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Reaction Products of Bisphenol-A-Diglycidyl Ether (BADGE) and Bisphenol-F-Diglycidyl Ether (BFDGE) with Hydrochloric Acid and Water in Canned Foods with Aqueous Matrix

1. Analytical Methods

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Introduction

Bisphenol-A-diglycidyl ether (BADGE) and Bisphenol-F-diglycidyl ether (BFDGE) are compounds used in the production of can coatings as well as other polymers. They have two epoxy groups which may be hydrolyzed, e.g. in aqueous foods and beverages, or react e.g. with hydrochloric acid, cleaved from organosol (PVC) polymers. The resulting products of BADGE are shown in figure 1. BFDGE is composed of three isomers with two methyl groups less than BADGE. They are components of technical products called epoxy Novolac or Novolac glycidyl ether (NOGE), a highly complex mixture including compounds with more than two aromatic rings and glycidyl groups (1) (fig. 2).

Analytical methods

Most methods described in literature for the analysis of BADGE, BFDGE and their reaction products were designed for food simulants and involve reversed phase liquid chromatography (RPLC) on C18 or C8 silica gels with mixtures of acetonitrile/water as mobile phase. Mostly Fluorescence Detection (FD) was applied (2–5),

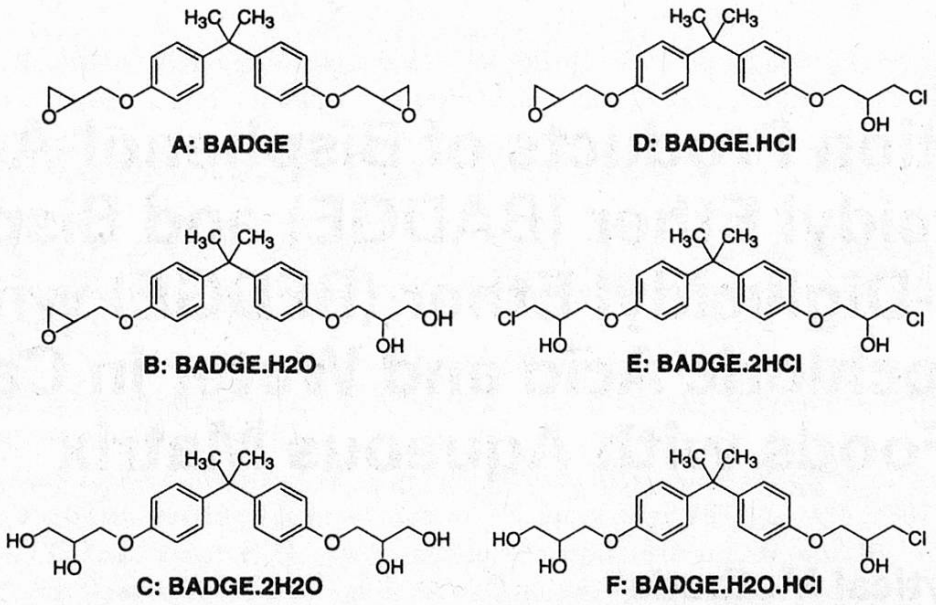

Figure 1 **Structures of BADGE and products resulting from hydrolysis or reaction with hydrochloric acid. A-F, denomination by the EU-SCF**

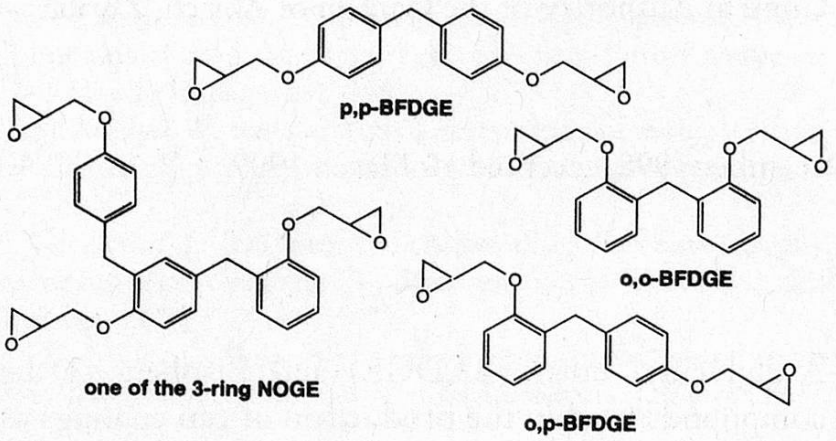

Figure 2 **Structures of the three isomers of BFDGE and of one out of seven 3-ring isomers of Novolak Glycidyl Ether (NOGE)**

but also RPLC coupled to Mass Spectrometry (MS) (6). RPLC-MS-MS was proposed for the analysis of BADGE in foods after freeze-drying of the product (7). While RPLC requires a preliminary removal of fat and oil (e.g. by partitioning between acetonitrile and hexane, e.g. (8)), Normal Phase LC (NPLC) enabled direct injection of organic extracts from oily foods (9–11). GC-MS of NPLC fractions was mostly used for peak identification or confirmation (12, 13).

This paper describes a set of three methods designed for the routine analysis of BADGE and BFDGE as well as their H_2O and HCl derivatives in canned foods and beverages. Products in aqueous phase were of primary interest, such as sweet corn,

vegetables, tomatoes and fruits. RPLC-FD provided the principal analysis. Positive results were confirmed by acetylation and NPLC-FD. When results disagreed, NPLC fractions were collected and analyzed by GC-MS. These methods were used for a survey of cans on the Swiss market, the results of which are described in Part 2 (14).

