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# Application News

# No. AD-0131

*Food Safety for Packaging Material / HS-20 GC-2010 Plus*

# Detection of 27 Residual Solvents in Food Packaging using Parallel Dual-Column Headspace Gas Chromatography

## ❑ Introduction

Food safety has gained escalated interest worldwide in recent years. It involves the whole process of food production, from the start of food processing to the end of food packaging. Food packaging is a barrier between food and the atmosphere that prolongs the shelf life of food, particularly for the perishables. Other than functioning as a physical barrier, the packaging is often printed with information labels or artwork. The use of inks for these prints leaves a possibility that residual solvents from the inks may migrate to the food, which affects not only the taste and flavour, but more importantly, causes toxicity to users [1]. Current food safety regulations specify that the amount of residual solvents present in packaging material to be controlled [2]. For instance, Korea Ministry of Food and Drug Safety regulates the residual toluene in packaging material should be less than 2mg/m$^2$ [2]. Headspace (HS) technique coupled with gas chromatography (GC) and flame ionization detector (FID) is routinely used for such measurement to eliminate the tedious sample preparation. In this application news, an automated parallel dual-column HS-GC technique was applied for simultaneous confirmation and quantitation of 27 residual solvents in packaging materials.

## ❑ Experimental

### Instrumental and analytical conditions

HS-20 headspace autosampler paired with GC-2010 Plus (Shimadzu Corporation, Japan) was used in this study. One column is not sufficient to achieve baseline separation for some targeted solvents. To avoid the inconvenience of changing column, an automated parallel dual-column HS-GC technique was developed in this study to separate a mixture of 27 solvents. Both columns were connected in parallel to the HS-20 interface using ferrules and nuts (Figure 1) to separate FIDs. Columns with the same diameter and length were used to ensure even carrier gas flow into both columns. The analysis conditions are presented in Table 1.

### Chemicals and samples

The 27 solvents (Table 2) were either obtained from Kanto Chemical (Tokyo, Japan) or Sigma Aldrich (City, USA). The solvents mixture was diluted to 0.02% using ethyl acetate, while measurement of ethyl acetate utilised methanol as diluent. Five microliters of 0.02% residual solvents mixture was pipetted into a 20-mL HS vial and sealed with a crimp cap. This was equivalent to an absolute weight of 1µg of each residual solvent in the crimped HS vial and served as a 1-point calibration standard by full evaporation technique.

Three packaging materials (samples) from company X were analysed. The sample preparation was carried out in accordance to ASTM 1884-04 [3]. Each sample was cut into an area of 100cm$^2$ and subsequently cut into smaller pieces before they were placed into a 20-mL HS vial. The HS vial was then crimped tightly for subsequent HS-GC analysis. No pre-treatment step was needed. Three vials were prepared for each sample to check for its repeatability.

Table 1: HS-GC analytical conditions for residual solvent analysis

| **Instrumentation** | |
|---|---|
| GC-FID | GC2010 Plus |
| Auto Injector | HS-20 |
| Column1 | SH-Rtx™-VMS<br>60m x 0.25mm ID x 1.4µm df |
| Column2 | SH-Rxi™-1MS<br>60m x 0.25mm ID x 1.0µm df |
| **HS** | |
| Oven Temperature | 120°C |
| Sample Line Temperature | 150°C |
| Transfer Line Temperature | 150°C |
| Pressurizing Gas Pressure | 50kPa |
| Equilibrating Time | 15min |
| Pressurizing Time | 1min |
| Pressure Equilibration Time | 0.1min |
| Load Time | 0.5min |
| Load Equilibration Time | 0.1min |
| Shaking Level | Off |
| Injection Time | 1min |
| **GC** | |
| Injection Mode | Split mode<br>Split ratio 20 |
| Standards Amount in Vial | 5µL of 0.02% solvents mixture |
| Sample Amount in Vial | 100cm$^2$ |
| Carrier Gas | Helium |
| Gas Flow Condition | Constant linear velocity mode<br>Linear velocity 25cm/s<br>Purge flow 5mL/min |
| Oven Temperature Programming | 35°C (10min)<br>→20°C/min to 90°C (5min)<br>→20°C/min to 180°C (7min) |
| **FID** | |
| Detector Temperature | 200°C |
| Hydrogen Flow | 40mL/min |
| Synthetic Air Flow | 400mL/min |
| Make-up Gas Flow (Nitrogen) | 30mL/min |

