Multiple Headspace Extraction for the Quantitative Determination of Residual Monomer and Solvents in Polystyrene Pellets Using the Agilent 7697A Headspace Sampler

Application Note

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Abstract

A multiple headspace extraction (MHE) method using the Agilent 7697A Headspace Sampler coupled with an Agilent 7890A Gas Chromatograph has been developed for quantitative determination of residual monomers and solvents in polystyrene pellets. The polystyrene pellets were freeze-ground before analysis by the MHE procedure. The optimization of headspace temperature and time for sample equilibration are discussed in detail. The repeatability was generally better than 2% RSD for each analyte in the same sample batch and the reproducibility was better than 5.6% RSD for different sample batches.

Introduction

Polystyrene is one of the most useful plastics used in various common consumer products as food containers, drinking cups, cutlery, and toys. Residual styrene can migrate from the product and therefore come in contact with the user. The acute toxicity of styrene has been well studied. It is a skin and mucous membranes irritant and also has narcotic properties. The presence of styrene monomer in the polystyrene must be as low as possible. Therefore, a fast, reproducible analytical method for the analysis of residual styrene content in polystyrene is essential for optimizing polymer production processes and controlling polystyrene product quality.

The analysis of residual impurities and monomers in solid polymers is always challenging. Traditionally, the sample is dissolved in a suitable solvent and injected directly into a gas chromatograph. However, the biggest problem with the direct injection of a polymer solution is the need of frequent maintenance including changing the column and replacing the inlet liner to ensure a clean analytical system. Also, there is a potential risk of decomposition of the sample in the injection port at high temperature. An easy alternate method is to use a headspace technique to do an analysis of the gas phase over the solid sample at a fixed temperature and equilibration time. This method will require compensation for the sample matrix, as calibration standards cannot be created with the same matrix interaction. Multiple headspace extraction (MHE) is a technique to exhaustively extract a sample and calculated the amount of analyte by comparison to an external standard.

This application note discusses the MHE procedure for the analysis of residual monomer like styrene, and solvents like ethyl benzene and cumene in polystyrene pellets.

Experimental

Sample Preparation

The SPEX 6879 Freezer/Mill was used for grinding 3 mm × 4 mm polystyrene (PS) pellets without thermal degradation of the polystyrene. Approximately 3 g of PS pellets was weighted into a 25-mL grinding vial. For this analysis, the following method was found to be the optimum grinding program:

Pre-cooling	10 minutes
Run	2 minutes
Cycle cool	1 minute
Cycles	5
Rate	25 Hz

Approximate 0.4 g of PS powder was weighted accurately into a 20-mL headspace vial. Ethylbenzene (EB), cumene, and styrene monomers (SM) are discussed here. Therefore, 2 µL DMF solution containing 10% v/v EB, cumene, and SM was transferred in a 20-mL headspace vial as an external standard.

Configuration

All experiments were performed using a 7697A Headspace Sampler (HSS) with a 7890A GC. The 7890A GC was configured with a split/splitless inlet and a flame ionization detector. A DB-FFAP column (30 m × 0.32 mm, 1.8 µm) was used for separation. Figure 1 shows a system diagram.

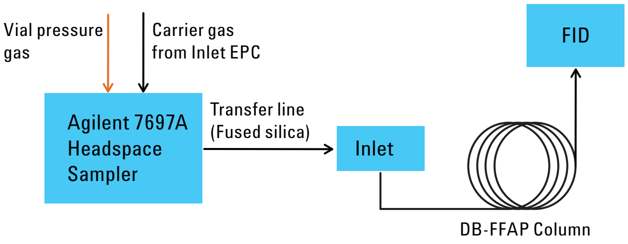

Figure 1. System diagram of the analysis of residual monomer and solvents in polystyrene pellets.

Helium is used as carrier gas and vial pressurization gas. The 7890A GC supplies the carrier gas control that allows carrier flow is routed from inlet EPC to the 7697A HSS and back to the inlet through the transfer line. Pre-cut inlet weldments are supplied for through-the-septum connection between the HSS transfer line (0.53 mm id deactivated fused silica) and the GC. A Pneumatic Control Module (PCM) integrated into the 7697A supplies the vial pressurization gas control.

