Application Note 252

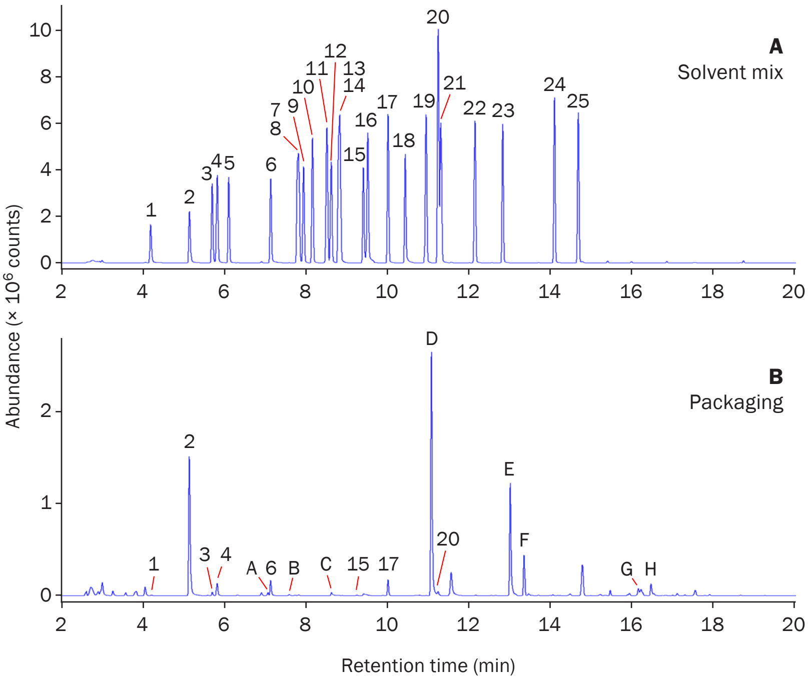
Quantitation of residual solvents in food packaging by automated headspace–trap GC–MS

This study shows that headspace samples acquired on the new Centri® sample extraction and enrichment platform for gas chromatography–mass spectrometry (GC–MS) can be used to screen food packaging for residual solvents and other additives. Analysis of a sample of a thin composite polymer used to contain savoury snacks found ethanol at 1.92 mg/m^2, in addition to a number of other volatile compounds resulting from the manufacturing process.

The vast majority of foodstuffs consumed today use packaging to convey information about the product and to protect it during shipping and storage. However, the packaging itself can be a source of contaminants, including residual solvents, monomers and additives. As well as off-odours, such contaminants can also give rise to health concerns, and for these reasons residual solvents in food packaging are regulated in the US (under 21CFR175) and the EU (under EC 1935/2004). The analysis of flexible packaging for the determination of residual solvents typically uses static headspace–GC in accordance with EN 13628-1 or -2.

In this study we demonstrate the fully automated sampling and detection of residual solvents and additives in the headspace of thin flexible packaging for savoury snacks, using syringe headspace extraction with trap-based focusing on the new Centri sample extraction and enrichment platform, in conjunction with GC–MS.

Figure 1A shows the HS–trap GC–MS profile for a standard containing 25 solvents commonly found in food packaging, which shows elution of all components within 15 min. Figure 1B shows the HS–trap profile from a 64 cm^2 sample of food packaging, which indicates the presence of a number of



Solvents

1 Methanol
2 Ethanol
3 Acetone
4 Propan-2-ol
5 Methyl acetate
6 Propan-1-ol
7 Butan-2-one
8 Ethyl acetate
9 Butan-2-ol
10 Tetrahydrofuran
11 Cyclohexane
12 2-Methylpropan-1-ol
13 2-Methoxyethanol
14 Isopropyl acetate
15 Butan-1-ol
16 1-Methyoxypropan-2-ol
17 n-Propyl acetate
18 2-Ethoxyethanol
19 4-Methylpentan-2-one
20 Toluene
21 Isobutyl acetate
22 n-Butyl acetate
23 2-Methoxyethyl acetate
24 2-Ethoxyethyl acetate
25 Cyclohexanone

Other contaminants

A Methacrolein
B 3-Ethylpropan-2-ol
C Acetic acid
D 1-Ethoxypropan-2-ol
E 1-Propoxypropan-2-ol
F 1-Methoxyprop-2-yl acetate
G 1-(2-Methoxy-1-methylethoxy)-propan-2-ol
H 1-(2-Methoxypropoxy)-propan-2-ol

Figure 1: HS–trap GC–MS analysis of: (**A**) a standard mix of solvents; (**B**) food packaging, identifying solvents and other contaminants.

