Residual Monomers in Polymers by Multiple Headspace Extraction using the Agilent 7697A Headspace Sampler

Application Note

Petrochemicals

Author

Roger L Firor
Agilent Technologies, Inc.
Wilmington, DE 19808

Abstract

Residual monomers are determined in a series of polymers including poly methyl methacrylate, poly acrylic, styrene co-methyl methacrylate, and styrene co-butadiene. Minimal sample preparation is required by using the well established technique of Multiple Headspace Extraction (MHE). The instrumental configuration consists of the Agilent 7697A Headspace Sampler interfaced to an Agilent 7890 Series GC with split/splitless inlet. An Agilent 5975C MSD was used for detection and confirmation.

Introduction

Residual monomer determination in polymers is an essential measurement in polymer production and quality control. From a sample preparation point of view, headspace is the method of choice. Sample dissolution is not required. Simply weigh the sample and place it in a 10 or 20 mL vial. In MHE a series of multiple extractions, each with decreasing analyte concentration, is used to determine the amount of analyte present in a complex matrix where calibration standards in that given matrix is not feasible. An external standard of the analyte is prepared for comparison to the real sample and for determination of a response factor. Cryo milling may be advantageous to produce a small homogeneous particle size. Cryo milling was not used in this work, and, as a result, longer headspace equilibration times were employed. Multiple Headspace Extraction has been used for the determination of leachable compounds in packaging materials in previously reported work [1].

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Experimental

The system configuration is shown in Figure 1. The headspace sampler is interfaced through the inlet septum using 0.45 mm ID deactivated fused silica. Headspace sampling vial pressure is controlled by a PCM module on-board the 7697A. Helium carrier is controlled by a 7890 s/s inlet EPC interfaced to the headspace sampler. The column used was a HP-FFAP, 30 m × 0.25 mm, 0.25 µm, part number 19091F-433.

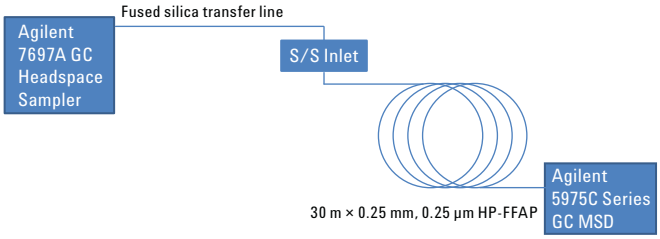


Figure 1. System diagram for MHE experiments.

In Tables 1 and 2, headspace sampling and GC/MSD parameters, respectively are shown. Typically, 0.02 to 0.09 grams of polymer was placed in 10-mL vials for analysis. PTFE lined septa with aluminum caps were used to seal the vials. Before sealing, the vials were purged with nitrogen. Pure monomers were purchased from Sigma-Aldrich. These were analyzed by full evaporation in 10-mL headspace vials as external standards. Typically, 0.1 µL of the pure monomer was injected directly into a sealed headspace vial. A regression analysis of the pure monomers using MHE is required as part of the calculations used to determine residual monomer amounts in the polymers or resins.

Table 1. Headspace Sampling Parameters for Monomer Determinations

Parameter	Poly acrylic	Poly methyl methacrylate	Styrene co-butadiene	Styrene co-methyl methacrylate
HS oven equil. temp., °C	200	75	120	120
Loop temp., °C	200	75	120	120
Transfer line temp., °C	210	85	130	130
HS equil. time, min	35	60	60	60
Vial size, mL	10	10	10	10
Vial shaking	Level 1	Level 1	Level 1	Level 1
Fill mode	To pressure	To pressure	To pressure	To pressure
Fill pressure	15 psi	15 psi	15 psi	15 psi
Fill time	0.1 min	0.1 min	0.1 min	0.1 min
Loop ramp rate	20 psi/min	20 psi/min	20 psi/min	20 psi/min
Loop final pressure	0 psi	2 psi	2 psi	2 psi
Loop equil. time	0.05 min	0.05 min	0.05 min	0.05 min
Extraction mode	MHE	MHE	MHE	MHE
Post Injection purge	100 mL/min, 5 min.	100 mL/min, 5 min.	100 mL/min, 5 min.	100 mL/min, 5 min.
Vent after last extract.	Yes	Yes	Yes	Yes

