

## Gas Chromatography/ Mass Spectrometry

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# Integrated Microextraction, Syringe Headspace, and SPME Characterization of Organic Contamination from Plastic Bags by GC

**Introduction**

Many industries, such as semiconductor, nanotechnology, forensics, and scientific instrumentation, need to store raw materials or high precision assembly components in a clean and protected environment prior to processing.

For reasons of cost, availability, convenience, and minimization of cross-contamination the container of choice is often a resealable plastic bag. These bags may be rated for human safety, particulates, or metal contamination, but rarely for volatile or semivolatile organics. In addition to accidental contaminants, there may also be processing-related contaminants from additives (e.g. anti-oxidants, lubricants, monomers, plasticizers, slip agents, stabilizers, etc.) which are often undocumented.

The food and pharmaceutical industries have numerous tests for extractables and leachables using test conditions relevant to their products. This paper examines three simple but sensitive tests for organic contamination using gas chromatography/mass spectrometry (GC/MS) for detection and identification.

Plastic bags are sampled by solvent micro-extraction, static syringe headspace, and headspace Solid Phase Microextraction (SPME) in an automated process using the PerkinElmer TurboMatrix MultiPrep+, a multi-function GC auto-sampler. Contamination is found at sufficiently high concentration to raise concern about possible transfer to the stored items with potentially adverse consequences.

## Experimental

All samples were 2 x 3 inch, 4 mil “press to close” industrial-grade FDA-compliant polyethylene bags.

### Solvent Microextraction

Add 1.5 mL of methanol (99.98% LC/MS grade) to bag with a new glass Pasture pipette, move it quickly but gently around the interior surface for one min. Open and tilt bag, allowing the solvent to collect in a bottom corner, transfer with the same pipet to an autosampler vial, and cap with Teflon®-faced silicon septum. Repeat procedure with the same bag using n-hexane (pesticide grade).

### Static Syringe Headspace and SPME Headspace

Turned bag inside-out (using nitrile gloves) to minimize exposure of the exterior to the headspace. Fold in half lengthwise, roll, insert into a 20 mL headspace vial, and cap Teflon®-faced silicon septum. All samples were processed and injected with a PerkinElmer TurboMatrix™ MultiPrep + autosampler.

## Instrumental Conditions

Instrument conditions are shown in Table 1. Liquid injection used different oven and injector split conditions than the headspace syringe and SPME methods because of the solvent peak.

## Results

### Solvent Microextraction

Chromatograms from the methanol solvent microextraction are shown in Figure 1. The top shows *m/z* 45 to 300 (avoiding Ar and CO<sub>2</sub>), and the bottom shows extracted and summed ions characteristic of alkanes. Most of the components appear to be alkanes. No analyte peaks were observed after 12 min.

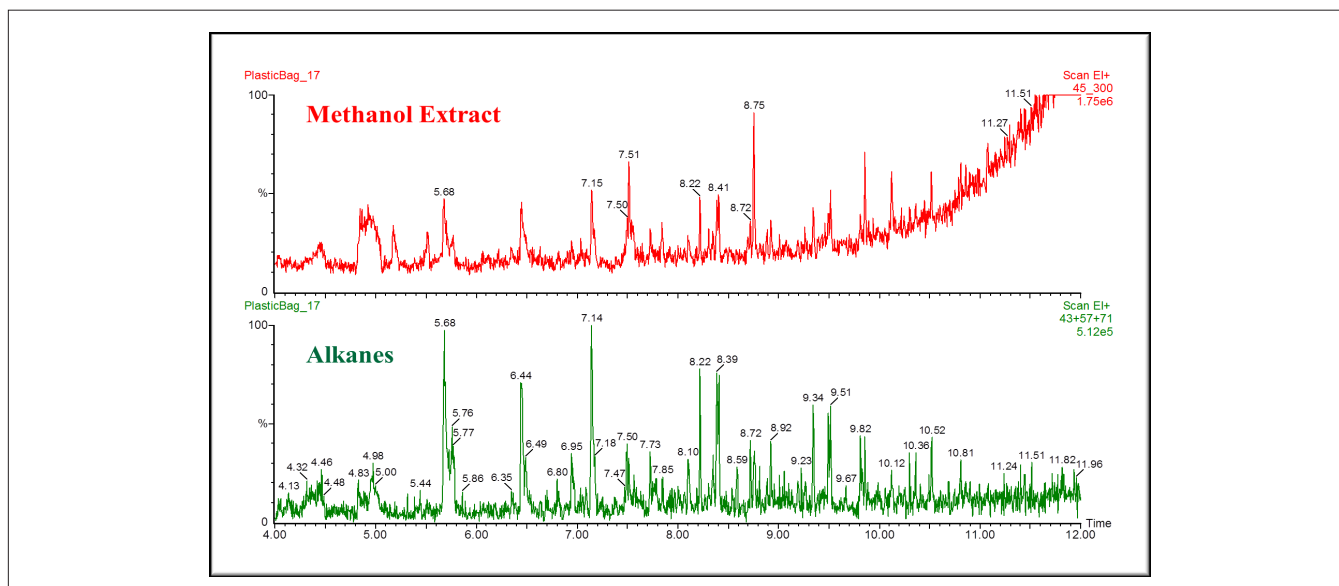
The peak at 7.5 min and a few smaller ones are silicones also present in the solvent blank. Using the averaged response factor of several TIC peaks of an EPA 8260 standard (5 ng on-column), the total peak area is used to calculate about 1.4 mg of contaminants extracted from the bag.

