Identification of Unknown Polyester Oligomers in New Polyester Food Can Coatings by LC/TOF-MS Using Molecular Feature Extraction and Database Searching

Application

Food Safety

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Abstract

This application illustrates how time-of-flight mass spectrometry (TOF-MS) can help in the safety evaluation of new and existing polyester-based coatings used on the inside of food cans. A database of over 1,000 possible migrants based on small polyester oligomers that may not be incorporated into the polymer network of the coating was prepared from likely starting materials and the exact mass of each one was calculated. Automated database searching using the Agilent Data Analysis software and molecular feature extraction (MFE) compared the accurate mass information provided by the TOF-MS analysis to the database to identify previously unknown chromatographic peaks.

Introduction

The development of new and improved internal coatings for food and beverage cans must be cognizant of the legislative requirements on food contact materials [1]. If not, otherwise promising developments with good technical performance could come to a wasteful dead end. Coating formulations usually contain various components such as resins, cross-linking agents, catalysts, lubricants, wetting agents, and solvents. The potential exists for these ingredients, or by-products of reactions between them, to migrate from the can coating into foods. Thus, existing and especially new coatings must be evaluated for their safety for contact with food and beverages.

An earlier application described the analysis of a can coating based on epoxy resins [2]. Polyester-based coatings provide an alternative to epoxy resins and in these systems the three-dimensional polymer network is built up from a number of possible poly-functional alcohol and carboxylic acid monomers [3]. Oligomers are by-products of the polymerization process and can migrate from the coating into the food [4]. These oligomers can be formed from all possible combinations of the monomers used to construct the polymer. Some of the most common monomers used to prepare polyester resins are given in Table 1.

Combination of the different monomers provides a large number of possible polyester oligomers with the potential to migrate from the can coating into food. The accurate mass measurements provided by TOF-MS makes the identification of potential migrants possible without the need for authentic standards of every possible polyester oligomer. The Agilent MFE data analysis tool allows very fast searching of the unknown chromatographic peaks against a large user-prepared database of possible polyester oligomers.

Experimental

Sample Extraction

A metal panel (250 cm^2) coated with a polyester lacquer and stoved under industrial conditions was cut into pieces (approximately 1 cm^2) and extracted by immersion in acetonitrile (100 mL). After 18 h the extract was concentrated to a small volume (1 mL) for LC/TOF-MS analysis.

LC Conditions	
Instrument	Agilent 1200 SL
Column	Agilent ZORBAX XDB-C18 100 mm × 2.1 mm, 3.5 µm Agilent p/n: 961753-902
Mobile phases	A: Water B: Acetonitrile
Gradient	20% B to 50% B over 25 min, hold 20 min, 100% B at 60 min, hold 10 min, return to 20% B over 10 min
Flow rate	0.2 mL/min
Injection volume	5 µL
MS Conditions	
Instrument	Agilent 6210 TOF-MS in positive ion ESI mode
Nebulizer pressure	30 psi
Capillary:	4000 V
Gas temperature	325 °C
Drying gas	10 L/min
Data Analysis (DA) Parameters	
DA operation	Molecular Feature Extraction
Report type	Include confirmation screening by database search
Processing option/peak detection	
S/N threshold	50
Minimum relative volume	2.5%
Adduct	H, NH_4, Na, K
Confirmation screen	
Mass tolerance	5 ppm

Results and Discussion

Figure 1 shows the total ion chromatogram (TIC) of the polyester coating extract. Although the amounts detected are low, these peaks need to be identified for a complete safety evaluation of the coating intended for food cans.

Because an unknown number of different polyols and polyacids can be used to make polyester resins (see Table 1 for some common examples), many polyester oligomers are theoretically possible. An Excel spreadsheet was prepared to calculate the exact mass of all possible oligomers and this contained over 1,000 possibilities [2,3]. An excerpt is given in Table 2. Although this is seemingly a very cumbersome and time-consuming process, once the database is constructed it allows very rapid and efficient data analysis and identification of unknown peaks in all further polyester-based coatings analyzed. The Excel spreadsheet was converted to .CSV format and used with the Agilent Data Analysis software to automatically search the chromatogram of unknown peaks (Figure 1) and compare it to the oligomer masses. Use of MFE, even with over 1,000 entries, makes this process very fast.

