Chimia 56 (2002) 295–297

ISSN 0009–4293

Residual Printing Solvents in Packaging Materials

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Abstract: Analysis of residual printing solvents in packaging materials. The aim was to define an analytical method based on the static headspace gas chromatography (HS-GC) method with a mass spectrometric detector (MSD) to qualify and quantify residual printing solvents. The quantitations are compared for mono headspace extraction and multi headspace extraction (MHE).

Keywords: Mass spectrometry detection · Mono and multi (MHE) headspace extraction · Residual printing solvents in packaging materials · Static headspace gas chromatography · Thermodynamic equilibrium

Introduction

The identification and quantitation of residual printing solvents in packaging materials are very important for the material packaging suppliers, the printers and the packaging users of food and pharmaceutical products. As it is obvious that the inks are not in direct contact with the packed product, indirect contamination may occur through the external layers of the packaging materials during storage before transformation into packages. In this case, the solvents may present a toxicity risk or modify the organoleptic quality of the packed product.

Given the fact that there are numerous packaging materials and a large range of relevant solvents used in the printing and laminating process, we have tried to evaluate the global properties of solubility and diffusion of these solvents in packaging materials.

To do this, an analytical method must be able to:

– desorb the residual printing solvents,
– qualify the residual printing solvents,
– quantify the residual printing solvents.

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Monitoring the limits of solvent content in packaging materials as selected by the users, requires a method that is applicable to a range of relevant solvents used in printing and laminating processes. According to current industrial practices, a list (see Table 1) of 28 solvents could be established.

Experimental

An analytical method based on static headspace gas chromatography (HS-GC) coupled with a mass spectrometer (MS) as detector (see Table 2) has been developed to:

1. create an authorized solvents database (MSDATA) in printing ink,
2. propose an identification and quantitation method (HS-GC-MS) for the residual printing solvents in packaging materials,
3. compare the quantitation results obtained by mono and multi headspace extraction (MHE).

Measuring Conditions and Analytical Method

The samples were taken from a film roll in the centre of the web. A piece of 1 dm^2 of material was placed in a 20ml vial, which was then sealed. The sample was equili-

Table 1. List of solvents

Solvents	CAS N°	Solvents	CAS N°
Cyclohexane	110-82-7	Vinyl acetate	108-05-4
Methanol	67-56-1	Propyl acetate	109-60-4
Ethanol	64-17-5	Isopropyl acetate	108-21-4
1-Propanol	71-23-8	Methoxy-2-ethyl acetate	110-49-6
2-Propanol	67-63-0	Ethoxy-2-ethyl acetate	111-15-9
1-Butanol	71-36-3	Methyl glycol	109-86-4
2-Butanol	15892-23-6	Ethyl glycol	110-80-5
Isobutanol	78-83-1	1-Methoxypropan-2-ol	107-98-2
Ethanediol	107-21-1	1-Ethoxypropan-2-ol	1569-02-4
Acetone	67-64-1	*m*-Xylene	108-38-3
Methylethylketone	78-93-3	*o*-Xylene	95-47-6
Methylisobutylketone	108-10-1	*p*-Xylene	106-42-3
Cyclohexanone	108-94-1	Toluene*	108-88-3
Ethyl acetate	141-78-6	Tetrahydrofurane	109-99-9

*Toluene is still used in Asia, not in Europe

brated with its gas phase at 85 °C for a period of 60 min. After preliminary results, a preconditioning, before the equilibration, was realized in an oven at 85 °C for a defined period. The head space, HS, *i.e.* the gaseous phase, was then injected into a gas chromatograph with a mass spectrometric detector (Table 2).

The analysed materials are, *e.g.*:

– Surface print PET
– Surface print PP
– PET/internal print/PE/Al/PE(PE/EVA)
– Surface print paper/PE

Table 2. Apparatus and method

Apparatus	Reference	Parameters
Static headspace auto sampler	HS 40XL, Perkin Elmer	Thermostatisation: 60 min at 85 °C, Injection: 0.1 min
Gas chromatograph	Auto sampler, Perkin Elmer	5 min at 40 °C, 5 °C/min to 120 °C and 10 °C/min to 240 °C Injector: CAP at 140 °C
Column	Supelcowax™-10 capillary column	PEG Stationary Phase, 30 m × 0.2 mm × 0.2 µm film thickness Carrier gas: Helium 100 kPa at 25 cm/s
Mass spectrometer	TurboMass, Perkin Elmer	Masses: 10–250; Interface: 200 °C; Source: 180 °C

Results

Thermodynamic Equilibrium

The thermodynamic equilibrium useful for the quantitation depends on:

– the chemical nature of the solvent,
– the printing process,
– the chemical nature of the packaging material,
– the interaction between solvent and packaging material,

and was reached after a preconditioning time from 1 to 24 h at 85 °C.

For example, in case of the reverse printed sample PET/internal print/PE/ Al/ PE (PE/EVA), the thermodynamic equilibrium required for the identified solvents is reached after at least a 12 h preconditioning period at 85 °C.

