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Food Packaging Compendium

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Importance of DSC Rapid Cooling for the Analysis of Plastic Microwave Food Trays

DSC 8500

Introduction

Differential scanning calorimetry (DSC) is widely used to characterize the thermophysical properties of polymers. DSC can measure important thermoplastic properties including:

- Melting temperature
- Heat of melting
- Percent crystallinity
- Tg or softening
- Crystallization
- Presence of recyclates/regrinds
- Nucleating agents
- Plasticizers
- Polymer blends (presence, composition and compatibility)

Most DSC experiments on polymers are conducted by heating from ambient conditions to above the melting temperature. But, for some thermoplastics, which do exhibit differences during processing, standard heating DSC may not show any significant differences. A more sensitive test, for detecting subtle, but important differences between different batches of a given thermoplastic, is the DSC isothermal crystallization test.

During the manufacture of plastic products, such as bottles, fibers, films, containers, housings, pipes and trays, the thermoplastic is melted, cooled, thermoformed and crystallized. The complete

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study of the behavior of plastics, which are melt-processed, requires having a DSC instrument that is capable of rapid cooling to simulate and fully explore the properties of these materials.

To study the melt-crystallization properties of polymers, several informative DSC tests can be conducted:

• Isothermal crystallization (at a single or multiple temperatures)

• Cooling (at different rates from very fast to normal)

• Reheating after cooling (at different rates)

The successful measurement of these particular tests requires a DSC instrument with a very fast response time. This is because many thermoplastics can crystallize rapidly when cooling from the melt. It is important that the DSC be able to cool and equilibrate as fast as possible in order to detect the complete crystallization exothermic peak. The DSC with the fastest response time is the Pyris™ Power Compensated DSC from PerkinElmer.

Power Compensated DSC

The Pyris Diamond DSC from PerkinElmer uses the Power Compensated approach. This DSC uses two independently controlled, low mass (1 g) sample and reference furnaces. The low mass of the Power Compensated furnaces yields a DSC with low thermal inertia and the fastest response time of any DSC instrument available.

The Power Compensated DSC allows samples to be linearly heated and/or cooled at rates as fast as 500 ˚C/min. This is important when measuring isothermal crystallization times and behaviors of polymers.

In contrast, heat flux DSC instruments employ a large mass furnace. Some DSC devices use a silver block with a mass of 100 g or more. This provides a much higher thermal inertia and a slower inherent DSC response time. The heat flux DSC instruments cannot achieve the very fast cooling and heating provided by the Power Compensated DSC.

Need for Fast Cooling for Microwave Food Trays

The thermophysical properties of plastic microwave food trays were studied using Power Compensated DSC. The microwave food trays must be capable of withstanding large and rapid extremes in temperatures. The trays are generally thermoformed from polyethylene terephthalate (PET) since this polymer is semicrystalline and exhibits the desired end-use properties such as stability, ease of processing and impact resistance. However, to further enhance the thermal stability of the PET polymer for use as microwave food trays, the crystallinity of the polymer is increased by adding nucleating agents. These agents induce a higher level of crystallization of the PET resin during cooling from the melt. Higher concentrations of a given nucleating agent will result in a higher level of crystallinity of the plastic during processing.

DSC cooling experiments are important for the assessment of the effects of these nucleating agents on the crystallization properties of the PET resin. Standard DSC may not reveal obvious differences between two different nucleated resins, whereas these differences will become evident during DSC cooling experiments. For the highly nucleated and fast crystallizing PET microwave food trays, the Power Compensated DSC is necessary for the best in-depth study of the rapid crystallization of the resin.

Experimental

The heat flow properties of two different PET microwave food trays (Tray 1 and Tray 2) were studied, along with the non-nucleated PET precursor resin. The experiment conditions presented in the table were used to study the cooling properties of the PET resins.

The outstanding rapid response of the Power Compensated DSC may be seen in Figure 1. This plot shows the heating and cooling performance of the Power Compensated DSC at heating and cooling rates of 400 and 200 ˚C/min between 200 and 0 ˚C. The DSC was equipped with the refrigerated cooling system, Intracooler II and a helium purge was applied. The actual sample temperature (red) and program temperature (blue) are displayed as a function of time. The sample temperature tracks the program temperature very well even at the ballistic cooling rate of 400 ˚C/min and the use of a refrigerated cooling system, rather than liquid nitrogen. No other DSC instrument can match this level of performance.

| Experimental Conditions	
Instrument	Pyris 1 DSC
Cooling system	Intracooler II
Sample pan	Crimped aluminum standard pan
Sample mass	Approximately 10 mg
Purge gas	Helium
Cooling rate (isothermal crystallization studies)	500 ˚C/min from 300 ˚C
Cooling rates for cool-reheat experiments	400, 300, 100 and 50 ˚C/min between 300 and 0 ˚C
Heating rate for heating experiments	20 ˚C/min
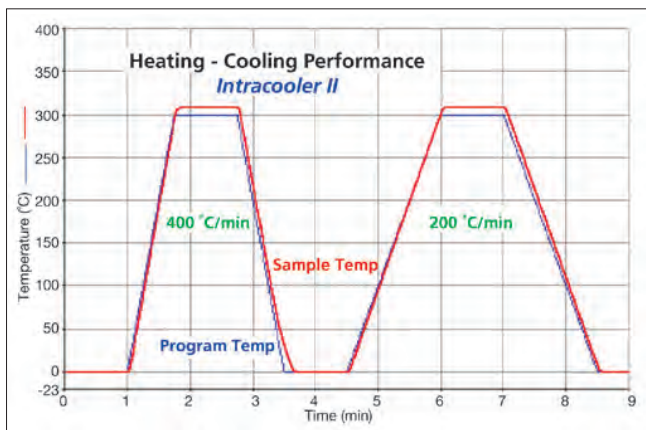
Figure 1. Fast heating and cooling performance of the Power Compensated DSC.

