Determination of the Diglycidyl Ether of Bisphenol A and Its Derivatives in Canned Foods

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Migration of the diglycidyl ether of bisphenol A (DGEBA) to food from can enamels and can pull-top seals is reported. Derivatives of DGEBA are also determined in some foods. Levels of DGEBA in the foods surveyed in this study range from nondetected (<0.3 ppb) to 50 mg/kg as determined by liquid−liquid extraction or solid-phase extraction coupled with high-pressure liquid chromatography using fluorescence detection. Confirmation of the analytes is by gas and/or liquid chromatography with mass spectral analysis. Fourier transform infrared spectroscopy with 30° specular reflectance/transmittance is used to characterize the coated food contact surfaces. Stability studies with DGEBA in water, acid, and saline solutions show conversion to the hydrolysis products and chloro adducts occurs readily. The presence of DGEBA derivatives in food demonstrates that analysis for DGEBA migration alone is not a good indicator of total migration from can coatings to foods.

Keywords: *Diglycidyl ether of bisphenol A; epoxy; vinyl plastisol; can coating; migration*

INTRODUCTION

The diglycidyl ether of bisphenol A, CAS Registry No. 1675-54-3, more commonly known as DGEBA (or BADGE in the European Community), is used in a number of food-packaging applications where migration to food can occur. Epoxy polymers based on DGEBA are used in a wide range of applications because they are resistant to solvents and can bond to a variety of substrates, especially metals (Gannon, 1990). DGEBA is also used as a stabilizer in vinyl plastisols and organosols to scavenge hydrogen chloride, which is formed during the decomposition of poly(vinyl chloride) (Pschorr, 1962; Perry, 1962). Whenever a polymeric material is in contact with food, the residual monomer, solvents, and additives in the polymer may migrate to the food. This is especially true when polymers are exposed to foods and beverages at elevated temperatures, that is, heat process canning operations. Previous work has shown that DGEBA migrates to various media from a variety of applications in which it is a component of a polymeric material, that is, adhesives used in microwave susceptor packaging (Begley et al., 1991; Sharman et al., 1995), vinyl coatings (Biedermann et al., 1996; Cottier et al., 1997), can enamels (Paseiro Losada et al., 1991; Simal Gandara et al., 1993), water pipe coatings (Crathorne et al., 1986), and dental sealants (Olea et al., 1996).

Recently, Biedermann et al. (1996) and MAFF (1997) have reported DGEBA migration from the vinyl organosol coatings of pull-top cans to fish products. Some of these reported amounts are well above the 1 mg/kg specific migration limit for DGEBA and its hydrolysis products set by the European Union. Cottier et al. (1997) have reported methods for the determination of DGEBA as well as the monochloro and dichloro adducts of DGEBA and the diglycidyl ether of bisphenol F (DGEBF) in coating extracts. Our present work demonstrates that in addition to DGEBA, both the mono- and dichloro adducts of DGEBA are present in some of the surveyed foods. We also performed tests that show DGEBA is hydrolyzed under relatively mild conditions, compared to those encountered in the food canning processes. Five hydrolysis products of DGEBA were identified in the course of this study (Figure 1).

We have developed protocols to characterize the coating on the food contact surface (FCS) of a can and to determine the potential migrants from the can surface. Additionally, protocols for determining DGEBA and its derivatives in canned fish products, cola beverages, and infant formula have been developed. The FCS of a can is analyzed by Fourier transform infrared spectroscopy (FT-IR). The FCS is also extracted with chloroform and the extract qualitatively analyzed by high-pressure liquid chromatography with fluorescence detection (HPLC). DGEBA and its derivatives in the liquid portion of the canned fish products were determined by separating the liquid from the food followed by a liquid−liquid extraction (LLE) before the extract was analyzed by HPLC. Canned diet cola beverages were also prepared for analysis by LLE and analyzed by HPLC. Canned liquid infant formula was tested for DGEBA by using a solid-phase extraction (SPE) concentration step prior to HPLC analysis. Food extracts found to be presumptive-positive for DGEBA and its derivatives by HPLC were then analyzed by gas chromatography with mass selective detection (GC/MS) and/or liquid chromatography with mass spectrometric detection (LC/MS) for confirmation.