Table 3 gives the identities of the 13 polyester oligomers detected and identified using the MFE software. The confidence in the identification is good as all mass error values (difference between the measured and theoretical masses) are less than 5 ppm. Analysis revealed the polyester was based on phthalic acids esterified with five of the polyols listed in Table 1. Twelve of the 13 oligomers are cyclic and only one is linear. This is reasonable because cyclic oligomers cannot be incorporated into the polymeric network of the coating, making them more readily available to migrate.

The TIC (Figure 1) shows more peaks than the 13 polyester oligomers identified in Table 2. This is due to isomeric forms of the oligomers that chromatograph differently. These can arise from (a) different isomers of the starting substances (for example, ortho-, meta-, or para-phthalic acid, or isomeric polyols); (b) oligomers having the same composition but different structures (for example, linear PA+EG+PA+EG+PA+NPG versus linear PA+EG+PA+NPG+PA+EG); (c) two or more oligomers having the same empirical formula but a different identity (for example, 3PA+2EG+NPG and 3PA+3PG both have the formula $C_{33}H_{30}O_{12}$); (d) diastereoisomers formed when incorporating the chiral 1,3-propylene glycol monomer.

The identity of those peaks not assigned as polyester oligomers were proposed based on chemical knowledge and analysis of the starting materials for the lacquer. One of these was proposed to be a plasticizer found in a starting material, three were from lubricants (two found in starting materials) and two from surfactant-type molecules (not found in starting materials).

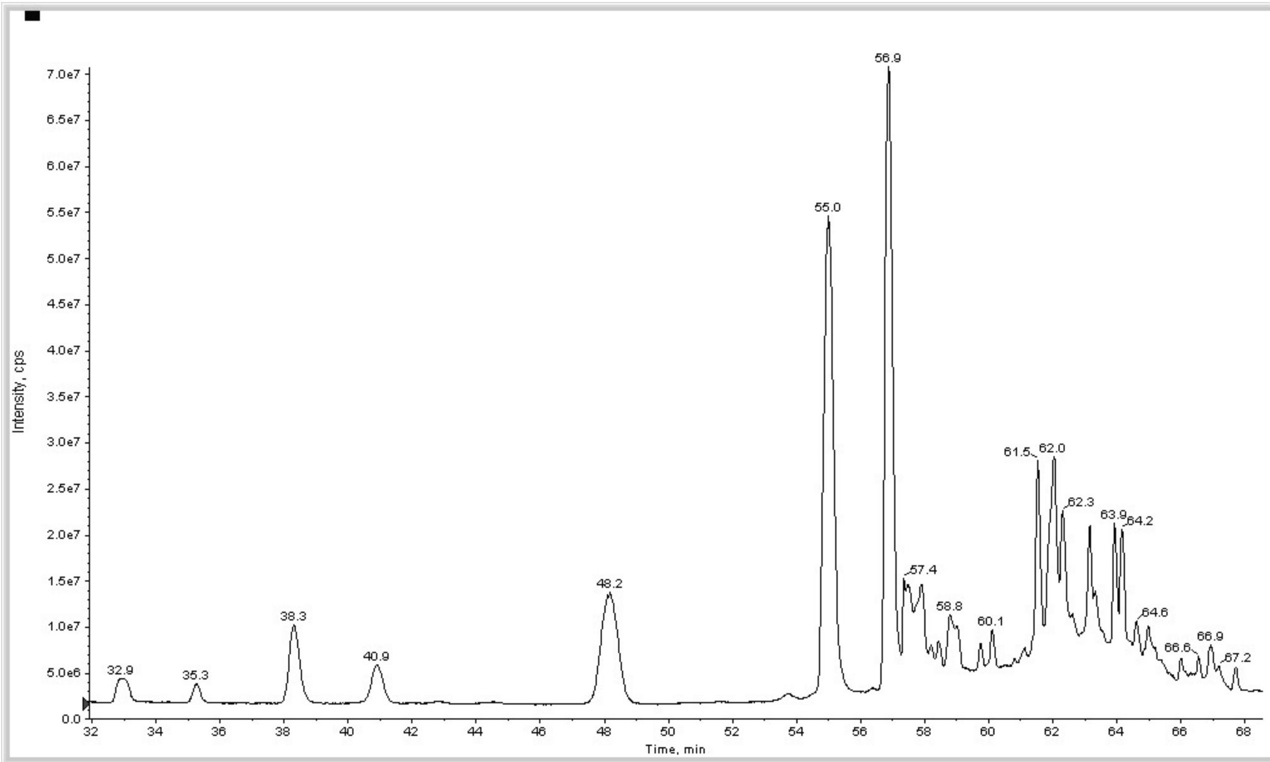

Figure 1. Total ion chromatogram (TIC) of the polyester coating extract.