System Parameters

Table 1 shows the parameters of headspace sampler and gas chromatograph.

Table 1. System Parameters for the Analysis of Residual Monomers in Polystyrene Pellets

Gas chromatograph	**Agilent 7890A GC**
Inlet	Split/splitless: 200 °C; carrier gas, He; split ratio, 5 to 1
Column	DB-FFAP column: 30 m × 0.32 mm, 1.8 µm, constant flow, 4 mL/min
Oven	50 °C (5 min) to 95 °C at 5 °C/min, then to 200 °C at 40 °C/min
Detector	FID: 230 °C; H_2, 40 mL/min; Air, 350 mL/min; N_2, 25 mL/min
Headspace sampler	**Agilent 7697A Headspace Sampler**
Temperature	HS oven, 120 °C; valve/loop, 120 °C; transfer line, 120 °C
Time	Vial equilibration: 120 minutes for PS powder, 30 minutes for standard, inject time, 0.5 minute
Vial	20-mL HS vial; vial shaking setting, 9; vial pressurize from 15 psi to 10 psi at 20 psi/min by a filling flow 50 mL/min
Extraction mode	Multiple; 12 times per vial

In the MHE mode, the headspace analytes are extracted stepwise. After one headspace extraction is completed, the vial is vented to atmosphere, re-equilibrated, and the next subsequent extraction performed. Between two consecutive extractions, the vial is being equilibrated on probe, that is, during this period, the sample probe remains in the vial after its first piercing of the vial septum to avoid leakage that could result from multiple piercing. The 7697A HSS is fully controlled by headspace control software integrated in the ChemStation. All the processes are carried out automatically and precisely.

Results and Discussion

Chromatographic Optimization

Typical chromatograms of the headspace result for the standard and the freeze-ground PS pellets (PS powder) are shown in Figure 2. A 2 µL DMF solution containing 10% v/v EB, cumene, and SM was used for external standard calibration. Note that DMSO can also be used as a solvent which does not impact the target peaks.

