RESIDUAL SOLVENTS IN FOOD PACKAGING
DHS Dynamic Headspace Sampler & Static Headspace Sampler Approaches
APPLICATION NOTE AN_176

Introduction

The increased awerness for safe and not contaminated food has led the food safety monitoring to become one of the most important applications for the analytical chemistry.

Food packaging can be a possibile source of contamination in case toxic substances are released to the foodstuff.

Most of the food products are nowadays, as well known, provided with some form of packaging material. ALso, the use of semi-processed food has become more popular, raising the need for advanced packaging solutions. The primary intent of food packaging is to protect the foodstuff from possible contamination resulting from the contact with the external environment. Such food packaging materials are composed of several layers of different materials that guarantee certain physical qualities (robustness, strenght, flexibility...). Residual solvents can be absorbed in food packaging during printing and lamination processes. In both cases the hazard is represented by excessive solvent retention in packaging and the subsequent migration to the foodstuff. Excessive migration of these substances can affect the flavor of food and cause health problems in humans.

In this work, two different configurations have been used to perform the analysis of food packaging in 6 real samples. The first configuration is based on DANI Master GC Coupled with DANI Master SHS Static Headspace Sampler. In the second one the Dynamic Headspace Sampler is used. Both solutions have been proved to be reliable tools able to be implied for the analysis of two critical aspects:

- the **quality control** of flexible packaging through the determination of residual solvents from manufactoring process, adhesives, inks and dyes;
- the study of the **migration** of chemicals from the packaging to foodstuff.

Food Packaging

DANI

Master SHS Static Headspace Sampler
EXPERIMENTAL CONDITIONS

Instrumentation

The first system configuration is composed of the DANI Master SHS Static Headspace Sampler coupled to the Master GC Fast Gas Chromatograph equipped with a Split/Splitless injector and a FID detector.

In the Static Headspace, the sample is placed in a sealed vial and heated to a suitable temperature for a certain amount of time. After this period, a portion of the gaseous phase is withdrawn and then injected into the chromatographic column. In this work, conditioning temperature was optimized in order to have the greatest yield of extraction in the shortest time considering the effects of thermal decomposition that could occur at such temperatures. The static headspace sampling technique provides highly reproducible results, but in case of solid samples quantitation can be challenging due to the difficulty in reproducing the sample matrix for external standard calibration. This limit can be resolved using the Multiple Headspace Extraction (MHE) technique that allows the proper calibration for solid samples for which it is difficult to reproduce the matrix.

Method conditions and instrumental parameters are shown in ***Tables 1 and 2***.

Master GC Fast Gas Chromatograph	
Injector	Split-Splitless
Injector Temperature	230°C
Column	VOCOL 60 m x 0.25 mm i.d. x 1.5 um d_f
Carrier (He)	1 mL/min (split 1:60)
Detector	FID (250°C)
Oven	40°C, 4°C/min, 170°C (2 min)

Table 1 : Master GC operative conditions

Master SHS Static Headspace Sampler	
Oven Temp	125°C
Manifold Temp	125°C
Transfer Line Temp	150°C
Equilibration time	30 min
Shaking	Medium
Pressurization Mode	Pressure
Aux Pression	1 bar
Pressure Eq. Time	0.2 min
Loop Fill Mode	Pressure
Loop Pressure	0.5 bar
Pressure Loop Eq .Time	0.2 min
Injection Time	0.2 min
Injection Mode	Standard
Vial Venting	Yes
Purge Time	0.3 min
Purge Flow	50 mL/min

Table 2 : Master SHS operative conditions

Master DHD Dynamic Headpsace Sampler
EXPERIMENTAL CONDITIONS

Instrumentation

The second system configuration is composed of the the DANI Master DHS Dynamic Headspace coupled to the Master GC Fast Gaschromatograph equipped with a Split/Splitless injector and a FID detector.

In the Master DHS the sample is directly placed into a conventional 20 mL vial. The vial is then introduced into a heated oven for incubation. When combined with the Master AS, the system delivers complete automation of all the operational steps (e.g. standard addition and incubation).

The vial is then pierced by a dual coaxial volumes needle in which a flow of inert gas blows through the headspace vial stripping the volatiles out of the sampling matrix. The gaseous phase, flowing into the needle external secondary volume, is led to a "valve and trap" focusing system which performs the concentration of the volatiles.

