

Determination of Bisphenol A, Bisphenol F, Bisphenol A Diglycidyl Ether and Bisphenol F Diglycidyl Ether Migrated from Food Cans using Gas Chromatography-Mass Spectrometry

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Abstract

JORDÁKOVÁ I., DOBIÁŠ J., VOLDŘICH M., POUSTKA J. (2003): **Determination of bisphenol A, bisphenol F, bisphenol A diglycidyl ether and bisphenol F diglycidyl ether migrated from food cans using Gas Chromatography-Mass Spectrometry.** Czech J. Food Sci., 21: 85–90.

Varnishes used for the inner coatings of food cans are mostly based on epoxy resins or vinylic organosols. The epoxy resins are produced from bisphenol A and bisphenol F and they also contain BADGE or BFDGE as stabilising components. A simple method for the quantitative determination of bisphenol A (BPA), bisphenol F (BPF), bisphenol A diglycidyl ether (BADGE), and bisphenol F diglycidyl ether (BFDGE) migrated from food packaging materials was optimised. The can sample was extracted with acetonitrile or with food simulants (distilled water, 3% acetic acid and 10% ethanol) and the extract obtained was analysed by gas chromatography coupled with mass spectrometric detector. The limits of detection and quantification ranged between 0.15–0.86 and 0.51–2.77 µg/dm², respectively. The migrating levels of bisphenols found in various can samples were for BPA and for BADGE in the range from 0.63×10^{-3} to 0.34 mg/dm², and from 1.49×10^{-3} to 3.67 mg/dm², respectively. BPF and BFDGE were practically not detected in the can samples.

Keywords: bisphenol A; bisphenol F; bisphenol A diglycidyl ether; bisphenol F diglycidyl ether; migration; gas chromatography; mass spectrometry

One of the ways of the can inner coating preservation employs varnishes based on epoxy resins or vinylic organosols. These resins are obtained from bisphenol A (BPA, CAS 80-05-7) and bisphenol F (BPF, CAS 620-92-8) and they also contain bisphenol A diglycidyl ether (BADGE, CAS 1675-54-3) or bisphenol F diglycidyl ether (BFDGE, CAS 2095-03-6) as stabilising materials. The molecular structures of bisphenol-type compounds are presented in Figure 1. Epoxy-based coatings are used in a great number of applications: as tank coatings, structural steel coatings, aircraft finishes, can and drum linings, furniture finishes, in printing inks, in dental, surgical and prosthetic applications etc. (TICE & MCGUINNESS 1987; LOSADA *et al.* 1992, 1993).

At higher temperatures (sterilisation, microwave heating), the resin can decompose and, as a result, the migration of bisphenols from packaging to food can be more intensive and rapid. A similar situation can be encountered, for example, in the case of imperfectly thermally stabilised can lacquers.

As regards the presumed toxic effects of the compounds mentioned, BPA shows estrogenic activity, BADGE has been classified as a carcinogen and a mutagenic compound. The potential target tissues are the central neural system, kidney and liver (LOSADA *et al.* 1997; SALAFRANCA *et al.* 1999).

Migration tests of food packages are usually realised by means of food simulants. The simulants are chosen as models of the basic food categories

