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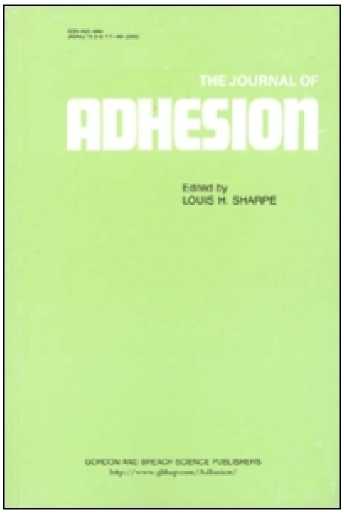

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The Determination of Solvents in Polymers by a Simple Direct GC/MS Method

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The Determination of Solvents in Polymers by a Simple Direct GC/MS Method

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INTRODUCTION

Small amounts of residual solvents may cause disproportionately large effects on the properties of polymers and adhesives. A number of methods for determining occluded solvents have been proposed. Suzuki *et al.*[1] have used a vaporizing attachment that was directly connected to the inlet of a gas chromatograph. Vapor desorbed from the polymer was introduced periodically into the gas chromatograph through a multiport valve by a stream of nitrogen. Residual solvents in samples were determined in the 10–50 ppm. range.

More recently Myers[2] has used a desorption apparatus that is made up of an external heater and cold trap. The volatiles are removed from the polymer by the diverted carrier gas of the gas chromatograph and collected in the cold trap. When the desorption of the solvent is complete the sample is transferred to the gas chromatograph with a heat gun.

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This method has the advantage of the thermal desorption technique in that all the solvent that is occluded in the polymer is transferred to the gas chromatograph, and maximum sensitivity can be attained.

Eiceman and Carpen[3] have reported the determination of the oganic impurities in polystyrene food containers. Samples were placed in a Pyrex tube, the tube was attached to the gas chromatograph valve, preheated and switched in series with the analytical column at 0°C, then heated with a heat gun for 2 minutes. After sampling, the GC valve was returned to the original position. The same introduction method was used when samples were analyzed with a Hewlett-Packard 5992A GC/MS.

Mieure and Dietrich[4] used adsorption tubes packed with solid adsorbents such as Tenax-GC and charcoal to concentrate organic pollutants from water samples and then used these tubes as the injection port liner in a gas chromatograph. Our experience with this technique in the sampling and analysis of organic pollutants in the atmosphere is that the desorption from the Tenax-GC was neither quantitative nor reproducible. To improve the reproducibility, we installed a three-way valve in the carrier gas line so that the carrier gas could be passed through the heated injection port liner packed with Tenax-GC, purging the pollutants from the Tenax-GC and depositing them at the head of the GC column which was held at -50°C. After the purging was complete, the gas flow was returned to the normal mode, and the GC analysis carried out. By modifying the procedure in this manner, we obtained sharp chromatographic peaks and reproducible results. A complete report on this work is in preparation.[5] For the study of occluded solvents in polymers we have used the same concept of sample introduction, but we have replaced the packing in the injection port liner with the polymer sample.

EXPERIMENTAL

Test samples were prepared by spreading a solution of polyisobutylene in hexane onto Mylar (0.001 in. thick) using a coater similar to a Gardner applicator with a gap set to give a film thickness of 0.0025 ± 0.0005 in. after drying. These sheets were placed on glass plates to facilitate handling, and the plates were placed in a vacuum drying oven. One inch x 4 inch samples were removed from the drying oven at intervals, rolled, and placed in the injection port liner/sample tubes

