A Survey of Residual Solvents in Various Inks used in Consumer Product Packaging

Application Note

Abstract

Food manufacturers use various printing inks on their consumer product packaging. These inks are typically used on the outside of the package, but are now also included on the packaging material used in the microwave. These inks can contain residual solvents currently monitored in food and drinking water.

This application note will present a survey of consumer product packaging and the residual solvent released from the printing ink using both static and dynamic headspace techniques.

Introduction

Printing inks are routinely used in consumer product packaging for baking and microwaving to enhance the shelf appeal to consumers. As more products are cooked in the microwave for quick snacks and meals, these printing inks are being placed on the package used in the microwave to assure proper heating. Printing on the microwave package also assist the consumer to properly place the package in the microwave with the correct side up.

These printing inks may contain volatile organic compounds (VOCs) which, depending on the type and amount left on the package, can cause concern to consumers. To minimize these concerns, many regulatory agencies around the world restrict the type of inks and their respective VOCs allowed in consumer products.

Four common consumer products were evaluated for this application note. The first is common microwavable gourmet popcorn with a colorful outer wrap. The second is a microwaveable sandwich with a crisping sleeve. The third is a potato chip bag and the final is a decorative printed paper baking cup for use in a conventional oven.

A Teledyne Tekmar HT3™ Headspace Analyzer was used for this application note in the both the static and the dynamic mode along with a Thermo Focus GC/DSQ™ II MS for the identification of VOCs found in typical consumer product packaging. An environmental column was used to assist in the detection and preliminary identification of volatile organic compounds (VOCs) released from the samples. These VOCs, including benzene and toluene can be quickly identified with the environmental column and confirmed with an EPA Method standard.

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com

Experimental-Instrument Conditions

HT3 Headspace Instrument Parameters			
Static		Dynamic	
Variable	Value	Variable	Value
Valve Oven Temp	200°C	Valve Oven Temp	180°C
Transfer Line Temp	200°C	Transfer Line Temp	200°C
Platen/Sample Temp	90°	Platen/Sample Temp	90°
Sample Equil Time	40.00 min	Sweep Flow Rate	150 mL/min
Pressurize	10 psig	Sweep Flow Time	5.00 min
Loop Fill Pressure	5 psig	Desorb Temp	250°C
Inject Time	2.00 min	Desorb Time	1.00 min
		Trap Material	#9

Table 1: Static and Dynamic HT3™ Parameters

Thermo Focus GC/DSQ™ II MS Parameters	
Column	Restek Rtx® VMS, 20m, 0.18mm ID, 1µm; Constant Flow 1.0 mL/min
Oven Program	35°C for 4 min; 16°C/min to 160°C, 25°C/min to 250°C hold for 4 min, run time 19.1 min
Inlet:	Temperature 220°C, Helium Carrier Gas, Split Flow –Dynamic 30 mL/min, - Static 10mL/min
MS	Source and Transfer Line Temp 230°C, Full Scan 35.0 *m/z* to 270.0 *m/z* Scan Rate 1492.11

Table 2: Thermo Focus GC/DSQ II MS Parameters

Sample Preparation

A variety of consumer product packages, most of which contain printing that is exposed to the product during cooking were investigated for this application note. The first is a typical gourmet microwave popcorn bag with an outer wrapper. The outer wrapper was test, even though it is not left on during microwaving. The top of the popcorn bag and the bottom cooking surface of the bag were tested separately.

The second sample is a typical microwaveable sandwich with a crisping sleeve. The crisping sleeve has printed instruction and a seam that may be sealed with a form of glue. Both the area of the crisping sleeve with printing and the sealed seam were tested separately.

The third sample is an individual serving potato chip bag. The bag was a foil appearing inner lining with printing on the outside of the bag. The potato chip bag was placed in to the headspace vial so that the inner lining was exposed. The bag was rinsed with deionized water and wiped dry with a laboratory grade wiper to remove as much food residue from the bag as possible.

The final sample is a printed paper baking cup. The paper baking cup was cut in half.

