APPLICATION NOTE

Gas Chromatography/
Mass Spectrometry

Author

Meng Yuan

PerkinElmer, Inc.
Shelton, CT 06484 USA

Increasing Sensitivity in the Determination of Volatile Organics in Toys with Headspace Trap-GC/MS

Introduction

The safety of toys has gained publicity on a global scale, with numerous recalls and new regulations. One aspect of toys which needs to be considered under European Union regulations (EN-71) is the content of volatile organic compounds (VOCs). These compounds, such as benzene and toluene, are residual after the manufacture of various types of polymers, additives and coatings. VOCs are potentially hazardous to the health of children if present at high levels in toys. As a result, it is necessary to accurately determine the level of VOCs in toys to ensure safety.

This application note will present an approach developed to measure VOCs at low levels using headspace trap (HS Trap) sample introduction with gas chromatography/mass spectrometry (GC/MS). This technique is based on European standard method EN-71 Part 11,[1] which specifies details for the analysis of toy and toy-material extracts – included in this method are headspace-GC/MS parameters for VOC analysis. In this application note, the sensitivity of the method presented in EN-71 is improved with the use of headspace-trap instrumentation.

In addition to method optimization and calibration, a variety of toys are analyzed and the level of VOCs determined.

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Experimental

VOCs in toys are identified and the amount is determined by HS Trap-GC/MS. Samples are heated in a sealed vial to 80 °C, allowing the volatile organics to migrate from the toy material into the headspace of the vial. The sample is equilibrated at this temperature for 40 minutes while this process occurs. Using the automated headspace trap technology of the PerkinElmer® TurboMatrix™ HS Trap, the headspace gas is extracted from the vial, concentrated on an adsorbent trap, and injected into a GC/MS system. In this application, a PerkinElmer Air Toxics trap was used.

The technique is very sensitive because the trap provides focusing before instrument introduction and remains clean because of limited sample contact. Table 1 shows the instrumental setup parameters for the HS Trap-GC/MS system.[2]

The headspace transfer line was passed through the GC injector port and connected to the GC column using a universal capillary-column connector.

Calibration-Standards Preparation

A 20 ng/µL standard stock solution was prepared by diluting 0.200 mL of a 1000 µg/mL VOC standard to 10.0 mL with methanol. From this, a working solution of 1 ng/µL was prepared by diluting 0.50 mL of the 20 ng/µL standard stock solution to 10 mL with methanol. Working calibration standards at 5, 10, 20, 50, and 100 ng/µL were prepared fresh each day.

An internal standard solution of toluene-d8 at 20 ng/µL was prepared by diluting 0.2 mL of a 1000 µg/mL toluene-d8 solution to 10 mL with methanol.

The working curve was prepared by injecting 5 µL and 10 µL of each working calibration standard and 1 µL, 2.5 µL and 5 µL of each standard-stock solution into headspace vials. Additionally, 5 µL of the 20 ng/µL internal standard solution was injected into each headspace vial. All headspace vials were sealed immediately and transferred to the headspace-trap vial tray.

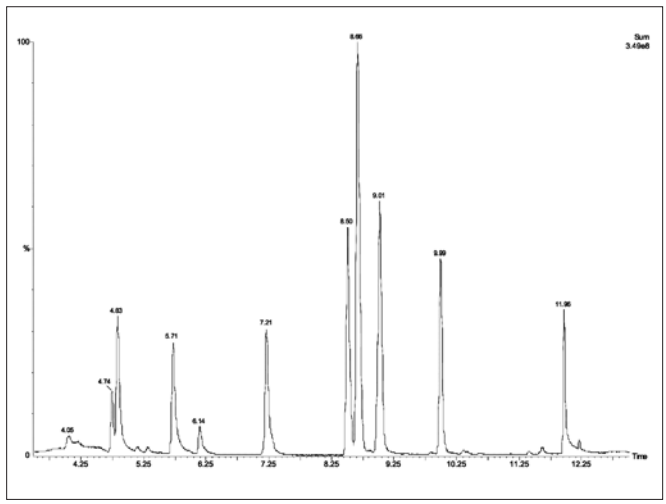

Figure 1. 50 ng injection of a reference standard for volatiles analysis by EN-71 with HS Trap.