EXPERIMENTAL PROCEDURES

Reagents. All solvents, unless otherwise specified, were of HPLC grade and purchased from Burdick and Jackson, Inc. (Muskegon, MI). Hydrochloric acid was of ACS reagent grade from J. T. Baker (Philipsburg, NJ). Sodium chloride was of Baker analyzed reagent grade from J. T. Baker. The DGEBA was of high purity, supplied by Shell Chemical Co. (Houston,

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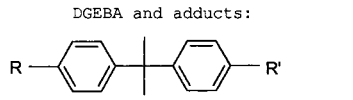

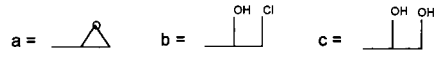

R=	R'=	[1]MW	Abbreviation	CAS registry #
a	a	340	[2]DGEBA	16754-54-3
a	b	376	[3]DGEBA-Cl	13836-48-1
b	b	412	[4]DGEBA-2Cl	4809-35-2
a	c	358	[5]DGEBA-2OH	76002-91-0
b	c	394	[6]DGEBA-Cl-2OH	---------
c	c	376	[7]DGEBA-2OH-2OH	5581-32-8

1) LC-MS observed all molecular ion species as the water ([M+] + 18) adduct.

2) 2,2-Bis[4-(2,3-epoxy-propanyl-oxy)phenyl]propane

3) 2-[4-(2,3-epoxy-propanyl-oxy)phenyl]-2-[4-(2-hydroxy-3-chloro-propanyl-oxy)phenyl]propane

4) 2,2-Bis[4-(2-hydroxy-3-chloro-propanyl-oxy)phenyl]propane

5) 2-[4-(2,3-epoxy-propanyl-oxy)phenyl]-2-[4-(2,3-dihydroxy-propanyl-oxy)phenyl]propane

6) 2-[4-(2-hydroxy-3-chloropropanyloxy)phenyl]-2-[4-(2-hydroxy-3-chloropropanyloxy)phenyl]propane

7) 2,2-Bis[4-(2,3-dihydroxypropanyloxy)phenyl]propane

Figure 1. Molecular structures, weights, abbreviations used in text, and CAS registry numbers (supplied by the authors) for DGEBA and DGEBA adducts.

TX). Water was distilled and then purified by a Milli-Q water purification system from Millipore Corp. (Milford, MA).

Foods Tested. *Canned Food Products.* Canned fish and meat products were purchased from local Washington, DC, area grocery stores. Anchovies in olive oil, herring in tomato sauce, tuna in vegetable oil, sardines in soy oil, sardines in olive oil, and sardines with hot peppers in oil were tested.

Diet Cola. The canned diet cola beverages were purchased from local Washington, DC, area grocery stores.

Infant Formula Concentrates. The canned liquid formula products were purchased from around the United States as part of an FDA field assignment not related to DGEBA. Ages of the canned formulas were no less than the expiration date plus 6 months.

FT-IR Apparatus and Operating Conditions. A Nicolet Magna 550 Series II (Nicolet Analytical Instruments, Madison, WI) FT-IR equipped with a 30° horizontal specular reflectance/transmittance attachment (Janos Optical Corp., Townshend, VT) and interfaced with a personal computer running Omnic (Nicolet Analytical Instruments) software was used to prescreen all of the cans surveyed in this study. The FT-IR was set to average 32 scans.

