ENVIRONMENT

APPLICATION NOTE

chromatec

Analysis of VOC and FOG Emissions from Vehicle Interior Materials by TD-GC-MS

Abstract

This study demonstrates the efficiency of Chromatec's TD-GC-MS system for determination of volatile organic compounds and condensable substances in car trim components.

Introduction

A variety of materials used in the vehicle interior generates the typical 'new car smell'. Occupants are concerned about the release of chemicals and their potential health risks.

The German Association of the Automotive Industry (VDA) consists of more than 600 companies involved in production for the automotive industry, among them are Audi, BMW, Man, Mercedes-Benz, Volkswagen. The association has developed the VDA 278 standard for determination of volatile organic compounds (VOC) and semivolatile condensable substances (FOG) in automotive interior materials. The term 'FOG' is used as these less volatile substances can condense at ambient temperature and contribute to fogging on the windshield. In turn, General Motors uses GMW 15634 standard. Both standards suggest Thermal Desorption – Gas Chromatography – Mass Spectrometry (TD-GC-MS) analysis and provide semi-quantitative values of VOC and FOG emissions.

The sample is placed in an empty glass tube and two tests are carried out:

- VOC value is determined by sample heating at 90°C for 30 minutes. Chromatographic elution range from n-pentane (n-C5) to n-eicosane (n-C20) is detected. The concentration is expressed as toluene equivalent.
- FOG value is determined in the second desorption at 120°C for 60 minutes. Chromatographic elution range from n-hexadecane (n-C16) to n-dotriacontane (n-C32) is detected. The concentration is expressed as n-hexadecane equivalent.

Methods

VDA 278 Thermal Desorption Analysis of Organic Emissions for the Characterization of Non-Metallic Materials for Automobiles

GMW15634 Determination of Volatile and Semi-Volatile Organic Compounds from Vehicle Interior Materials

Equipment

- Chromatec Crystal 9000 GC/MSD
- Thermal Desorber Chromatec TDA
- Injection unit for TD tubes
- Capillary column BP5 (60 m × 0.25 mm × 0.25 µm)
- Empty glass tubes (for samples)
- Sorbent tube Tenax TA (for calibration)
- Focusing trap Tenax TA/Carbopack B

VOC conditions

GC			
Analysis time		55 min	
Column			
Carrier gas		Helium	
Constant flow		1.3 mL/min	
Column temperature			
	40 °C	2 min	3 °C/min
	92 °C	0 min	5 °C/min
	160 °C	0 min	10 °C/min
	280 °C	10 min	
Inlet			
Split		1:60	
Gas saver		10 mL/min	
MSD			
Mass range		29-450	
Ion source temperature		250 °C	
Transfer line temperature		280 °C	
Thermal Desorber			
Valve temperature		300 °C	
Transfer line temperature		300 °C	
Carrier gas		Helium	
Purge gas		Helium	
Desorption temperature		90 °C	
Desorption flow		40 mL/min	
Desorption time		30 min	
Trap low temperature		-20 °C	
Trap high temperature		300 °C	
Trap heating rate		3000 °C/min	
Trap heating time		5 min	

FOG conditions

GC			
Analysis time		48 min	
Column			
Carrier gas		Helium	
Constant flow		1.3 mL/min	
Column temperature			
	50 °C	2 min	25 °C/min
	160 °C	0 min	10 °C/min
	280 °C	30 min	
Inlet			
Split		1:60	
Gas saver		10 mL/min	
MSD			
Mass range		29-450	
Ion source temperature		250 °C	
Transfer line temperature		280 °C	
Thermal Desorber			
Valve temperature		300 °C	
Transfer line temperature		300 °C	
Carrier gas		Helium	
Purge gas		Helium	
Desorption temperature		120 °C	
Desorption flow		40 mL/min	
Desorption time		60 min	
Trap low temperature		-20 °C	
Trap high temperature		300 °C	
Trap heating rate		3000 °C/min	
Trap heating time		5 min	

