

Determination of bisphenol A in, and its migration from, PVC stretch film used for food packaging

J. López-Cervantes and P. Paseiro-Losada*

Departamento de Química Analítica, Nutrición y Bromatología,
Facultad de Farmacia, Universidad de Santiago de Compostela,
E-15782, Santiago de Compostela, La Coruña, Spain

(Received 29 November 2002; revised 11 March 2003; accepted 12 March 2003)

Bisphenol A (BPA) is used as an additive in polyvinyl chloride (PVC) products, including stretch films used for food packaging. The BPA contents were investigated of several brands of stretch film bought locally but marketed internationally or throughout Spain and which were presumably produced at different manufacturing plants. Their major components were identified by FTIR (Fourier Transform Infrared Spectrometry) and horizontal attenuated total reflectance, and the migration of BPA from these materials into the standard European Union food simulants was determined by high-performance liquid chromatography (HPLC) using both fluorescence (FL) and ultraviolet (UV) detection, the identity of the analyte being confirmed by gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-mass spectrometry (LC-MS). The two HPLC detection methods had different detection limits ($30 \mu\text{g l}^{-1}$ for UV, $3 \mu\text{g l}^{-1}$ for FL), but afforded virtually identical BPA determinations for the samples tested. BPA contents ranging from 40 to 100 mg kg^{-1} were found in three of the five PVC-based films analysed, and a content of 500 mg kg^{-1} was found in a fourth; for these determinations, extraction into acetonitrile was used. In standard tests of migration into water, 3% acetic acid and olive oil over 10 days at 40°C , migration from a given film was in all cases greatest into olive oil. Migration from the films with non-zero BPA contents ranged from 3 to $31 \mu\text{g dm}^{-2}$, values higher than those reported for many other food-contact materials, but lower than the European Union specific migration limit for BPA. PVC stretch film nevertheless may make a

significant contribution to contamination of foodstuffs by BPA, and should be taken into account in estimating BPA intake or exposure to this substance.

Keywords: bisphenol A, PVC, migration, food simulants, HPLC, fluorescence, UV

Introduction

World production of 2,2-bis(4-hydroxyphenyl)propane (bisphenol A, BPA CAS No. 80-05-7, EEC Ref. No. 13480) has increased from about 73 000 tonnes to an expected total in excess of 1 million tonnes in 2002 (González-Casado *et al.* 1998). Some 63% of this production is used to produce polycarbonate plastic resins, 27% for production of epoxy resin monomers and the remaining 10% in various other applications, including use as an antioxidant or inhibitor in the manufacture and processing of polyvinyl chloride (PVC) (Bisphenol A Global Industry Group of The Society of the Plastics Industry, Inc. 2002, UK Health and Safety Executive and Environment Agency 2002). Many of the products manufactured from BPA-based resins are designed for contact with food: polycarbonates, for example, are used in returnable beverage containers and in infant feeding bottles; and epoxy resins, following reaction with appropriate curing agents, are used as can liners.

The US National Institute for Occupational Safety and Health's Registry of Toxic Effects of Chemical Substances describes BPA as a primary irritant, a mutagen and an agent affecting the reproductive system (Registry of Toxic Effects of Chemical Substances, RTECS 1997). In recent years, BPA has been shown to mimic natural oestrogens, and there is concern about whether it may affect the endocrine system even at very low doses (Krishnan *et al.* 1993, Nagel *et al.* 1997, Howdeshell *et al.* 1999,

* To whom correspondence should be addressed.
e-mail: qnpaseir@usc.es

Laws *et al.* 2000, McNeal *et al.* 2000). While the plastics industry claims that BPA is safe when used in accordance with current regulations (Bisphenol A Global Industry Group of The Society of the Plastics Industry, Inc. 2002), leading independent environmental organizations consider that current legal limits are not stringent enough to protect humans and wildlife, and that the use of BPA should be discontinued wherever practicable (Friends of the Earth in London 2002, World Wildlife Fund 2002).

European Commission Directive 90/128 (1990) permits the use of BPA as a monomer or starting substance in the manufacture of plastic materials or articles intended to come into contact with foodstuffs provided that its migration from such materials or articles into food or food simulant does not exceed a specific migration limit (SML) of 3 mg kg^{-1} food, a limit treated as equivalent to 0.5 mg dm^{-2} when the plastic is a container, container lining or film (90/128/EEC). The European Commission's Scientific Committee on Food (2002) recently issued the opinion that in the light of the most recent toxicological information (UK Health and Safety Executive and Environment Agency 2002), the tolerable daily intake (TDI) specification for BPA should be lowered, at least provisionally, from the present 0.05 mg kg^{-1} to 0.01 mg kg^{-1} , and that research on the effects of BPA on humans should be continued (Scientific Committee on Food 2002). The 0.01 mg kg^{-1} limit would imply a new SML of 0.1 mg dm^{-2} , five times less than the current limit, for migration of BPA from plastic materials.

Numerous studies have been carried out on the concentration of BPA in environmental samples (Olmo *et al.* 1997, Lee and Peart 2000, Fukazawa *et al.* 2001, Yoshida *et al.* 2001), its residual concentration in polycarbonates and surface coatings, and its migration from these latter materials into foodstuffs or food simulants (Biles *et al.* 1997, Howe and Borodinsky 1998, Poskrobko *et al.* 2000, Sun *et al.* 2000, D'Antuono *et al.* 2001, Yoshida *et al.* 2001), but as far as is known, no analogous studies of materials in which BPA is used as an additive rather than as a major starting substance have been published (possibly because its use as an additive is subject to national legislations but has not been specifically regulated by European law). The present study determined BPA concentrations in PVC stretch film and its migration from this food packaging material into food and food simulants.

