APPLICATION NOTE

Gas Chromatography

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Determination of Residual Solvents in Flexible Packaging According to EN 13628-2:2004

Introduction

The reference standards for food contact materials are rapidly evolving in favor of increasing consumer protection.

The Commission Regulation (EC) No. 1935/2004 is the main reference legislation in the European community. This regulation establishes that any materials that come into contact with food must not release chemicals in quantities which could:

- Pose a danger to the health of consumers
- Result in an unacceptable change in the composition of food
- Change the organoleptic properties

Part 2 of the regulation focuses the attention of food contact material producers on the need to operate in terms of quality assurance. The Commission Regulation (EC No. 2023/2006) has made it mandatory to adopt a system of Good Manufacturing Practice (GMP); with GMP referring to the set of actions to ensure a consistently high quality both in production and control process. This requires not only a deep knowledge of the materials used but also of the entire production and control process.

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Flexible Packaging

In case of printed flexible packaging, Commission Regulation (EC) No. 2023/2006 Annex I prohibits the printed side of the materials to come into contact with food. Verification by GMP is also required in order to prevent any "Set-off" (process transfer of substances, from the printed side of a film to the non-printed side, due to the fact that these materials are normally produced in coils) that could ultimately transfer these chemicals onto foods.

The solvents in the inks used to print flexible packaging may represent a possible source of food contamination and therefore must be controlled.

For the determination of residual solvents from printed materials, it is highly recommended that an analytical method such as the official UNI EN 13628-2:2004[1] is followed. If the application of a non-official method is adopted, it requires validation by the laboratory; a task that is often long, complex and expensive.

Experimental Instrumentation

The analysis was performed using a PerkinElmer Clarus® 580 gas chromatograph equipped with a capillary column injector and an FID detector coupled to an automatic TurboMatrix™ 40 Headspace sampler. The capillary column used was a PerkinElmer Velocity-1 (30 m, 0.32 mm, 3 um – P/N N9306329).

Figure 1. Clarus 580 GC and TurboMatrix 40 Headspace sampler.

Analytical Conditions

The instrument conditions are given below:

Table 1. Instrument Conditions.

HS Conditions:	
Thermostatting Temperature	110 °C
Needle Temperature	130 °C
Transfer line Temperature	150 °C
Thermostatting Time	20 min
Pressurization Time	3 min
Injection Time	0.06 min
Pressure	21 psi
Mode	Constant
GC Conditions:	
Carrier Gas	He 1.7 ml/min
Split Ratio	1:20
Injector Temperature	230 °C
Detector Temperature FID	280 °C
Ramp	50 °C for 5 min, ramp to 100 °C @ 5 °C/min, ramp to 250 °C @ 10 °C/min

Standard Preparation

Standards are prepared together as a stock mixture. Using the Total Vaporization Technique[2], different levels of the calibration curves were obtained analyzing increasing amounts of the standard mixture added to the vial prior to analysis.

Table 2. Calibration Amounts.

Solvent	Level 1 mg	Level 2 mg	Level 3 mg	Level 4 mg
Ethanol	0.0065	0.0130	0.0260	0.0390
Isopropanol	0.0064	0.0128	0.0256	0.0384
MEK	0.0066	0.0132	0.2640	0.0396
Ethyl Acetate	0.0074	0.0148	0.0296	0.0444
Isobutanol	0.0065	0.0130	0.0260	0.0390
Methoxy Propanol	0.0075	0.0150	0.0300	0.0450
Ethoxy Propanol	0.0073	0.0146	0.0292	0.0438
Toluene	0.0058	0.0116	0.0232	0.0348
Butyl Acetate	0.0073	0.0146	0.0292	0.0438
m-Xylene	0.0071	0.0142	0.0284	0.0426
o-Xylene	0.0073	0.0146	0.0292	0.0438

Analytical Results

The software runs the standards/sample, calibrates the instrument and automatically produces the report. In the real world, samples can widely vary in concentration, therefore it is paramount that a high level sample does not carryover and contaminate the following samples and give false high results. The inert flow path and post sampling needle purge ensures the lowest possible carryover, producing quality results day after day. Another important area to consider is that the instrument's natural background levels are as low as possible, thus enabling ultra-low level detection when needed for those difficult analyses.