Qualitative Analysis of Can Coatings by FT-IR. The inside of the empty can was rinsed and cleaned with soap and water to remove any food residues. The inside surface of the can was dried with a paper towel and then air-dried for several hours. Tin snips were used to remove a coupon measuring ~5 cm × 1.5 cm from each side (body and lid or ends) of the cleaned dried cans. One coupon at a time was placed flat on the horizontal specular reflectance/transmittance attachment mounted in the FT-IR so the infrared radiation was incident on the food contact surface of the can coupon. The spectra of the can coupons were recorded, analyzed, and compared with infrared spectra of known polymers.

HPLC Apparatus and Operating Conditions. The HPLC system consisted of a Spectra Physics model 8800 pump (Spectra-Physics, San Jose, CA), a Rheodyne model 7125 injector valve (Rheodyne, Inc., Cotati, CA) equipped with a 50-μL injection loop, a Spectra-Physics SP8792 column heater set at 60 °C, a 5-μm particle size, 250 mm × 3.2 mm Alltima C_{18} column (Alltech Associates, Inc., Deerfield, IL), a Waters model 470 fluorescence detector (Waters Division of Millipore Corp., Milford, MA) operated at 235 nm excitation and 317 nm emission, and a PE-Nelson Analytical model 3000 data system (Cupertino, CA) interfaced to a personal computer. The HPLC mobile phases were solvent A, water/acetonitrile (95:5), and solvent B, acetonitrile. At a flow of 0.9 mL/min, the mobile phase program was the following: linear gradient starting at t_0 from 50% A and 50% B to 75% B in 5 min; linear gradient from 75% B to 100% B from 5.1 to 15 min; isocratic from 15.1 to 27 min; linear gradient to 50% A and 50% B in 1 min; followed by re-equilibration of the column for 10 min.

HPLC Quantitation. Quantitation was based on an external calibration curve using chromatographic responses of at least five standard concentrations of DGEBA ranging from 0.01 to 0.5 μg/mL. The calibration curve of concentrations versus chromatographic peak areas was calculated from a linear regression program.

Extraction for Qualitative Can Coating Analysis. The coupon used for FT-IR analysis, described above, was rinsed with chloroform on the non-FCS side, dried, and placed in a 100 mL beaker with 25 mL of chloroform. The beaker was heated on a steam bath for several minutes until ~2 mL of chloroform remained. The liquid was decanted into a 15 mL conical tube and evaporated to dryness by using carborundum boiling chips to prevent bumping. The residue in the bottom of the tube was redissolved in ~5 mL of acetonitrile and diluted as appropriate with t_0 mobile phase to produce on-scale HPLC detector response. The presence of DGEBA and DGEBA derivatives was confirmed by GC/MS and/or LC/MS.

Liquid−Liquid Extraction of Food. The liquor (combined aqueous and oil layers) from a canned fish product was decanted into a 250 mL Erlenmeyer flask. It was mixed until a homogeneous blend of the liquid layers was produced, and a 5 g aliquot was then placed in a tared 125 mL separatory funnel. The combined mass of the funnel and liquor was recorded to determine the mass of the liquor. The liquor in the funnel was diluted with 25 mL of hexane to which 25 mL of acetonitrile was added. The mixture was shaken for 30 s, and the layers were allowed to separate. A total of three extractions of the liquor/hexane were carried out with acetonitrile. The three acetonitrile extracts were combined in a 125 mL Kuderna-Danish concentrator equipped with a three-ball Snyder column and evaporated to 3 mL. A 0.1−2 mL aliquot (depending on the amount of DGEBA in the extract) of the concentrated extract was diluted to 10.0 mL with t_0 mobile phase and filtered through a 0.45 μm nylon 66 filter. The filtered extract was quantitatively analyzed by HPLC by using fluorescence detection with external calibration. This procedure was performed in triplicate for each canned fish product tested. Recoveries were calculated by fortifying the liquor (in duplicate) with an amount of DGEBA equal to the average amount quantitated in the same liquor. The average DGEBA concentration in the unfortified liquor was subtracted from the total DGEBA concentration in the fortified liquor to determine the net amount of DGEBA recovered. Olive oil was extracted as an analytical blank for the canned fish liquor.