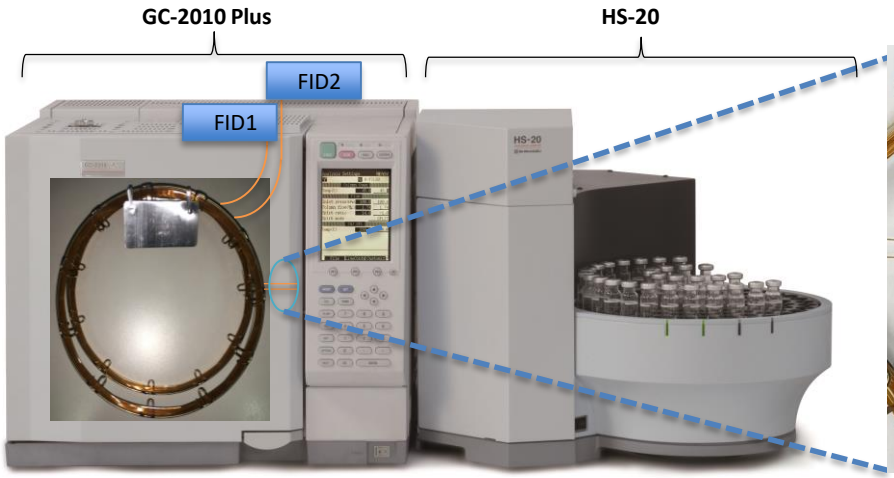


Figure 1a: Parallel dual-column configuration for HS-GC allows a single injection into 2 columns simultaneously

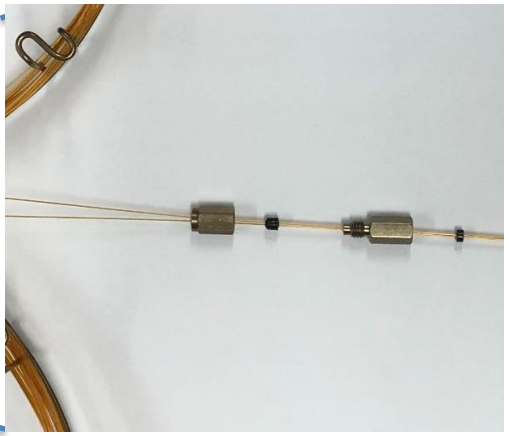

Figure 1b: Shimadzu Twin Line Kit (P/N: 225-20201-91) connects two columns to the HS sampler using special nuts and ferrules

## ❑ Results and Discussion

### Selection of diluents and separation

The chromatographic peak shapes of the residual solvents dissolved in two diluents (methanol and ethyl acetate) were investigated. Higher peak tailing of polar compounds were observed in methanol compared to ethyl acetate (Figure 2), thus, ethyl acetate was selected as the diluent. For quantitation of ethyl acetate, methanol was used as diluent since good peak shape was still obtained as shown in Figure 2.

The chromatogram of the solvents mixture separated by two different columns are displayed in Figure 3. Neither columns could achieve baseline separation for 1-butanol and methoxy propanol. In addition, the unresolved isomers m- and p-xylene were quantified as a group.

