QUANTIFICATION OF BISPHENOL RELATED COMPOUNDS IN POLYMERIC CAN COATINGS AND IN BEVERAGE SAMPLES BY HPLC-FLD AND CONFIRMATION BY LC-MS/MS

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INTRODUCTION

Major types of internal can coatings used for food and beverages are made from epoxy-based resins, which contain among their components bisphenol A (BPA) or bisphenol A diglycidyl ether (BADGE). These components can be released and reach the food. There is no specific European legislation for coatings, but there is legislation on specific substances setting migration limits. Many investigations have paid attention to BPA due to its classification as endocrine disruptor, however, studies are available concerning other analogues developed to replace it in the manufacture of these resins [1].

The objective of the present work was to apply an analytical method based on high performance liquid chromatography with fluorescence detection (HPLC-FLD) to the simultaneous identification and quantification of fourteen compounds including bisphenol analogues (BPA, BPB, BPBP, BPC, BPE, BPF, BPG) and BADGEs (BADGE, BADGE.H_2O, BADGE.$2H_2O$, BADGE.HCl, BADGE.2HCl, BADGE.H_2O.HCl, cyclo-di-BADGE) in the material (cans) and in the beverage samples. In addition, a liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) method was optimized for confirmation purposes.

EXPERIMENTAL

CODE	DESCRIPTION	ORIGIN	TYPE OF MATERIAL			
			Lateral External	Lateral Internal	Lid Internal	Lid External
BC01	Traditional Beer	Spain	Polyurethane	Phenoxy resin	Phenoxy resin	Phenoxy resin
BC02	Vodka mixed drink	Italy	Polyurethane	Phenoxy resin	Epoxy resin	Epoxy resin
BC03	Mixed lemon flavour	Spain	Polyurethane	Phenoxy resin	Phenoxy resin	Phenoxy resin
BC04	Energy drink zero	Ireland	Polyurethane	Phenoxy resin	Epoxy resin	Epoxy resin
BC05	Star wars space punch	Germany	Polypropylene	Acrylic resin	Polyester	Phenoxy resin
BC06	Green cola	Spain	Polyurethane	Phenoxy resin	Phenoxy resin	Phenoxy resin
BC07	Tonic original	Spain	Polyurethane	Phenoxy resin	Epoxy resin	Epoxy resin
BC08	Tonic water original	Spain	Polyurethane	Phenoxy resin	Epoxy resin	Epoxy resin
BC09	Premium tonic water	Germany	Polyurethane	Acrylic resin	Polyester	Phenoxy resin
BC10	Natural mineral water drink	Spain	Polyurethane	Phenoxy resin	Epoxy resin	Epoxy resin

Table 1: Information about the samples included in the study.

The type of coating was verified using an 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).

EXTRACTION PROCEDURE

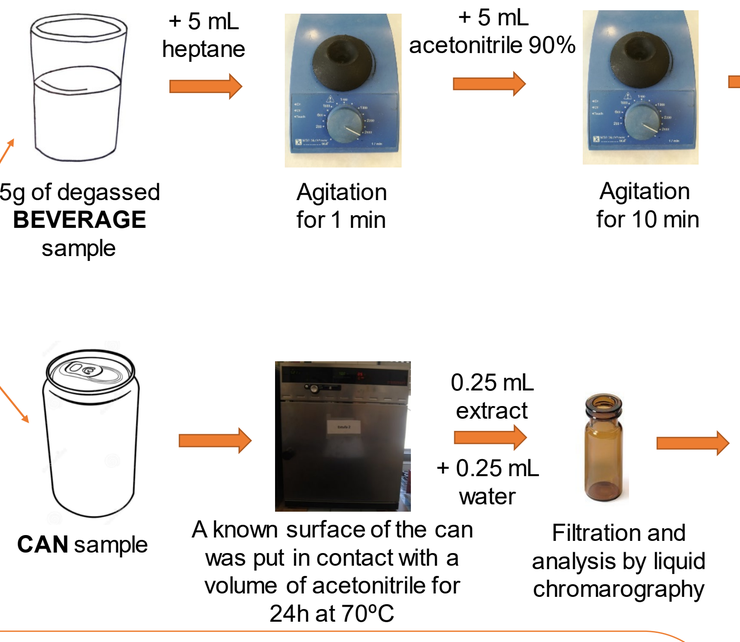

Figure 1: HPLC-FLD.

CONFIRMATION

Figure 2: LC-MS/MS.

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
Gradiente 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
Fluorescence detection	Excitation: 225 nm Emission: 305 nm
Data acquisition	Selected reaction monitoring (SRM)
Source	Positive and negative atmospheric pressure chemical ionisation (APCI)
Vaporizer Tª	400ºC
Capillary Tª	350ºC

Table 2: Experimental condition of HPLC-FLD and LC-MS/MS methods.