Superior sensitivity is obtained through the constant sweeping of the thermostatted vial, promoting the enrichment of the volatile compounds on the adsorbent trap. Analytes are focused in a sorbent packed trap, rapidly thermally desorbed and introduced into the gaschromatographic column.

After the injection, the trap is baked to a higher temperature to clean it, avoiding, thus, any risk of carryover effect.

Method conditions and instrumental parameters are shown in ***Tables 3 and 4***.

Master DHS Dynamic Headspace Sampler	
Trap Material	Carbotrap - Carbosieve SIII
Valve Temp.	250°C
Transfer Line Temperature	225°C
Stripping Time	10 min
Stripping Flow	30 mL/min
Trap Temp	30°C / 310°C
Injection Time	1 min
Baking Time	10 min
Trap Baking Time	350°C

Table 3 : Master DHS Parameters

Master GC Gas Chromatograph	
Injector	Split-Splitless
Injector Temperature	250°C
Column	VOCOL 60 m x 0.25 mm i.d. x 1.5 um d_f
Carrier (He)	1,5 mL/min (split 1:80)
Detector	FID (250°C)
Oven	35°C (4 min), 4°C/min, 200°C (2 min)

Table 4 : Master GC Parameters

Samples

Real packaging samples of 50 cm^2 were placed into 20 mL vials and conditioned for one hour at 100°C before the analysis.

A 14-components mixture containing equal volumes was used to prepare 6 calibration levels in the range of 0.5-20.0 mg/m^2. Packaging samples and standard vials were stripped for 10 minutes at 30 mL/min.

REAL SAMPLES ANALYSIS

Sample 1

Master SHS Static Headspace Sampler

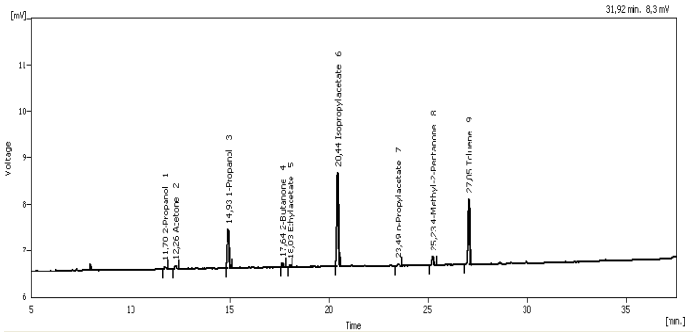

Figure 1: Chromatogram of Sample 1 [SHS-GC]

	Compound	Response	Amount [mg/m2]	Amount [%]
1	2-Propanol	0.493	0.181	2.8
2	Acetone	0.474	0.164	2.5
3	1-Propanol	4.272	1.434	21.9
4	2-Butanone	0.511	0.143	2.2
5	Ethylacetate	0.292	0.120	1.9
6	Isopropylacetate	9.383	3.113	47.6
7	n-Propylacetate	0.315	0.098	1.5
8	4-Methyl-2-Pentanone	1.041	0.234	3.6
9	Toluene	6.949	1.057	16.2

Table 5: List of Compounds and results for Sample 1 [SHS-GC]

Master DHS Dynamic Headspace Sampler

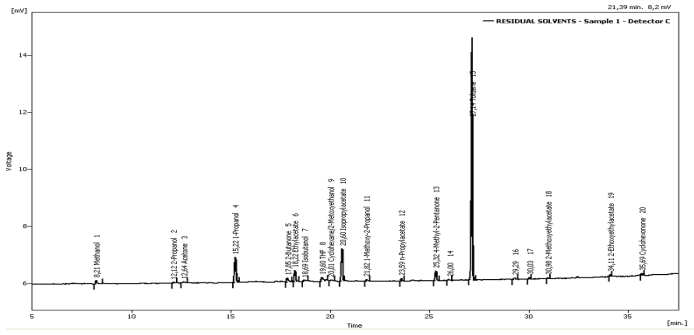

Figure 2: Chromatogram of Sample 1 [DHS-GC]

