



APPLICATION NOTE

Gas Chromatography/ Mass Spectrometry

Author:

Kira. Yang

PerkinElmer, Inc.
Shanghai, China

Determination of VOC in Artificial Runway by Multiple Headspace Extraction-GC/MS

Introduction

There has been an increase in public concern about the safety of artificial runway used to pave school playgrounds, sports stadiums and so on in China since the raw materials of artificial runway are mainly recycled tire

crumb rubber. Recycled tires may contain several substances of high concern, and the associated adhesives may also contain various volatiles, so the environmental and health compatibility of plastic track should be satisfied when it is to be used^{1,2}. The EPA and the CDC/ATSDR are conducting a characterization of the components in tire crumb rubber including volatile organic chemicals (VOCs), semi-volatile organic chemicals (SVOCs) and heavy metal species, which is critical to quality control and understanding the potential for exposure³. Chamber testing as a method included by the EPA and the CDC/ATSDR is a qualitative method to assess the emissions of VOC in tire crumb rubber³. But the quantitation of VOC in samples can't be determined. The determination method of VOC in raw materials of plastic and rubber sports surface is by solvent extraction-GC in many local standards in China⁴. This method measures the amount of VOC but it is complicated and consumes significant quantities of organic solvent.

This application note discusses the alternative technique of, multiple headspace extraction (MHE), which is a procedure to quantify target compounds in solid or difficult matrices independent of matrix effects. The theory of MHE has been described by Kolb⁵⁻⁸ et al. and McAuliffe⁹. Using MHE, the analytes in samples and standard are extracted exhaustively. The total amount in the sample is calculated using a report template by inputting the peak area of each MHE injection, concentration and volume of standard and the sample weight in the vial. Presented in this paper is a quantitative determination of VOCs like toluene, xylene, naphthalene and some non-target compounds in artificial runway.

Experimental

A Fritsch (p-14) Mill with liquid nitrogen refrigeration was used to grind the runway sample from which approximately 0.06 g of sample powder was placed into a 20-ml headspace vial. The vial was then immediately sealed with the PTFE side of the septum facing toward the sample and placed into the PerkinElmer TurboMatrix™ HS-40 Headspace Sampler (HS). Five target compounds including toluene, o-xylene, m-xylene, p-xylene and naphthalene are discussed in this application note. Therefore, 3 µL DMF solution was added into a vial as an external standard containing 34.64 µg/mL of toluene, 1.76 µg/mL of o-xylene, 8.68 µg/mL of m-xylene, 1.03 µg/mL of p-xylene and 430 µg/mL of naphthalene. The system precision was investigated by running six identical calibration standards.

The conditions used for the PerkinElmer Clarus® SQ 8 GC/MS operating in electron ionization mode with PerkinElmer TurboMatrix HS-40 Headspace Sampler are presented in Table 1. SIFI MS mode was used which combines SIM with a full scan over a desired mass range. Table 2 shows the SIM quantitation and qualifier ions.

Results and Discussion

The sample analytes were extracted five times in this study to generate the quantitation curves. Figure 1 shows the total ion chromatogram (TIC) of the initial extraction cycle. There are many

Table 1. Analytical parameters.

Headspace Sampler Parameters	
Headspace Mode	MHE
Oven Temperature	90 °C
Needle Temperature	120 °C
Transfer Line Temperature	135 °C
Thermostat Time	60 min
Vial Pressurization Time	1 min
Withdraw Time	0.2 min
Injection Time	0.05 min
Column Pressure	21 psi

GC Parameters			
Analytical Column	Perkinelmer Elite-WAX (30 m x 0.25 mm x 0.25 µm)		
Injector Type	Capillary injector with capillary split deactivated glass liner		
Inlet Temp	200 °C		
Carrier Gas Flow	1 mL/min		
Split Flow	20 mL/min		
Oven Program	Temp.	Hold Time	Rate
	35 °C	5 min	15 °C/min
	200 °C	2 min	END

MS Parameters	
Mass Range	45 to 300 amu
GC Inlet Line Temp	200 °C
Ion Source Temp	200 °C
Solvent Delay	0 min
Function Type	SIFI