Materials and methods

Reagents

Bisphenol A, 99+% pure (Aldrich-Chemie, Steinheim, Germany); water obtained using Milli-Q apparatus from Millipore Ireland B.V. (Carrigtwohill, Ireland); glacial acetic acid (Scharlau, Barcelona, Spain); HPLC-grade *n*-heptane (Aldrich-Chemie, Darmstadt, Germany); HPLC-grade acetonitrile (Merck, Darmstadt, Germany); N-50 He and B-50 N₂ (Sociedad Española de Oxígeno, Madrid, Spain). Where 90% v/v acetonitrile is referred to below, it was obtained by diluting HPLC-grade acetonitrile with Milli-Q water.

Samples

Seven samples of food wrapping stretch film without any indications of composition or instructions about food-contact conditions (temperature, duration, etc.) were obtained from two local supermarkets. Five (identified in what follows as films 1, 2, 3, 6 and 7; see table 1) were rolls of different brands of domestic Clingfilm marketed internationally or throughout Spain (and presumably produced at different manufacturing plants), and two stretch films (samples 4 and 5) taken from large rolls used by the supermarkets, which gave no information about their suppliers. In subsampling the above material for analysis, care was always taken to cut subsamples from an unrolled length of film without stretching or folding it.

Table 1. Characteristics of the stretch films studied.

Film	Format	Composition*	Thickness (μm)
1	30 cm \times 30 m roll	PVC + phthalate	16
2	30 cm \times 60 m roll	PVC + phthalate	9
3	30 cm \times 100 m roll	PVC + phthalate	10
4	Large roll	PVC + phthalate	12
5	Large roll	PVC + phthalate	13
6	30 cm \times 30 m roll	PE	2
7	30 cm \times 30 m roll	PE	28

* As determined by FTIR and HATR.

Apparatus and operating conditions

- *Infrared spectrometry* was performed on a Mattson Genesis II FTIR apparatus running under WINFIRST software and equipped with a Pike Technologies horizontal attenuated total reflectance (HATR) accessory. Conventional transmission mode IR spectra were run over the range 400–4000 cm⁻¹ on film samples consisting of discs 1 cm in diameter, and HATR spectra were run on 1 × 8 cm strips placed on a ZnSe crystal.
- *Liquid chromatography with mass spectrometry (LC-MS)* was performed using a Spectra-Physics P200 binary pump and a Fisons VG Biotech Platform mass detector. The conditions used for identification of BPA are listed in table 2.
- *Gas chromatography with mass spectrometry (GC-MS)* was performed using a Fisons GC 8000 chromatograph with an MD 800 mass detector. The conditions used for identification of BPA are listed in table 3.
- *High-performance liquid chromatography with UV and fluorescence detection (HPLC-UV-FL)* was performed using a Hewlett-Packard HP 1100 chromatograph equipped with a diode array

Table 2. Conditions and instrument settings for identification of BPA by GC-MS.

Constant flow	2 ml min ⁻¹
Carrier gas	He
Column:	
Dimensions	30 m × 0.253 mm
Temperature limits	–60 to 325°C
Film surface	1.00 µm
Liquid phase	DB-5MS
Injector temperature	275°C
Split mode	1:20
Injection volume	1 µl
Column temperature programme	150°C (2 min) to 5°C min ⁻¹ to 270°C (5 min)
Mass spectrometer, FISIONS Instrument MD800	
Interphase temperature	500°C
Electron energy	50 eV
Electron multiplier	200 V
Full-scan	<i>m/z</i> 20–500
SIR mode	<i>m/z</i> 213, 228
<i>m/z</i> range	20–500
Electron impact	El + mode
Spectrum library	Wiley
Software	MassLab version 1.3, Windows 95

detector and a fluorescence scanning detector arranged in series. Conditions are listed in table 4.

- *Micrometry* was performed with a Palmer digital micrometer (Ref. 5900602).
- *Migration cells*, consisting of 20 ml, 23 × 75 mm glass tubes that were hermetically closed with Teflon septa, were purchased from Afora. S.A. (Barcelona, Spain) (Ref. No. 237501). Discs of film were mounted with an exposed disc diameter of 1.3 cm.

Procedures

Preliminary studies

Each film sample was subjected to an accelerated migration test in which a 4 dm² sample was immersed in 100 ml water in an hermetically closed glass vial that was then kept for 72 h in an oven at 60°C (82/711/CEE); after removal from the oven, the migration

Table 3. Conditions and instrument settings for identification of BPA by LC-MS.

Ionization mode	APCI (–)		
Mass range	20–500		
Probe temperature (optimized)	500°C		
Ionization source temperature	125°C		
Cone voltage (optimized)	50 eV		
Electron multiplier voltage	700 V		
Drying gas	N ₂ at 175 l h ^{–1}		
Selective ion recording (SIR)	<i>m/z</i> 213 base peak, 227		
Binary pump	Thermo Separation Products SpectraSERIES P200		
Injection volume	50 µl		
Column	Kromasil 100 C18 5 µ (15 cm × 0.4 cm)		
Mobile phase	A: acetonitrile B: Milli-Q water		
Flow rate	1 ml min ^{–1}		
Gradient	Time (min)	%A	%B
	0.00	30	70
	2.00	30	70
	20.00	80	20
	23.00	100	0.00
	30.00	100	0.00
Software	MassLynx version 1.03, Windows 3.1		

Table 4. Conditions and instrument settings for determination of BPA by HPLC.

Pump	Hewlett-Packard Quaternary HP 1100 pump		
Injection volume	50 μ l		
Thermostat	HP 1100		
Detector	Fluorescence (FL) HP 1100		
	Scan excitation range 220–380 nm		
	Ultraviolet HP 1100		
Degasser	Scan range 190–400 nm		
	HP 1100 Vacuum degasser		
	Wavelength		
Column	Fluorescence: excitation 225 nm, emission 305 nm		
	Ultraviolet: Sig. 225 nm, Ref. 360.1 nm		
	Kromasil 100 C18 5 μ (15 cm \times 0.4 cm)		
Mobile phase	A: acetonitrile		
Flow velocity	B: Milli-Q Water		
	1 ml min ⁻¹		
Gradient	Time (min)	%A	%B
	0.00	30	70
	2.00	30	70
	20.00	80	20
	23.00	100	0.00
	30.00	100	0.00
Software	HP Chem Station		

solution was filtered and analysed by scan-mode HPLC using both UV detection (scan range 200–340 nm) and fluorescence detection (excitation scan range 200–280 nm, emission wavelength 305 nm). The presence of BPA in the films was also investigated by extraction with acetonitrile for 24 h at 60°C.

