

Determination of Volatile Organic Compounds (VOCs) present in the interiors of car by using GCMS/MS with static and dynamic headspace

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Introduction

Volatile Organic Compounds (VOCs) are a large group of carbon-based chemicals that have high vapor pressure at room temperature. They are widely present in both outdoor and indoor air, and are considered to be an important group of air pollutants. They are reported to have a negative impact on human health, and their concentration in indoor air is higher than outdoor air⁽¹⁾. The level of VOCs indoors is generally 3 to 4 times higher than the level of VOCs outdoors. The interior of vehicle (Refer Figure 1) is regarded as a specific microenvironment where the concentration of VOCs may be much higher than in public or private buildings.

Inside the car, sources of VOCs are air fresheners, paints, adhesives, air conditioners, plastic and leather materials etc. Exposure of VOCs may increase risk of cancer, damage to liver, kidney and central nervous system. The extent and nature of the effect on health will depend on many factors including level and duration of exposure. Some of the potential VOCs were measured by Shimadzu GCMS-TQ8040 equipped with HS-20 Loop (Static) and Trap (Dynamic) headspace sampler and by using Multiple Reaction Monitoring (MRM) mode to obtain reliable analytical data.



Figure 1. Interior of car



Figure 2. Headspace vial and monotrapp

Method of analysis

Extraction of VOCs by using static and dynamic headspace

1) Standard stock solution:

Standard solution mixture of VOCs (2000 ppm) were procured from Restek® (P/N:VOC kit #30221). Using this standard solution, 2000 ppb standard stock solution was prepared in methanol containing mixture of 17 VOCs.

2) Calibration curve:

Standard stock solution was further diluted with methanol to make eight linearity levels with different concentration ranging from 5 ppb to 500 ppb. Calibration curve was plotted using above linearity level standard solutions (Refer Figure 5 and 6) in the

concentration range of 5 ppb, 10 ppb, 25 ppb, 50 ppb, 75 ppb, 125 ppb, 250 ppb and 500 ppb. 20 μ L of each level standard solution was transferred in separate 20 mL headspace vials and crimped with automated crimper.

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3) Sample preparation:

RSC18 monotraps from GL Sciences P/N:1050-71201 (4 units each) in 20 mL headspace vial was placed inside the car with vial mouth open for 24 hrs ^[2] (Refer Figure 2). 20 µL of methanol was added in the vial and crimped with automated crimper.

Method was partly validated to support the findings by performing precision, linearity, LOD and LOQ determination as summarized in Table 1.

Table 1. Method validation parameters

Parameter	Concentration (ppb)
Linearity (Dynamic)	5, 10, 25, 50, 75, 125, 250 and 500
System precision (Dynamic)	100 (n=6)
Sample precision (Dynamic)	(n=5)
System precision (Static)	100 (n=6)



Figure 3. GCMS-TQ8040 equipped with HS-20 by Shimadzu

Key Features of GCMS-TQ8040 equipped with HS-20

- Static and dynamic both modes are available in HS-20.
- Advanced Pressure Controller (APC) pressure programming enables removal of carryover.
- Can work on high temp range of Loop (300 °C), trap (350 °C), oven (300 °C) and transferline (350 °C).
- ASSP™ (Advanced Scanning Speed Protocol) enables high-speed scan and data acquisition for accurate quantitation at 20,000 u/sec.
- Ultra Fast UF sweeper® technology efficiently sweeps residual ions from the collision cell for fast, efficient ion transport ensuring no cross-talk.
- Acquisition modes including MRM, Scan/MRM, Precursor Ion, Product Ion, Neutral Loss Scan and SMART MRM Software helps to create method and sequence automatically.

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HS-GCMSMS Analytical Conditions

The analysis was carried out using Shimadzu GCMS-TQ8040 equipped with HS-20 (Figure 3) as per conditions given in Table 2.

