From ppt to high Levels of Residual Solvents in Food Packaging through HS-GC-FID

APPLICATION NOTE AN_173

Introduction

Healthy, pure, and fresh food is one of the essential necessities for human health. For this reason monitoring is of primary importance. One possible source of contamination is the packaging that envelopes about the totality of the food consumed nowadays. Packaging for food is intended to be a food protection from external environment with the objective to supply safe, fresh, and contaminant-free food to the consumers. Food packaging legislation aims to ensure that this objective is achieved establishing the maximum quantity of chemicals transferred from the packaging into the food.

It has been demonstrated that a number of substances, considered indirect food additives, migrate from packaging into the food. Food packaging legislation regulates the control of such contaminants, among which particular attention has to be paid to residual solvents.

The preferred analytical technique for the determination of residual solvents in food packaging is gas chromatography coupled to different extraction systems. Among those, Static Headspace is certanly the most popular for its simplicity and for its capability of providing quantitative data in a short time, and as such responding to the industry production needs.

In this work a system composed by DANI HSS 86.50 Plus Static Headspace Sampler and DANI Master GC Gas Chromatograph with SL/IN and FID is presented as a easy to use and reliable tool for the determination of residual sovents in food packaging.

DANI

EXPERIMENTAL CONDITIONS

Instrumentation

The system is composed of the DANI HSS 86.50 Plus 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 After this period, a portion of the gaseous phase is withdrawn and then injected into the chromatographic column.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.

MHE technique consists in sampling more than once from the same sample after subsequent incubations. As the peak area decreases at each injection, the total amount of the correspondent analyte is obtained by extrapolation, from the linear response obtained by plotting the logarithm of the area counts of the repeated injections against the number of samplings. The calibration factors are obtained by the analysis, under the same conditions, of a standard solution of the components and are therefore independent from the presence of 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
Carrier (He)	1 mL/min (split 1:60)
Detector	FID (250°C)
Oven	40°C, 4°C/min, 170°C (2 min)
Column	Supelco Vocol 60m, 0.25mm, 1,5µm

Table 1 : Master GC operative conditions

HSS 86.50 Plus Static Headspace Sampler	
Oven Temp	125°C
Manifold Temp	125°C
Transfer Line Temp	150°C
Equilibration time	30 min
Aux Gas	1bar
Press.	10s
Venting	10s
Sampling	10s
Vial	20mL
Sample	0.5dm^2

Table 2 : HSS 86.50 Plus operative conditions

Samples

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-component standard mixture containing equal concentrations was used to prepare 4 calibration levels in the range of 2-20.0 mg/m^2 by spiking a sheet of white paper (printer type) with a size of 50 cm^2 (5x10cm) as support to simulate the migration of solvents from packaging. Paper was checked "as is" in a blank injection.

The pieces of paper were placed into sealed vials, and spiked with the standard mixture at 7.14% v/v (mixture 1) added as follows (see Table 3):

0.2 µL
0.6 µL
1 µL
2 µL

Another standard was prepared at 3 different levels of concentration with compounds usually searched as impurities in ethyl acetate solvent (mixture 2).

Mixture 2 at 9.09% v/v has been added to the white paper (printer type - 50x10cm) as follows (see table 4):

0.5 µL
1 µL
2 µL

Based on the density of each compound in the standard mixture, and since they are at identical concentrations, weights of each compound are as follows:

approximately 2.5mg/m^2, 7.5 mg/m^2, 11.5 mg/m^2 , 24 mg/m^2

	Standard Mix 1 Compounds	0.2 µL	0.6 µL	1 µL	2 µL
1	Methanol	2.26	6.78	11.30	22.59
2	Ethanol	2.25	6.76	11.27	22.53
3	Methyl Acetate	2.68	8.04	13.40	26.79
4	Sec-butanol	2.31	6.92	11.54	23.08
5	2-Butanone	2.30	6.90	11.50	22.99
6	Ethylacetate	2.58	7.73	12.88	25.76
7	Cyclohexane	2.22	6.67	11.12	22.25
8	n-Butanol	2.31	6.94	11.57	23.13
9	2-Ethoxyethanol	2.66	7.97	13.28	26.56
10	Isobutylacetate	2.49	7.47	12.45	24.90
11	Toluene	2.47	7.41	12.35	24.70
12	n-Butyl acetate	2.51	7.54	12.57	25.13
13	Metilcellosolve acetate	2.77	8.31	13.85	27.70
14	Cyclohexanone	2.70	8.11	13.52	27.05