Calibration and control standard conditions

GC			
Analysis time		55 min	
Column			
Carrier gas		Helium	
Constant flow		1.3 mL/min	
Column temperature			
	40 °C	2 min	3 °C/min
	92 °C	0 min	5 °C/min
	160 °C	0 min	10 °C/min
	280 °C	10 min	
Inlet			
Split		1:60	
Gas saver		10 mL/min	
MSD			
Mass range		29-450	
Ion source temperature		250 °C	
Transfer line temperature		280 °C	
Thermal Desorber			
Valve temperature		300 °C	
Transfer line temperature		300 °C	
Carrier gas		Helium	
Purge gas		Helium	
Desorption temperature		300 °C	
Desorption flow		40 mL/min	
Desorption time		5 min	
Trap low temperature		-20 °C	
Trap high temperature		300 °C	
Trap heating rate		3000 °C/min	
Trap heating time		5 min	

Experimental

Control standard containing 18 compounds (Table 1) at a concentration of 0.45 µg/µL was prepared in methanol from individual compounds (purity more than 99%).

Table 1. List of compounds for control standard.

No	Compound	CAS number
1	Benzene	71-43-2
2	n-Heptane	142-82-5
3	Toluene	108-88-3
4	n-Octane	111-65-9
5	p-Xylene	106-42-3
6	o-Xylene	95-47-6
7	n-Nonane	111-84-2
8	n-Decane	124-18-5
9	2-Ethyl-1-hexanol	104-76-7
10	n-Undecane	1120-21-4
11	2,6-Dimethylphenol	576-26-1
12	n-Dodecane	112-40-3
13	n-Tridecane	629-50-5
14	n-Tetradecane	629-59-4
15	Dicyclohexylamine	101-83-7
16	n-Pentadecane	629-62-9
17	n-Hexadecane	544-76-3
18	Bis(2-ethylhexyl) adipate	103-23-1

In this study two series of calibration standards were used – for toluene and n-hexadecane. Calibration standards with concentrations of 0.01, 0.05, 0.1, 0.5 and 1 µg/µL in methanol were prepared.

The sorbent tubes Tenax® TA were conditioned using Desorber (P/N 400-1903) under nitrogen flow rate of 50 mL/min at 320 °C for 120 min.

Calibration solutions and control standard were injected into the sorbent tube Tenax® TA. The volume of each solution was 1 µL. The solvent was purged with nitrogen using Injection Unit for Thermal Desorption Tubes (IUTD, P/N 400-1931), as shown in Figure 1. The purge gas flow was 50 mL/min for 2 min.

Figure 1 – Loading the calibration standard into the Tenax® TA tube using an injection unit for TD tubes.

Three samples were analyzed – genuine leather, artificial leather and polyurethane foam.

Each sample was cut into pieces with a width of 3 mm and weighed. A piece of the sample was placed directly into a glass tube and fixed with glass wool (Figure 2).

Figure 2 – Samples placed into glass tubes.

Results and discussion

Analysis of control standard

A chromatogram of the control standard in shown in Figure 3. It demonstrates good separation and system inertness. According to VDA 278 requirement, o-xylene and n-nonane are almost baseline separated.

1	Benzene	10	n-Undecane
2	n-Heptane	11	2,6-Dimethylphenol
3	Toluene	12	n-Dodecane
4	n-Octane	13	n-Tridecane
5	p-Xylene	14	n-Tetradecane
6	o-Xylene	15	Dicyclohexylamine
7	n-Nonane	16	n-Pentadecane
8	n-Decane	17	n-Hexadecane
9	2-Ethyl-1-hexanol	18	Bis(2-ethylhexyl) adipate