	Compound	Retention Time (min)	Response	Amount [mg/m2]	Amount [%]
1	Methanol	8.213	0.852	0.031	2.3
2	2-Propanol	12.117	0.258	0.026	2.0
3	Acetone	12.640	0.329	0.018	1.4
4	1-Propanol	15.220	4.724	0.500	37.7
5	2-Butanone	17.853	0.908	0.022	1.7
6	Ethylacetate	18.223	2.004	0.066	5.0
7	Isobutanol	18.693	0.379	0.024	1.8
8	THF	19.603	1.154	0.061	4.6
9	Cyclohexane/2-Metoxyethanol	20.013	0.267	0.014	1.0
10	Isopropylacetate	20.597	5.598	0.190	14.3
11	1-Methoxy-2-Propanol	21.823	0.387	0.071	5.4
12	n-Propylacetate	23.590	0.507	0.017	1.3
13	4-Methyl-2-Pentanone	25.320	1.779	0.040	3.0
14	Unknown	26.003	0.272		
15	Toluene	27.140	38.496	0.213	16.1
16	Unknown	29.290	0.418		
17	Unknown	30.033	0.359		
18	2-Methoxyethylacetate	30.980	0.186	0.009	0.7
19	2-Ethoxyethylacetate	34.107	0.246	0.021	1.6
20	Cyclohexanone	35.687	0.271	0.002	0.2

Table 6: List of Compounds and results of Sample 1 [DHS-GC]

Sample 2

Master SHS Static Headspace Sampler

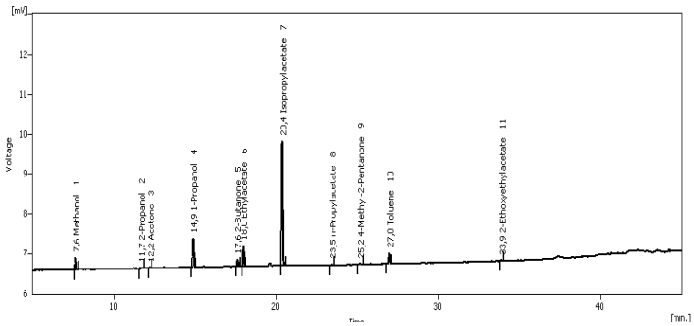

Figure 3: Chromatogram of Sample 2 [SHS-GC]

	Compound	Response	Amount [mg/m2]	Amount [%]
1	Methanol	1.105	0.644	8.6
2	2-Propanol	0.249	0.091	1.3
3	Acetone	0.197	0.068	1.0
4	1-Propanol	3.062	1.028	13.4
5	2-Butanone	0.924	0.258	3.5
6	Ethylacetate	2.254	0.925	12.3
7	Isopropylacetate	12.577	4.173	55.0
8	n-Propylacetate	0.251	0.079	1.1
9	4-Methyl-2-Pentanone	0.210	0.047	0.6
10	Toluene	1.171	0.178	2.4
11	2-Ethoxyethylacetate	0.169	0.085	1.1

Table 7: List of Compounds and results for Sample 2 [SHS-GC]

Master DHS Dynamic Headspace Sampler

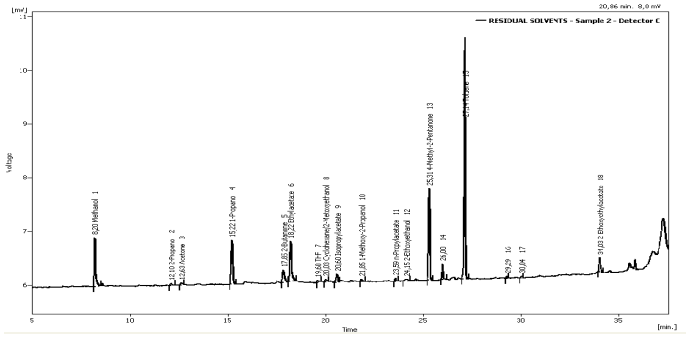

Figure 4: Chromatogram of Sample 2 [DHS-GC]