Table 3 : Mix 1 - mg/m^2 assuming 50 cm^2 of paper

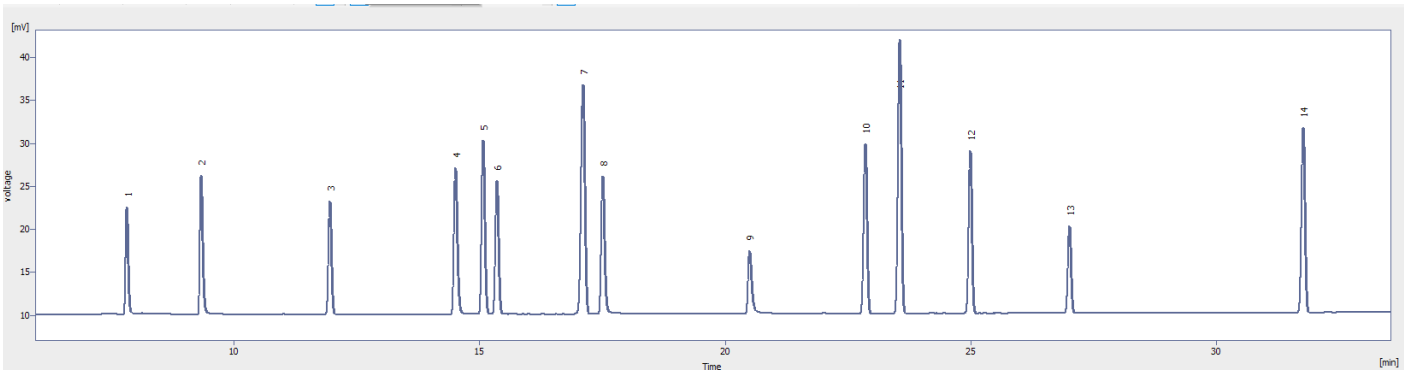

Figure 1 : FID chromatogram of spiked white paper with 1 µL of Mix 1

The calibration for three different levels of concentration was carried out through the same method of sample preparation for all the compounds in Mixture two, also.
These compounds are usually researched as impurities in the ethyl acetate solvent.
Through the use of suitable syringe the amount of the standard mixture 2 at 9.09% v/v was added as shown in the present document.
As a support, to simulate the migration of solvents from packaging to the headspace, a sheet of white paper (printer type) with a size of 50cm^2 was used.

	Standard Mix 2 Compounds	0.5 µL	1 µL	2 µL
1	2-propanol	7.14	14.29	28.58
2	Acetone	7.18	14.36	28.72
3	1-Propanol	7.31	14.62	29.23
4	Isobutanol	7.29	14.58	29.16
5	THF	8.06	16.13	32.25
6	2-Methoxyethanol	8.64	17.27	34.54
7	Isopropyl acetate	7.93	15.85	31.71
8	1-methoxy-2-propanol	8.64	17.27	34.54
9	n-propylacetate	8.07	16.14	32.29
10	4-methyl-2-Pentanone	7.27	14.54	29.09
11	2-Ethoxy ethyl acetate	8.82	17.63	35.27