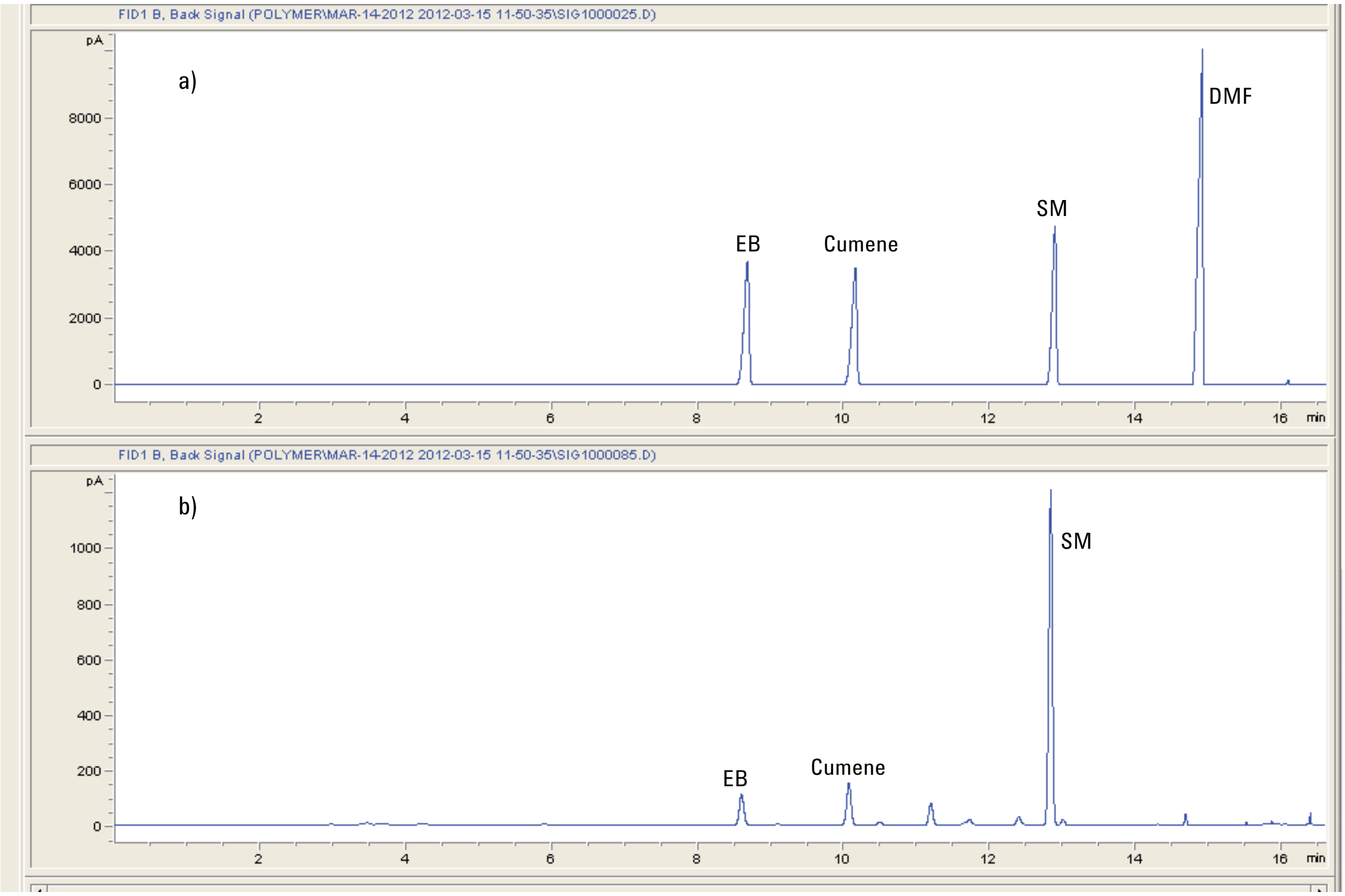

Figure 2. The headspace chromatograms of a) the standard (2 µL DMF solution containing 10% v/v EB, cumene, and SM), and b) the freeze-ground PS pellets.

Headspace Parameter Optimization

In these experiments, the PS pellets are equilibrated at 120 °C. This equilibration temperature is 20 °C higher than the glass transition temperature of polystyrene (100 °C) [1]. Glass transition occurs over a narrow temperature region of which the glass transition temperature is the midpoint. This phase change increases the speed of diffusion of the solid sample that makes the thermal equilibrium in a relatively short time. Normally, the equilibration temperature is determined to be equal or a little higher than the glass transition temperature of the polymer samples [2]. For polymers, it is not recommended using too high temperature since depolymerization or side reaction would take place. This is especially true in air. Different headspace equilibration thermostatting temperatures up to 250 °C for the analysis of polystyrene were tested. The solid matrix turned dark after it was equilibrated at 150 °C or above. Gudat's experiment also showed that when the polystyrene sample was thermostatted at 150 °C for 60 minutes, degradation could probably occur [3].

3 mm × 4 mm polystyrene pellets require a very long equilibration time for the residual SM, cumene, and EB to be released from the matrix. Different equilibration times were tested for the pellets at 120 °C. The peak area-versus-thermostating time plot shown in Figure 3a demonstrates that the analytes in the PS pellets cannot reach two-phase equilibrium in 7.5 hours. Kolb, *et al*, also demonstrated in their experiments that PS pellets could not reach equilibrium after 10 hours at 120 °C [4]. Shaking the vial is helpful but quite limited. In order to decrease the diffusion path of the analytes, 3 mm × 4 mm polystyrene pellets are applied by a Freezer/Mill cryogenic grinder under cooling with liquid nitrogen or solid carbon dioxide. Freeze-grinding can prevent the thermal degradation of the polystyrene during milling into micro size. The resulting particle size of the PS powder is less than 500 µm and will reach equilibrium in a short time frame. As shown in Figure 3b, 90-minute thermostatting is long enough to make each analyte's concentration stable in the headspace when the matrix is polystyrene powder. The large surface area of the powder makes the speed of diffusion faster than that for the pellets, so it takes relatively shorter time to reach thermal equilibrium. However, since the vial system cannot be completely sealed, especially at high temperature, a small amount of the volatile analytes could escape from the vial after too long of a thermostatting time. It probably explains the small decline of the SM amounts (shown as peak area) when the thermostatting time is 360 minutes or above. Considering the multiple measurements with the same vial in these experiments, a headspace equilibration time of 120 minutes was used at a temperature of 120 °C for the freeze-ground PS pellets.