Results

Displayed in Figure 2 are the DSC results obtained on the PET precursor polymer before the nucleating agents are added. The plot shows the first and second heating results. The PET resin was rapidly cooled at a rate of 200 °C/min between the first and second heats. During the first heating, no crystallization exothermic peak is observed reflecting the fact that the polymer has a high level of crystallinity in its as received state. The resin undergoes melting at 261 °C with a heat of melting of 66.7 J/g.

When the PET sample is rapidly cooled down to room temperature and then reheated, a well-defined cold crystallization peak is obtained at 173 °C, which is typical for this polymer. The heat of crystallization is found to be 30.1 J/g. During the second heating segment, the PET undergoes melting at 257 °C with a heat of melting of 33.0 J/g. The net heat of crystallization (melting – cold crystallization) is 2.9 J/g, which is reflective of a nearly amorphous polymer. This demonstrates the ability of the Power Compensated DSC to yield an amorphous polymer directly in the DSC with the application of a fast cooling rate. In comparison, many heat flux DSC instruments require that the sample be physically removed from the hot cell in order to generate an amorphous state by manual quench cooling.

To make the PET resin suitable for the manufacture of the microwave food trays, nucleating agents are added to the polymer. The presence of these nucleating additives drastically changes the morphology of the polymer allowing it to crystallize much more rapidly. Displayed in Figure 3 are the DSC results obtained from the PET sample extracted from a microwave food tray (Tray 1). The sample was heated through its melt temperature and then cooled at a rate of 200 °C/min back to room temperature.

When the cooled food tray is reheated, the cold crystallization exothermic peak occurs at a much lower temperature (134 °C) and is much smaller than that of the PET chip. These major differences are reflective of the changes caused by the presence of the nucleating agents.
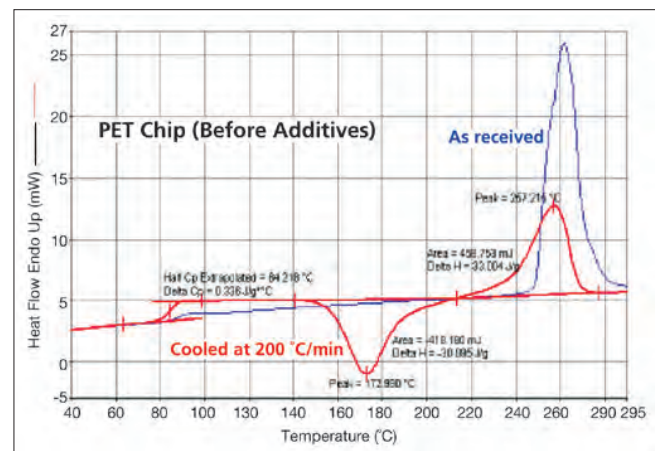

Figure 2. DSC results for PET chip (before additives) showing as received resin and resin after being melted and cooled at 200 °C/min.
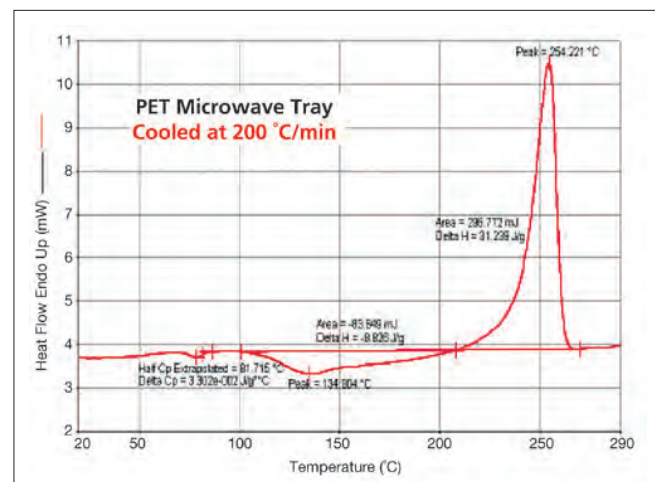

Figure 3. DSC heating results for PET microwave tray resin after cooling from the melt at 200 °C/min.

For quality assurance purposes, the manufacturers of the plastic microwave food trays like to induce a more well-defined cold crystallization peak for the nucleating resin. This provides a sensitive indicator as to the effectiveness of the nucleating agents based on the peak shape, magnitude and temperature. However, this requires ballistically cooling the PET resin from the melt to develop an amorphous material. Displayed in Figure 4 are the DSC results obtained on the food tray PET resin when cooled at the very fast rate of 400 °C/min. It may be seen that a well-defined cold crystallization peak is observed at 131 °C. This is possible only with the cooling capability provided by the Power Compensated DSC for such heavily nucleated polymers.

In contrast, most heat flux DSC units can heat at a maximum rate of only 100 ˚C/min. This is not fast enough to avoid crystallization for fast crystallizing polymers such as nylon or nucleated PET. Shown in Figure 5 are the DSC results generated for the PET tray resin when cooled from the melt at a rate of 100 ˚C/min. The cold crystallization peak is just barely observed, as these results demonstrate. Much valuable characterization information on the effects of the nucleating agents is lost when required to use the slower heating rates necessitated with heat flux DSC. The Pyris Power Compensated DSC provides the ability to cool over an extremely wide range of rates for the most comprehensive characterization information.
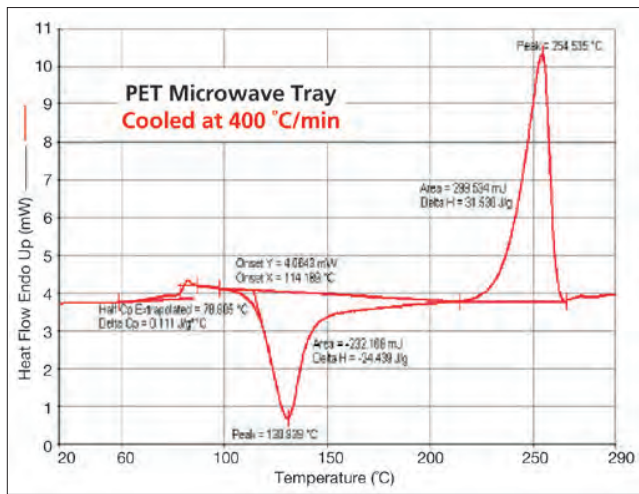

Figure 6. Overlay of DSC results on PET tray after cooling at rates of 400, 200, 100 and 50 ˚C/min.