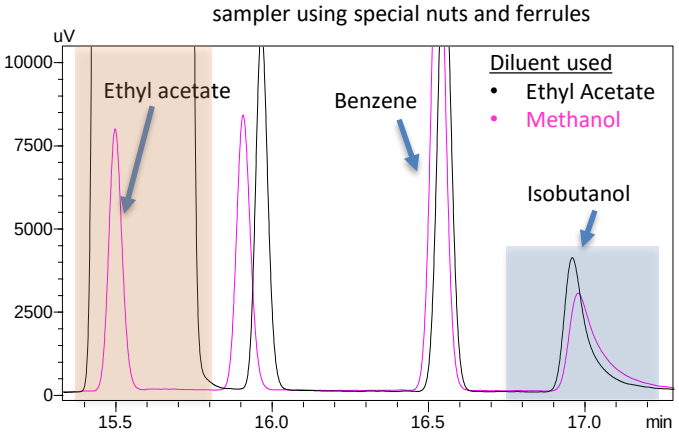


Figure 2: Separation of solvents mixture in methanol (red) and ethyl acetate (black) with SH-Rtx-VMS column by HS-GC (ethyl acetate (shaded in orange) and an example of polar compound, isobutanol, (shaded in blue))

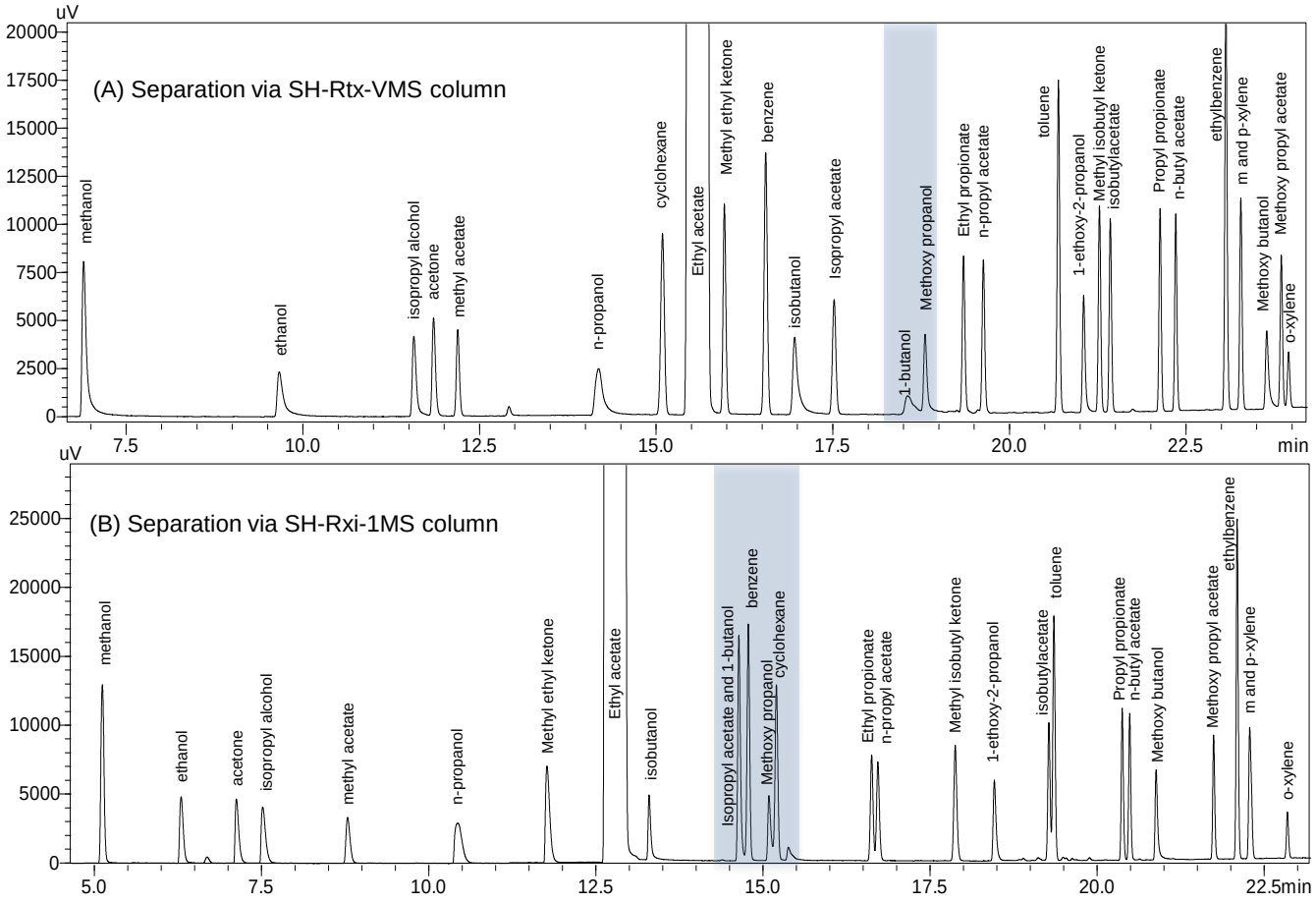


Figure 3: Chromatograms of solvents mixture in ethyl acetate (absolute 1µg of solvent each in HS vial) separated via (A) SH-Rtx-VMS column and (B) SH-Rxi-1MS column

Table 2: The mean RT, mean S/N & % RSD of 1µg standard solvent each and amount of residual solvents in µg per 100cm$^2$ of packaging materials detected by parallel column HS-GC analysis

| No | Solvents | Standard solvents mixture (1µg each) n=10 | | | | | | Amount of solvents detected in packaging materials (µg) n=3 | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | SH-Rtx-VMS column | | | SH-Rxi-1MS column | | | | | |
| | | Mean RT | Mean S/N | Area %RSD | Mean RT | Mean S/N | Area %RSD | Sample A | Sample B | Sample C |
| 1 | Methanol | 6.896 | 293 | 6.1 | 5.117 | 484 | 5.0 | 0.97 | 1.36 | 0.71 |
| 2 | Ethanol | 9.666 | 79 | 2.5 | 6.295 | 170 | 1.3 | 0.09 | 0.09 | 1.02 |
| 3 | Isopropyl Alcohol | 11.571 | 143 | 1.8 | 7.516 | 145 | 1.9 | 0.08 | 1.28 | 0.11 |
| 4 | Acetone | 11.850 | 175 | 1.1 | 7.122 | 164 | 1.2 | 0.06 | 0.64 | 0.10 |
| 5 | Methyl Acetate | 12.192 | 157 | 1.9 | 8.785 | 121 | 2.1 | Not Detected | 0.08 | Not Detected |
| 6 | n-Propanol | 14.191 | 81 | 3.0 | 10.438 | 101 | 2.1 | Not Detected | Not Detected | Not Detected |
| 7 | Cyclohexane | 15.090 | 321 | 1.2 | 15.201 | 423 | 1.1 | 0.34 | 0.57 | 0.42 |
| 8 | Ethyl Acetate | 15.498 | 299 | 2.2 | 16.686 | 241 | 1.8 | 4.31 | 1.17 | 0.52 |