Concepts of the methods

Partitioning into aqueous phase; RPLC

Extraction of the compounds of interest from the foods into an aqueous phase is suitable for subsequent analysis by RPLC. A modifier must be added that fulfills the requirements of providing efficient extraction as well as of complying with RPLC analysis.

Extraction from the foods into the modified aqueous phase presupposes favorable partitioning with waxy surfaces of solids, fat and oil even for the components of low polarity. Some 50 % of methanol or 40 % of acetonitrile were needed in the aqueous phase in order to well extract BADGE.H_2O. However, these two modifiers turned out not being suitable, because RPLC with mobile phases containing methanol or acetonitrile did not separate BADGE.H_2O from BADGE.HCl.H_2O, neither on a C18 nor on a C8 or a phenyl phase. Complete separation of these components was achieved with ethanol, and equivalent extraction was obtained with 40 % ethanol.

The other critical aspect concerned the suitability of the resulting solvent mixture for injection. For sensitivity reasons, 80–100 µl of extract had to be introduced into a 25 cm x 2 mm i.d. column used with a flow rate of 150 µl/min. This called for a solvent mixture behaving as a weak eluent in order to avoid band spreading. After separation from the food, the extract was diluted 1:1 with water. Further dilution resulted in loss of solute material on the wall of the vial or on the filter. The aqueous extract containing about 20 % of ethanol was found to be acceptable for the RPLC gradient used.

Partitioning into organic solvents; NPLC

For the confirmation of the results from RPLC by NPLC, food homogenates were extracted by an organic solvent. Fat and oil are co-extracted and eluted long before the components of interest, not disturbing the analysis. Extraction of the most polar component, BADGE.2H_2O, from a homogenized sample of tuna in oil and water showed that Methyl tert-Butyl Ether (MTBE) achieved an acceptable yield (table 1).

For sensitivity reasons, 80 µl of the extract had to be introduced into the 25 cm x 2 mm i.d. NPLC column (flow rate of 400 µl/min). Using MTBE, this caused strong band broadening. Evaporation of MTBE and re-dissolution in a weaker solvent was not successful since no compromising solvent was found that was a sufficiently

Table 1
Extraction yields with various organic solvents for BADGE.2H_2O spiked into a sample of homogenized tuna in oil (1 g of sample + 1 ml of water + 5 ml of solvent)

Solvent	*Extraction yield*
10 % CH_2Cl_2/heptane	46 %
20 % MTBE/heptane	13 %
50 % MTBE/heptane	55 %
100 % MTBE	80 %

weak eluent and at the same time quantitatively picked up all solutes (particularly BADGE.2H_2O) from a crude extract.

Acetylation

Incompatibility of solvents was the first reason to acetylate the hydroxyl groups of the solutes: after derivatization, the samples could be picked up in heptane, which resulted in efficient reconcentration of the solute material in the head of the NPLC column to produce sharp initial bands. The second reason was the possibility of confirming the identity of LC peaks by GC-MS.

The hydroxyl groups must be derivatized without opening epoxy groups. This could be achieved neither by silylation (BSTFA/1 % TMCS) nor by trifluoroacetylation. Even for acetylation with Acetic Anhydride (AA), careful optimization of the conditions was needed and some loss of BADGE had to be accepted (see fig. 3). As no additional peak showed up in NPLC-FD, GC-MS or Size Exclusion Chromatography (SEC)-FD, the loss remained unexplained; it did not involve opening of the epoxy group and formation of acetates.

Pyridine was added not only for scavenging protons from acetylation, but also for the reliable dissolution of the evaporated food extracts. However, it must be re-

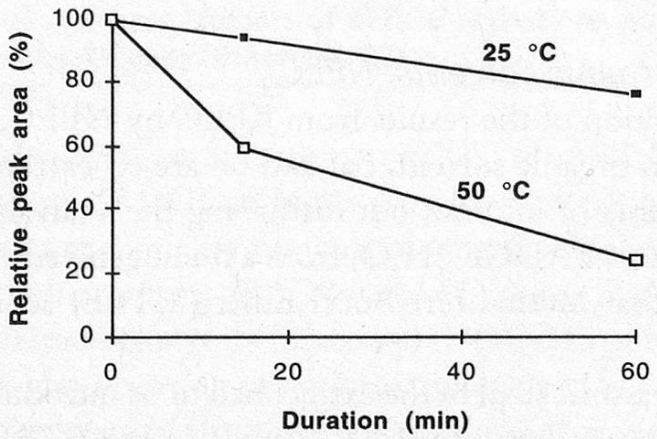

Figure 3 **Decreasing recovery of BADGE after treatment with acetylation reagent**

moved before injection because it is eluted in the region of the acetylated BADGE.HCl and BFDGE.HCl and quenches their fluorescence. Removal occurred by extraction into an acidic aqueous medium.

GC-MS of NPLC fractions

Even with short (3 m) and thin-film columns, GC of BADGE.HCl and BADGE.2HCl mostly resulted in partial elimination of HCl and the formation of epoxy groups. BADGE.H_2O and BADGE.$2H_2O$ were strongly adsorbed. Hence a derivatization (acetylation) of the hydroxyl groups was required.

