# IDENTIFICATION OF POTENTIAL MIGRANTS PRESENT IN POLYMERIC COATINGS IN FOOD CANS

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## INTRODUCTION

Polymeric coatings are commonly used in metal food cans to protect food from corrosion. However, there is a risk that coatings used in cans release complex chemical mixture into foodstuff including monomers, oligomers, additives, impurities, reaction products, etc. It is important to develop analytical tools for the identification of these potential migrants in the food packaging with the ultimate objective of ensure the consumer safety. A GC-MS screening method was performed to identify potential migrants in polymeric coatings and a LC-MS/MS method was developed for the determination of bisphenols and BADGEs. A total of twelve food cans that cover several types of food including fish, seafood, vegetables and fruit were selected as study samples.

## EXPERIMENTAL

### Identification of the type of coating (ATR-FTIR)

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

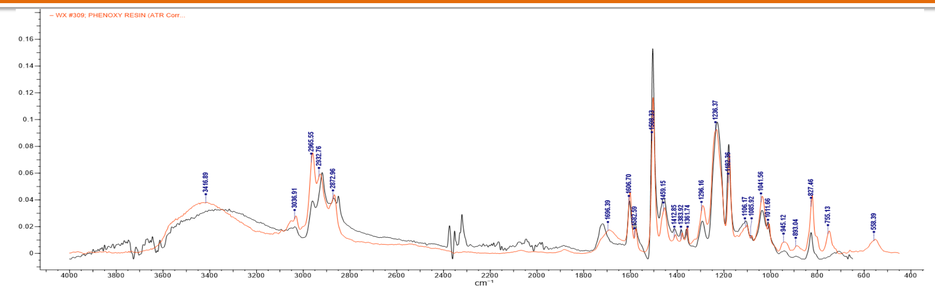



**Figure 1.** IR spectrum of the internal side of one sample (dark) compared to the IR of the Spectral Library (red)

### Identification of potential migrants (GC-MS)

A non-targeted screening by gas chromatography coupled to mass spectrometry (GC-MS) was performed for migrant identification.

Can sample

A known surface of the packaging was put in contact with a volume of acetonitrile for 24 h at 70◦C

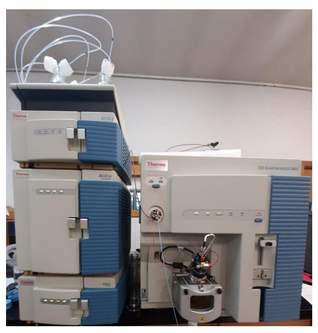
An aliquot of the extracts (10 mL) was evaporated down to 1 mL by a stream of nitrogen

An aliquot was filtered and analysed by GC-MS

| | |
|---|---|
| Column | ZB-5MS (30 m × 0.25 mm × 0.25 µm) |
| Carrier gas | Helium 1mL/min |
| Injection mode | Splitless |
| Injection volume | 1µL |
| Tª program | 40ºC/2min, 9ºC/min to 300ºC, 300ºC/3min |
| Data acquisition | Full scan (range m/z 35-500) |
| Mass detector | Electron impact |
| Transfer line Tª | 300ºC |
| Detector Tª | 300ºC |
| Mass spectrum library | Wiley 8th & NIST/EPA/NIH 11 |

### Multi-target analysis (LC-MS)

A targeted analysis was carried out for the simultaneous determination of thirteen compounds including bisphenols and BADGEs by liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS).



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

**Table 2:** Experimental conditions of LC-MS/MS method

| Compound | Retention Time (min) | APCI mode | Parent ion | Product ion | Collision energy (V) |
|---|---|---|---|---|---|
| BPF | 4.27 | - | 198.9 | 93.0 | 24 |
| | | | | 105.0 | 23 |
| $BADGE.2H_2O$ | 4.72 | - | 374.8 | 226.8 | 28 |
| | | | | 300.6 | 16 |
| BPE | 5.54 | - | 212.9 | 196.8 | 33 |
| | | | | 197.8 | 20 |
| BPA | 6.92 | - | 226.9 | 133.0 | 28 |
| | | | | 211.8 | 20 |
| BPB | 9.03 | - | 240.9 | 210.7 | 31 |
| | | | | 211.8 | 20 |
| $BADGE.H_2O$ | 9.45 | + | 399.9 | 106.9 | 45 |
| | | | | 134.8 | 26 |
| $BADGE.H_2O.HCl$ | 9.96 | - | 283.0 | 211.0 | 30 |
| | | | | 226.0 | 21 |
| BPC | 10.62 | - | 254.9 | 146.9 | 33 |
| | | | | 239.8 | 21 |
| BADGE | 14.23 | + | 381.9 | 134.9 | 31 |
| | | | | 190.8 | 25 |
| BADGE.HCl | 14.50 | + | 417.9 | 106.9 | 43 |
| | | | | 134.9 | 28 |
| BADGE.2HCl | 14.77 | + | 382.2 | 191.1 | 16 |
| | | | | 135.2 | 26 |
| BPG | 16.90 | - | 311.0 | 174.9 | 33 |
| | | | | 294.9 | 37 |
| CYDBADGE | 18.74, 18.99 | + | 569.0 | 134.8 | 29 |
| | | | | 106.9 | 39 |