Table 2. Agilent 7890 Series GC and Agilent 5975C Series GC/MSD Parameters

Parameter	Poly acrylic	Poly methylmethacrylate	Styrene co-butadiene	Styrene co-methylmethacrylate
Inlet	Split/splitless	Split/splitless	Split/splitless	Split/splitless
HS interface	Fused silica through septum	Fused silica through septum	Fused silica through septum	Fused silica through septum
Liner #5190-2292	Ultra Inert, single taper	Ultra Inert, single taper	Ultra Inert, single taper	Ultra Inert, single taper
Inlet temperature	220 °C	135 °C	135 °C	135 °C
Split ratio	100 to 1	100 to 1	100 to 1	100 to 1
HS sample loop size	1 mL	1 mL	1 mL	1 mL
5975C scan	19–250 amu	19–250 amu	19–250 amu	19–250 amu
MS source	320 °C	320 °C	320 °C	320 °C
MS quad	200 °C	200 °C	200 °C	200 °C
Agilent 7890 column	30 m × 0.25 mm, 0.25 µm HP-FFAP	30 m × 0.25 mm, 0.25 µm HP-FFAP	30 m × 0.25 mm, 0.25 µm HP-FFAP	30 m × 0.25 mm, 0.25 µm HP-FFAP

Discussion

The popularity of static headspace analysis is due in large part to the simple and fast sample preparation that is adequate for most materials. MHE is somewhat more involved compared to standard headspace analysis in that a standard of the analyte that requires quantitative analysis in a given matrix must be analyzed in pure form using a full evaporation technique. MHE should be used when a complex matrix is encountered and a standard in that given matrix cannot be reliably made or purchased. The MHE technique is matrix independent and therefore the standard and analyte are not required to be in the same matrix.

In this work, six extractions each of standard and polymer sample were made. The vial remains in the oven between extractions. Venting of the vial between extractions was not performed; vial venting occurred only after the last extraction. With each extraction, the peak area should show an exponential decrease. Because a cryo mill was not used, particle sizes were larger than ideal. As a result, peak area of the first headspace extraction from the polymeric material was typically low by a few percent from examination of an initial exponential plot of area versus the extraction number. Longer headspace oven sample equilibration times help, to some extent, minimize the effect of a higher than ideal surface area to volume ratio of the particles. When this is seen, a modification of the equation for total peak area (Appendix) can be used as given below.

Total peak area = $A_1 + A_2 / (1 - e^{-k})$

The second part of this equation calculates the total peak area for the second through last extraction (6th in this work). In the semi-logarithmic plots presented in this work, the first extraction point was corrected so that it fell onto the regression line calculated from the 2nd to 6th extractions.

All polymers in this study were equilibrated above their glass transition temperature regions with the exception of poly acrylic acid (T*g* = 102 °C) and poly methyl methyacrylate (approximately T*g* = 105 °C).

MHE calculations are made using an Excel spreadsheet. Inputs for the user consists of the following:

1. Areas from each extraction of the pure monomer
2. Areas of each extraction of the identified monomer peak in the polymer sample
3. Amount of the pure monomer in the headspace vial
4. Weight of the polymer sample in the vial

A total of six extractions from each vial were made. In this spreadsheet, the LOGEST array command is used to calculate the regression statistics. This command calculates an exponential curve from the MHE data. A semi-logarithmic plot of area versus the extraction number is made to visually check the results. Regression statistics from the exponential curve fit is shown on the right side of the Excel spreadsheet for both standard and sample (see Tables 4 to 7).

