Application Note 10396

Static Headspace Analysis of Residual Solvents in Flexible Packaging and Quantitation with Multiple Headspace Extraction Following EN 13628-1: 2002

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Key Words
Flexible packaging, TRACE 1310 GC, TriPlus 300 HS, Chromeleon CDS, static headspace, EN 13628-1, MHE, cling film, plastic wrap

Introduction

Flexible packaging is essential in ensuring the safety, quality and shelf-life of packaged consumer products. Such packaging, commonly referred to as cling film or plastic wrap, is often comprised of layers bonded together with adhesives (multilayer) and imprinted with product information. During the process of manufacturing, shipping or storage, the packaging itself might leach solvents from the adhesives and printing inks or finishes into the very product it was meant to protect. When these are food products, those solvents can pose significant health risks and negatively impact the taste, aroma, or appearance of the product.

Food manufacturers need to both ensure the quality of their food for commercial success and to comply with government food safety standards. For this and other applications with non-food products, headspace (HS) gas chromatography is the recommended method of analysis.

The method for the quantitative determination of residual solvents in flexible packaging by static headspace is reported in the European Standard absolute method EN 13628-1: 2002.

EN 13628-1: 2002 in particular specifies methods for the quantitative determination of residual solvents in flexible packaging by static headspace chromatography where the chemical identities of the residual solvents are known before commencing analysis.[1]

Quantification is achieved by the multiple headspace extraction (MHE) procedure using external or internal standards. MHE eliminates any effect of the sample matrix by extracting the *whole* amount of analytes in a few consecutive extraction cycles of the same sample.[2]

EN 13628-1: 2002 applies to flexible packaging materials that may consist of mono- or multilayer plastic films, paper or board, foil or combinations thereof and does not apply to residual solvents with amounts lower than 0.5 mg/m².

Using headspace autosamplers like the Thermo Scientific™ TriPlus™ 300 Headspace Autosampler, quantification is achieved by MHE. The advantage of using MHE is high precision in the determination of the residual solvents with a relatively light work load, thanks to a fully automated process. No external calibration solutions or standard additions are required.

Goal

The goal of this application note is to demonstrate the applicability of a modern, high-throughput valve-and-loop static headspace autosampler to obtain full compliance with EN 13628-1:2002.

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Materials and Methods

Headspace analysis was conducted using a TriPlus 300 Headspace Autosampler equipped with the standard 1 mL loop and connected to a Thermo Scientific™ TRACE™ 1310 Gas Chromatograph (GC). The system was further configured with an instant connect Split/Splitless (SSL) injector and an instant connect Flame Ionization Detector (FID) module.

The Thermo Scientific™ Dionex™ Chromeleon™ 7.2 Chromatography Data System was used to control the system, acquire data and generate all reports.

For the headspace analyses, 20 mL headspace vials (P/N 60180-506) with magnetic caps and PTFE/silicone septa (P/N 60180-520) were used. For the SSL injector, the HS/SPME straight liner (P/N 453A1335) was used and a capillary column with a phase dedicated for the separation of volatile compounds was chosen. An example of this kind of column is the Thermo Scientific™ TraceGOLD™ TG-624 (60 m × 0.25 mm id × 1.4 um, PN 26085-3330).

Standard mixtures specifically prepared for residual solvents analysis in packaging were purchased:

- Residual Solvents in Packaging Material Mixture 1, analytical standard, 7.14% (v/v) (Sigma-Aldrich® cat# 48994-U)
- Residual Solvents in Packaging Material Mixture 2, analytical standard, 9.09% (v/v) (Sigma-Aldrich cat# 48995-U)

Method Development

To find the proper equilibration time, 1 µL of each standard mixture was placed in five 20 mL headspace vials, then capped and crimped. The headspace vial equilibration times were increased, and the peak area of each compound versus the equilibration time was reported.

To find the optimum heating time, the Method Development Optimization (MDO) function of TriPlus 300 Headspace Autosampler was used.

The MDO function automatically increments the heating time in consecutive runs by an amount set by the user. Here, the starting heating time was 20 min and increased in 10 min increments, so the five vials were heated respectively for 20, 30, 40, 50 and 60 min.