	Compound	Retention Time (min)	Response	Amount [mg/m2]	Amount [%]
1	Methanol	8.197	4.412	0.161	11.4
2	2-Propanol	12.100	0.312	0.031	2.2
3	Acetone	12.627	0.285	0.016	1.1
4	1-Propanol	15.223	4.196	0.444	31.3
5	2-Butanone	17.847	1.569	0.038	2.7
6	Ethylacetate	18.223	4.483	0.148	10.4
7	THF	19.603	0.240	0.013	0.9
8	Cyclohexane/2-Metoxyethanol	20.027	0.290	0.015	1.1
9	Isopropylacetate	20.597	0.813	0.028	1.9
10	1-Methoxy-2-Propanol	21.850	0.307	0.056	4.0
11	n-Propylacetate	23.593	0.295	0.010	0.7
12	4-Methyl-2-Pentanone	25.310	8.169	0.186	13.1
13	Unknown	26.000	1.413		
14	Toluene	27.140	0.172		
15	Unknown	29.290	0.172		
16	Unknown	30.043	0.180		
17	2-Ethoxyethylacetate	34.030	1.434	0.121	8.5

Table 8: List of Compounds and results of Sample 2 [DHS-GC]

Sample 3

Master SHS Static Headspace Sampler

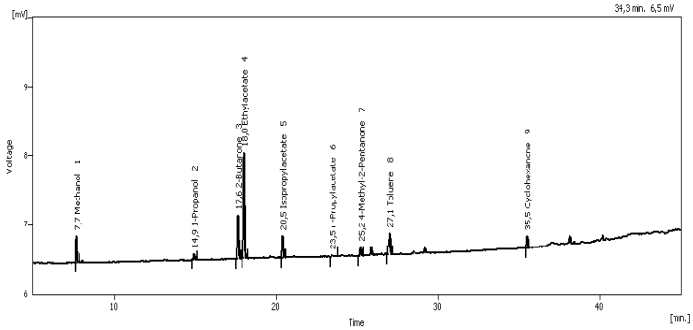

Figure 5 : Chromatogram of Sample 3 [SHS-GC]

	Compound	Response	Amount [mg/m2]	Amount [%]
1	Methanol	1.425	0.831	14.9
2	1-Propanol	0.499	0.168	3.0
3	2-Butanone	2.771	0.773	13.9
4	Ethylacetate	6.525	2.687	48.0
5	Isopropylacetate	1.175	0.390	6.9
6	n-Propylacetate	0.270	0.085	1.6
7	4-Methyl-2-Pentanone	0.769	0.173	3.2
8	Toluene	2.145	0.326	5.9
9	Cyclohexanone	0.780	0.163	2.9

Table 9: List of Compounds and results for Sample 3 [SHS-GC]

Master DHS Dynamic Headspace Sampler

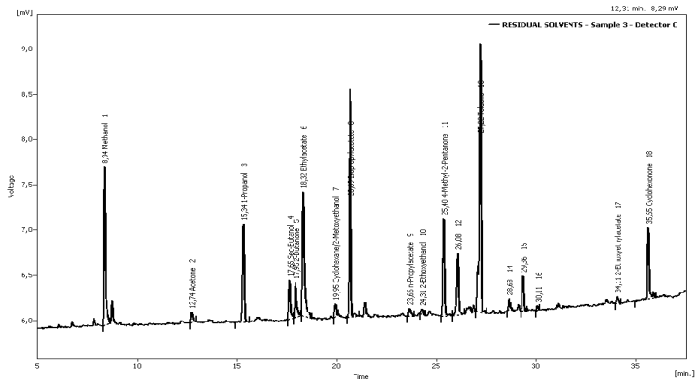

Figure 6 : Chromatogram of Sample 3 [DHS-GC]

	Compound	Retention Time (min)	Response	Amount [mg/m2]	Amount [%]
1	Methanol	8.343	8.561	0.313	14.0
2	Acetone	12.740	0.749	0.042	1.9
3	1-Propanol	15.337	5.864	0.620	27.8
4	Sec-Butanol	17.653	2.375	0.037	1.6
5	2-Butanone	17.947	2.647	0.065	2.9
6	Ethylacetate	18.317	9.325	0.304	13.6
7	Cyclohexane/2-Metoxyethanol	19.950	0.873	0.045	2.0
8	Isopropylacetate	20.690	12.442	0.421	18.9
9	n-Propylacetate	23.660	0.729	0.025	1.1
10	2-Ethoxyethanol	24.310	0.470	0.046	2.1
11	4-Methyl-2-Pentanone	25.397	5.516	0.125	5.6
12	Unknown	26.077	4.076		
13	Toluene	27.223	16.186	0.090	4.0
14	Unknown	28.677	0.532		
15	Unknown	29.363	1.931		
16	Unknown	30.107	0.281		
17	2-Ethoxyethylacetate	34.107	0.652	0.055	2.5
18	Cyclohexanone	35.653	5.030	0.043	1.9