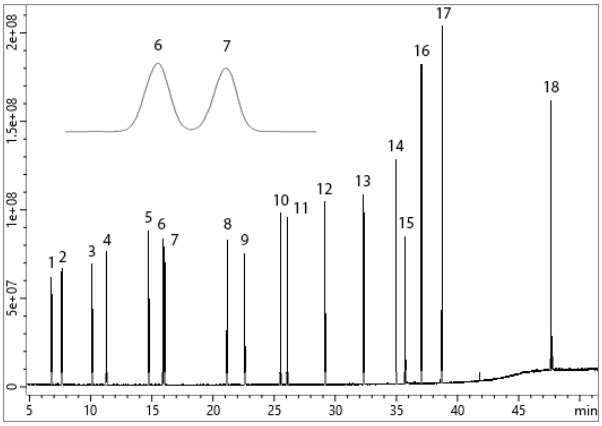


Figure 3 –Chromatogram of control standard.

Calibration

Five-point calibration was carried out over the range from 0.01 to 1 µg. Calibration curves for toluene and n-hexadecane showed excellent linearity with R^2 values 0.9999 and 0.9998, respectively (Figure 4).

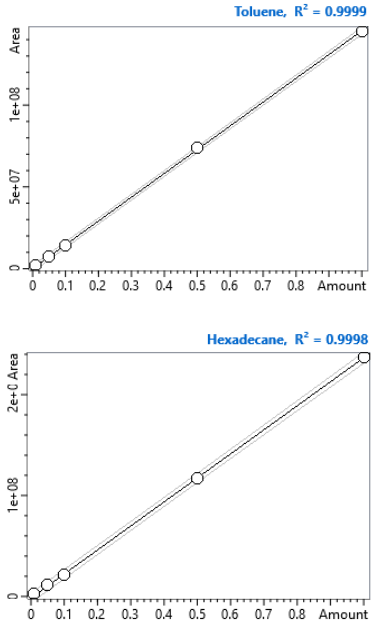


Figure 4 – Calibration curves of toluene and n-hexadecane.

Recovery

As required by VDA 278, the recovery rates of the individual substances in the control standard should be between 60 and 140%, with the exception of toluene, which should be in the range 80-120%. The experimental data for the recovery rates are summarized in Table 2.

Table 2. Recovery rates of substances in control standard.

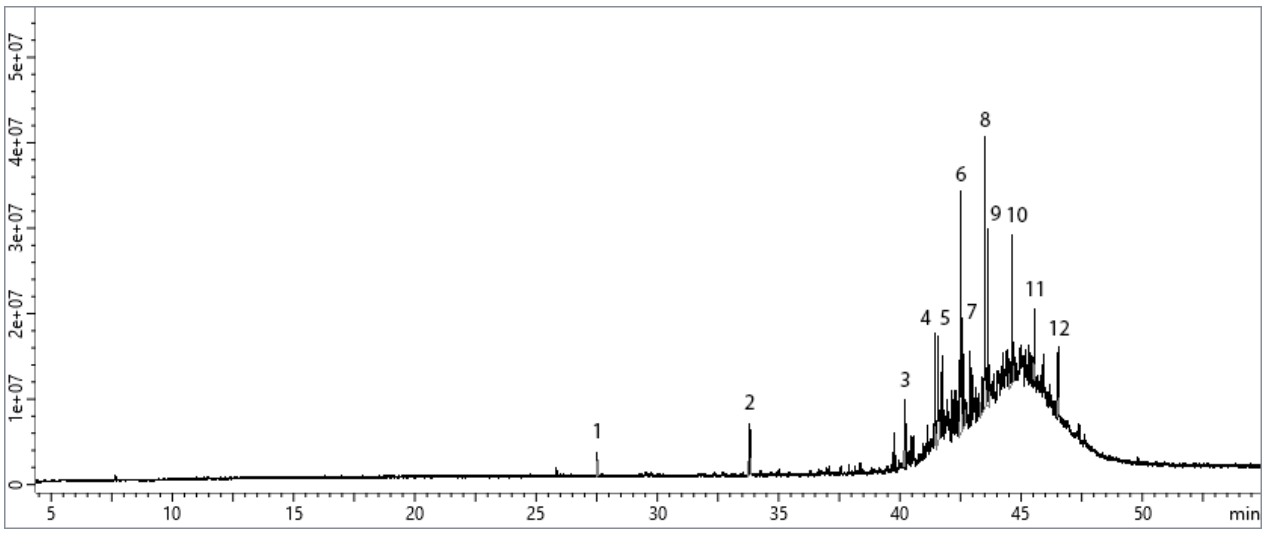
Compound	Recovery rate, %
Benzene	94.7
n-Heptane	102.9
Toluene	95.8
n-Octane	102.7
p-Xylene	108.9
o-Xylene	110.0
n-Nonane	103.5
n-Decane	112.9
2-Ethyl-1-hexanol	90.2
n-Undecane	116.7
2,6-Dimethylphenol	104.2
n-Dodecane	121.3
n-Tridecane	123.1
n-Tetradecane	114.0
Dicyclohexylamine	109.8
n-Pentadecane	109.3
n-Hexadecane	111.1
Bis(2-ethylhexyl) adipate	112.9