The samples were cut into appropriate sizes. These were carefully placed into 22mL headspace vials folding or positioning the sample to ensure that the product contact surface was more exposed to the headspace area. Each sample was prepared in duplicate to allow one of the samples to be spiked with 5µL of an internal standard solution.

The internal standard solution consisted of a 100ppm mix of containing chlorobenzene-d5, 1,4-dichlorobenzene-d4, toluene-d8, 1,4-difluororbenzene, pentafluorobenzene, dibromofluoromethane, and 4-bromofluorobenzene. To assist in the identification of common environmental VOCs, a headspace vial containing 10µL of a 50ppm standard containing an 8260B Mega Mix, 8260B Acetate Mix, California Oxygenates Mix, and a 502.2 Calibration Mix (gases) was tested as the last vial of the run.

All of the samples and standard were tested with Teledyne Tekmar HT3 with both dynamic and static headspace methods and the Thermo Focus GC/DSQ II MS. The headspace parameters are listed in Table 1 and the GC/ MS are listed in Table 2.

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com

Results

The total ion current (TIC) chromatograms from both the dynamic and static headspace methods were evaluated using Thermo EnviroLab Forms 3.0 software with the NIST 8 spectral database. The TIC chromatograms were first evaluated to detect VOCs in the samples that were consistent with the EPA 8260 standard and to estimate their concentration in the samples.

These VOCs were first confirmed to be the VOC by ensuring that ratio of the peak area of the secondary ion to the peak area of the primary ion from the sample was consistent with the ratio obtained for the VOCs standard ions. The peak area of the primary ions of the sample and the standard were then used to calculate the concentration in ppb of the VOC. The concentrations of the found VOCs are listed in Table 3 for the potato chip package and the three components of the popcorn package. Table 4 lists the concentration of the VOC's found in the baking cup and the sandwich crisping sleeve.

			Popcorn Packaging					
	Potato Chip Package		Outer Wrapper		Bag Top		Bag Bottom	
VOCs	Dynamic	Static	Dynamic	Static	Dynamic	Static	Dynamic	Static
Acetone	5861		1283	331.5	227.8	74.8	598.9	221.7
t-Butanol	253.9		253.7		605.2	181.8	934.4	183.3
Tetrahydrofuran			141.1	42.2				
2-Butanone	84.8	16.0	85.7		16.9		116.3	
Ethyl Acetate							341.8	
Benzene							2.9	
n-Propyl Acetate	124.0	109.9	62.8		2.0			
Toluene	3.1	1.6	16.6	11.8	5.9	1.5	21.3	8.8
Tetrachloroethane	6.6							
4-Methyl-2-2pentanone	34.8	8.0	131.8		17.1	4.2	25.6	
Ethylbenzene	1.5		4.4		1.8		3.5	
m-, p-Xylene	1.5		7.5	3.5	4.5	1.3	42.1	12.1
o-Xylene	1.5		5.8	17.8	2.5	0.5	4.5	2.5
Stryene					2.4		5.4	2.2
n-Propylbenzene			4.3		2.0		3.5	
4-Isopropyltoluene	7.5							
1,2,4-Trimethylbenzene	4.1	0.9	26.4	6.3	10.1	1.7	18.1	5.9

Table 3: Calculated Approximate ppb (based on Sample Weight) of Identified Volatile Organic Compounds in the Potato Chip Bag and the Three Different Parts of the Popcorn Bag Packaging.