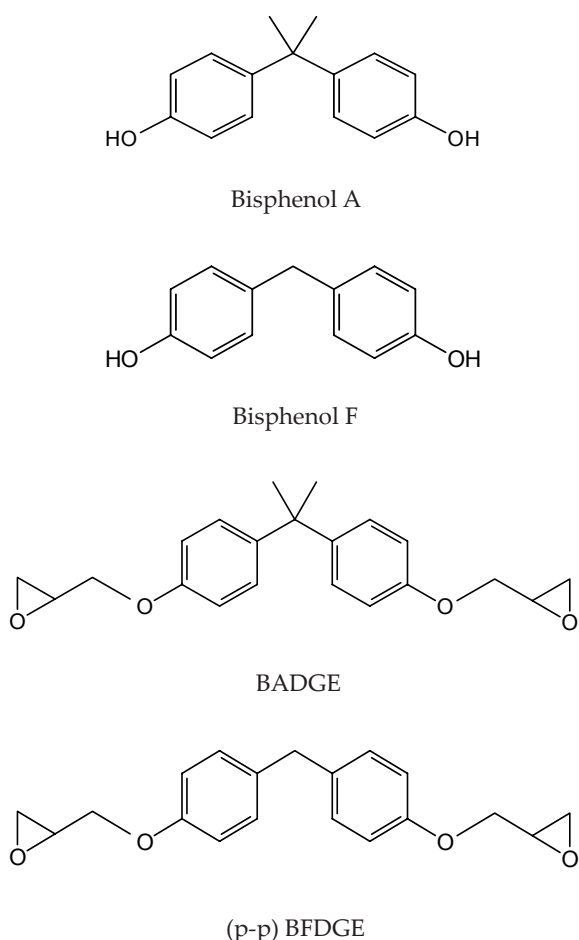


Figure 1. Molecular structures of bisphenol A (BPA), bisphenol F (BPF), bisphenol A diglycidyl ether (BADGE) and bisphenol F diglycidyl ether (BFDGE)

(i.e. aqueous, acidic, alcoholic and fatty). The former European Community Commission Directive (90/128/EEC, 1990) established specific migration limits in food or in food simulants: 0.5 mg/dm² for BPA and 0.02 mg/dm² for BADGE, the maximal permitted quantity of the residual BADGE in the material (lacquer) of 0.17 mg/dm². This directive is nowadays amended by new issues (1999/91/EC, 2001/61/EC, 2001/62/EC, 2002/16/EC, 2002/17/EC, 2002/72/EC) in which are established specific migration limits for BADGE, BFDGE and certain of their derivatives: the sum of the migration levels of the following substances: BADGE, BADGE.H₂O, BADGE.HCl, BADGE.2HCl, BADGE.H₂O.HCl shall not exceed the following limits: 1 mg/kg in foodstuffs or in food simulants or 1 mg/6 dm² of food simulants, the sum of the migration levels of the following substances: BFDGE, BFDGE.H₂O,

BFDGE.HCl, BFDGE.2HCl, BFDGE.H₂O.HCl shall not exceed the following limits: 1 mg/kg in foodstuffs or in food simulants or 1 mg/6 dm² of food simulants. In the Czech directive No. 38/2001 Collection of Law (Decree No. 38, 2001) are included only BPA and BADGE, but novel directive is awaited. The limits for BPF and BFDGE have not yet been established.

The results have been published of intensive investigations of the bisphenols contents in the food contact materials such as microwave susceptors (SHARMAN *et al.* 1995) or in foods (BIEDERMANN *et al.* 1996; SIMONEAU *et al.* 1999; HAMMARLING *et al.* 2000), as well as of their stability (LOSADA *et al.* 1991). The techniques most commonly used for the routine analysis of bisphenols are high performance liquid chromatography coupled with fluorescence detection (HPLC/FLD) (SIMONEAU *et al.* 1999; SCHMALZ *et al.* 1999; NERÍN *et al.* 2002) or gas chromatography with mass spectrometric detection (GC/MS) (COTTIER *et al.* 1997; DEL OLMO *et al.* 1997).

In this paper, a method is reported based on GC/MS for the determination of bisphenol A, bisphenol F, bisphenol A diglycidyl ether and bisphenol F diglycidyl ether migrated from food cans.

MATERIALS AND METHODS

Bisphenol A (99%) and bisphenol F (98%) were obtained from Aldrich (Sigma Aldrich, Germany), bisphenol A diglycidyl ether (97%), bisphenol F diglycidyl ether (97%, a mixture of 3 isomers: ortho-ortho, ortho-para, para-para) and acetonitrile (99%) were obtained from Fluka (Switzerland). Standard solutions in acetonitrile were prepared of all the compounds investigated (concentrations in the range from 1 to 80 µg/ml). The 99% acetic acid was obtained from Penta (Czech Republic) and 96% ethanol was obtained from Lachema (Czech Republic). The vials containing the calibration solutions or the samples were sealed with the PTFE faced septum. The calibration was measured in the range from 10 to 80 µg/ml.

During the experiments various kinds of samples were analysed: lacquers (lacquer on the glass plate), cans, can lids, metal tubes, metal barrels etc. The materials tested are commonly used in the food industry and were investigated because of the existing legislation requirements.

