

## **Application Note**

### **Abstract**

Printing inks have been used extensively to enhance the visual appearance of packing materials of consumer products. These inks are typically comprised of colorants and pigments, binder systems, solvents, and additives. ASTM International is recognized for developing and delivering international voluntary consensus standards. They provide packaging material suppliers with a standardized test method, ASTM F 1884-04<sup>1</sup> to determine residual solvents remaining in their packaging materials from printing processes utilizing solvent-based printing inks. Test method A, recommends an autosampler to perform the headspace-gas chromatography examination of residual solvents in packaging materials.

This application note will demonstrate the capability of the Teledyne Tekmar Versa and HT3 automated headspace sampler to meet the rigorous demands of ASTM F 1884-04. These scientific instruments can provide packaging material suppliers with quality analysis following ASTM F1884-04 with minimal sample preparation.

### **Introduction**

This application note evaluates ASTM F 1884-04 using both the Versa and HT3 Automated Headspace Analyzers. A 624-phase GC column was used for this study. The FDA recently standardized residual solvent testing on this type of column. Calibrations were evaluated by the addition of a standard solution by itself and with a blank film. A sample of printed film was used to determine the effects that water has on residual solvent recoveries, by testing the dry sample film and the sample film with water added.

ASTM F 1884-04 does not prescribe a carrier gas to use for determining residual solvents in packaging material. The calibration standards were evaluated on both headspace systems with helium and nitrogen.

### **Experimental-Instrument Conditions**

The Versa and the HT3 Automated Headspace Analyzers were connected to a Shimadzu 2010 Plus GC/FID system for this study. Both analyzers were tested with helium and nitrogen, depending on the carrier gas used for each evaluation. Table 1 displays the Versa and HT3 method parameters, while Table 2 displays the Shimadzu GC/FID parameters.

Teledyne Tekmar Automated Headspace Sampler Parameters		
Variable	Versa Value	HT3 Value
Constant Heat Time	N/A	On
GC Cycle Time	27.00 min	27.00 min
Valve Oven Temp	105 °C	105 °C
Transfer Line Temp	110 °C	110 °C
Standby Flow Rate	N/A	100 mL/min
Platen/Sample Temp	90 °C	90°C
Platen Temp Equil Time	0.10 min	0.50 min
Sample Equil Time	20.00 min	20.00 min
Pressurize	13.0 psig	13.0 psig
Pressurize Time	1.00 min	1.00 min
Pressurize Equil Time	0.25 min	0.20 min
Loop Fill Pressure	9.0 psig	9.0 psig
Loop Fill Time	1.00 min	1.00 min
Inject Time	0.50 min	0.50 min

Table 1: Versa and HT3 Headspace Conditions for ASTM F 1884-04

Shimadzu GC/FID Parameters	
Column	Restek Rxi-624Sil MS, 30 m, 0.32 mm ID, 1.8 µm df, Carrier gas – Helium or Nitrogen
Oven Program	40 °C for 2 min, 8 °C/min to 104 °C, 15 °C/min to 164 °C, 30 °C/min to 250 °C, hold for 4 min, run time – 20.87 min
Inlet:	Temperature - 250 °C, Split Ratio - 10:1 Constant Velocity – 40 cm/sec
Detector	Temperature - 250 °C, Sampling rate 40msec
Flows	Makeup (Same as Column) – 30.0 mL/min, Hydrogen – 40.0 mL/min, Air Flow – 400 mL/min

Table 2: Shimadzu 2010Plus GC/FID Parameters

## Standard Preparation

An internal standard solution was prepared by diluting 80 µL of 4-heptanone into 4 L of water. A five-point calibration curve was prepared by diluting 1 µL of a commercially available packaging material residual solvent standard mix into various volumes of the internal standard solution. Table 3 lists these dilutions, the total residual solvent concentrations (volume/volume) and the concentration range of the constituents (µg/mL).

Standard Volume (mL)	Concentration (v/v)	Concentration Range (µg/mL)
1000	0.00004	0.031 to 0.040
500	0.00008	0.062 to 0.081
250	0.00016	0.125 to 0.161
100	0.00040	0.312 to 0.404
50	0.00080	0.623 to 0.807

Table 3: Concentrations for the Five Standard Calibration Points

## **Sample Preparation**

A printable polypropylene film was obtained and prepared, following the ASTM F 1884-04 Section 9.1.1, by heating the film in a vacuum oven at 90 °C for 24 hours. When cooled, the film was stored tightly sealed in aluminum foil.

Two calibration curves were prepared; one using the calibration standards only and one matrix-matched calibration using blank film. The first set consisted of 2.0 mL of each standard and the blank internal standard solution added to separate 22 mL headspace vials. The second set contained strips of the blank film totaling 25 in<sup>2</sup>. 2.0 mL of each standard and the blank internal standard solution was added separately to the film containing vials.