With the method applied, an NPLC peak corresponding to 20 µg/kg in the food represented about 1 ng of material. In order to obtain full mass spectra, almost the whole material available from NPLC had to be injected. Fractions typically had a volume of 200–500 µl, of which 100 µl were injected, possibly after slight reconcentration. The on-column technique was chosen to rule out degradation in a hot injector chamber. The low volatility of the compounds enabled the application of fully concurrent solvent evaporation. This merely requires a short, coated precolumn, which is more inert than a long, uncoated one.

Fluorescence detection

For LC, FD was chosen because of its high sensitivity, good selectivity and the nearly equal response for all compounds of interest. The latter enabled to extrapolate the FD response for all compounds which were not available as pure standards.

Separation of BADGE.H_2O and BADGE.H_2O.HCl

The work described below focused on canned foods without a relevant fat and oil phase. It started with the puzzling result that canned sweet corn and asparagus seemed to contain up to 3 mg/kg of BADGE.H_2O. Synthesis and HPLC of BADGE.HCl.H_2O revealed, however, that under most LC-conditions underivatized BADGE.H_2O and BADGE.HCl.H_2O are not separated (neither in normal nor in reversed phase) and that the material found was, in fact, BADGE.HCl.H_2O.

Methods

Reference materials

Standards of BADGE, BFDGE, BADGE.$2H_2O$, BADGE.2HCl, BFDGE.$2H_2O$ and BFDGE.2HCl were from Fluka (Buchs, Switzerland). The other products of interest were prepared as mixtures from BADGE and BFDGE. Conversions must occur in highly dilute aqueous solutions and only tolerate small additions of organic mediator solvents. The following procedures were used:

- Synthesis of BADGE.HCl and BADGE.2HCl as well as of BFDGE.HCl and BFDGE.2HCl (main products): 5 ml of BADGE or BFDGE, 1 mg/ml in

tetrahydrofurane (THF), were added to 500 ml of water. 40.5 ml of concentrated hydrochloric acid were added, resulting in a concentration of about 3 %. After 1 min reaction time, the products were extracted into 500 ml of MTBE. The MTBE phase was washed with 200 ml of 8 % sodium bicarbonate.

- BADGE.H_2O, BADGE.$2H_2O$ as well as BFDGE.H_2O and BFDGE.$2H_2O$ (main products): 5 ml of BADGE or BFDGE, 1 mg/ml in THF, were added to 500 ml of 3 % acetic acid and allowed to stand at 40 °C during 3 days. Then the aqueous phase was saturated with sodium chloride and extracted with 500 ml of MTBE. The extract was washed with 200 ml of 8 % sodium bicarbonate.
- BADGE.$2H_2O$, BADGE.HCl.H_2O and BADGE.2HCl as well as BFDGE.$2H_2O$, BFDGE.HCl.H_2O and BFDGE.2HCl were obtained by adding 5 ml of BADGE or BFDGE (1 mg/ml in THF) to 500 ml of 0.5 % hydrochloric acid. After 3 days at ambient temperature, the products were extracted with 500 ml MTBE.

Complete mixtures of BADGE or BFDGE derivatives were obtained by combining the products and evaporating the solvent together with 10 ml of 1-propanol for the removal of residual water.

Sample preparation

Analysis was performed on the part of food expected to be consumed. From vegetables like peas, sweet corn or mushrooms, the aqueous phase was removed, while fruits in syrup were analyzed with the aqueous phase, the same as tomatoes (from which usually no well defined aqueous phase can be separated), sauces and soups.

The can content (with or without aqueous phase) was weighed into a beaker. Before mixing, an equal amount of water was added in order to obtain a rather fluid, well extractable homogenate. In the interest of a standardized procedure, water was added also to liquid samples such as soups.

Samples containing some oil or fat in coherent phases (e.g. soups with droplets of oil) may contain epoxy compounds. Homogenization splits the fat or oil into small droplets, which strongly accelerates hydrolysis (and possibly other reactions). For this reason, samples were stored by deep freezing. Of products suspected to contain epoxy compounds, an aliquot of the homogenate was extracted with 15 % dichloromethane/heptane immediately after mixing. Extracts were analyzed for BADGE, BADGE.HCl, BADGE.H_2O and the corresponding BFDGE analogs by NPLC-FD without acetylation according to the method used previously (11), though with the gradient applied to the analysis of the acetates.

Analysis by RPLC

Extraction

For RPLC, 2 g of homogenate (including 1 g of sample) were extracted with 3 ml of an ethanol-water mixture 2:1 (v/v) by vigorous stirring and treating with ultrasound, over all diluting with 50 % ethanol. Since the samples mainly consisted of water, the resulting liquid phase contained approximately 40 % ethanol. For calculating the results it was assumed that the sample was diluted 1:5. The solids were removed by centrifugation and the supernatant diluted with an equal amount of water for injection. Liquid products (beverages) were diluted with ethanol to form a 20 % ethanolic solution. Turbid samples were filtered through a material which does not retain the compounds of interest (Chromafil O-20/25, 0.2 µm, Macherey-Nagel, Oensingen, Switzerland). Since linearity of FD was limited to concentrations in the solution injected of below 100 µg/l, more concentrated samples were diluted with 20 % ethanol/water.