Table 1. Commonly Used Monomers for Polyester Resins [2,3]

Common name	Abbreviation	Formula
Polyols		
Ethylene glycol	EG	$C_2H_6O_2$
Propylene glycol (1,2- and 1,3-)	PG	$C_3H_8O_2$
Butanediol (1,3- + isomers)	BD	$C_4H_{10}O_2$
Diethylene glycol	DEG	$C_4H_{10}O_4$
Neopentyl glycol	NPG	$C_5H_{12}O_2$
1,6-Hexanediol	HD	$C_6H_{14}O_2$
Tris(hydroxymethyl)propane	HMP	$C_6H_{14}O_3$
Cyclohexyldimethanol	CHDM	$C_8H_{16}O_2$
2,2,4-Trimethylpentane-1,3-diol	TMP	$C_8H_{18}O_2$
Polyacids		
Adipic acid	AA	$C_6H_{10}O_4$
Phthalic acid (o, m, and p-isomers)	PA	$C_8H_6O_4$
Trimellitic acid	TMA	$C_9H_6O_6$

Table 2. Excerpt from the Polyester User-Prepared Database (See Table 1 for Abbreviations)

		AA	TMA	PA	CHDM	BD	EG	DEG	PG	HD	HMP	TMP	NPG	H_2O	MW
PA+EG	Linear			1			1							1	210.0528
EG+PA+EG	Linear			1			2							2	254.0790
PA+EG+PA+EG	Linear			2			2							3	402.0951
PA+EG+PA+EG	Cyclic			2			2							4	384.0845
PA+EG+PA+EG+PA	Linear			3			2							4	550.1111
PA+EG+PA+EG+PA+NPG	Linear			3			2						1	5	636.1843
PA+EG+PA+NPG+PA+EG	Linear			3			2						1	5	636.1843
PA+PG+PA+PG+PA+PG	Linear			3					3					5	636.1843
PA+PG+PA+PG+PA+PG	Cyclic			3					3					6	618.1737

Table 3. Polyester Oligomers Identified Using Molecular Feature Extraction and Database Searching

Mass of compound	Formula predicted	Mass error (ppm)	Proposed identity	Notes
384.0845	$C_{20}H_{16}O_8$	1.4	2PA+2EG	Cyclic
426.1315	$C_{23}H_{22}O_8$	1.4	2PA+EG+NPG	Cyclic
428.1107	$C_{22}H_{20}O_9$	1.1	2PA+EG+DEG	Cyclic
466.1630	$C_{26}H_{26}O_8$	0.36	2PA+CHDM+EG	Cyclic
468.1784	$C_{26}H_{28}O_8$	0.50	2PA+2NPG	Cyclic
508.2114	$C_{29}H_{32}O_8$	3.3	2PA+CHDM+NPG	Cyclic
618.1737	$C_{33}H_{30}O_{12}$	0.84	3PA+2EG+NPG or 3PA+3PG	Cyclic
660.2238	$C_{36}H_{36}O_{12}$	4.6	3PA+EG+2NPG	Cyclic
700.2520	$C_{39}H_{40}O_{12}$	0.82	3PA+CHDM+EG+NPG	Cyclic
702.2703	$C_{39}H_{42}O_{12}$	4.8	3PA+3NPG	Cyclic
704.2469	$C_{38}H_{40}O_{13}$	0.79	3PA+CHDM+2PG	Linear
742.3003	$C_{35}H_{50}O_{17}$	0.74	3PA+CHDM+2NPG	Cyclic
782.3330	$C_{45}H_{50}O_{12}$	4.2	3PA+2CHDM+NPG	Cyclic

Conclusions

Solvent extracts of polyester can coatings have been analyzed by LC/TOF-MS to identify potential migrants into food and beverages. Accurate mass data of the parent compounds and automated data analysis software with MFE allowed confident assignment of previously unknown peaks by searching a user-prepared database of possible polyester oligomers. The database allows rapid identification of these oligomers in many complex samples. In this work LC/TOF-MS has helped to ensure the safety of food can coatings and has guided the development of new coating chemistries.

References

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