Sample measurements

Chromatograms of the samples with total ion current are shown in Figures 5 – 10. Different plasticizers were found in each sample – diisobutyl phthalate (DIBP), dibutyl phthalate (DBP), bis(2-ethylhexyl) phthalate (DEHP), bis(2-ethylhexyl) adipate (DEHA), bis-(2-ethylhexyl) terephthalate (DEHT). They are used to make the material more flexible. Many hydrocarbons were obtained in the genuine leather sample. These compounds improve waterproof property, coating feel, wear-resistance, and increase luster. Flame retardants (tris(2-chloroisopropyl) phosphate and triphenyl phosphate) were identified in artificial leather and polyurethane foam.

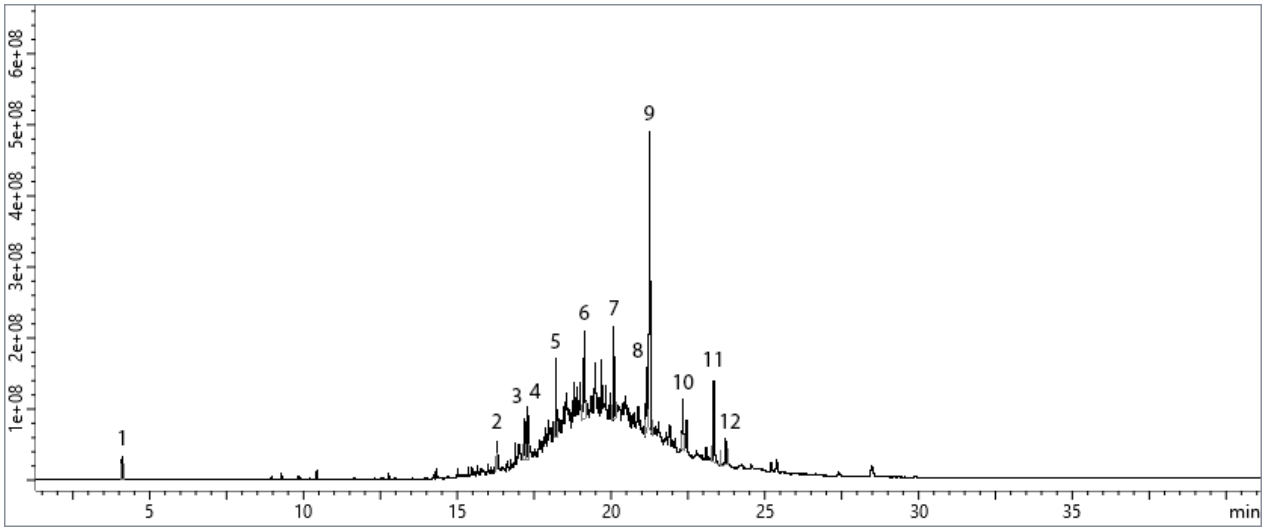
Conclusion

The application has illustrated the use of the Chromatec TDA thermal desorber in combination with Chromatec Crystal GC/MSD for analysis of VOC and FOG in vehicle interior materials. A wide linear range and analytical performance were shown.