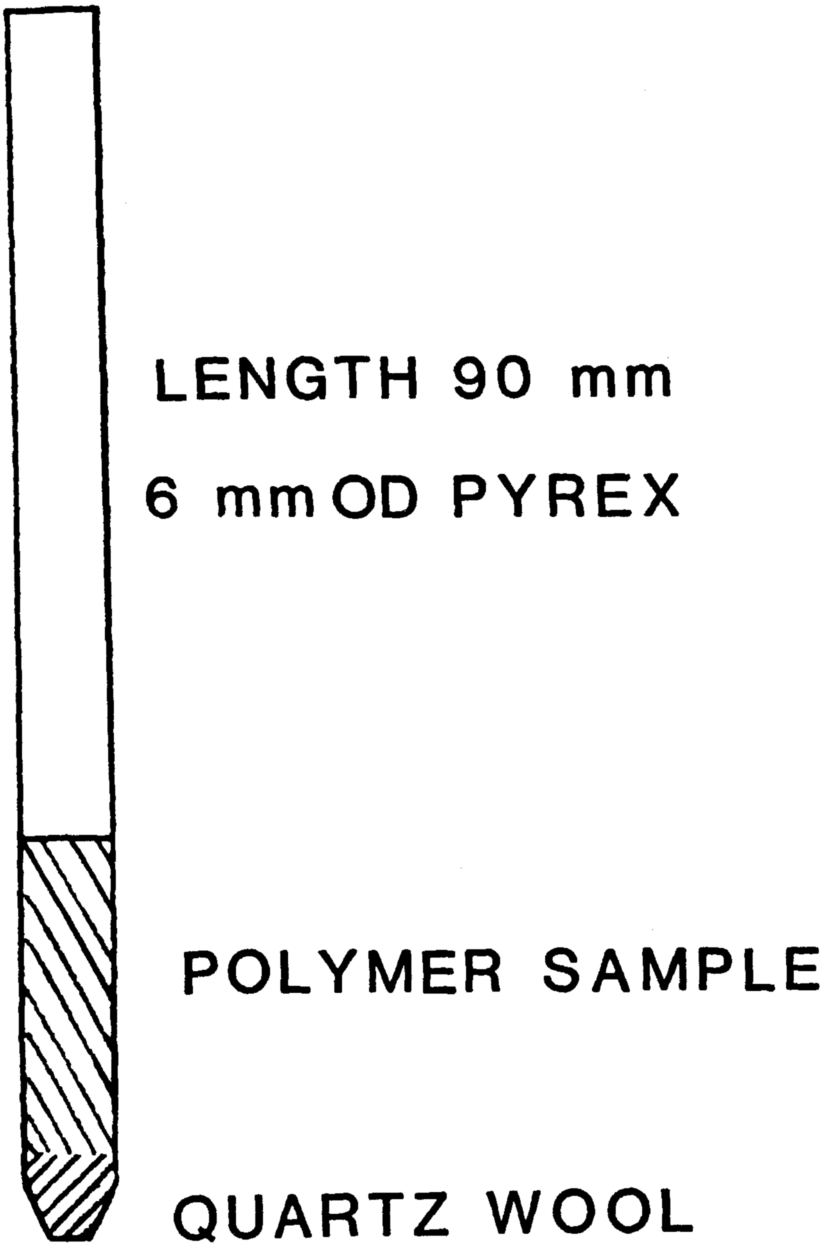

FIGURE 1 Injection port liner/sample tube.

shown in Figure 1. The tubes were closed with plastic caps until the samples were to be analyzed.

The analyses were carried out with a Hewlett-Packard 5985B gas chromatograph/mass spectrometer/data system. The gas chromato-