Table 10: List of Compounds and results for Sample 3 [DHS-GC]

Sample 4

Master SHS Static Headspace Sampler

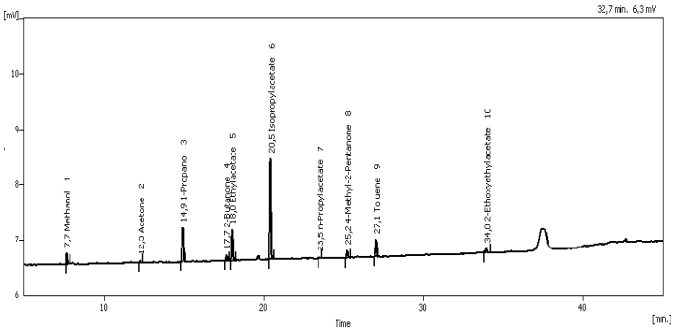

Figure 7: Chromatogram of Sample 4 [SHS-GC]

	Compound	Response	Amount [mg/m2]	Amount [%]
1	Methanol	0.860	0.501	7.4
2	Acetone	0.293	0.101	1.5
3	1-Propanol	3.292	1.105	16.4
4	2-Butanone	0.924	0.258	3.5
5	Ethylacetate	2.717	1.115	16.5
6	Isopropylacetate	9.408	3.122	56.1
7	n-Propylacetate	0.218	0.068	1.0
8	4-Methyl-2-Pentanone	0.728	0.164	2.4
9	Toluene	1.445	0.220	3.3
10	2-Ethoxyethylacetate	0.433	0.217	3.2

Table 11: List of Compounds and results for Sample 4 [SHS-GC]

Master DHS Dynamic Headspace Sampler

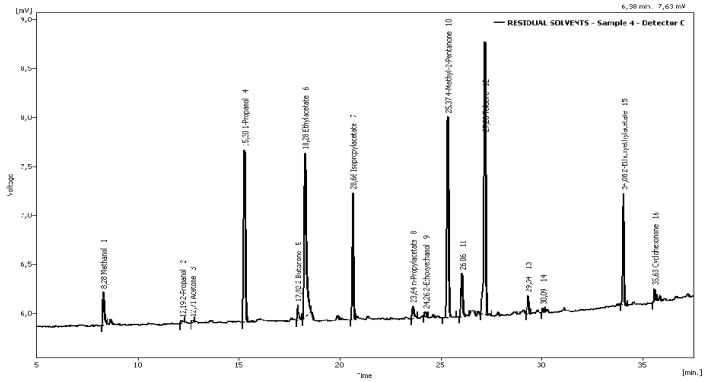

Figure 8: Chromatogram of Sample 4 [DHS-GC]

	Compound	Retention Time (min)	Response	Amount [mg/m2]	Amount [%]
1	Methanol	8.280	1.601	0.058	2.4
2	2-Propanol	12.190	0.213	0.021	0.9
3	Acetone	12.710	0.173	0.010	0.4
4	1-Propanol	15.297	8.822	0.933	39.0
5	2-Butanone	17.923	1.006	0.025	1.0
6	Ethylacetate	18.283	10.466	0.344	14.4
7	Isopropylacetate	20.663	6.104	0.207	8.6
8	n-Propylacetate	23.643	0.687	0.024	1.0
9	2-Ethoxyrthanol	24.257	0.297	0.029	1.2
10	2-Methyl-2-Pentanone	25.370	9.959	0.226	9.4
11	Unknown	26.060	2.384		
12	Toluene	27.200	13.839	0.077	3.2
13	Unknown	29.340	0.888		
14	Unknown	30.093	0.230		
15	2-Ethoxyethylacetate	34.077	5.177	0.436	18.2
16	Cyclohexanone	35.630	0.630	0.005	0.2