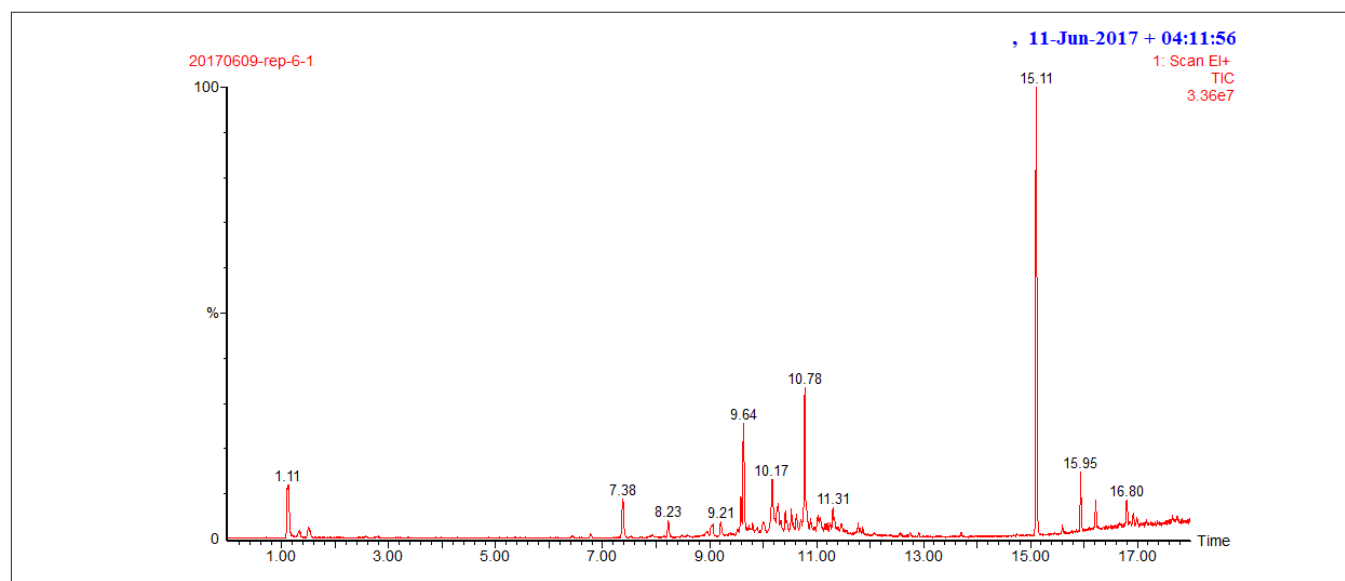


Figure 1. The total ion chromatogram (TIC) of the initial extraction cycle from a 0.0608 g sample powder of artificial runway.

Table 2. SIM ions used in this method.

Compound Name	Quantitation Ion (m/z)	Qualifier Ion (m/z)	Retention Time (min)
Toluene	91	92	7.38
o-Xylene	91	106	9.64
m-Xylene	91	106	9.04
p-Xylene	91	106	8.95
Naphthalene	128	-	15.11

compounds extracted when the sample is equilibrated at 90 °C. The compound eluted at 15.11 min is naphthalene which shows the strongest response in the chromatogram. Naphthalene is a carcinogenic polycyclic aromatic hydrocarbon with high volatility and a pungent odor; therefore, it is analyzed and quantified in this application note. Since the TIC is complex and many peaks are composed of multiple overlapping components between nine to 12 min which covers the retention time range of three xylenes, SIR mode is used to quantify the five target compounds. The five chromatograms obtained for toluene in the sample powder are shown in Figure 2. The amount of each analyte is calculated by an Excel® macro available from PerkinElmer (Figure 3-7). The

sample was determined to have 1498 µg/kg of toluene, 60.27 µg/kg of o-xylene, 183.3 µg/kg of m-xylene, 39.42 µg/kg of p-xylene and 124791 µg/kg of naphthalene. The correlation coefficients for the target compounds in the sample and calibration standard are better than 0.99 which means that thermal equilibrium was established after 60 minutes at 90 °C. Analytes with high volatility and low amount would be extracted until nothing remains after only a few MHE cycles. Therefore there are only four peak areas for p-xylene in the standard, as shown in Figure 6. The result for precision is shown in Table 3, the RSD % is in the range of 1.38 – 1.89 which demonstrate high reliability.