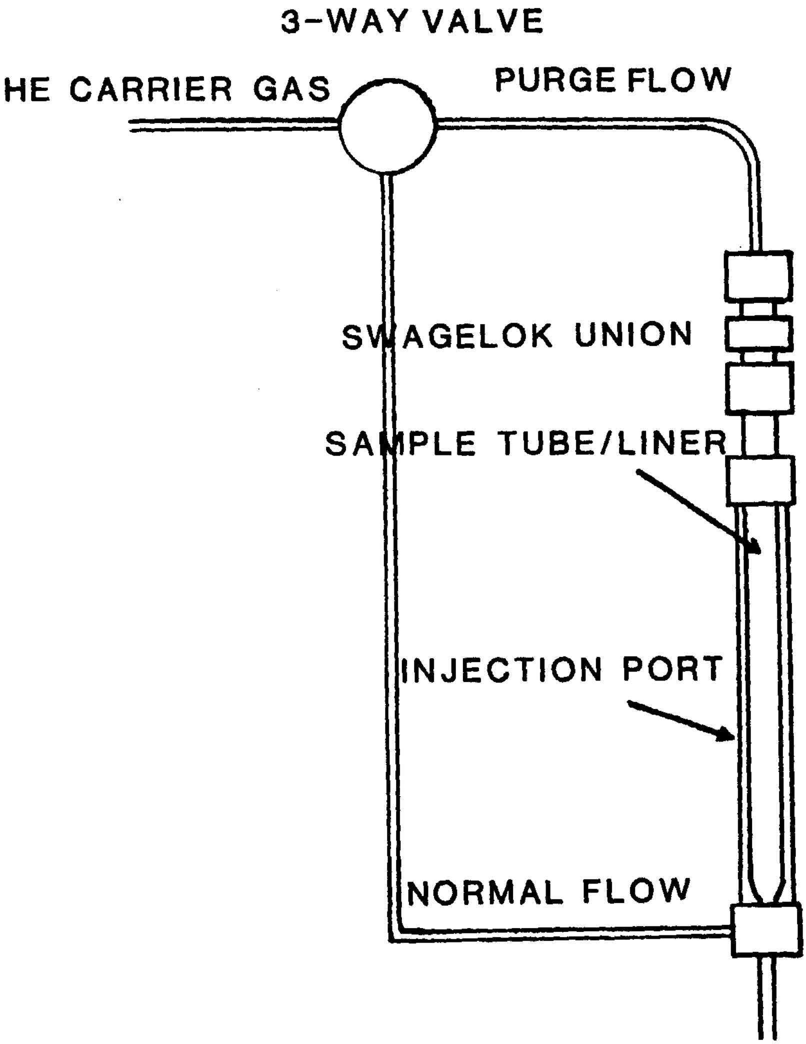

FIGURE 2 Modification of carrier gas flow for injection port liner/sample tube.

graph of this system is a Hewlett-Packard 5840A equipped with both packed and capillary columns. For this work only the packed column was used, and it was connected to the 1/4" ID injection port. The carrier gas flow system was modified as shown in Figure 2, so that the carrier gas could be diverted to the top of the sample tube to purge the sample onto the head of the column.

Prior to inserting the injection port liner/sample tube in the injection port, the gas chromatograph oven was cooled at −50°C. The sample injection port liner/sample tube was connected to the carrier gas line with a Swagelok connector as shown in Figure 2, inserted into the injection port and secured with a Swagelok nut. When the sample was positioned, the gas flow was diverted to the purge mode and the sample was purged for 10 minutes. For this work the injection port temperature was 275°C which was sufficient to melt the polymer and hence – desorb the solvent rapidly and completely[2]. To confirm this fact some samples were desorbed a second time and the amount of hexane found on the

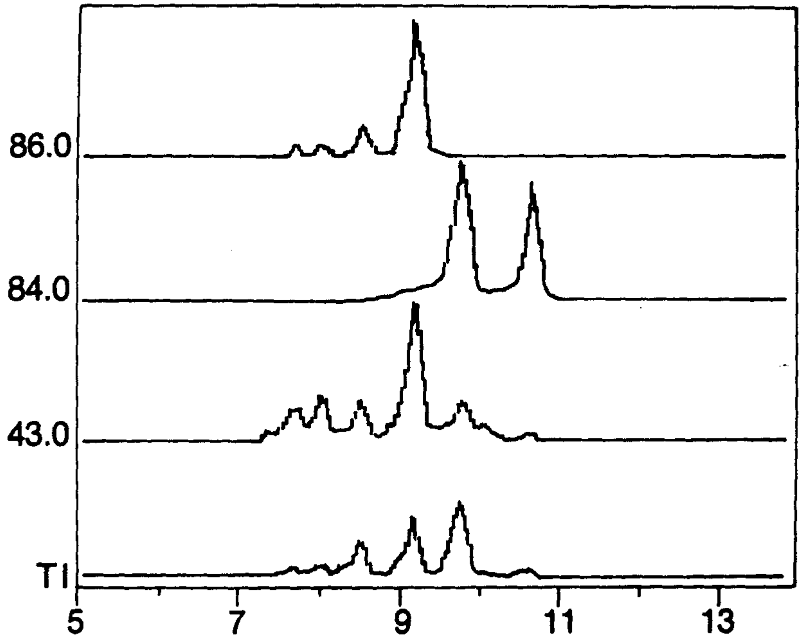

FIGURE 3 Total ion chromatograms at masses 43, 84 and 86 of solvent desorbed from polymer.

second introduction was always less than 5% of that found on the first introduction.

