

Determination of polymer additives and migration products prevalent in food packaging material

Using the Agilent 1260 Infinity SFC System with the Agilent 6130 Single Quadrupole LC/MS System

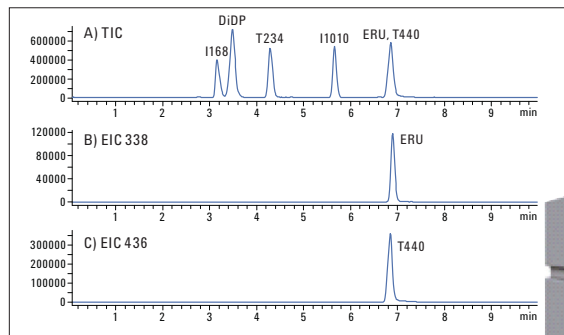
Application Note

Consumer Product, Food Safety

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Abstract

According to EU directive 2002/72, materials that come into contact with food products should be tested for possible leachables. Supercritical fluid chromatography (SFC) is a complimentary separation technique to HPLC for the analysis and potential detection of polymer additives that might be released out of packaging material. This Application Note demonstrates the applicability of SFC for typical polymer additives using the Agilent 1260 Infinity Analytical SFC System in combination with an Agilent 6130 Single Quadrupole LC/MS System.



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Introduction

According to EU Directive 2002/72/EC, materials that are intended to come into contact with food products should be tested for potential leach out of the plastic material¹. This directive contains a list of additives, along with global and specific migration limits (SMLs). The list contains volatiles, such as acetic acid and monomers (for example, butadiene), semivolatiles (phenols) and nonvolatile components. An additional directive describes four simulants that can be used for migration testing².

Specific migration of solutes is determined by analyzing the simulants. Obviously, different analytical methods are used for these tests. While the volatile solutes can be analyzed by gas chromatography, for example, in combination with headspace sampling, semivolatiles and nonvolatiles require other analytical methods. For some compounds, HPLC can be used. Several additives, however, are quite apolar and have a high molecular weight (> 300 Da). For the analysis of this class of solutes, supercritical fluid chromatography (SFC) is an excellent technique. Since several additives do not contain a chromophore, MS detection is often required.

In this Application Note, the analysis of some typical polymer additives by SFC/MS is demonstrated. Additionally, the potential of the SFC/MS approach is illustrated for the analysis of unknown (non-UV absorbing) solutes that leached out of a polymer intended to be used as food packaging. Based on the SFC/MS analysis, the material was rejected.

Experimental

Solutions and sample preparation

A mixture containing six typical polymer additives, belonging to different

classes, was prepared at a concentration of 50 µg/mL in methanol. The solutes are listed in Table 1, with their abbreviation, molecular formula, and molecular weight.

The SFC/MS method was applied to the analysis of solutes released from a polymer intended to be used for food packaging. Approximately 1.5 g of the polymer was weighed and placed in a 20 mL vial; 10 mL of a 85/15 water/ethanol solution was added to the vial, and the vial was placed in an oven at 40 °C for 24 hours. After removal of the polymer, the extract was analyzed as such.

Name	Abbrev.	Formula	MW (g/mol)	Ion APCI (+)	Ion mass	Ion APCI (-)	Ion mass
Diisodecyl Phthalate	DiDP	C ₂₈ H ₄₆ O ₄	446.66	M+H	447	N/A	N/A
Irganox 1010	I1010	C ₇₃ H ₁₀₈ O ₁₂	1177.67	M+H+NH ₃	1195	M-H	1176
Tinuvin 440	T440	C ₂₅ H ₄₅ N ₃ O ₃	435.64	M+H	436	M-H	434
Tinuvin 234	T234	C ₃₀ H ₂₉ N ₃ O	447.63	M+H	448	M-H	446
Erucamide	ERU	C ₂₂ H ₄₃ NO	337.58	M+H	338	N/A	N/A
Irgafos 168	I168	C ₄₂ H ₆₃ O ₃ P	646.90	M+H	647	N/A	N/A

Table 1
List of compounds in test mixture.

Experimental

The analyses were performed on an Agilent 1260 Infinity Analytical SFC System coupled to an Agilent 6130 Single Quadrupole LC/MS System. The system configuration is listed in Table 2. Details on the coupling of the Agilent 1260 Infinity SFC to MS systems can be found in another Agilent publication³.