Figure 1 shows the optimal equilibration time was determined to be 40 min, after which a slight decrease of the peak areas was observed for a few analytes.

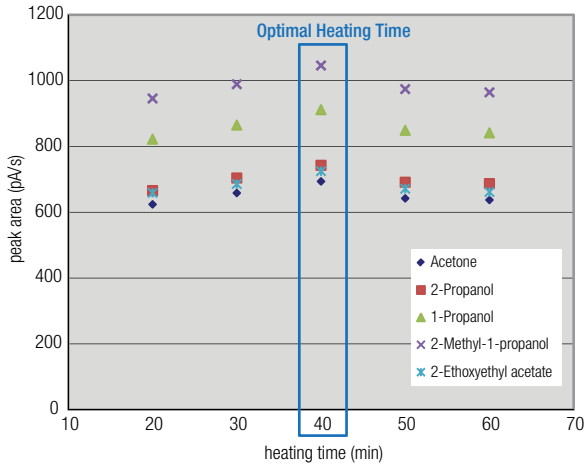


Figure 1. Heating times shown in five increments of 10 min each through MDO.

Next, 1 µL of each standard mixture was placed into a 20 mL headspace vial, then capped and crimped to run an MHE experiment with 4 extraction repetitions on the same vial.

For each compound tested, EN 13628-1 requires the correlation coefficient of the natural logarithm of the peak area from the consecutive four analyses plotted against the number of MHE cycles to be at least -0.98.

Particular instrument parameters (equilibration time and temperatures) had to be used to run the analysis for the determination of residual solvents in the samples to allow the required correlation coefficient to be obtained. Table 1 shows the system parameters that were used for method development, and for the method used to produce the data in this note.

To analyze real samples and determine the residual solvents, the flexible packaging material (plastic films or paper) was trimmed into a piece with a surface of 30 cm^2, placed into a 20 mL headspace vial, capped and crimped. If this analysis is repeated using different headspace vial volumes, it must be considered that EN 13628-1 requires the ratio between the specimen area (in cm^2) and the vial volume (in mL) to be between three and five.

Table 1. GC and headspace parameters used in this method.

TriPlus 300 Headspace Analyzer		
parameters	**for MDO* heating time optimization**	**for standard mixtures/ sample analysis**
oven temp	125 °C	125 °C
manifold temp	125 °C	125 °C
transfer line temp	150 °C	150 °C
equilibration time	from 20 min to 60 min, increments of 10 min	40 min
shaking	medium	medium
pressure mode	pressure	pressure
aux pressure	1 bar	1 bar
pressure eq. time	0.2 min	0.2 min
loop fill mode	pressure	pressure
other parameters	loop pressure: 0.5 bar; loop eq.time: 0.2 min	loop pressure: 0.5 bar; loop eq.time: 0.2 min
injection time	0.2 min	0.2 min
injection mode	standard	standard
vial venting	on	on
purge time	0.5 min	0.5 min
purge flow	50 mL/min	50 mL/min
others		for Multiple Headspace Extraction: *MHE multiple*, 4 repetitions
TRACE 1310 Gas Chromatograph		
SSL mode	split	
SSL temperature	200 °C	
split flow	30 mL/min	
splitless time	1 min	
constant purge	on	
carrier mode	helium, constant flow	
carrier flow	1 mL/min	
FID temperature	220 °C	
oven program	35 °C (4 min), 4 °C/min to 200 °C (3 min)	

Quantification of the residual solvent(s) found in a sample was done on the first and second extraction cycles of the MHE analysis using the equations below, which are reported in EN 13628-1:

$$e_n = \frac{(e_1)^2}{(e_1 - e_2)}$$

where:

e_n is the total peak area of one solvent of the standard mix

e_1 is the peak area of the same solvent in the first desorption

e_2 is the peak area of the same solvent in the second desorption

$$a_n = \frac{(a_1)^2}{(a_1 - a_2)}$$

where:

a_n is the total peak area of one residual solvent of the sample

a_1 is the peak area of the same solvent in the first desorption

a_2 is the peak area of the same solvent in the second desorption

$$Q = (a_n \times p)/(e_n \times S)$$

where:

Q is the quantity of one residual solvent (in mg/m^2) of packaging material

p is the mass of solvent in the standard mix expressed in milligrams (mg)

S is the area of specimen expressed in square meters (m^2)

Results and Discussion

The elution order of the compounds of the two standard mixtures (Figure 2) and their retention times (Table 2) were determined using a Thermo Scientific™ ISQ™ LT Single Quadrupole GC-MS running in full scan mode (mass range 35-400 m/z).

