IDENTIFICATION OF MIGRANTS IN EPOXY CAN COATINGS BY LC-MS/MS

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INTRODUCTION

A variety of different materials are used for the coating of cans, but epoxy polymers are the type of coating most widely used. Epoxy resins are obtained by the condensation of epichlorohydrin and bisphenol A (BPA), which yields bisphenol A diglycidyl ether (BADGE). These compounds can potentially migrate from the food contact material into the food and they are regulated with their specific migration limits. However, migrants from epoxy coatings may also contain oligomers, adducts with chain stoppers or reaction products of either solvents or phenolic monomers, among others.

The objective of this work is the identification of these potential migrants in polymeric coatings including intentionally added substances (IAS) such as monomers, additives and non-intentionally added substances (NIAS) such as oligomers by liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS). It is a difficult task due to the lack of information about the formulations used in the manufacture of the coatings as well as the lack of commercially available standards of these compounds.

The two-piece cans used in this study were provided by industrial partners. One for use in beverage samples (BC) and other for food samples (FC).

EXPERIMENTAL

Identification of the type of coating

To identify the type of coating, infrared spectra were acquired using an ATR (attenuated total reflectance)-FTIR spectrometer equipped with a diamond optical crystal. The spectra identification was performed by comparing recorded spectra with several commercial spectral libraries (IR Spectral Libraries of Polymers & Related Compounds from Bio-Rad Laboratories).

Can sample

FTIR-ATR

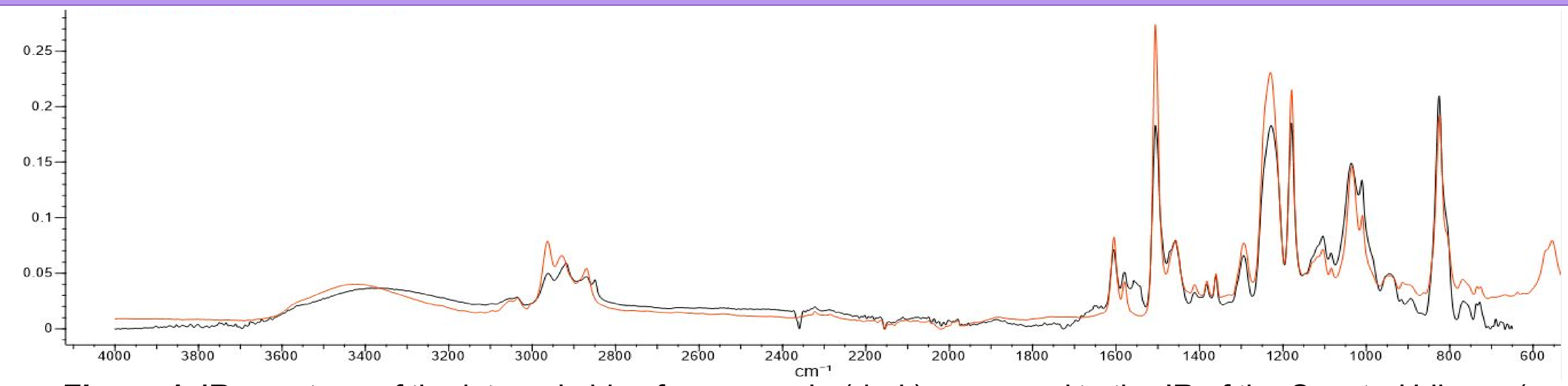


Figure 1. IR spectrum of the internal side of one sample (dark) compared to the IR of the Spectral Library (red)

Identification of potential migrants

A non-targeted screening by liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) was performed for migrant identification.

Can sample

A known surface of the can was put in contact with a volume of acetonitrile for 24h at 70ºC

0.25 mL extract
+ 0.25 mL water

Filtration and analysis by LC-MS/MS

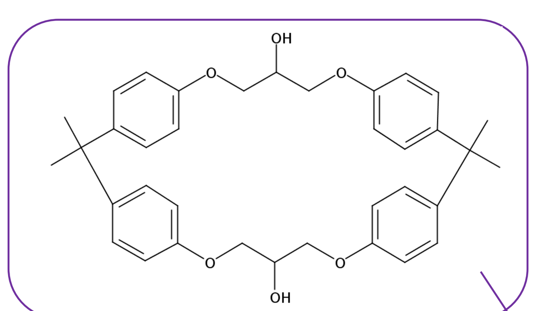
LC-MS/MS Thermo Scientific

Column	Phenosphere 80A ODS (150 mm × 3.2 mm, 3 µm)
Column Tª	30ºC
Mobile phase	MeOH: ACN (50:50, v/v) and water
Flow rate	0.5 mL/min
Injection volume	10 µL
Gradient elution	55% water and 45% MeOH:ACN for 2 min, MeOH:ACN was increasing until 75% for 14 min, and another gradient to 100% MeOH:ACN for 7 min
Data acquisition	Full scan (400-1000 m/z)
Source	Positive and negative atmospheric pressure chemical ionisation (APCI)
Vaporizer Tª	400ºC
Capillary Tª	350ºC

Table 1: Experimental conditions of LC-MS methods.