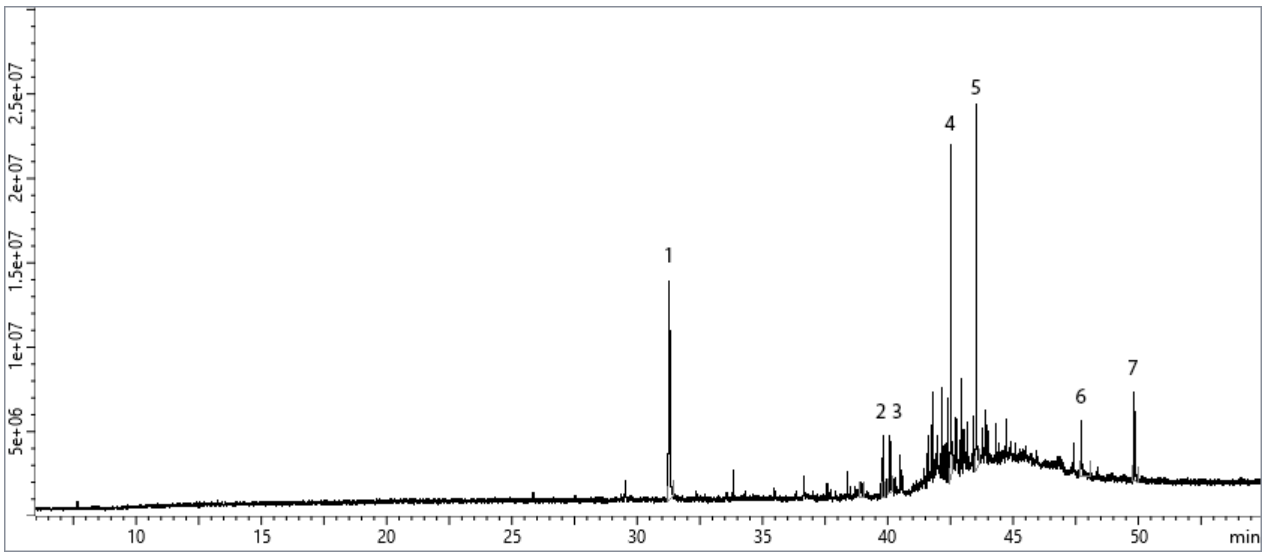
	Compound	CAS No	Description	Amount, µg/g
1	2-Ethylhexyl acetate	103-09-3		2.5
2	1,2-Diacetin	102-62-5		5.3
3	n-Heptadecane	629-78-7		5.3
4	n-Octadecane	593-45-3		9.0
5	2-Hexyl-1-decanol	2425-77-6		10.2
6	Diisobutyl phthalate	84-69-5	Plasticizer	30.3
7	n-Nonadecane	629-92-5		10.1
8	Dibutyl phthalate	84-74-2	Plasticizer	33.6
9	n-Eicosane	112-95-8		17.4
10	n-Heneicosane	629-94-7		19.9
11	n-Docosane	629-97-0		8.1
12	2,6-Diphenylphenol	2432-11-3		6.9

Figure 5 – VOC analysis of a genuine leather sample.