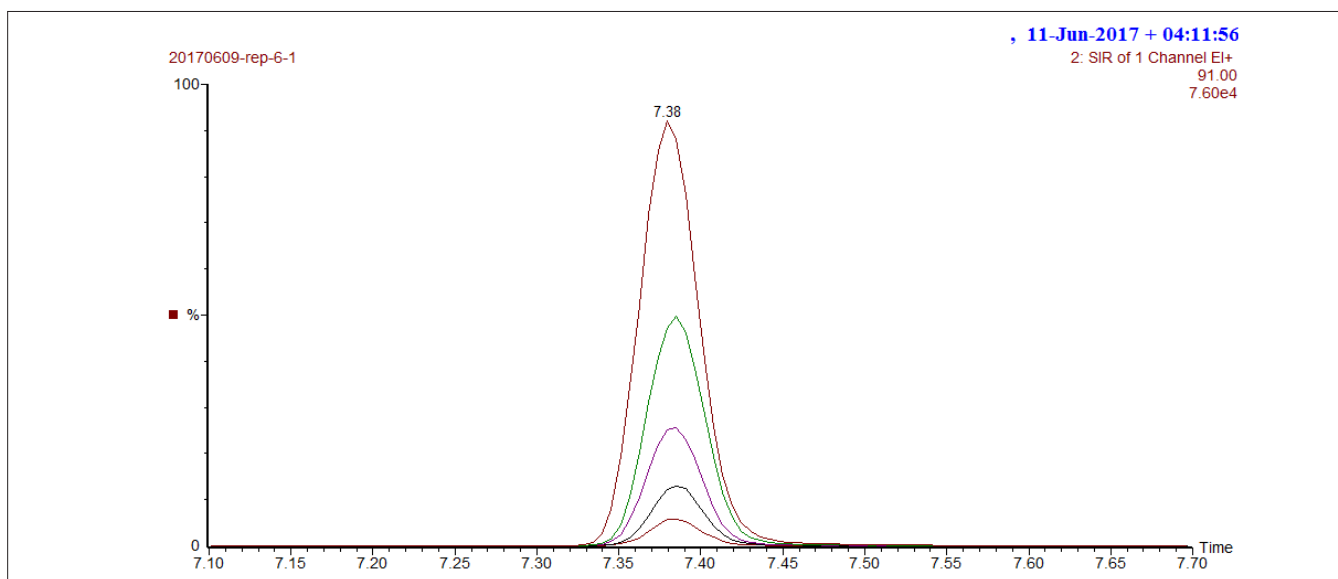


Figure 2. Multiple headspace extraction data for the toluene peak in sample powder.

Table 3. The result for precision of six calibration standards.

No.	Toluene (µg/ml)	o-Xylene (µg/ml)	m-Xylene (µg/ml)	p-Xylene (µg/ml)	Naphthalene (µg/ml)
1	35.34	1.78	8.72	1.04	433.25
2	34.68	1.77	8.70	1.03	431.15
3	34.58	1.72	8.55	1.01	427.00
4	35.22	1.77	8.77	1.04	438.14
5	34.47	1.71	8.49	1.01	425.02
6	35.68	1.79	8.84	1.05	440.12
Mean	35.00	1.76	8.68	1.03	432.45
StDev	0.49	0.03	0.13	0.02	5.97
RSD %	1.39	1.89	1.53	1.62	1.38