RPLC determination

RPLC was performed on a HPLC-System from Thermo Separation Products (San Jose, CA, USA), consisting of a SpectraSYSTEM P4000 pump, a SpectraSYSTEM AS3000 autosampler and a FL3000 SpectraSYSTEM fluorescence detector. Raw data was collected and evaluated using a PC1000 System control and data management software. The 25 cm x 2 mm i.d. column was packed with Hypersil MOS (C8), 5 µm (Macherey-Nagel). A gradient with water (A) and ethanol (B) was applied at a flow rate of 0.15 ml/min: 0–10 min: 20 %–50 % B; 10–35 min: 50 %–57 % B; 35–40 min: 57 % –100 % B, 40–45 min: 100 % B; 45–50 min: 100 %–20 % B; 50–60 min: 20 % B. Injection volume, 100 µl; FD at 224 nm/294 nm. In order to improve the reproducibility of retention times, the column was thermostatted at 35 °C. Chromatograms of the mixture of all BADGE compounds of interest as well as of the most important BFDGE derivatives are shown in figure 4.

Quantitative determinations were based on BADGE as external standard. A 1 mg/l BADGE solution in MTBE was diluted with ethanol/water 20/80 to 10 µg/l and 100 µg/l. Since BADGE, BADGE.2H_2O and BADGE.2HCl resulted in similar FD-response at equal molarity (table 2), the same molar response factor was assumed for all compounds including those not available as reference substances.

Analysis by NPLC

Extraction

In a 10 ml screw cap flask, 2 g of homogenate (including 1 g of sample) was extracted with 5 ml of MTBE by vigorous stirring on a vortex during 30 s. For samples tending to form lumps or foods with well emulgated fat (such as cremes), extraction required up to 5 min.

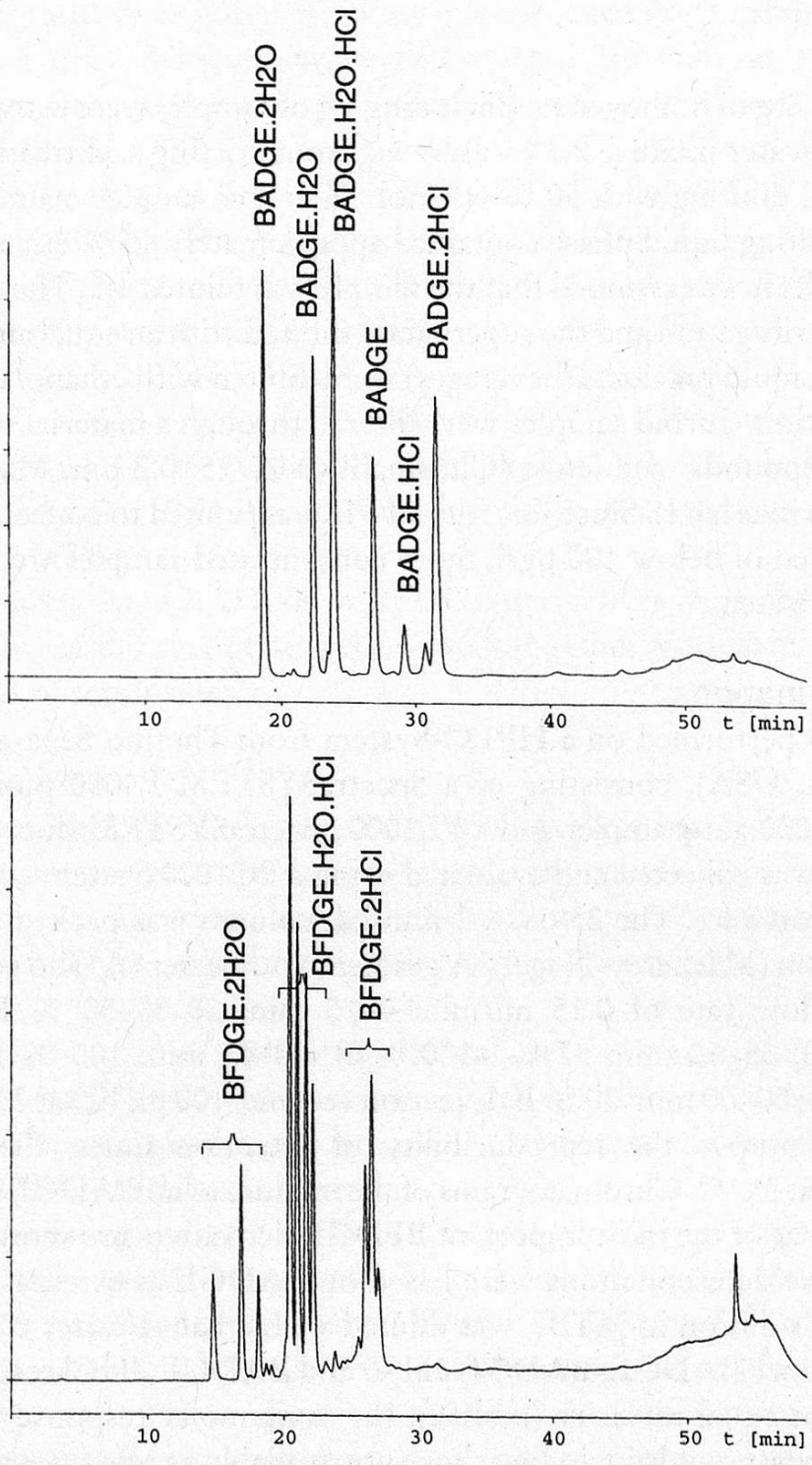

Figure 4 **RPLC-FD of the most important BADGE and BFDGE reaction products**

Acetylation

In a 1.5 ml autosampler vial, 1 ml of MTBE extract was evaporated to dryness by a stream of nitrogen. 80 µl each of pyridine and acetanhydride were added and the vial kept in a warmed aluminum block at 35 °C for 30 min. Then 1 ml of heptane and

Table 2
FD-responses of reference substances: Area Points (AP) related to molar concentrations

	Conc. in the solution ($x\ 10^{-7}$ *M)*	*Peak area* ($x\ 10^{6}$ *AP)*	*FD-Response* (10^{6} *AP/*10^{-7} *M)*
BADGE	2.94 (0.1 mg/l)	4.1	1.6
BADGE.2H_2O	2.66 (0.1 mg/l)	4.6	1.5
BADGE.2HCl	2.42 (0.1 mg/l)	3.8	1.6

500 µl of 20 % phosphoric acid (extraction of pyridine) were added. After shaking, the aqueous phase was withdrawn by a Pasteur pipette and the heptane phase analyzed by NPLC.