Table 12: List of Compounds and results for Sample 4 [DHS-GC]

Sample 5

Master SHS Static Headspace Sampler

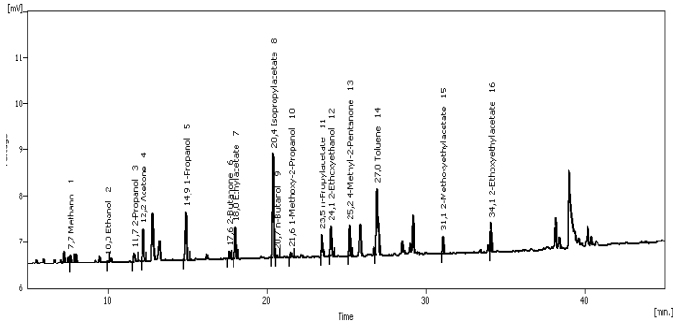

Figure 9: Chromatogram of Sample 5 [SHS-GC]

	Compound	Response	Amount [mg/m2]	Amount [%]
1	Methanol	0.709	0.413	2.5
2	Ethanol	0.211	0.086	0.5
3	2-Propanol	1.203	0.442	2.6
4	Acetone	3.245	1.122	6.7
5	1-Propanol	5.602	1.881	11.2
6	2-Butanone	0.850	0.237	1.4
7	Ethylacetate	3.212	1.318	7.8
8	Isopropylacetate	10.301	3.417	20.3
9	n-Butanol	0.340	0.095	0.6
10	1-Methoxy-2-Propanol	0.592	0.399	2.4
11	n-Propylacetate	2.075	0.649	3.9
12	2-Ethoxyethanol	3.549	2.572	15.2
13	4-Methyl-2-Pentanone	3.108	0.698	4.2
14	Toluene	10.065	1.532	9.1
15	2-Methoxyethylacetate	1.553	0.797	4.7
16	Ethoxyethylacetate	2.470	1.236	7.3

Table 13: List of Compounds and results for Sample 5 [SHS-GC]

Master DHS Dynamic Headspace Sampler

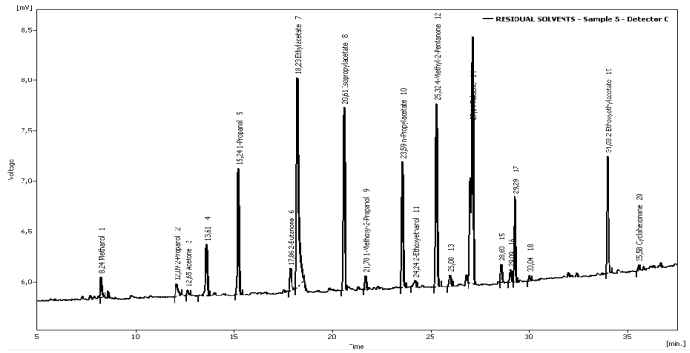

Figure 10: Chromatogram of Sample 5 [DHS-GC]

	Compound	Retention Time (min)	Response	Amount [mg/m2]	Amount [%]
1	Methanol	8.237	0.976	0.036	1.3
2	2-Propanol	12.093	1.071	0.108	3.9
3	Acetone	12.650	0.403	0.023	0.8
4	Unknown	13.613	3.605		
5	1-Propanol	15.337	5.864	0.620	27.8
6	2-Butanone	18.863	1.451	0.035	1.3
7	Ethylacetate	18.230	13.814	0.455	16.4
8	Isopropylacetate	20.607	8.634	0.292	10.5
9	1-Methoxy-2-Propanol	21.700	0.672	0.123	4.5
10	n-Propylacetate	23.587	5.629	0.194	7.0
11	2-Ethoxyethanol	24.240	0.574	0.057	2.0
12	4-Methyl-2-Pentanone	25.317	8.702	0.198	7.1
13	Unknown	26.000	0.663		
14	Toluene	27.143	16.195	0.090	3.2
15	Unknown	28.600	0.819		
16	Unknown	29.087	1.931		
17	Unknown	29.293	3.981		
18	Unknown	30.037	0.316		
19	2-Ethoxyethylacetate	34.030	5.294	0.442	16.0
20	Cyclohexanone	35.583	0.269	0.002	0.1