Table 4: Mix 2 - mg/m^2 assuming 50 cm^2 of paper

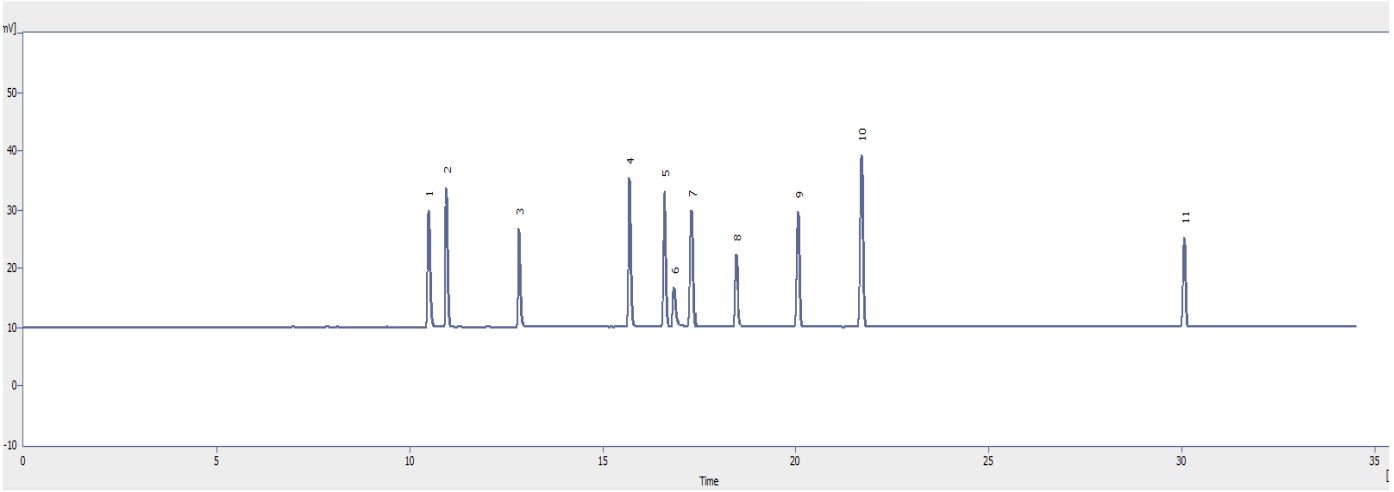

Figure 2: FID chromatogram of spiked white paper with 1 µL of Mix 2

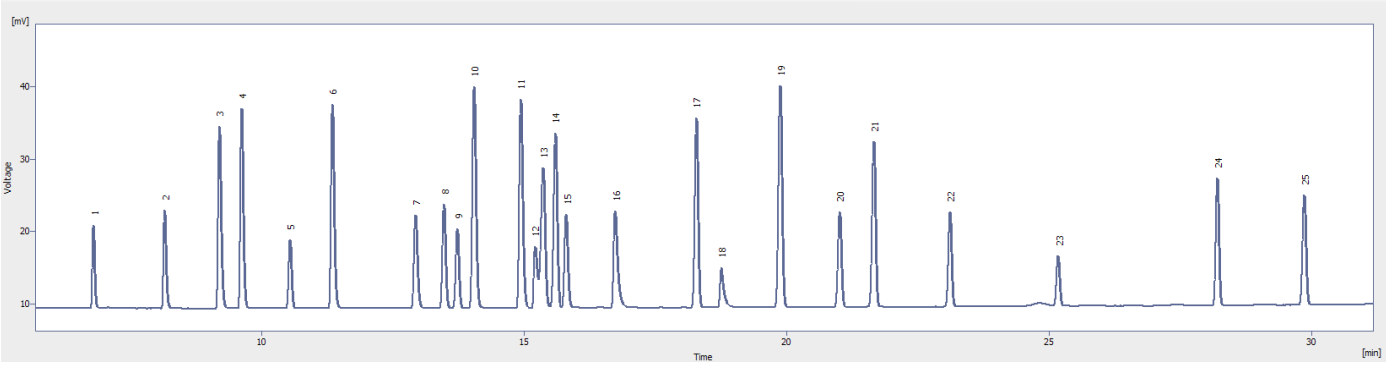

Figure 3: FID chromatogram of spiked white paper with Mix1 and Mix2