The packed column used in the gas chromatograph was a 6 ft × 1/8 in stainless steel column packed with 5% SE-30 on 80–100 mesh Chromosorb WAW DMCS. Helium was used as the carrier gas with a flow rate of 30.0 cc/min. The oven temperature was programmed to hold for 2 minutes at −50°C and increase at 10°/min to 250°C. The mass spectrometer was operated in the electron impact mode and the data were collected in the regular "AQUIRE" mode for samples that might have relatively large amounts of solvent, or in the "SIM" (single ion monitor) mode for samples with only traces of solvent.

This method of introducing the sample gives an excellent plug injection. An example of the data display is shown in Figure 3. On the lower trace is displayed the total ion chromatogram. The hexane solvent gave several isomer peaks which eluted between 7.5 and 9.5 minutes. The

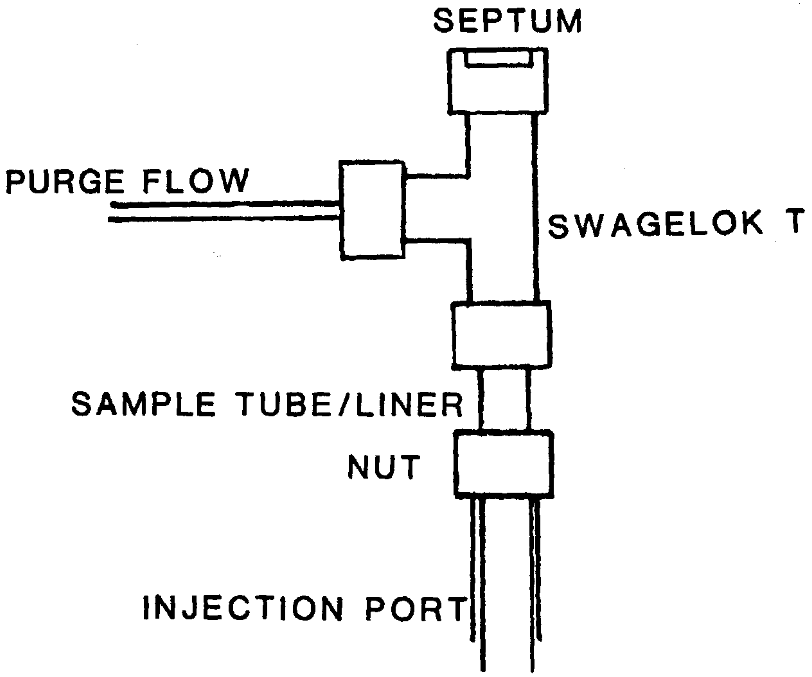

FIGURE 4 Modification for the simultaneous addition of a standard sample with solvent desorbed from a polymer.

identity of these peaks was confirmed by monitoring the characteristic ions at masses 43 and 86 as seen in Figure 3. The identity of the hexane was further confirmed by the mass spectra of the compounds that gave rise to these peaks and by the retention times on the SE-30 column. The peaks on the total ion chromatogram between 9.5 and 10.5 minutes are hexene isomers as identified from the mass spectra and the molecular ion at mass 84 (see below).

The amount of solvent was quantified by measuring the peak areas and comparing these areas to standard samples. In one modification of this technique a standard sample can be added as the solute is being desorbed from the polymer, Figure 4.

RESULTS AND DISCUSSION

The reproducibility of the technique was measured by placing known amounts of hexane on pre-washed and conditioned Poropak Q that was packed in the injection port liner in the place of the polymer sample. The results of these tests are shown in Table I.

The results of three runs with polymer samples are listed in Table II. The amount of hexane desorbed from the polymer sample is listed in micrograms of hexane/gram polymer sample. The peak areas on the total ion chromatogram were calibrated with standard samples of hexane in isooctane.