An actual printed film sample was obtained to evaluate the ASTM method. The sample was tested in triplicate by placing 25 in<sup>2</sup> into separate headspace vials. One of the vials was capped without the addition of solvent. The second had 2 mL of water added, and the third had 2 mL of internal standard solution added.

The calibration levels and samples were tested on both headspace systems using helium and nitrogen. Most of the solvents in the standard were confirmed with known standard solvents. Peak numbers were used to label the unconfirmed compounds.

## **Results**

The correlation coefficients ( $r^2$ ) for the peaks were calculated by the external standard method using five-point calibration curves on both automated headspace autosamplers. This data is presented in Table 4.

Since this assay was performed using an FID, with retention time as the only form of confirmation, unknown compounds and coelutions are potentially problematic. 2-Methoxyethanol and isopropyl acetate could not be resolved, but still maintained linearity. An unconfirmed solvent in the standard mix also coeluted with the internal standard, biasing the internal standard calibration data.

Autosampler	Versa				HT3			
Carrier Gas	Helium		Nitrogen		Helium		Nitrogen	
Solvent \ Standard	Clean	Film	Clean	Film	Clean	Film	Clean	Film
Methanol - 1	0.486	0.792	0.993	0.982	0.988	0.974	0.977	0.987
Ethanol - 2	0.993	0.982	0.998	0.992	0.997	0.997	0.995	0.997
Acetone - 3	0.996	0.991	0.999	0.997	0.996	0.996	0.995	0.996
Isopropanol - 4	0.993	0.989	0.999	0.997	0.992	0.995	0.992	0.992
Methyl Acetate - 5	0.998	0.997	1.000	0.997	0.996	0.996	0.996	0.999
n-Propanol - 6	0.993	0.999	0.998	0.996	0.996	0.996	0.994	0.997
Ethyl Acetate - 7	0.999	0.997	0.999	0.996	0.999	0.998	0.996	0.999
2-Butanone - 8	0.995	0.997	0.999	0.997	0.996	0.997	0.9995	0.993
Tetrahydrofuran - 9	0.998	0.999	0.999	0.998	0.998	0.998	0.994	0.999
Cyclohexane - 10	0.993	0.996	0.999	0.998	0.996	0.998	0.996	0.994
Isopropyl Acetate - 11	0.999	0.998	0.997	0.996	1.000	0.999	0.998	0.999
Peak 12	0.991	0.998	0.999	0.995	0.996	0.997	0.996	0.996
Propyl Acetate - 13	0.999	0.998	0.999	0.998	0.9999	0.997	0.996	0.999
4-Methyl-2-pentanone - 14	0.999	0.999	0.999	0.997	0.999	0.998	0.996	0.999
Toluene - 15	1.000	0.998	0.997	0.997	1.000	0.997	0.998	0.999
Butyl Acetate - 16	0.999	0.997	0.998	0.998	0.999	0.997	0.997	0.999
Peak 17	0.997	0.995	0.995	0.996	0.996	0.996	0.894	0.996
Peak 18	0.995	0.998	0.999	0.998	0.996	0.998	0.995	0.998

Table 4: Correlation Coefficient for Residual Solvent Standards Analyzed Following ASTM F1884-04

The lowest detectable limit for all of the residual solvents was at or just below the 1  $\mu$ L in 1000 mL of water standard. This equates to 1 mg/ream of packaging material. Figure 1 is an overlay chromatogram of the 1000 mL, 500 mL and 250 mL residual solvent standard levels.