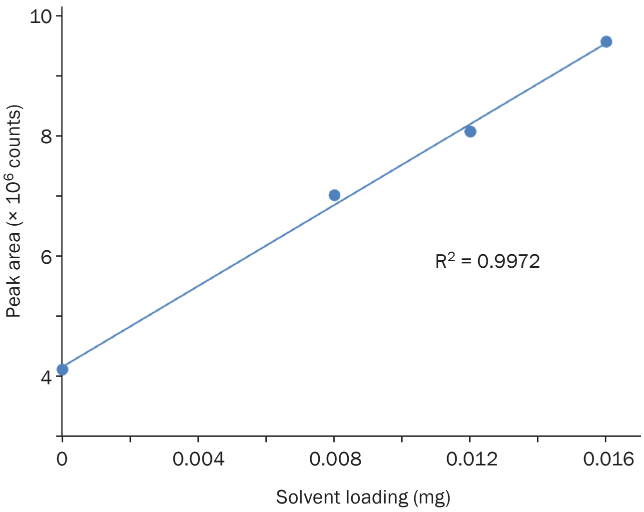


Figure 2: Example of a calibration plot (for ethanol) used to determine solvent loading on the sample of packaging, using four standard additions of 0, 0.008, 0.012 and 0.016 mg, respectively.

solvents and some other components that likely derive from the manufacturing process.

The solvents in the packaging were quantified on the basis of a calibration using standard addition into four vials, an example of which is shown in Figure 2. The resulting levels of residual solvents in the packaging are listed in Table 1, and show that ethanol is the most significant component (at 1.92 mg/m^2), with seven other solvents at trace levels. This quantitation process would typically also be performed for other chemicals identified in the food packaging sample, such as 1-ethoxypropan-2-ol (#D) and 1-propoxypropan-2-ol (#E).

No.	Compound	Loading (mg/m^2)
1	Methanol	0.005
2	Ethanol	1.92
3	Acetone	0.024
4	Propan-2-ol	0.059
6	Propan-1-ol	0.102
15	Butan-1-ol	0.093
17	n-Propyl acetate	0.135
20	Toluene	0.061

Table 1: Loadings of residual solvents identified in the food packaging sample.

Two features of this analysis combine to allow determination of residual solvents at the sub-mg/m^2 level:

- The use of analyte re-focusing on the Centri focusing trap results in better GC–MS peak shape compared to headspace methods that do not use analyte focusing.
- The use of a very low 3.5:1 split ratio for the injection means that a large proportion of the sample is sent to the GC–MS. On many trap-based systems, the use of such a low ratio would result in poor peak shape, but this is avoided with Centri because of the optimised design and highly efficient backflush desorption of the focusing trap.

Background to Centri®

Markes International's Centri system for GC–MS is the first platform to offer high-sensitivity unattended extraction and enrichment of VOCs and SVOCs in solid, liquid and gaseous samples.

Centri allows full automation of immersive and headspace extraction using HiSorb™, high-capacity sorptive extraction probes. It also offers full automation of headspace, SPME and tube-based thermal desorption with enrichment. Leading robotics and analyte-trapping technologies are used to improve sample throughput and maximise sensitivity for a range of applications – including profiling of foods, beverages and fragranced products, environmental monitoring, clinical investigations and forensic analysis.

In addition, Centri allows samples from any injection mode to be split and re-collected onto clean sorbent tubes, avoiding the need to repeat lengthy sample extraction procedures and improving security for valuable samples, amongst many other benefits.

For more on Centri, visit www.markes.com.

In conclusion, we have shown the ability of Centri to allow highly sensitive headspace–trap analysis of food packaging for improved detection of residual solvents and other additives. This capability is complemented by the other extraction modes available with Centri – HiSorb high-capacity sorptive extraction, thermal desorption and SPME – all of which can benefit from cryogen-free trapping for enhanced sensitivity. In addition, by allowing unattended sequential analysis of multiple sample types using different injection modes (with 'prep-ahead' functionality), Centri greatly improves efficiency for high-throughput laboratories.

Experimental

Sample:
Unused flexible packaging for baked savoury snacks was cut into 64 cm^2 sections, which were rolled up and inserted into a 20 mL headspace vial. The vial was capped and crimped to form an air-tight seal.

Standard:
A standard containing 25 common solvents was prepared in accordance with EN 13628-1. Calibrations were performed in duplicate by injecting appropriate volumes of the standard solution into the crimped vials. Loadings were 0, 0.008, 0.012

and 0.016 mg for ethanol and 1-methoxypropan-2-ol, and 0, 0.000150, 0.000225 and 0.000300 mg for all other compounds.

Headspace–trap:

Instrument:	Centri (Markes International)
Equilibration:	60 min at 100°C
Extraction volume:	1 mL
Inlet:	180°C
Focusing trap:	'TO-15/TO-17 Air toxics' (part no. U-T15ATA-2S)
Trap flow:	50 mL/min
Trap desorption:	25°C to 290°C (3 min)
Outlet split:	5 mL/min (3.5:1)
Flow path:	180°C

GC:

Column:	DB-624™, 60m × 0.32mm × 1.8 µm
Column flow:	2 mL/min (constant-flow)
Oven program:	40°C (2 min), 10°C/min to 200°C (5 min)
Aux heater:	210°C

Quadrupole MS:

Scan mode:	m/z 15–300
Source:	300°C
Transfer line:	280°C

Calculations:

Amounts of residual solvent in the packaging (in mg/m^2) were determined from linear regression plots from the four levels of each solvent analysed in the calibration standard, in accordance with the standard addition procedure in EN 13628-1.

Applications were performed under the stated analytical conditions. Operation under different conditions, or with incompatible sample matrices, may impact the performance shown.

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