This demonstrates the great importance of the need for the very fast cooling to get a complete picture of the crystallizable nature of this PET resin material.

Additional supplementary characterization information can be obtained by performing isothermal crystallization measurements on the nucleated PET resins. With this test, a sample of polymer is heated up through its melt and held under isothermal conditions for several minutes to destroy the existing crystalline structure. The sample is then ballistically cooled to a temperature below the melting temperature to allow the polymer to crystallize under tightly controlled conditions. DSC monitors the resulting crystallization exothermic peak as a function of time.

Figure 4. DSC results for PET tray resin after cooling at 400 ˚C/min.

The isothermal crystallization test provides valuable information on polymers including:

- Average molecular weight
- Molecular weight distribution
- Presence of recyclates/regrinds
- Plasticizers
- Nucleating agents, pigments or other additives
- Copolymers
- Injection molding lubricants or flow enhancers

Because of its very fast response time and ability to cool quickly, the Power Compensated is ideally suited for the measurement of the isothermal crystallization of polymers.
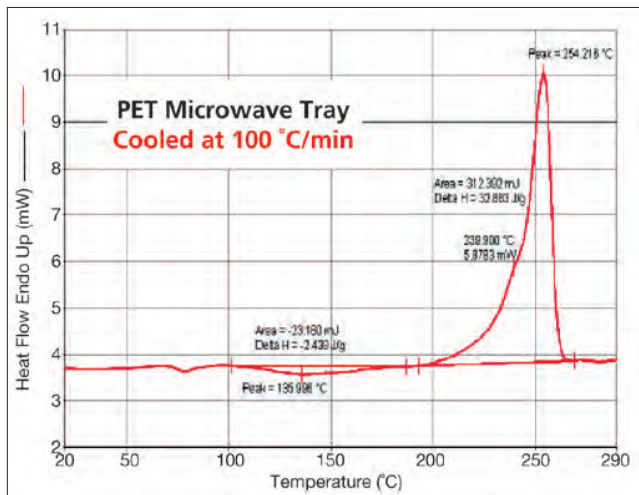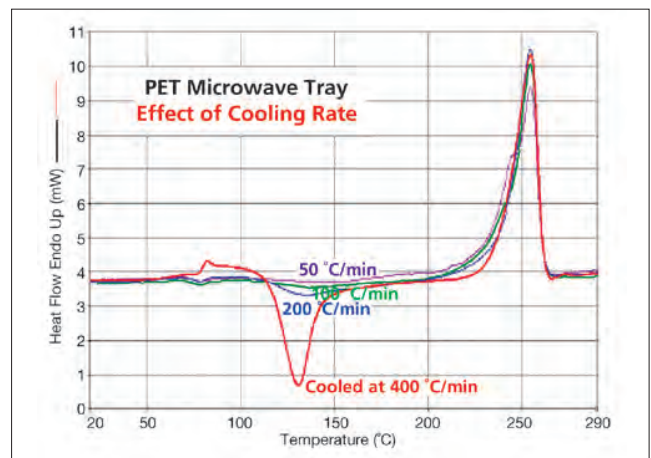

Figure 5. DSC results for PET tray resin after cooling at 100 ˚C/min.

The effects of the applied cooling rate for the PET tray resins may be seen in Figure 6. This shows a direct overlay of the heating curves obtained after cooling from the melt at 400, 200, 100 and 50 ˚C/min. Due to the heavy nucleation of the PET resin, there is a major change in the results when the cooling is slowed from the very fast 400 ˚C/min to 200 ˚C/min.

Displayed in Figure 7 are the isothermal crystallization results generated for Tray 1. The sample was cooled from 300 ˚C to the target isothermal temperatures at a cooling rate of 500 ˚C/min. The crystallization behavior was monitored at temperatures of 230, 225, 220, 215 and 210 ˚C. At the temperature of 210 ˚C, the resin reached its maximum rate of crystallization in about 30 seconds. This demonstrates the ultra fast responsiveness of the Power Compensated DSC.
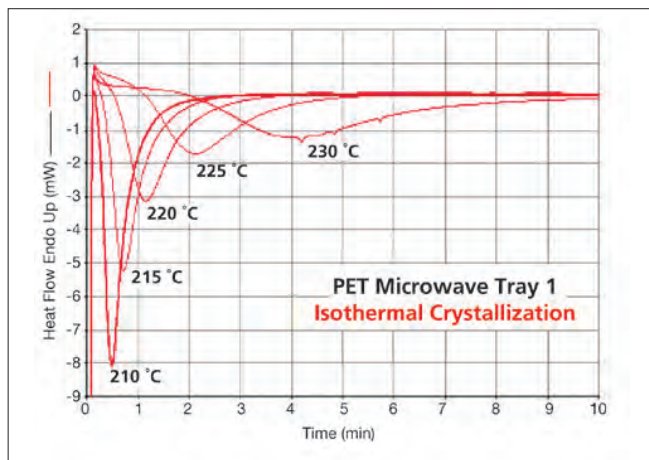
Figure 7. Isothermal crystallization results for PET Tray 1.

Figure 9. Overlay of DSC isothermal crystallization results at 220 ˚C for PET microwave trays 1 and 2.

Another PET microwave tray (Tray 2) was analyzed using the DSC isothermal crystallization test and these results are displayed in Figure 8. This resin was clearly different in its resulting crystallization behavior as compared to the Tray 1 sample in that it took longer for it to crystallize under identical conditions. This indicates that the Tray 1 resin was more heavily loaded with nucleating agents as compared to Tray 2.

