An Easy Solution to Monitor Printing Residual Solvents in Packaging Material using an Agilent 7820 GC system and an Agilent 7697A Headspace Sampler

Application Note

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Abstract

Printing inks have been used extensively to enhance the visual appearance of packing materials of consumer products, however due to its toxicity, the manufacturing process of printing ink has been heavily regulated. This application note demonstrates the capability of one automatic Headspace/Gas Chromatograph (HS/GC) system to meet the demands of such residual solvents detection. These scientific instruments provide quality analysis to packing material suppliers, with minimal sample preparation and short cycle times at an affordable price.

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Introduction

Solvents can play an important role in various stages of the manufacturing of flexible packaging, ranging from laminating through printing to coating. Solvent-based inks are created with the solvent comprising up to 95% of the ink. The identification and quantitation of residual printing solvents in packaging materials are very important for the material packaging suppliers, users, and printers. The constituents in the links can migrate into packed products and endanger human health, or change the packed products, or cause a deterioration of the organoleptic characteristic of packed products. The manufacturing of print inks has been heavily regulated worldwide, and solvent analysis is one of the items listed in the regulations.

This application note describes a method for the detection of such solvents using the Agilent 7820GC-7697HS system. With ASTM F 1884-04 as reference standard method [1], this solution can:

- Desorb the residual printing solvents by 7697A headspace
- Qualify the residual printing solvents by retention time on Agilent 7820 GC with Flame Ionization Detection (FID)
- Quantify the residual printing solvents by the peaks area produced by 7820GC and ChemStation software

Key points of this application

- Fast analysis by Optimized method
- Reliable 7820 GC/FID performance
- Cycle time savings and excellent performance with 12 vials on the 7697A headspace sampler.

Experimental

Reagents and Standards

All of the standards and reagents used in this application were obtained from J&K. According to current industrial practice, a list of 13 solvents was established (Table 1).

Table 1. Thirteen Solvents Used

Name	Cas.	R.T (min)
Acetone	67-64-1	0.869
Methyl acetate	79-20-9	0.901
Ethyl acetate	141-78-6	1.098
MEK	78-93-3	1.151
Isopropanol	67-63-0	1.314
Ethanol	64-17-5	1.342
n-propyl acetate	109-60-4	1.517
Toluene	108-88-3	1.862
n-propanol	71-23-8	1.896
Isobutanol	78-83-1	2.188
Methoxypropanol	107-98-2	2.386
n-butanol	71-36-3	2.484
Ethoxypropanol	1569-02-4	2.589

Instruments

This method was developed using an Agilent 7820 GC with a 7697A Headspace Sampler. The carrier gas flow was controlled with the 7820 EPC module. The system incorporated a split/splitless inlet and a flame ionization detector. Agilent OpenLAB CDS ChemStation software was used for data acquisition and analysis. The 7697A transfer line was installed through the inlet septum.

Component	Part number
Agilent 7697A Headspace Sampler	p/n G4556A
Agilent 7820GC	p/n G4350A
OpenLAB CDS ChemStation	p/n M8301AA
OpenLAB CDS instrument driver for Agilent GC	p/n M8400AA
7697A headspace control GC ChemStation	p/n G7318AA
GC liner is direct 2 mm id	p/n 5181-8818
20-mL vials	p/n 5190-2288
20-mm crimper	p/n 5040-4669
Headspace Al crimp cap (PTFE/Si sep, 20 mm)	p/n 5183-4477

Table 2 shows the instrument conditions used.

Standard preparation

Mix 10 µL of each solvent in a 2-mL sampler vial. Add 100 µL of this solution into 10 mL of DMSO to make a 0.8 g/mL solution. Dilute this solution with DMSO to make standards of 5.0, 2.5, 1.0, 0.5, 0.05, and 0.005 mg/mL solutions. Use 1 mL in headspace vials to obtain 5.0, 2.5, 1.0, 0.5, 0.05, and 0.005 mg calibration levels. Calibration curves for this application were made by external standard mode.

Sample preparation

Insert 10 × 10 cm clean soft package paper into vials, then add calibration solutions to check the method reliability.