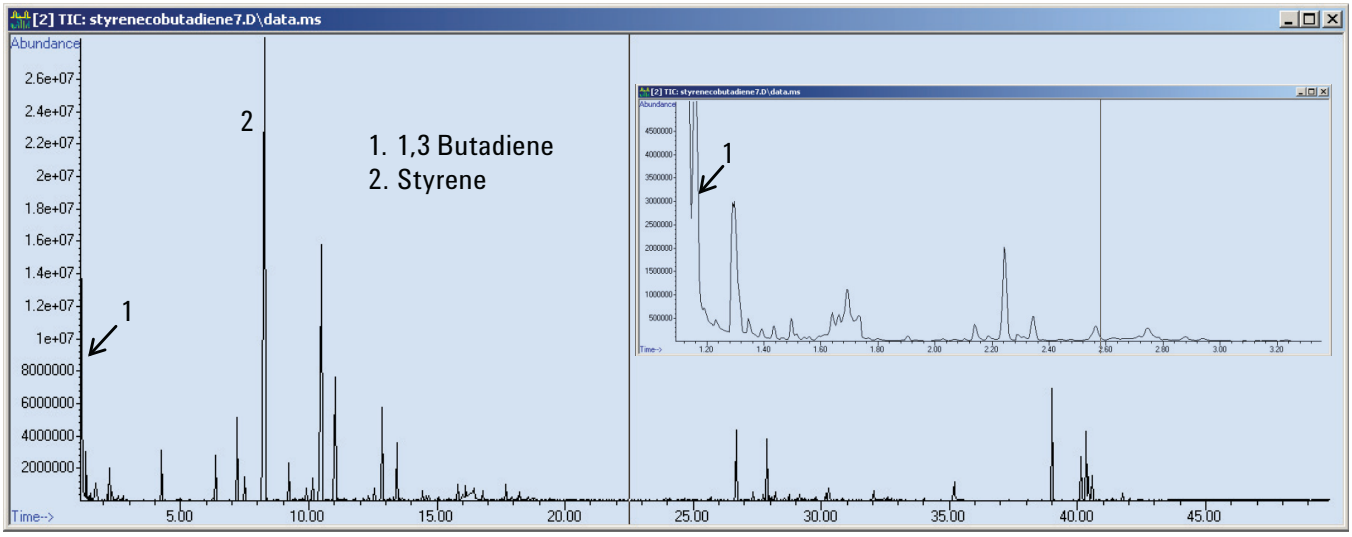


Figure 2. TIC for the analysis of Styrene cobutadiene.

Table 3 maps the four polymers studied in this work to their respective residual monomer calculations and semi log plots of peak area versus the extraction number. The TIC for styrene co-butadiene polymer is shown in Figure 2. 1, 3 Butadiene elutes at approximately 1.15 minutes. Extracted ion confirmation for 1, 3 butadiene is seen in Figure 3. For the sample, only calculations for styrene residual monomer is shown in Table 6.