RESULTS AND DISCUSSION

- FTIR-ATR results illustrate that the internal and external side of the can samples correspond with an epoxy-based resin.
- Acetonitrile was selected as solvent for the extraction of the unreacted compounds remaining in the coating based on our laboratory experience and in previous studies.
- Mass spectrometry detection resulted to be a powerful tool for the determination of molecular weight and structure elucidation of unidentified compounds.
- Only compounds with a molecular weight up to 1000 m/z were included in the study because it is generally recognized that compounds, except perfluoroalkyl compounds, above this mass range are typically not absorbed through the gastrointestinal tract.
- Several non-intentionally added substances, were tentatively identified in the two samples analysed (Figure 2 for the beverage can extract and Figure 3 for the food can extract), including BADGE.H_2O.BPA, cyclo-di-BADGE, BADGE(n=1)H_2O.BPA, BADGE.BPA.BuOH or BADGE(n=1)BPA among others.
- Further studies are required to confirm these results, such as using a high resolution mass detector. Further, migration assays will be required in order to identify these compounds in foodstuffs.



cyclo-di-BADGE

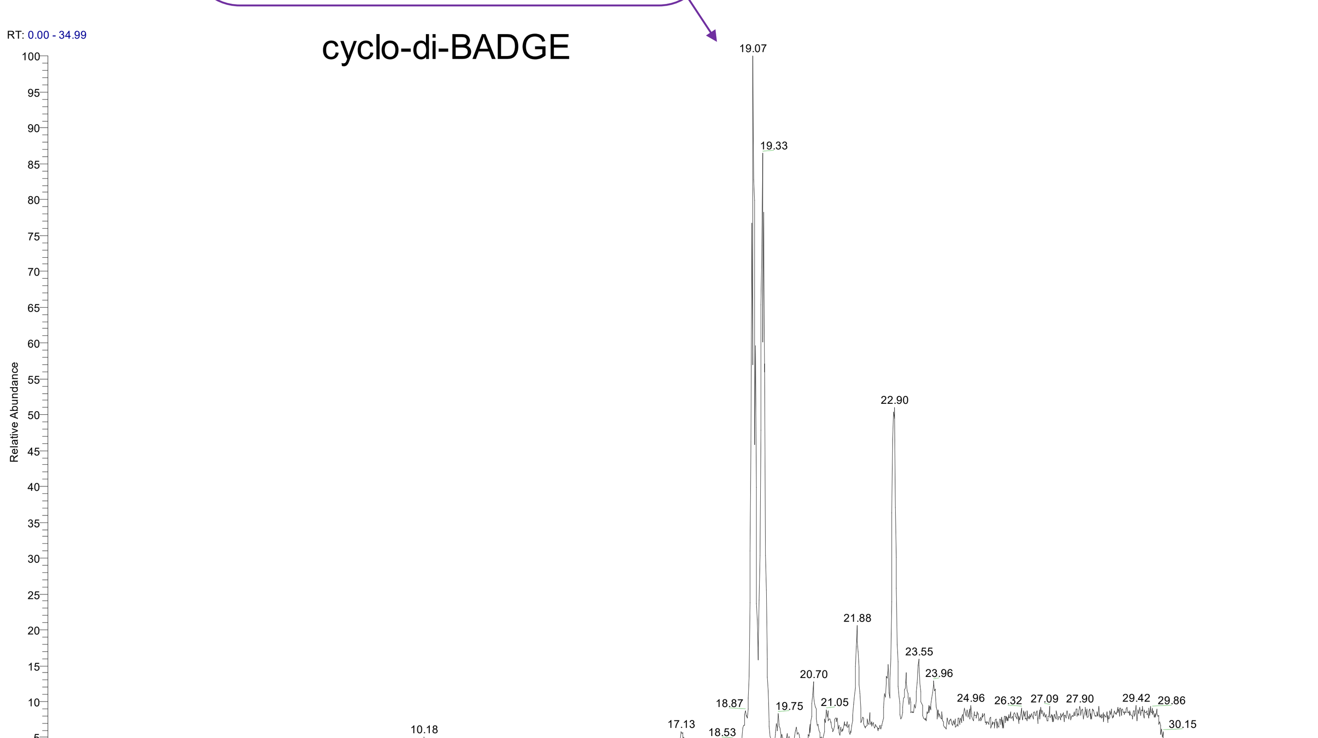
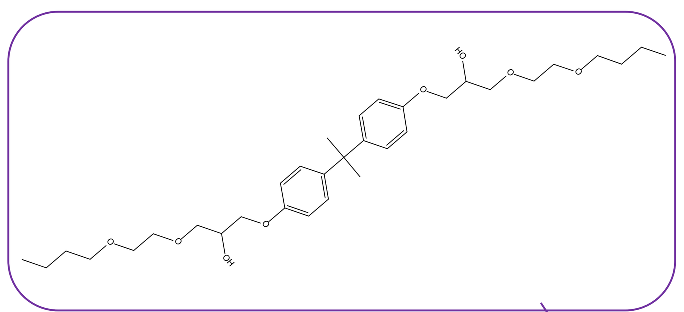


Figure 2: TIC chromatogram for the extract of the beverage sample in positive mode.