Table 2. Agilent 7697A headspace and GC/MS Run Conditions

Agilent 7697A HS GC/MS System		
Temperature	Oven	85 °C
	Loop	95 °C
	Transfer line	105 °C
Time	Vial equilibration	5 minutes
	Injection time	0.5 minutes
	GC cycle	7 minutes
Vial	20 mL	
	Fill mode	default
	Fill pressure	He, 15 psi
	Extraction mode	single extraction
GC run conditions		
Inlet	180 °C; split: 100:1	
Carrier gas	He, flow mode: 0.8 mL (3 minutes), 100 mL/min, 1.5 mL (running end)	
Injection volume	1 mL from a 1-mL headspace loop	
Column	DB-WAX 10 m × 0.18 mm, 0.18 µm (p/n 121-7012)	
Oven temperature gradient	1.0 minute hold at 40 °C, 40 °C to 110 °C at 30 °C/min, hold for 0 minutes 110 °C to 140 °C at 40 °C/min, hold for 0 minutes	
FID	250 °C; H_2: 35 mL/min; make up + constant flow: He, 24.5 mL/min; air: 350 mL/min	
FID Signal	50 Hz/0.004 minutes	

Results and Discussion

Fast method optimization

To develop a fast method for monitoring volatiles in packaging, the target list of volatile compounds shown in Table 1 was developed based on compounds detected in processed packaging materials [2]. We selected a short, narrow id DB-WAX to get a fast analysis time and acceptable separation. Figure 1 shows a 10-µg calibration chromatogram and Table 1 shows the retention time.

The elution time of the target compound is within 3 minutes under constant 0.8 mL/min flow. A change to program flow mode quickly pushed the higher boiling point unknowns out. Once all of the targets eluted from the column, a higher carrier gas flow rate shortened cycle time. If it is not necessary to analyze the higher boiling point compounds ignore the program flow, just use constant flow mode.

Because concentration of solvents in ink is relatively high, 5 minutes headspace equilibration time was sufficient. We also used a high split ratio in inlet for high concentration solvents and narrow id column. Under these conditions, the method detection limit is lower than 0.005 µg. The split ratio can be adjusted according to application needs.

The 12-vial 7697A headspace can reduce cycle time and provide an applicable fast solution with these conditions. An applicable fast solution was developed. In this method, it should be noted that methanol may coelute with MEK.

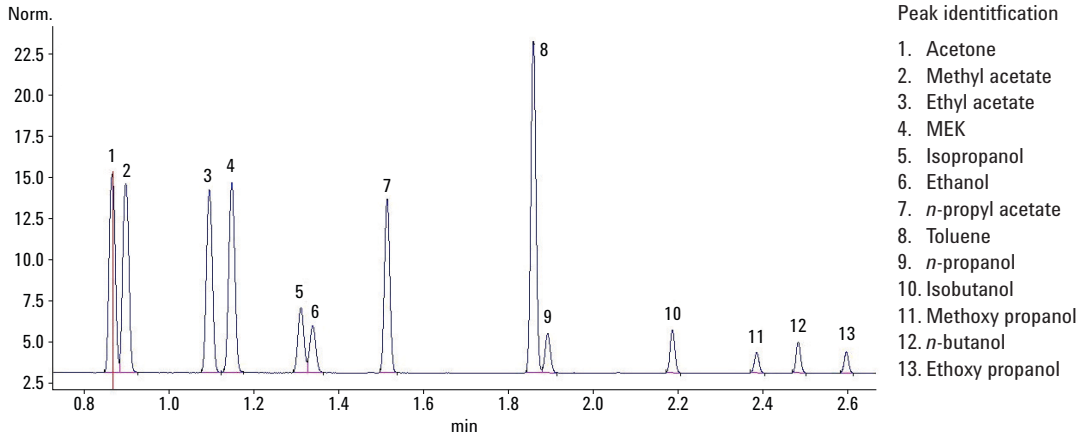

Figure 1. 10.0 µg solvents chromatogram.

Accuracy of quantitative and qualitative analysis

The calibration samples prepared were used to construct calibration curves for the 13 solvents with the standard mix added to soft packing materials. The correlation coefficients (R^2) for all 13 compounds were ≥ 0.9990 for the range of 0.005 mg to 5 mg (Table 3), and the calibration curves for two compounds are shown in Figures 2 and 3. The calibrations show that a 7820GC-7697 HS system produces reliable quantitation results.

We placed 10 µg of solvent directly onto the 10 × 10 cm soft packaging paper and inserted them into seven headspace vials. Seven injections were done to calculate retention time and area RSD%. Table 3 shows that the 7820GC -7697A headspace system provides excellent retention time stability. This is important because the retention time is the only specification in a GC's qualitative capability, especially in unknowns application.

Table 3.