Table 14: List of Compounds and results for Sample 5 [DHS-GC]

Sample 6

Master SHS Static Headspace Sampler

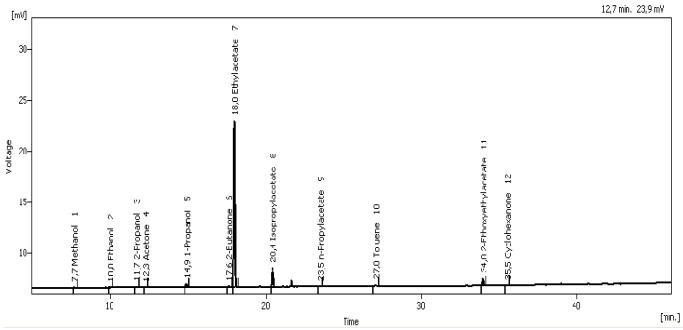

Figure 11: Chromatogram of Sample 6 [SHS-GC]

	Compound	Response	Amount [mg/m2]	Amount [%]
1	Methanol	0.351	0.204	0.6
2	Ethanol	0.356	0.146	0.4
3	2-Propanol	0.454	0.167	0.5
4	Acetone	0.147	0.051	0.1
5	1-Propanol	2.316	0.778	2.1
6	2-Butanone	0.544	0.152	0.4
7	Ethylacetate	72.484	29.745	81.1
8	Isopropylacetate	10.028	3.327	9.1
9	n-Propylacetate	0.373	0.117	0.3
10	Toluene	0.922	0.140	0.4
11	2-Ethoxyethylacetate	3.605	1.804	5.0
12	Cyclohexanone	0.289	0.060	0.2

Table 15: List of Compounds and results for Sample 6 [SHS-GC]

Master DHS Dynamic Headspace Sampler

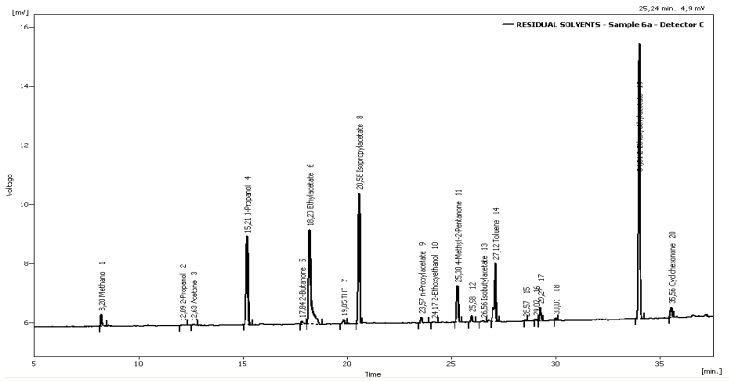

Figure 12: Chromatogram of Sample 6 [DHS-GC]

	Compound	Retention Time (min)	Response	Amount [mg/m2]	Amount [%]
1	Methanol	8.203	1.978	0.072	1.0
2	2-Propanol	12.090	0.303	0.030	0.4
3	Acetone	12.627	0.223	0.012	0.2
4	1-Propanol	15.210	15.175	1.605	22.7
5	2-Butanone	17.840	0.573	0.014	0.2
6	Ethylacetate	18.200	24.811	0.816	11.5
7	THF	19.847	0.999	0.053	9.9
8	Isopropylacetate	20.583	20.807	0.705	9.9
9	n-Propylacetate	23.570	1.138	0.039	0.6
10	2-Ethoxyrthanol	14.173	0.223	0.022	0.3
11	4-Methyl-2-Pentanone	25.297	5.945	0.135	1.9
12	Unknown	25.983	1.223		
13	Isobutylacetate	26.560	0.344	0.002	0.0
14	Toluene	27.123	11.344	0.063	0.9
15	Unknown	28.570	0.188		
16	Unknown	29.067	0.362		
17	Unknown	29.273	2.129		
18	Unknown	30.013	0.381		
19	2-Ethoxyethylacetate	34.007	41.568	3.501	49.4
20	Cyclohexanone	35.560	1.781	0.015	0.2

Table 16: List of Compounds and results for Sample 6 [DHS-GC]

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