Canned diet cola was extracted in a manner similar to that used for the canned fish liquor. An ~50 mL portion of canned diet cola was degassed by sonication for 10 min in an unstoppered 250 mL Erlenmeyer flask. A 40.0 mL aliquot of the cola was placed into a 125 mL separatory funnel and partitioned three times with 25 mL of chloroform. The three chloroform (lower) layers were combined, then concentrated with a Kuderna-Danish apparatus as described above, and analyzed by HPLC with confirmation of selected extracts by GC/MS or LC/MS. Recoveries were calculated by fortifying a 40.0 mL aliquot of the beverage with known amounts of DGEBA, followed by LLE and concentration. The concentrate was analyzed by HPLC, and the percent recovery was calculated from the ratio of the observed and theoretical amounts of DGEBA. Water was substituted for the cola for analytical reagent blank analysis.

SPE of Liquid Infant Formula. Solid-phase extraction tubes consisting of 6 mL of styrene/divinylbenzene porous polymer packing available as Supelclean Envi-chrom P (Supelco, Inc., Bellefonte, PA) were used. A 30.0 mL aliquot of

liquid infant formula was removed from a can; the remainder was stored in a refrigerator at 4 °C and reserved for additional testing. The aliquot was diluted to 100.0 mL with distilled deionized water and transferred to a 100 mL buret. An SPE cartridge was rinsed and prewetted with a total of 20 mL of water. Enough water was retained on the cartridge so that the bed remained completely covered. The buret was placed above the cartridge, and a flow from the buret to the cartridge was adjusted to be compatible with a flow of ~5 mL/min through the cartridge produced from a vacuum source. The total volume of diluted formula was passed through the cartridge. The buret was washed with 5 mL of water and the wash allowed to pass completely through the cartridge. The total aqueous eluate was drained and discarded, and the residual water was removed from the cartridge by air-drying with vacuum for 5 min. The buret was then washed with 5 mL of hexane and the wash allowed to pass through the cartridge. The cartridge was eluted with three 5 mL volumes of chloroform into a calibrated 15 mL conical tube. The cartridge was drained between each volume. The chloroform was evaporated (by gently heating over a steam bath after each elution of the column with chloroform) to dryness. The addition of two or three carborundum boiling chips helps prevent bumping during successive evaporation processes. The concentrated extract was then redissolved with 2.0 mL of acetonitrile. Vortexing aided dissolution of the extract, after which a volume of water was added equal to the volume of acetonitrile, making the solvent compatible with the t_0 mobile phase composition. The concentrated extract was analyzed by HPLC. The extraction/concentration was performed in triplicate for each canned formula tested. Recoveries were calculated by fortifying the formula (in duplicate) with a known amount of DGEBA. The DGEBA quantitated in the fortified formula was compared with the amount added and the ratio expressed as a percentage to report the net amount of recoverable DGEBA.

Estimation of DGEBA Aqueous Solubility. The concentration of DGEBA to make a saturated aqueous solution at ambient conditions in the laboratory was estimated. To a 100 mL volumetric flask was added ~100 mg of DGEBA; the flask was filled with water, shaken vigorously for 30 s, and allowed to settle for 1 h. (Undissolved DGEBA remained in the bottom of the flask.) An aliquot was removed and diluted 1000-fold in t_0 mobile phase. The concentration of DGEBA in the saturated aqueous solution was determined by HPLC analysis.

DGEBA Stability in Solution. The stability of DGEBA in three different aqueous solutions was investigated. In triplicate, 20 mL test vials were filled with water or 0.05 M hydrochloric acid or 50 mg/mL sodium chloride solution in water. The vials, fortified with 20 μL of a ~8 mg/mL stock solution of DGEBA prepared in chloroform, were sealed and placed into a preheated 90 °C oven for 1 h. After the 1 h heating, the vials were cooled to room temperature and allowed to remain at ambient conditions for 72 h. An aliquot was removed from each vial, diluted 100-fold in t_0 mobile phase, and analyzed for DGEBA by HPLC. The identity of DGEBA degradation products was confirmed by LC/MS.