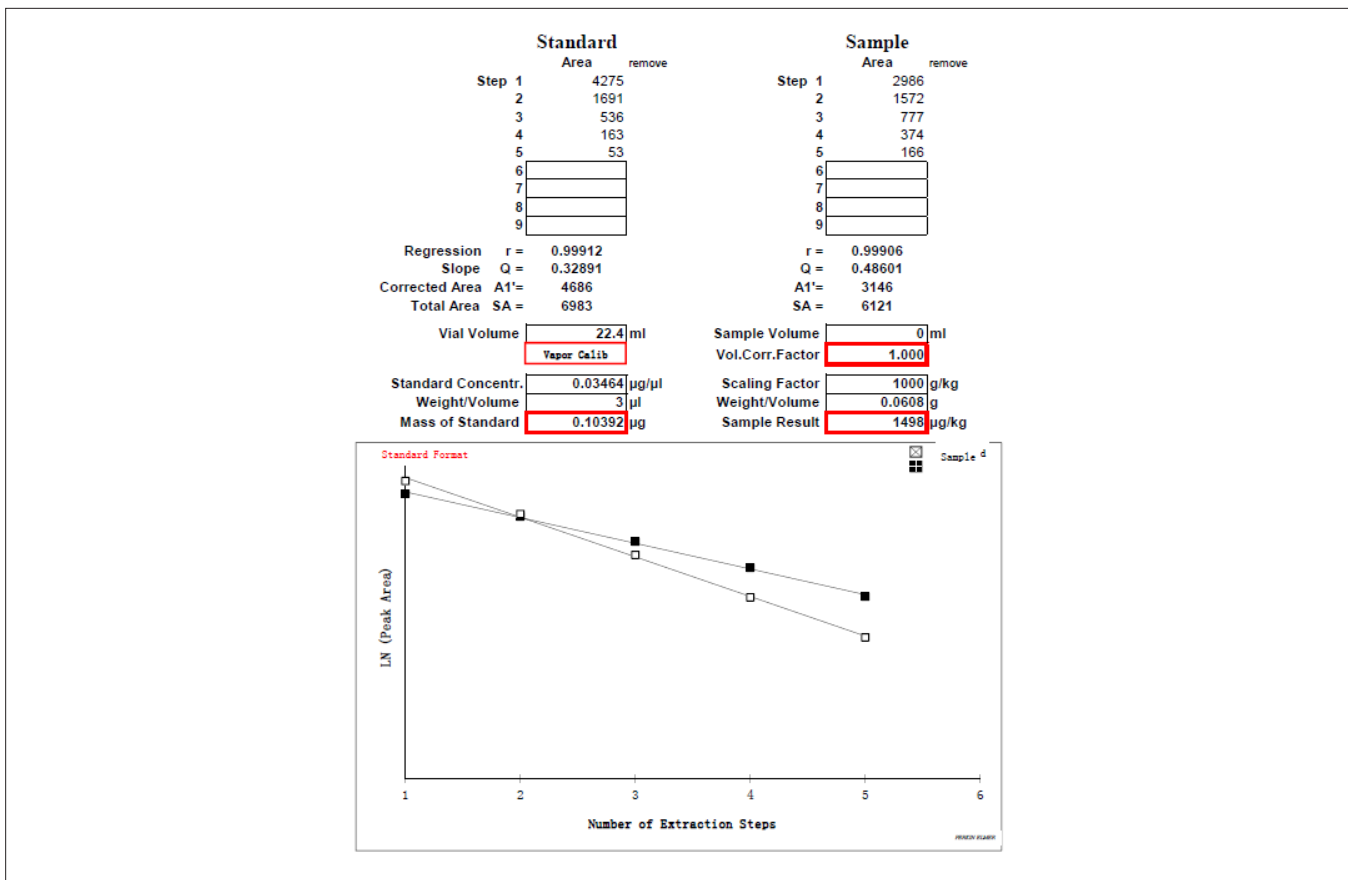


Figure 3. Example of the Excel®-based macro used to calculate concentration of toluene in MHE.