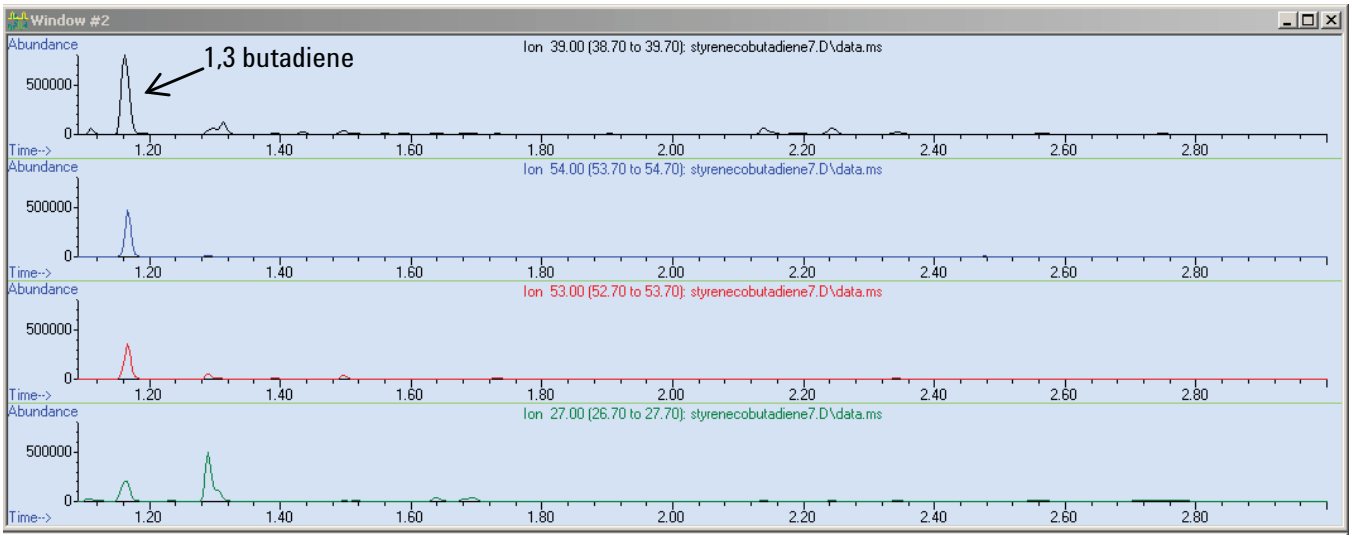


Figure 3. Extracted ion chromatograms for 1,3 butadiene at a retention time 1.15 minutes.

Table 3. Figure and Table Assignments for the Four Studied Polymers

Polymer	MHE calculations	Plot - standard	Plot - residual monomer
Poly acrylic	Table 4	Figure 4a	Figure 4b
Poly methyl methacrylate	Table 5	Figure 5a	Figure 5b
Styrene co-butadiene	Table 6	Figure 6a	Figure 6b
Styrene co-methyl methacrylate	Table 7	Figures 7a, 7c	Figures 7b, 7d

Table 4. MHE Calculations for Poly Acrylic Acid

Extraction no.	Sample poly acrylic	Standard acrylic acid
1	17900000	73398095
2	13356229	37321132
3	9537816	19097365
4	6887156	9701384
5	4913843	4761376
6	3380211	2400283
Regression correlation	0.999404389	0.999870049
Slope (k) = ln(E2 or E9)	–0.324781342	–0.681801371
Total area = (A(1)/(1-e(-k)))	64547619	148490529
Analyte in vial (mg)	0.003764431	0.00866
Sample amt (mg) in vial	345	
Concentration (ppm) in wt/wt	10.91	
Concentration (wt-%)=ppm * (10 ^ -4)	0.00109	

Standard	Stats
0.505705	1.46E+08
0.004488	0.014884
0.99987	0.014191
23082.55	3
4.648531	0.000604

Sample	Stats
0.722685	25156003
0.004578	0.015182
0.999404	0.014476
5033.84	3
1.054829	0.000629

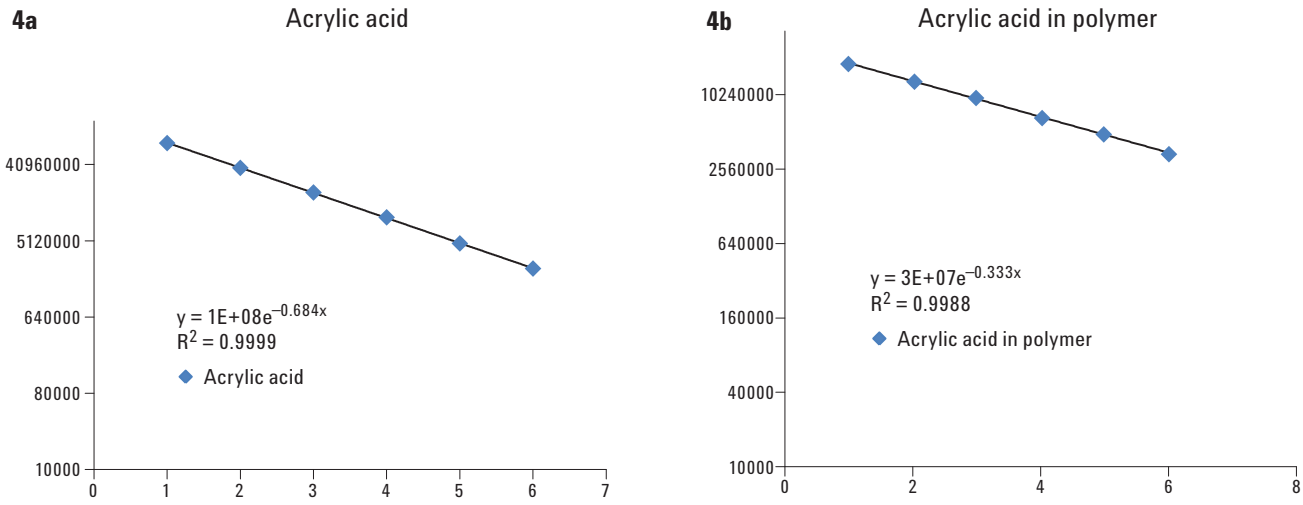


Figure 4. Regression plots for Acrylic acid standard and residual monomer.

