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Analysis of styrene leached from polystyrene cups using GCMS coupled with Headspace (HS) sampler

ASMS 2014 TP763

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Introduction

Worldwide studies have revealed the negative impacts of household disposable polystyrene cups (Figure 1) on human health and environment.
Molecular structure of styrene is shown in Figure 2. Styrene is considered as a possible human carcinogen by the WHO and International Agency for Research on Cancer (IARC).[1] Migration of styrene from polystyrene cups containing beverages has been observed.[2] Styrene enters into our body through the food we take, mimics estrogens in the body and can therefore disrupt normal hormonal functions. This could also lead to breast and prostate cancer.
The objective of this study is to develop a sensitive, selective, accurate and reliable method for styrene determination using low carryover headspace sampler, HS-20 coupled with Ultra Fast Scan Speed 20,000 u/sec, GCMS-QP2010 Ultra to assess the risk involved in using polystyrene cups.

Figure 1. Polystyrene cup

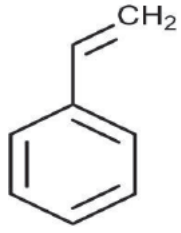

Figure 2. Structure of styrene

Method of Analysis

Extraction of styrene from polystyrene cups

This study was carried out by extracting styrene from commercially available polystyrene cups and recoveries were established by spiking polystyrene cups with standard solution of styrene. Solutions were prepared as follows,

1) Standard Stock Solution:
   1000 ppm of styrene standard stock solution in DMF: Water-50:50 (v/v) was prepared. It was further diluted with water to make 100 ppm and 1 ppm of standard styrene solutions.
2) Calibration Curve:
   Calibration curve was plotted using standard styrene solutions in the concentration range of 1 to 50 ppb with water as a diluent. 5 mL of each standard styrene solution was transferred in separate 20 mL headspace vials and crimped with automated crimper.
3) Sample Preparation:
   150 mL of boiling water (around 100 °C)[1] was poured into polystyrene cups. The cup was covered with aluminium foil and kept at room temperature for 1 hour. After an hour, 5 mL of sample from the cup was transferred into the 20 mL headspace vial and crimped with automated crimper.

Method was partly validated to support the findings by performing reproducibility, linearity, LOD, LOQ and recovery studies. For validation, solutions of different concentrations were prepared using standard stock solution of styrene (1000 ppm) as mentioned in Table 1.

Table 1. Method validation parameters

Parameter	Concentration (ppb)
Linearity	1, 2.5, 5, 10, 20, 50
Accuracy / Recovery	2.5, 10, 50
Precision at LOQ level	1
Reproducibility	50

HS-GCMS Analytical Conditions

Figure 3 shows the analytical instrument, HS-20 coupled with GCMS-QP2010 Ultra on which samples were analyzed with following instrument parameter.

Figure 3. HS-20 coupled with GCMS-QP2010 Ultra by Shimadzu

HS-GCMS analytical parameters

Headspace parameters

- Sampling Mode : Loop
- Oven Temp. : 80.0 °C
- Sample Line Temp. : 130.0 °C
- Transfer Line Temp. : 140.0 °C
- Equilibrating Time : 20.00 min
- Pressurizing Time : 0.50 min
- Pressure Equilib. Time : 0.10 min
- Load Time : 0.50 min
- Load Equilib. Time : 0.10 min
- Injection Time : 1.00 min
- Needle Flush Time : 10.00 min
- GC Cycle Time : 23.00 min

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Chromatographic parameters

• Column	: Rxi-5Sil MS (30 m L x 0.25 mm I.D., 0.25 µm)		
• Injection Mode	: Split		
• Split Ratio	: 10.0		
• Carrier Gas	: Helium		
• Flow Control Mode	: Linear Velocity		
• Linear Velocity	: 36.3 cm/sec		
• Pressure	: 53.5 kPa		
• Column Flow	: 1.00 mL/min		
• Total Flow	: 14.0 mL/min		
• Total Program Time	: 12.42 min		
• Column Oven Temp.	: Rate (°C /min)	Temperature (°C)	Hold time (min)
		50.0	0.00
	40.00	200.0	1.00
	30.00	280.0	5.00

Mass Spectrometry parameters

• Ion Source Temp.	: 200 °C
• Interface Temp.	: 230 °C
• Ionization Mode	: EI
• Event Time	: 0.20 sec
• Mode	: SIM
• m/z	: 104,103 and 78
• Start Time	: 1.00 min
• End Time	: 5.00 min

Results

Fragmentation of styrene

Mass spectrum of styrene is shown in Figure 4. From the mass spectrum, base peak of m/z 104 was used for quantitation where as m/z 103 and 78 were used as reference ions.
SIM chromatogram of 50 ppb standard styrene solution with m/z 104, 103 and 78 is shown in Figure 5.
Method validation data is summarized in Table 2. Figures 6 and 7 show overlay of SIM chromatograms for m/z 104 at linearity levels and calibration curve respectively.

