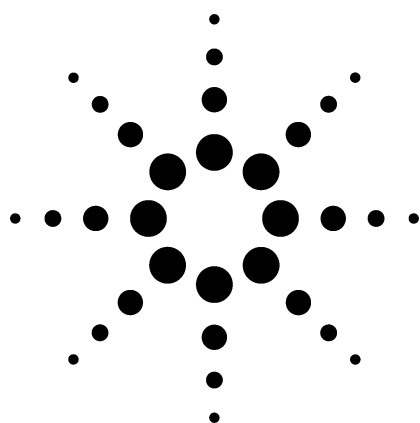# Multiple Headspace Extraction-Capillary Gas Chromatography for the Quantitative Determination of Volatiles in Solid Matrices

Application

Gas Chromatography

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Abstract

A multiple headspace extraction capillary gas chromatographic (MHE-CGC) method for the quantitative, accurate, and rapid determination of volatile components in solids such as polymers, resins, and activated carbon has been developed. A five-step MHE determination was performed using the Agilent 7694 headspace sampler and a 5890 Series II GC with EPC. A Microsoft ® Excel spreadsheet was used to quickly perform the required calculations. Details of the procedure and implications affecting the analysis of polymeric materials are discussed.

Introduction

U.S. producers supplied 75.3 billion lb. of plastics in 1994[1]. Packaging is a major end-use for the four primary plastics: high-density polyethylene, low-density polyethylene, polystyrene, and polypropylene. Thermoplastic polyesters such as bottle-grade polyethylene terephthalate (PET) find extensive use in the soft-drink bottle market. Knowledge about impurities and monomers in such plastics is important if the material is used in the packaging of food products. The low levels (ppm or ppb) of impurities or monomers present may not influence the bulk physical characteristics of the plastic; however, they may affect the quality of the food stored inside, if they migrate through the plastic.

The analysis of residual solvents, impurities, and monomers in solid matrices such as polymers, resins or pharmaceutical products is always challenging. Typically, the sample is dissolved in a suitable solvent and injected directly into a gas chromatograph. There are several inherent disadvantages with this approach including: difficulty in dissolving the sample, decomposition of the sample in the injection port, and increased maintenance. Sometimes direct injection does not work simply because the broad solvent peak interferes with the peaks of interest from the solid matrix. Since we are usually measuring trace levels of the analytes, we would like the large solvent peak to elute after the analytes of interest in order to minimize interference from the large solvent tail. Careful selection of the solvent and the type of stationary phase on the column becomes critical. Injection of a polymer solution may also be difficult due to the high viscosity and adhesion of the solution. Many polymers are difficult to dissolve in common solvents and may decompose at comparatively low temperatures. However, the biggest problem with the direct injection of a polymer solution is the need to perform frequent maintenance to ensure a clean analytical system. This involves changing the analytical column and replacing the injection-port liner as often as once per day. This is required because the non-volatile, long-chain polymers irreversibly contaminate the front portion of the GC system causing adsorption of active compounds, loss of resolution, and poor peak symmetry. The simplest fix to all these problems is to not do a direct injection of

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a solution; but do an analysis of the gas phase over the solid sample, a headspace (HS) analysis.

Both external (ESTD) and internal (ISTD) standard techniques are commonly used in quantitative headspace gas chromatography of many sample types. These techniques, however, require the preparation of homogeneous samples and standards. For the ESTD method, the sample matrix effects must also be duplicated in the standard. This becomes an almost impossible task when dealing with polymers because of the difficulty of homogeneously and reproducibly mixing trace quantities of very volatile substances into a solid polymer matrix. This application note discusses an alternative method, the multiple headspace extraction (MHE) procedure, which facilitates the quantitative determination of volatile analytes in solid matrices independent of matrix effects. MHE circumvents the many complications associated with the analysis of volatiles in polymers.

Experimental

Solid samples to be analyzed included: polymers such as polyethylene terephthalate (PET) from a film used for video tape applications; polyphenol oxide (PPO) powder; polystyrene (PS) from a coffee cup; polymeric resin powder (containing approximately 75% inorganic materials); and also micro-encapsulated activated carbon from a hemoperfusion tube. The MHE methodology illustrated here can be applied to any solid matrix. 0.5-1.0 grams of each sample were placed into 22-mL headspace vials and analyzed according to the conditions given in Table 1.