Retention time (min)	Proposed compound	m/z	Ion/Adduct	Sample
14.22	BADGE.H_2O.BuEtOH	477 494	H^+ NH_4^+	FC
15.00	BADGE.BuEtOH.tBuPh	609 626	H^+ NH_4^+	BC
15.74	BADGE.H_2O.Ph	453 470	H^+ NH_4^+	FC
17.13	BADGE.H_2O.BPA	585	H^-	FC, BC
19.00+19.26	Cyclo-di-BADGE	569 567	H^+ H^-	FC, BC
19.72	BADGE(n=1)H_2O.PrOH	701	H^-	BC
20.52	BADGE.2BuEtOH	577 594	H^+ NH_4^+	FC
20.71	BADGE(n=1)H_2O.BPA	869	H^-	BC
21.01	BADGE(n=1)	625 642 666	H^+ NH_4^+ ACN^+	BC
21.34	BADGE.BPA.BuOH	641	H^-	BC
21.14	BADGE.BuEtOH.BPA	687 704 685	H^+ NH_4^+ H^-	FC
21.48	BADGE.2BPA	795	H^-	FC, BC
22.83	BADGE(n=1)BPA	853 870 851	H^+ NH_4^+ H^-	FC, BC
22.88	BADGE(n=2)	909	H^+	BC

Table 2: Substances tentatively identified in the extracts. BuEtOH: butoxyethanol; Ph: phenol; tBuPh: tert-butylphenol; BuPH: butanol; PrOH: propanol.



BADGE.2BuEtOH

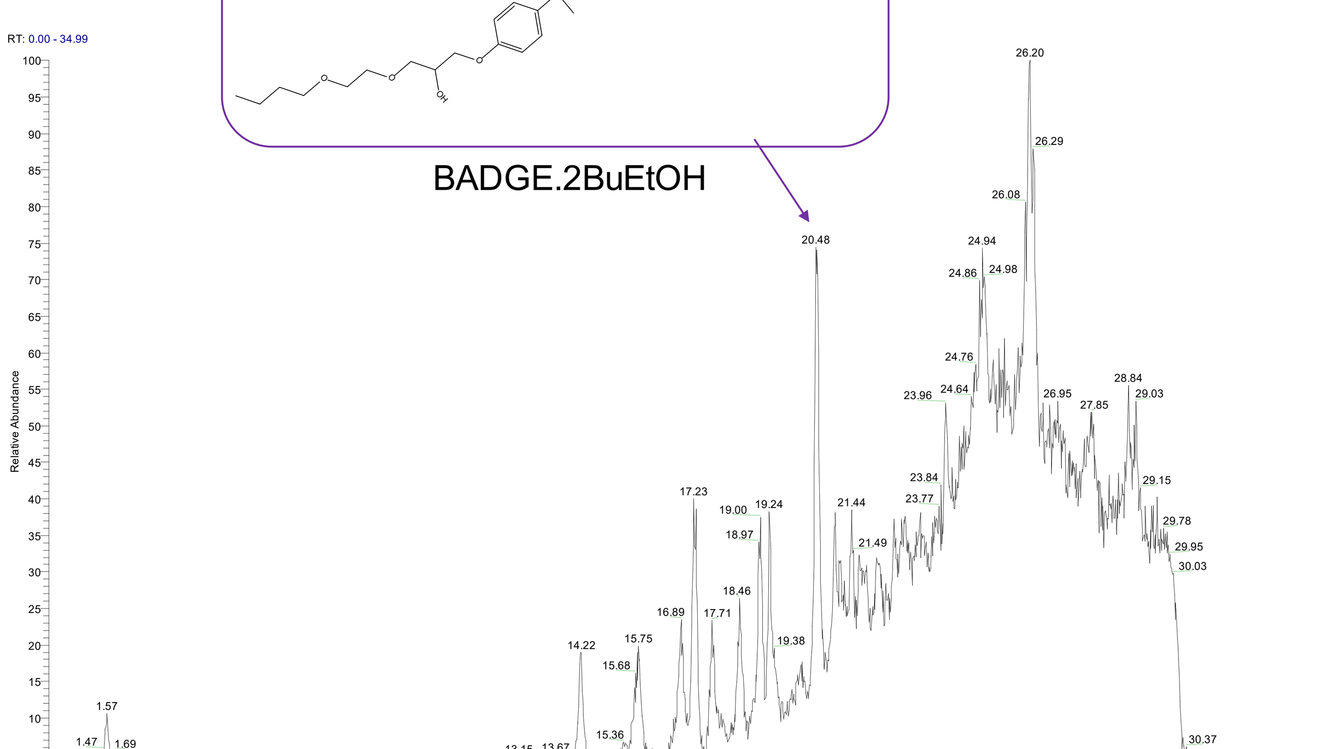


Figure 3: TIC chromatogram for the extract of the food sample in positive mode.

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