Table 1. **Instrument Parameters.**

Sample Introduction	**PerkinElmer TurboMatrix HS-40 Trap**
Needle Temp	90 °C
Transfer Line Temp	120 °C
Oven Temp	80 °C
Trap Low Temp	45 °C
Trap High Temp	280 °C
Dry Purge (Helium)	5 min
Trap Hold Time	6 min
Desorb Time	0.5 min
Thermostatting Time	40 min
Pressurization Time	1 min
Decay Time	2 min
Column Pressure	15 psi
Vial Pressure	35 psi
Desorb Pressure	10 psi
Transfer Line	Fused Silica 2 m x 320 µm (Part No. N9301357)

Gas Chromatograph	**PerkinElmer Clarus® 600 GC**
Headspace Connector	Universal Connector (Part No. N9302149)
Oven Program Initial Temp	50 °C
Hold Time 1	1 min
Ramp 1	15 °C/min to 210 °C
Hold Time 2	5.33 min
Vacuum Compensation	On
Column	Elite™ Volatiles 30 m x 0.25 mm x 1.4 µm (Part No. N9316388)
Carrier Gas	Helium
Mass Spectrometer	**PerkinElmer Clarus 600 MS**
Mass Range	45-220 u
Solvent Delay Time	0.1 min
Scan Time	0.20 sec
InterScan Delay Time	0.05 sec
Transfer Line Temp	200 °C
Source Temp	200 °C
Multiplier	400 V

Results

Five calibration levels are recommended for method EN-71 Part 11. The standard deviation of response should be below 15 %RSD (relative standard deviation). Table 2 shows %RSD data of a 50 ng standard. All compounds meet the specified criteria of RSD less than 15%. Figure 1 is an example chromatogram of a 50 ng standard injection.

Toluene-d8 was used as an internal standard. Peak-area ratio was used to calculate amounts of VOC.

The peak-area ratio for the component in the sample was calculated by dividing the peak area of the component (target ion) by the peak area (target ion) of the internal standard toluene-d8 (IS):

$$\text{peak-area ratio} = \frac{\text{peak area of the component ion}}{\text{peak area of the IS ion}}$$

Amounts of VOC (concentration in ng) were calculated by plotting the peak area ratio in the following calibration functions:

$$\text{conc(x)in ng} = \frac{\text{y(peak-area ratio)} - b^{y=ax+b}}{a}$$

Method detection limits (MDL) were calculated to give an indication of the measurement capability. The quantification limit is generally 10x above the MDL. The method detection limits were calculated using the following equation:

$$\text{MDL} = t_{(n-1,\ a = .99)} \times s$$

An empty vial was analyzed to determine the baseline and seven samples were prepared at 5 ng. Each individual MDL was obtained by multiplying the standard deviation by the 99% t-statistic. Table 2 also shows the list of calculated MDLs.

Following the calibration of the system, 4 toy samples (toy ball, noise putty, modeling compound, crab) obtained from the local market were analyzed. The resultant chromatogram for the analysis of the toy-ball sample is pictured in Figure 2. The sample preparation with headspace analysis is very simple.

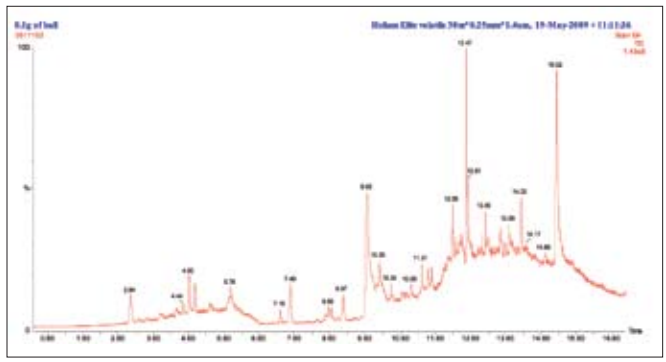

Figure 2. Total ion chromatogram of 0.1 g of toy-ball sample.