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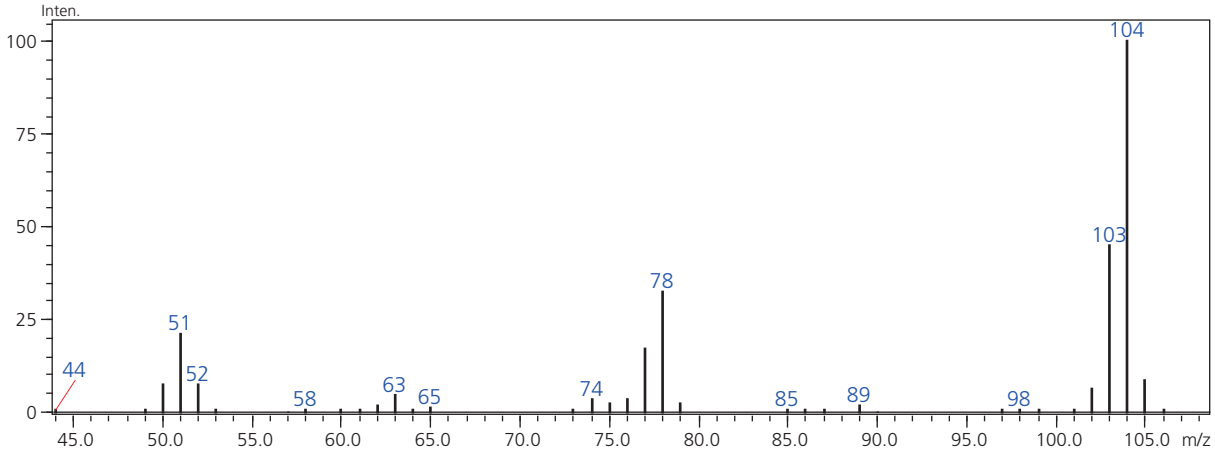

Figure 4. Mass spectrum of styrene

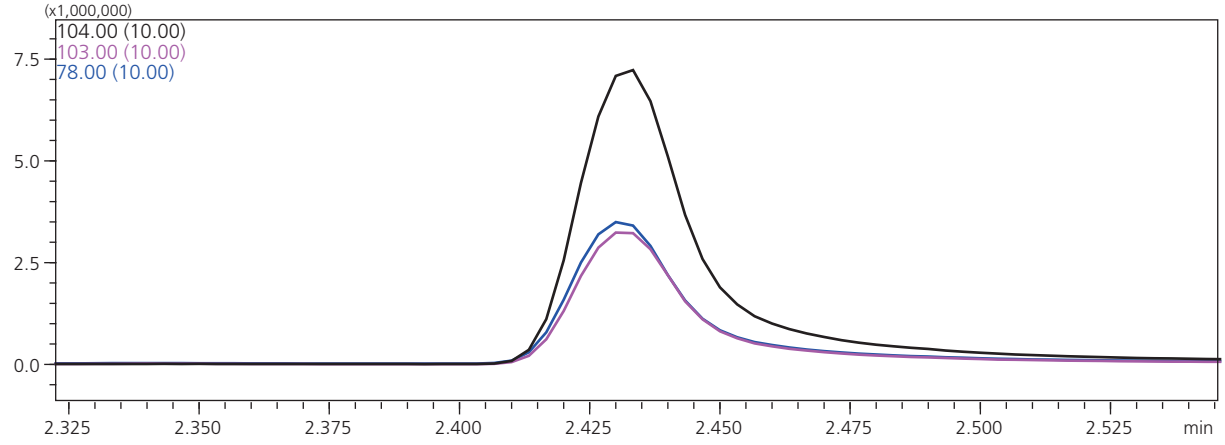

Figure 5. SIM chromatogram of 50 ppb standard styrene solution

Summary of validation results

Table 2. Validation summary

Sr. No.	Compound Name	Parameter	Concentration in ppb	Result
1	Styrene	Reproducibility (% RSD)	50	% RSD : 1.74 (n=6)
2		Linearity* (R^2)	1 – 50	R^2 : 0.9996
3		LOD	1 – 50	LOD : 0.2 ppb
4		LOQ		LOQ : 1 ppb
5		Precision at LOQ	1	S/N ratio : 38 (n=6)
				% RSD : 3.2 (n=6)

* Linearity levels – 1, 2.5, 5, 10, 20 and 50 ppb.