Identification of BPA by GC-MS

To establish the optimal operational mode and limitations of the identification of BPA by GC-MS, successive dilutions of a standard 500 mg l⁻¹ solution of BPA in acetonitrile were run in full-scan mode and by single ion recording (SIR) of the MS base peak under the conditions listed in table 2. GC BPA peaks were identified by comparison of their mass spectra with that of the BPA standard and with a spectrum in the Wiley library.

Identification of BPA by LC-MS

Optimal conditions and limitations of the identification of BPA by LC-MS were established by procedure similar to that used for GC-MS, although for LC-MS, additionally, MS optimization trials were run with probe temperatures ranging from 200 to 500°C and

cone voltages ranging from 20 to 70 eV. Fixed parameters in these trials are listed in table 3.

Determination of BPA by HPLC-FL and HPLC-UV

Calibration

A stock 1 mg ml⁻¹ solution of BPA in acetonitrile was made up by weighing 100 mg BPA into a 100-ml volumetric flask to the nearest 0.1 mg and filling to the mark with acetonitrile on water. Intermediate standards (0.1 mg ml⁻¹) were prepared as required by 10-fold dilution of the stock solution, and calibration standards by transferring 0.15, 0.5, 1.0, 2.0 or 4.0 ml of an intermediate standard to a 100 ml volumetric flask and making up to the mark with acetonitrile. Calibration lines were constructed by running these standards under the conditions listed in table 4, determining the area of the peak eluting at around 9.8 min, and regressing this area on concentration; two samples of each standard were each run three times.

Limit of detection

The noise of the analytic signal was estimated as the maximum height of a chromatogram of acetonitrile in the 9.3–10.3-min region. The limit of detection was estimated by running successive dilutions of the stock BPA solution until the height of the BPA peak was about three times this noise level (Momson 1990).

Precision

Measurement precision was estimated by running a 0.26 mg l⁻¹ solution of BPA in acetonitrile 10 times and calculating the relative standard deviation.

Recovery

The accuracy of the method for determining migration into acidic simulant was estimated by performing a standard migration test (see below) for migration from PVC film No. 1 into 3% acetic acid spiked with 0.2 mg l⁻¹ BPA. Its accuracy for determining migration into olive oil was estimated similarly, except that the migration solution was in this case made up by dissolving 0.1 mg BPA in 100 ml tetrahydrofuran, making 50 ml of this solution up to 100 ml with *n*-heptane, and making 1 ml of this intermediate solution up to 40 ml with olive oil.

Determination of BPA contents of PVC stretch films

A total of 1 dm² samples were cut from the PVC films, weighed and extracted with 100 ml acetonitrile for 24 h in a hermetically sealed glass flask at 60°C. The extract solutions were filtered and analysed by HPLC-UV-FL, and when a BPA peak was found, the identity of the analyte was confirmed by both GC-MS and LC-MS.

Determination of migration from PVC films into official EU food simulants

Migration of BPA from PVC films into the official EU simulants of aqueous, acid and fatty foods (water, 3% w/v acetic acid and olive oil, respectively; 82/711/EEC) was determined by subjecting film discs 13 mm in diameter (contact area 0.01327 dm²) to the standard test conditions (10-day exposure at 40°C) in migration cells containing 1 ml simulant. Migration into the EU simulant of alcoholic beverages, 10% ethanol, was not investigated because of the unlikelihood of stretch film being used as a contact material for alcoholic beverages. Six replicate tests were performed for each stretch film. The aqueous and acidic migration solutions were analysed directly by HPLC-UV-FL, while migration into olive oil was determined by diluting a 1 ml sample of the migration solution with 1 ml *n*-heptane, adding 2 ml 90% v/v acetonitrile, shaking the mixture for 2 min, centrifuging for 5 min, and analysing the denser acetonitrile layer by HPLC-UV-FL. Whenever a BPA peak was found, the identity of the analyte was confirmed by both GC-MS and LC-MS.

Results and discussion

Identification of stretch film material by FTIR

The seven stretch films listed in table 1 were analysed by FTIR transmission spectroscopy and HATR spectroscopy of both sides of the film. Films were judged to be monolayers if the HATR spectra of the two sides coincided (as was the case for all seven). Comparison of the IR spectra with those published in polymer spectrum libraries identified five of the films (three domestic brands, two used in the supermarkets)

as PVC containing a phthalate plasticizer, and the other two as polyethylene (PE). Measured film thicknesses are shown in table 1.

Preliminary studies

In the accelerated test of migration into water, four PVC samples showed a main peak at a retention time of 9.3 ± 0.3 min. Both the UV and fluorescence spectra of this peak had maxima at 225 and 275 nm (figures 1 and 2). For some samples fluorescence detection also showed a minor peak at 4.3 ± 0.2 min with spectral maxima at 215 and 265 nm (figures 1 and 3A). Figure 3 shows typical chromatograms obtained at the wavelengths of the main spectral peak of each detection method ($\lambda_{\text{ex}} = 225$ nm, $\lambda_{\text{em}} = 305$ nm for FL, $\lambda = 225$ nm for UV). Comparison of the spectra of figure 2 with others contained in our personal HPLC library suggested the presence in the main peak of compounds related to BPA, of which our laboratory has broad experience (Paseiro-Losada *et al.* 1991, 1993). That this peak in fact consisted of BPA was confirmed by concentrating migration solutions to dryness, redissolving the residue in acetonitrile, and analysing this solution by GC-MS under conditions in which BPA elutes with a retention time of 16.45 min (see below). The chromatograms afforded by the PE films showed no significant peaks of interest, and no further experiments were performed on these PE films.