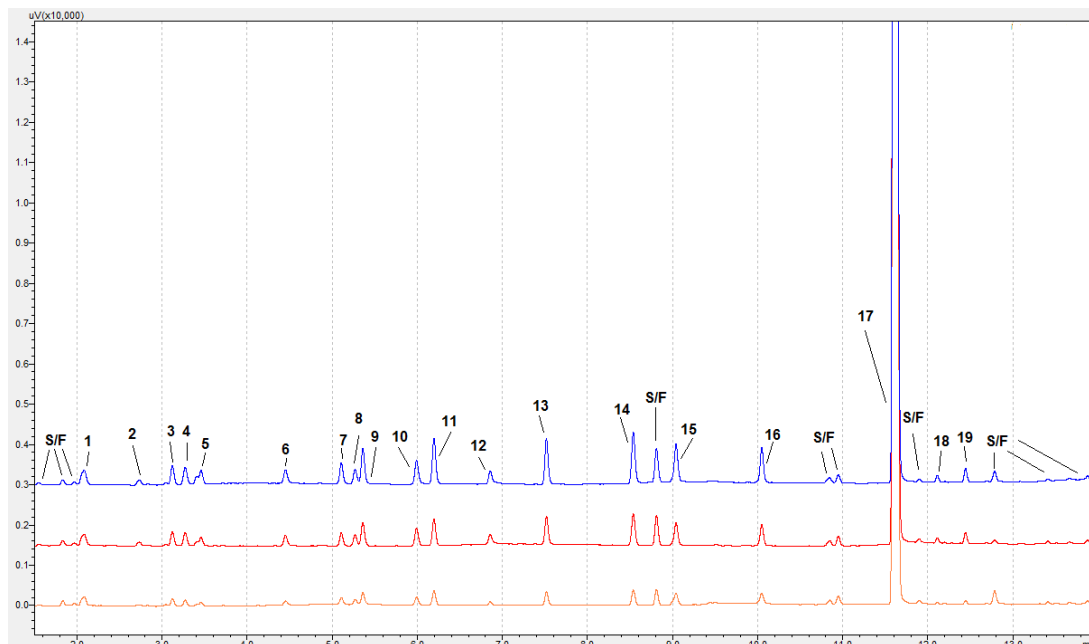


Figure 1: Comparison of the FID Chromatograms of the 1 L Mixed Standard diluted in 1000 mL (Bottom), 500 mL (Middle) and 250 mL (Top) of Internal Standard. The numbers correspond to the compounds in Table 4. The S/F indicates that this peak was part of the system/film background.

The actual printed film sample contained 11 of the solvents identified by the standards and numerous unknown peaks. The addition of water enhanced several of the early eluting residual solvent peaks, while decreasing some of the later eluting residual solvent peaks. Figure 2 shows a comparison of chromatograms of the film sample with and without water and a low-level standard.

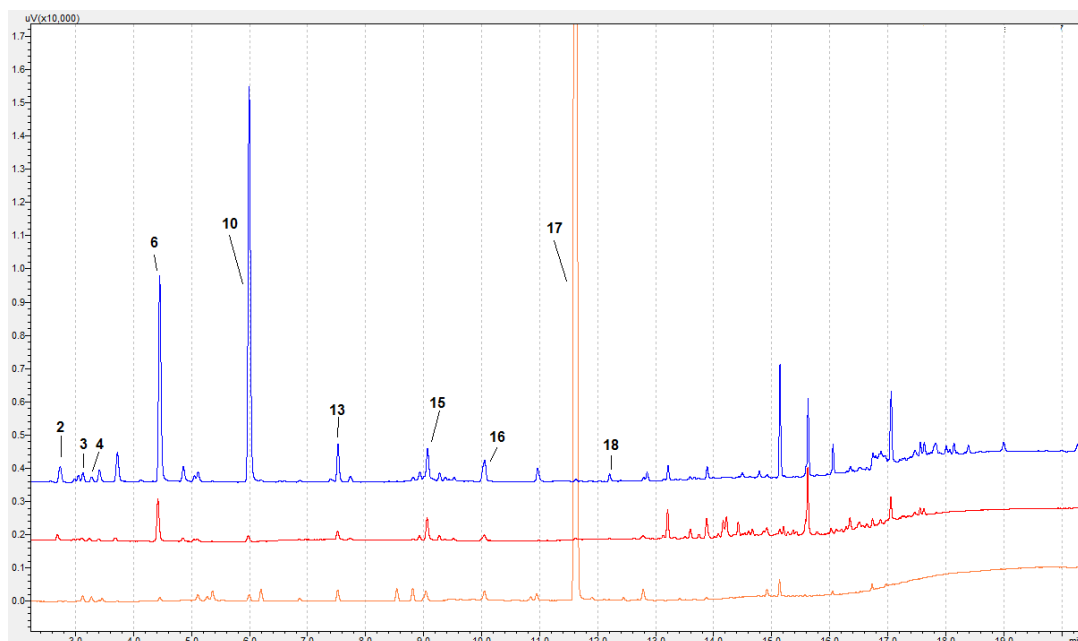


Figure 2: Comparison of the FID Chromatograms of the 1 L Mixed Standard diluted in 1000 mL of Internal Standard (Bottom), the Dry Sample Film (Middle) and Sample Film with Water (Top). The numbers correspond to the compounds in Table 4.

## **Conclusions**

The Teledyne Tekmar Versa and HT3 Automated Headspace Analyzers provide excellent linearity for residual solvent standards used in the analysis of residual solvents in packaging material as defined by ASTM method F 1884-04, Standard Test Methods for Determining Residual Solvents in Packaging Materials. This application note demonstrates detection of less than 1 mg/ream of residual solvents using either helium or nitrogen as supply gases for the headspace GC/FID system. This allows packaging material manufacturers to achieve lower detection levels to meet the ever-increasing regulatory demands, which push for lower and lower levels of residual solvents in their products.

This study indicates an enhancement of some residual solvent peaks with the addition of water using the sample temperature and heating times recommended by the ASTM method, but had a detrimental effect on other residual solvent peaks. Further method optimization may prove useful depending on the particular compounds of interest.

## **References**

1. ASTM Method F1884-04, Standard Test Methods for Determining Residual Solvents in Packaging Materials, ASTM International, West Conshohocken, PA, United States.