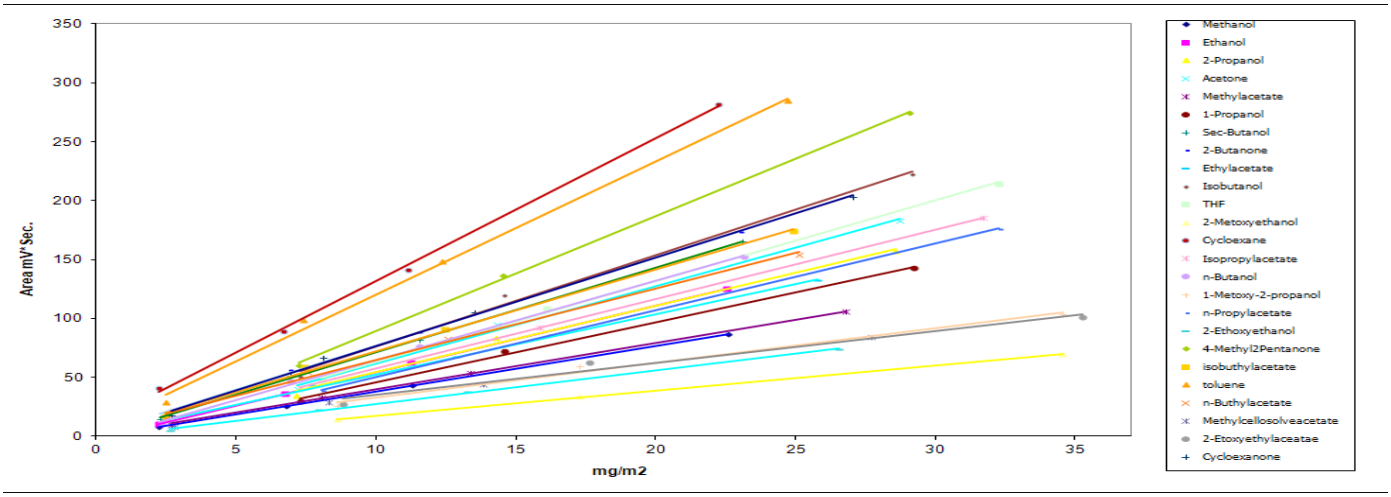

Figure 4 : Linear Calibration Curves obtained for Mix1 and Mix respectively range between 2-20 mg/m² and 4-30 mg/m²

REAL SAMPLES ANALYSIS

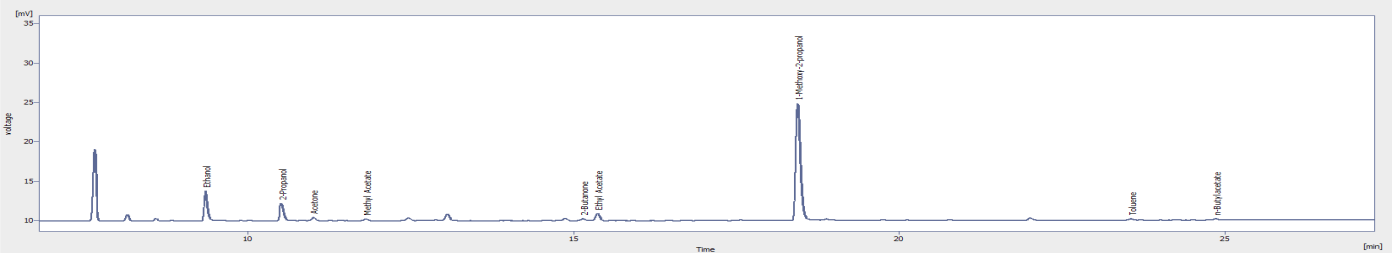

Figure 5 : 50 cm² of sample A. Results, expressed in mg/m² are reported in Table 5

