Application News

No. AD-0233

Environmental/ TD-30 & GCMS-QP2020 NX

Indoor Air Monitoring of Volatile Organic Compounds by Thermal Desorption - GCMS

❑ Introduction

Volatile organic compounds (VOCs) are considered to be indoor air pollutant, which could be generated from paints, household products or sometimes from outdoor air pollution [1]. It is important to monitor VOCs as it can potentially pose serious health issue to human, such as eye or nose irritation and damage to liver or even to central nervous system [1]. VOCs in air can be identified using thermal desorption system paired with gas chromatography mass spectrometer (TD-GCMS). The International Organization for Standardization (ISO) 16000-6-2011 allows quantitation of single VOC to be done using either SCAN or SIM mode [2]. However, when SIM mode is used, only VOCs which are in the targeted list can be identified. Other detected VOCs will be left unidentified. On the other hand, if only SCAN mode is used, lower quantitation limits cannot be achieved. Therefore, a method capable of running both SCAN and SIM simultaneously would be ideal. Here, we describe TD-GCMS method for the analysis of VOCs in indoor air. FASST mode (Fast Automated SCAN/SIM Type) was utilised to enable the quantitation of targeted VOCs, and at the same time, the identification of untargeted VOCs. In this study, the comparison of VOCs present in different locations (rooms) was also done.

❑ Experimental

Analytical conditions

TD-30 thermal desorption system paired with GCMS-QP™2020 NX (Shimadzu Corporation, Japan) was used in this work. Details of analytical conditions were shown in Table 1.

Standard preparation

All the chemicals were mixed and diluted with methanol into a stock solution. The stock solution was then further diluted with methanol to different concentrations (2.5, 5, 10, 25 and 50 ng/µL). For preparation of calibration curves, 1 µL of each standard mixture solution was injected into different TD sample tubes containing TenaxTA adsorbent material. In total, there were 5 sample tubes with different concentrations in term of absolute weight (2.5, 5,10, 25 and 50 ng). The injection of standard into sample tube was performed only when sample preparation had been completed to avoid possible loss of targets.

Table 1. Analytical Condition for indoor air monitoring

Analytical Condition	
GCMS™ Parameters	
Flow control mode	Pressure
Linear velocity	33.1 cm/s
Injection mode	Split (split ratio 10)
Carrier gas	Helium
Column	SH-Rxi™-624Sil MS (60 m length, 0.32 mm ID, df =1.80 mm)
Column temp program	35℃ (hold time: 5 min) → rate: 5℃/min → 280℃ (hold time: 5 min) →-10℃/min until 100⁰C
Ion source temp	230℃
Interface temp	200℃
Acquisition mode	FASST (Scan/SIM)
Scan m/z range	20-600 amu
SIM ions	Refer to Table 2.
TD-30 Parameters	
Tube desorb temp	250℃ (10 min)
Tube desorb flow	70 mL/min
Second trap	TenaxTA
Second trap cooling temp	-25℃
Second trap desorb temp	250℃ (2 min)
Joint temp	75℃
Valve temp	185℃
Transfer line temp	220℃

Table 2. SIM ions of the targeted VOCs

No.	Compound	Target ion (m/z)	Reference Ions (m/z)
1	Chloroform	83	85, 47
2	Benzene	78	77, 50
3	1,2-dichloroethane	62	64, 27
4	Ethyl Acrylate	55	73
5	Methyl Isobutyl Ketone	43	58, 100
6	Toluene	91	92
7	Ethylbenzene	91	106
8	m-Xylene and p-xylene	91	106
9	o-Xylene	91	106
10	1,2-dichlorobenzene	146	111, 148
11	Hexadecane	57	71, 85

Sample Preparation

To collect air sample, a sampling pump (GL Sciences, P/N: 2702-17576) with controllable flow rate (10~100mL/min) and a TD sample tube with TenaxTA adsorbent (P/N: 223-57102-91) were utilised (Fig.1). The flow rate of the sampling pump was adjusted to 66.7 mL/min and the surrounding air was continuously pumped into the sample tube for 1 hour. In total, about 4 L of air was collected.

The air of three different rooms (Room A, B and C) was collected separately. Room A was located beside a laboratory, Room B was a room far from the laboratory, and Room C was a newly renovated room, far from the laboratory. Room B air was collected before and after painting work was done on its walls. To prevent confusion, Room B before painting will be called as Room B1 while Room B after painting will be called as Room B2. The air of Room A, B1 and C were collected on the same day.