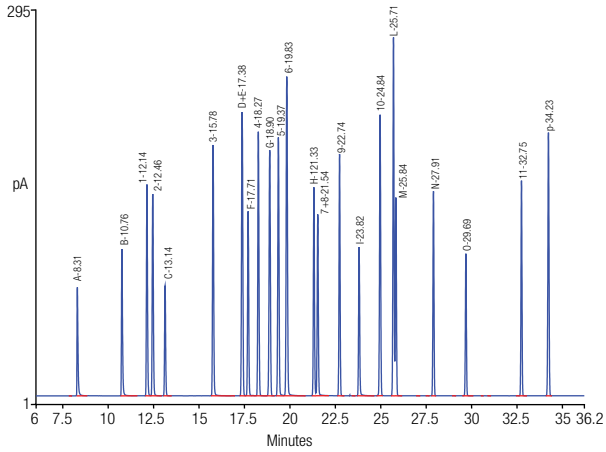


Figure 2. The elution order of the compounds in the two standard mixtures.

Table 2. Compound retention times in the two standard mixtures.

Peak	RTs (min)	Compound
A	8.32	Methanol
B	10.76	Ethanol
1	12.147	Acetone
2	12.463	2-Propanol
C	13.15	Methyl acetate
3	15.78	1-Propanol
D+E	17.39	Ethyl acetate & 2-Butanone
F	17.72	2-Butanol
4	18.275	Tetrahydrofuran
G	18.91	Cyclohexane
5	19.367	2-Methyl-1-propanol
6	19.833	Isopropyl acetate
H	21.33	1-Butanol
7+8	21.533	1-Methoxy-2-propanol & 2-Methoxyethanol
9	22.738	Propyl acetate
I	23.82	2-Ethoxyethanol
10	24.97	4-Methyl-2-pentanone
L	25.71	Toluene
M	25.84	Isobutyl acetate
N	27.91	Butyl acetate
O	29.69	2-Methoxyethyl acetate
11	32.748	2-Ethoxyethyl acetate
P	34.23	Cyclohexanone

Figure 3 shows the chromatograms and Figure 4 shows the MHE results of the two standard mixtures.

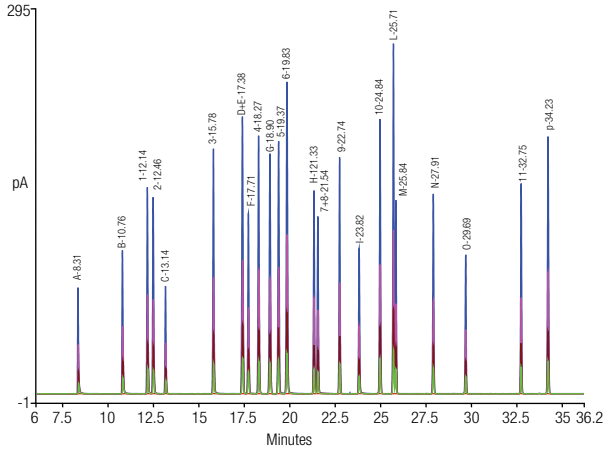
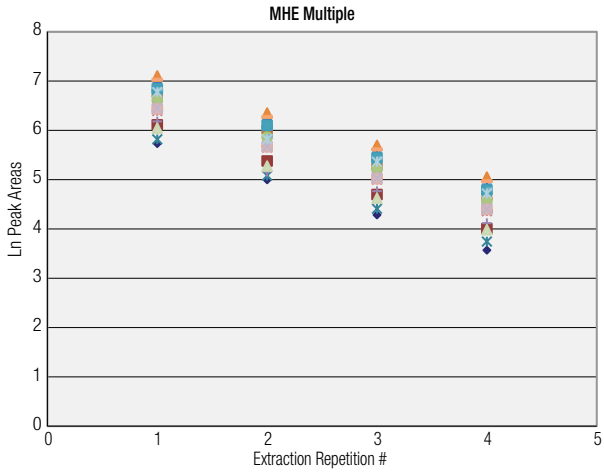