| 9 | Methyl Ethyl ketone | 15.968 | 379 | 1.7 | 11.769 | 245 | 1.7 | 0.37 | 0.48 | 0.18 |
| 10 | Benzene | 16.551 | 475 | 1.8 | 14.781 | 605 | 1.7 | 0.01 | 0.03 | 0.02 |
| 11 | Isobutanol | 16.961 | 139 | 2.4 | 13.298 | 162 | 1.7 | Not Detected | Not Detected | Not Detected |
| 12 | Isopropyl Acetate | 17.519 | 209 | 2.0 | Overlap | | | 0.97 | 0.78 | 0.21 |
| 13 | 1-Butanol | 18.575 | 30 | 7.1 | | | | Not Detected | 0.08 | 0.10 |
| 14 | Methoxy Propanol | 18.806 | 140 | 9.5 | 15.088 | 156 | 3.0 | Not Detected | 0.43 | Not Detected |
| 15 | Ethyl Propionate | 19.350 | 287 | 1.8 | 16.625 | 264 | 2.0 | 0.11 | 0.33 | 0.09 |
| 16 | N-Propyl Acetate | 19.631 | 282 | 2.1 | 16.718 | 240 | 2.0 | 0.05 | 0.04 | 0.06 |
| 17 | Toluene | 20.693 | 605 | 2.1 | 19.353 | 594 | 2.1 | 22.17 | 3.35 | 20.37 |
| 18 | 1-Ethoxy-2-propanol | 21.050 | 215 | 2.3 | 18.461 | 214 | 2.4 | 0.02 | 0.05 | 0.11 |
| 19 | Methyl Isobutyl ketone | 21.274 | 377 | 2.2 | 17.875 | 303 | 2.0 | 0.71 | 0.40 | 0.66 |
| 20 | Isobutylacetate | 21.428 | 353 | 2.2 | 19.278 | 319 | 2.2 | 0.07 | 0.84 | 0.05 |
| 21 | Propyl Propionate | 22.132 | 373 | 2.2 | 20.375 | 395 | 2.2 | Not Detected | 0.05 | 0.75 |
| 22 | n-Butyl Acetate | 22.354 | 360 | 2.3 | 20.487 | 382 | 2.3 | Not Detected | 0.11 | 0.05 |
| 23 | Ethylbenzene | 23.064 | 748 | 2.3 | 22.095 | 895 | 2.3 | 0.02 | Not Detected | 0.03 |
| 24 | m- & p-Xylene | 23.275 | 389 | 2.4 | 22.283 | 343 | 2.3 | Not Detected | Not Detected | 0.66 |
| 25 | Methoxy Butanol | 23.641 | 143 | 2.4 | 20.882 | 236 | 2.4 | 0.11 | Not Detected | 0.14 |
| 26 | Methoxy Propyl Acetate (MPAC) | 23.848 | 279 | 2.4 | 21.743 | 325 | 2.2 | 0.08 | 1.12 | 0.39 |
| 27 | O-Xylene | 23.951 | 103 | 2.6 | 22.848 | 121 | 2.3 | Not Detected | 0.04 | 0.09 |