When acetonitrile was used as extractant, an HPLC peak with a retention time of 26.7 min appeared in addition to the two peaks produced by migration into water. GC-MS chromatograms showed the BPA peak at 16.45 min and a peak identified as due to the plasticizer di(2-ethylhexyl)phthalate (DEHP) at 14.45 min. It was concluded that the analyte composing the minor HPLC peak at 4.3 min was not resolved as a distinct peak by GC-MS, and that the new HPLC peak at 26.7 min was DEHP, which had failed to migrate into water under the conditions of the accelerated test. These conclusions were corroborated by LC-MS (see below), which in both positive- and negative-ion full-scan modes likewise failed to detect the HPLC-UV-FL peak at 4.3 min.

As noted above, the use of BPA as an additive is not regulated by European law, and the same holds of DEHP. However, whereas a number of studies have approached the determination of DEHP in plastic materials and foodstuffs, this is not the case for BPA

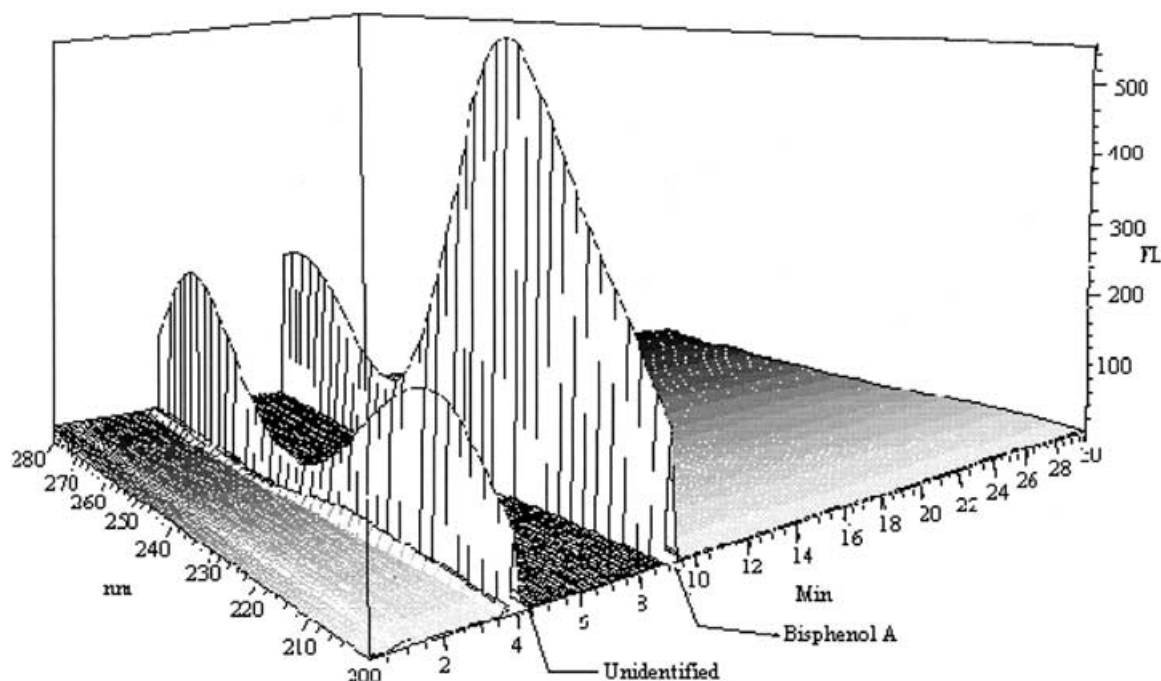


Figure 1. Spectrographic sections of a 3D spectrochromatogram afforded by HPLC-FL analysis of an aqueous extract of a PVC stretch film. The spectrum obtained at 9.3 min identifies bisphenol A.

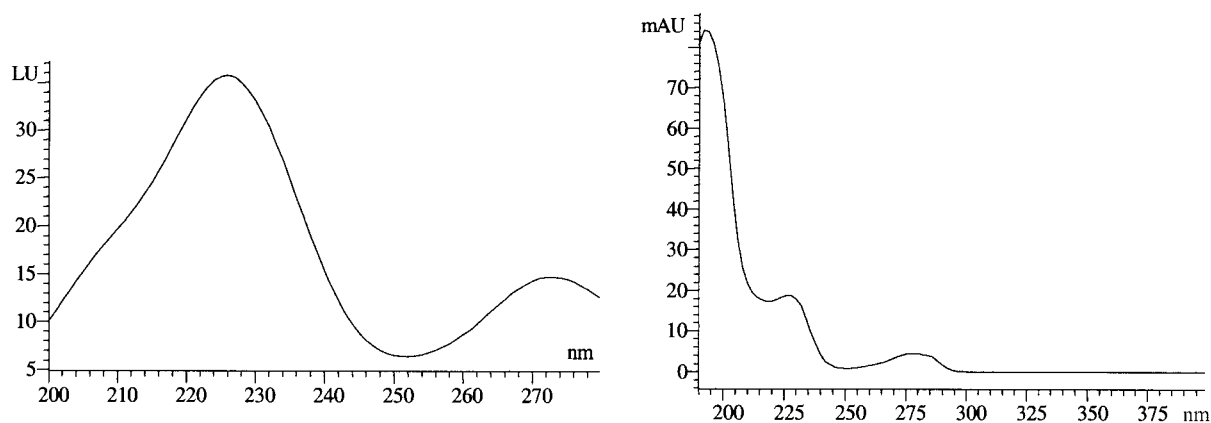


Figure 2. Fluorescence excitation ($\lambda_{em}=305$ nm) and UV spectra (left and right, respectively) of the peak occurring at 9.3 min in the HPLC-UV-FL chromatograms of an aqueous extract of a PVC stretch film.

used as an additive. Its presence in the PVC films studied here may have been due either to its being used as a stabilizer in the preparation of DEHP (Abudillin *et al.* 1984, Cerbulis and Byler 1986, Castle 1988, 1989, ATSDR 2000) or to its direct addition to the PVC resin as an antioxidant.