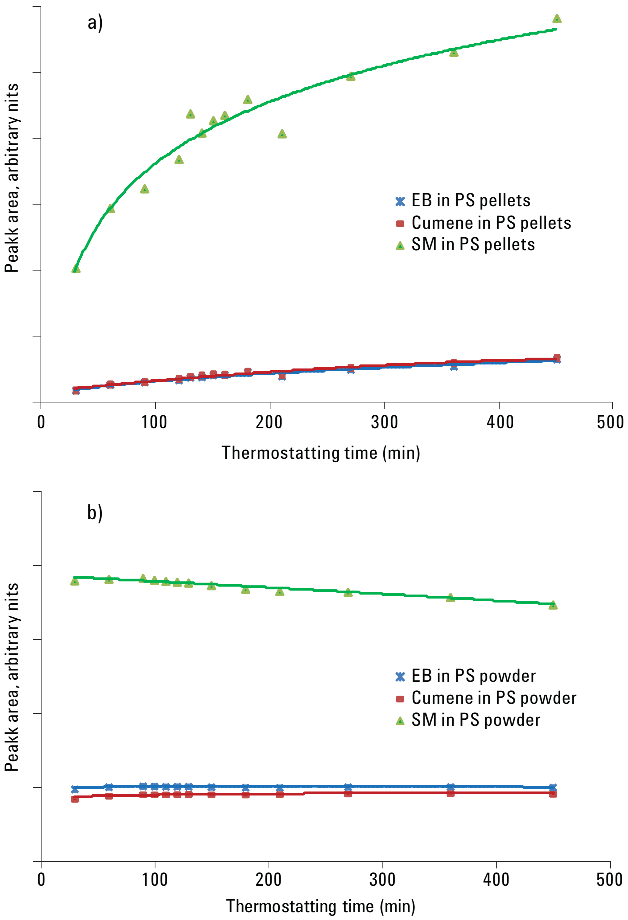

Figure 3. Thermostatting time for the analysis of residual monomer and solvents a) in the PS pellets and b) in the PS powder thermostatted at 120 °C.