Table 2. Analytical conditions

Headspace parameters												
Sampling Mode	:	Static and dynamic										
Oven Temp.	:	90.0 °C										
Sample Line Temp.	:	100.0 °C										
Transfer Line Temp.	:	110.0 °C										
Trap Cooling Temp	:	-25.0 °C										
Trap Desorb. Temp	:	220 °C										
Trap Equilib. Temp	:	25.0 °C										
Multiple Injection Count	:	3										
Equilibrating Time	:	15.00 min										
Pressurizing Time	:	2.00 min										
Injection Time	:	10.00 min										
GC Cycle Time	:	45.00 min										
Gas Pressure	:	65.0 kPa										
Dry Purge Pressure	:	20 kPa										
Chromatographic parameters												
Column	:	Rxi-VMS (60 m L x 0.45 mm I.D. x 2.55 µm)										
Injection Mode	:	Split										
Split Ratio	:	3:0										
Carrier Gas	:	Helium										
Linear Velocity	:	57.0 cm/sec										
Pressure	:	48.6 kPa										
Column Flow	:	4.99 mL/min										
Total Program Time	:	21.00 min										
Column Oven Temp.	:	<table border="1"> <thead> <tr> <th>Rate (°C /min)</th> <th>Temperature (°C)</th> <th>Hold time (min)</th> </tr> </thead> <tbody> <tr> <td></td> <td>40.0</td> <td>2.00</td> </tr> <tr> <td>10.00</td> <td>230.0</td> <td>0.00</td> </tr> </tbody> </table>		Rate (°C /min)	Temperature (°C)	Hold time (min)		40.0	2.00	10.00	230.0	0.00
Rate (°C /min)	Temperature (°C)	Hold time (min)										
	40.0	2.00										
10.00	230.0	0.00										
Mass Spectrometry parameters												
Ion Source Temp.	:	200.0 °C										
Interface Temp.	:	230.0 °C										
Ionization Mode	:	EI (Electron ionization)										
Mode	:	MRM										

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Results

MRM method preparation

Mixtures of different VOC standards (four standard solutions - 2000 ppm) were procured from Restek®. For MRM optimization, about 2 ppm of standard stock solution was prepared using above standard solutions. Further above standard stock solution was analyzed using scan mode. For 17 components, retention time and precursor ions were identified and selected. Using selected precursor ions, product ion scan was performed with different Collision Energies (CE). For each

component, MRM transitions with appropriate CEs were determined (Refer Table 3). All the above steps were simplified with the help of Smart MRM optimization tool. These MRM transitions were registered to Smart Database and the final MRM method with optimum segments was generated. Further this optimized MRM method was used to analyze samples (Refer Figure 4) by using both static and dynamic mode of HS-20 headspace sampler.

Table 3. MRM and CE table

Sr. No.	Name of VOCs	Target MRM (m/z)	CE	Reference-1 MRM (m/z)	CE	Reference-2 MRM (m/z)	CE
1	Ethylene, 1,2-dichloro	95.95>61.00	18	97.95>63.00	18	97.95>61.00	18
2	Benzene	78.05>52.10	18	77.05>51.00	18	78.05>39.00	18
3	Ethane, 1,2-dichloro-	62.00>27.00	18	64.00>27.10	18	62.00>60.90	42
4	Trichloroethylene	129.95>95.00	15	131.95>97.00	18	131.95>95.00	15
5	Propane, 1,2-dichloro-	63.00>27.00	15	76.00>41.00	12	76.00>39.00	21
6	Methane, bromodichloro-	82.95>48.00	24	82.95>82.00	33	84.95>47.90	27
7	Toluene	92.10>91.10	18	91.10>65.10	18	91.10>39.00	24
8	Tetrachloroethylene	165.90>130.90	18	163.90>128.90	15	163.90>94.00	27
9	Ethane, 1,1,2-trichloro-	97.00>61.00	18	99.00>61.00	18	99.00>63.00	18
10	Methane, dibromochloro-	128.90>48.00	27	126.90>48.00	27	128.90>127.90	42
11	Ethylbenzene	91.10>65.10	18	106.10>91.10	18	91.10>39.10	27
12	p-Xylene	106.10>91.10	18	91.10>65.10	18	91.10>39.10	27
13	o-Xylene	106.10>91.10	18	91.10>65.10	18	91.10>39.10	27
14	Styrene	104.10>78.10	18	104.10>103.10	18	103.10>77.00	18
15	Benzene, 1,4-dichloro-	146.00>111.00	18	146.00>75.10	27	148.00>75.00	27
16	Benzene, 1,2-dichloro-	146.00>111.00	18	146.00>75.10	27	148.00>75.00	27
17	Benzene, 1,2,4-trichloro-	179.95>145.00	18	179.95>109.00	27	181.95>147.00	15

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Summary of validation results

On the basis of statistical data obtained, the method was proved to be highly selective, sensitive and reliable.