All experiments were performed using a 7694 headspace sampler interfaced to an 5890 Series II GC with electronic pressure control (EPC) and a flame ionization detector (FID).

Table 1. Instrument Configuration and Conditions

Instrumentation	
Gas chromatograph:	5890 Series II with EPC
Injection port:	Split/splitless
Column:	HP-5, 25-m x 0.32 mm x 1.0 μm
Detector:	FID
Sample introduction:	7694 headspace sampler
Data collection:	ChemStation

7694 Headspace Conditions	
GC cycle time:	60 minutes
Oven temperature:	150°C
Transfer line temperature:	175°C
Loop temperature:	175°C
Vial equilibration time:	60 minutes
Shaking speed:	Off
Loop size:	1.0 mL
Loop fill time:	0.2 minutes
Loop equilibration time:	0.02 minutes
Inject (or vent) time:	0.3 minutes
Pressurization time:	0.4 minutes
Advanced functions:	#8 multiple headspace extractions
	extractions/vial = 5
	puncture (0 = S 1 = M) = 0

5890 Series II GC Conditions	
Carrier gas (EPC):	Helium
Inlet temperature:	250°C
Inlet pressure:	9.5 psi
Split ratio:	1:10
Flow mode:	Constant flow
FID temperature:	250°C
Oven Program:	40°C, hold for 5 min; ramp to 250°C at a rate of 20°C/min; hold for 5 minutes.

The headspace instrument and gas chromatographic parameters are shown in Table 1. The identity of the peaks was established by HS/GC/MSD and confirmed by running pure substances by HS/GC/FID. The advanced function #8 of the 7694 headspace sampler was activated to do MHE, performing five headspace extractions with a single puncture of the septum.

Results and Discussion

The theory of MHE has been described in various forms by Kolb et al.[2-5], McAulife[6], and Suzuki et al.[7]. Appendix 1 gives a summary of the salient features of the MHE technique and an example for calculating an analyte's concentration. Since standard chromatography software does not usually include a MHE quantitation procedure, an Excel template (Figure 3) was designed to calculate statistics for the semilogarithmic plot, the correlation coefficients, slopes, total peak areas, and the concentration of the analytes given the sample weight in the vial and the amount of standard used for the calibration.

A typical chromatogram of the headspace and MHE results for toluene in the PET sample are shown in Figures 1 and 2. The average toluene concentration in the PET sample was thus calculated from the regression analysis (Eqn. 6) to be 13.1 ppm with a 3.5% RSD for five representative samples taken from different locations of the PET film. This RSD value includes
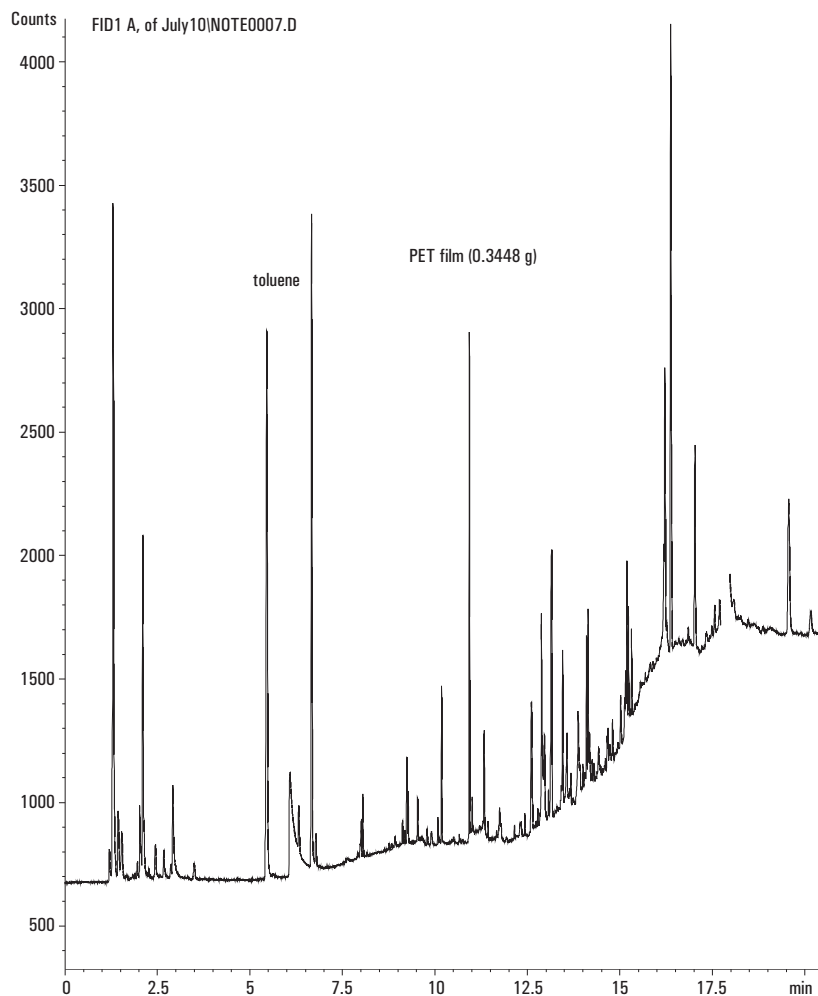
Figure 1. Gas chromatogram of the headspace above the polymer PET.