Note: The solvents amount in samples highlighted with blue font were determined using SH-Rtx-VMS column and those in red font were quantitated by SH-Rxi-1MS column
Quantitation of ethyl acetate for sample was performed with methanol as diluent

**Target analyte identity confirmation and quantitation**

Two columns with different stationary phases aided the separation of the residual solvents. At the same time, the analysis using the second column served as a confirmatory method. Since GC/FID does not produce mass spectrum (unlike GC/MS), analysis using the second column confirmed the presence of the solvents. Subsequently, the confirmed residual solvent were quantified easily by using the peak areas obtained from either one of the columns that had no partial peak overlap with the sample matrices. If both columns were able to give isolated target peaks, the peak with better profiles (sharper and more symmetrical) was selected to ensure good quantitative sensitivity and accuracy.

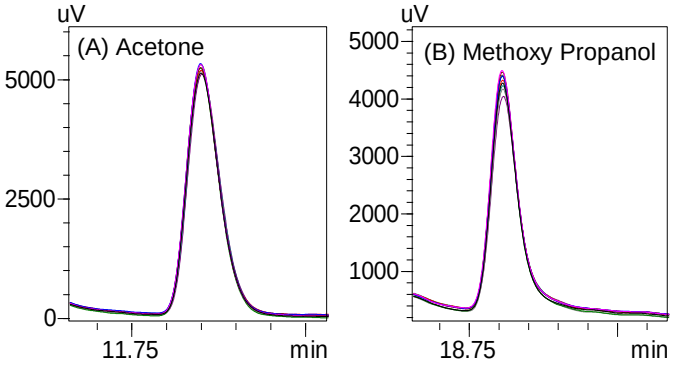


Figure 4: Overlay of 10 chromatograms for (A) acetone and (B) methoxy propanol with %RSD of 1.1 (A) and 9.5 (B)

**Sensitivity and precision**

All the solvents (1µg each) except 1-butanol produced signal to noise ratio (S/N) greater than 100 (Table 2) in either one of the columns. This demonstrated that solvents below 1µg in a HS vial were still detectable via parallel dual-column analysis. The repeatability (%RSD of n=10) for most solvents was between 1.0% to 3.0% (Table 2). An overlay of 10 chromatograms for two selected solvents with the lowest and the highest %RSD is displayed in Figure 4.