The chromatogram in Fig. 2 was obtained from the standard mixture Level 3 (blue) as compared with a blank (red) that was obtained by the analysis of an empty vial. The blank is clean and void of extraneous peaks, thus simplifying the reporting of data.

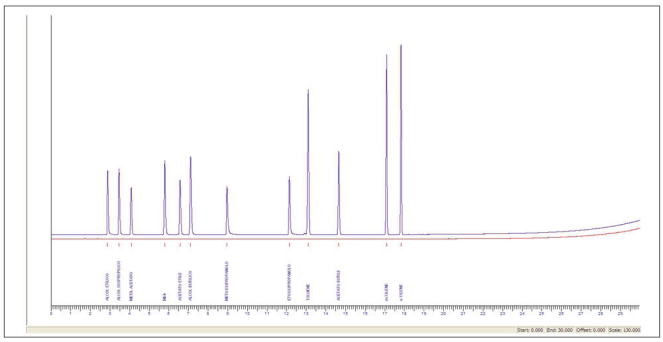

Figure 2. Chromatogram of Level 3 Standard.

Figures 3 and 4 represent the calibration curves for two example analytes: methyl acetate and toluene, both showing excellent linearity of the four calibration levels, thus enabling easy operation for the end user and improved accuracy of the results.

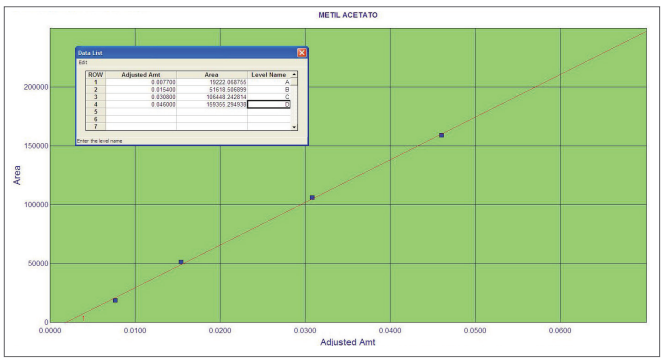

Figure 3. Methyl Acetate Calibration Curve.

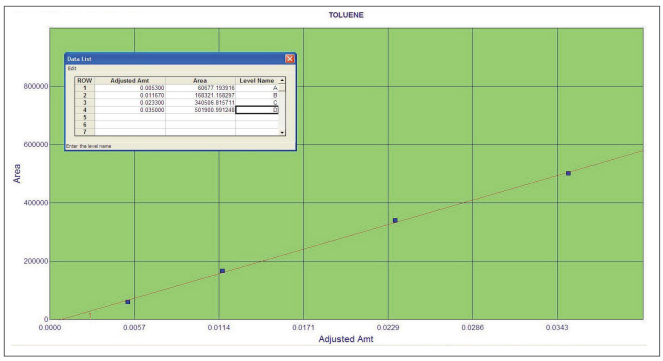

Figure 4. Toluene Calibration Curve.

Example of a Real Sample

A known Area (1 dm2) of the unknown sample is introduced into the vial and analyzed using the same analytical conditions as the standards above. The quantitative result obtained is then reported as the overall amount of solvents per m2 of material.

Figure 5 below shows the analysis of a real sample. For this sample the total content of solvent is found to be equal to 7.20 mg / m2.

Figure 5 also shows there is the presence of several unknown peaks, the one in the center is labeled "incognito." This is investigated further in the next section.