Identification of BPA by GC-MS

Under the GC conditions used (table 2), BPA eluted at 16.45 min. The detection limit in full-scan mode was $500 \mu\text{g l}^{-1}$, but a limit of $50 \mu\text{g l}^{-1}$ was achieved by single-ion recording (SIR) of the demethylated

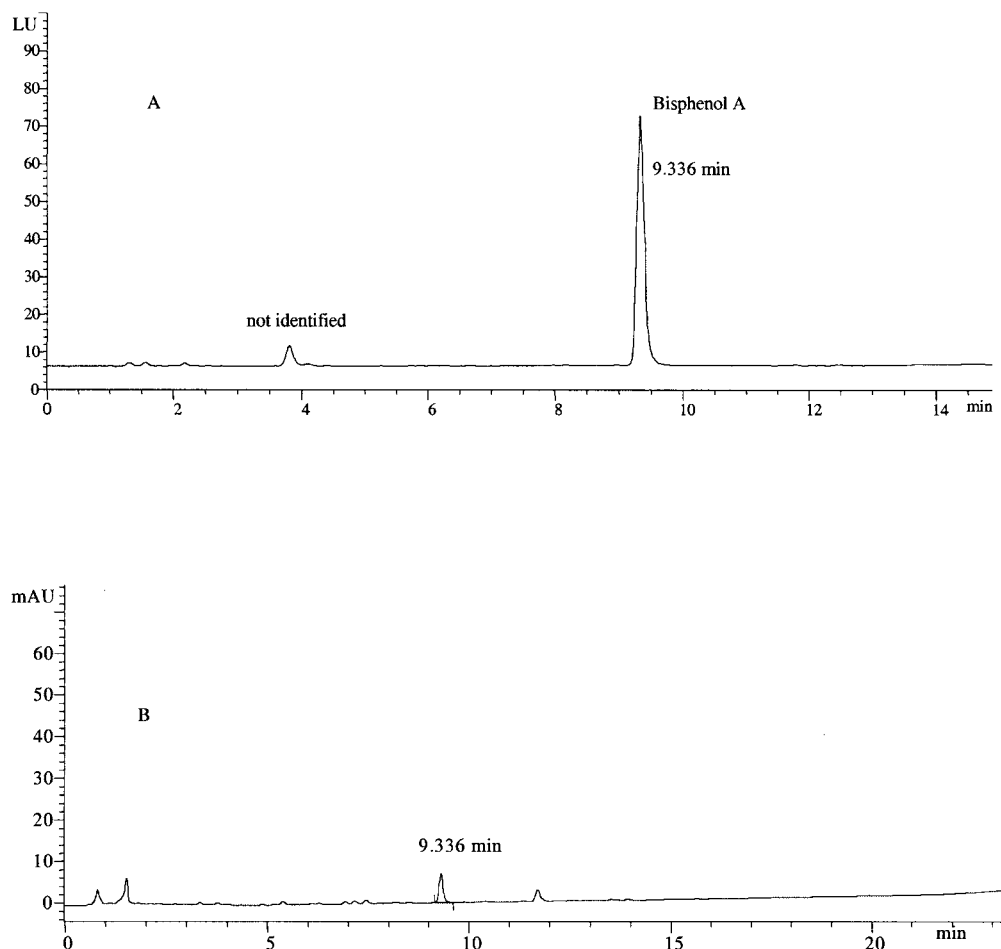


Figure 3. HPLC chromatograms of an aqueous extract of a PVC stretch film: (A) with fluorescence detection ($\lambda_{ex} = 225$ nm, $\lambda_{em} = 305$ nm); (B) with UV detection ($\lambda = 225$ nm).

fragment at $m/z = 213$ (the MS base peak) (figure 4B). SIR mode has the additional advantage of reducing the risk of interferences. Figure 4A shows the result of using these latter detection conditions to obtain a GC-MS chromatogram of the acetonitrile extract of a PVC film, and figure 4B shows the mass spectrum of its 16.45 min peak, which was identified as corresponding to BPA as described above. A similar spectrum was reported by Olmo *et al.* (1997) in a study of BPA in water.

Identification of BPA by LC-MS

Under the LC conditions used (table 3), BPA eluted at 10.38 min. Figure 5A shows a chromatogram run under the optimal conditions (probe temperature

500°C, cone voltage 50 eV) in full-scan mode, and figure 5B shows the mass spectrum of the peak at 10.38 min. The detection limit in full-scan mode was $500 \mu\text{g l}^{-1}$, but a limit of $50 \mu\text{g l}^{-1}$ was achieved using SIR mode for the deprotonated fragment at $m/z = 227$ (the MS base peak). Figure 6A shows the result of using these conditions to obtain a chromatogram of the acetonitrile extract of a PVC film, and figure 6B shows the mass spectrum of the 10.38 min peak of this chromatogram.

Determination of BPA by HPLC-FL or HPLC-UV

Table 5 lists the parameters of the calibration lines constructed as described above when calibration standards made up in acetonitrile were used.

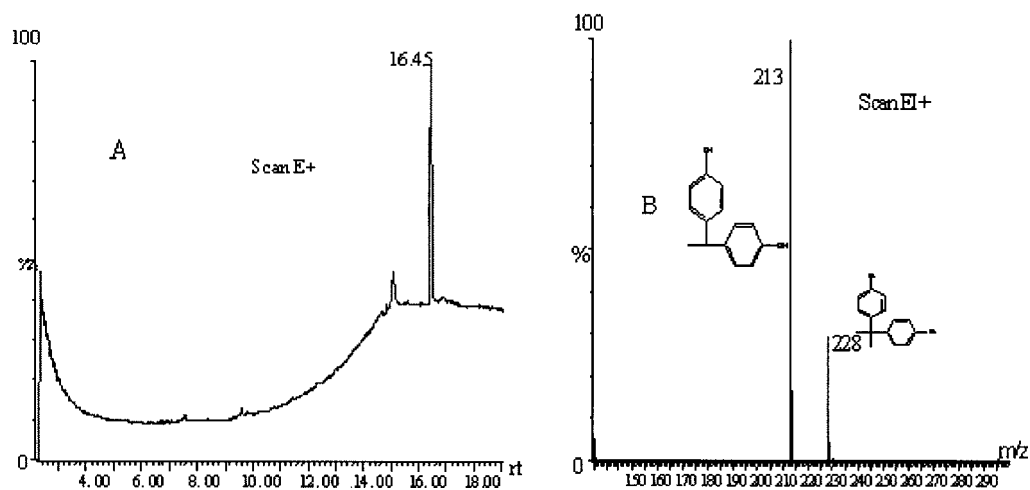


Figure 4. (A) GC-MS chromatogram of an acetonitrile extract of a PVC stretch film; (B) mass spectrum of the 16.45 min peak of A.