Table 1. Instrumental Conditions tables.

Gas Chromatograph	PerkinElmer Clarus GC	Mass Spectrometer	PerkinElmer Clarus SQ 8 GC/MS
Injector Type	Programmable Split/Splitless	GC Transfer Line	250 °C
Injector Temperature	280 °C (liquid), 200 °C (headspace)	Ion Source	250 °C
Analytical Column	PerkinElmer Elite™ - 5 MS 30 m x 0.25 mm ID x 0.25 µm	Ion Source Type	Electron Ionization
Liquid Injection	80 °C for two min, then ramp to 280 °C at 20 °C/min, hold five min	Acquisition Range	<i>m/z</i> 35-500
Oven	Splitless until two min, then 50 mL/min	Scan Time	0.20 sec
Split Flow	40 °C for 1.5 min, then ramp to 250 °C at 20 °C/min	Inter-Scan Delay	0.05 sec
Headspace Injection	10 mL/min	Solvent Delay	1.5 min
Oven			
Split Flow			
Carrier Gas	1 mL/min Helium, 99.999+% purity		

Autosampler		PerkinElmer TurboMatrix™ MultiPrep +			
Syringe & SPME Headspace	Syringe Headspace	Syringe Headspace	SPME Headspace	SPME Headspace	
Sample Equilibration	20 min	Sample Volume	20 min	65 µm PDMS/DVB Fiber	
Equilibration Temperature	70 °C	Syringe Temperature	70 °C	Conditioning Temperature	250 °C
Agitation	1.5 min	Injection Rate	1.5 min	Pre/Post conditioning Time	5 min
				Desorb Time	2 min



2 Figure 1. Methanol extract from plastic bag.

Figure 2 shows the hexane extract. Most of these peaks appear to be the same as in the methanol extract.

The integrated area of these peaks yields about 13.7 mg of contaminants, for a methanol + hexane total of about 15.1 mg of extracted impurities.

### Syringe Headspace

Figure 3 shows the syringe static headspace chromatogram. Most of the peaks appear to be alkanes. Library searching tentatively identifies the peak at 10.16 min as the octyl ester of decanoic acid or similar, and 10.67 min as xylene or ethyl benzene.

The change in injection and GC methods improved resolution of the GC peaks earlier than 7 min. Less material equilibrated into the headspace than was extracted into the solvent. Accounting for injecting 1 mL of the 20 mL headspace volume with a 10:1 split, the integrated peak area represents about 86.5 ng, or 0.57% of the amount of material calculated as extracted into the solvents. However, the liquid injection was only 1  $\mu$ L of the 1.5 mL extract, so only a very small portion was injected. The headspace chromatographic background was much lower because of the absence of solvent.