both the variation observed between different solid samples and the precision of the instrument system. The precision of the system was demonstrated by running 10 identical calibration standards though the MHE procedure and calculating the total peak area of toluene for each standard. The calculated RSD was 1.7%.

On those occasions when speed of analysis is more important than accuracy, a modified procedure using only two extractions to calculate the total peak area (Eqn. 9) can be used. Using this method we calculated the toluene concentration in the PET sample to be 14.8 ppm with an RSD of 10.7%. In addition, the error observed in using

only two extractions versus five extractions, was 13%. Generally, highly volatile analytes would require only a few extractions to accomplish complete extraction; whereas, less volatile analytes would require many such extractions. It should be noted that in the MHE procedure, once a specific sample type is characterized and the slope is determined for the analyte from the regression analysis of the semilogarithmic plot, only one extraction per sample is needed to calculate the concentration of the analyte as long as the physical nature of the sample (film thickness or particle size) and the experimental conditions remain the same.

In these experiments the required peak areas for the analyte in the sample and the standard, the sample weight, and the amount of standard used in the calibration were entered manually into the Excel template (Figure 3, cells outlined with heavy borders) and then plotted as ln peak-area vs. extraction-number. However, if a large number of samples needs to be analyzed by MHE, the required data can be automatically entered into the Excel template by dynamic data exchange (DDE) using a post-run macro. The best-fit semilogarithmic plot of the MHE results for toluene in the sample and the standard, and the equation for the curves and the correlation coefficients are given in Figure 4. The correlation coefficient for the calibration standard is usually very high and indicates the instrument precision; whereas, that of the sample includes additional problems associated with the sample such as adsorption or a lack of equilibrium. Since the correlation coefficients for toluene in the sample and standard are 0.99 or better, thermal equilibrium was established at the experimental conditions (150°C for 60 min.) and quantitation by the MHE procedure is valid. Should the correlation for the sample be closer to or below 0.98, then thermal equilibrium was probably not reached (possibly fixable by an increase in time or temperature or both) or adsorptive chemistry is complicating the analysis. The latter may sometimes be corrected by adding a polar solvent such as water to the sample[4]. Since the slope of the semilogarithmic plot is used to calculate the total peak area, the slope defines the practical limit for the application of the MHE technique. A steep slope is desirable for good precision and accuracy. The slope is anticipated to increase with increases in the equilibration temperature of the solid matrix, and to decrease with

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increases in the boiling point of the analyte.

An attempt was made to prepare a solution of the PET sample for direct injection to obtain comparative quantitative data for the toluene peak. However, the sample was insoluble in most of the common solvents available in the laboratory such as THF, DMF, DMSO, acetone, and methylene chloride. Selecting a suitable solvent for the polymer for direct injection thus becomes a serious challenge. The MHE technique applied to solid samples (films and powders) avoids this and other problems because we don't need to select a solvent and, therefore, observe no interference from a large solvent peak nor from the impurities present in the solvent. Furthermore, since the size of the sample used in the MHE procedure is not limited by the sample solubility, a large weight of the solid sample may be analyzed to increase sensitivity for samples with low-analyte concentration.

A new toluene standard did not have to be run for the PPO, resin, and polystyrene samples since the calibration data derived from the PET experiment was still valid. MHE data for these samples are given in Figure 5. The corresponding toluene concentrations were calculated to be 2.5 ppm, 0.2 ppm, and 1.3 ppm, respectively. Since the peak areas of toluene were very small, especially for the resin sample, the calculated concentration of toluene is very much dependent on the placement of the integration baseline. Thus, a larger uncertainty than 3.5% is expected for these concentrations. Other peaks in the chromatograms could easily be quantitated if calibration standards were prepared and subjected to the same MHE procedure.