Initially we attempted to remove the solvent from the polymer in a vacuum oven set at 60°C, but when we realized that the solvent could

TABLE I

Reproducibility of Desorption and Measurement of Hexane from Poropak Q

Ng hexane added to Poropak Q	Mass spectrometer response to hexane in arbitrary units	Std Dev
6.6	72,140	
	76,468	
	72,446	
	73,685	2,415 (±3.3%)
33.	373,046	
	379,017	
	364,082	
	372,048	7,517 (±2.0%)

TABLE II

Measurement of Hexane in Polymer Sample after Desorption in Vacuum

Run	Temperature	Time in Vacuum Oven	μg hexane/g polymer sample
1	60°C	95 min	1.9×10^3
		48 hr	4.2×10^2
2	80°C	0	1.2×10^3
		1 hr	2.3×10^1
		2 hr	1.7×10^1
		4 hr	1.7
		8 hr	2.3
		24.5 hr	1.1
3	80°C	0	1.7×10^3
		0	1.3×10^3
		0	6.1×10^3
		5.5 hr	1.2×10^3
		5.5 hr	1.3×10^2
		27.5 hr	6.0×10^1
		27.5 hr	1.3×10^1
		74 hr	2.5
		74 hr	5.3
		95 hr	1.7
		95 hr	5.6

not be removed in a reasonable time at 60°C, further work at this temperature was discontinued. Data were acquired at 80°C, and the data for Run #3 are plotted in Figure 5.

The mass of the 1" × 4" polymer sample is 0.150 g; thus 0.1 μg of hexane corresponds to about 0.5 p.p.m. This is nowhere near the limit of sensitivity, since with the Hewlett-Packard 5985 gc/ms in the single ion monitor mode it is possible to detect 10 picograms.

The hexane used in this work contained hexene as an impurity; the ratio of the areas of the hexene the hexane peaks was 0.15. During vacuum drying hexane was removed more readily than hexene from the polyisobutylene films. In samples that had been dried about 90 hours, the ratio of hexene to hexane was 0.80 ± 0.40.

The method is a simple, highly sensitive method to determine solvent or volatile impurities in polymers. For those not wishing to replumb the gas chromatograph, purging with an external source of helium gives satisfactory results. We have used this procedure in the preliminary experiments in the study of solvents occluded in polymers. In cases

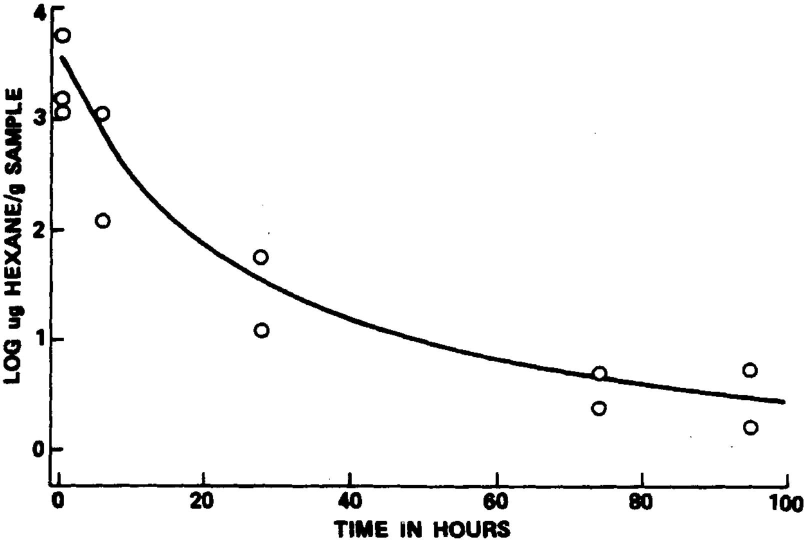

FIGURE 5 Log μg hexane/g polymer sample *vs* time in vacuum oven.

where the identity of the solvent is known, any suitable GC detector can be used in place of the mass spectrometer detector.

Since the samples were completely desorbed, the variations in the amounts of hexane from samples desorbed for the same time is probably due to non-uniform amounts of hexane dispersed throughout the polymer.

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