NPLC determination

NPLC was performed on an instrument designed for on-line LC-GC (Dualchrom 3000, CE Instruments, Milan, Italy) with two syringe pumps and a fluorescence detector (Merck/Hitachi F1000). The 25 cm x 2 mm i.d. column was packed with Gromsil 100 cyano 2 PR 5 µm (Stagroma, Wallisellen, Switzerland). A gradient (400 µl/min) was used with 1 % 1-propanol/pentane (A) and 50 % 1-propanol/MTBE (B), programming as follows: A, 10 min, then 1 %/min B up to 10 % and 5 %/min B up to 30 % (2 min). Sample volume injected, 80 µl; FD at 225/295 nm. For confirmation, detection at 275/320 nm can be used, calibrating the ratio of the peak area obtained at the two wave lengths with a standard solution of BADGE. Chromatograms of the mixture of all BADGE compounds of interest as well as of the fully reacted BFDGE derivatives are shown in figure 5. BADGE and its derivatives are eluted with a retention time similar to that of the first eluted corresponding BFDGE compound.

Concentrations were calculated through BADGE as external standard. From a 1 mg/ml solution of BADGE in MTBE, a solution of 100 ng/ml in heptane was prepared. These solutions were stable for more than an year. Calculations involved a correction/response factor of 1.25 for all components, compensating for the loss of epoxy compounds during the acetylation procedure and a reduced response by FD (see below).

GC-MS

An UltraTrace gas chromatograph equipped with an autosampler for large volume on-column injection and a vapor exit was coupled to a mass spectrometer MD-800 working in the EI mode (all CE Instruments, Milan, Italy). GC separation involved an 8 m x 0.25 mm i.d. capillary column coated in the laboratory with an 0.2 µm film of PS-255, a dimethyl polysiloxane (Fluka).

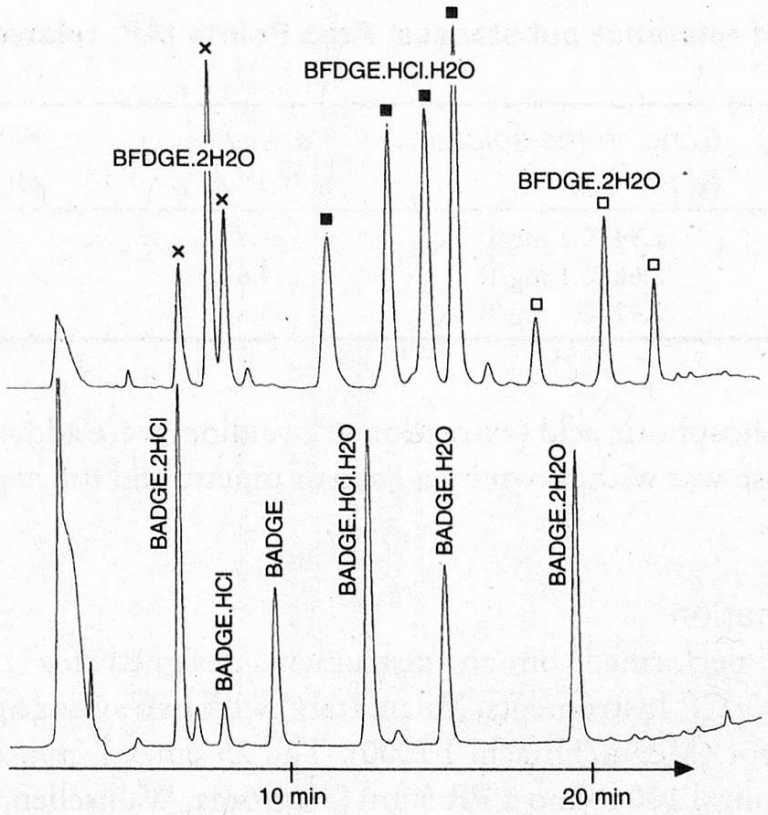

Figure 5 **NPLC-FD of the most important solutes**

Large volume injection

For large (100 µl) volume on-column injection, the separation column was equipped with a 1.5 m x 0.53 mm i.d. retaining precolumn coated with an 0.15 µm film of OV-1701-OH (Fluka). It was connected to a screw type T-piece leading to the 0.5 mm i.d. vapor outlet and the separation column. The vapor exit was equipped with a 50 cm x 75 µm i.d. fused silica resistance capillary.

During solvent evaporation, the oven temperature was at 80 °C; the inlet pressure was 30 kPa. After closure of the vapor exit, pressure was increased to 80 kPa. The injection rate by the autosampler was 1 µl/s, which resulted in fully concurrent evaporation for all solvents used, including (as a worst case) 1-propanol. The vapor exit was closed 2 min after starting injection. 1.5 min later, the column temperature was programmed at 15 °/min to 350 °C (10 min, removing triglycerides).