GC/MS Apparatus and Operating Conditions. The GC/MS system consisted of a Hewlett-Packard (HP) 5890B gas chromatograph (GC) with an HP 7673 automated liquid sampler; a capillary split−splitless injector; a 30 m × 0.25 mm i.d. HP-5MS, cross-linked 5% diphenyl−95% dimethyl polysiloxane, fused silica open tubular capillary column with 0.25 μm film thickness (Hewlett-Packard Corp, Avondale, PA); and an HP 5970B mass selective detector (MSD) with capillary direct interface to GC. The GC operating parameters were as follows: UHP helium carrier gas at ~12 psi column head pressure (1 mL/min); injection volume, 2 μL; split vent open after 1 min; injector temperature, 275 °C; interface temperature, 280 °C; oven program, initial temperature 40 °C, program at 10 °C/min to 280 °C, and hold 4 min (DGEBA t_r ~27.76 min); the MSD was operated in the scan mode; scan range, 40−450 *m*/*z*; scan rate, 1.05 scans/s. The GC/MS system was controlled with a Pascal Chemstation data system.

Confirmation of the presence of DGEBA by GC/MS was made by injecting 2 μL of the concentrated pull-top can enamel and anchovy liquor extracts in chloroform using the retention time and the relative response ratio of the integrated responses of ions *m*/*z* 309, 325, and 340, 0.07:1.00:0.20.

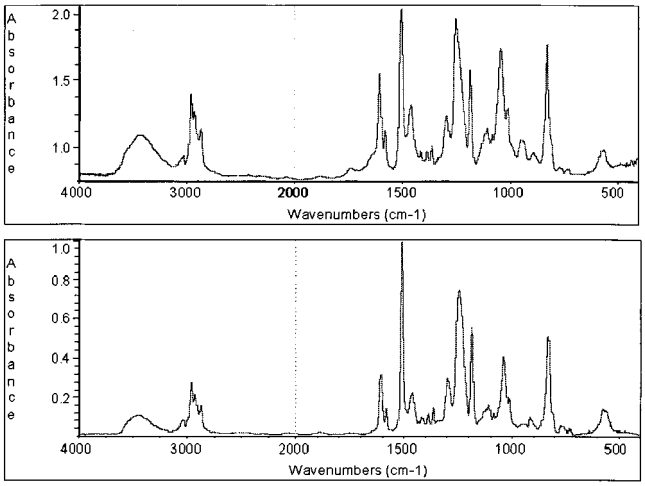

Figure 2. Infrared spectra: (top) food contact surface of a sardine can pull-top lid; (bottom) "known" DGEBA-based epoxy coating.

LC/MS Analysis. LC/MS data were collected using a Finnigan TSQ 7000 (Thermo Quest, Austin, TX) equipped with an atmospheric pressure chemical ionization (APCI) interface and a Hewlett-Packard (Hewlett-Packard, Wilmington, DE) 1050 liquid chromatograph. Chromatographic separation was achieved with a YMC (YMC, Inc., Wilmington, NC) J'sphere ODS-M80 column (250 × 2.0 mm i.d., S-4 μm, 80A) heated to 40 °C. A linear gradient employing water/methanol as the mobile phase was pumped at 200 μL/min. Initial mobile phase composition of 40% A (95:5 water/methanol), 60% B (methanol), was increased to 75% B over 5 min. The final mobile phase composition of 100% B was reached at 15 min, which was maintained for another 12 min. Ionization conditions were as follows: vaporizer, 450 °C; heated capillary, 200 °C; corona discharge needle, 5.0 μA; and tube lens voltage, 80 V. Nitrogen was employed, at a sheath gas pressure of 70 psi and auxiliary gas pressure at 50 mm on the flow tube (maximum flow 65 mm = 12 L/min), to assist in nebulization. The mass spectrometer was operated in the scan mode, scan range 110−900 *m*/*z*, scan rate, 1 scan/s. Response of DGEBA by APCI was superior using methanol versus acetonitrile; therefore, alternate mobile phase and program gradient were needed, which differed from those used for HPLC quantitation with fluorescence detection.