The differences between the crystallization behaviors of the Tray 1 and Tray 2 PET resins is more evident in an overlay (Figure 9) of the isothermal crystallization behaviors at 220 ˚C. Tray 1 clearly crystallizes more rapidly as compared to Tray 2.
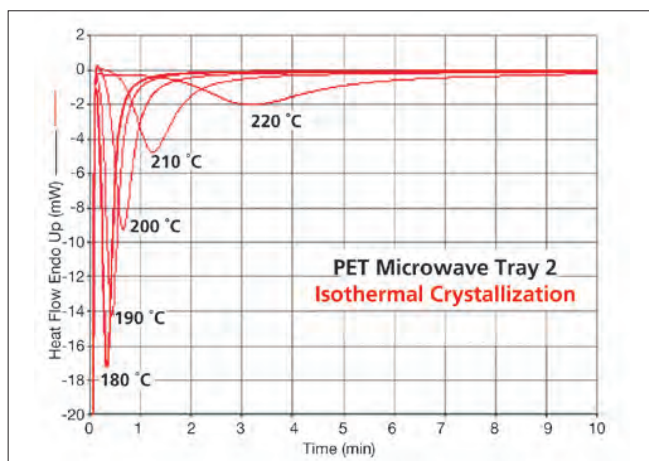
These differences would not be apparent with standard heating DSC, but are very noticeable with the DSC isothermal crystallization measurements. The measurement of the very fast crystallization responses of these nucleated resins requires a DSC with an ultra-fast response time, and this is the Power Compensated DSC.

Summary

Most plastic processes require that the polymer be melted and cooled during the thermoforming stage. The most comprehensive characterization of plastics undergoing melt processing necessitates that the material be studied under both heating and cooling conditions. The cooling analysis allows the effects of nucleating and plasticizing agents to be more fully quantified. Oftentimes thermoplastics may not exhibit any significant differences by standard heating DSC. However, when cooling studies are performed, significant differences, due to the presence of nucleating agents or flow enhancers, may become apparent. Such DSC data is extremely valuable for quality assurance or for process control purposes. The successful performance of cooling studies requires a DSC with a fast response time so that the sample can be analyzed at ballistic cooling rates. The DSC instrument with the fastest response time and the ability to heat and cool ballistically (up to 500 ˚C/min) is the Diamond Power Compensated DSC from PerkinElmer.

Figure 8. Isothermal crystallization results for PET Tray 2.

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Quantitation of BADGE: An Epoxyphenol-based Food Can Coating in Canned Tuna Extracts Using UHPLC-TOF

Introduction

Metal cans are often coated with a resin barrier to prevent contact between food and the can. Components from these coatings can migrate into the food affecting its safety and quality. Polyepoxyphenol coatings on the inside of cans based on bisphenol A epoxy resins can release the epoxy monomer bisphenol A diglycidyl ether (BADGE) into food (1,2). Bisphenol A and its derivatives are considered as endocrine disruptors (3). Both Europe and the U.S. have set regulations on the limit of BADGE migration into food at 1 mg/Kg. Using the quantitative capability of the AxION® 2 Time-of-Flight (TOF) mass spectrometer, we were able to set up a calibration curve and quantitate BADGE in a tuna extract. In addition, the high mass accuracy capability of the TOF along with the proprietary AxION EC ID software, allowed us to identify an unknown impurity cyclo-di-BADGE without having an authentic standard of this compound.

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Experimental

Sample preparation:

10 g of tuna was transferred into a 50 mL tube and spiked with BADGE standard (200 ng). To this, 10 mL of acetonitrile was added and shaken. Salts (1 g sodium chloride, 4 g magnesium sulfate, 1 g trisodium citrate, 0.5 g disodium hydrogen citrate) were added to the sample, which was shaken and centrifuged (3700 rpm) for 5 min. The supernatant (1 mL) was transferred to a dispersive SPE micro-centrifuge tube containing primary and secondary amine (PSA, 25 mg) and magnesium sulfate (150 mg) and C18 (25 mg). Sample was vortexed and centrifuged at 3000 rpm for 5 min. The supernatant was carefully removed, pH adjusted with 5 µL of 5% formic acid and used for analysis.

LC conditions:

Pump: PerkinElmer® Flexar™ FX-15 pump
Flow: 0.4 mL/min
Mobile phase A: Water containing 0.1% formic acid
Mobile phase B: Acetonitrile containing 0.1% formic acid
Gradient conditions: 70% A/30% B to 10%A/90%B in
    5 mins in a linear gradient
Injection volume: 5 µL in partial fill mode.
Column used: PerkinElmer Brownlee™ SPP C-18, 2x50 mm,
    2.7 µm, 25 °C

MS conditions:

Mass spectrometer: PerkinElmer AxION 2 TOF MS
Ionization source: PerkinElmer Ultraspray™ 2
    (Dual ESI source)
Ionization mode: Positive
m/z range: 90-700
Capillary exit voltage: 100 V
Internal calibration was performed using m/z 118.08625
    and 622.02896 as lock mass ions.

Results

The mass spectrum showed BADGE was predominantly observed as the [M+NH4$^+$] ion (Figure 1). We were easily able to detect as low as 2 ppb concentration of BADGE (S/N = 52) standard. Excellent linearity (r^2 > 0.995) was observed for the calibration curve generated between 2 to 500 ng/mL (Figure 2) of BADGE standard. The intra assay %RSD for triplicate injections at the 2 ppb concentration was <10%. Tuna extracts spiked with 20 ng/mL of BADGE standard were easily detected by UHPLC-TOF (Figure 3). A 94% recovery of BADGE was observed in the spiked tuna extracts suggesting little or no ion suppression of the analyte in the extracts.