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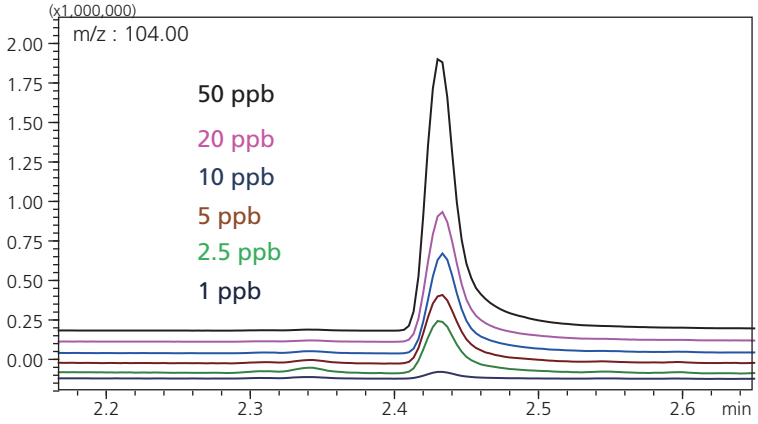

Figure 6. Overlay of SIM chromatograms for m/z 104 at linearity levels

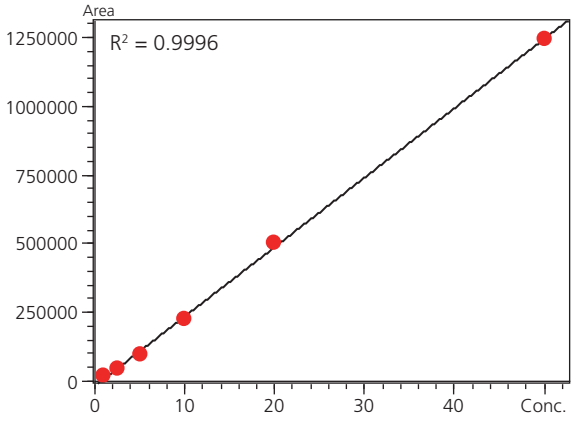

Figure 7. Calibration curve for Styrene

Quantitation of styrene in polystyrene cup sample

Analysis of leachable styrene from polystyrene cups was done as per method described earlier. Recovery studies were carried out by spiking 2.5, 10 and 50 ppb of standard styrene solutions in polystyrene cups. Figure 8 shows overlay SIM chromatogram of spiked and unspiked samples. Table 3 shows the summary of results.

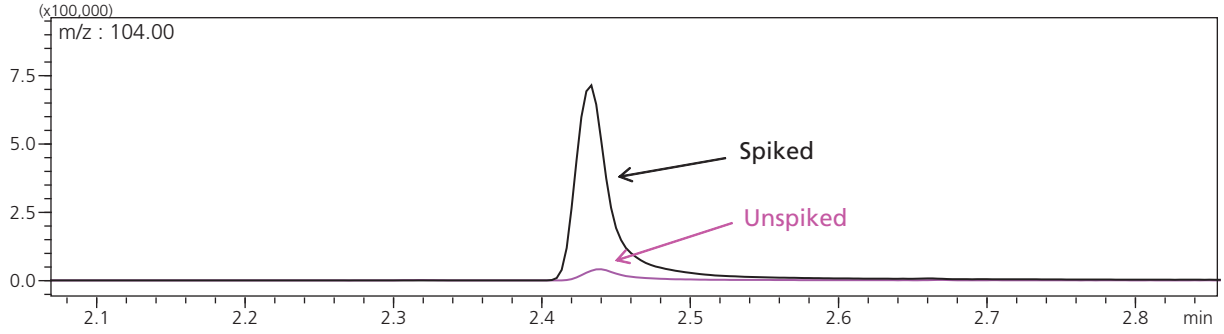

Figure 8. Overlay SIM chromatograms of spiked and unspiked samples

Table 3. Summary of results for sample analysis

Sr. No.	Sample Name	Parameter	Observed Concentration in ppb	Spiked Concentration in ppb	% Recovery
1	Unspiked sample	Precision	9.8	NA	NA
2	Spiked polystyrene cups	Recovery	12.0	2.5	88.0
			18.5	10	87.0
			55.9	50	92.2

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Conclusion

- HS-GCMS method was developed for quantitation of styrene leached from polystyrene cup. Part method validation was performed. Results obtained for reproducibility, linearity, LOQ and recovery studies were within acceptable criteria.
- With low carryover, the characteristic feature of HS-20 headspace, reproducibility even at very low concentration level could be achieved easily.
- Ultra Fast Scan Speed 20,000 u/sec is the characteristic feature of GCMS-QP2010 Ultra mass spectrometer, useful for quantitation of styrene at very low level (ppb level) with high sensitivity.

References

[1] Maqbool Ahmad, Ahmad S. Bajahlan, Journal of Environmental Sciences, Volume 19, (2007), 422, 424.
[2] M. S. Tawfika; A. Huyghebaerta, Journal of Food Additives and Contaminants, Volume 15, (1998), 595.

First Edition: June, 2014

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