

Gas Chromatography/
Mass Spectrometry

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Determination of Monomers in Polymers by Multiple Headspace Extraction – GC/MS

Abstract

Polymer production and quality control (QC) requires a variety of analytical testing – one common QC test is the analysis of residual monomers in the final polymer material. This analysis is well suited for headspace sampling because headspace eliminates the sample preparation. The sample is analyzed directly with no need to dissolve the polymer.

The analysis of solid samples with headspace does require compensation for the sample matrix, as calibration standards cannot be created with the same matrix interactions. Multiple headspace extraction (MHE) is a technique to exhaustively extract a sample and calculate the amount of analyte by comparison to an external standard.

This application note will discuss the testing of polymers for residual monomers by MHE-GC/MS. The polymers tested in this application are used for the manufacturing of corrective eyeglass lenses. This material is monitored for acrylic acids, such as methylmethacrylic acid methyl ester (MMA).

Introduction

Multiple headspace extraction is used because it is a technique to quantify samples in a solid or difficult matrix without matrix matching the calibration standards. The standard is analyzed, without matrix, in a total evaporation headspace with MHE, determining a response factor (Figure 1, Page 3). MHE is an option the user selects in the method which initiates a specific extraction process in the instrument.

In MHE, the HS method follows the standard extraction steps in the first round of extraction. The vial is equilibrated, pressurized, an injection is made, and the vial is vented. Following the first round of extraction, the MHE method differs from a standard HS method – rather than ejecting the vial after venting, the vial remains into the headspace oven, it is re-equilibrated, and the injection process repeated. The instrument can run this process unattended for the number of times, up to nine, that the operator selects in the method.

With this technique, the sample is extracted until nothing remains – this data is used to determine the total amount of analyte within the sample and the rate of extraction specific to the sample matrix. This data is input into a report template (Figure 2, Page 3) and used to calculate the amount of analyte in each sample of similar matrix.

Experimental

Headspace sample preparation is simple. A sample of known weight is placed into a headspace vial, then the vial is crimped and placed into the PerkinElmer® TurboMatrix™ HS-40 Headspace Sampler (HS). The headspace method was created with the parameters listed in Table 1. The conditions used for the PerkinElmer Clarus® 600 GC/MS system are presented in Tables 2 and 3. A PerkinElmer Elite™-5MS column achieved the necessary separation, while the Clarus 600 MS operated in full-scan mode, providing both qualitative and quantitative data.

Table 1. Headspace Conditions Used in Analysis of Monomers in Polymers.

Headspace Unit:	PerkinElmer TurboMatrix HS-40
Headspace Mode:	MHE
Oven Temperature:	180 °C
Needle Temperature:	185 °C
Transfer Line Temperature:	190 °C
Thermostat Time:	30 min
Vial Pressurization Time:	2 min
Withdraw Time:	0.2 min
Injection Time:	0.03 min
Column Pressure:	120 kPa
Injection Pressure:	160 kPa
Vial Pressure:	160 kPa
Vial Vent:	On
Transfer Line:	Fused Silica (0.32 mm)

Table 2. GC Conditions Used in Analysis of Monomers in Polymers.

Gas Chromatograph:	PerkinElmer Clarus 600 GC												
Analytical Column:	PerkinElmer Elite-5MS (30 m x 0.25 mm x 0.25 µm)												
Injection Port Type:	Programmable Split/Splitless												
Injector Temperature:	200 °C												
Injection Type:	HS-Control												
Carrier Gas Type:	Helium												
Carrier Gas Program:	80 kPa Constant												
Oven Program:	<table><thead><tr><th>Temp.</th><th>Hold Time</th><th>Rate</th></tr></thead><tbody><tr><td>40 °C</td><td>4 min</td><td>5 °C/min</td></tr><tr><td>160 °C</td><td>5 min</td><td>20 °C/min</td></tr><tr><td>260 °C</td><td>2 min</td><td>End</td></tr></tbody></table>	Temp.	Hold Time	Rate	40 °C	4 min	5 °C/min	160 °C	5 min	20 °C/min	260 °C	2 min	End
Temp.	Hold Time	Rate											
40 °C	4 min	5 °C/min											
160 °C	5 min	20 °C/min											
260 °C	2 min	End											

Table 3. MS Conditions Used in Analysis of Monomers in Polymers.

Mass Spectrometer:	PerkinElmer Clarus 600 T MS
GC Inlet Line Temperature:	180 °C
Ion Source Temperature:	200 °C
Function Type:	Full Scan
Full-Scan Range:	<i>m/z</i> 45-350
Full-Scan Time:	0.35 sec
InterScan Delay:	0.05 sec
Solvent Delay:	0 min

Results

MHE is used because it is a technique to quantify samples in a solid or difficult matrix without matrix matching the calibration standards. The standard is analyzed, without matrix, in a total evaporation headspace with MHE, determining a response factor (Figure 1).

In this case, 1 µL of MMA was vaporized in the vial; the amount of 935 µg was calculated with the known density. The sample was exhaustively extracted over several MHE steps, in this case 5.

A sample, 0.688 g, of polymethyl methacrylate (PMMA) was placed into a headspace vial and analyzed by MHE. The total peak area of the analyte was calculated and the concentration of analyte in the sample determined by comparison to this response factor. The necessary calculations for MHE are completed using an Excel® macro available from PerkinElmer and pictured in Figure 2. The sample was determined to have 1726 µg/kg of MMA.