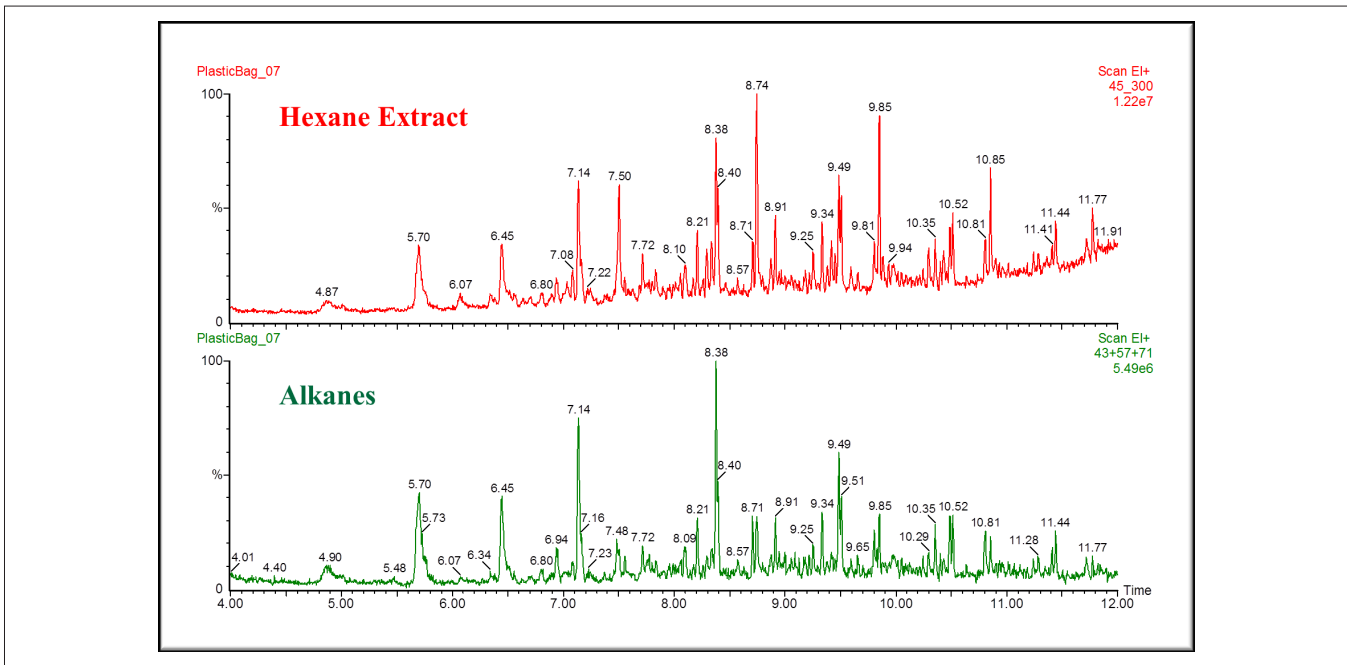


Figure 2. Hexane extract from plastic bag.

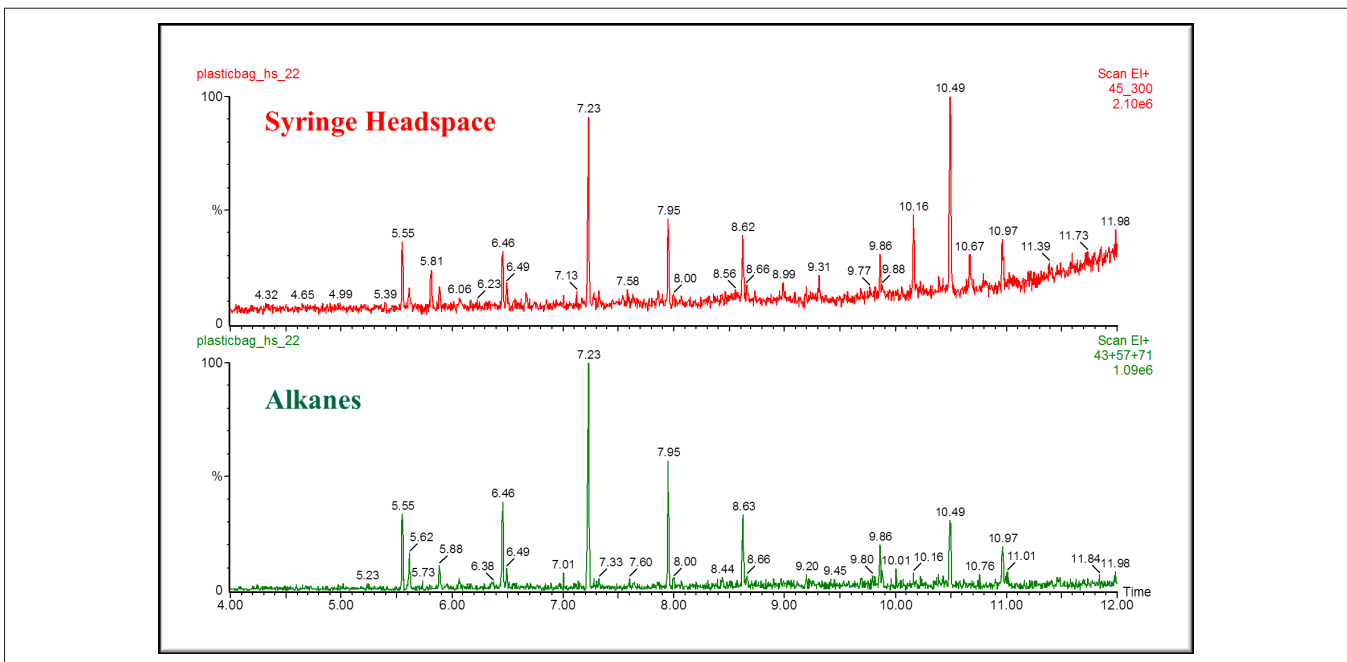


Figure 3. Syringe Headspace of plastic bag.