We tried to identify two unknown peaks with same exact masses eluting between 2.5 to 3 mins (Figure 4) using the exact mass capability of the AxION 2 TOF. The accurate mass and isotope profile was entered into the AxION EC ID calculator of the software. The software uses this
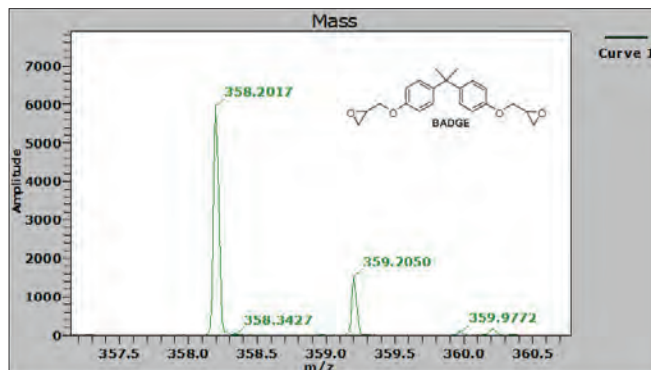

Figure 1. Mass spectrum shows [M+NH4]+ as the predominant peak for BADGE. Expected accurate mass of BADGE is 358.2013 (mass error < 2 ppm).
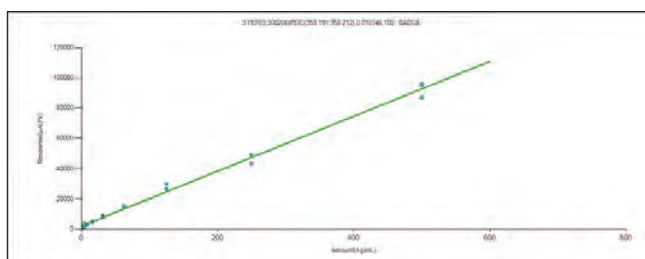

Figure 2. Shows calibration curve for BADGE analysis (r2 0.995).
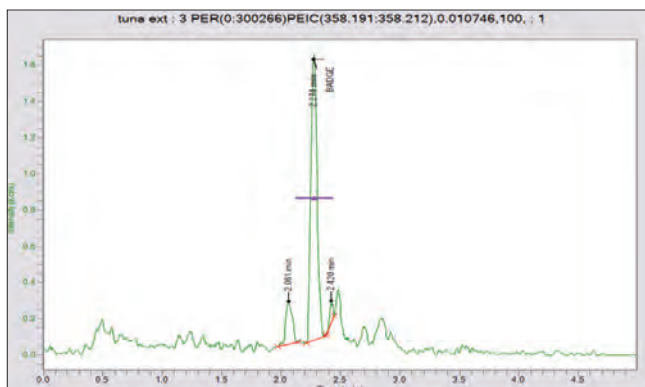

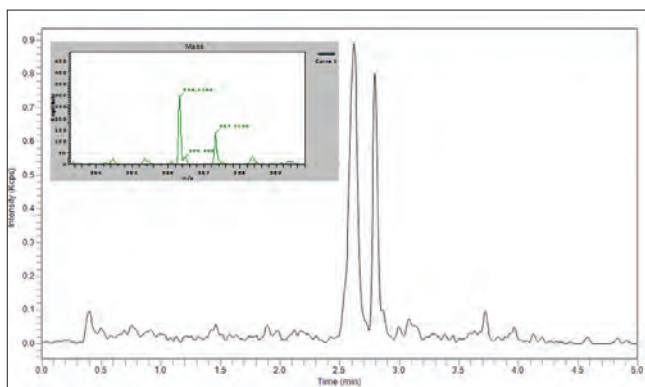Figure 3. Analysis of BADGE by UHPLC-TOF in tuna extracts spiked at 0.2 mg/Kg .

Figure 4. Unknown peaks in tuna extracts with the same m/z 586.3164 eluting at 2.6 and 2.8 min. Inset shows mass spectrum.
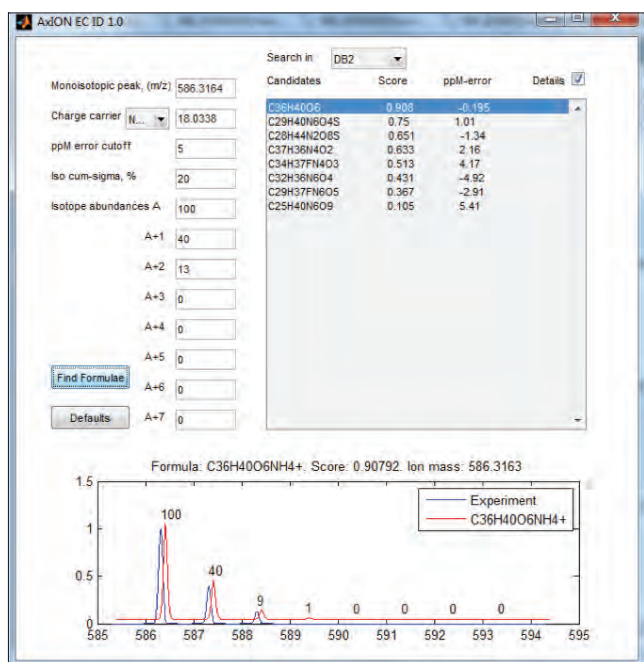
Figure 5. AxION EC ID software gave the elemental composition C36H40O6 as the top choice for the unknown mass 586.3164.

information and searches against the PubChem database and identifies potential molecular formulae matches. The first potential match with the highest score was identified with the elemental composition $C_{36}H_{40}O_6$ within a mass error of < 1 ppm (Figure 5). The software also provides a list of possible structures for the given elemental composition and one of the listed structures that related to bisphenol family of compounds was the BADGE.BPA linear structure (Figure 6a). However, an isomeric structure cyclo-di-BADGE compound described in the literature could also be possible (Figure 6b). Based on the fragmentation pattern and the retention time matching with an authentic standard, the presence of linear versus cyclo structure could be further confirmed.

Conclusion

Using the high sensitivity AxION 2 TOF, we were able to detect 0.2 mg/Kg of BADGE in tuna extract well below the regulation limits set at 1 mg/Kg. Using the high mass accuracy capability of AxION 2 TOF along with the AxION EC ID software, we were able to detect unknown peaks and match them to the isomers BADGE.BPA linear structure/cyclo-di-BADGE structures without the use of authentic standards.