Mass spectra

The mass spectra of acetylated compounds differ from the non-acetylated BADGE derivatives inasfar as the positive charge is largely transferred to the glycidyl fragments, leaving little response to the bisphenol backbone. Figure 6 shows the mass spectrum of the BADGE.HCl.H_2O triacetate. The dominating signal m/z 159 represents the acetylated diol (diacetylpropyl), m/z 135 the acetylated

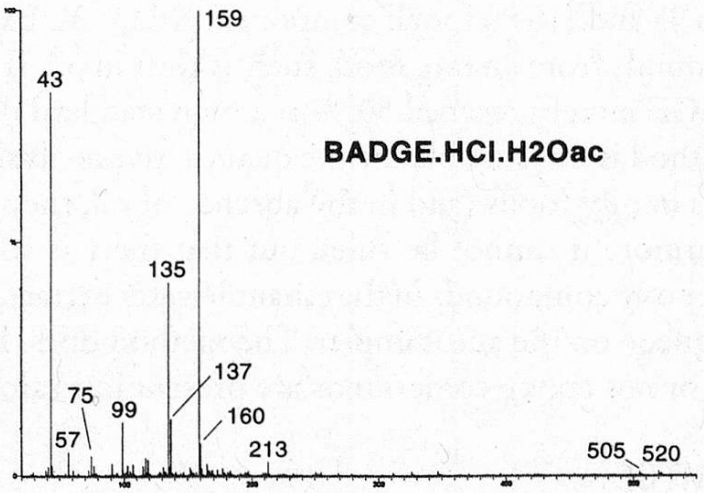

Figure 6 **EI Mass spectrum of triacetylated BADGE.HCl.H_2O**

chlorohydroxy group (2-chloro-3-acetylpropyl). The isotope signal (m/z 137) confirms the presence of the chloro atom. This is important since m/z 135 is also a key fragment in chlorine-free BADGE and its non-acetylated derivatives.

For the confirmation of the Bisphenol A or F structure, the molecular ion may be used. The corresponding signal (m/z 520 for BADGE.HCl.H_2O) is small, however. Often the signal m/z 213 is more easily detected. It is an important signal of non-acetylated BADGE derivatives and results from loss of both side chains and a methyl group in the center of the molecule, i.e. corresponds to Bisphenol A after loss of a methyl unit.

Quantitation

GC-MS was merely used in a semiquantitative manner, aiming at the conclusion whether or not the NPLC peak to be confirmed at least largely represented the compound identified by the mass spectrum. For calibration, an amount of acetylated standards was injected into NPLC that produced a peak of similar size for the component to be confirmed. This fraction was recovered, the eluent evaporated to less than 200 µl and the volume brought back to 200 µl with MTBE. The component to be verified was handled in the same way.

Quantitative performance

Extraction yields

Extraction into the aqueous/ethanolic phase

Food samples were spiked with the mixture of BADGE standards at concentrations ranging from 15 µg/kg to 950 µg/kg. Extracts were analyzed by RPLC and recoveries determined by comparison with unspiked material.

For products in essentially aqueous matrices, such as sweet corn and beer, recoveries were between 95 and 115 % for all components (table 3). Extraction of the less polar epoxy compounds from an oily food, such as tuna in oil, is more difficult: the recovery for BADGE merely reached 50 % at a high standard deviation. It is concluded that the method is not suitable for the quantitative analysis of BADGE type epoxy components in oily foods (and in the absence of oil, they are hydrolyzed in the foods). Furthermore it cannot be ruled out that there is some hydrolysis (or other reaction) of epoxy compounds in the ethanol/water extract, particularly when waiting in a long queue on the autosampler. The method does, however, enable to conclude whether or not epoxy compounds are present in a sample.

Extraction with MTBE

Table 4 shows the recoveries for the extraction from homogenated food samples with MTBE. Mixing on the vortex lasted 30 s unless stated otherwise. Concentrations of the BADGE standards varied between 600 and 1400 µg/kg.

Yields determined for sweet corn were around 90 % for all components except BADGE.2H_2O, where the average was 77 %. Similar results were obtained for peas and apricots. Regarding fruits and vegetables, the worst results were obtained for asparagus, where some yields remained below 70 %. Prolonged mixing (5 min) did not improve. Since results were particularly low for the epoxy compounds, problems were hardly related to unfavorable partitioning. Extraction from oily samples (tuna in oil) gave similar results as that from vegetables.

Cremes required more time, presumably because the emulgators slow down the extraction from the fatty phase (also explaining why the hydrophilic components were extracted faster than BADGE and its HCl adducts). Another potential problem concerns samples tending to form lumps (e.g. meat). They must be homogenated with more water or extracted during longer times. Visual observation of the mixing process during extraction enables to recognize the difficult samples.

Acetylation

As mentioned above, acetylation must be performed under conditions minimizing the loss of BADGE. It was optimized using a mixture of BADGE, BADGE.2H_2O and BADGE.2HCl standards. After removal of the solvent in an autosampler vial, 50 or 80 µl of pyridine and AA were added and allowed to react at various conditions. The yields of the acetylation shown in table 5 were calculated from the peak areas of the incompletely acetylated compounds.