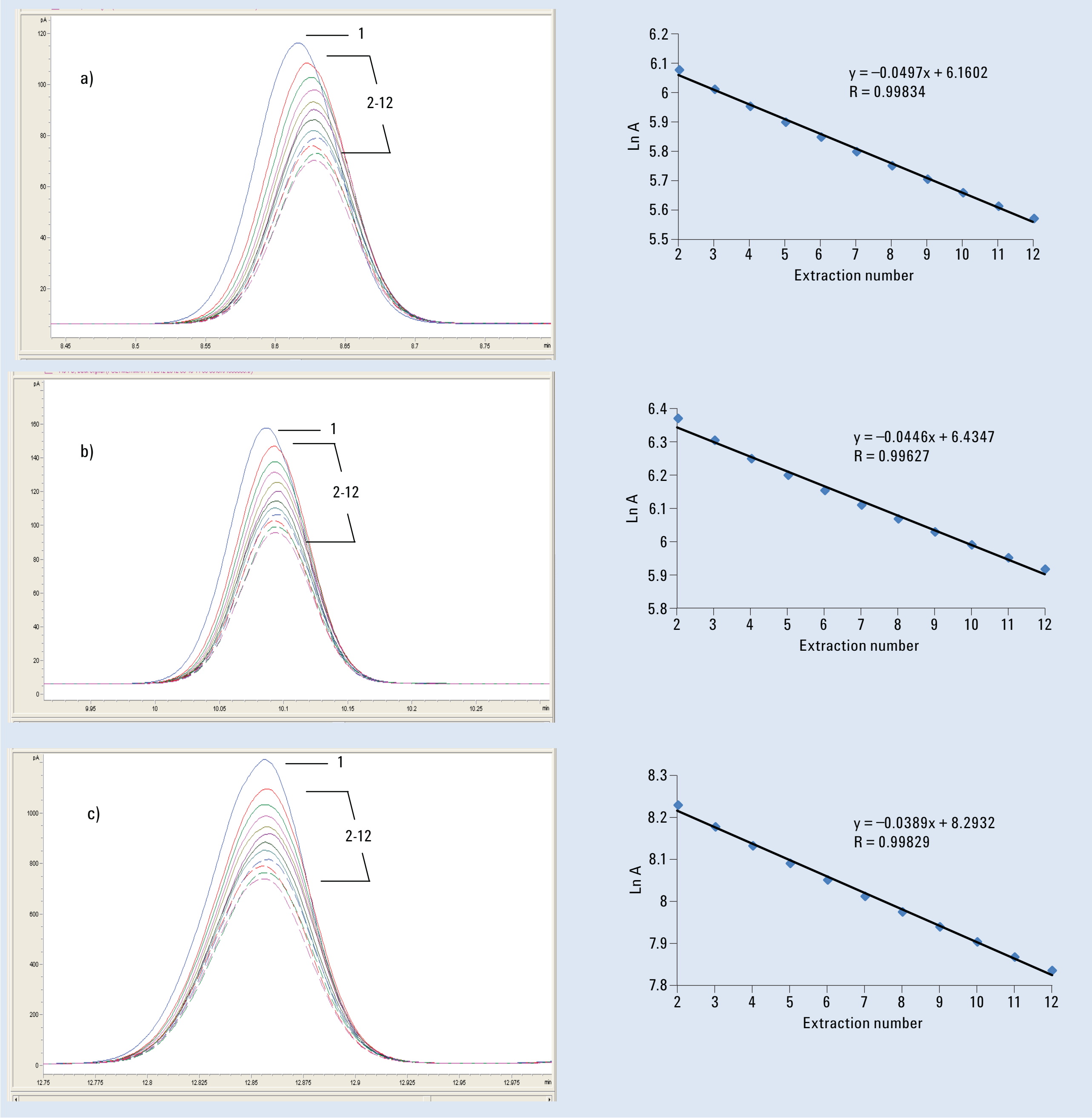

Figure 4. Multiple headspace extraction data for the peak of a) EB, b) cumene, and c) SM in the freeze-ground PS pellets, respectively. Ln A represents Napierian Logarithm of peak area.

MHE Measurements

For quantitative determination, a calibration standard using a matrix identical to the sample is needed. However, it is very difficult to simulate the solid matrix, especially for the polymer sample. The total peak area of the headspace analyte can represent the amount of the analyte in the solid sample after an infinite number of extractions. If the total peak area can be calculated, the matrix effect can be eliminated. The MHE technique, which calculates the total peak area from a limited number of consecutive headspace analysis from the same sample vial, is an ideal way to quantitatively analyze the solid sample. Hence, the freeze-ground sample was carried through the MHE process. The MHE measurements on the PS sample are discussed in Appendix A.

Figure 4 shows the MHE chromatograms for the analytes in the PS sample. The freeze-ground sample was extracted 12 times. A modified MHE calculation template was introduced by Gudat, and so forth [3]. Since the 1st peak is particularly prone to experimental errors [5], it is recommended using data from the 2nd to the last extraction to integrate the linear regression plots. Therefore, the linearity is better than 0.996 for each logarithmic peak area-versus-extraction number plot.

Different headspace gas composition between the 1st equilibrium and the subsequent equilibriums can account for the 1st data point deviation. For the 1st extraction procedure, the main headspace gas matrix is air, so the equilibrium is established between air and the PS powder. After the 1st extraction procedure, helium, the vial pressurization gas, dominates the headspace gas composition, so the subsequent equilibrium takes place in a helium environment.

Complete evaporation of the standard can eliminate the matrix effect. Hence, a 2-µL vapor standard was carried through the MHE process similar to that for the sample described above. Since the standard is vaporized immediately when it is thermostatted under 120 °C, it reaches equilibrium quickly. Therefore, a 30-minute equilibration is long enough to be used for the standard system. Figure 5 shows the MHE results of the standard containing the chromatograms and the corresponding plots. The MHE measurement data of both the sample and the standard are listed in Table 2. Calibrated by the standard with the given amounts, the concentration of each analyte in the PS sample is determined. A gram of this PS contains 28.48 µg EB, 41.32 µg cumene, and 280.37 µg styrene monomer.