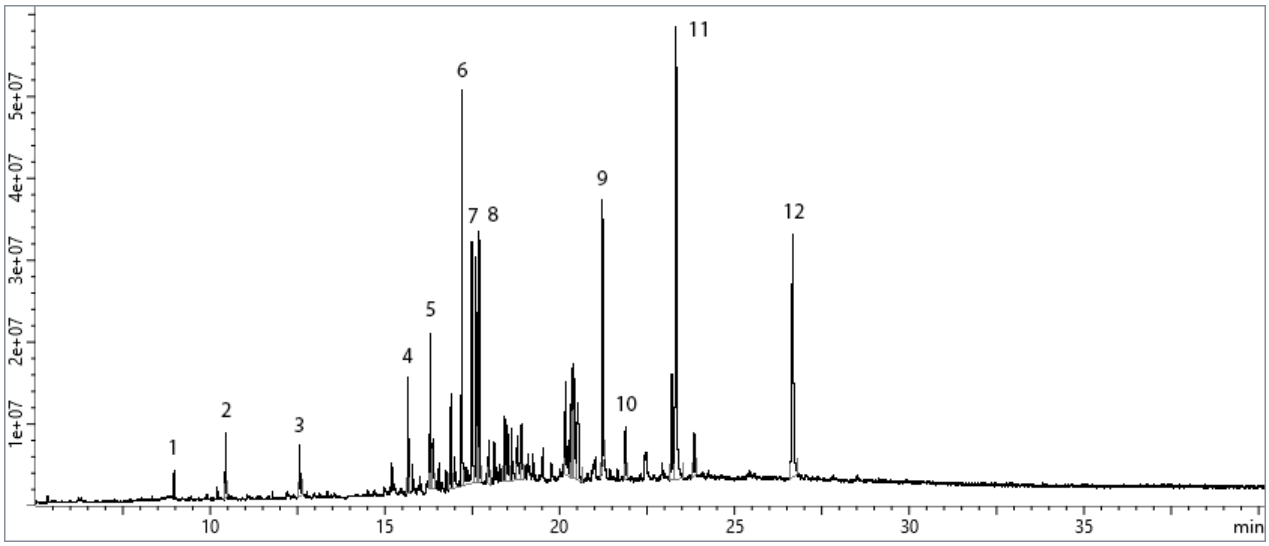
	Compound	CAS No	Description	Amount, µg/g
1	Formic acid	64-18-6		17.1
2	Diisobutyl phthalate	84-69-5	Plasticizer	19.9
3	Dibutyl phthalate	84-74-2	Plasticizer	24.4
4	n-Eicosane	112-95-8		30.5
5	n-Heneicosane	629-94-7		44.2
6	n-Docosane	629-97-0		60.9
7	n-Tricosane	638-67-5		57.6
8	n-Tetracosane	646-31-1		50.9
9	Bis(2-ethylhexyl) adipate	103-23-1	Plasticizer	272.4
10	n-Pentacosane	629-99-2		41.2
11	Bis(2-ethylhexyl) phthalate	117-81-7	Plasticizer	81.2
12	n-Hexacosane	630-01-3		26.3

Figure 6 – FOG analysis of a genuine leather sample.