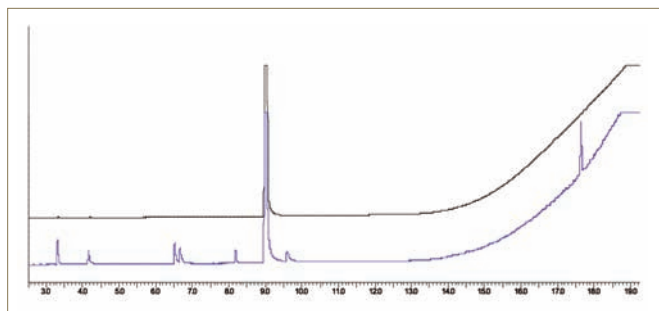


Figure 1. Chromatogram of a MMA calibration standard by total vaporization (top); and chromatogram of the MMA in a PMMA sample (bottom).

In this application, two samples of polycarbonate lenses were analyzed, both demonstrating MMA peaks. In routine analysis of the same polymer, in this case polycarbonate, the number of extraction steps can be reduced and the formula from a previous sample used. This is an acceptable practice, because the matrix will behave in a predictable fashion under specified experimental conditions. Reducing the number of extraction steps speeds up the analytical cycle time and continues to provide the accurate calibration of exhaustive extraction. Two samples of eye-glass lenses were analyzed (Figures 3 and 4) both containing MMA.

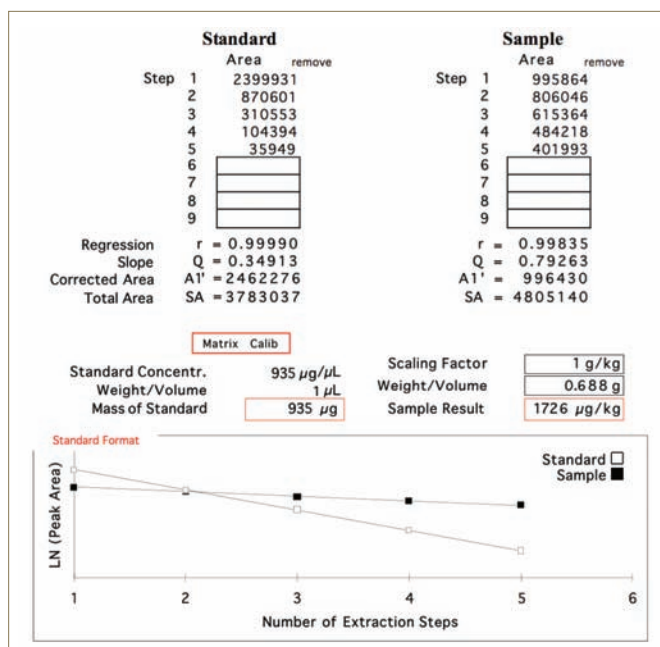


Figure 2. Example of the Excel®-based macro used to calculate concentration of MMA in MHE.

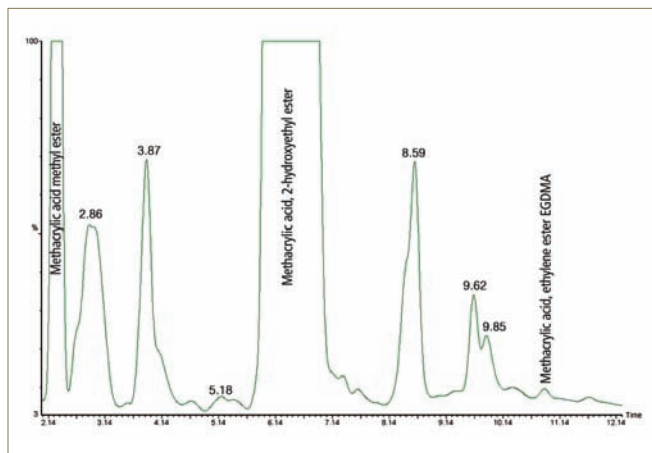


Figure 3. Chromatogram of Sample 1, demonstrating methacrylic acid methyl ester, methacrylic acid-2-hydroxyethyl ester, and methacrylic acid ethylene ester.

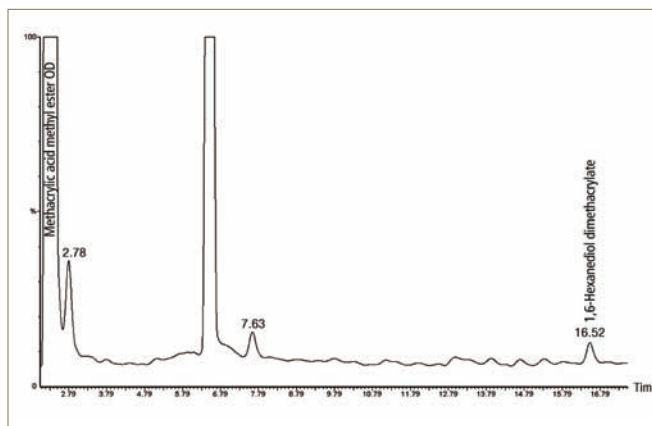


Figure 4. Chromatogram of Sample 2, demonstrating methacrylic acid methyl ester and 1,6-hexanediol dimethacrylate.

Conclusion

This paper has shown that multiple headspace extraction is a suitable and effective technique for the analysis of polymeric materials for residual monomers. The headspace sample introduction reduces sample preparation to an absolute minimum and solvent use is eliminated. Complicated matrix matching of calibration standards was replaced with an automated multiple headspace extraction technique. Additionally, mass spectral characteristics allowed for the identification of each analyte. Several samples were analyzed qualitatively and quantitatively here with a simple and effective headspace-GC/MS technique.