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com

			Sandwich Crisping Sleeve			
	Baking Cup		Top		Bottom with Seam	
VOCs	Dynamic	Static	Dynamic	Static	Dynamic	Static
Methylene Chloride			1.5			
Acetone	1316	265.1	6653	1724	1169	489.9
t-Butanol	105.7		132.0			
Chloroform			5.0	5.2	17.9	
2-Butanone	69.6		128.5		88.4	
Ethyl Acetate			13.6		55.1	
Benzene	3.5				2.1	
Toluene	3.2	1.9	10.9	5.3	17.3	0.4
Tetrachloroethane					1.2	
4-Methyl-2-pentanone	78.8	19.7	37.9	129.1	40.4	13.5
Dibromochloromethane					2.4	
Butyl Acetate			81.9		321.2	
Ethylbenzene	7.8	4.4	9.9	6.8	21.1	
m-, p-Xylene	6.9	3.8	34.7	13.9	33.7	0.5
o-Xylene	28.1	16.8	6.0	11.4	40.5	
Styrene	53.4	25.4			3.8	
Bromoform					2.6	
Isopropylbenzene			23.5	14.2	113.0	
n-Propylbenzene			21.9	11.8	72.8	
4-Isopropyltoluene			2.4		1.8	
n-Butylbenzene	2.3					
1,2,4-Trimethtlbenzene					19.7	

Table 4: Calculated Approximate ppb (based on Sample Weight) of Identified Volatile Organic Compounds in the Baking Cup and the Two Different Parts of the Sandwich Crisping Sleeve.

The TIC data was also evaluated to determine other compounds present in the sample that were not in the 8260 mixture and to compare the differences between the TIC data of the samples from the dynamic and static headspace method. The other compounds identified in the samples were only tentatively identified with the NIST 8 database and were not confirmed with actual standards.

Figure 1 to Figure 7 are the comparisons of the dynamic headspace TIC to the static headspace TIC for each of the samples.

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com

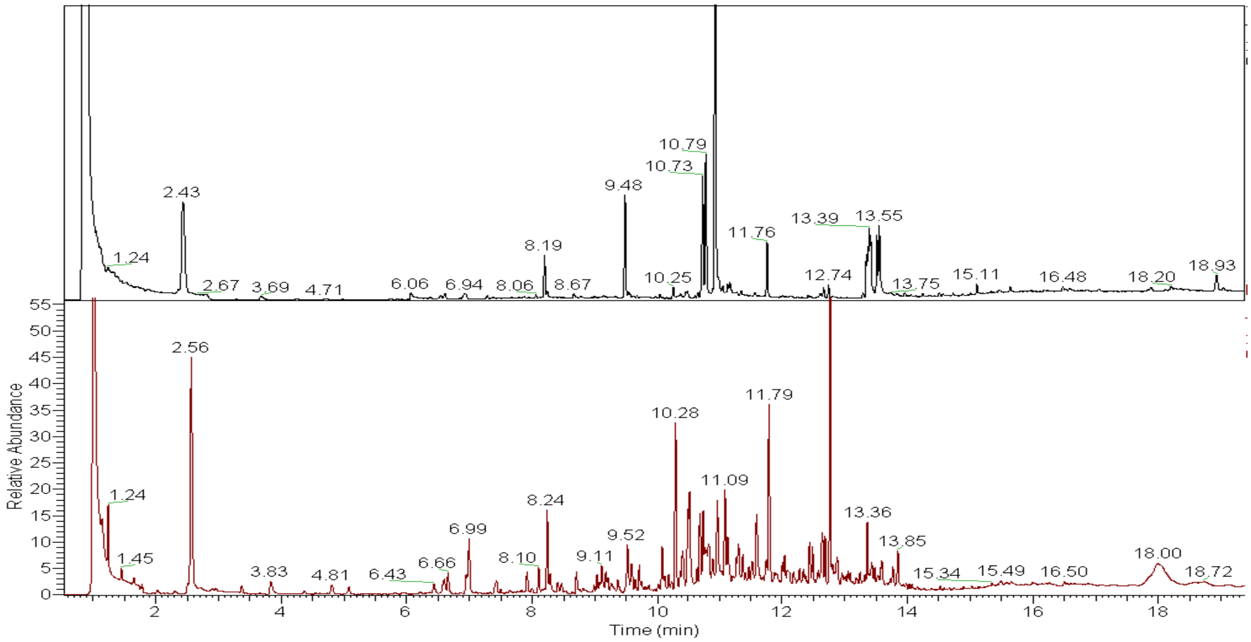

Figure 1: Comparison of the TIC data from the Dynamic Headspace (Bottom Chromatogram) to the Static Headspace Method (Top Chromatogram) for the Potato Chip Package. The peak at 2.56 minutes in the dynamic TIC is acetone. The small peak at 2.9 minutes in the dynamic TIC is t-butanol. The cluster at 13.39 to 13.55 in the static headspace TIC was identified by the NIST software as Dowanol 62b.

