APPLICATION NOTE

Gas Chromatography

Authors:

Guowei Fu

Kira. Yang

PerkinElmer, Inc.
Shanghai, China

Determination of Volatile Organic Compounds (VOCs) in Wallpapers Using ATD-GCMS

Introduction

Wallpaper is widely used throughout the world as an interior design choice that offers bright colors, rich designs and durability, all at an affordable price. Vinyl wallpaper has emerged as an especially durable choice over paper and non-woven varieties of wallpaper, however, its manufacturing poses many environmental concerns. When manufacturing wallpaper, a large amount of organic solvent is utilized in the treatment and printing processes. As a result, high levels of volatile organic compounds (VOCs) can be present in the product, which pose an inhalation risk to humans. Determination of VOC content in wallpapers is necessary to identify potential environmental and human health risks associated with the use of wallpaper. Several regulatory bodies have proposed methods and limitations for contaminants in wallpaper, such as the EU Standard EN12149:1997[1] and the Chinese Standard GB/T 35613-2017[2].

To identify potential levels of VOCs in wallpaper samples, a method was undertaken, targeting 35 volatile organic compounds using a PerkinElmer TurboMatrix™ 650 ATD and PerkinElmer Clarus® SQ8 GC/MS, with results and methodology introduced in this study. Results of the study indicate that this method is simple, efficient and reliable, with applicability in a number of industries and laboratory settings.

PerkinElmer®
For the Better

Experimental

Sample Preparation and Extraction

A standard mixture of 35 volatile organic compounds was purchased from ANPEL Laboratory Technologies Inc. (Shanghai).

Two wallpaper samples were provided by a private laboratory. VOCs emitted by wallpaper samples were sampled utilizing a bag method. The procedure used is as follows:

1. 90 cm^2 of wallpaper sample was placed in a 10-liter sampling bag.
2. The sampling bag was filled with 6 liters of nitrogen.
3. The sampling bag was placed in an incubator chamber at 23 °C for 24 hours.
4. VOC content was sampled utilizing Carbotrap® 300 tubes, with a sampling pump set at a 200 ml/min flow rate for 15 minutes.

Instrumentation

The PerkinElmer Clarus SQ8 GC/MS, equipped with a TurboMatrix 650 ATD, were used to perform these experiments, under the conditions presented in Table 1. A PerkinElmer Elite 624 column (60 m x 0.25 mm x 1.4 µm) was used to separate the eluting compounds, with a direct connection to the thermal desorber transfer line.

Calibration

Chromatographic grade methanol (HPLC grade) was obtained from Fisher Scientific™, and was used for all standard dilutions, to produce the 5, 10, 20, 50, 100 µg/ml of calibration standard required for the experiments. A group of standard sample tubes were prepared by adding 1 µl of calibration standards on Carbotrap® 300 tubes to establish the calibration curve.

Results and Discussion

The total ion chromatogram of the calibration standard is shown in Figure 1. Benefited by the fastest available GC cool-down rate, 35 °C of initial temperature was used to obtain better separation for the compounds with low boiling points. Table 2 summarizes the results for retention time (RT), quantitation ion, method dynamic range and signal to noise (S/N) at the reporting limit. The calibration curves were plotted as the peak area versus the amount of analyte. The determination coefficients (r^2) was over 0.999, showing the reliability of the analysis in the range of 5 – 100 µg/ml. A calibration curve for toluene is shown in Figure 2. The results for signal to noise at the reporting limit is calculated using extracted ion chromatograms by full scan function.

The concentration of VOCs in two wallpaper samples tested were determined based on the method described above, and results are displayed in Table 3. The contents of all targets are lower than the limits requested in GB/T 35613-2017 (Table 4).