Name	R^2	R.T RSD%	Area RSD%
Acetone	0.9998	0	1.21
Methyl acetate	0.9996	0	1.03
Ethyl acetate	0.9996	0	1.02
MEK	0.9998	0	1.01
Isopropanol	0.9996	0	1.25
Ethanol	0.9997	0	1.18
n-propyl acetate	0.9997	0	1.26
Toluene	0.9998	0	1.12
n-propanol	0.9990	0	1.13
Isobutanol	0.9996	0	1.07
Methoxypropanol	0.9998	0	1.35
n-butanol	0.9998	0.015	1.31
Ethoxypropanol	0.9997	0	1.16

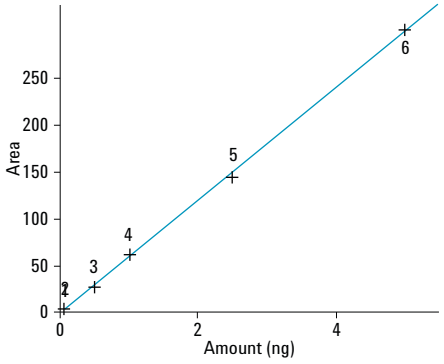

Figure 2. Ethanol calibration curve (R^2 = 0.9997).

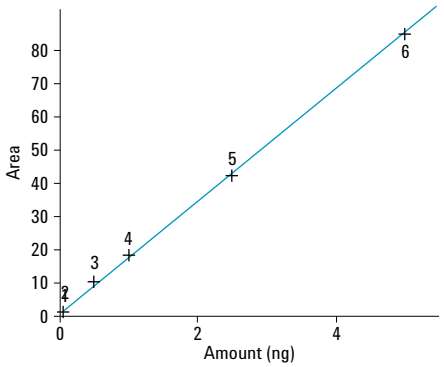

Figure 3. Methoxypropanol calibration curve (R^2 = 0.9998).

Real ink sample simulation analysis

Place 5 µg amounts of solvent into a 1.0-g blank ink carbon powder matrix to simulate a real ink sample. Figure 4 shows the chromatogram for the 13 solvents. The recoveries for all the compounds were between 98.0 to 101.5%.

Conclusion

The Agilent 7820 GC configured with an Agilent 7697A headspace meets the requirements of the standard test method for analyzing printing ink in packaging. The main requirement for this application is fast, easy, and quantitative solvent determination. Using the setup demonstrated in this application note, analysis of residual solvents (VOCs) in packaging materials can successfully be performed with high precision and accuracy. This solution allows the customer to achieve a fast total analysis cycle time to meet the requirement of packaging material process.

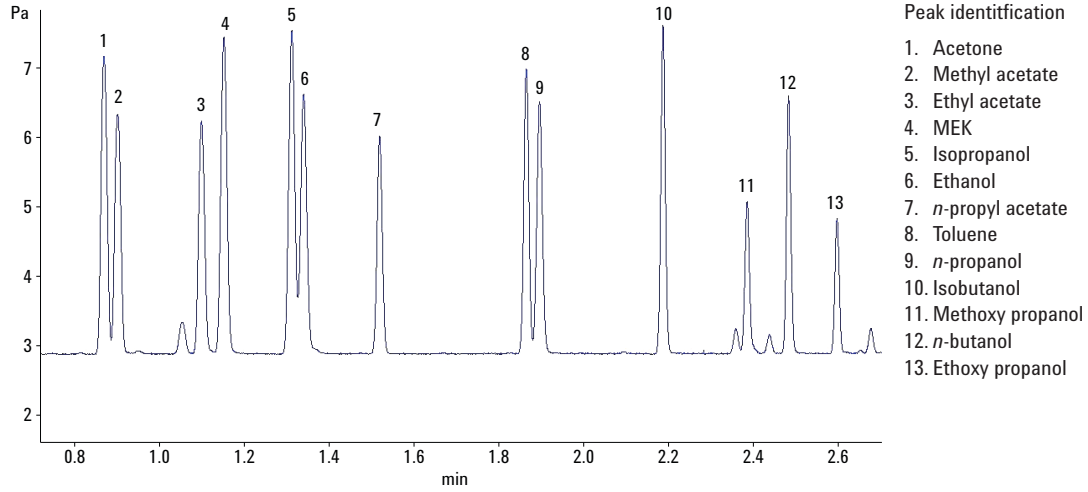

Figure 4. Chromatogram of 5.0 µg added to ink carbon matrix.

References

1. Standard Test Methods for Determining Residual Solvents in Packaging Materials ASTM F 1884-04
2. Didier Louvier and Eric Martine, "Residual printing solvents in packaging materials", *Chimia* 56 (2002), 295~297.

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