**Table 3:** MS/MS conditions and retention times

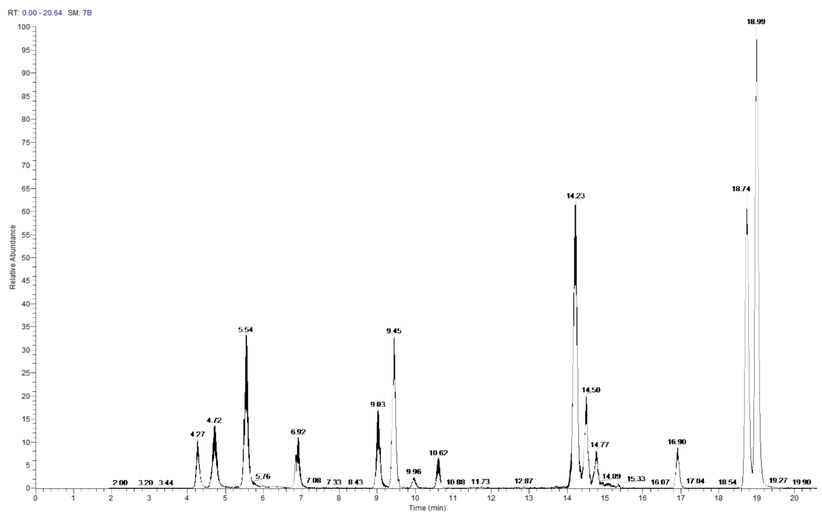



**Figure 2:** A LC-MS/MS chromatogram corresponding to a mix solution

## RESULTS AND DISCUSSION

The FTIR results confirmed that most of the samples examined in this study were coated with epoxy-phenolic resins.

The screening reveals the presence of a great variety of compounds including plasticizers (acetyl tributyl citrate, bis(2-ethylhexyl) adipate, phthalates such as diisobutyl phthalate, bis(2-ethylhexyl)phthalate, etc.), photoinitiators (benzophenone and 4-phenylbenzophenone), antioxidants (butylated hydroxytoluene), lubricants (butyl palmitate, glycerol tricaprylate), etc. Sixteen of the total of forty-five compounds were positively confirmed by injection of the respective standard. Several degradation products formed from antioxidants used as additives were identified in the can extracts, for example, 1,3-di-tert-butylbenzene and 2,4-di-tert-butylphenol.

The developed method by LC-MS/MS turned out to be an excellent analytical tool for the confirmation of the presence of bisphenol related compounds in the can extracts being cyclo-di-BADGE the predominant compound detected.

| Compound | Samples | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | AA | AH | AL | AN | AR | ES | MA | ME | MZ | SR | TO1 | TO2 |
| BPF | | | | | | | | | | | | |
| $BADGE.2H_2O$ | X | X | X | X | | X | X | X | X | X | X | X |
| BPE | | | | | | | | | | | | |
| BPA | | | | X | | X | | X | | | | X |
| BPB | | | | | | | | | | | | |
| $BADGE.H_2O$ | X | X | X | X | | X | X | X | X | X | X | X |
| $BADGE.H_2O.HCl$ | | | X | X | | | | X | | | | |
| BPC | | | | | | | | | | | | |
| BADGE | | X | X | X | | X | X | X | X | X | X | X |
| BADGE.HCl | | X | X | X | | | | | | | | X |
| BADGE.2HCl | | | | | | | | | | | | |
| BPG | | | | | | | | | | | | |
| CYDBADGE | X | X | X | X | X | X | X | X | X | X | X | X |

**Table 4:** Bisphenols and BADGEs identified in the extracts of the analysed cans by LC-MS/MS

## Acknowledgement

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