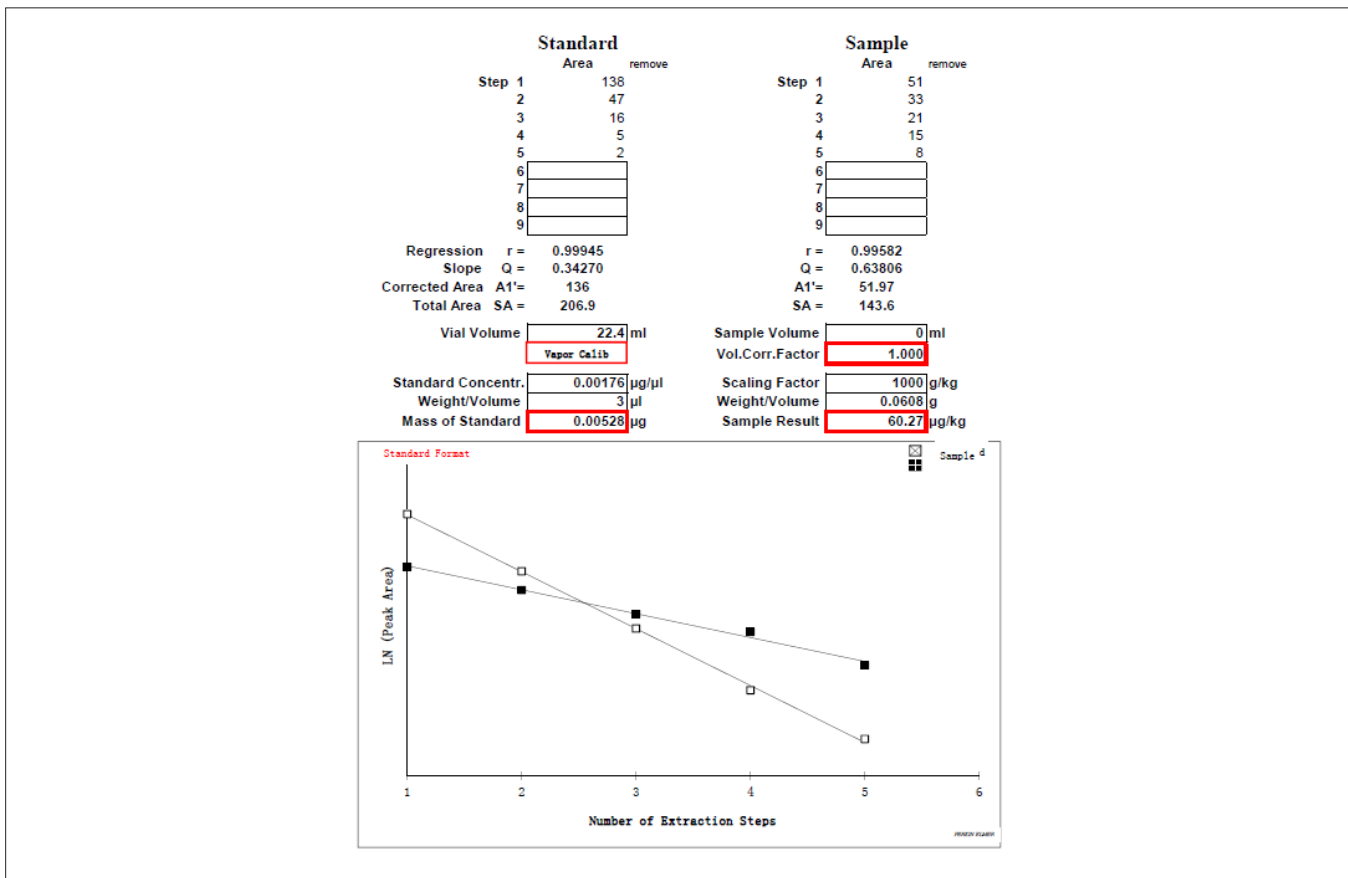


Figure 4. Example of the Excel®-based macro used to calculate concentration of o-xylene in MHE.

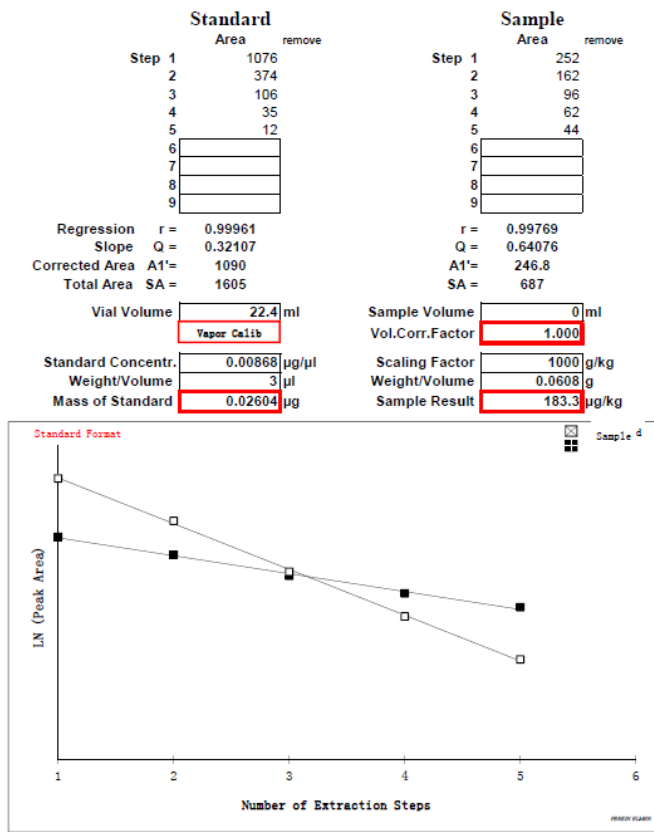


Figure 5. Example of the Excel®-based macro used to calculate concentration of m-xylene in MHE.