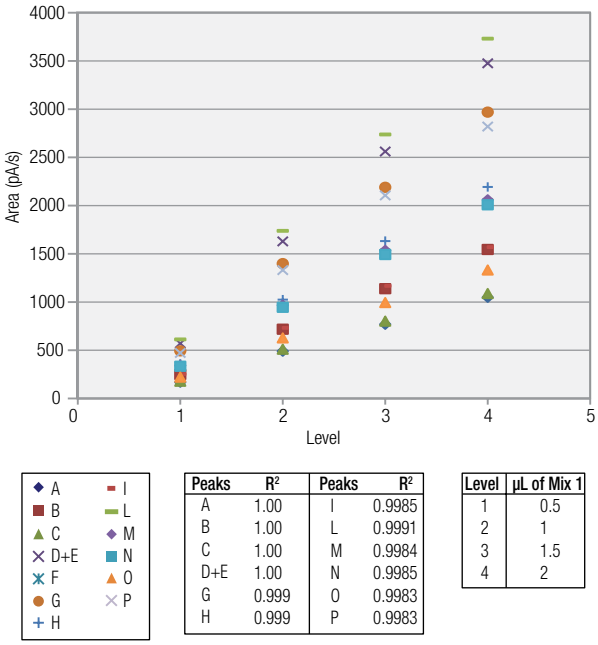
Figure 3. MHE chromatograms for the two standard mixtures with 4 extraction cycles.



Peaks	R^2	Peaks	R^2
A	1.00	H	0.999
B	1.00	7+8	0.999
1	1.00	9	0.998
2	1.00	I	0.989
C	0.999	10	0.987
D+E	0.999	L	0.999
F	0.999	M	0.998
4	0.999	N	0.998
G	0.984	O	0.998
5	0.999	11	0.997
6	0.999	P	0.998

Figure 4. MHE results for the two standard mixtures (overlay).

Although not specifically required by EN 13628-1, a linearity check was run by preparing 4 calibration levels with different volumes of Residual Solvents Mixture 1 (0.5 µL for Level 1, 1.0 µL for Level 2, 1.5 µL for Level 3, and 2 µL for Level 4) placed in 4 different 20 mL headspace empty vials. Figure 5 shows a graph of the excellent correlation coefficients obtained in the linearity check, proving the system can be used for the determination of residual solvents over a wide range of concentrations.



Peaks	R^2	Peaks	R^2
A	1.00	I	0.9985
B	1.00	L	0.9991
C	1.00	M	0.9984
D+E	1.00	N	0.9985
G	0.999	O	0.9983
H	0.999	P	0.9983

Level	µL of Mix 1
1	0.5
2	1
3	1.5
4	2

Figure 5. Correlation coefficients from the linearity check on Residual Solvents Mixture 1.

Next, samples of transparent plastic film used to wrap commercial magazines with a surface of 90 cm^2 each, were placed in a 20 mL headspace vial, capped and crimped. Then they were analyzed in MHE mode (Figure 6) with 4 extraction repetitions.

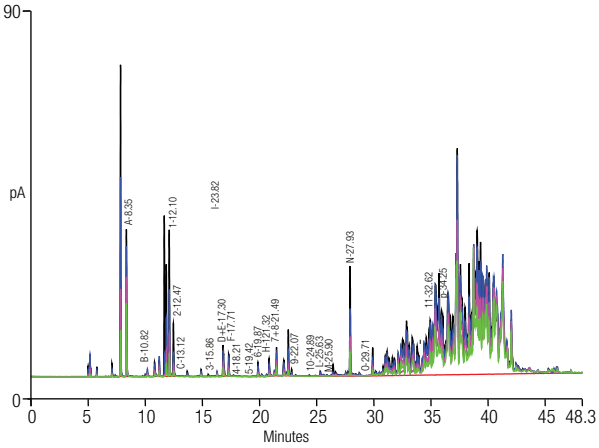


Figure 6. Chromatograms of MHE extractions from real samples of transparent plastic film.