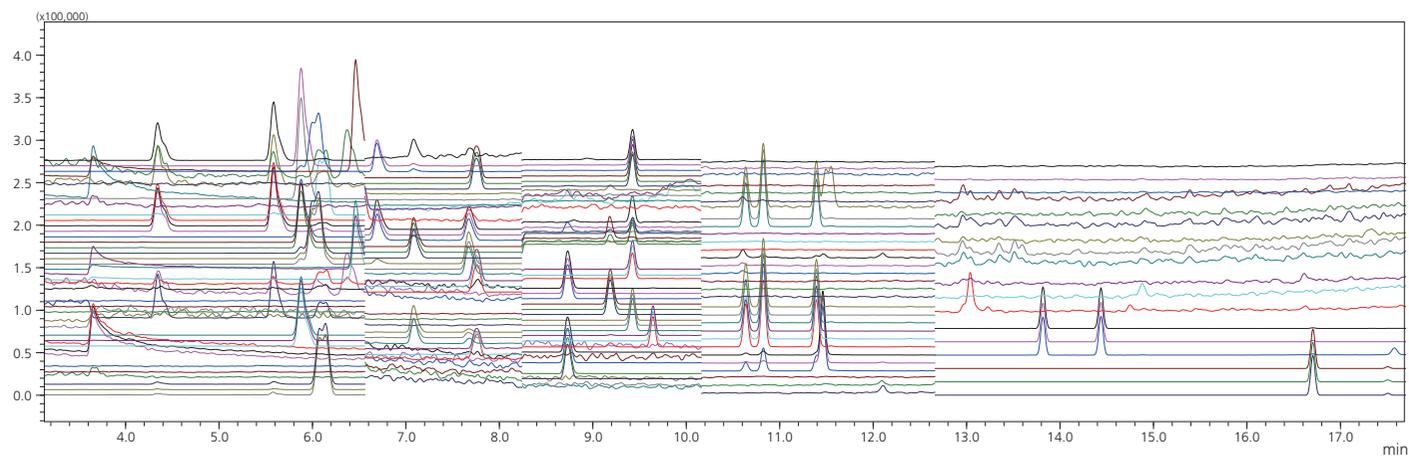


Figure 4. MRM Chromatogram of 100 ppb standard solution

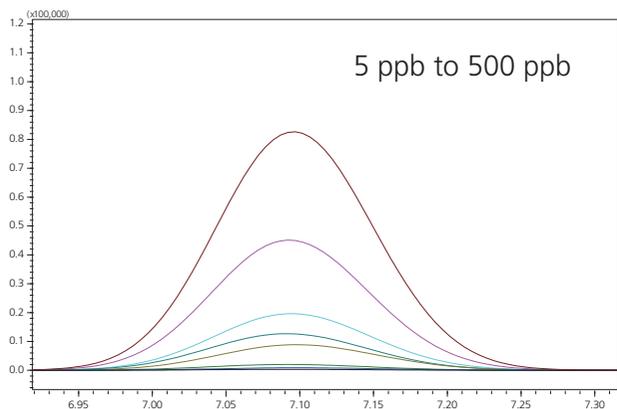


Figure 5. Overlay of linearity levels for Trichloroethylene

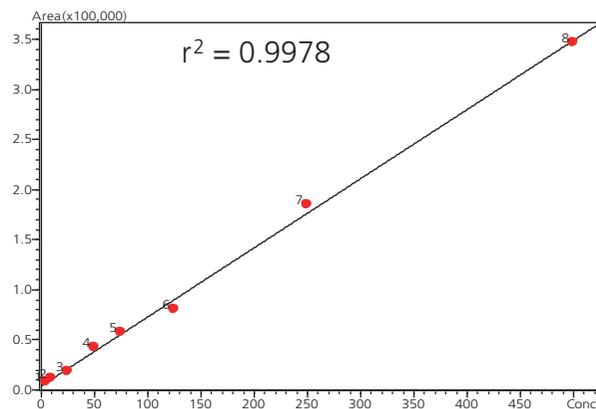


Figure 6. Calibration curve for Trichloroethylene

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Table 4. Comparative data for static and dynamic headspace mode