Two normal phase columns of the same stationary phase (Agilent ZORBAX RX-SIL: 4.6 × 250 mm, 5 μm) were coupled together to give a total column length of 50 cm. The modifier used was methanol with 20 mM ammonium formate. Detection was done in positive mode using an APCI source. The experimental conditions are summarized in Table 3.

Agilent 1260 Infinity SFC/MS solution	Part number
1260 Infinity Analytical SFC System consisting of:	G4309A
• 1260 Infinity Degasser	
• Aurora Fusion A5 module	
• 1260 Infinity SFC Autosampler	
• 1260 Infinity SFC Binary Pump	
• 1290 Infinity Thermostatted Column Compartment	
• 1260 Infinity Diode Array Detector VL Plus	
External heating device	Caloratherm heater
1260 Infinity Micro Degasser	G1379A
1100 Series Binary Pump	G1312A (used as make-up flow pump)
6130 Quadrupole LC/MS	G6130B

Table 2
System modules.

Conditions	
Column:	2 × Agilent ZORBAX RX-SIL (4.6 × 250 mm, 5 μm) (p/n 88097-901)
Supercritical fluid:	CO ₂
Modifier:	MeOH w. 20 mM NH ₄ COOH
Outlet pressure:	120 bar
Flow rate:	2.0 mL/min
Modifier gradient:	0–10 min: 10–20%
Temperature:	40 °C
Injection volume:	5 μL
Caloratherm heater (*):	60 °C
Make-up flow (*):	Isopropanol at 0.5 mL/min
Detection:	MS scan 200–1200 amu (screening) MS SIM (419 amu) (DiNP quantification)
APCI:	Capillary V ± 3,000 V Corona current = 4.0 μA(+), 15.0 μA(-) Drying gas flow: 8.0 L/min at 325 °C Nebulizer pressure: 50 psig Vaporizer temperature: 350 °C

(*): Caloratherm heater and make-up flow prevent solute deposition/condensation after the back-pressure regulator³.

Table 3
Experimental conditions.

Results and discussion

Analysis of polymer additives using SFC-APCI-MS in positive mode

The test mixture, containing six typical polymer additives, was analyzed using the separation conditions given in Table 3. The separation obtained using these generic SFC conditions in APCI (+) mode is shown in Figure 1. Sufficient resolution between all compounds is achieved in 10 minutes analysis time. The test mixture contains analytes typically added at different steps of the manufacturing process of the packaging material, including diisononylphthalate (a plasticizer), Irgaphos 168 (a tris-arylphosphite processing stabilizer), Irganox 1010 (a sterically hindered phenolic antioxidant), Tinuvin 234, and Tinuvin 440 (hindered amine light stabilizers/UV absorbers) and erucamide (a slip, antistatic, anti-sticking agent). All these compounds can be separated and detected using SFC and good quality mass spectra are obtained, as illustrated in Figure 2 for Irgaphos 168 and Irganox 1010. Typically, $[M+H]^+$ ions are prevalent, except for Irganox 1010 where an ammonium adduct is detected.

As shown in the TIC trace in Figure 1, erucamide and Tinuvin 440 are not chromatographically separated using the SFC conditions. However, based on their different mass spectrum, peak deconvolution using extracted ion chromatograms, clearly proves the presence of two different compounds as illustrated in Figure 1B (EIC 338 = erucamide) and Figure 1C (EIC 436 = Tinuvin 440).

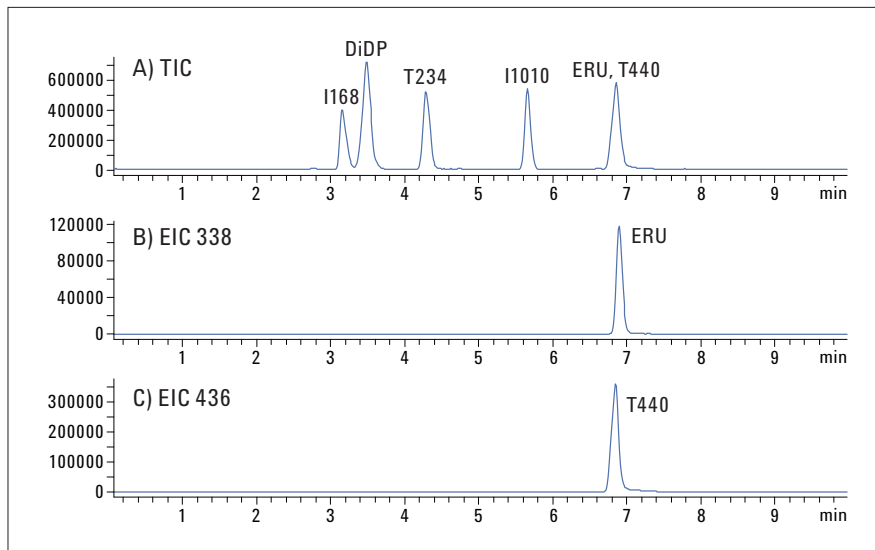


Figure 1
TIC of the SFC-APCI(+)-MS analysis of the polymer additive test mixture (A) and the EIC of the two coeluting compounds erucamide (B) and Tinuvin 440 (C).