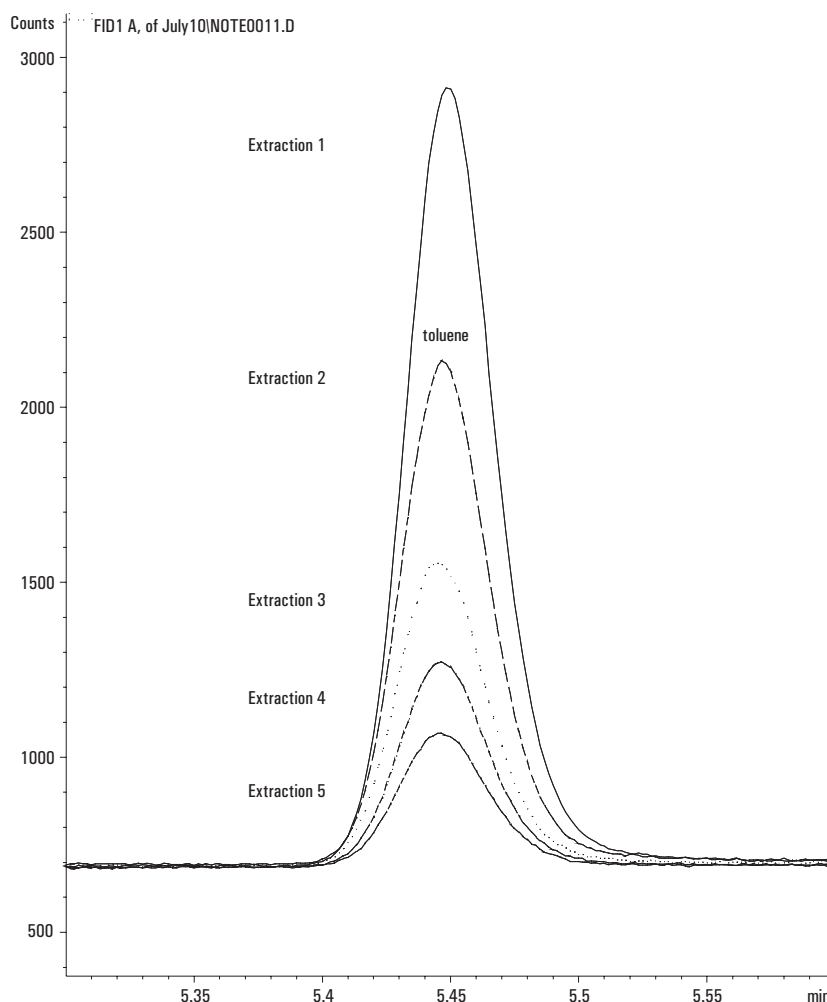A representative chromatogram and the MHE graphs for the ethanol peaks (1.44 min.) in both the activated

Figure 2. Multiple headspace extraction data for the toluene peak in PET.

Extraction number	Sample (toluene)	Standard (toluene)	Standard	Stats
1	5658	15609	0.514044	28365.24
2	3662	7279	0.023582	0.078212
3	2261	3526	0.996247	0.074572
4	1510	1966	796.2923	3
5	995	1078	4.428201	0.016683
6				
7			**Sample**	**Stats**
8			0.646484	8666.08
			0.007582	0.025146
regression correlation (E4 or E11)	0.999094519	0.99624668	0.999095	0.023976
slope (k) = ln (E2 or E9)	-0.436206582	-0.665447287	3310.157	3
			1.902762	0.001724
total area = (A(1)/(1-e(-k)))	16005	32120		
analyte in vial (mg)	0.004315133	0.00866		
sample amt (mg) in vial	345			
concentration (ppm) in wt/wt	12.51			
concentration				
(wt-%) = ppm * (10 ^ -4)	0.0856			

Figure 3. Excel template used for the calculations needed for the MHE procedure

carbon sample and the standard are given in Figures 6 and 7, respectively. Since the observed correlation coefficient for ethanol in the dry sample was 0.973, some adsorptive chemistry may be complicating the analysis. 25 mL of water was added to another sample and the experiment was repeated. The correlation coefficient became 0.995 and the MHE technique could then be used for accurate quantitation. The ethanol concentration was calculated both without and with water addition to be 18.2 ppm and 46.5 ppm, respectively. Furthermore, the total area under the ethanol peak increased by a factor of 1.86 upon adding the water to the sample. Apparently the water, being a more polar eluent, assisted in the desorption of the ethanol from the activated carbon surface.