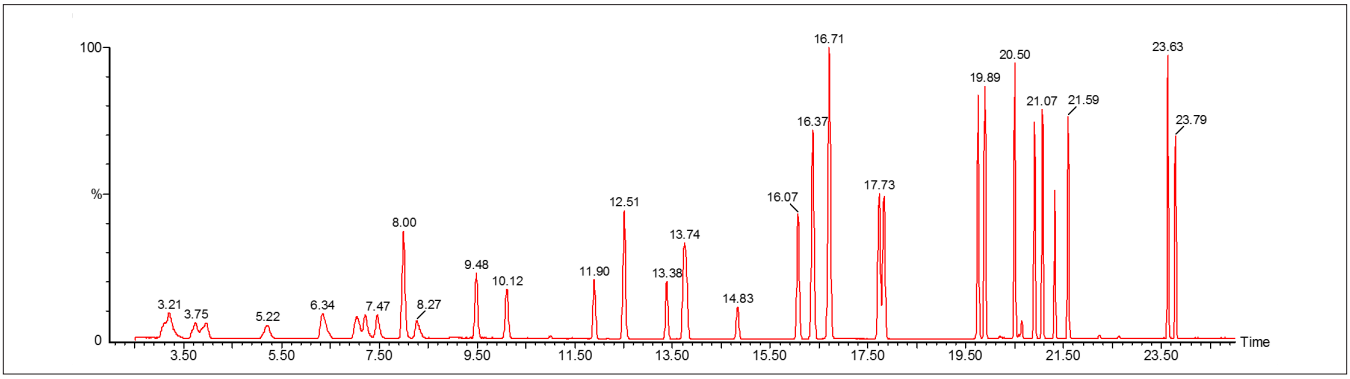

Figure 1. The total ion chromatogram of a 100 ng VOC standard desorbed from an ATD tube.

Table 1. Analytical parameters.

Thermal Desorber Parameters		GC Parameters	
Tube Desorb Temp	325 °C	Initial Oven Temp	35 °C
Tube Desorb Time	5 min	Oven Hold	5 min
Tube Desorb Flow	40 mL/min	Ramp	5 °C/min
Concentrator Trap Low	-30 °C	2nd Oven Temp	100 °C
Concentrator Trap High	325 °C	Oven Hold	0 min
Concentrator Trap Hold	10 min	Ramp	15 °C/min
Concentrator Trap Heating Rate	40 °C/min	3rd Oven Temp	200 °C
Valve Temp	220 °C	Oven Hold	5.33 min
Transfer Line Temp	220 °C	**GC Parameters**	
Column Flow	1.2 mL/min	Mass Range (Amu)	35 to 270
Inlet Split	OFF	Gc Inlet Line Temp	280 °C
Outlet Split	6.0 mL/min	Ion Source Temp	280 °C
Dry Purge Flow Rate	40 mL/min	Function Type	SIFI
Dry Purge Time	1 min	Ionization	EI

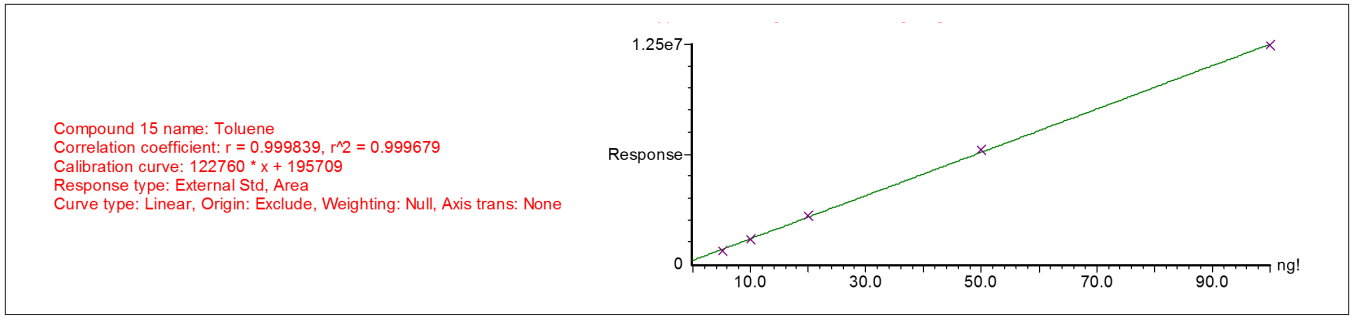

Figure 2. Calibration curve for toluene (5-100 ng).

Table 2. Results for retention time (RT), quantitation ion, method dynamic range and signal to noise (S/N) at the reporting limit.