References

1. Cao XL, Dufresne G, Clement G, Bélisle S, Robichaud A, Beraldin F. JAOAC Int 92 (2009) 1780.

2. Míguez J, Herrero C, Quintás I, Rodríguez C, Gigosos PG, Mariz OC. Food Chem. 135 (2012) 1310.

3. Schug T, Janesick A, Blumberg B, Heindel J Steroid Biochem Mol Biol. 127 (2011) 204.
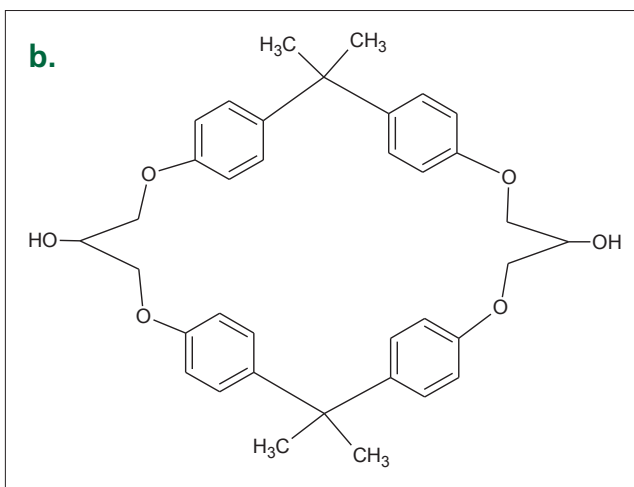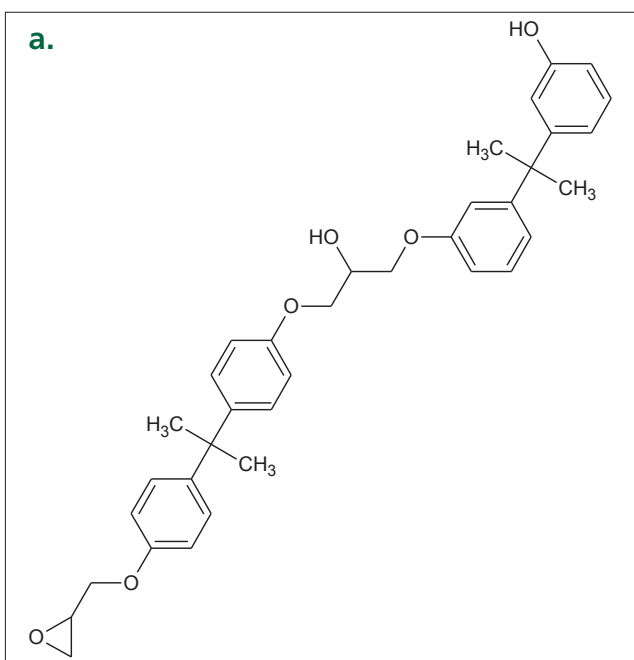
Figure 6 a and b. Structures that fit the elemental composition C36H40O6.
 a. Linear BADGE.BPA
 b. Cyclo-di-BADGE

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Gas Chromatography/
Mass Spectrometry

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Analysis of Food-Packaging Film by Headspace-GC/MS

Introduction

Food-packaging material is typically manu-factured as a thin film and coated with inks which usually contain multiple, harmful, vol-atile organics. Therefore, they must be care-fully monitored and quantitated to ensure that the amounts are limited.

Traditionally, the test for solvent materials in food-packaging film was performed using a technique of heating a square meter of the film material inside a mason jar. This jar is then opened and tested (by smell) for volatile organic compounds. Later, this test was expanded to extract a headspace sample out of the mason jar by syringe and then injected into a gas chromatograph (GC) for quantitative analysis. This produced significantly better results and provided laboratories with a quantitative number. This process is still very time-consuming and labor inten-sive as a result of the number of manual steps involved. The manual process of cutting food packaging, placing it in a mason jar, heating the jar, and manually collecting a sample for GC analysis dramatically limits the number of samples that can be analyzed each day. The technique demonstrated here will greatly improve the efficiency and throughput of this analysis.

This analysis can be completely automated using a PerkinElmer® TurboMatrix™ Headspace (HS) sampler with the Clarus® Gas Chromatograph/Mass Spectrometer (GC/MS). This system passed all the requirements for food-packaging analysis.

Experimental

The first food packaging film used for this experiment was from a typical package of cookies. This film was cut into squares: 325 cm² pieces. The typical volume used in a mason jar is a square meter but this volume is not required for the headspace sampler. The desired sensitivity can be reached with significantly lower quantities. The second packaging material tested was obtained from a shopping bag that you would typically find at a department store.

The 325 cm² pieces of film were added directly to a 22-mL headspace vial. The vial was then sealed with silicone/PTFE septa (PerkinElmer Part No. B0104241). In addition, a calibration standard was prepared to get an estimate of the expected concentration of the typical solvents. This standard was prepared by adding 4.7 µg of each solvent in a 22-mL headspace vial (Table 2).

The instrument used for this analysis was a TurboMatrix HS 40 Headspace Trap sampler run in headspace-only mode. This bypassed the trapping capability. If extra sensitivity is required, the trap option could be used for up to 100 times lower detection levels. The shaker option on the headspace was utilized for a faster equilibration of the solid film material. The headspace was controlled using the TurboMatrix remote control software and was coupled to the Clarus GC/MS. The Clarus GC was equipped with a programmable split/splitless (PSS) injector and programmable pneumatic control (PPC). Deactivated fused silica (0.32 mm) transfer line connects the TurboMatrix HS 40 Trap to the Clarus GC. The GC column was directly connected to this transfer line using a universal union (PerkinElmer Part No. N9302149). The Clarus MS was controlled via TurboMass™ 5.1 GC/MS software and operated in electron ionization (EI) mode.

Results

The TurboMatrix HS 40 Headspace sampler was successful in analyzing the solvents in food packaging. Six solvents were identified: 1 – MIBK (Methyl Isobutyl Ketone), 2 – NPAC (n-Propyl Acetate), 3 – ETAC (Ethyl Acetate), 4 – Propanol, 5 – ETOH (Ethanol) and 6 – Heptane (Figures 2 and 3). Ethanol and Propanol were the largest responders and over-loaded the system. However, the requirements of the testing were to only get semi-quantitative information. Therefore, the overloading was accepted. All components were positively identified using a NIST® library database.