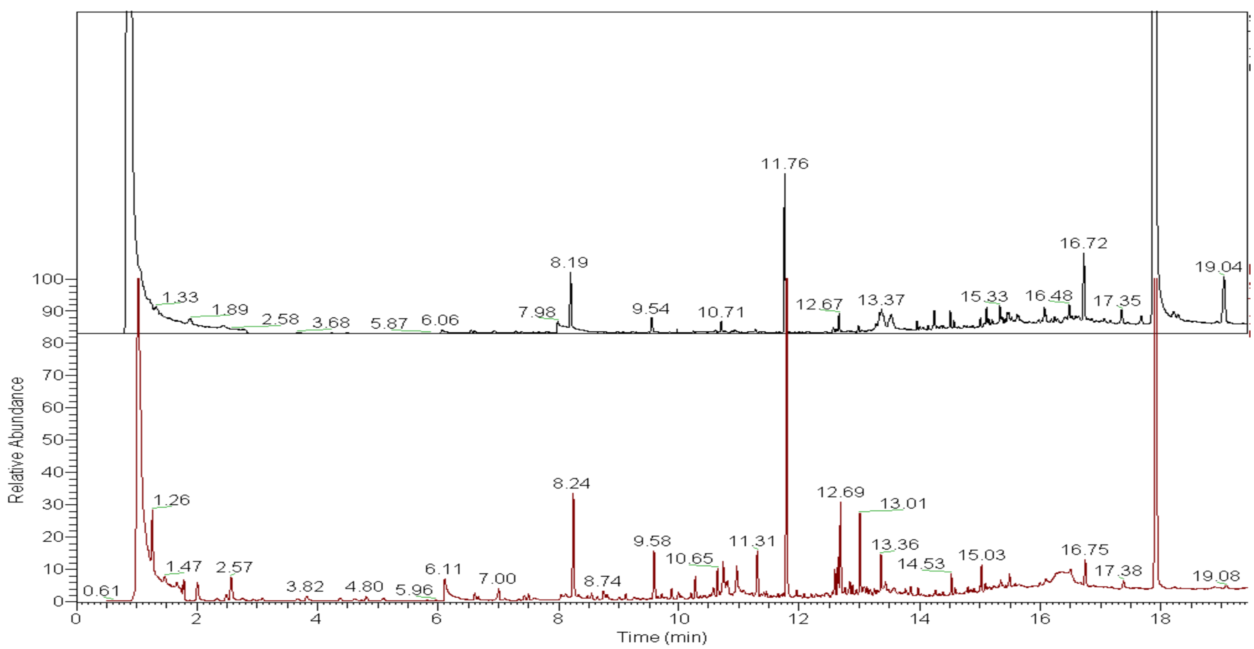

Figure 2: Comparison of the TIC data from the Dynamic Headspace (Bottom Chromatogram) to the Static Headspace Method (Top Chromatogram) for Non Microwavable Popcorn Outer Wrapper. The peak at 2.57 minutes in the dynamic TIC is acetone. The small peak at 2.9 minutes in the dynamic TIC is t-butanol. The cluster at 13.39 to 13.55 in the static headspace TIC was identified by the NIST software as Dowanol 62b. The peak at 18 minutes was identified by the NIST software as dibutyl phthalale.