Table 2. **Calibration Table for 12 Volatiles.**

Name	Retention Time	Quantifier Ion	Qualifier Ion 1	Qualifier Ion 2	%RSD	r^2	MDL (µg/g)
Dichloromethane	4.041	49	86	84	9.51	0.9962	0.002
Benzene	5.703	78	77	52	4.41	0.9939	0.002
Trichloroethylene	6.128	130	132	95	4.31	0.9970	0.003
Tolune-d8	7.134	98	100	–	Internal Standard		–
Toluene	7.192	91	92	65	2.62	0.9995	0.002
Ethylbenzene	8.487	91	106	51	5.45	0.9993	0.002
m,p-Xylene	8.649	91	106	105	6.42	0.9992	0.002
Cyclohexanone	8.972	55	98		6.76	0.9979	0.003
o-Xylene	8.997	91	106	105	5.94	0.9979	0.002
1,3,5-Trimethylbenzene	9.973	105	120	119	4.82	0.9983	0.002
Nitrobenzene	11.595	77	123	51	4.91	0.9956	0.010
Isophorone	11.958	82	138	54	8.42	0.9959	0.009

Table 3. **VOC Content (µg/g) for Four Toy Samples.**

	Sample	(µg/g)
Ball	Dichloromethane	68.0
	Benzene	11.1
	Toluene	26.5
	Ethylbenzene	10.5
	m,p-Xylene	10.4
	Cyclohexanone	94.3
	o-Xylene	13.2
	1,3,5-Trimethylbenzene	15.4
	Isophorone	15.1
Noise Putty		
	Benzene	26.1
	Toluene	19.4
	Cyclohexanone	84.5
	Nitrobenzene	9.5
Modeling Compound		
	Benzene	33.4
	Ethylbenzene	71.6
	m,p-Xylene	20.3
	o-Xylene	16.0
Crab	Benzene	20.1
	Toluene	62.8
	Ethylbenzene	16.4
	m,p-Xylene	11.9
	Cyclohexanone	303.0
	Isophorone	67.7

A known amount of the toy was cut into small (1 mm x 1 mm) pieces with a razor blade and placed into the headspace vial, internal standard was added and the vial was capped. Detectable solvents were seen in each sample (Table 3) – however, the levels determined in this application were below regulatory limits.

Discussion

Headspace trap is an additional sample-handling technology to improve upon the sensitivity of static headspace. In this article, HS Trap demonstrated high sensitivity and linearity across the range of 25–500 ng.

The HS Trap uses heat to extract compounds out of the toys into the headspace, offering three advantages: easy sample preparation, high sensitivity, and no cross-contamination of samples. After the analytes are extracted, the trap is dry-purged to eliminate the moisture. Then the trap is heated and carrier gas transfers a narrow band of the desorbed analytes into the GC/MS system.

Table 4 compares the guideline of EN-71 for selected compounds with the MDL achieved using this method. The method developed provides sufficient capability to measure with confidence at the concentrations lower than regulatory level.

Table 4. **MDL Guideline of EN-71 and MDL in this Method.**

	MDL in EN-71 (ng)	MDL in this Method (ng)
Dichloromethane	10	2.2
Benzene	30	1.7
Trichloroethylene	20	3.1
Toluene	20	2.2
Ethylbenzene	40	1.5
m,p-Xylene	30	1.8
Cyclohexanone	30	2.8
o-Xylene	20	1.9
1,3,5-Trimethylbenzene	10	2.0
Nitrobenzene	60	10.2
Isophorone	40	9.6

Conclusion

This application note shows that the Clarus 600 GC/MS system with TurboMatrix HS Trap meets and exceeds the requirements for method EN-71 Part 11, including minimum detection limits and calibration requirements. The calibration of the system was demonstrated across the range of 25–500 ng, with a linear response. Toy samples were analyzed and the VOC content was determined. Advantages of the headspace-trap technology for this application include ease of use, high sensitivity, ease of disposable sample vials, and no cross-contamination of samples. Plus, the novel GC oven design of the Clarus 600 GC improves separation and decreases run time.

References

1. EN-71 Part 11 "Safety of toys - Part 11: Organic chemical compounds – Methods of analysis" 2004-07-01

2. Yuan, Meng "Measuring Volatile Organic Compounds by Headspace Trap GC-MS in the Beijing Food Laboratory", American Laboratory, On-Line Edition, April 2009

3. Yuan, Meng "Reliably Detect 86 of Pesticides in a Single Run Down to 10pg with GC/MS in the Beijing Food Lab", PerkinElmer Field Application Report, available from www.perkinelmer.com

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

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For a complete listing of our global offices, visit www.perkinelmer.com/ContactUs

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