprehensive two-dimensional gas chromatography, *Anal. Chem.*, 2016, **88**, 8428–8432.

42 A. Rodríguez-Cuevas, I. Lara-Ibeas, A. Leprince, M. Wolf and S. Le Calvé, Easy-to-manufacture micro gas preconcentrator integrated in a portable GC for enhanced trace detection of BTEX, *Sens. Actuators, B*, 2020, **324**, 128690.

43 T. Salthammer, Analytical chemistry of carbonyl compounds in indoor air, *Analyst*, 2023, **148**, 3432–3451.

44 Q. Junwei, X. Kai, Z. Tao, Z. Huijun, Z. Shuo, L. Xinxin and L. Xiaoxu, Development of a portable gas chromatography linear ion trap mass spectrometer (GC-LIT-MS) for VOCs analysis in water, *Int. J. Mass Spectrom.*, 2024, **497**, 117189.