In the case of the real samples, 0.5 dm² of the packaging material tested was soaked with 50 ml

of acetonitrile for 24 hours at 25°C. The extract obtained was analysed by GC/MS. Another way was based on soaking with 50 ml of food simulants (distilled water, 3% acetic acid, and 10% ethanol) for 10 days at the temperature of 40°C. The extract obtained was evaporated to dryness using rotary vacuum evaporator (Büchi, Switzerland) and after reconstitution in 1 ml of acetonitrile, it was analysed by GC/MS. For each sample, two parallel determinations were carried out. Results calculation was based on the calibration dependence.

GC/MS system consisted of Hewlett Packard 5890 Series II gas chromatograph (Hewlett Packard, USA) with mass spectrometric detector 5972 Series (Hewlett Packard, USA). DB 5-MS (30 m × 0.32 mm i.d. with 0.25 µm film thickness) fused silica capillary column (J & W Scientific, USA) was used for

the chromatographic separation. GC conditions were as follows: initial oven temperature 150°C, initial time 2.0 min, oven temperature increase rate from 150°C to 270°C at 30°C/min after which the temperature was held at 270°C for 6 min. The carrier gas (helium) flow rate was held constant at 1.1 ml/min. The injector temperature was 260°C and the detector temperature was 300°C. Quantification was carried out under following conditions: electron ionisation at 70 eV, selected ion monitoring mode: m/z 228 for BPA, 200 for BPF, 325 for BADGE and 312 (for confirmation m/z 207) for BFDGE in the corresponding time windows.

RESULTS AND DISCUSSION

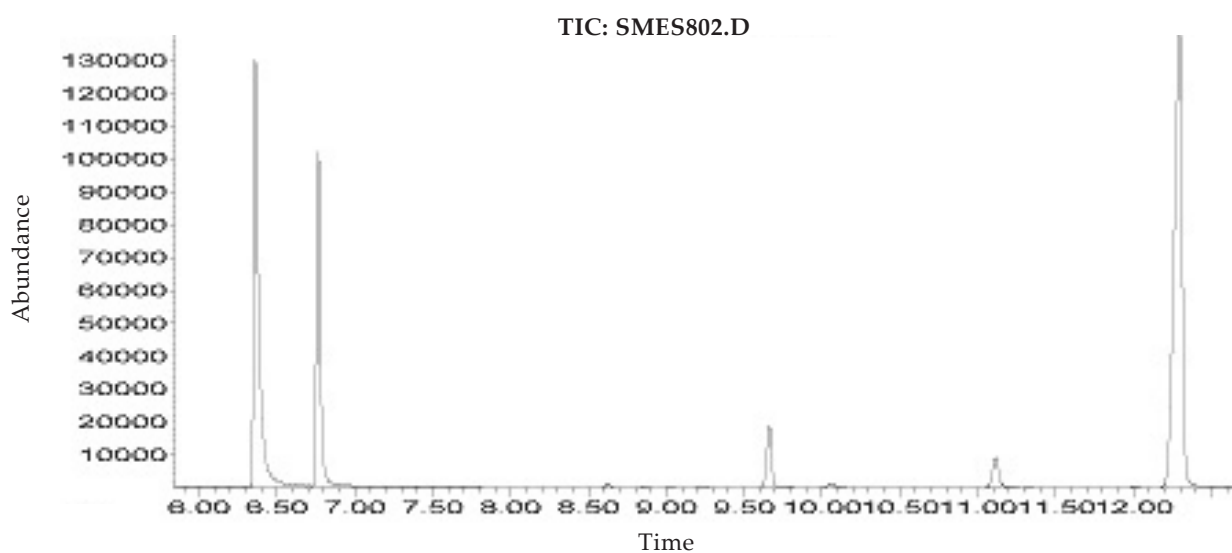
Repeatability, LOD (limit of detection), LOQ (limit of quantification)

Analytical characteristics, i.e. repeatability, LOD and LOQ, are summarised in Table 1. Repeatability of MS quantification expressed as RSD was measured with six replicates of standard solution injections for concentration 50 µg/ml.