Sr. No.	Name of VOCs	In Dynamic mode			System precision (n=6) for 100 ppb			
					Dynamic mode		Static mode	
		Linearity (r ²)	LOD* (ppb)	LOQ* (ppb)	Avg. Area	% RSD	Avg. Area	% RSD
1	Ethylene, 1,2-dichloro	0.9980	1.7	5.3	113064	2.8	40,714	4.3
2	Benzene	0.9654	0.7	2.1	449,500	2.1	157,837	5.3
3	Ethane, 1,2-dichloro-	0.9978	0.2	0.6	51,176	4.0	16,709	4.9
4	Trichloroethylene	0.9980	1.0	3.2	152,558	2.2	54,970	4.2
5	Propane, 1,2-dichloro-	0.9981	1.4	4.1	53,998	3.3	16,757	7.8
6	Methane, bromodichloro-	0.9967	0.6	1.8	33,745	2.9	9,431	7.5
7	Toluene	0.9956	0.8	2.4	199,811	2.3	66,624	4.3
8	Tetrachloroethylene	0.9978	1.8	5.4	55,502	2.3	17,653	4.2
9	Ethane, 1,1,2-trichloro-	0.9974	2.1	6.2	49,922	1.8	13,145	4.9
10	Methane, dibromochloro-	0.9976	1.1	3.4	9,310	1.7	2,617	6.7
11	Ethylbenzene	0.9981	1.1	3.3	85,477	2.1	26,866	4.2
12	p-Xylene	0.9980	0.6	1.9	222,067	2.7	69,309	4.1
13	o-Xylene	0.9969	1.0	3.1	184,205	1.6	50,763	4.8
14	Styrene	0.9974	0.8	2.5	122,897	3.3	32,467	4.8
15	Benzene, 1,4-dichloro-	0.9968	1.0	3.1	161,920	4.0	45,440	6.8
16	Benzene, 1,2-dichloro-	0.9971	1.0	3.1	163,283	4.5	41,228	4.6
17	Benzene, 1,2,4-trichloro-	0.9971	0.9	2.9	119,406	5.0	30,045	4.8

*As per software calculations.

Table 4 gives comparison of data obtained on standards using static and dynamic headspace analysis of VOCs.

Determination of VOCs in interior of car

RSC18 monotraps were kept inside a car for 24 hours to trap VOCs. Then these monotraps with trapped VOCs were analyzed as per instrument parameters given in Table 2. Precision (n=5) for sample analysis was carried out and %RSD for individual VOCs from five replicate injections was found to be less than 15% (Refer Table 5).

Table 5. Summary of sample analysis

Sr. No.	Name of VOCs	System precision (n=5)		
		Dynamic mode		
		Avg. Area	% RSD	Concentration (ppb)
1	Toluene	94,051	14.6	48
2	Ethylbenzene	16,347	14.8	18
3	o-Xylene	63,464	14.6	34
4	Benzene, 1,4-dichloro-	38,930	14.6	22

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Conclusion

- HS-GCMSMS method was developed for determination of VOCs from interior of the car by trapping on RSC18 monotraps. Part method validation was performed. Results obtained for reproducibility, linearity and LOQ studies were within acceptable criteria.
- Dynamic mode is almost 4 to 5 times sensitive than static mode and further can be optimized for more sensitivity by optimization of multi injection count.
- Ultra Fast Scan Speed 20,000 u/sec is the characteristic feature of GCMS-TQ8040 mass spectrometer, useful for quantitation of VOCs at very low level (ppb level) with high sensitivity.

References

- [1] A Study of Indoor air quality certified (IAQ) in Automobile Cabin Interiors GREENGUARD Environmental Institute Released May 31, 2006.
- [2] Easy Enrichment of the VOC in a New Car with MonoTrap® GC Technical Note 33 from GL Science Inc.