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com

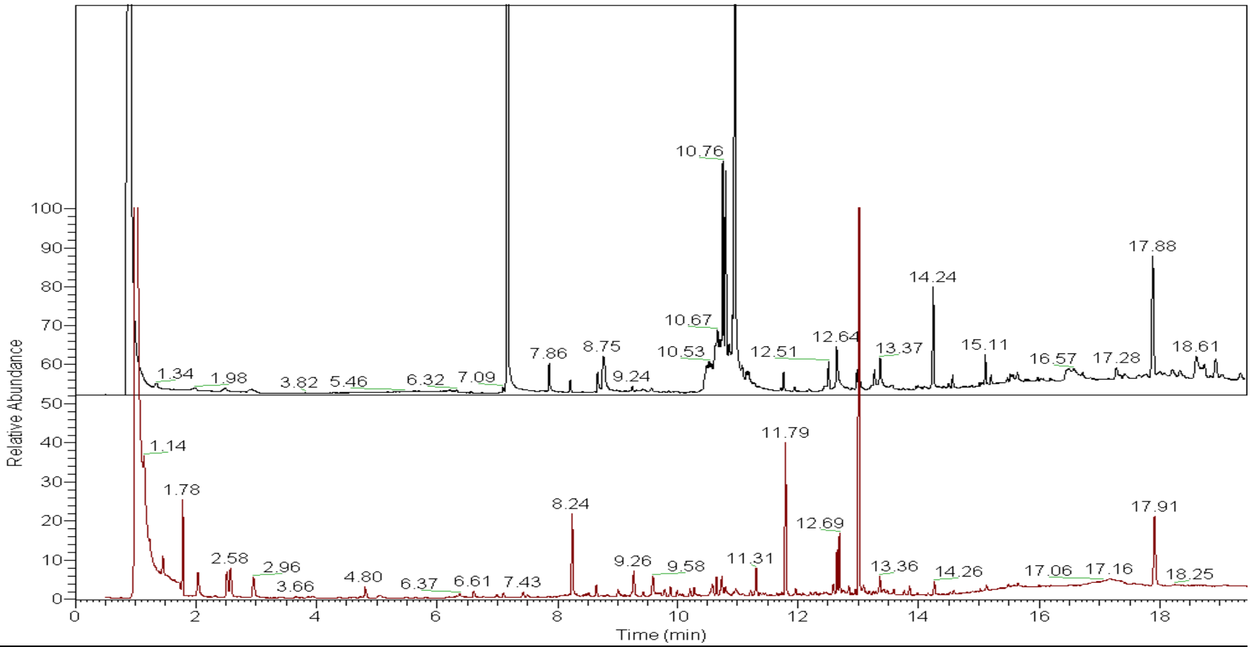

Figure 3: Comparison of the TIC data from the Dynamic Headspace (Bottom Chromatogram) to the Static Headspace Method (Top Chromatogram) for the Top Portion of the Microwavable Popcorn Bag. The peak at 2.56 minutes in the dynamic TIC is acetone. The peak at 2.96 minutes in the dynamic TIC is t-butanol. The cluster of peaks at 10.7 to 10.9 in the static headspace TIC was identified by the NIST software as a dipropylene glycol monomethyl ether. The peak at 10.96 minutes in the static TIC was identified by the NIST software as 1-(2-methoxypropoxl)-2-propanol.