Table 5. MHE Calculations for Poly Methyl Methacrylate

Extraction no.	Sample (PMMA)	Standard (methyl methacrylate)
1	12206500	120157970
2	11028812	69114398
3	9990828	39474218
4	8718874	22364001
5	7634967	12808405
6	6642230	7350760
Regression correlation	0.994725176	0.999987345
Slope (k)	–0.117348098	–0.56057219
Total area = (A(1)/(1-e(-k)))	110242171	280011696
Analyte in vial (mg)	0.036850844	0.0936
Sample amt (mg) in vial	55	
Concentration (ppm) in wt/wt	670	
Concentration (wt-%)=ppm * (10 ^ –4)	0.067	

Standard	Stats
0.571287	2.11E+08
0.000996	0.003878
0.999987	0.004166
316068.5	4
5.485311	6.94E-05

Sample	Stats
0.884842	14071909
0.004455	0.017348
0.994725	0.018635
754.3192	4
0.261948	0.001389

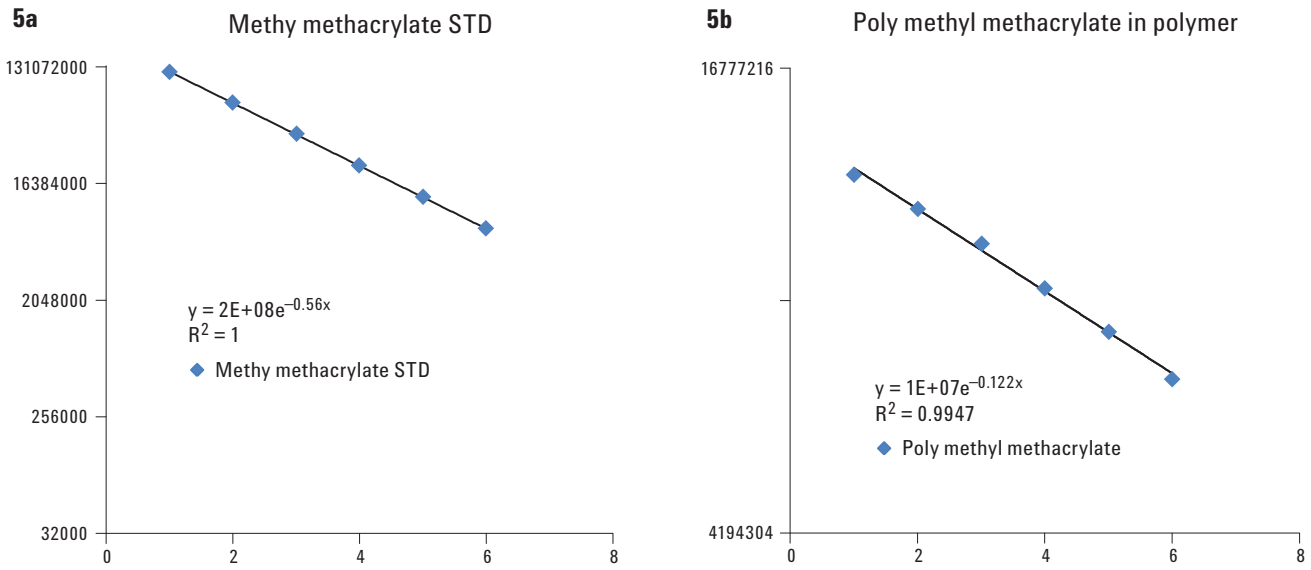


Figure 5. Regression plots for methy methacrylate standard and residual monomer.

