CASE STUDY
Multiple Headspace Extraction Gas Chromatography Mass Spectroscopy

OBJECTIVE

The objective of this work is to demonstrate the use of multiple headspace extraction for the quantitative determination of organic volatiles in solid matrices. Specifically, the residual styrene content in a sample of polystyrene foam is determined.

ANALYTICAL STRATEGY

Multiple Headspace Extraction GCMS is well suited for analysis of organic volatiles from a complex matrix. This technique can avoid some common problems encountered when trying to quantitate volatiles using traditional GCMS techniques, especially when the matrix is a polymer.

Read the following report to see the full analysis.

`

Final Report

Jordi Labs LLC
Case Study MHE-GCMS

Date

Prepared by:
Dr. Mark Jordi
President
Jordi Labs LLC

Report Number: J#### Case Study MHE-GCMS

Jordi Labs LLC Confidential


MATERIAL SOLUTIONS. UNCOMPROMISING INTEGRITY.
Tel: +1 (508) 966-1301 Fax: +1 (508) 966-4063
4 Mill St, Bellingham, MA. 02019 USA
JORDI

Date

Client Name
Company Name
Address

Dear Valued Client:

Please find enclosed the test results for your sample described as:

1. *Polystyrene Foam*

The following test was performed:

1. Multiple Headspace Extraction Gas Chromatography Mass Spectroscopy (MHE-GCMS)

Objective

The objective of this work is to demonstrate the use of multiple headspace extraction for the quantitative determination of organic volatiles in solid matrices. Specifically, the residual styrene content in a sample of polystyrene foam is determined.

Summary of Results

Multiple Headspace Extraction GCMS is well suited for analysis of organic volatiles from a complex matrix. This technique can avoid some common problems encountered when trying to quantitate volatiles using traditional GCMS techniques, especially when the matrix is a polymer. This technique also does not require replication of the matrix for standards, which is required in normal standardized headspace GCMS quantitative methods.

Using the Multiple Headspace Extraction GCMS technique the amount of residual styrene found in a sample of polystyrene foam was determined to be 1451 ppm.

Individual Test Results

A summary of the individual test results is provided below. All accompanying data, including spectra, has been included in the data section of this report.

MHE-GCMS

It can often be very difficult to quantify organic volatiles present in complex matrices, such as polymers. If a suitable solvent can be found, one may quantify volatiles by dissolving the sample and analyzing it directly by GCMS. However, this approach will require frequent instrument maintenance, as any polymeric portion of the samples will tend to collect in the GCMS injection port causing adsorption of analytes and poor chromatography. In some cases, additional problems such as discrimination of sample components can occur due to the presence of polymer in the GC injection port.

In order to avoid directly injecting dissolved polymers, a liquid phase extraction or a dissolution/precipitation experiment can be performed. Unfortunately, in the case of very low level volatile components it can be difficult to obtain an extract with sufficient concentration of the analyte(s) for detection by GCMS.

Often, especially for highly volatile analytes, analysis of the sample headspace is the best option. Both internal and external standardization can be used for quantitation of analytes, but will require preparation of homogeneous standards and samples. Also, in the case of external standardization, the sample matrix must be replicated for the standard. This is not always possible, especially with polymeric matrices.

However, this problem can be avoided by measuring the total amount of a specific analyte present in the sample. This is similar to performing a gas phase extraction of the analyte. A standard is also analyzed to relate peak area to analyte content (mass). This data can be obtained using dynamic headspace (purge & trap) analysis, as well as by multiple headspace extraction.

In the case of multiple headspace extraction, repeat extraction of sample headspace gasses is performed on the same sample vial. The total peak area can then be extrapolated based on a series (5-10) of these extractions. Separately, a standard is analyzed without the presence of the sample matrix which is used to relate the total peak area of the analyte observed to mass of the analyte. The actual calculations involved are discussed in further detail later.

For this analysis, the compound of interest is residual styrene, present on a portion of polystyrene foam packaging material. Approximately 130 mg of the sample was sealed in a 10 ml headspace vial. Five (5) repeat extractions were performed on this sample. The resulting series of peaks, all of which are identified as styrene by mass spectroscopy, are presented in **Figure 1**.