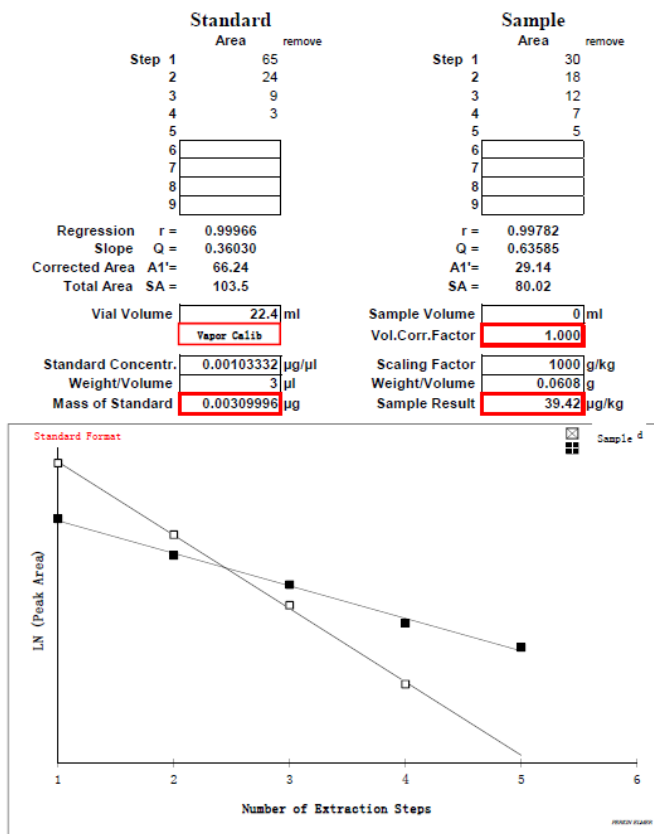


Figure 6. Example of the Excel®-based macro used to calculate concentration of p-xylene in MHE.