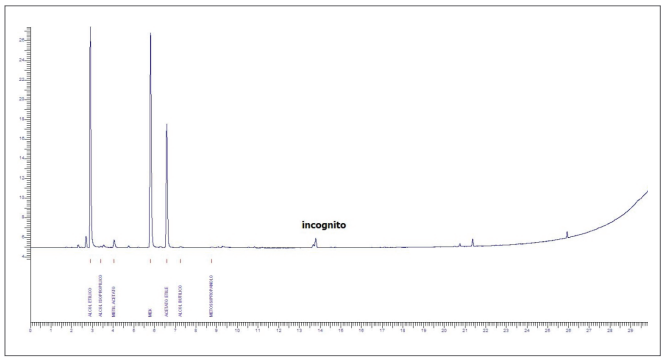

Figure 5. Chromatogram of Real Sample Showing Unknown Peak.

GC/MS

Although the standard UNI EN 13628-2:2004 requires the use of an FID detector, at times it may be necessary to identify an unknown solvent in a real sample, i.e. a solvent not included in the standard mixture. A mass spectrometer (MS) is a powerful detector for the determination of unknowns. We will use the same chromatographic system, vide supra, but coupled to a Clarus 560S MS. Figure 6 shows our target compound labeled as "incognito" at approximately five minutes into the chromatogram.

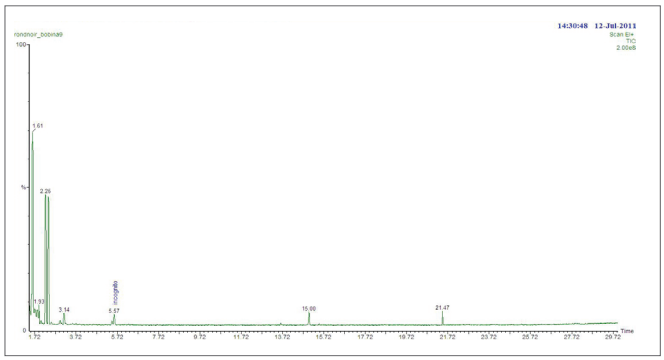

Figure 6. GC/MS Chromatogram of Sample Shown in Figure 5.

A mass spectrum of the unknown peak can easily be obtained by clicking on the peak. To assist in the identification of this unknown, the resulting mass spectrum was searched against a NIST mass spectra library that contains over 200,000 compounds. The NIST library software has selected the following solvent, 3-methyl heptane, as a possiblibility in Figure 7.

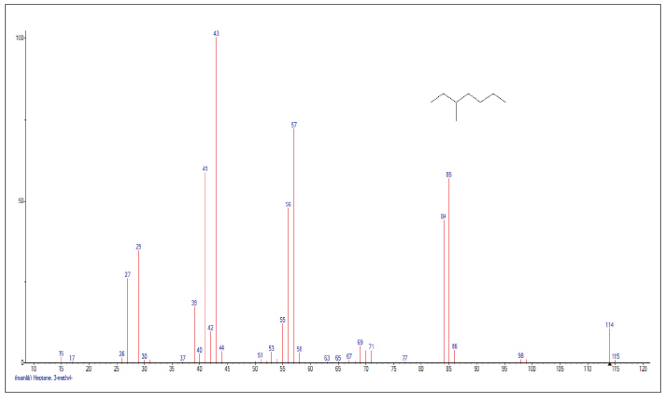

Figure 7. NIST Library Search Match of Peak Labeled "Incognito."

In order to verify and quantify this new solvent, it will be sufficient to have a small quantity of it added to the calibration mixture. Alternatively, in order to have a semi-quantitative result, you can compare the response factor to one of the other solvents inside the standard mixture.

Conclusion

The Clarus 580 GC and TurboMatrix HS system can easily and accurately quantify the amount of residual solvents according to the official method EN13628-2:2004.

References:

1. Uni En 13628-2:2004 Packaging - Flexible Packaging Material - Determination Of Residual Solvents By Static Headspace Gas Chromatography - Part 2: Industrial Methods.
2. Static Headspace-Gas Chromatography Theory and Practice by B. Kolb, L. Ettre, 1997 p. 142 Wiley-VCH.

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