RESULTS

Infrared analysis showed all cans had at least one of the FCS's coated with an epoxy or "modified" epoxy enamel. Several of the pull-top lids were coated with a PVC polymer; however, of all the cans in the test group characterized by FT-IR, only one was found to be a vinyl coating with a large proportion of plasticizer, that is, a plastisol.

All spectra were compared (visually and by a spectral matching algorithm) with standards in the High-Resolution Hummel Polymer Library and spectra acquired from the FCS of epoxy coated "customer ready" (unused) cans obtained from a major supplier. For example, Figure 2 illustrates the FT-IR spectra for an unused can and a pull-top lid.

Qualitative HPLC analysis of selected can coating extracts showed the coatings contained some DGEBA. The greatest amount of residual DGEBA was extracted from a can lid coated with a vinyl plastisol. DGEBA derivatives were also detected in this vinyl plastisol coating. DGEBA, DGEBA-Cl, and DGEBA-2Cl were

Table 1. DGEBA and Derivatives Extracted from Foods[a]

food				DGEBA					
	mass		can coating[b]	measd	fortfd			adducts (μg/g$_{liq}$)	
type	liq (g)	sol (g)	top/sides	(μg/g$_{liq}$)	(μg/g$_{liq}$)	rec (%)	CV (%)	Cl	2-Cl
anchovy[c]	40	56	Pl/Ep	50[f]	56	96	7	24[f]	8[f]
anchovy[c]	40	56	Pl/Ep	9[g]	10	87	1	8[g]	0.7
herring[c]	50	140	Es + PVC/Es + PVC	0.53	0.65	80	12	0.4	0.6
sardine 1[c]	21	85	PVC/Ep	ND[h]	0.65	118	14	ND[h]	ND[h]
sardine 2[c]	51	55	Ep + PVC/Ep + PVC	0.60	0.65	100	7	ND[h]	ND[h]
sardine 3[c]	21	85	Ep/Ep	0.15	0.14	91	8	ND[h]	ND[h]
sardine 4[c]	21	85	Ep/Ep	0.13	0.14	103	2	ND[h]	ND[h]
tuna w/oil[c]	85	76	PVC/PVC	0.13	0.65	91	16	ND[h]	ND[h]
cola 1[c]	355[e]		PVC/Ep	ND[i]	0.002	106	6	ND[i]	ND[i]
cola 2[c]	355[e]		PVC/Ep	ND[i]	0.002	100	6	ND[i]	ND[i]
inf form. 1[d]	946[e]		Ep/Ep	ND[j]	0.06	77	20	ND[j]	ND[j]
inf form. 2[d]	946[e]		Ep/Ep	ND[j]				ND[j]	ND[j]
olive oil[c] (blank)			N/A	ND[h]				ND[h]	ND[h]
HPLC water[c] (blank)			N/A	ND[i]				ND[i]	ND[i]

[a] Abbreviations: DGEBA-Cl, = monochloro adduct of DGEBA; DGEBA-2Cl, dichloro adduct of DGEBA; Ep, epoxy; inf form., infant formula; liq, liquid; ND, not detected; Pl, plastisol; rec, recovered; sol, solid; CV, coefficient of variation. [b] Results from FT-IR analysis. [c] Liquid−liquid extraction. [d] Solid-phase extraction. [e] Milliliters. [f] Confirmed by both GC/MS and LC/MS. [g] Confirmed by LC/MS. [h −j] Detection limits based on DGEBA: *h*, 20 ng/g; *i*, 0.6 ng/g; *j*, 0.3 ng/g.

confirmed to be in the vinyl plastisol coating by GC/MS. DGEBA, DGEBA-Cl, DGEBA-2Cl, DGEBA-2OH, DGEBA-2OH-2OH, and DGEBA-Cl-2OH were also confirmed by LC/MS to be in the coating.