Compound	Amount [mg/m²]
Ethanol	2.99
2-Propanol	2.06
Acetone	0.83
Methyl Acetate	0.19
2-Butanone	N/A
Ethyl-Acetate	0.59
1-Methoxy-2-Propanol	22.52
Toluene	N/A
n-Butylacetate	N/A

Table 5: List of Compounds and results for Sample A

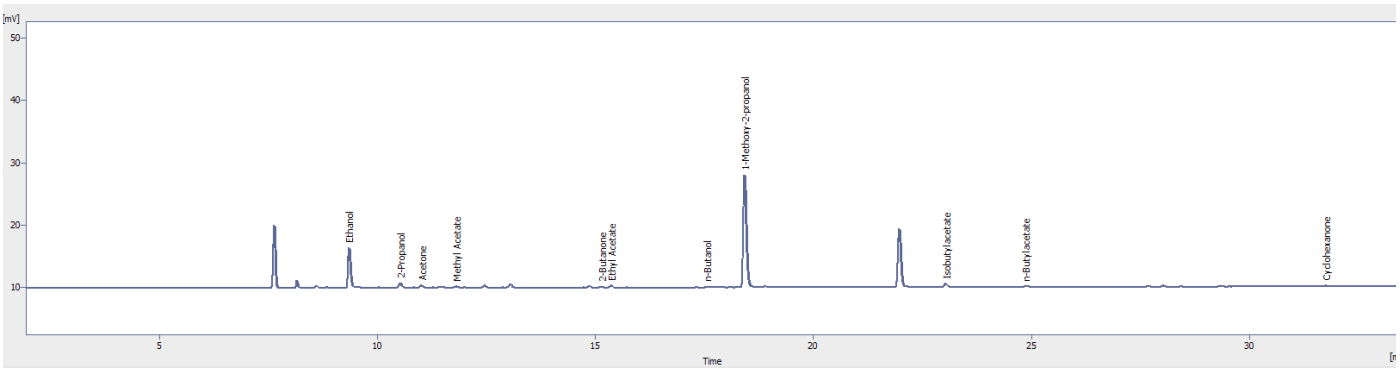

Figure 6 : 50 cm² of sample B. Results, expressed in mg/m² are reported in Table 6

Compound	Amount [mg/m²]
Ethanol	4.67
2-Propanol	1.00
Acetone	0.81
Methyl Acetate	0.13
2-Butanone	N/A
Ethyl-Acetate	0.07
1-Methoxy-2-Propanol	27.98
Isobutylacetate	0.01
n-Butylacetate	N/A
Cyclohexanone	N/A

Table 6: List of Compounds and results for Sample B

Compound	Amount [mg/m²]
Ethanol	3.48
2-Propanol	0.77
Acetone	0.80
Methyl Acetate	0.48
2-Butanone	0.24
Ethyl-Acetate	0.03
1-Methoxy-2-Propanol	0.34
Toluene	N/A
n-Butylacetate	N/A