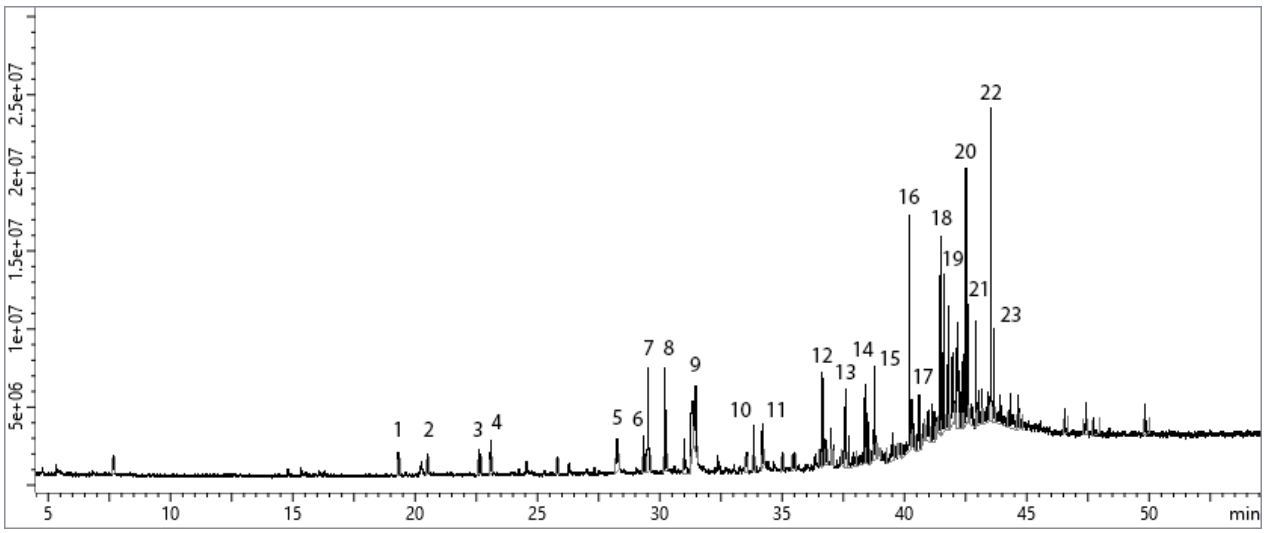
	Compound	CAS No	Description	Amount, µg/g
1	Caprolactam	105-60-2		22.4
2	Diethylene glycol adipate	58984-19-3		3.1
3	Diethylene glycol monododecyl ether	3055-93-4		3.8
4	Diisobutyl phthalate	84-69-5	Plasticizer	20.7
5	Dibutyl phthalate	84-74-2	Plasticizer	25.6
6	Bis(2-ethylhexyl) adipate	103-23-1	Plasticizer	4.8
7	Bis(2-ethylhexyl) phthalate	117-81-7	Plasticizer	7.2

Figure 7 – VOC analysis of an artificial leather sample.



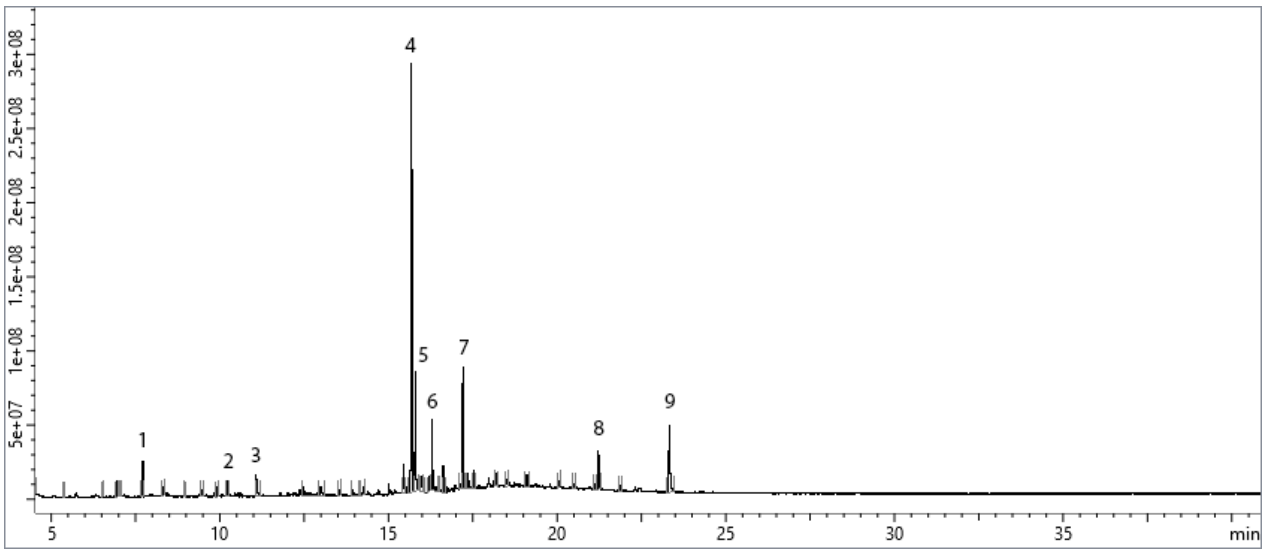
	Compound	CAS No	Description	Amount, µg/g
1	Nonanal	124-19-6		2.1
2	Caprolactam	105-60-2		4.9
3	N,N-Dimethyldodecylamine	112-18-5		3.3
4	Tris(2-chloroisopropyl) phosphate	13674-84-5	Flame retardant	5.6
5	Diisobutyl phthalate	84-69-5	Plasticizer	6.8
6	Dibutyl phthalate	84-74-2	Plasticizer	18.5
7	3-[1-(4-Cyano-1,2,3,4-tetrahydronaphthyl)]propanenitrile	57964-40-6		12.3
8	2-[1-(4-Cyano-1,2,3,4-tetrahydronaphthyl)]propanenitrile	57964-39-3		11.1
9	Bis(2-ethylhexyl) adipate	103-23-1	Plasticizer	20.2
10	Triphenyl phosphate	115-86-6	Flame retardant	4.2
11	Bis(2-ethylhexyl) phthalate	117-81-7	Plasticizer	38.9
12	Bis-(2-ethylhexyl) terephthalate	6422-86-2	Plasticizer	28.4