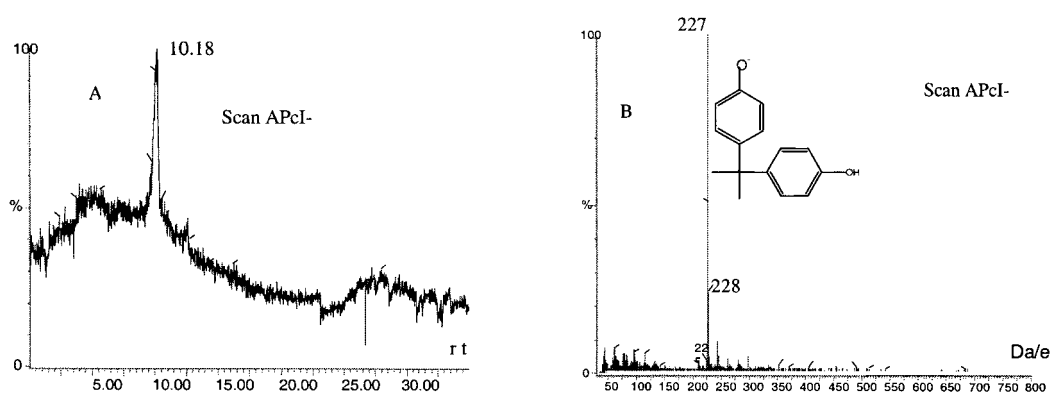


Figure 5. (A) LC-MS chromatogram of a 0.2 mg kg^{-1} solution of bisphenol A in acetonitrile (for conditions, see table 2); (B) mass spectrum of the 10.18 min peak of A.

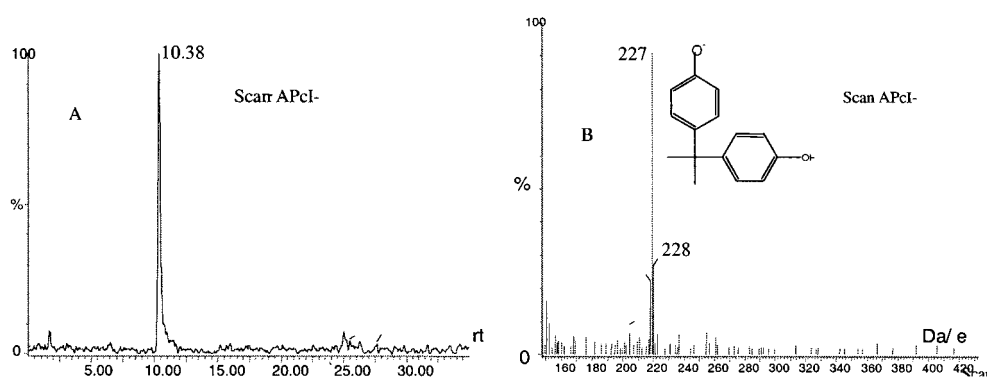


Figure 6. (A) LC-MS chromatogram of an acetonitrile extract of a PVC stretch film, run in SIR mode for $m/z = 227$; (B) mass spectrum of the 10.38 min peak of A.

For both UV and fluorescence detection, the correlation coefficient was >0.999 . Calibration lines with virtually identical parameters were obtained when the final calibration standards were made up using water instead of acetonitrile. The limits of detection were ($3\mu\text{g l}^{-1}$ for fluorescence detection and $30\mu\text{g l}^{-1}$ for UV), values similar to those obtained by others who have determined BPA in aqueous matrices (Olmo *et al.* 1997, González-Casado *et al.* 1998, Lee and Peart 2000). The relative standard deviation was 0.90% for fluorescence detection and 0.93% for UV. Recovery from 3% acetic acid was 109.5% with fluorescence detection and 105.1% with UV ($n=6$); recovery from olive oil was 100.4% with fluorescence detection ($n=6$).

BPA contents of PVC stretch films

BPA was not detected in film 2; was found at levels of $43\text{--}98\text{ mg kg}^{-1}$ film in films 3–5; and had a level of 483 mg kg^{-1} film in film 1 (table 6). This last figure is the highest free BPA content reported for a food-contact material, reusable polycarbonates having contents of $10\text{--}47\text{ mg kg}^{-1}$ (Biles *et al.* 1997) and polycarbonate infant feeding bottles contents of $10\text{--}136\text{ mg kg}^{-1}$ (Mountfort *et al.* 1997). It seems likely that in the manufacture of film 1 BPA was added

directly to PVC as an antioxidant, whereas in films 3–5 it was incorporated with DEHP. The EU has established no limit on the residual quantity of BPA in plastics; assuming that all BPA in film 1 would migrate, its migration would be less than the current EU SML of 0.5 mg dm^{-2} but comes close to the likely future limit of 0.1 mg dm^{-2} , which would probably be exceeded by thicker films.