Fig. 1a shows the peak area in function of the preconditioning time for the solvents of major amount while Fig. 1b shows the minority solvents.

In both cases, the thermodynamic equilibrium is reached after 12 h preconditioning at 85 °C for this kind of multi-layer material.

Mono Headspace Extraction in Function of the Thermodynamic Equilibrium

When the thermodynamic equilibrium is not reached, the determined concentrations are much lower and some solvent may not be detected (Table 3).

Mono-, Multi Headspace Extraction and Quantitation

When the thermodynamic equilibrium is determined, it is possible to quantify the solvents either in mono extraction or in MHE. Under this condition the theory of MHE is verified, so Ln (Peak Area) is a linear function of the number of extraction steps (Fig. 2, Table 4).

For this material, the thermodynamic equilibrium at 85 °C is reached after 3 h and the determined amounts for the two solvents are in the same range after 6 h of preconditioning.

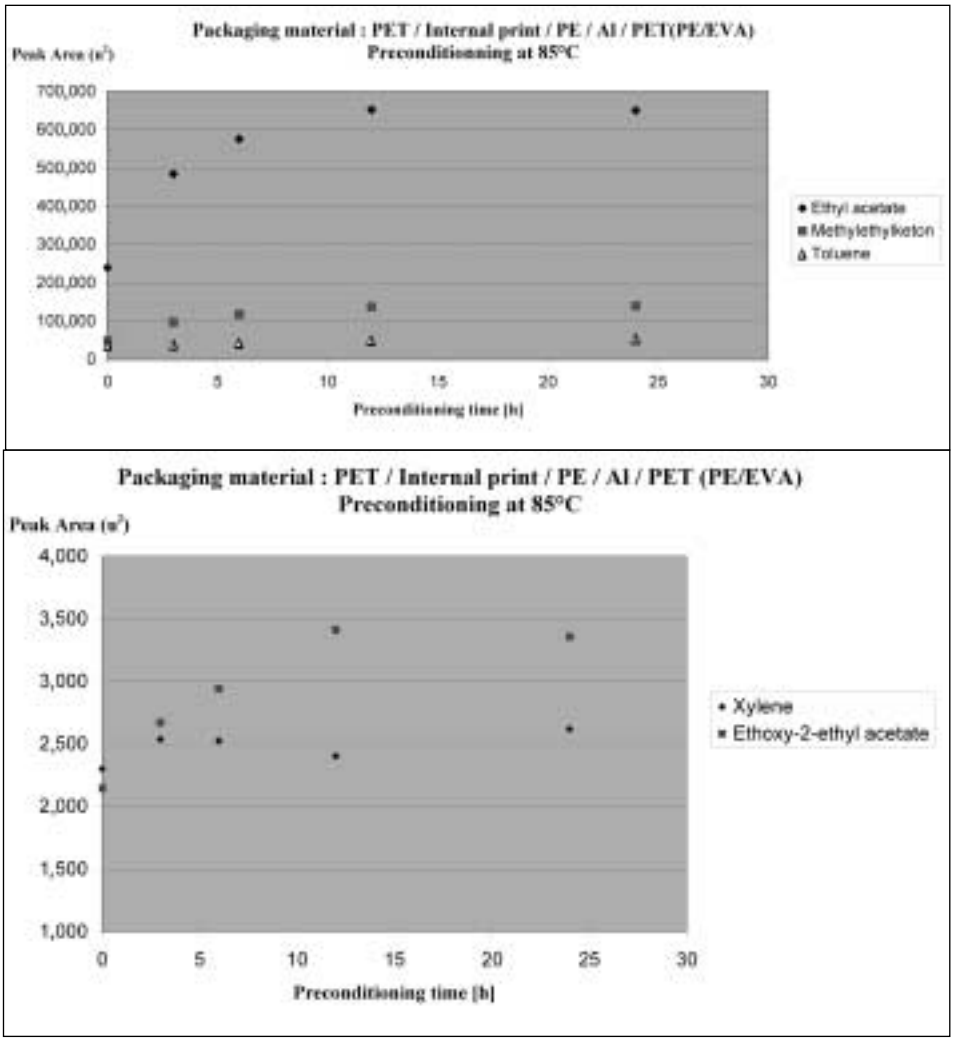

Fig. 1. a) Amount of residual solvents in function of preconditioning times at 85 °C. PET/Internal print/PE/Al/PE(PE/EVA). b) Amount of residual solvents in function of preconditioning times at 85 °C. PET/internal print/PE/Al/ PE(PE/EVA).