Table 1 gives the summarised performance characteristics of the optimised GC/MS method. As can be seen, the values of RSD indicate good repeatability and it is interesting that they are

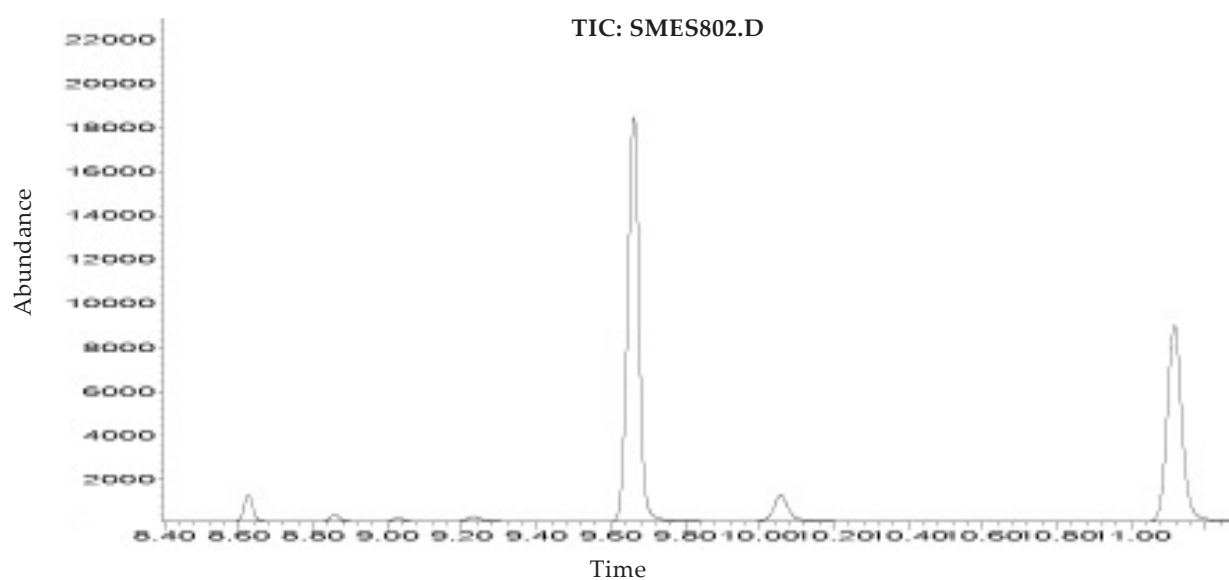
Table 1. Performance characteristics of GC/MS method

Compound	RSD (%)	LOD (µg/dm ²)	LOQ (µg/dm ²)
BPA	3.8	0.15	0.51
BPF	4.6	0.36	1.16
BADGE	4.4	0.28	0.88
BFDGE	5.0	0.86	2.77



*Retention times: BPF – 6.37 min, BPA – 6.76 min, BFDGE – 8.63 min, 9.66 min, 11.12 min, BADGE – 12.27 min

Figure 2. GC/MS chromatogram of a standard solution at the concentration level of about 50 µg/ml of bisphenol A, bisphenol F, bisphenol A diglycidyl ether and bisphenol F diglycidyl ether



*Retention times: BFDGE – 8.63 min, 9.66 min, 11.12 min

Figure 3. Detail of the previous GC/MS chromatogram

Table 2. Amounts of migrated bisphenols in packaging materials into acetonitrile (excluding samples 5^a, 5^b) (mg/dm²)

Sample	BPA	BPF	BADGE	BFDGE
Can No. 1	0.91×10^{-3}	3.41×10^{-3}	< LOD	< LOD
Can No. 2	< LOQ	< LOD	< LOD	1.86×10^{-3}
Can lid No. 1	2.02×10^{-3}	7.19×10^{-3}	1.49×10^{-3}	< LOD
Can lid No. 2	< LOQ	< LOD	0.01	< LOD
Lacquer No. 1	0.13	< LOD	3.67	0.13
Lacquer No. 2	4.7×10^{-3}	< LOD	2.93	0.03
Lacquer No. 3	1.91×10^{-3}	7.74×10^{-3}	0.06	< LOD
Lacquer No. 4	0.63×10^{-3}	< LOD	< LOD	0.01
Lacquer No. 5	0.34	< LOD	0.17	3.1×10^{-3}
Lacquer No. 5 ^a	0.19	< LOD	4.68×10^{-3}	0.08
Lacquer No. 5 ^b	0.23	< LOD	< LOD	< LOD
Metal barrel	< LOD	< LOD	< LOD	< LOD
Metal tube	< LOD	< LOD	< LOD	< LOD
Polycarbonate plastic piece	< LOQ	< LOD	< LOD	< LOD
Tin	< LOD	< LOD	< LOD	< LOD