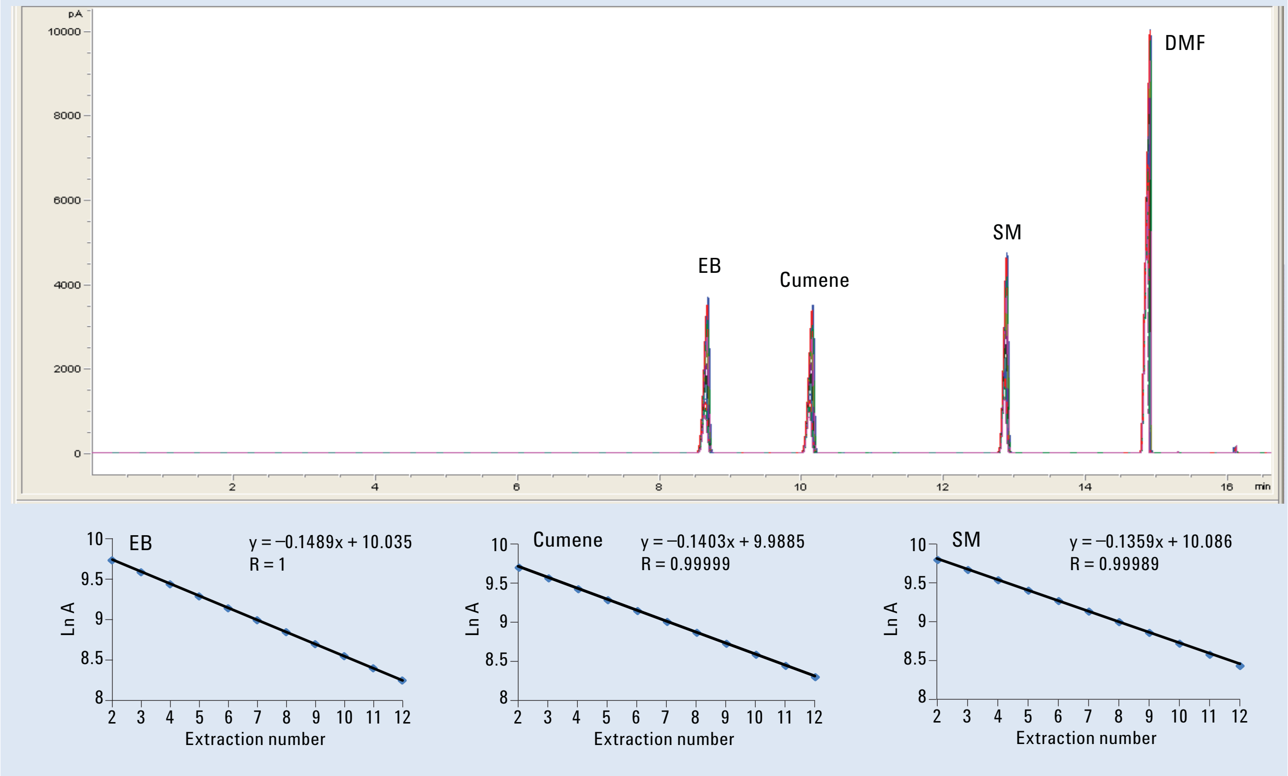

Figure 5. Multiple headspace extraction data of the standard (2 µL DMF solution containing 10% v/v EB, cumene, and SM).