The presence of DGEBA and DGEBA derivatives in food extracts was confirmed by GC/MS and/or LC/MS retention times and mass spectra that matched corresponding spectra of standards. Standards of the hydrolysis products or chloro adducts of DGEBA could not be obtained from commercial sources; however, compounds obtained from high-purity standards of DGEBA "treated" with 0.05 M HCl in water and/or 50 mg/mL NaCl in water served as reference standards for the DGEBA derivatives.

The levels of DGEBA quantitatively determined in foods in the test group are reported in Table 1. Due to matrix effects, LC/MS and GC/MS could confirm DGEBA and DGEBA adducts in only the foods with the highest concentrations. The highest amount of DGEBA measured in the products occurred in the liquor of the canned anchovies, 50 mg/kg. Figure 3A illustrates the HPLC chromatograms of the extracts from the anchovy can lid and the food liquor. In the same product, levels of DGEBA-Cl and DGEBA-2Cl adducts (based on the fluorescence detector response for DGEBA) were estimated to be 24 and 8 mg/kg, respectively. In the absence of authentic standards, quantitation of these chemicals was performed relative to DGEBA. Recoveries of DGEBA from the various matrices ranged from 77 to 118%. Coefficients of variation for the triplicate runs ranged from 2 to 20% for the products surveyed. The limit of detection, defined as 3 times the standard deviation of the baseline produced by the detector when measuring a blank, was 8 μg/L. Some foods were extracted and concentrated by as much as 30-fold using SPE before HPLC analysis. This concentration step lowered the effective limit of detection for DGEBA by as much as a factor of 30 to <0.3 μg/kg.

We found that DGEBA was unstable in aqueous, acidic, and saline solutions. Figure 1 illustrates the structures of DGEBA reaction products found in aqueous, acidic, and saline solutions. An 8 mg/kg stock solution of DGEBA prepared in water was heated, held for 1 h at 90 °C, and then stored at room temperature for 72 h. Twenty-four percent of the DGEBA had reacted. Similar results were obtained in saline and acidic conditions, in which 46 and 43%, respectively, of the DGEBA reacted. A series of chromatograms illustrated in Figure 3B shows the formation of the DGEBA degradation products in different solutions. The overall solubility of DGEBA in water was estimated at ambient conditions to be ~260 mg/L. Hydrolysis of DGEBA to form DGEBA-2OH and DGEBA-2OH-2OH