Migration from PVC stretch films into official EU food simulants

Given the difficulty of determining migration into complex matrixes, EU law regards substances and materials as complying with migration limits if they comply with these limits in tests of migration into the officially recognized simulants. In this work, no migration of BPA from film 2 was detected; no migration from film 4 into water or acetic acid was detected; migration from films 3 and 5, and from film 4 into olive oil, ranged from 3 to $7\mu\text{g dm}^{-2}$; while for film 1, migration into water and acetic acid was $11\text{--}12\mu\text{g dm}^{-2}$ and migration into olive oil $31\mu\text{g dm}^{-2}$ (table 7). Although some of these values are greater than those reported for migration of BPA from numerous other food-contact materials (Biles *et al.* 1997, $0.1\text{--}13\text{ ppb}$; D'Antuono *et al.* 2001, 1.2 ppb ;

Table 5. Analytical performance parameters for fluorescence and ultraviolet detection.

Parameter	Fluorescence	Ultraviolet
Calibration line*		
y -Intersect (a)	−18.3	−6.2363
Slope (b)	1795	158.37
Correlation coefficient (r)	0.9997	0.9995
Linear dynamic range (mg l^{-1})	0.015–4.00	0.125–4.00
Detection limit ($\mu\text{g l}^{-1}$)	3.00	30.00

Table 6. BPA contents of PVC stretch films.

Film*	BPA content (mg kg^{-1} film)	BPA content ($\mu\text{g dm}^{-2}$)
1	483	61.2
2	n.d.	n.d.
3	43	6.4
4	96	13.1
5	98	13.1

* For numbering, see table 1.
n.d., Not detected.

Table 7. Migration of BPA from PVC stretch films into food simulants ($\mu\text{g dm}^{-2}$), as determined by HPLC-FL.

Simulant	Film sample number*				
	1	2	3	4	5
Water	11.5 ± 0.98	n.d.	3.2 ± 0.29	n.d.	3.5 ± 0.34
Acetic acid (3% w/v)	11.9 ± 1.22	n.d.	4.2 ± 0.33	n.d.	3.1 ± 0.07
Olive oil	30.7 ± 1.75	n.d.	6.5 ± 0.80	5.3 ± 1.70	6.1 ± 0.80

* For numbering, see table 1.
n.d., Not detected.

Yoshida *et al.* 2001, 11 µg/can), they are all below both the current EU SML and the likely future SML.

Conclusions

The safety of BPA is currently controversial and its use is subject to legal limits. It is important to bear in mind that total intake of BPA by consumers may be contributed to not only by those products currently subject to legislation in this respect, but also by others in which BPA is employed. The present study developed methods for detecting the presence of BPA in film and confirming its identity, and for determining its concentration in these films and its migration from them into the official EU food simulants. Among the seven different film samples examined, BPA was only detected in PVC-based films. The BPA contents of these latter varied from undetectable to nearly 500 g kg⁻¹. Although migration from some of the PVC-based stretch films was greater than has been reported for numerous other food-contact materials, it was in all cases less than both the current EU SML for BPA (0.5 mg dm⁻²) and the more stringent limit likely to be imposed in the near future, 0.1 mg dm⁻².

Acknowledgements

Work was supported by the Spanish Interministerial Committee for Science and Technology (CICYT) and the European Commission under Project 1FD97-2167-C02-01.

References

- ABUDILLIN, M. I., ZUEVA, N. P., and MINSKER, K. S., 1984, Stabilization of plasticized poly(vinyl chloride) by phenolic compounds. *Plasticheskie Massy*, **1**, 15–17.
- AGENCY FOR TOXIC SUBSTANCES AND DISEASE REGISTRY (ATSDR), 2000, *Toxicological Profile for Di(2-ethylhexyl)phthalate (DEHP)* — Draft for Public Comment (Atlanta: US Department of Health and Human Services, Public Health Service) [http://www.atsdr.cdc.gov/tfacts9.html] (accessed 3 November 2002).
- BILES, J. E., MCNEAL, T. P., and BEGLEY, T. H., 1997, Determination of bisphenol A migrating from epoxy can coatings to infant formula liquid concentrates. *Journal of Agriculture and Food Chemistry*, **45**, 4697–4700.
- BISPENOL A GLOBAL INDUSTRY GROUP OF THE SOCIETY OF THE PLASTICS INDUSTRY, INC., THE BISPENOL A SECTOR GROUP OF THE EUROPEAN CHEMICAL INDUSTRY COUNCIL and the JAPAN CHEMICAL INDUSTRY ASSOCIATION, 2002, [http://www.bisphenol-a.org] (accessed 14 November 2002).
- CASTLE, L., MAYO, A., and GILBERT, J., 1989, Migration of plasticizers from printing inks into food. *Food Additives and Contaminants*, **6**, 437–443.
- CASTLE, L., MERCER, A., and STARTIN, J. R., 1988, Migration from plasticized film into foods. 3. Migration of phthalate, sebacate, citrate and phosphate esters from film used for retail food packaging. *Food Additives and Contaminants*, **5**, 9–20.
- CERBULIS, J., and BYLER, D. M., 1986, Isolation and detection of dialkyl 1 phthalates from pork. *Journal of Agriculture and Food Chemistry*, **34**, 198–200.
- D'ANTUONO, A., CAMPO, D. V., BALBO, L. A., SOBRAL, S., and REZAANO, I., 2001, Determination of bisphenol A (BPA) in food-simulating liquids using LCED with a chemically modified electrode. *Journal of Agriculture and Food Chemistry*, **49**, 1098–1101.
- DEL OLMO, M., GONZÁLEZ-CASADO, A., NAVAS, N. A., and VILCHEZ, J. L., 1997, Determination of bisphenol A (BPA) in water by gas chromatography-mass spectrometry. *Analytica Chimica Acta*, **346**, 87–92.
- EUROPEAN COMMISSION, 1982, Commission Directive 82/711/EEC of 18 October 1982, Laying down the basic rules necessary for testing migration of the constituents of plastic materials and articles intended to come into contact with foodstuffs. *Official Journal of the European Communities*, **L 297**.
- EUROPEAN COMMISSION, 1990, Commission Directive 90/128/EEC of 23 February 1990, Relating to plastics materials and articles intended to come into contact with foodstuffs. *Official Journal of the European Communities*, **L 75/19**.
- FRIENDS OF THE EARTH IN LONDON, 2002 [http://www.foe.co.uk/] (accessed 10 November 2002).
- FUKAZAWA, H., HOSHINO, K., SHIOZAWA, T., MATSUSHITA, H., and TERAOKA, Y., 2001, Identification and quantification of chlorinated bisphenol A in waste water from waste paper recycling plants. *Chemosphere*, **44**, 973–979.
- GONZÁLEZ-CASADO, A., NAVAS, N., DEL OLMO, M., and VILCHEZ, J. L., 1998, Determination of bisphenol A in water by micro liquid-liquid extraction followed by silylation and gas chromatography-mass spectrometry analysis. *Journal of Chromatographic Sciences*, **36**, 565–569.
- HOWDESHELL, K. L., HOTCHKISS, A. K., THAYER, K. A., VANDENBERGH, J. G., and VOM SAAL, F. S., 1999, Exposure to bisphenol A advances puberty. *Nature*, **401**, 763–764.
- HOWE, R. S., and BORODINSKY, L., 1998, Potential exposure to bisphenol A from food-contact use of polycarbonate resins. *Food Additives and Contaminants*, **15**, 370–375.
- KRISHNAN, A. V., STATHIS, P., PERMUTH, S. F., TOKES, L., and FELDMAN, D., 1993, Bisphenol A: an estrogenic substance is released from polycarbonate flasks during autoclaving. *Endocrinology*, **132**, 2279–2286.
- LAWS, S., CAREY, S. A., FERRELL, J. M., BODMAN, G. J., and COOPER, R. L., 2000, Estrogenic activity of octylphenol, nonylphenol, bisphenol A and methoxychlor in rats. *Toxicological Sciences*, **54**, 154–167.
- LEE, H.-B., and PEART, E. T., 2000, Determination of bisphenol A in sewage effluent and sludge by solid-phase and supercritical fluid extraction and gas chromatography/mass spectrometry. *Journal of AOAC International*, **83**, 290–297.
- MCNEAL, T. P., BILES, J. E., BEGLEY, T. H., CRAUN, J. C., HOPPER, M. L., and SACK, C. A., 2000, Determination of suspected endocrine disruptors in foods and food packaging