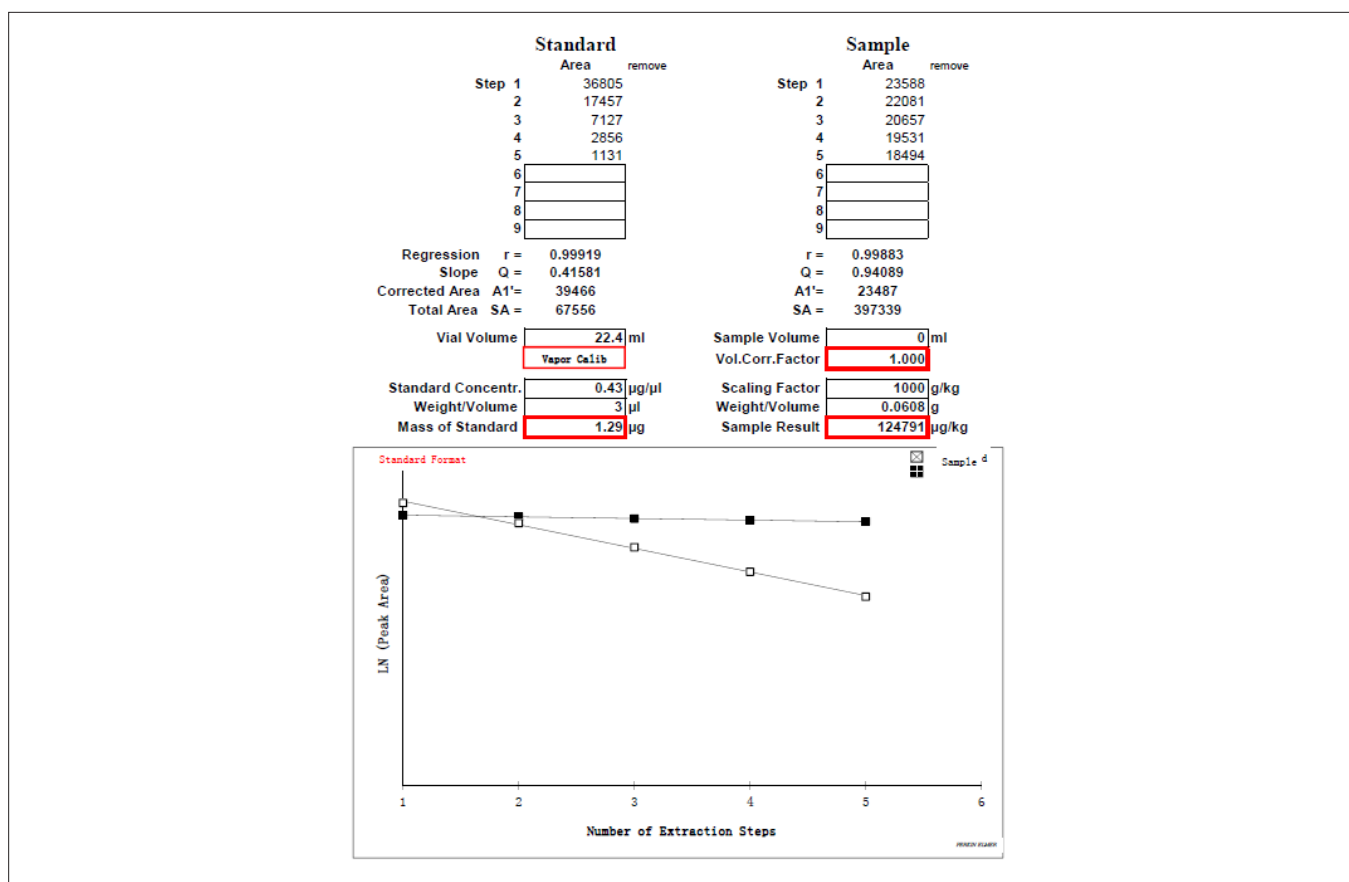


Figure 7. Example of the Excel®-based macro used to calculate concentration of naphthalene in MHE.

The regression lines of logarithmic plots for nine non-target peaks present good linearity also (Figure 8). The amounts of the non-target peaks are calculated using the peak area of the extracted ion chromatogram and reported as equivalents of toluene in Table 4.

A minimum of three extractions are required to quantify the target analytes by the MHE technique. Increasing the number of extraction steps increases the accuracy of the quantitative determination, however, fewer extraction steps can be used when throughput is more important than accuracy. Table 5 shows the difference in quantitation when using two extractions vs. five extractions.

Table 4. The corresponding equivalent to toluene amounts of nine non-target peaks.

No.	Retention Time (min)	Quantitation Ion (m/z)	Amount ($\mu\text{g}/\text{kg}$)
1	8.24	57	971.3
2	9.21	57	868.6
3	9.60	57	2649
4	9.65	57	6830
5	10.18	57	5103
6	10.79	57	10910
7	11.79	57	993
8	15.95	142	4728
9	16.24	142	2292

Table 5. The difference in quantitation using two extractions vs. five extractions.

Extraction number	Toluene ($\mu\text{g}/\text{kg}$)	o-Xylene ($\mu\text{g}/\text{kg}$)	m-Xylene ($\mu\text{g}/\text{kg}$)	p-Xylene ($\mu\text{g}/\text{kg}$)	Naphthalene ($\mu\text{g}/\text{kg}$)
5	1498	60.27	183.3	39.42	124791
2	1544	62.31	188.3	36.95	115955
Error %	3.07	3.38	2.73	-6.27	-7.08