RT	Compound Name	Quantitation Ion	Linearity (5 – 100 ng)			Reporting Limit
			Slope	Intercept	r^2	(S/N at 5 ng)
3.06	1,1,2-Trichloro-1,2,2Trifluoroethane	151	152556	646.6	0.9996	113.08
3.12	1,1-Dichloroethene	61	28316.3	6930.7	0.9994	157.86
3.74	Allyl Chloride	41	37485	50599.1	0.9995	195.24
3.96	Methylene Chloride	49	138747	245927	0.9998	190.05
5.22	1,1-Dichloroethane	63	34808	-33869.2	0.9999	142.08
6.34	Cis-1,2-Dichloroethene	61	21745	23133.3	0.9992	1037.94
7.05	Trichloromethane	83	42562.7	17177.5	0.9998	78.13
7.22	1,1,1-Trichloroethane	97	24338.7	8891.7	0.9997	334.60
7.46	Carbon Tetrachloride	117	24360.3	742.0	0.9997	426.40
8.00	Benzene	78	135260	311230	0.9992	658.25
8.28	1,2-Dichloroethylene	62	26515.4	-3954.7	0.9992	401.56
9.48	Trichloroethylene	130	33779.3	47640.7	0.9993	1036.96
10.12	1,2-Dichloropropane	63	26024.1	25768.4	0.9994	702.16
11.90	Cis-1,3-Dichloropropene	75	48795.8	-15258.5	0.9999	593.69
12.51	Toluene	91	122760	195709	0.9997	1590.88
13.38	Trans-1,3-Dichloropropene	75	42130	-36029.3	0.9998	722.99
13.73	Tetrachloroethane	166	23726.5	28345.4	0.9993	681.27
13.79	1,1,2-Trichloroethane	97	37839.3	39876.8	0.9992	517.60
14.83	1,2-Dibromoethane	107	28423.5	-4782.8	0.9998	513.71
16.07	Chlorobenzene	112	87605	106246	0.9993	554.27
16.36	Ethylbenzene	91	133003	170031	0.9997	736.40
16.37	1,1,2,2-Tetrachloroethane	131	28550.6	5709.3	0.9992	450.05
16.71	M, P-xylene	91	210940	289853	0.9997	723.59
17.72	O-xylene	91	108665	127970	0.9996	759.57
17.83	Styrene	104	84146.2	38025.7	0.9992	1656.35
19.75	4-Ethyltoluene	105	134380	10846.3	0.9998	3064.09
19.89	1,3,5-Trimethylbenzene	105	118951	13935	0.9998	2790.07
20.50	1,2,4-Trimethylbenzene	105	120852	-17395.3	0.9999	2563.70
20.90	1,3-Dichlorobenzene	146	73398.3	41962.1	0.9996	2224.47
21.07	1,4-Dichlorobenzene	146	74510.3	46792	0.9995	2335.71
21.32	Benzyl Chloride	91	77826.9	-194542	0.9999	771.35
21.59	1,2-Dichlorobenzene	146	71144.1	26534.8	0.9994	2291.94
23.63	1,2,4-Trichlorobenzene	180	325768	-90529.9	0.9992	1448.78
23.79	Hexachlorobutadiene	225	108423	260323	0.9996	1097.30

Table 3. Results for two wallcovering samples.

RT	Concentration (mg/m²)	
	Sample 1	Sample 2
1,1,2-Trichloro-1,2,2Trifluoroethane	-	-
1,1-Dichloroethene	-	-
Allyl Chloride	-	-
Methylene Chloride	-	-
1,1-Dichloroethane	0.003	-
Cis-1,2-Dichloroethene	0.006	0.007
Trichloromethane	-	-
1,1,1-Trichloroethane	0.005	0.010
Carbon Tetrachloride	-	0.008
Benzene	0.008	0.008
1,2-Dichloroethylene	-	0.006
Trichloroethylene	0.005	0.007
1,2-Dichloropropane	-	-
Cis-1,3-Dichloropropene	-	0.005
Toluene	0.013	0.020
Trans-1,3-Dichloropropene	-	-
Tetrachloroethane	-	-
1,1,2-Trichloroethane	-	0.004
1,2-Dibromoethane	-	-
Chlorobenzene	-	-
Ethylbenzene	0.002	0.002
1,1,2,2-Tetrachloroethane	-	0.002
M,p-xylene	0.010	0.015
O-xylene	0.005	0.006
Styrene	0.009	0.009
4-Ethyltoluene	0.002	-
1,3,5-Trimethylbenzene	0.002	0.002
1,2,4-Trimethylbenzene	-	0.002
1,3-Dichlorobenzene	-	0.002
1,4-Dichlorobenzene	0.002	0.004
Benzyl Chloride	-	0.002
1,2-Dichlorobenzene	0.002	0.002
1,2,4-Trichlorobenzene	0.002	-
Hexachlorobutadiene	-	-

Table 4. The limits for VOCs requested in GB/T 35613-2017.

Compound Name	Unit	Limit
Benzene	mg/m²	≤ 0.01
Toluene	mg/m²	≤ 0.5
xylene	mg/m²	≤ 0.25
TVOC	mg/m²	≤ 0.50

Summary

In this study, the analysis of 35 VOCs in wallpaper is performed effectively and efficiently by the PerkinElmer TurboMatrix 650 ATD and Clarus SQ8 GC/MS system. This method demonstrates results with good linearity for VOCs analysis. It satisfies the needs of the environmental protection and indoor decoration materials industry.

References

1. EN12149:1997, Wallcoverings in roll form - Determination of migration of heavy metals and certain other elements, of vinyl chloride monomer and of formaldehyde release.
2. GB/T 35613-2017, Green product assessment-Paper and paper products.

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

014772_01 PKI