During MHE some analytes may have a smaller peak area from the first extraction than that observed for the second extraction, while the remaining extractions show the expected exponential decrease in the peak areas. Such behavior was observed for the peak at 2.07 minutes in the PPO sample and the data are presented in Figure 8. Since headspace analysis involves a gas phase extraction, we should be aware that the first extraction is always done with air as the extraction fluid, while subsequent extractions are done with helium. The extraction efficiency using air may be less than that observed for helium and thus cause the peak area of the first extraction to be lower than what the graphical extrapolation would indicate. In such cases a modified form of the equation for the total area may be used for the quantitation calculation of the analyte. Total

$$\text{peak area} = A_1 + \frac{A_2}{(1 - e^{-K})}$$

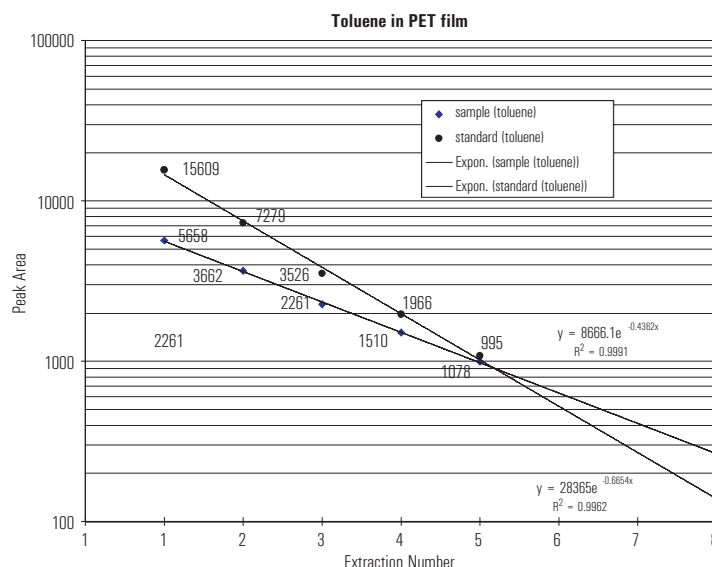where the 2nd half of the equation (the ratio) gives the total peak area

Figure 4. Semilogarithmic plot of the MHE results for toluene in PET sample and standard.
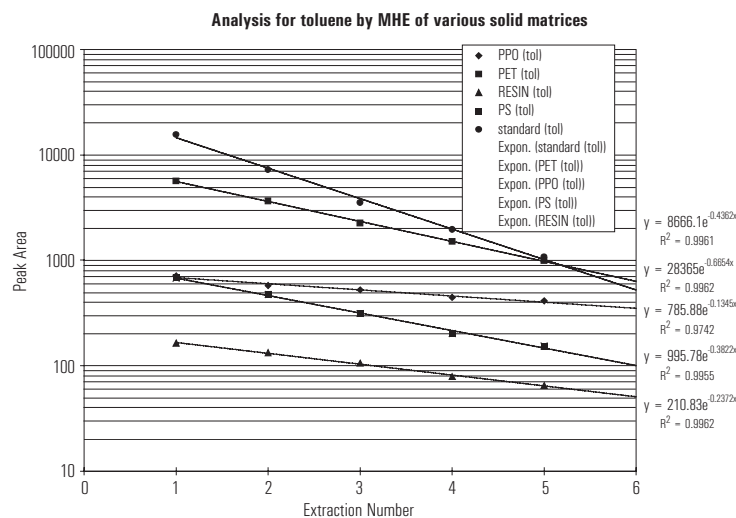