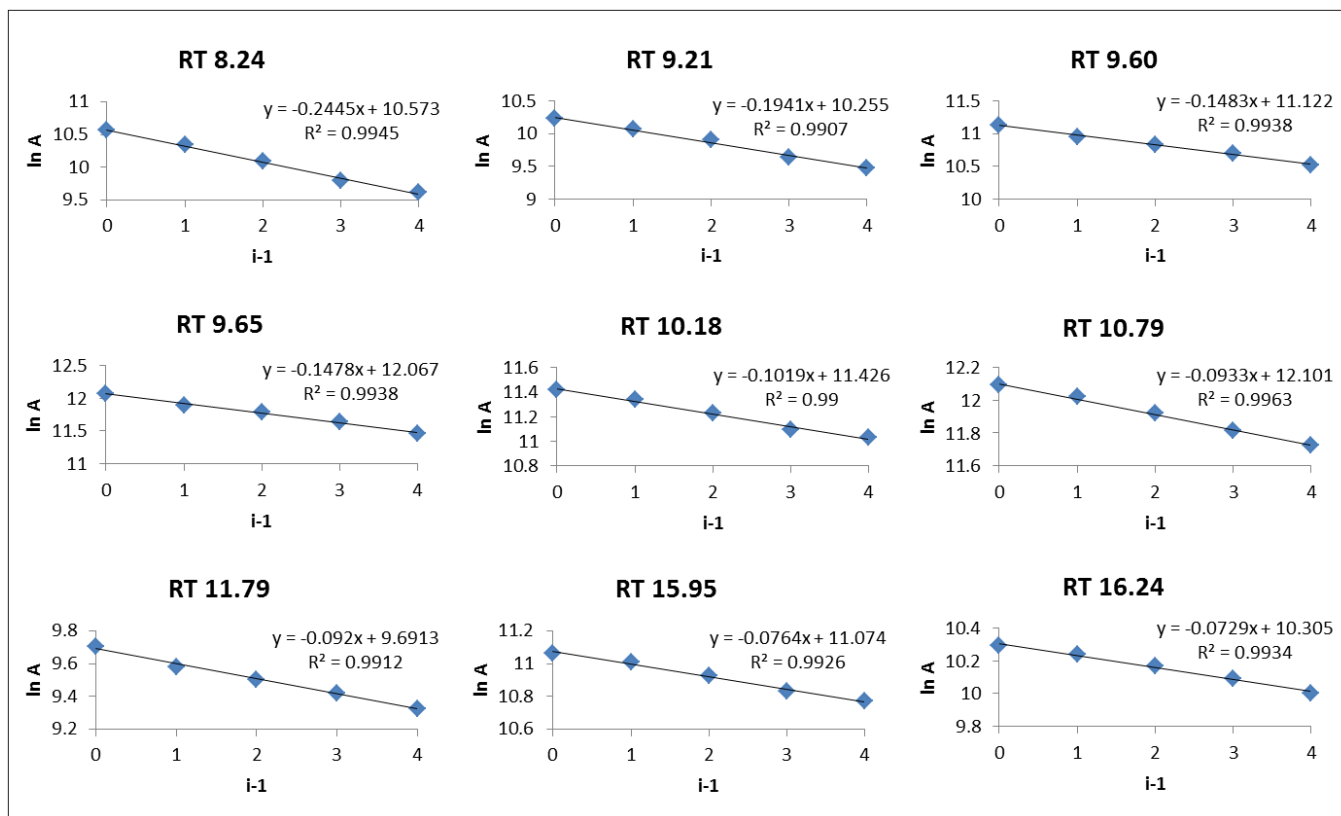


Figure 8. Logarithmic plots of peak area vs. extraction number for nine non-target peaks.

Summary

In this study, the quantitative determination of VOC in artificial runway is performed easily by the MHE technique. The MHE technique minimizes the sample preparation for solid samples and accurately quantifies samples when standard matrix matching can be challenging. The quantitative values for target compounds can be generated by an Excel[®] macro quickly for risk evaluation. High reliability of the method in this paper is demonstrated by good repeatability for the standard batch.

References

1. B. Bocca, G. Forte, F. Petrucci, S. Costantini, P. Izzo, Metals contained and leached from rubber granulates used in synthetic turf areas, *Sci. Tot. Env.*, 2009.
2. Chapter 159: Control of volatile organic compounds from adhesives and sealants, department of environmental protection, 2014.
3. Federal research action plan on recycled tire crumb used on playing fields and playgrounds status report, 2016.
4. Limit of harmful substances of plastic and rubber sports surface for school, Shanghai Chemical Building Materials Trade Association, 2016.
5. B. Kolb, Multiple headspace extraction - A procedure for eliminating the influence of the sample matrix in quantitative headspace, gas chromatography, *Chromatographia* 1982.
6. L. S. Ettre, E. Jones, B. S. Todd, Quantitative analysis with headspace gas chromatography using multiple headspace extraction. *Chromatography Newsletter*, 1984.
7. B. Kolb, P. Pospisil, M. Auer, Quantitative headspace analysis of solid samples; a classification of various sample types, *Chromatographia*, 1984.
8. B. Kolb, L. S. Ettre, Theory and practice of multiple headspace extraction, *Chromatographia*, 1991.
9. C. McAuliffe, Gas chromatographic determination of solutes by multiple phase equilibrium, *Chemical Technology*, 1971.