Table 2. MHE Measurement of Residual Monomer Content in the Freeze-Ground PS Pellets

	Sample peak area			Standard peak area		
Extraction number	**EB**	**Cumene**	**SM**	**EB**	**Cumene**	**SM**
1	478.75	639.22	4150.68	18106.14	17164.89	18997.45
2	437.20	585.14	3755.83	16920.50	16384.76	18087.56
3	409.41	547.74	3566.36	14593.47	14291.51	15906.75
4	386.47	518.17	3408.88	12568.54	12428.93	13949.11
5	366.21	492.89	3269.04	10816.05	10797.69	12201.94
6	348.18	470.76	3142.70	9331.66	9397.79	10678.74
7	331.38	450.45	3022.54	8045.16	8170.70	9327.00
8	315.97	432.03	2912.28	6937.82	7107.78	8147.35
9	301.91	415.34	2810.70	5978.39	6174.36	7097.75
10	288.32	399.43	2711.77	5150.82	5362.73	6180.31
11	275.46	384.13	2615.65	4432.28	4649.07	5361.72
12	264.21	371.10	2533.06	3809.31	4023.95	4640.97
Correlation coefficient R^2	0.99668	0.992555	0.996586	0.999994	0.999972	0.999775
Slope q	0.05	0.04	0.04	0.15	0.14	0.14
Intercept B	6.16	6.43	8.29	10.03	9.99	10.09
Correlation coefficient R	0.998338	0.99627	0.998292	0.999997	0.999986	0.999888
Q = exp(-q)	0.95	0.96	0.96	0.86	0.87	0.87
1-Q	0.05	0.04	0.04	0.14	0.13	0.13
total area A	9498.28	14055.93	102700.7	140403.7	142345.9	161352.3
Density, g/mL	--	--	--	0.87	0.86	0.91
2 µL standard containing, µg	--	--	--	173.42	172.40	181.48
Sample mass, µg	0.412					
Concentration in PS µg/g	28.48	41.32	280.37	--	--	--

The MHE measurement calculation template requires at least three data plots, that is, more than three consecutive extractions need to be processed. More data points increases accuracy of the quantitative determination. However, in practice, significant amounts of sample could escape from the system under high temperature when it is thermostatted for long times as discussed above. It is practical to process 6–12 extractions for the quantitative determination. If high accuracy is not required (error margin ~10%), it is acceptable to process eight extractions for this application.

Repeatability and Reproducibility

The PS pellets were freeze-ground into three batches and each batch of the resulting powder was carried through the MHE procedure for six trials. Applying all MHE data to the calculation template (Table 2), calculates the results and RSD's of different trials from the same batch of sample as well as the different batches of sample. The resulting data is shown in Table 3. Good repeatability (RSD better than 2%) and reproducibility (RSD better than 5.6%) demonstrate high reliability of the established MHE method using the 7697A.

Table 3. Analysis of Different Freeze-Grinding Batches of PS Pellets

Sample batch	**Trials**	**EB in PS (µg/g)**	**Cumene in PS (µg/g)**	**SM in PS (µg/g)**
1st batch PS powder	1st trial	28.45	40.16	278.36
	2nd trial	28.50	41.28	280.12
	3rd trial	28.27	40.26	278.76
	4th trial	28.61	41.68	282.34
	5th trial	28.48	41.32	280.37
	6th trial	27.35	39.65	269.09
2nd batch PS powder	1st trial	29.25	40.61	314.00
	2nd trial	29.27	41.20	312.43
	3rd trial	29.02	41.20	309.66
	4th trial	29.32	41.41	313.81
	5th trial	29.14	41.12	312.69
	6th trial	28.84	40.88	308.03
3rd batch PS powder	1st trial	29.27	40.77	313.57
	2nd trial	29.23	40.51	313.14
	3rd trial	29.19	40.84	311.38
	4th trial	29.06	40.39	310.89
	5th trial	29.34	40.96	314.79
	6th trial	28.94	39.98	310.20
Mean (1st batch)		28.28	40.73	278.17
STDev (1st batch)		0.46	0.81	4.67
RSD% (1st batch)		1.64	1.99	1.68
Mean (2nd batch)		29.14	41.07	311.77
STDev (2nd batch)		0.18	0.28	2.40
RSD% (2nd batch)		0.63	0.69	0.77
Mean (3rd batch)		29.17	40.58	312.33
STDev (3rd batch)		0.15	0.36	1.78
RSD% (3rd batch)		0.50	0.89	0.57
Mean (all batches)		28.86	40.79	300.76
STDev (all batches)		0.51	0.55	16.71
RSD% (all batches)		1.77	1.34	5.55

Conclusion

The MHE procedure using the 7697A Headspace Sampler provides an easy to use solution for the quantitative determination of residual monomer and solvents in polystyrene pellets. Polymer pellets require freeze-grinding into a powder before being analyzed by the MHE procedure. This is needed in order to reach equilibrium in a relatively short time frame. The required calibration and calculations can be easily performed using the template. The linearity of the logarithmic peak area-versus-extraction number plots is better than 0.996, illustrating that the freeze-grinding PS pellets is suitable for MHE analysis. High reliability of the solution established here shows good repeatability (better than 2%) for the same sample batch and the good reproducibility (better than 5.6%) for the different sample batches.