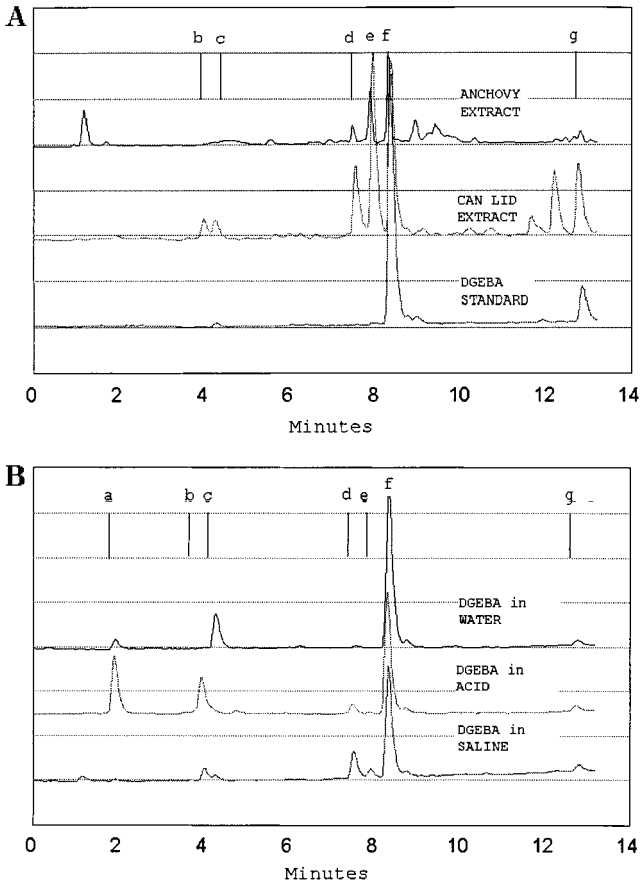

Figure 3. (A) HPLC fluorescence chromatograms of DGEBA standard, anchovy can pull-top lid extract made in chloroform and anchovy liquor extract. (B) HPLC fluorescence chromatograms of DGEBA treated with saline solution, acid, and water: (a) DGEBA-2OH-2OH; (b) DGEBA-Cl-2OH; (c) DGEBA-2OH; (d) DGEBA-2CL; (e) DGEBA-Cl; (f) DGEBA (n = 0 oligomer); (g) oligomer of DGEBA (n = 1).

occurred in solutions made in the t_0 mobile phase after storage for several days at ambient conditions. Working standards in aqueous solvents should be prepared fresh each day and checked for changes in DGEBA concentrations or the appearance of DGEBA adducts.

DISCUSSION

The qualitative FT-IR data presented here show that epoxy is used as a component of the coating on at least part of the FCS's of all of the cans in the test group. These data, coupled with the migration data, show that cans coated with vinyl plastisols demonstrate the highest migration to food.

Qualitative HPLC analysis of the coating extracts confirmed that DGEBA could be extracted from each can in the test group. The highest levels of DGEBA extracted from a FCS were from the vinyl plastisol coating, which coincided with the highest levels of DGEBA observed to migrate to food in the test group.

This limited survey of DGEBA in canned meat products, liquid infant formulas, and colas has shown that low levels to 50 mg/kg are extracted, concentrated, determined, and confirmed by using the combined techniques described here. Derivatives of DGEBA can be extracted from canned fish liquor that has been in contact with vinyl plastisol coatings. Migration of DGEBA from epoxy can enamels occurs at levels ~2 orders of magnitude below those determined in the foods that came in contact with vinyl plastisols. Neither DGEBA nor its derivatives could be detected in canned infant formula or canned cola beverages. However, when infant formula and colas were fortified with low levels of DGEBA and analyzed promptly, recoveries were 77 and 106%, respectively.

When can specimens were stored for 3 months and tested, the levels of DGEBA and DGEBA adducts were observed to decrease with time. Controlled testing in food was not performed to determine the stability of DGEBA in food matrices, nor were tests performed to determine the degree to which DGEBA or its derivatives partition between the aqueous and organic phases present in the food "liquor". DGEBA appears to be unstable in food. This is not surprising as the hydrolysis products and chloro adducts of DGEBA were shown to form under relatively mild conditions compared with those encountered in heat-processed food canning operations. On the basis of the data presented here as well as by Paseiro Losada et al. (1997) and Simal Gandara et al. (1993), it is likely that much of the DGEBA migrating to aqueous foods during the retort process was converted to DGEBA adducts other than those investigated here. The reactivity of the epoxide groups with nucleophiles likely present in foods (e.g., proteinaceous materials, fatty acids and esters) would result in derivatives of DGEBA other than those explored here (Yurawecz, 1987; Collier et al., 1991).

Our data illustrate that DGEBA migrates from vinylic, polyester, and epoxy coatings. Any attempt to determine the total amount of DGEBA migrating to foods must also consider the reactivity of DGEBA and the formation of derivatives with components of the food matrix as well. Future research will continue on the topic of migration from can coatings to foods and beverages.

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