The correlation coefficients obtained by plotting the natural logarithms of the peak areas of the residual solvents found in the film sample against the number of MHE cycles are shown in Figure 7.

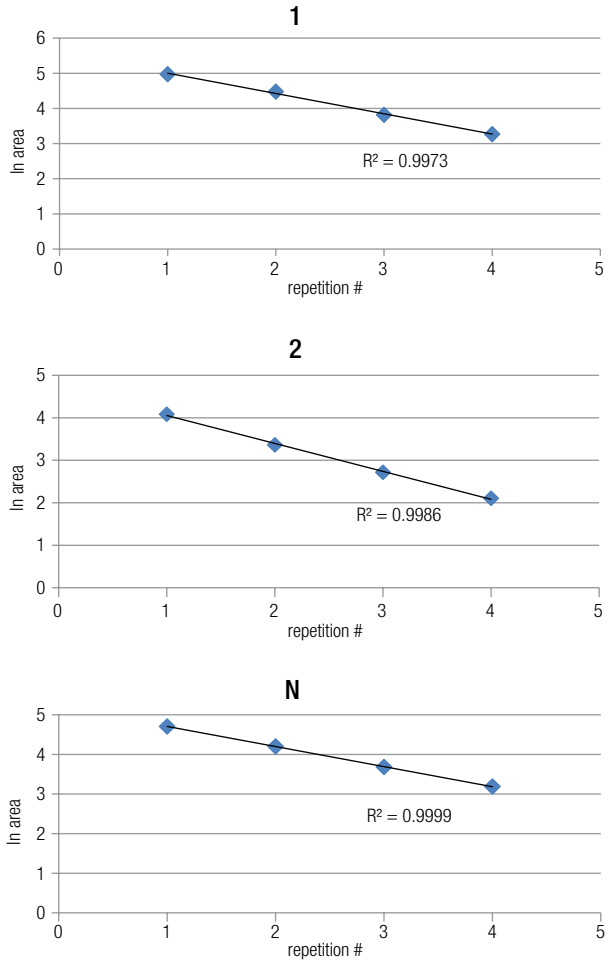


Figure 7. Correlation coefficients of MHE extractions on the identified solvents from real samples of transparent plastic film.

Each residual solvent present in the sample was quantified using Chromeleon CDS (Table 3).

Table 3. Amount of residual solvents present in the real samples of transparent plastic film.

Residual Solvent Found	Amount mg/m²
A	13.15
B	0.46
1	2.31
2	0.72
D+E	0.76
6	0.20
H	0.38
7+8	2.69
N	1.68

Conclusion

The data obtained in this application demonstrate that the technique of headspace gas chromatography using MHE in an automated fashion easily meets the requirements of the EN 13628-1: 2002 standard and provides excellent quantitation results without any sample preparation. All the quality criteria requested by the method were verified, including the linearity of MHE curves for all solvents tested.

The system configuration of the TRACE 1310 GC, TriPlus 300 Headspace Autosampler, and Chromeleon CDS proved to be a solid, fully integrated, easy-to-use and reliable platform to perform this analysis with a great degree of automation, from sample analysis to data reporting.

With its 120-vial sample tray and the large 18-vial incubation oven overlap capacity, the TriPlus 300 Headspace valve-and-loop autosampler guarantees excellent throughput allowing the analysis of multiple samples at once and ensuring true weekend-long operations.

Reference

1. EN 13628-1 October 2002 *Packaging. Flexible packaging material — Determination of residual solvents by static headspace gas chromatography.* Part 1: Absolute methods.
2. Kolb, B., Ettre, L.S., *Static Headspace Chromatography, Theory and Practice*. Wiley-VCH 2006, pp. 40–43.

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