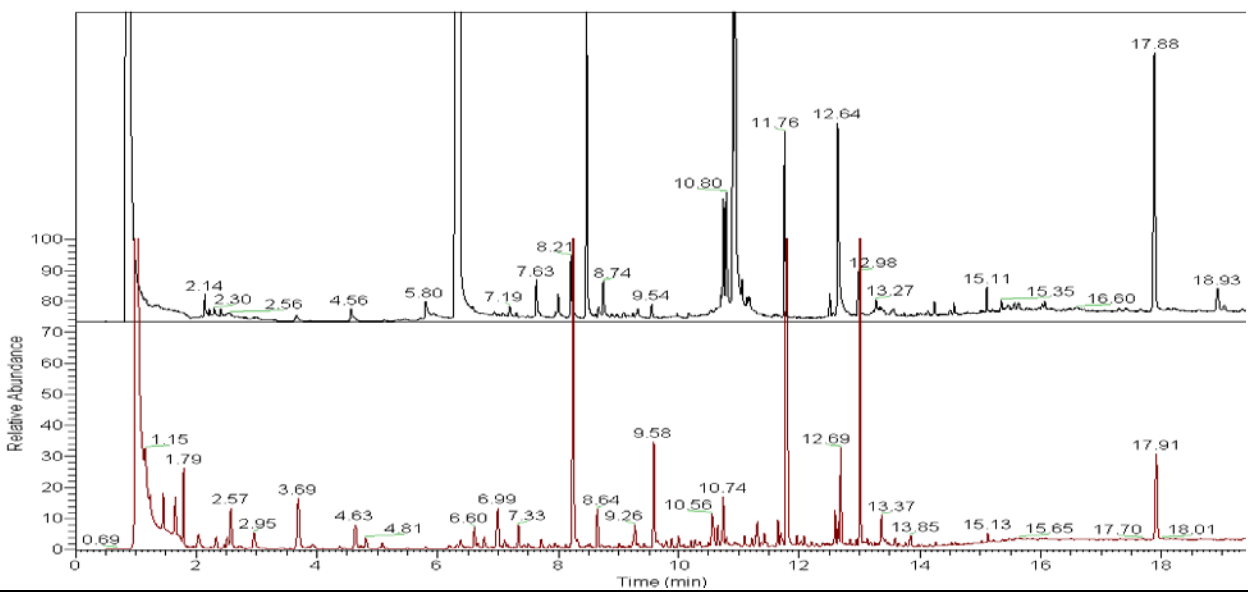

Figure 4: Comparison of the TIC data from the Dynamic Headspace (Bottom Chromatogram) to the Static Headspace Method (Top Chromatogram) for the Bottom Portion of the Microwavable Popcorn Bag. The peak at 2.57 minutes in the dynamic TIC is acetone. The peak at 2.95 minutes in the dynamic TIC is t-butanol. The cluster of peaks at 10.7 to 10.9 in the static headspace TIC was identified by the NIST software as a dipropylene glycol monomethyl ether. The peak at 10.96 minutes in the static TIC was identified by the NIST software as 1-(2-methoxypropoxl)-2-propanol.