Figure 5. Semilogarithmic plot of the MHE results for toluene in PET, PPO, PS, and resin.
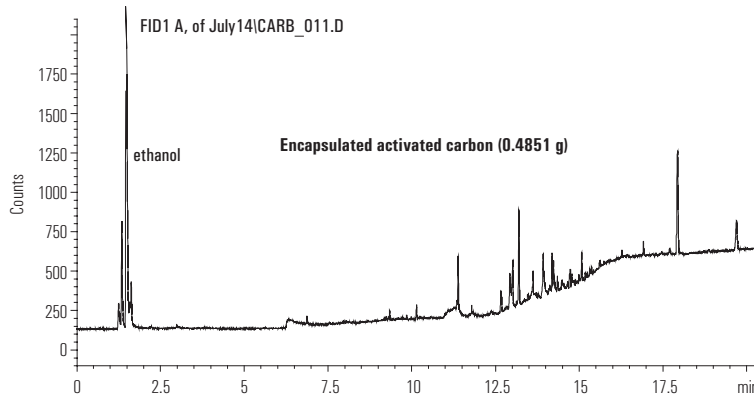

Figure 6. Gas chromatogram of the headspace above encapsulated activated carbon.

derived from the regression analysis using the results from the second and subsequent extractions.

The MHE technique requires that the solid polymer sample be heated at a given temperature for some length of time so that the analyte exists in thermal equilibrium between the condensed and the gas phases. The temperature is often determined experimentally to be high enough to reach equilibrium in a reasonable time but low enough not to degrade the polymer. Figure 9 shows the chromatograms for a polystyrene sample equilibrated for 60 minutes at 150°C and at 105°C. At 150°C the sample melted and showed a large number of intense peaks, probably degradation compounds. A significant amount of labor can be avoided if, as a first approximation, the polymer is heated to, or just above, its glass transition temperature. At or above the glass transition temperature, a polymer changes from a semi-crystalline structure into a rubber-like state; and the sample, though still solid, behaves like a quasi-liquid[4]. Since liquid samples, especially if agitated, attain thermal equilibrium in a very short time; such quasi-liquids should also reach equilibrium in a relatively short time. Table 2 lists glass transition temperatures for a few representative polymers[9]. Thin films, fine powders, or samples with a porous structure are ideal solid matrices for MHE because they should reach thermal equilibrium in a relatively short time, even if below the glass transition temperature. For the PET film sample described above, a time of 60 minutes at 105°C was quite adequate.

Conclusion

Using a HS-GC(FID) and an MHE procedure presents a good solution for those who need to quantitate volatile compounds in solid matrices, espe-
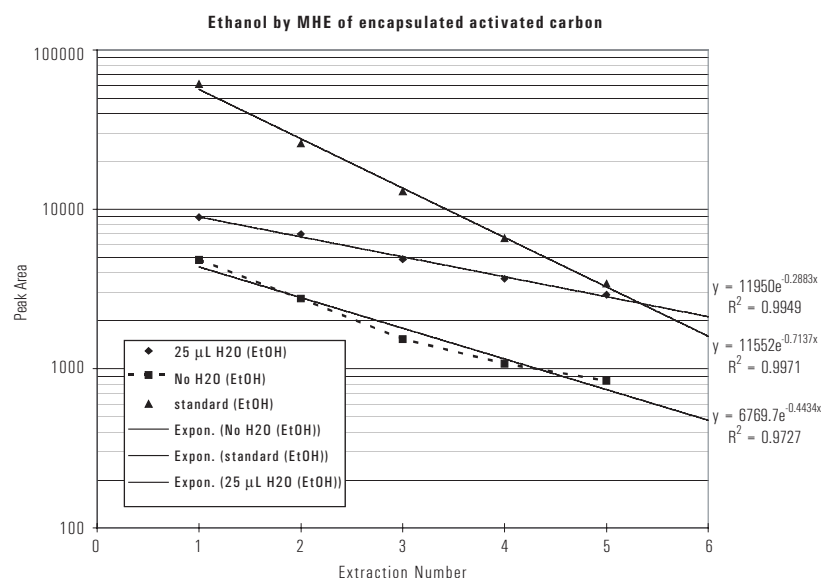