Compound	CAS N°	Molecular Weight (g/mol)	APCI mode	Parent ion	Product ions
BPA	80-05-7	228.29	-	226.9	133.0, 211.8
BPB	77-40-7	242.31	-	240.9	210.7, 211.8
BPC	79-97-0	256.34	-	254.9	146.9, 239.8
BPE	2081-08-5	214.26	-	212.9	196.8, 197.8
BPF	620-92-8	200.23	-	198.9	93.0, 105.0
BPG	127-54-8	312.45	-	311.0	174.9, 294.9
BADGE	1675-54-3	340.41	+	381.9	134.9, 190.8
BADGE.H_2O	76002-91-0	358.43	+	399.9	106.9, 134.8
BADGE.$2H_2O$	5581-32-8	376.44	-	374.8	226.8, 300.6
BADGE.HCl	13836-48-1	376.87	+	417.9	106.9, 134.9
BADGE.2HCl	4809-35-2	413.33	+	382.2	191.1, 135.2
BADGE.H_2O.HCl	227947-06-0	394.89	-	283.0	211.0, 226.0
CYDBADGE	20583-87-3	568.71	+	569.0	134.8, 106.9

Table 3: Compounds analyzed in this work with their MS/MS conditions.

RESULTS AND DISCUSSION

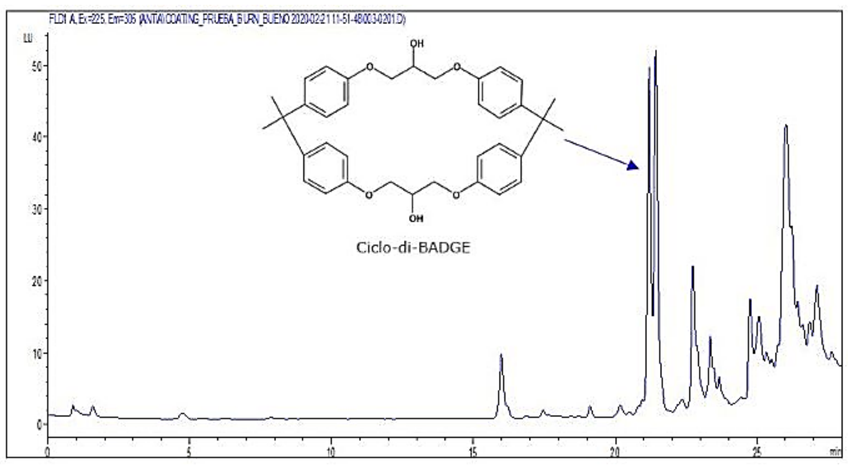

Figure 3: A HPLC-FLD chromatogram corresponding to an extract of a can sample.

	BC01	BC02	BC03	BC04	BC05	BC06	BC07	BC08	BC09	BC10
BPF	-	-	-	-	-	-	-	-	-	-
BADGE.$2H_2O$	0.002	-	0.004	0.003	-	0.002	0.006	0.004	-	0.004
BPE	-	-	-	-	-	-	-	-	-	-
BPA	-	-	0.003	0.003	-	-	0.003	-	-	0.003
BPB	-	-	-	-	-	-	-	-	-	-
BADGE.H_2O	-	-	-	-	-	-	-	-	-	-
BADGE.H_2O.HCl	-	-	-	<LOQ	-	-	<LOQ	-	-	-
BPC	-	-	-	-	-	-	-	-	-	-
BADGE	-	-	-	-	-	-	<LOQ*	-	-	-
BADGE.HCl	-	-	-	-	-	-	-	-	-	-
BADGE.2HCl	-	-	-	-	-	-	-	-	-	-
BPG	-	-	-	-	-	-	-	-	-	-
Ciclo-di-BADGE	0.26	0.17	0.36	0.43	0.006	0.37	0.60	0.40	0.004	0.30

Table 4: Concentrations obtained in can samples (mg/dm²).
LOQ*: limit of quantification considering the signal by LC-MS/MS.

The HPLC-FLD method developed to determine the migrants in the samples was validated showing low detection levels (LOD = 0.005 mg/L), good repeatability (RSD % < 5) and acceptable recoveries (>75 %) determined by spiking experiments on food samples at three concentrations (0.05, 0.1 and 0.2 µg/g) during three consecutive days (n=6).

- In the extracts from the can coatings BPA, BADGE, BADGE.$2H_2O$, BADGE.H_2O.HCl and cyclo-di-BADGE were detected.
- No analytes were detected above the detection limit in any of the beverage samples.
- These results were confirmed by LC-MS/MS.
- From the food safety point of view, it can be concluded that they comply with the European legislation respect to the compounds analyzed.

Acknowledgement

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References

[1] Lestido Cardama A. et al., Polymers 11 (2019) 2086.