Once the samples and standards were prepared, the standards were analysed first followed by the samples. Freshly prepared standards were used for quantitation of Room B2 after it had been painted. Results of the samples will be expressed in both ng/L and parts-per-billion-volume (ppbv).
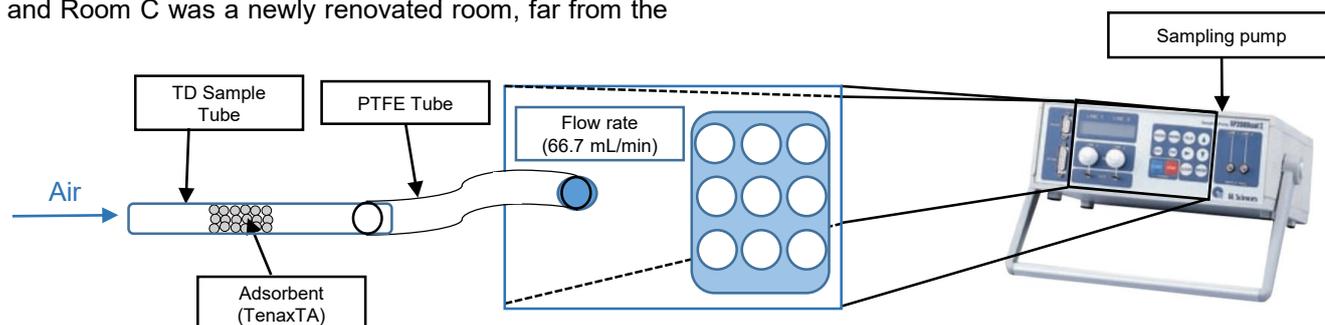

Fig. 1: Sampling pump experimental setup for indoor air sampling

❑ Results and Discussion

Thermal Desorption robustness results

In this experiment, a few compounds (listed in either ISO-16000-6 or Compendium Method TO-17) were selected for quantitation [2][3]. Chromatographic separation and mass separation were not possible for m-xylene and p-xylene (Fig. 2, Peak 8). Hence, these 2 compounds were quantified as a group.

To ensure the robustness of the analytical system, peak area repeatability test (n=5) was conducted on all the targets at concentration of 2.5 ng in sample tube. All the targeted compounds %RSD (n=5) were less than 5.0 % except for toluene (6.1 %) and 1,2-dichlorobenzene (5.0 %). This is due to short transfer line in the TD-30 system which prevent possible loss of compounds through interaction with active site. Furthermore, TD-30 sample line with no cold spots helps to prevent condensation of compound in the system. This allows semi-volatile compound like hexadecane to have %RSD (n=5) of less than 4%.

Table 3. Peak area Repeatability (n=5) and average (n=5) S/N ratio for standard mixtures at concentration of 2.5 ng

No.	Compound	Retention Time (Min)	%RSD (n=5)	Average S/N ratio
1	Chloroform	13.285	2.6	241
2	Benzene	14.655	3.3	477
3	1,2-dichloroethane	14.801	4.2	47
4	Ethyl Acrylate	16.648	4.0	314
5	Methyl Isobutyl Ketone	19.442	4.5	731
6	Toluene	20.017	6.1	1255
7	Ethylbenzene	24.485	4.2	2605
8	m-Xylene and p-xylene	24.891	4.3	1537
9	o-Xylene	26.068	4.3	538
10	1,2-dichlorobenzene	32.700	5.0	576
11	Hexadecane	48.780	3.9	361

Signal to noise ratio (S/N) value of greater than 10 was used to determine the quantitation limit in this application. At 2.5 ng, most of the compounds had signal to noise ratio values of greater than 100 while the lowest was 47. Therefore, concentration of 2.5 ng was suitable to be used as limit of quantitation (lowest calibration point).
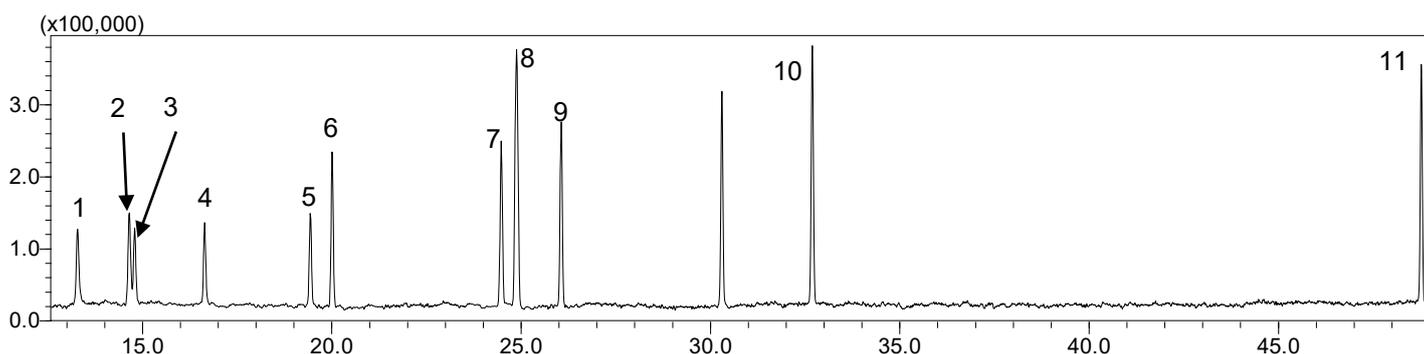