## SPME Headspace

Figure 4 shows the SPME headspace chromatogram. The majority of the peaks appear to be alkanes. Several appear to be terminal aldehydes or alcohols, and 5.81 min is 4-Cyanocyclohexene.

The SPME chromatogram visually appears to have fewer peaks than the earlier ones, but this is misleading because the major alkane peaks are much larger. When graphically scaled the same as the hexane extract chromatogram the SPME chromatogram has even more small peaks.

The peaks correspond to about 322 ng of extracted material on-fiber, or about 3.7x the calculated extracted quantity from the syringe headspace. SPME has about 75x the syringe headspace GC peak area because only 1/20 of the syringe headspace was injected. Similarly, while the combined liquid extraction amount is about 47x higher than SPME, the integrated SPME peak area is about 3.9x larger than the combined methanol and hexane peaks because of the high liquid sample dilution.

## Discussion

Liquid extraction models contamination from direct physical contact of the bag and its contents over a prolonged period of time. The extraction period was kept short (1 min) in an attempt

to sample only the bag surface. Syringe and SPME headspace modeled vapor phase deposition. Thermostating at 70 °C was chosen to simulate storage at elevated temperatures. The SPME fiber extracts analytes from the headspace, concentrating the analytes and improving detection limits.

Liquid extraction removed the most contamination from the bags, but the requisite dilutions reduced its sensitivity relative to the headspace techniques. Syringe headspace required no solvents and was simpler to use than SPME, but less sensitive. SPME was the most complicated to use, but gave the best chromatography and detection limits.

The timings, temperatures, and other conditions used here are not optimized. Sensitivity could be improved or analysis time significantly reduced.

## Conclusion

Three methods of contamination extraction from industrial-grade polyethylene bags were used with a robotic GC/MS autosampler. The bags were shown to be capable of contaminating high-purity objects both through direct contact and through the vapor phase.

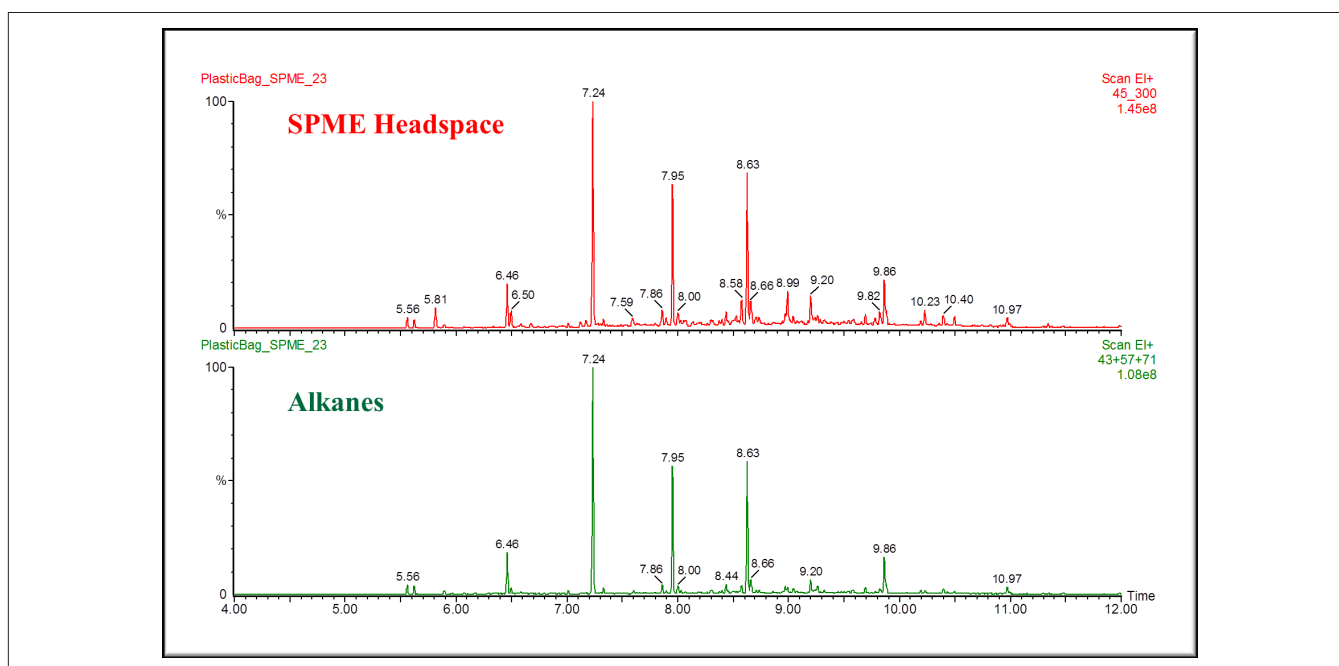


Figure 4. SPME Headspace Chromatogram.