Figure 7. **Semilogarithmic plot of the MHE results for ethanol in encapsulated activated carbon.**
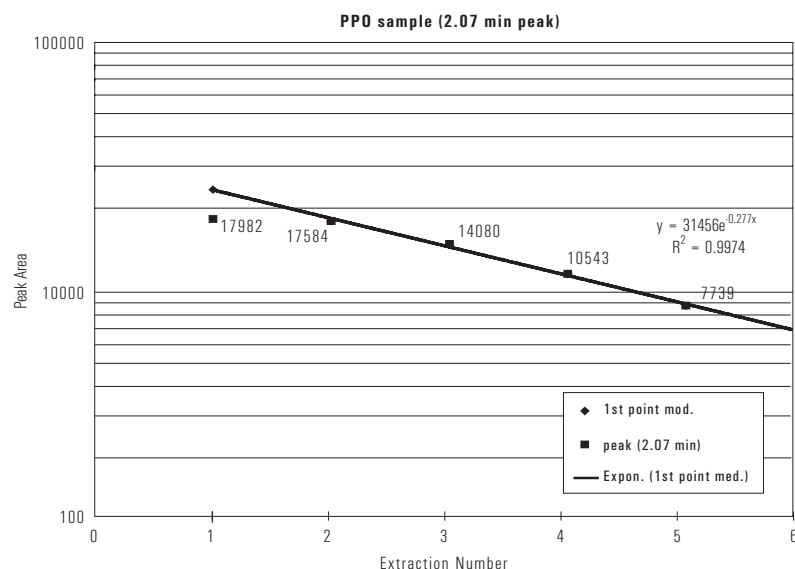

Figure 8. Semilogarithmic plot of the MHE results of the 2.07 min. peak in PPO.

cially ones not amenable to direct injection. The required calculations, though complex, are quickly performed using an Excel template. If the correlation coefficient for the semilogarithmic plot of peak-area vs. extraction-number for a specific type of solid material is close to or better

than 0.99, then a simpler and more cost-effective two-step MHE can be used for quantitation. The headspace technique offers great potential for characterizing volatiles in solid samples and facilitating the quality assurance programs in the polymer industries.

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Table 2.   Glass Transition Temperature of Some Polymers (8)

Polymer	Tg(°C)
Poly(oxyethyleneoxyterephthaloyl), [PET]	60 - 85
Poly(styrene), [PS]	100
Poly(ethylene), [PE]	(-135) - (-33)
Poly(propylene), [PP]	(-13) - (-1)
Poly(vinyl Chloride), [PVC]	79 - 98
Poly(oxy-2,6-dimethyl-1,4-phenylene), [PPO]	209 - 234
Poly(methyl methacrylate)	5
Poly(ethyl methacrylate)	65
Poly(methacrylic acid)	209 - 234

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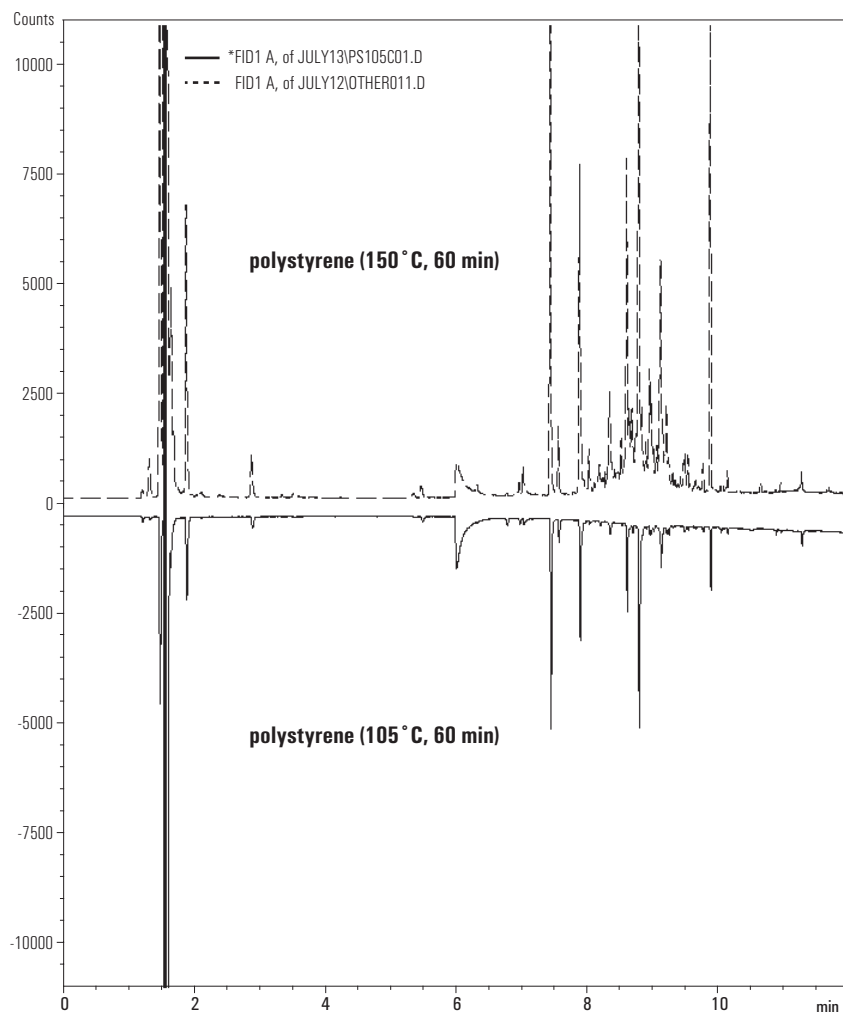
Figure 9.   Gas chromatograms of the headspace for PS equilibrated at 150°C and 105°C.