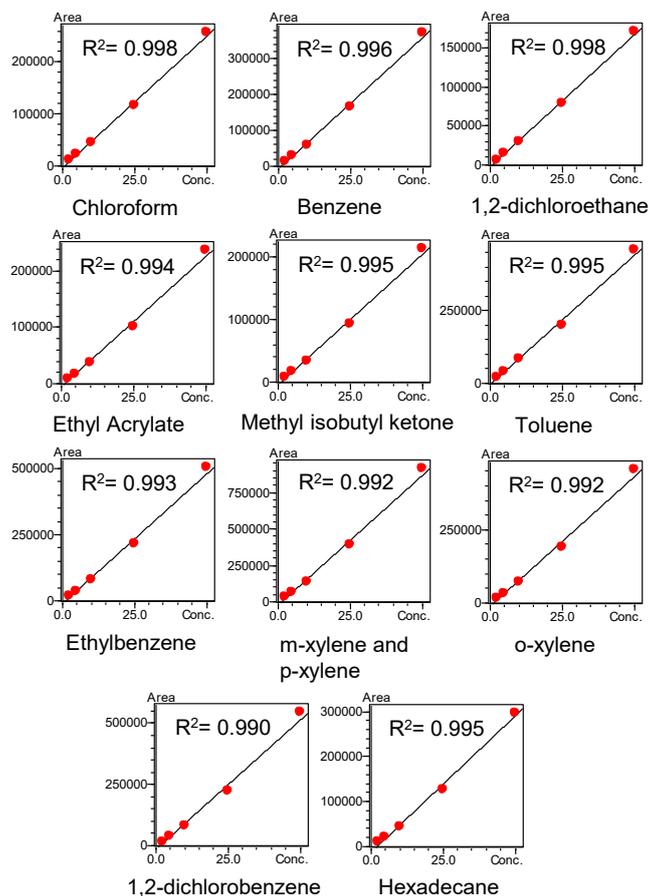**Fig. 2: Total Ion Chromatograms (TIC) of all the 11 targeted compounds at 50 ng**

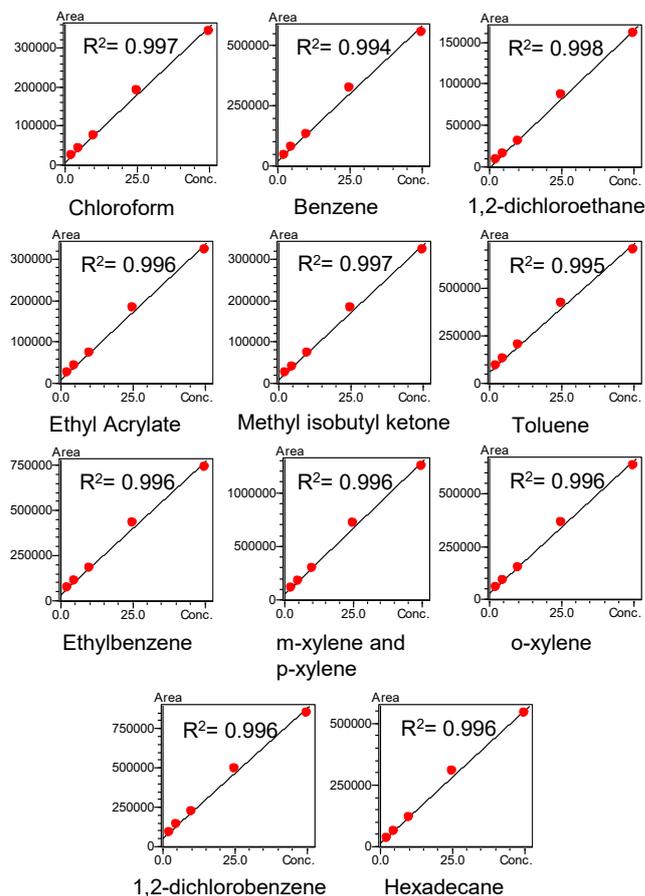**Fig. 3A: 5-points calibration curves for sample analysis on Room A, B1 and C**