Oil and maybe other material extracted from the food samples slow down the acetylation. This was taken into consideration when repeating the above experiments after adding to the standards 60 mg of an oily residue obtained by extracting a sample of tuna in oil (60 mg correspond to 30 % in a sample). As shown in table 6, reaction during 30 min at 25 °C is now no longer sufficient. With 30 µl each of pyridine and AA, yields were low primarily because the extract from tuna was not

Table 3

Recoveries (%) for the extraction of BADGE and its reaction products into ethanol/water from an aqueous and an oily food (relative standard deviations)

	.2H_2O	*.H_2O*	*.HCl.H_2O*	*BADGE*	*.HCl*	*.2HCl*
Sweet corn (n = 4)	105 (1.3 %)	107 (1.5 %)	107 (0.7 %)	112 (1.6 %)	96 (1.6 %)	102 (0.5 %)
Tuna in oil (n = 4)	112 (11.4 %)	101 (6.0 %)	110 (8.3 %)	50 (63.9 %)	72 (56.3 %)	72 (37.4 %)

Table 4

Extraction yields with MTBE (%), (relative standard deviations)

	.2HCl	*.HCl*	*BADGE*	*.HCl.H_2O*	*.H_2O*	*.2H_2O*
Sweet corn (n = 5)	90 (2.5 %)	91 (3.2 %)	89 (2.2 %)	87 (1.8 %)	97 (2.1 %)	77 (1.8 %)
Asparagus 30 s	60	58	65	91	85	88
5 min	64	69	67	93	75	82
Tuna in oil (n = 5)	80 (1.6 %)		93 (6.1 %)	78 (1.8 %)	88 (3.8 %)	76 (4.2 %)
Creme 30 s (n = 2)	35	44	65	92	93	90
5 min	109	102	104	112	110	95

Table 5
Yields of the acetylation tested with standards

			Yield (%)	
°C	Py/AA (µl)	Duration	BADGE.2HCl	BADGE.2H_2O
25	50/50	5 min	50	< 50
25	50/50	15 min	88	80
25	50/50	30 min	98.5	97
35	50/50	15 min	92	87
35	80/80	15 min	96	95
35	80/80	30 min	> 99	> 99
50	50/50	15 min	> 99	> 99

Table 6
Yields of the acetylation tested with standards in 60 mg of an extract from tuna in oil

	Conditions		Yield (%)	
°C	Py/AA (µl)	Duration	BADGE.2HCl	BADGE.2H_2O
25	50/50	30 min	90	75
35	50/50	15 min	84	85
35	80/80	15 min	89	92
35	80/80	30 min	> 99	98
40	30/30	15 min	50	< 50
50	30/30	15 min	97	89
50	80/80	15 min	99	99

dissolved well enough in the acetylation medium. 50 µl of pyridine solved this problem, but addition of 80 µl each of pyridine and AA was preferred, since it accelerates derivatization (at a constant loss of BADGE). The reaction is virtually complete after 30 min at 35 °C.

Response factors in NPLC

Calculation of concentrations in the samples was based on BADGE injected as an external standard in a solution which has not gone through acetylation (100 ng/ml). The response/correction factors related to this BADGE were determined for a mixture of treated BADGE, BADGE.2HCl and BADGE.2H_2O (100 ng/ml). Figure 7 shows results for the acetylation at 35 °C calculated as percent peak area. Areas of BADGE decrease with extended duration of the reaction, whereas those of BADGE.2H_2O and BADGE.2HCl reach a maximum after some 30 min reaction time. The results indicate that the response of all three compounds is around 0.8 times that of the external standard. For BADGE this is the result of degradation whereas the acetates are assumed to show a reduced response in FD. In fact,

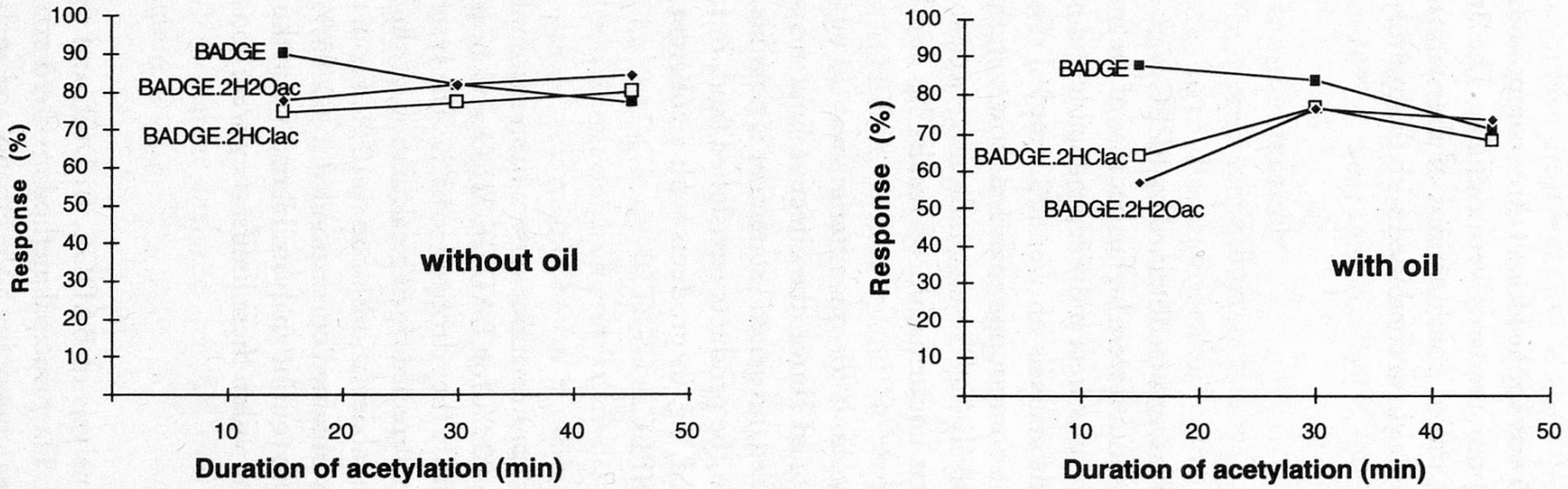

Figure 7 **Response of a mixture of BADGE, BADGE.2HCl and BADGE.2H_2O after acetylation with or without presence of an extract from tuna in oil; peak areas expressed as percentage of BADGE as external standard**

BADGE derivatives trifluoroacetylated in position 2 of the glycidyl group are no longer detected by FD at all.