Table 3. Comparison between concentrations when the thermodynamic equilibrium is not reached or is reached for three solvents in surface print PET film.
Note: Concentrations given are the amount of solvent per square meter of printed packaging material

Solvents	Thermodynamic equilibrium not reached Concentration [mg/m^2]	Thermodynamic equilibrium reached Concentration [mg/m^2]	ΔC [%]
1-Methoxypropan-2-ol	1.45	1.69	+17
Ethyl acetate	0.06	0.13	+117
Methanol	Not detectable	0.10	-

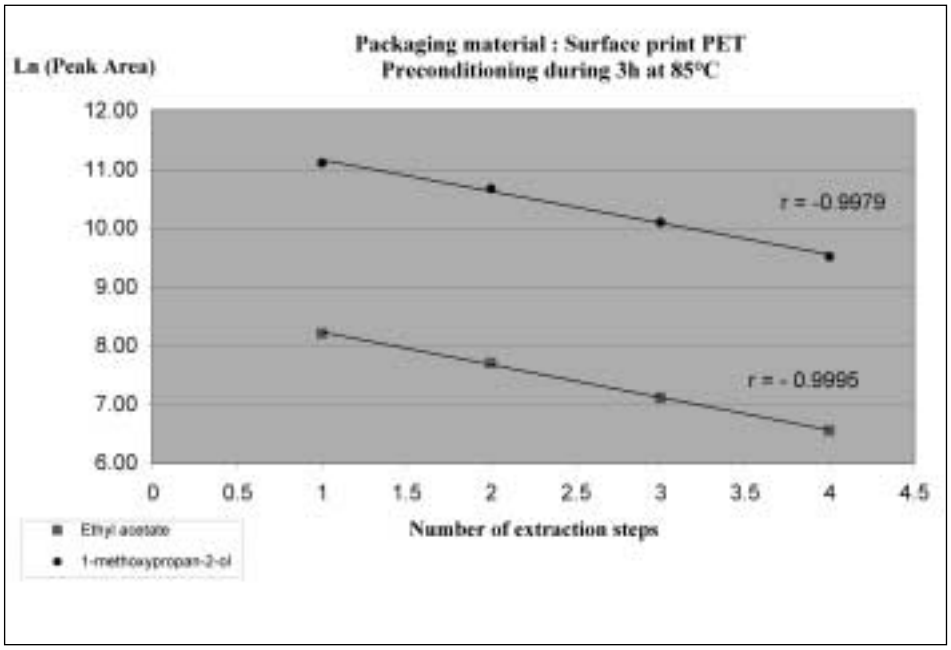

Fig. 2. Semi-log relationship between peak area and the number of extraction steps in MHE measurements of a sample of a surface print PET.

Table 4. Quantitation of residual printing solvent of surface print PET [mg/m^2]

Solvents	Preconditioning time [h]	C_1 [mg/m^2]	C_2 [mg/m^2]	C_3 [mg/m^2]	C_4 [mg/m^2]
1-Methoxypropan-2-ol	3	1.65	1.38	1.61	1.64
	6	1.73	1.50	1.61	1.64
Ethyl acetate	3	0.11	0.10	0.11	0.11
	6	0.14	0.16	0.20	0.17

C_1: Concentration determined with the 1st extraction A_1-Mono Headspace Extraction
C_2: Concentration determined with the first two extractions by using the simplified MHE relation: $S_A = A_1^2/(A_1-A_2)$
C_3: Concentration determined with the first three extractions by using linear regression
C_4: Concentration determined with the four extractions by using linear regression:
A_1: Peak area of the 1st extraction
A_2: Peak area of the 2nd extraction
S_A: Sum of the peak areas for the first two extractions

Discussion

For the analysis of any new packaging material, the following points must be addressed:

1. Whatever the structure of the packaging material, the thermodynamic equilibrium must be defined in order to be as close as possible to the real amount of residual printing solvents. To reach the thermodynamic equilibrium, a *preconditioning time* must be set. If the thermodynamic equilibrium is not reached, the error in the amount of solvent determined would be enormous. If the thermodynamic equilibrium is not reached, some solvents could not be detected at 85 °C. To work either in Mono or in MHE, the thermodynamic equilibrium has to be reached.
2. Moreover, when MHE is applied, a minimum of three extraction steps has to be realized.
3. According to the above points, the MHE at this preconditioning time will allow the quantification and qualification of the residual printing solvents in a new packaging material.
4. In order to specify the parameters of the analytical method, the temperature and the time of the preconditioning in particular, it is important to know:

– how the material will be stored before use (time, temperature …),
– what will be the conditions of use of the packaging material in its final configuration?

Bearing in mind that a printed packaging material must not be a solvent 'tank'.

Even though MHE could be too time-consuming for routine analyses, the results show that the MHE HS-GC-MS method is well adapted for the quality control in residual printing solvents for packaging materials.

Received: April 23, 2002

[1] B. Kolb, 'Multiple Headspace Extraction – A Procedure for Eliminating the Influence of the Sample Matrix in Quantitative Headspace Gas Chromatography', *Chromatographia* **1982**, *154*(9), 587–594.
[2] B. Kolb, L.S. Ettre, 'Static Headspace-Gas Chromatography', Wiley-VCH, **1997**.
[3] L. Spack. A. Collet, R. Buffat, 'Residual Solvents in Packaging Materials', Nestlé Research Center, **2000**.
[4] B. Kolb, P. Pospisil, M. Auer, 'Quantitative Bestimmung von Restlösemitteln in bedruckten Verpackungsfolien nach dem Verfahren der Mehrfach-Gasextraktion', Perkin Elmer, **1981**.