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com

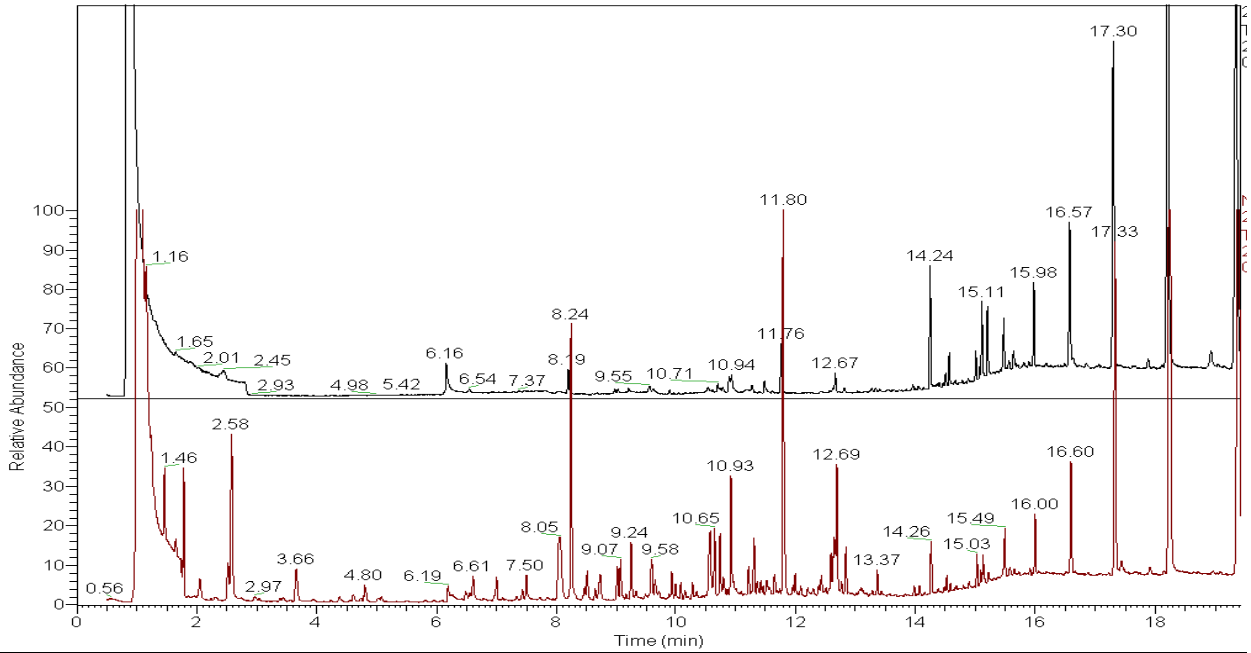

Figure 5: Comparison of the TIC data from the Dynamic Headspace (Bottom Chromatogram) to the Static Headspace Method (Top Chromatogram) for the Baking Cup. The peak at 2.58 minutes in the dynamic TIC is acetone. The small peak at 2.97 minutes in the dynamic TIC is t-butanol. The peak at 8.24 in the dynamic TIC (8.19 minutes for the static TIC) was identified by the NIST software as hexanal. The peak at 11.8 minutes in both chromatogram was identified by the NIST software as nonanal. The pattern peaks at 15.5, 16.0, 16.6, 17.3, 18.2 and 19.4 minutes were identified by the NIST software as long chain aliphatic hydrocarbons.

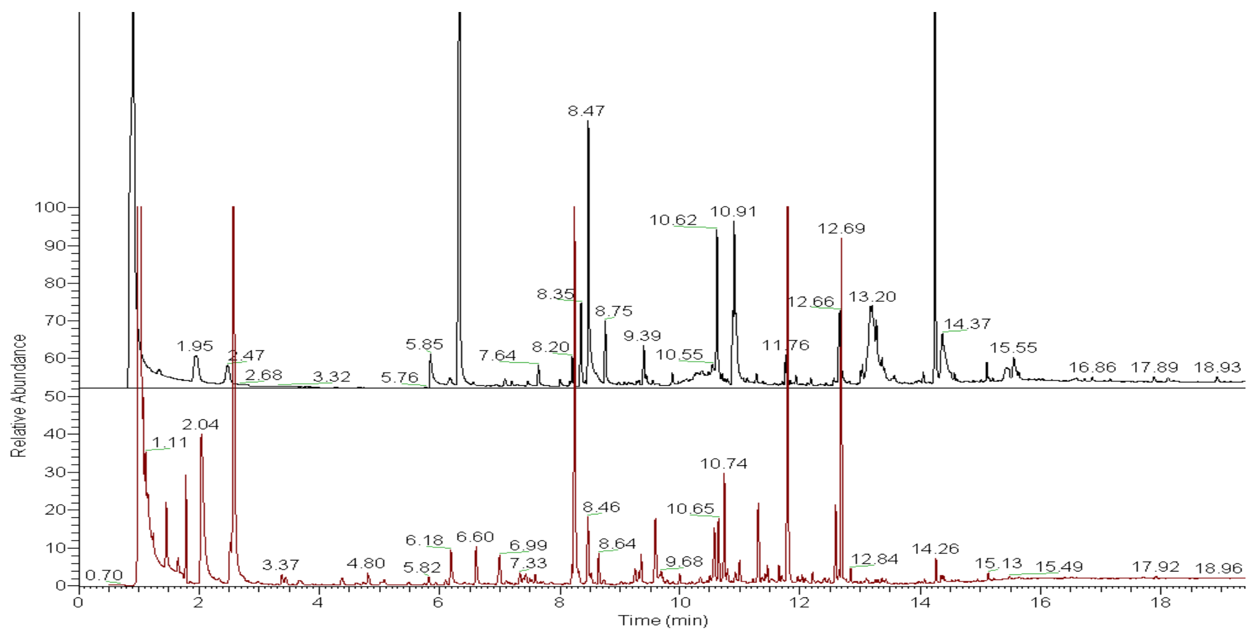

Figure 6: Comparison of the TIC data from the Dynamic Headspace (Bottom Chromatogram) to the Static Headspace Method (Top Chromatogram) for the Top Portion of the Microwavable Sandwich Crisping Sleeve. The peak at 2.56 minutes in the dynamic TIC (2.47 minutes in the static) is acetone. The small peak at 2.9 minutes in the dynamic TIC is t-butanol.