- (Washington, DC: US Food and Drug Administration), **747**, pp. 33–52.
- MOMSON, G. H., 1990, Accuracy and precision revisited. *Analytical Chemistry*, **52**, 2242–2249.
- MOUNTFORT, K. A., KELLY, J., JICKELLS, S. M., and CASTLE, L., 1997, Investigations into the potential degradation of polycarbonate baby bottles during sterilization with consequent release of bisphenol A. *Food Additives and Contaminants*, **14**, 737–740.
- NAGEL, S. C., VOM SAAL, F. S., THAYER, K. A., DHAR, M. G., BOECHLER, M., and WELSHONS, W. V., 1997, Relative binding affinity-serum modified access (RBA-SMA) assay predicts the relative *in vivo* bioactivity of the xenoestrogens bisphenol A and octylphenol. *Environmental Health Perspectives*, **103**, 734–742.
- PASEIRO-LOSADA, P., LÓPEZ-MAHIA, P., VAZQUEZ-ODORIZ, L., SIMAL-LOZANO, J., and SIMAL-GÁNDARA, J., 1991, Sensitive and rapid reversed-phase liquid chromatography — fluorescence method for determining bisphenol A diglycidyl ether in aqueous-based food simulants. *Journal of AOAC International*, **74**, 925–928.
- PASEIRO-LOSADA, P., SIMAL-LOZANO, J., PAZ-ABUIN, S., LÓPEZ-MAHIA, P., and SIMAL-GÁNDARA, J., 1993, Kinetics of the hydrolysis of bisphenol A diglycidyl ether (BADGE) in water-based food simulants. Implications for legislation on the migration of BADGE-type epoxy resins into foodstuffs. *Fresenius' Journal of Analytical Chemistry*, **345**, 527–532.
- POSKROBK, J., DEJNEGA, M., and KIEDIK, M., 2000, High performance liquid chromatography with multi-wavelength detection of the bisphenol A impurities. *Journal of Chromatography A*, **883**, 291–297.
- REGISTRY OF TOXIC EFFECTS OF CHEMICAL SUBSTANCES (RTECS), 1998, National Institute for Occupational Safety and Health (NIOSH), [<http://www.cdc.gov/niosh/rtecs.htm>] (accessed 5 November 2002).
- SCIENTIFIC COMMITTEE ON FOOD, 2002, *Opinion on Bisphenol A* (Brussels: European Commission). SCF/CS/PM/3936 Final [http://europa.eu.int/comm/food/fs/sc/scf/out128_en.pdf] (accessed 15 November 2002).
- SUN, Y., WADA, M., AL-DIRBASHI, O., KURODA, N., NAKAZAWA, H., and NAKASHIMA, K., 2000, High performance liquid chromatography with peroxyoxalate chemiluminescence detection of bisphenol A migrated from polycarbonate baby bottles using 4-(4,5-diphenol-1H-imidazol-2-yl)benzoyl chloride as a label. *Journal of Chromatography B*, **749**, 49–56.
- UK HEALTH AND SAFETY EXECUTIVE and ENVIRONMENT AGENCY, 2002, *Risk Assessment of Bisphenol A*. European Chemical Bureau Draft Report R325_0202_env_hh [<http://ecb.jrc.it/existing-chemicals/>] (accessed 2 November 2002).
- WORLD WILDLIFE FUND (WWF), 2002 [<http://www.worldwildlife.org/>] and WWF Global network [<http://panda.org/>] (accessed 12 November 2002).
- YOSHIDA, T., HORIE, M., HOCINO, Y., and NAKAZAWA, H., 2001, Determination of bisphenol A (BPA) in canned vegetables and fruit by high performance liquid chromatography. *Food Additives and Contaminants*, **18**, 69–75.