Figure 8 – FOG analysis of an artificial leather sample.



	Compound	CAS No	Description	Amount, µg/g
1	2-Hydroxypropyl acetate	627-69-0		2.5
2	Phenol	108-95-2		1.7
3	2-Ethylhexanol	104-76-7		2.6
4	Benzyl alcohol	100-51-6		3.4
5	Octanoic acid	124-07-2		8.0
6	4-Hydroxy-3-hexanone	4984-85-4		4.3
7	(4,5-Dimethyl-1,3-dioxan-5-yl)methanol	54063-15-9		12.9
8	2-Phenoxyethanol	122-99-6		11.6
9	Nonanoic acid	112-05-0		11.3
10	1,2-Diacetin	102-62-5		3.8
11	Decanoic acid	334-48-5		5.0
12	n-Pentadecane	629-62-9		8.8
13	Dimethyl terephthalate	120-61-6		7.9
14	1,6-Dioxacyclododecane-7,12-dione	777-95-7		10.8
15	n-Hexadecane	544-76-3		8.5
16	n-Heptadecane	629-78-7		22.8
17	2-Ethylhexyl benzoate	5444-75-7		8.2
18	n-Octadecane	593-45-3		25.4
19	Nonyl benzoate	5451-95-6		14.7
20	Diisobutyl phthalate	84-69-5	Plasticizer	22.6
21	n-Nonadecane	629-92-5		8.4
22	Dibutyl phthalate	84-74-2	Plasticizer	26.1
23	n-Eicosane	112-95-8		7.2

Figure 9 – VOC analysis of a polyurethane foam sample.



	Compound	CAS No	Description	Amount, µg/g
1	Acetoxyacetone	592-20-1		11.3
2	Nonanoic acid	112-05-0		6.0
3	Decanoic acid	334-48-5		11.1
4	Tris(2-chloroisopropyl) phosphate	13674-84-5	Flame retardant	203.7
5	Tris(2-chloropropyl) phosphate	6145-73-9	Flame retardant	50.9
6	Diisobutyl phthalate	84-69-5	Plasticizer	28.8
7	Dibutyl phthalate	84-74-2	Plasticizer	44.5
8	Bis(2-ethylhexyl) adipate	103-23-1	Plasticizer	20.8
9	Bis(2-ethylhexyl) phthalate	117-81-7	Plasticizer	47.7

Figure 10 – FOG analysis of a polyurethane foam sample.