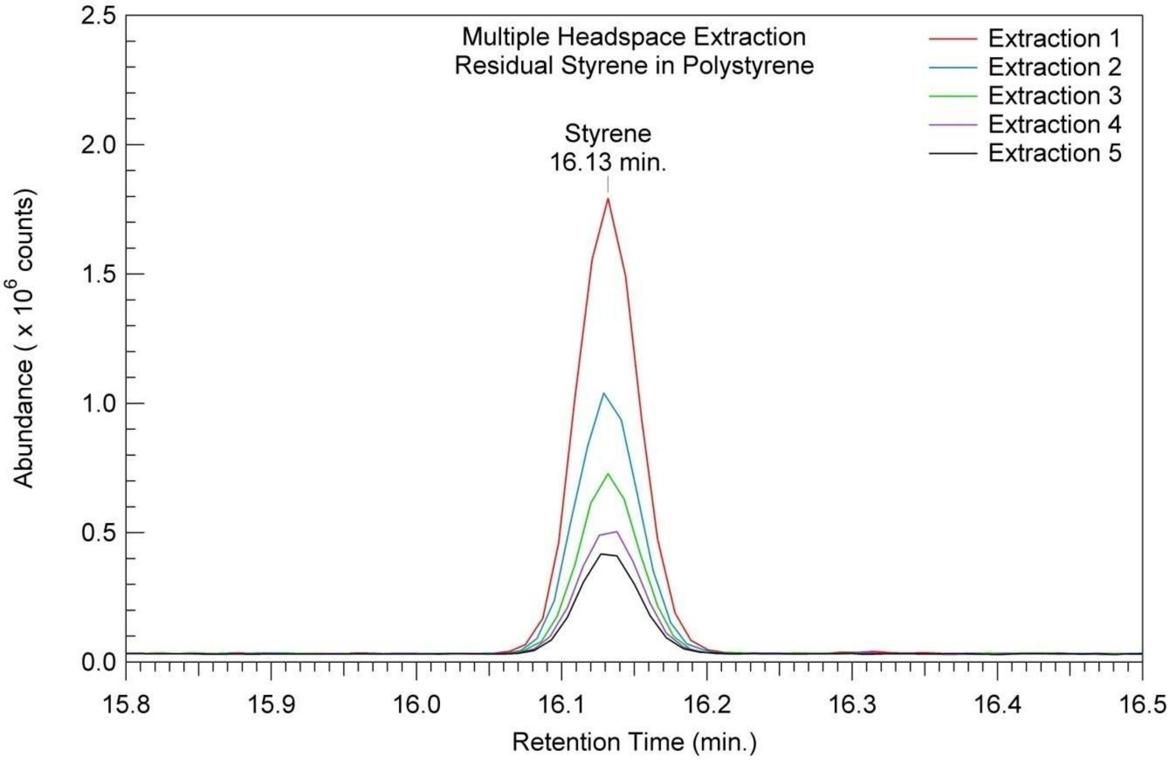

Figure 1 - Overlay of the five headspace extractions performed on the sample.

The individual peaks are then integrated, and the resulting peak areas are plotted as the natural log of the observed peak area *(ln A_i)* versus the extraction number minus 1 *(i-1)*. **Figure 2** contains the *ln A_i* vs *i-1* plot for the polystyrene sample and styrene standard analyzed. From this plot the constant *q'* for the slope of the linear regression line can be determined. **Equations 1** and **2** below relate the area of a peak after *i* injections, based on an exponential decrease in area with successive injections of the same sample vial. **Equation 2** is in the form *y=mx+b*, where *m* (the slope of a linear regression line of the semi-logarithmic plot for the sample and standard data) is equal to *q'*.

$$A_i = A_1 \times e^{q'(i-1)} \qquad \mathbf{(1)}^2$$
$$\ln A_i = lnA_1 + q'(i-1) \qquad \mathbf{(2)}^2$$

A_1 = Peak Area of the analyte in the first extraction
A_i = Peak Area of the i^{th} extraction
q' = constant determined from a linear regression of the semi-logarithmic plot.