Table 6. MHE Calculations for Styrene co-butadiene

Extraction no.	Sample (styrene)	Standard (styrene)
1	2950000	242387425
2	2660000	135439623
3	2443870	76792496
4	2236942	43866719
5	2062892	25754414
6	1881711	15293635
Regression correlation (E4 or E11)	0.998100414	0.999734755
Slope (k) = ln(E2 or E9)	–0.088860895	–0.561123272
Total area = (A(1)/(1-e(-k)))	34694797	564437006
Analyte in vial (mg)	0.005587439	0.0909
Sample amt (mg) in vial	92	
Concentration (ppm) in wt/wt	60.73	
Concentration (wt-%) = ppm * (10 ^ -4)	0.00607	

Standard	Stats
0.570568	4.19E+08
0.005277	0.017501
0.999735	0.016687
11307.31	3
3.148593	0.000835

Sample	Stats
0.914973	3200059
0.002238	0.007423
0.9981	0.007078
1576.292	3
0.078963	0.00015

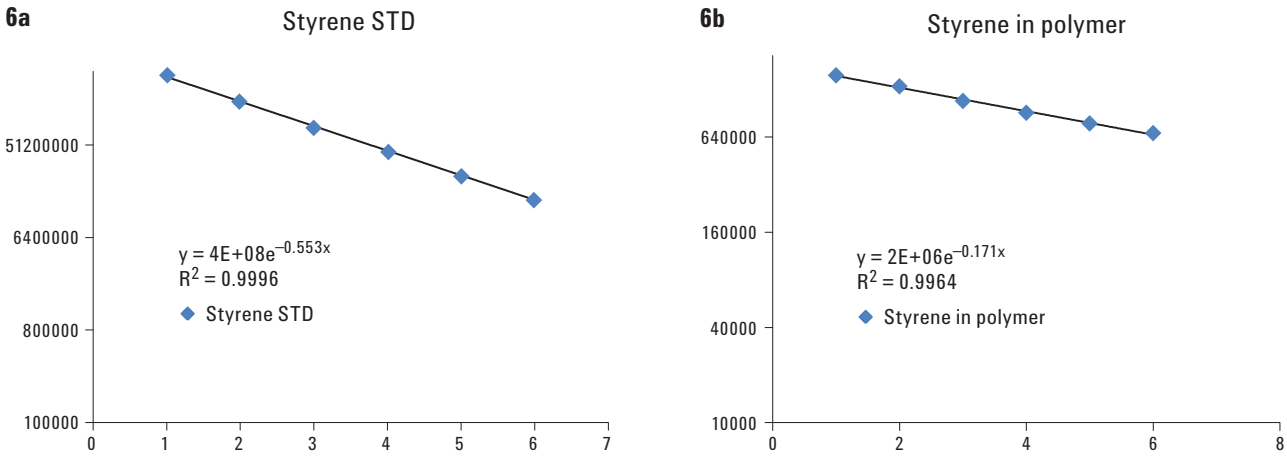


Figure 6. Regression plots for styrene standard and styrene monomer.

Table 7. MHE Calculations for Styrene co-methyl Methacrylate

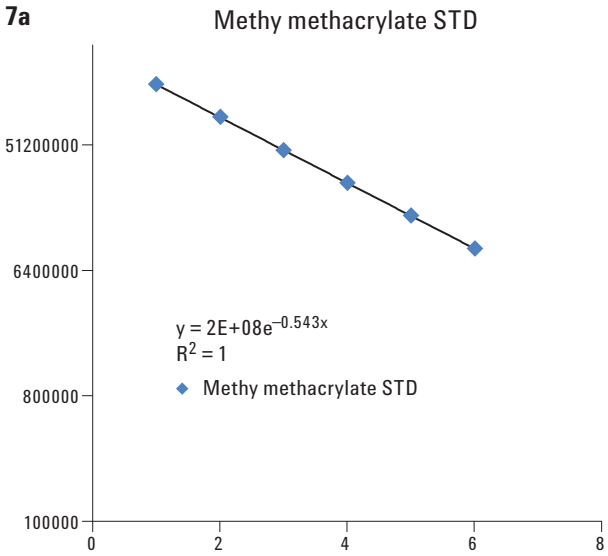
Extraction no.	Methyl methacrylate sample	Styrene sample	Methyl methacrylate STD	Styrene STD
1	1809940	1604252	139277886	242387425
2	1544357	1341511	80950927	135439623
3	1308275	1085316	46957098	76792496
4	1120663	912787	27223930	43866719
5	953713	778087	15802381	25754414
6	814080	676849	9227813	15293635