In conclusion, a correction factor of 1.25 was applied for all three compounds as well as for all other derivatives of which no pure standards were available. The latter is justified by the fact that they represent mixed combinations of the standards tested, such as an epoxy or chlorohydroxy side chain combined with the hydrolysis product.

Estimated accuracy

RPLC method

For the fully extracted BADGE derivatives, results obtained by RPLC were superior to those of NPLC: the concentrations found were higher because of the more complete extraction and (linked with this) results were more reproducible and reliable. As shown above and confirmed by the analysis of over 400 samples, results were accurate within 20 %. For most of the compounds analyzed, however, there were about 5 % wrongly positive or excessively high results, indicating occasional co-elution with food components and that confirmation of results by another method is required.

In the absence of interfering peaks, the limit for quantitation was 20 µg/kg. However, owing to the co-elutions mentioned above, the effective limit may be higher. For the wide variety of foods analyzed, no general statement is possible.

No epoxy compounds were expected in the products envisioned (and, in fact, none were found). In case they are detected, e.g. in products with a coherent fat phase, their quantitation should occur by NPLC.

NPLC method

The NPLC method, primarily used for confirmation, suffers from incomplete extraction. Mostly yields were around 75–80 % for BADGE.$2H_2O$ and near to 90 % for the other compounds, but occasionally they dropped to 65 %. The systematic deviations caused by acetylation were corrected during calculation of the results. They may, however, introduce additional deviations of up to 10 %. From this error budget it is concluded that the results obtained corresponded to 60–95 % of the true values, which was, in fact, observed in routine analysis. Hence, when the results of the RPLC analysis were reproduced within these limits, they were considered as confirmed.

Summary

Three methods are described for the analysis of BADGE, BFDGE and their derivatives with water or hydrochloric acid. The principal method involved extraction of the components into an aqueous phase containing 50 % ethanol and analysis by RPLC with fluorescence detection (FD). With the exception of the epoxy com-

pounds in oily foods, results were accurate within an estimated 20 %. For individual compounds, the lower limit of quantitation was 20 µg/kg.

Owing to occasional co-chromatography with food components, positive results were confirmed by extraction of the food homogenates with MTBE, acetylation and normal phase HPLC (NPLC)-FD. With this method, some 60–95 % of the true values were obtained. In the case of disagreement, fractions from NPLC were analyzed by GC-MS using large volume on-column injection.

Zusammenfassung

In Konservenprodukten mit wässeriger Matrix wurden BADGE, BFDGE sowie deren Reaktionsprodukte mit Wasser und Chlorwasserstoff mit drei Methoden bestimmt. Als Hauptmethode wurden die Komponenten in die mit 50 % Ethanol modifizierte wässerige Phase extrahiert und mittels RPLC und Fluoreszenzdetektion (FD) analysiert. Mit Ausnahme der Epoxyverbindungen in öligen Lebensmitteln wurde eine Richtigkeit innerhalb geschätzten 20 % erreicht. Die untere Quantifizierungsgrenze für Einzelkomponenten betrug 20 µg/kg.

Wegen gelegentlicher Co-chromatographie mit Lebensmittelkomponenten wurden die positiven Befunde über eine Extraktion der Lebensmittelhomogenate mit MTBE, Acetylierung und Normalphasen HPLC (NPLC)-FD bestätigt. Mit dieser Methode wurden 60–95 % des richtigen Wertes gefunden. Bei mangelnder Übereinstimmung wurden die NPLC-Fraktionen mit GC-MS und grossvolumiger on-column-Einspritzung überprüft.

Résumé

Le BADGE, le BFDGE et ses produits de réaction avec l'eau et l'acide chlorhydrique ont été mesurés dans des aliments en solution aqueuse en conserve au moyen de trois méthodes. Par la méthode principale, les composés ont été extraits dans la phase aqueuse modifiée avec 50 % d'ethanol et analysés par RPLC avec détection fluorimétrique (FD). A l'exception des composés époxidiques dans les aliments huileux, la fiabilité des résultats était de l'ordre de ± 20 %; la limite de quantification par substance était de 20 µg/kg.

A cause d'occasionelles co-chromatographies avec des composés de l'aliment, les résultats positifs étaient confirmés par extraction des homogénats de l'aliment par MTBE, acétylation et HPLC en phase normale (NPLC)-FD. Par cette méthode, 60 à 95 % des «valeurs justes» étaient trouvées. En cas de différences, les fractions NPLC étaient analysées par GC-MS utilisant l'injection de large volumes on-column.

Key words

Canned foods, Bisphenol-A-diglycidyl ether, Bisphenol-F-diglycidyl ether, Hydrolysis products, Hydrochlorination products, Large volume on-column injection

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