**Sample analysis**

Three different food packaging materials, namely A, B and C were analysed. The chromatograms for Sample C with three replicate analyses are displayed in Figure 5. The quantitative results of residual solvents in the samples are tabulated in Table 2. The most abundant residual solvent detected was toluene with a concentration of 22.2µg (2.2mg/m$^2$), 3.4µg (0.3mg/m$^2$) and 20.4µg (2.0mg/m$^2$) for Sample A, B and C respectively.

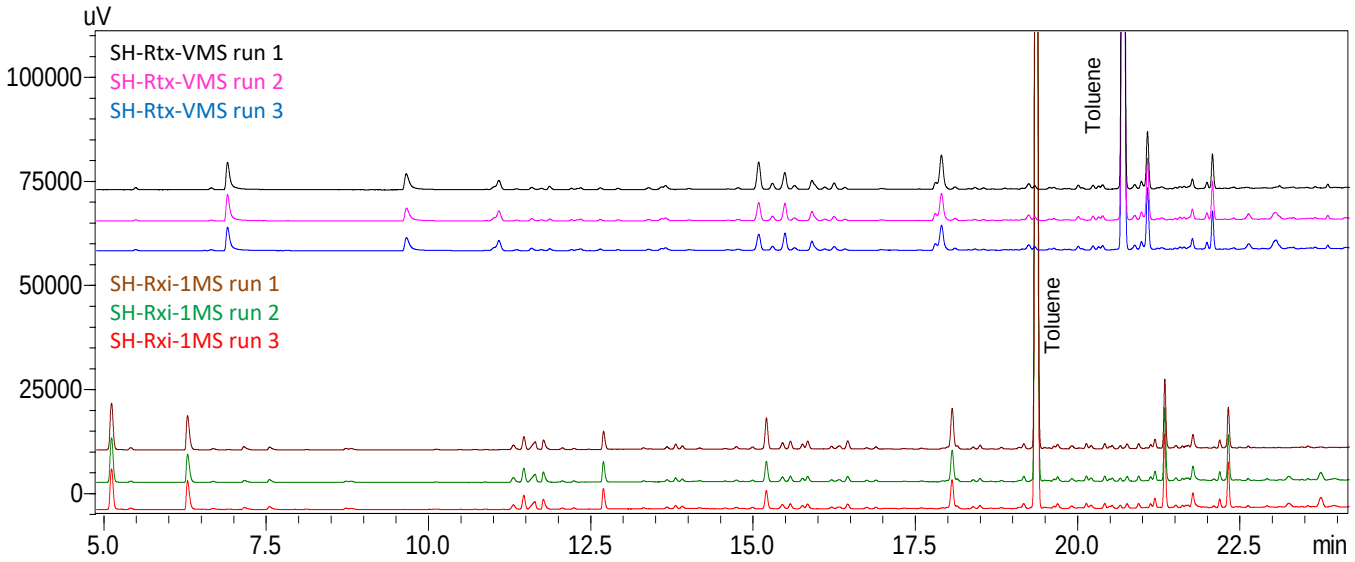


Figure 5: Chromatogram of Sample C with triplicate runs using three fresh sample and vial per run

## ❑ Conclusions

Determination of residual solvents in packaging materials was successfully carried out with a parallel dual column HS-GC technique. The S/N for each solvent at 1µg was more than 100, which indicate that the current system can detect residual solvents (except 1-butanol) at concentrations below 0.1mg/m$^2$ in food packaging material.

## ❑ References

1. Seo. I, Shin. H.S. Food Sci. Biotechnol. 19(6): 1429-1434 (2010)
2. Standards and Specifications for Food Utensils, Containers and Packages [March 2015] (https://www.mfds.go.kr/eng/eng/index.do?nMenuCode=120&page=1&mode=view&boardSeq=70089, retrieved 3 May 2017)
3. ASTM F1884-04(2011), Standard Test Method for Determining Residual Solvents in Packaging Materials, ASTM International, West Conshohocken, PA, 2011



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