©Cambridge Polymer Group, Inc.(2014). All rights reserved

Summary
This application note describes residual methyl methacrylate monomer analysis in polymethyl methacrylate-based bone cement using head space gas chromatography-mass spectroscopy (GC-MS).

Background
The orthopedic and dental community often use polymethyl methacrylate (PMMA) resins as grout, fillers, and cements. Usually supplied as a two component package, with one package containing pre-polymerized PMMA powder and the second package containing liquid methyl methacrylate monomer, the two components are mixed in the operating theater or dental office and are cured in their application area. For the dental community, curing is normally achieved through exposure to ultraviolet light, while in the orthopedic industry, free radical initiators in the powder package (normally benzoyl peroxide) initiate the free radical polymerization process. However, some methyl methacrylate may remain unpolymerized which could potentially leach out of the cured cement. For this reason, manufacturers and regulators are interested in knowing the amount of monomer that could potentially leach out of the cured PMMA.

Headspace GC/MS analysis is perfectly suited to measuring volatile and semi-volatile components of polymers and other compounds. Compounds that may be measured by this technique include residual solvents or residual monomers that are strictly regulated and must be present below certain concentrations for health and safety reasons.

In headspace GC/MS, a solid or liquid sample is placed in a sealed vial and heated. As the sample equilibrates at the target temperature, the volatile compounds present in the sample will partition between the sample phase and the gas phase within the vial. After equilibration, a heated, gas-tight syringe is used to sample the headspace in the vial and then inject the gas into a gas chromatograph equipped with a mass spectrometer. The gas chromatogram (GC) separates the compound mixture according to volatility, boiling point, and polarity, while the mass spectrometer ionizes the compounds and measures the mass-to-charge ratio of the ion fragments. The measured mass spectra are compared against the NIST/EPA/NIH Mass Spectral Library for compound identification.

Procedure
Figure 1 shows the headspace GC/MS analysis of commercial poly (methyl methacrylate) bone cement after curing. The dominant compound present in the headspace is the residual, unreacted monomer methyl methacrylate, present in more than 99% of the volatile material based on peak height. Trace quantities of other identified compounds are shown in Table 1. Match qualities above 80 are very strong and indicate a very close spectral match between the unknown peak and the NIST library entry. Definitive identification, however, requires comparison against analytical standards.

For each of the compounds identified, quantitation may be performed by preparing headspace calibration curves using reference standards. Using selective ion monitoring techniques, the limit of quantitation for most compounds is approximately 100 ppb.

Following the procedure described in ASTM F451, quantification of eluted methyl methacrylate monomer as a function of either cure time or days following cure can be monitored with this technique.

Table 1: Compounds identified in PMMA bone cement by headspace GC/MS.

Retention Time [min]	Compound	Peak percentage [%]
2.013	Methyl Propionate	<1
2.244	Benzene	<1
2.667	Methyl Methacrylate	>99
13.064	Benzenamine, N,N,4-trimethyl	<1

©Cambridge Polymer Group, Inc.(2014). All rights reserved

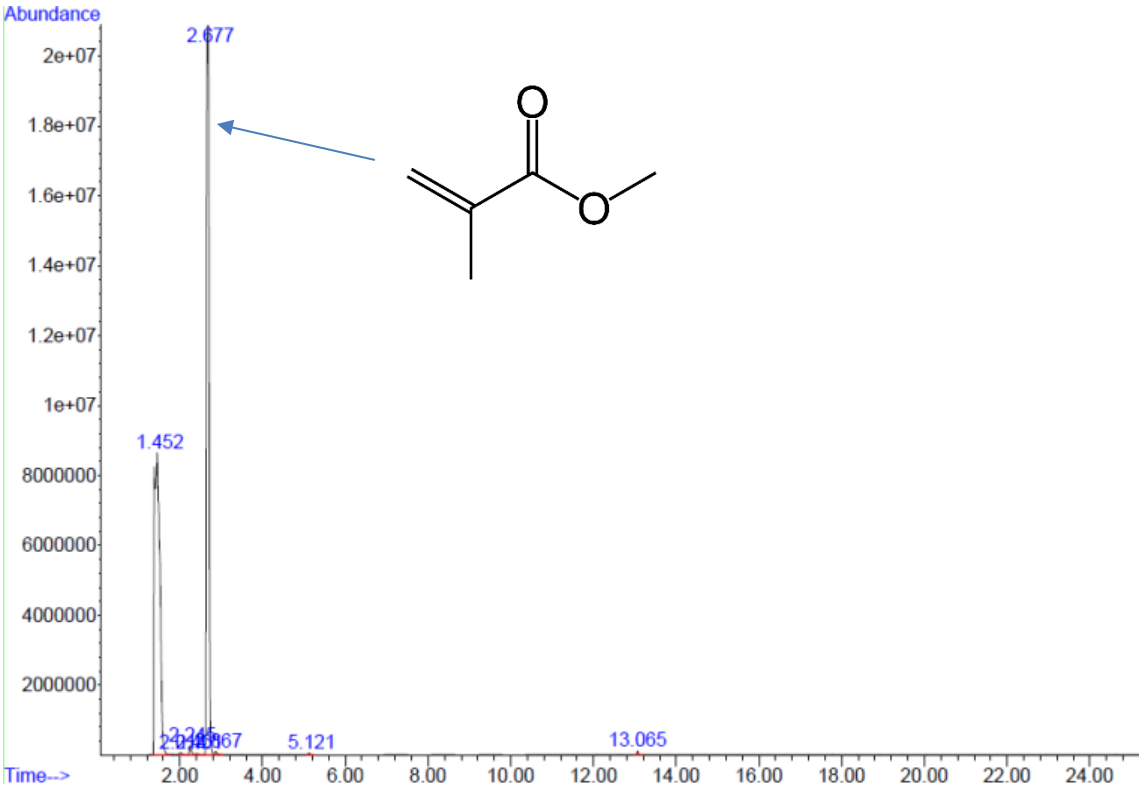

Figure 1: Total ion chromatogram of PMMA by headspace GC/MS.

Other applications of headspace GC/MS include:

- Polymer identification/deformulation.
- Residual monomer analysis of other polymers such as PLA, polyacrylamide, acrylics, styrenes, PVC
- Tracking curing dynamics by sampling the headspace at multiple time points.