The cookie package/wrapper had approximately 0.22 mg/m² of solvents found. However, Propanol was very significant, making up the large majority of the total solvents identified. The cookie wrapper also had a lower level of interferences from outside sources (Figure 1). The shopping bag (purple) had approximately 0.32 mg/m² of total solvent material (of the six solvents tested) – Table 2. This represented a very good response of all six solvents. In addition, there is a significant amount of other materials found in the food film. This is evident in the chromatogram shown on Figure 2. Because of the ability of the MS to extract only the required ion from the component of interest, this interference was not an issue.

The headspace system enabled the method to be set up and run unattended with no sample preparation. This eliminated the need for mason jars and operator attention. In addition, the system showed a significant amount of sensitivity for the required components, demonstrating the ease of setup methodologies of many types of food packaging at many different levels.
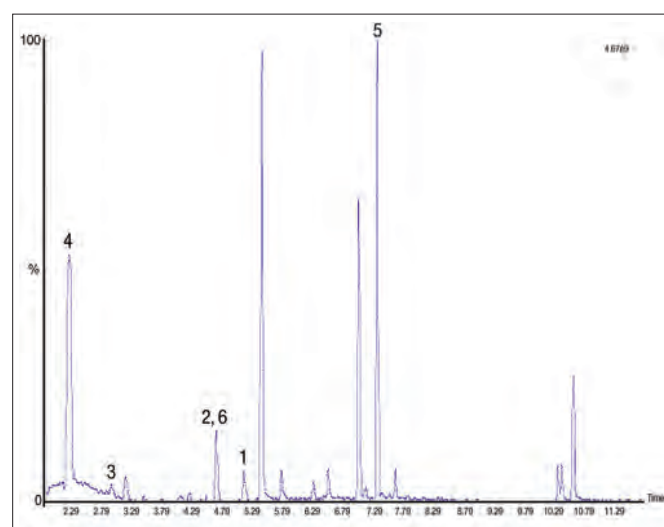

Figure 1. Chromatogram of cookie wrapper.

The significant response of the volatile solvent material by this heated headspace technique would allow for a flame ionization detector (FID) to be used as a substitute for the MS detector. While the MS gives a positive identification as well as selectivity, the FID can be used in a majority of standard QA/QC environments.

Conclusions

The PerkinElmer TurboMatrix Headspace Trap with the Clarus GC/MS meets all the requirements for food-packaging analysis. The main requirement for this application is fast, easy and quantitative solvent determination. Using the setup demonstrated here, the sample is placed into a vial and placed in the autosampler tray of the headspace. Then the automated analysis is completed without operator attention. In addition, the headspace's overlapping thermostatting allows up to 12 samples to be processed simultaneously, thus allowing 50-75 analyses per day.
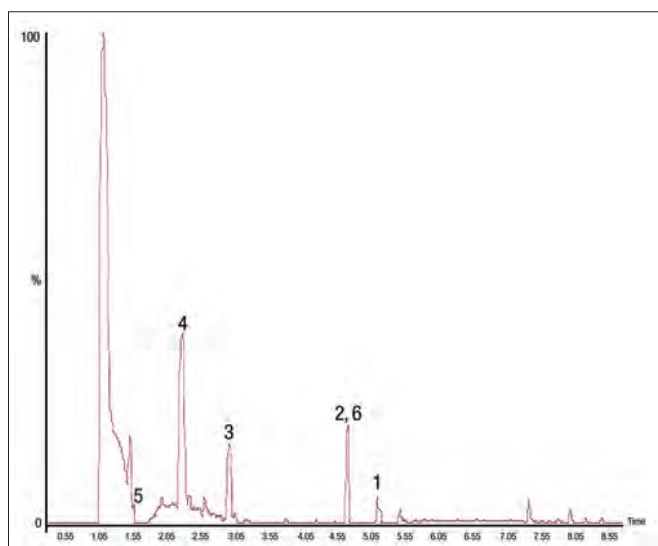

Figure 2. Chromatogram of shopping-bag film – with expanded ethanol chromatogram.

Table 1. Instrument Parameters.

GC		Headspace Trap	
Injector Temp:	120 ˚C	Needle Temp:	85 ˚C
Oven Program – Initial Temp:	35 ˚C	Transfer-Line Temp:	85 ˚C
Initial Time:	Hold 2 mins	Oven Temp:	80 ˚C
Ramp:	10 ˚C/min	Shaker:	On
Final Temp:	200 ˚C	High-Pressure Injection:	On
Final Time:	Hold 5 mins	Trap Option:	Off
Column:	Elite 200*	Constant Mode:	On
MS	**SIFI Conditions EI**	Thermostatting Time:	30 min
Mass Range:	30-300 amu	Pressurization Time:	1 min
Scan Time:	0.41 sec	Withdrawal Time:	1 min
InterScan Delay:	0.01 sec	Injection Pressure:	20 psi
Transfer-Line Temp:	200 ˚C	Column Pressure:	25 psi
Electron Energy:	70 eV	Injection Time:	0.08 min
Detector Voltage:	400 V	GC Cycle Time:	35 min
Threshold:	0	Carrier Gas:	Helium at 99.999%
*PerkinElmer Part No. – N9316630 (30 m, 0.32 mm, 1 μ).			

Table 2. Semi-Quantitative Results.

