Determination of compounds migrated from epoxy and polyester coatings into canned foods

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INTRODUCTION

Metal cans are often coated in the internal side to protect the food. Some of the most widely used coatings applied to metal substrates are epoxy resins, which are produced by condensation of epichlorohydrin and bisphenol A (BPA), or polyester resins, which are produced by condensing an acid with one or more alcohols. During the polymerization process residual monomers can remain and also oligomers can be formed and be present in the final product, therefore they have the potential to migrate to the food.

In this work, 22 canned food samples including fish, meat, pasta, and vegetables were analyzed for the determination of compounds migrated from the polymeric coatings. Firstly, a characterization of the material was made using an ATR-FTIR spectrometer and then, an extraction of the cans was made to identify potential migrants which can be susceptible to migrate to the food.

In the second part of the work, canned foods were extracted to identify and quantify the compounds of interest selected previously. Bisphenols including BPA, BPE, and BPG and BADGEs derivatives migrating from epoxy resins were extracted by solid liquid extraction and quantified by HPLC-FLD. Acids including, adipic acid (AA), terephthalic acid (TPA) or Trimellitic acid (TMA) identified in polyester resins, were extracted from the food using a QuEChERS method and quantified by LC-MS -ESI in negative mode.

EXPERIMENTAL

Characterization of the coating

Identification of potential migrants in cans

Figure 1. Different samples analysed in this study

Figure 2. ATR-FTIR Spectrometer

24 h, ACN, 40 °C

Quantification of potential migrants in food

Extraction of bisphenol compounds and BADGE derivatives

5 g+ 5 mL Heptane

1 min

+ 10 mL ACN 90 % v/v

4500 rpm, 10 min

Figure 3. HPLC-FLD

Extraction of the polyester monomers

10 g + 10 mL ACN

10 min Ultrasound

QuEChERS

1 min

3000 rpm, 20 min

X 10, 40 °C

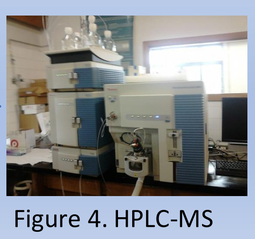

Figure 4. HPLC-MS

RESULTS AND DISCUSSION

IR identification

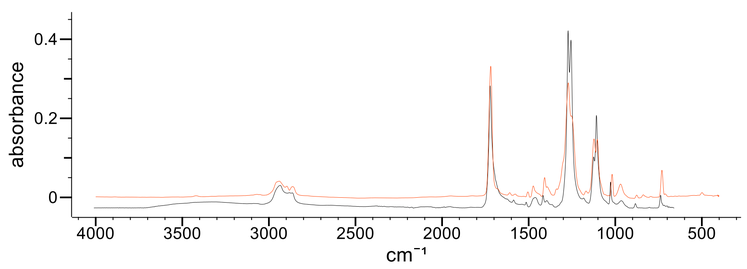

Figure 5. IR spectrum corresponding to the internal side of the sample LE (black line) compared to the first entry of the spectral libraries corresponding to a polyester spectrum (red line).

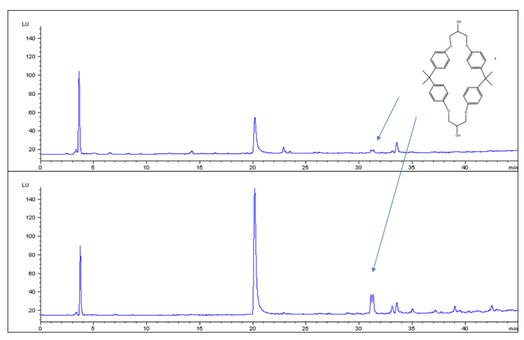

Figure 6. Chromatogram of ME_A and ME_L analysed by HPLC-FLD.

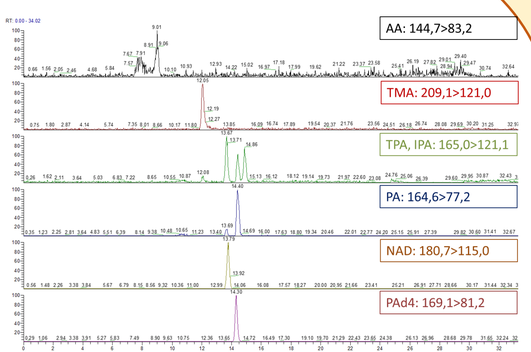

Figure 7. Chromatogram of carboxylic acids analysed by HPLC-MS.

Epoxy resins coated samples

Compound	TR/min	BN_A mg/kg	BN_L mg/kg	CH_A mg/kg	CH_L mg/kg	SCO_A mg/kg	SCO_L mg/kg	ME_A mg/kg	ME_L mg/kg
BADGE.2$H_2$0	14.2	0.65	0.16	0.11	< LOD	0.52	0.26	0.09	< LOD
BPF	16.4	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
BPE	17.9	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
BPA	19.3	0.05	0.02	0.04	< LOD	0.04	< LOD	< LOD	< LOD
BADGE.H_2O.HCl	19.8	0.04	< LOD	< LOD	< LOD	0.06	< LOD	< LOD	< LOD
BADGE.$H_2$0	20.2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
BPB	21.3	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
BPC	23.1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
BP	26	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
BADGE.2HCl	26.5	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
BADGE.HCl	27.4	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
BADGE	28.3	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
BPG	30.3	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
CyclodBADGE	31.2	0.41	0.49	0.30	2.78	0.44	2.44	0.11	0.72

Table 1. Concentrations of bisphenols and BADGE derivatives detected in food and covering liquids. LOD: 0.01 mg/kg; LOQ: 0.025 mg/kg

Polyester resins coated samples

Tr/min	Acid	LEV mg/kg	LE mg/kg	GUIB mg/kg	GUIB_L mg/kg	SCA mg/kg	SCA_L mg/kg	GUIM mg/kg	GUIM_L mg/kg
9.1	AA	< LOD	<LOQ	0.10	0.11	< LOD	< LOD	<LOQ	0.098
12.1	TMA	0.014	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	<LOQ
13.7	TPA	0.018	0.047	0.025	0.03	< LOD	< LOD	<LOQ	<LOQ
14.5	PA	<LOQ	< LOD	<LOQ	<LOQ	< LOD	< LOD	<LOQ	<LOQ
15	IPA	< LOD	< LOD	<LOQ	< LOD	< LOD	< LOD	< LOD	<LOQ
13.7	NAD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD

Table 2. Concentrations of monomers in food. LOD: 0.004 mg/kg; LOQ: 0.01 mg/kg

CONCLUSIONS

- Most of the coatings identified were based on epoxy and/or polyester resins.
- BADGE.2H_2O and CdB were the most abundant compound detected in all of samples analysed
- BPA was detected in 13 samples
- TMA and TPA were the main monomers identified in the polyester can samples analysed as well as in food
- Future work will be focused on the identification of oligomers formed during the polymerization in the coating as well as in the food samples.

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