Fig. 3B: 5-points calibration curves for sample analysis on Room B2

Sample Results

Five-point calibration curves were built for all the targeted compounds (Fig. 3A and Fig. 3B). Sample results calculated from these calibration curves were reported in term of absolute weight (ng). Next, to get concentration in ng/L, the absolute weight of each target was divided by the total volume of air collected. Finally, a unit conversion between ng/L (equivalent to μg/m^3) and ppbv was done using the following equation (1).

$$ppbv = \frac{ug}{m^3} \times \frac{Molecular\ Volume\ (litres)}{Molecular\ Weight} \quad (1)$$

$Where$:

$Molecular\ volume\ (litres)$
$$= 22.41 \times \frac{sample\ collection\ Temp\ (K)}{273.15} \times \frac{101325}{sample\ collection\ Pressure(Pa)} \quad (2)$$

The temperature of the room was 25 $^\circ$C when the sampling was done. The pressure was set to 101325 Pa since the sampling was done at around sea level elevation.
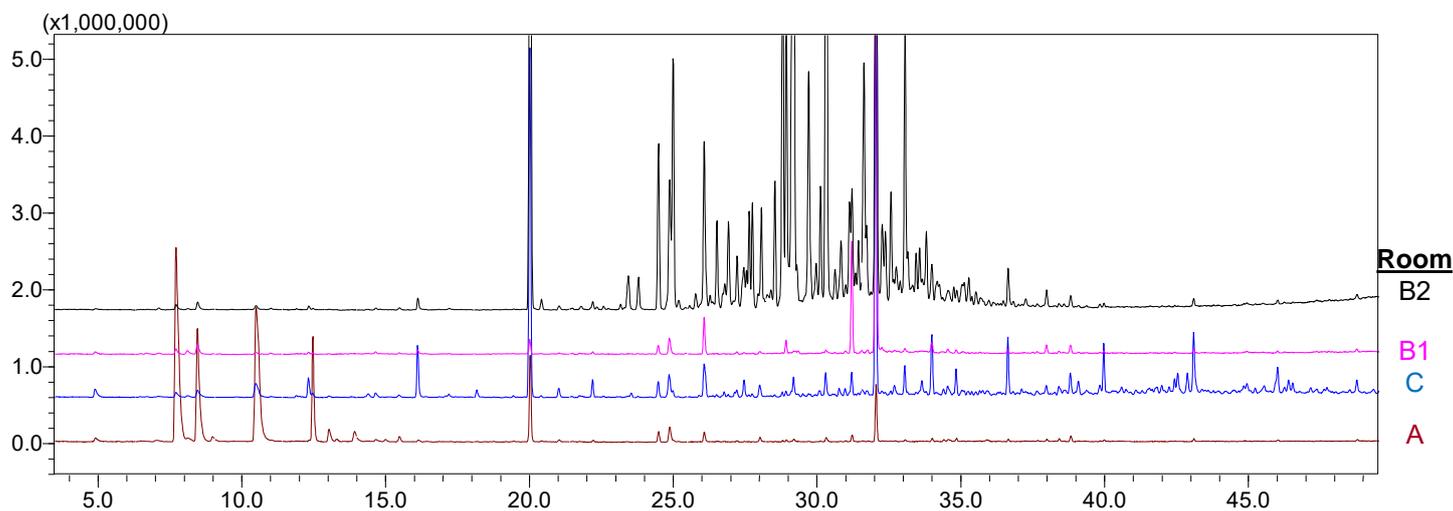

Fig. 4: Overlay Total Ion Chromatograms (TIC) of Room B2 (Black, after painting), B1 (pink, before painting) and C (blue) and A (brown)

Table 4: Concentration in term of ng/L and ppbv of the targeted compound for different rooms