Sample: Standard

Peak #	Solvent Name	RT (min)	Area	µg in Vial
1	MIBK	5.104	15165890	4.7
2	NPAC	4.663	19381950	4.7
3	ETAC	2.932	14047220	4.7
4	Propanol	2.256	16693610	4.7
5	ETOH	1.518	31902978	4.7
6	Heptane	4.69	12375010	4.7

Sample: Purple Shopping Bag 300 cm²

Peak #	Solvent Name	RT (min)	Area	µg in Vial	mg/m²
1	MIBK	5.12	162823	0.05	0.00
2	NPAC	4.665	4010297	0.97	0.03
3	ETAC	2.927	4236236	1.42	0.04
4	Propanol	2.244	19894030	5.6	0.17
5	ETOH	1.526	15599010	2.3	0.07
6	Heptane	4.686	14941	0.01	0.00
Total					**0.32**

Sample: Cookie Wrapper 325 cm²

Peak #	Solvent Name	RT (min)	Area	µg in Vial	mg/m²
1	MIBK	5.112	30410	0.01	0.00
2	NPAC	4.664	2320430	0.56	0.02
3	ETAC	2.947	472144	0.16	0.00
4	Propanol	2.243	21689300	6.11	0.19
5	ETOH	1.533	2630198	0.39	0.01
6	Heptane	4.692	211345	0.08	0.00
Total					**0.22**

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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.

For the Better

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.
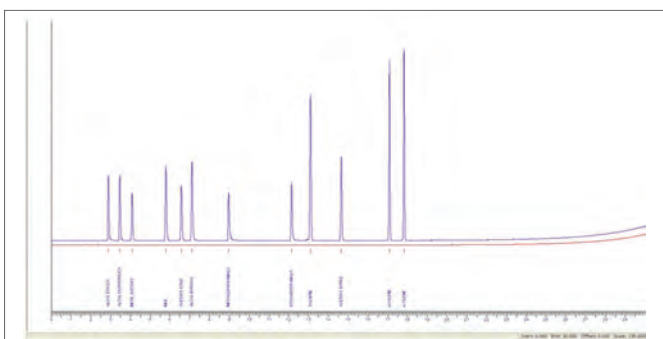

Figure 2. Chromatogram of Level 3 Standard.

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.
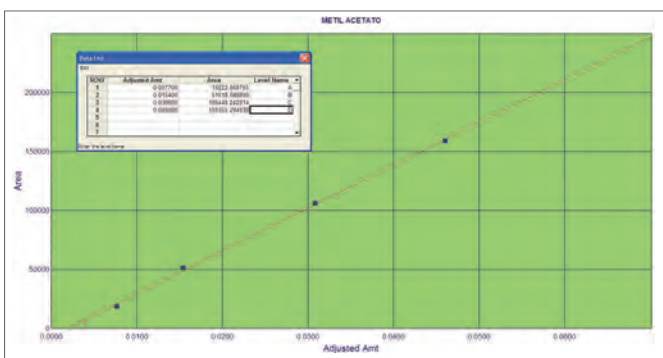

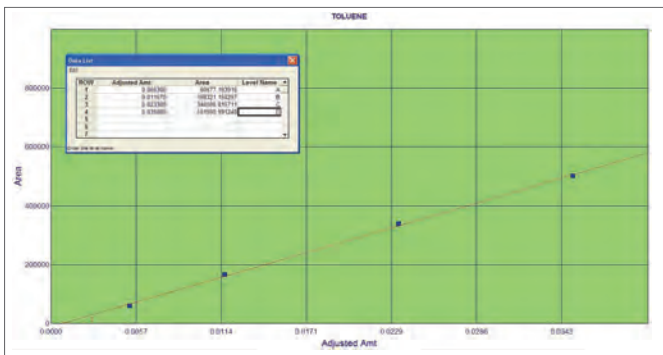*Figure 3.* Methyl Acetate Calibration Curve.

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.
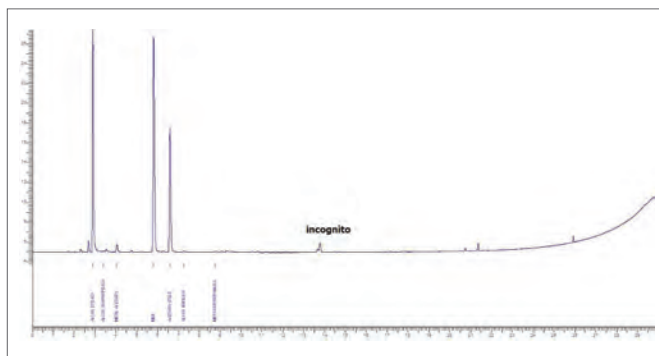

Figure 5. Chromatogram of Real Sample Showing Unknown Peak.

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.
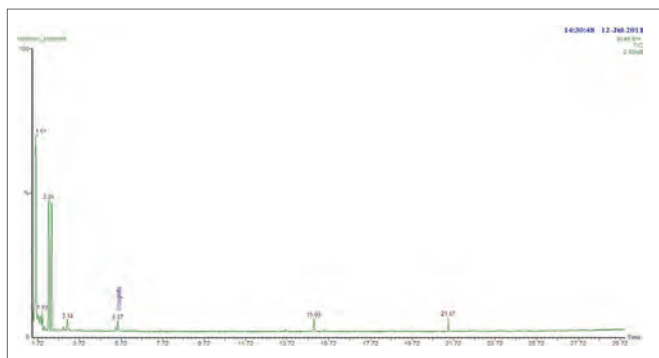

Figure 6. GC/MS Chromatogram of Sample Shown in Figure 5.

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.
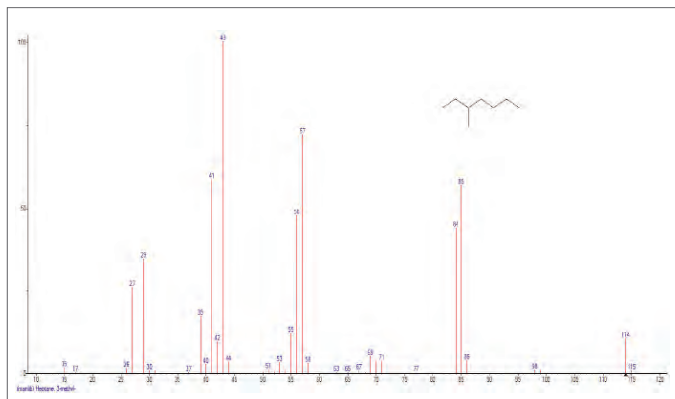

Figure 7. NIST Library Search Match of Peak Labeled "Incognito."

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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