Table 7: List of Compounds and results for Sample C

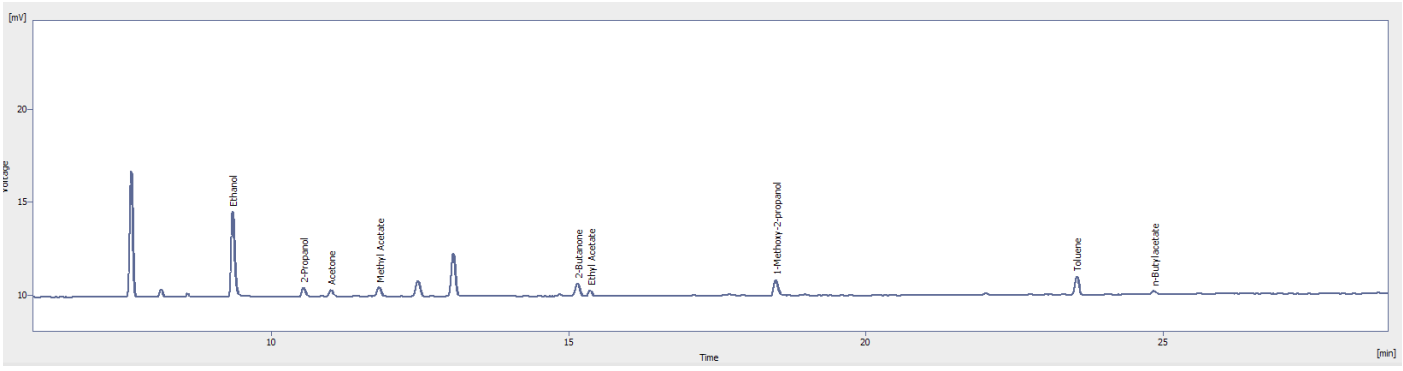

Figure 7 : List of Compounds and results for Sample C. Results, expressed in mg/m² are reported in Table 7

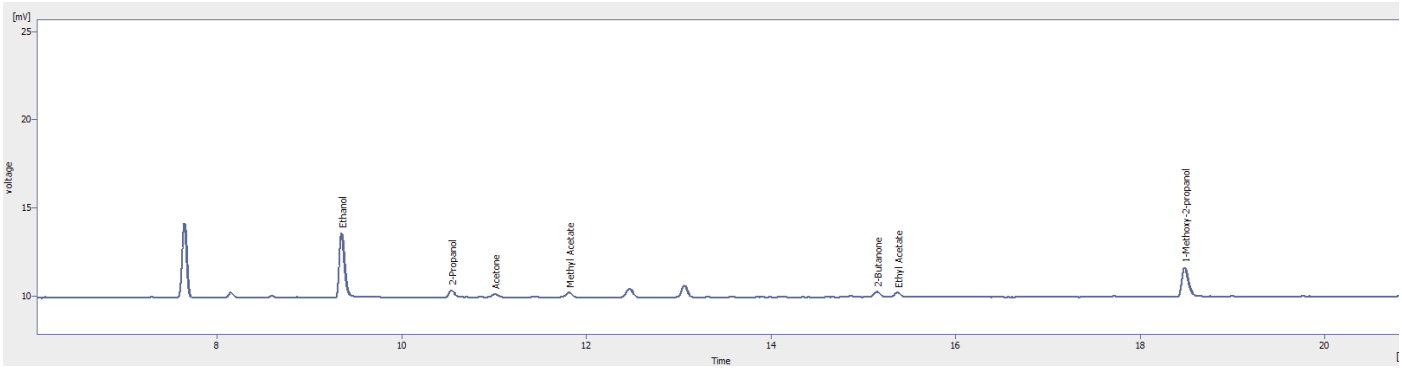

Figure 8 : 50 cm² of sample D. Results, expressed in mg/m² are reported in Table 8

Compound	Amount [mg/m²]
Ethanol	2.85
2-Propanol	0.71
Acetone	0.69
Methyl Acetate	0.30
2-Butanone	N/A
Ethyl-Acetate	N/A
1-Methoxy-2-Propanol	1.74

Table 8: List of Compounds and results for Sample D

Conclusions

DANI HSS 86.50 Plus Headspace Sampler coupled with Master GC Fast Gas Chromatograph is a simple and reliable tool for the determination of residual solvents in food packaging.

Master SHS Static Headspace Sampler permits a complete automatic sampling and guarantees to reach minimum detectable levels even below those currently recommended by the norms.

The Fast GC significantly reduces the analysis time if compared to conventional GC Analysis, thus facilitating Process Quality Control.

A suitable capillary column with shorter length is employed (30 meters instead of 60 meters) to reduce retention time.

Besides, faster separation allows to reduce peak width and increase peak height for better detectability.

The Flame Ionization Detector is enabled with fast data acquisition capability up to 300 Hz, for a suitable description of narrow peaks and optimum Fast GC analysis.

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