^aextracted with 10% ethanol

^bextracted with distilled water

slightly increasing from BPA to BFDGE which is probably caused by the increase of the retention time and, consequently, by a greater band broadening of the peaks. The chromatographic separation of the compounds investigated is documented in Figures 2 and 3.

Levels determined in packaging materials

Table 2 gives the summarised results obtained with various kinds of packaging materials and different extraction media. As can be seen, acetonitrile proved to be a more efficient solvent than food simulants as compared in the case of lacquer No. 5. Based on this knowledge, the sample was first analysed using acetonitrile extraction, and only if the level exceeded the limit, the sample was repeatedly extracted with food simulants. A problem occurred with 3% acetic acid: after 10-days extraction, the lacquer was dissolved and thus GC analysis was practically impossible. In the case of the metal barrel designated for beer or of the metal tube, bisphenols migration was not detected but in the case of some epoxy based lacquers, the specific migration limit was exceeded with BADGE. Migration of BFDGE also occurred. Because no specific migration limits exist for BPF and BFDGE, any migration of these compounds detected is evaluated case to case.

Conclusions

The migrating levels of bisphenols as found in various can samples ranged in the case of BPA from 0.63×10^{-3} to 0.34 mg/dm^2 and in the case of BADGE from 1.49×10^{-3} to 3.67 mg/dm^2 , respectively. BPF and BFDGE were practically not detected in the can samples. The optimised GC/MS method proved to be a suitable technique for the routine and fast analysis of bisphenols.

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Souhrn

JORDÁKOVÁ I., DOBIÁŠ J., VOLDŘICH M., POUSTKA J. (2003): **Stanovení migrace bisfenolu A, bisfenolu F, bisfenolu A diglycidyletheru a bisfenolu F diglycidyletheru z potravinových konzervových plechovek pomocí plynové chromatografie s hmotnostním detektorem.** *Czech J. Food Sci.*, **21**: 85–90.

Laky používané na vnitřní povrch konzervových plechovek jsou převážně typu epoxidových polymerů nebo polyvinylchloridových organosolů. Tyto polymery jsou složeny z bisfenolu A (BPA) a bisfenolu F (BPF) a obsahují bisfenol A diglycidyl ether (BADGE) a bisfenol F diglycidyl ether (BFDGE) jako stabilizátory. Za vyšších teplot (autoklávování, mikrovlnný ohřev) je možná degradace těchto polymerů, a tím zvýšení rizika migrace bisfenolů z obalu do potravin. Byla vyvinuta jednoduchá metoda pro kvantitativní stanovení migrace BPA, BPF, BADGE a BFDGE z obalových materiálů. Vzorek polymeru byl extrahován acetonitrilem nebo potravinovými simulanty (destilovaná voda, 3% kyselina octová a 10% ethanol) a dále analyzován pomocí plynové chromatografie s hmotnostním detektorem (GC/MS). Tato metoda poskytuje pro sledované sloučeniny mez detekce v rozmezí 0,15–0,86 $\mu\text{g per dm}^2$ a mez stanovitelnosti v rozmezí od 0,51 do 2,77 $\mu\text{g/dm}^2$. Nalezená množství bisfenolu A a BADGE v různých vzorcích konzervových plechovek byla v rozmezí od $0,63 \times 10^{-3}$ do $0,34 \text{ mg/dm}^2$ a od $1,49 \times 10^{-3}$ do $3,67 \text{ mg/dm}^2$. Nálezy bisfenolu F a BFDGE prakticky nebyly ve vzorcích zaznamenány.

Klíčová slova: bisfenol A; bisfenol F; bisfenol A diglycidyl ether; bisfenol F diglycidyl ether; migrace; plynová chromatografie; hmotnostní spektrometrie

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