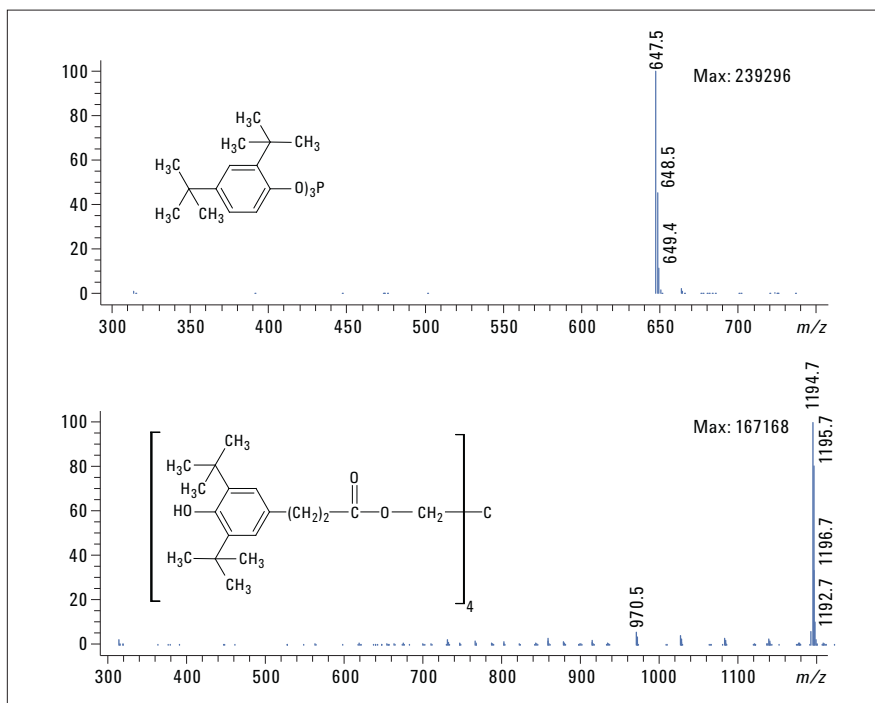


Figure 2
APCI(+)-MS mass spectra of A) Irgaphos 168 giving a clean spectra of the $M+1$ ion (647) and B) Irganox 1010 giving a spectra of the ammonium adduct (1195). Note that the spectra have different x-axis scales.

Repeatability of the SFC/MS analysis was demonstrated by analyzing the test mixture six times. As illustrated in Table 4, excellent retention time reproducibility was obtained. Peak area repeatability was in the order of 5–10% taking into consideration that this is measured on raw peak areas obtained on extracted ion chromatograms from (APCI) scan acquisition.

The analysis of the standard mixture of typical polymer additives clearly illustrates that SFC/MS is a useful tool for these type of applications. The described generic SFC/MS method can be applied to different classes of additives. It is also applicable for the analysis of other irganox, tinuvin, phthalate or amide type polymer additives. Since most polymers do not contain very complex cocktails of additives, it is in most cases not necessary to use slower modifier programs which results in increased analysis time.

Screening of polymer extract

The potential of SFC/MS is also demonstrated by the analysis of an extract obtained from a polymer intended to be used for food packaging. The polymer was extracted in 15% ethanol. After 24 hours at 40 °C, the solution was analyzed. The total ion chromatogram obtained by SFC-APCI(+)MS in scan mode is shown in Figure 5. The first eluting compound was determined as an antioxidant (sterically hindered phenol).

	Ion	Retention time Average	% RSD	Peak area Average	% RSD
I168	647	3.168	0.52	1870000	9.62
DiNP	447	3.489	0.41	4995000	8.23
T234	448	4.296	0.29	3702500	8.08
I1010	1195	5.670	0.22	2417500	7.60
T440	436	6.832	0.27	2622500	8.00
ERU	338	6.899	0.21	599875	7.99

Table 4
Reproducibility data.