Methyl methacrylate stats sample		Styrene stats sample	
0.852247	2122259.1	0.839527	1880461
0.000579	0.002255	0.005838	0.022735
0.999948	0.0024222	0.995564	0.024422
76241.7	4	897.7288	4
0.447319	2.347E-05	0.535428	0.002386

	Methyl methacrylate	Methyl methacrylate STD
Regression correlation ()	0.999947538	0.999996157
Slope (k) = ln()	–0.159878316	–0.543355164
Ttotal area = (A(1)/(1-e(-k)))	12249808.6	332243943.1
Analyte in vial (mg)	0.003524765	0.0956
Sample amt (mg) in vial	17	
Concentration (ppm) in wt/wt	207.34	
Concentration (wt-%) = ppm * (10 ^ -4)	0.02073	

methyl methacrylate stats STD		Styrene stats STD	
0.580796	239706284	0.575218	4.11E+08
0.000533	0.0020742	0.005822	0.022674
0.999996	0.002228	0.999557	0.024356
1040803	4	9022.019	4
5.16661	1.986E-05	5.351776	0.002373

	Styrene	Styrene STD
Regression correlation (E4 or E11)	0.995564077	0.999556837
Slope (k) = ln(E2 or E9)	–0.174916797	–0.553006115
Total area = (A(1)/(1-e(-k)))	9997013.166	570616095.6
Analyte in vial (mg)	0.001592539	0.0909
Sample amt (mg) in vial	17	
Concentration (ppm) in wt/wt	93.68	
Concentration (wt-%) = ppm * (10 ^ -4)	0.00937	



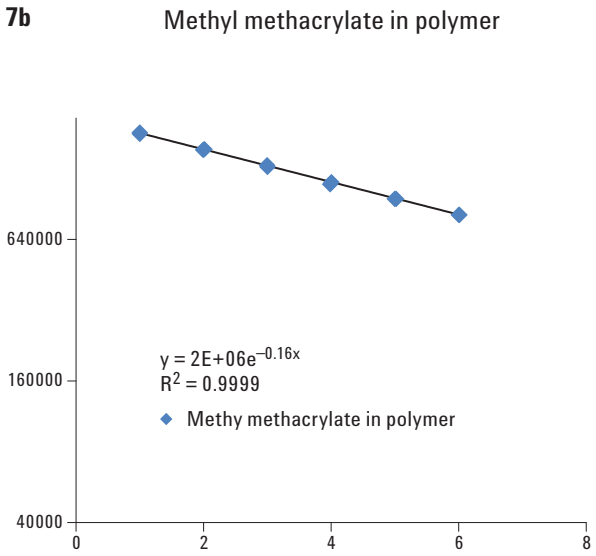
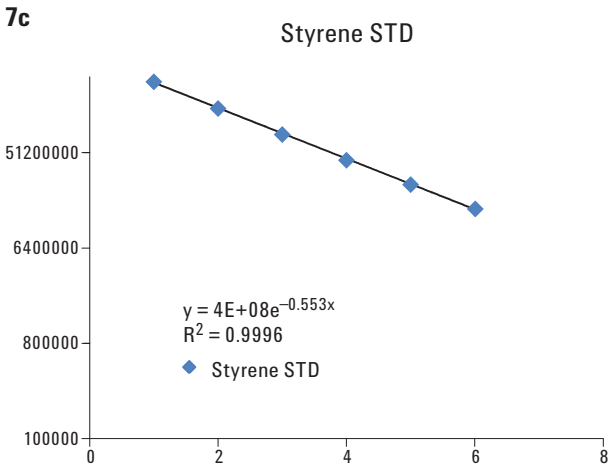