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Appendix 1

In the multiple headspace extraction technique the sample is equilibrated at some temperature for a given amount of time and the headspace above the sample is analyzed. This equilibration and measurement process is repeated multiple times and an exponential decrease in the peak areas is observed. If we perform an infinite number of extractions, all the volatile impurities will be converted into the gas phase and the total peak area (eqn. 1) will correspond to the total content of the analyte in the sample:

Total peak area = (1)

$$\sum_{n=1}^{\infty} A_n = A_1 + A_2 + A_3 + ... + A_n.$$

However, such a large number of extractions per sample becomes impractical and we are forced to use arguments from kinetics to get the total peak area.

The rate of conversion of the analyte from the solid matrix into the gas phase is assumed to follow 1st order kinetics,

$$- \frac{dc}{dt} = k c , \qquad (2)$$

which upon integration becomes:

$$c = c_0 \, e^{-kt} \qquad (3)$$

The concentration of the analyte in the solid matrix thus changes over time according to this exponential law.

If the gas extraction is carried out carefully and for equal times, and equal portions of the headspace gas are introduced into the chromatograph, then the peak areas of a given analyte in the chromatogram will follow the same exponential law 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 phases, respectively. For a discontinuous or stepwise gas extraction performed at equal time intervals, eqn. 3 now becomes:

$$A_n = A_1 e^{(1-n)K} \qquad (4)$$

Note: n = 1 at t = 0 since t = n - 1

A_n = the peak area of the nth injection

A_1 = the peak area of the 1st injection

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

$$\sum_{n=1}^{\infty} A_n = \qquad (5)$$
$$A_1(1 + e^{-K} + e^{-2K} + e^{-3K} + ...).$$

This decreasing geometric progression in eqn. 5 converges to:
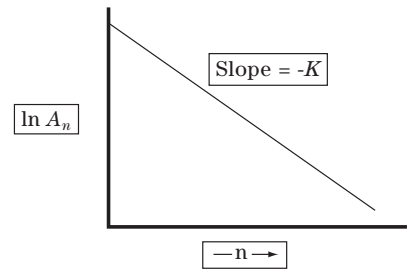
$$\sum_{n=1}^{\infty} A_n = \frac{A_1}{(1 - e^{-K})} . \qquad (6)$$

We therefore do not need to do a complete gas extraction to obtain the total peak area, but we must obtain values for A_1 and K. The A_1 value is the measured peak area of the analyte after the 1st gas extraction and K is the slope obtained from a regression analysis of the semilogarithmic plot of eqn. 4:

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

or

$$ln \ A_n = -K \ (n - 1) + ln \ A_1 \qquad (8)$$

For two measurements eqn. 6 simplifies to:

$$\sum_{n=1}^{\infty} A_n = \frac{A_1^2}{(A_1 - A_2)} \qquad (9)$$

Example Calculation:

Solid sample (337 mg in vial)	**Analyte Standard** (0.00866 mg in vial)

$$\sum_{n=1}^{\infty} A_n = \frac{A_1}{(1 - e^{-K})} = \frac{6072}{(1 - e^{-0.4615})} = 16423 \qquad \sum_{n=1}^{\infty} A_n = \frac{15609}{(1 - e^{-0.6654})} = 32120$$

$$\frac{Total\ Area_{analyte}}{Amount_{analyte}} = \frac{Total\ Area_{standard}}{Amount_{standard}}$$

$$Amount_{analyte} = \frac{16423}{32120} * 0.00866 = 0.00443\ mg$$

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