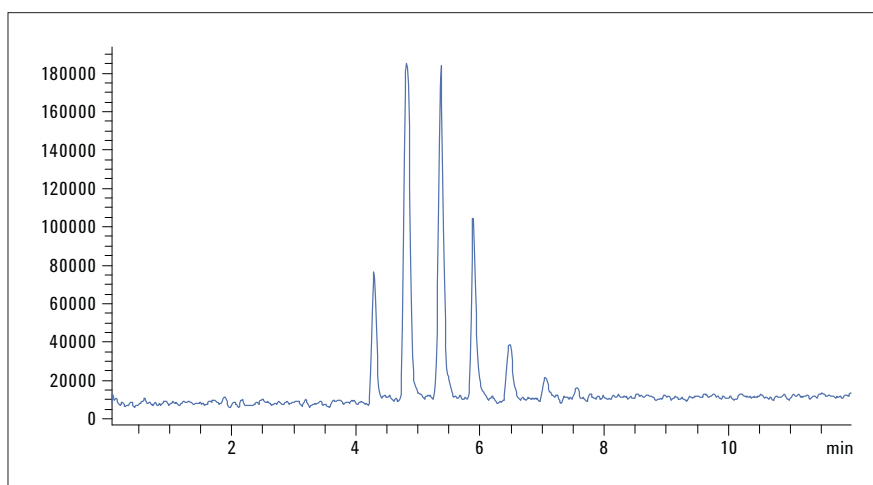


Figure 5
TIC of the SFC-APCI(+)MS analysis of ethanol/water extract of polymer.

The mass spectra of the other peaks showed most abundant ions at 306, 378, 450, 522, and 594, as illustrated in the extracted ion chromatograms in Figure 6. The difference between these masses is 72 Da, which most likely corresponds to poly-THF oligomers.

This example clearly illustrates how the SFC/MS system can be used for screening of solutes released from polymers in different simulants. It should also be noted that the extract was also analyzed by GC/MS and HPLC/UV and that neither of these techniques were able to detect all these compounds, either due to lack of volatility or lack of chromophore.

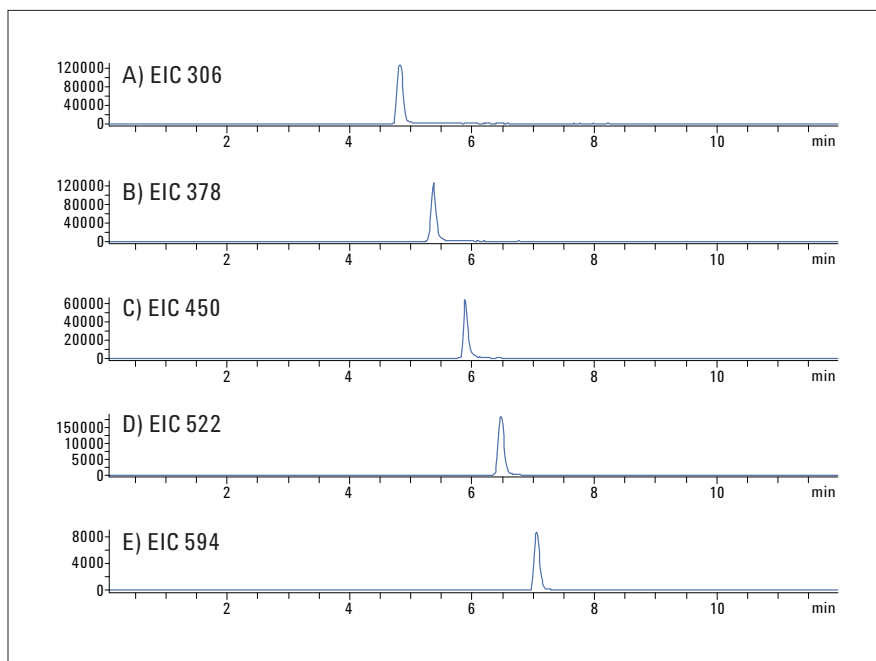


Figure 6
EICs from Figure 5 showing the homologues series with a mass difference of 72 Da.

Conclusion

The combination of the Agilent 1260 Infinity Analytical SFC System with the Agilent 6130 Single Quadrupole LC/MS System is an interesting tool to screen and quantify polymer additives and solutes that can migrate out of packaging material consisting of polymeric material. Using the SFC/MS conditions described, general screening of a wide range of polymer additives and oligomers (typically in a MW range from 200-1500) SFC/MS is very useful.

References

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2.
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3.
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