Figure 7a and 7b. *Regression plots for Methyl methacrylate standard and residual monomer.*



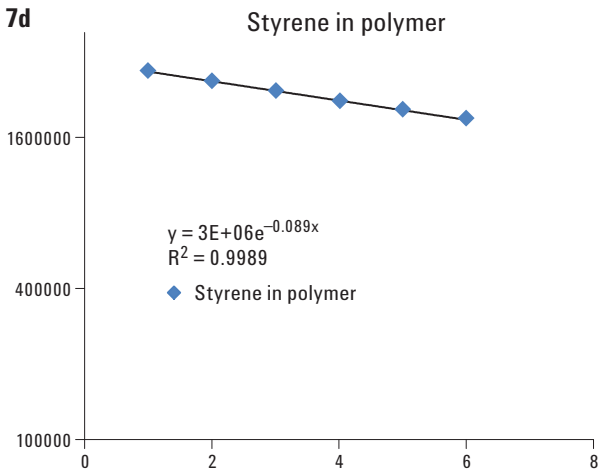


Figure 7c and 7d. *Regression plots for Styrene standard and residual monomer.*

Conclusions

MHE is a relatively easy technique for the determination of residual monomer content. Reducing the levels of residual monomer is highly desirable among polymer producers. Pricing, commercial value, and material properties are affected by the level of monomers in the final product. Safety concerns are also relevant as long-term exposure in the manufacturing environment may need to be considered. The system described here should assist in the study of monomer reducing techniques to quickly check their effectiveness.

Appendix

In classical MHE, the sample is equilibrated at a given temperature for a specified time in the headspace oven prior to sampling. The cycle time should be equal to or shorter than the vial equilibration time so that each extraction experiences the same heating time. An exponential decrease in peak area should be observed. An infinite number of extractions to remove all of a given analyte from the matrix will yield the total amount of analyte present as shown in equation (1)

$$\text{Total peak area} = \sum_{n=1}^{\infty} A_n = A_1+A_2+A_3+ \ldots + A_n \quad (1)$$

Because a large number of extractions are impractical, first order kinetics is assumed and it follows that:

$-dc/dt = kc$, (2) which integrated becomes $c = c_0\, e^{-kt}$ (3)

If the gas extraction is carried out carefully and for equal times, and equal portions of the headspace are introduced into the GC, then the peak area of a given analyte will follow the same exponential rule since at equilibrium the distribution coefficient K_d is a constant, $K_d = c_c/c_g$ where c_c and c_g are the concentrations of the analyte in the condensed and gas phase, respectively. For a discontinuous or stepwise gas extraction performed at equal time intervals, equation 3 becomes:

$A_n = A_1 e^{(1-n)k}$ (4)
A_n = peak area of nth injection,
A_1 = peak area of 1st injection

For an infinitely large number of extractions, the total peak area for an analyte becomes

$$\sum_{n=1}^{\infty} A_n = A_1(1 + e^{-k} + e^{-2k} + e^{-3k} + \cdots) \quad (5)$$

This decreasing geometric progression in equation 5 converges to

$$\sum_{n=1}^{\infty} A_n = A_1/(1 - e^{-k}) \quad (6)$$

Therefore a complete gas extraction is not necessary to obtain the total peak area; only values for A_1 and K are needed. The A_1 value is the measured peak area of the analyte after the 1st extraction and K is the slope obtained from a regression analysis (equation 4).

$$\ln A_n = \ln A_1 + (1 - n)K \quad (7)$$

Once the total area of the analyte in the matrix sample is know, it follows that:

Calculations, T area = total area, and Am = amount

$$\text{T area}_{\text{analyte}}/\text{Am}_{\text{analyte}} = \text{T area}_{\text{standard}}/\text{Am}_{\text{standard}}$$

or

$$\text{Am}_{\text{analyte}} = \text{T Area}_{\text{analyte}}/\text{T Area}_{\text{standard}} * \text{Am}_{\text{standard}}$$

Reference

Roger L Firor and Albert E. Gudat, “The determination of extractables and leachables in pharmaceutical packaging materials using headspace GC/MS”, Application Note 5989-5494EN, 2006.

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