Compound names	Concentration (ng/L)				Concentration (ppbv)			
	Room A	Room B1	Room B2	Room C	Room A	Room B1	Room B2	Room C
Chloroform	5.053	0.453	0.042	1.028	1.035	<LOQ	<LOQ	0.211
Benzene	3.705	2.844	1.366	7.547	1.160	0.891	0.428	2.364
1,2-dichloroethane	ND	<LOQ	<LOQ	<LOQ	ND	<LOQ	<LOQ	<LOQ
Ethyl Acrylate	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Methyl Isobutyl Ketone	1.310	0.762	0.310	2.816	0.320	0.186	0.076	0.688
Toluene	76.871	11.922	707.54*	322.171	20.398	3.165	187.86*	85.538
Ethylbenzene	8.379	6.533	85.889	11.455	1.930	1.505	19.790	2.639
m-Xylene, p-xylene	6.916	7.307	40.292	9.445	1.593	1.684	9.285	2.177
o-Xylene	5.035	5.241	48.027	7.737	1.160	1.208	11.067	1.783
1,2-dichlorobenzene	<LOQ	<LOQ	ND	<LOQ	<LOQ	<LOQ	ND	<LOQ
Hexadecane	1.255	1.808	0.871	5.114	0.136	0.195	0.094	0.553

*Toluene target ion was saturated for Room B2. Hence, toluene in room 2B was re-calculated again using reference ion that was not saturated.

A comparison study was done between Room B1 with the other 3 rooms (A, B2 and C) to demonstrate the capability of TD-GCMS in differentiating the air quality. Room B1 was the longest existing room that had not undergone any refurbishment and was not located near to any factory or room that could generate VOCs content. Hence, the VOCs content in Room B1 (Fig. 4 and Table 4) were generally low as compared to the other rooms.

For Room A, there were more VOCs content as compared to Room B1 even though there was no recent renovation. The main reason was due to its location (beside a laboratory). Moreover, there was no complete partition to significantly isolate both rooms separately. The data shows that there were more peaks detected at the front part of chromatogram (Fig. 4) in Room A as compared to Room B1. Based on the library search, these four major early eluting compounds were acetone (7.713 min), acetonitrile (8.462 min), hexane (10.489 min) and ethyl acetate (12.468 min). These four solvents might be commonly used in the laboratory and could have diffused to Room A.

Room B2, a freshly painted version of Room B1, had the highest VOCs content out of the other three rooms (Table 4). The air sample was collected on the following week after the painting had been completed. Notably, there were more compounds eluting between retention time of 24 mins to 36 mins. Compounds like toluene (saturated at 20.017 min), mesitylene (30.321 min) and some aliphatic hydrocarbons (within 24 mins to 36 mins) could be identified in the chromatogram. These compounds are commonly used in paint, either as paint thinner, additives or binding agent. Hence, it may be possible to corelate that the room had just been painted with the presence of these compounds. The toluene concentration was high which resulted in saturation of the detector for the target ion. Therefore, a different target ion (non-saturated) was used for quantitation of toluene for Room B2.

For Room C, the air sample was collected 2 months after the renovation was completed. Thus, the VOCs content was not as high as Room B2. Probably, most of the VOCs content may have already been dissipated within these 2 months. However, toluene content was still much higher as compared to Room B1 even though no laboratory or factory was in the proximity. Another major compound found was 1-butanol (16.107 min). 1-butanol could have been generated from the water-proofing cement used during renovation [4]. All these suggest that this room could have undergone some renovation or painting work not long ago.

With TD-GCMS combined with FASST method, it is possible to do not only qualitative profiling of air sample, but also quantitation to ppbv level. Additional requirement like semi-quantitation of total volatile organic compound (TVOC) can be done if a suitable column is selected [3].

❑ Conclusion

TD-GCMS with FASST method successfully analysed VOCs in indoor air. Good sensitivity and repeatability were achieved with the SIM mode at the concentration of 2.5 ng. Furthermore, with the SCAN result, other potential toxic VOCs that were not in the targeted list could be identified for further investigation.

❑ References

1. United States Environmental Protection Agency. Introduction to Indoor Air Quality. Retrieved From the Environmental Protection Agency website: https://www.epa.gov/indoor-air-quality-iaq/introduction-indoor-air-quality
2. International Organization for Standardization 16000-6-2011. Determination of volatile organic compounds in indoor and test chamber air by active sampling on Tenax TA sorbent, thermal desorption and gas chromatography using MS or MS-FID, 2011
3. Compendium Method TO-17, Determination of Volatile Organic Compounds in Ambient Air using Active Sampling Onto Sorbent Tubes, 1999
4. Kozicki et al,. Emission of Volatile Organic Compounds (VOCs) from Dispersion and Cementitious Waterproofing Products. *Sustainability*. 10, 2178 (2018)

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