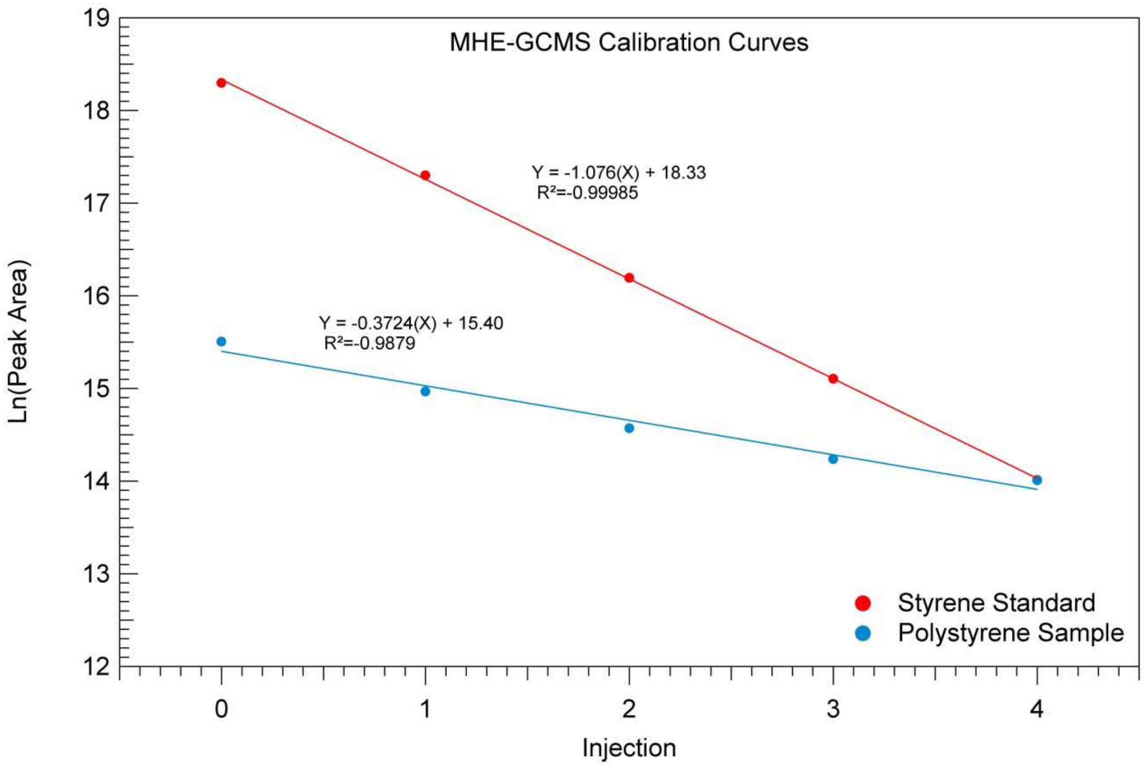

Figure 2 - Semi-logarithmic plots used to determine the parameter q', which is the slope of the best fit line.

Once q' has been determined the total peak area (A_T) can be calculated using **Equation 3**.

$$\sum_{i=1}^{n} A_i = A_T = \frac{A_1'}{1-e^{-q'}}$$

(3)[2]

A corrected value *(A_1')* for A_1 is obtained based on the linear regression, which is then used to calculate the total area for the sample and the standard. Because the amount of standard added is known, a *Factor* in counts/mg can be determined, which relates the observed peak area for the standard to the known mass. This factor can then be used to calculate the amount of the analyte present in the sample.

Applying this process to the sample under study resulted in a value of 1451 ppm residual styrene. **Table 1** shows the calculation of this value. This value is consistent with values obtained from other, more labor intensive extraction methods performed on commercial polystyrene foam products.[1]

Table 1
HS-GCMS Results

	Standard	Sample
Corrected Area (A_1')	91689576	4885981
Total Area (A_T)	139102937	15715099
Analyte mass (mg)	1.682	--
Factor (counts/mg)	82700914	--
Analyte in sample (mg)		0.190023
Starting Sample Mass (mg)	--	131
ppm styrene	**1451**	
wt% styrene	0.1451%	

Works Cited

1. *J.R. Withey; Quantitative Analysis of Styrene Monomer in Polystyrene and Foods Including Some Preliminary Studies of the Uptake and Pharmacodynamics of the Monomer in Rats;* Environmental Health Perspectives Vol. 17, pp. 125-1.53, 1976

2. B. Kolb and L.S. Ettre; *Theory and Practice of Multiple Headspace Extraction*; Chromatographia Vol. 32, No. 11/12, pp. 505-513, 1991

Closing Comments

Deformulation of an unknown material is intended to provide a best estimate of the chemical nature of the sample. All chemical structures are supported by the evidence presented but are subject to revision upon receipt of additional evidence. Additional factors such as material processing conditions may also affect final material properties.

Jordi Labs’ reports are issued solely for the use of the clients to whom they are addressed. No quotations from reports or use of the Jordi name is permitted except as authorized in writing. The liability of Jordi Labs with respect to the services rendered shall be limited to the amount of consideration paid for such services and do not include any consequential damages.

Jordi Labs specializes in polymer testing and has 30 years experience doing complete polymer deformulations. We are one of the few labs in the country specialized in this type of testing. We will work closely with you to help explain your test results and solve your problem. We appreciate your business and are looking forward to speaking with you concerning these results.

Sincerely,

Mark Jordi

Mark Jordi, Ph. D.
President
Jordi Labs LLC