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3. A. E. Gudat, S. M. Brillante, Multiple Headspace Extraction-Capillary Gas Chromatography for the Quantitative Determination of Volatiles in Solid Matrices, Agilent Technologies publication 5965-0978E.
4. B. Kolb, L. S. Ettre, Static Headspace-Gas Chromatography-Theory and Pratice, Second Edition, John Wiley & Sons 2006, 171-174.
5. B. Kolb, L. S. Ettre, Static Headspace-Gas Chromatography-Theory and Pratice, Second Edition, John Wiley & Sons 2006, 221-222.

Appendix A

The MHE measurements on the PS sample will be discussed in the following sections. The theory of MHE supports that the decrease in the peak area obtained from MHE is exponential (Equations 1 and 2). If the linearity of Equation 1 is sufficient and quotient Q in Equation 2 is close to constant, the total peak area can also be calculated by a few consecutive measurements, that is, the total peak area can be calculated by the slope of the plot q and the 1st peak area A_1 (Equation 3). After numerous consecutive measurements, the slope q and the intercept B, and A_1 value can be obtained from linear regression equation (Equations 1 and 4). However, since the 1st peak is particularly prone to experimental errors,[i] the calculation equation or method should be optimized. Different headspace gas matrix of the 1st equilibrium and the subsequent equilibrium can probably explain this deviation. For the 1st extraction procedure, the main headspace gas matrix is air, so the equilibrium is between air and the PS powder. After the 1st extraction procedure, helium, the vial pressurization gas, becomes the main headspace gas matrix, so the subsequent equilibrium is between helium and the PS powder.

$$\ln A_i = -q(i-1) + \ln A_i \qquad \text{Equation 1}$$

$$Q = \frac{A_2}{A_1} = \frac{A_3}{A_2} = \frac{A_{i+1}}{A_i} = e^{-q} \qquad \text{Equation 2}$$

$$\sum_{i=1}^{i\to\infty} A_i = \frac{A_1}{1-e^{-q}} = \frac{A_1}{1-Q} \qquad \text{Equation 3}$$

$$\ln A_1 = B - q \qquad \text{Equation 4}$$

q: The slope of the logarithmic peak area-versus-extraction number plot

B: The intercept of the logarithmic peak area-versus-extraction number plot

A: Peak area of the headspace analyte

i: The i^{th} extraction

A modified MHE calculation template was introduced by Gudat, etc.[ii] Use data from the 2nd to the last extraction to integrate the linear regression plots, and then use the modified equation for the total area (Equation 5). This template requires at least three data points. Using this calculation template, every gram of this PS sample remains of 28.48 µg EB, 41.32 µg Cumene, and 280.37 µg SM. The linearity of the logarithmic peak area-versus-extraction number plots (R > 0.996) is better than that using the all 12 data plots, since the 1st peak data which is slightly derived from the linear trend is not included. To achieve high accuracy in this application, use this template for all the samples.

$$\sum_{i=1}^{i\to\infty} A_i = A_1 + \frac{A_2}{1-Q} \qquad \text{Equation 5}$$

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[i] B. Kolb, L. S. Ettre, Static Headspace-Gas Chromatography-Theory and Pratice, Second Edition, John Wiley & Sons 2006, 221-222.

[ii] A. E. Gudat, S. M. Brillante, Multiple Headspace Extraction-Capillary Gas Chromatography for the Quantitative Determination of Volatiles in Solid Matrices, Agilent Technologies publication 5965-0978E.

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Printed in the USA
August 10, 2012
5991-0974EN

Agilent Technologies