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com

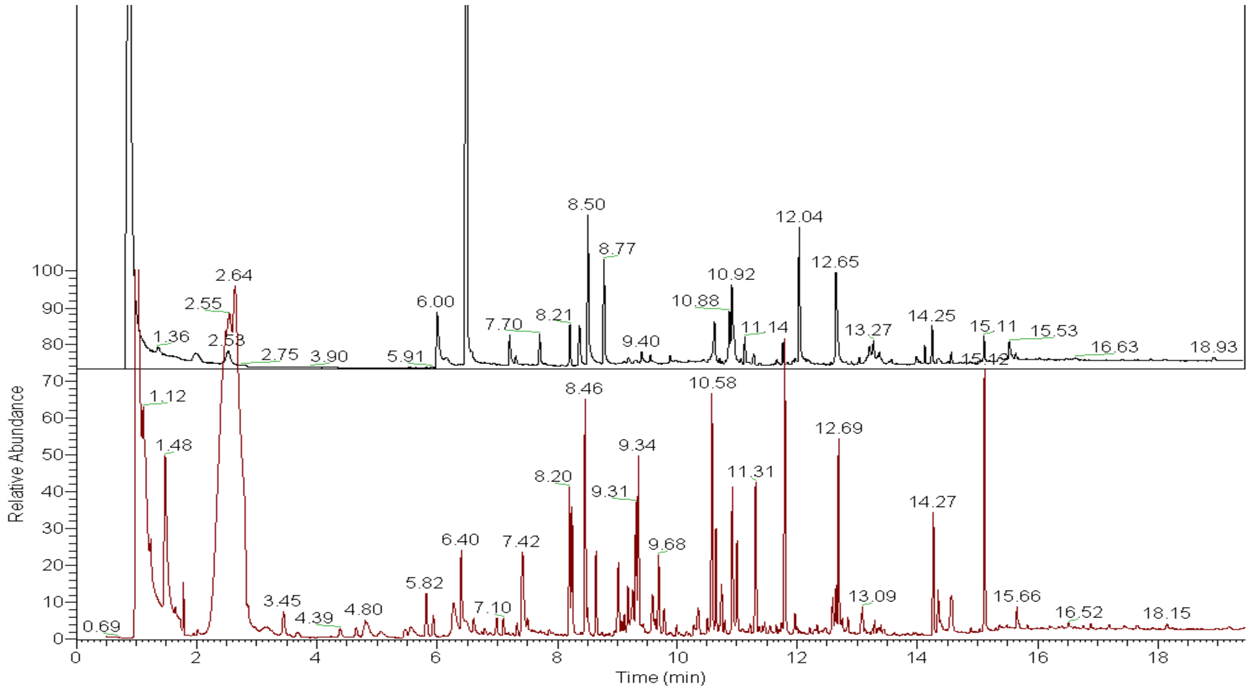

Figure 7: Comparison of the TIC data from the Dynamic Headspace (Bottom Chromatogram) to the Static Headspace Method (Top Chromatogram) for The Bottom Portion of the Microwavable Sandwich Crisping Sleeve Including the Seam.

Conclusions

Various consumer product packaging were tested for residual solvents with both the dynamic option and the static option of a Tekmar HT3 headspace instrument. Both the dynamic and the static mode were capable of detecting numerous volatile organic compound released from these consumer products.

The HT3 in either the static or dynamic mode is an excellent headspace instrument for the detection of VOCs in printing inks used on consumer product packaging.

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com