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Diglycidyl Ethers of Bisphenol-F and Novolac in Canned Oily Foods

Key words: Canned foods, Bisphenol-F-diglycidyl ether (BFDGE), Chlorohydroxy derivatives of BFDGE, Novolac Glycidyl Ethers (NOGE)

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Introduction

A recent paper (1) reported problems related to the release of Bisphenol-Adiglycidyl ether (BADGE) from the internal coating of cans into fat- or oil-containing foods. BADGE is a monomer for the production of epoxy polymers (2). More important for the problem, however, is its use as an additive to organosol and polyester coatings, where it serves as a scavenger to remove hydrochloric acid released during the heat treatment of the coating procedure. Swiss food regulation requires that BADGE is not detectable in foods at a detection limit of 20 µg/kg. In a large number of samples, primarily fish in oil, this limit was far exceeded. After forcing the distributors to control their products in this respect, BADGE concentrations in canned products from the Swiss market dropped radically.

In a second paper (3) it was shown that BADGE is often accompanied by dimers and trimers, as well as chlorohydroxy compounds derived from the reaction with hydrochloric acid. In some samples, these compounds far exceeded the concentration of BADGE and reached several 1000 µg/kg, compelling us to widen the range

of compounds kept under control.

This paper describes the analysis of the glycidyl ethers of Bisphenol-F and Novolac, as well as the concentrations found in canned foods.

Bisphenol-A is formed by reaction of phenol with acetone, whereas Bisphenol-F is produced from phenol and formaldehyde, i.e. the aromatic rings are interconnected via a methylene instead of a propylene unit. While acetone reacts with the para-position of the phenol almost exclusively, formaldehyde is also bonded to the ortho-carbon. As a consequence, Bisphenol-F exists in 3 isomers, with ring connections in para-para, para-ortho and ortho-ortho positions to the phenol. Since the ortho-position is still less reactive than para, the 0,0-isomer is the least abundant component.

The reaction of phenol with acetone results in a compound with two aromatic rings (Bisphenol-A) almost exclusively. This is different when using formaldehyde: owing to the accessibility of more than one carbon atom of the ring, two (or theoretically three) phenols may be connected to one ring. This provides a way for polymerization over ring-ring connections. In fact, technical products are usually mixtures of the 2-ring isomers (Bisphenol-F) and compounds with 3 and more phenolic building blocks. They are called Novolacs. According to *Oldring* (2), the term Novolac includes Bisphenol-F as the basic member.

Novolacs are complex mixtures of components with varying numbers of aromatic rings as well as of positional isomers. For instance, there are 4 major isomers of the 3-ring system, with the center phenol substituted in ortho and para and the other rings attached with their ortho or para carbon atom. 4-ring systems consist of many more isomers.

After reaction with epichlorohydrin, Bisphenol-F-diglycidyl ether (BFDGE) and Novolac glycidyl ether (NOGE), also called «Epoxy Novolac», are formed, some structures of which are shown in figure 1.

The complexity of NOGE materials is further increased considering that polymerization is possible also over the oxygen: Epoxy compounds reacting with

Figure 1. Some structures of BFDGE and NOGE, as well as of a glycidoxypropyl group hydrolyzed with HCl

phenols yield oligomers as they exist for BADGE, with the difference that there is

a large number of isomers.

If NOGE is used for stabilizing organosols, reaction with hydrochloric acid opens the epoxy group and produces a large number of chlorohydroxy compounds. The position of the hydroxyl and the chloro group shown in figure 1 corresponds

to that determined by Schönenberger (4).

NOGE seems to be of interest for replacing BADGE, probably because Swiss (and other countries') legislation does not define a limit. However, BFDGE or NOGE is not even listed as an accepted component of food contact materials. Since there is no satisfactory toxicological evaluation and the material contains glycidoxypropyl groups as BADGE, Swiss food control authorities apply the same limit as for BADGE, i.e. «not detectable at a detection limit of 20 μ g/kg» related to the can content.

Methods

LC and LC-LC were performed on a Dualchrom 3000 (C.E. Instruments, Milan, Italy), basically an automated LC-GC system, equipped with 3 valves in the LC part and a fluorescence detector (Merck F1050). For GC-MS, an UltraTrace gas chromatograph equipped with an autosampler for large volume on-column injection and an early vapor exit was used, coupled to a mass spectrometer MD-800 (all C.E. Instruments).

Standards of BFDGE and NOGE were obtained from Vernicolor (Grüningen, Switzerland). In the near future, Fluka (Buchs, Switzerland) will offer BFDGE (15144), Bisphenol-F-bis-(2-hydroxy-3-chloropropyl) ether (BFDGE.2HCl, 15139), and Bisphenol-F-bis-(2,3-dihydroxypropyl) ether (15142). Pentane of technical grade (Siegfried, Zofingen, Switzerland) and methyl *tert*. butyl ether

(MTBE, Merck, zur Synthese) were used after redistillation.

BFDGE was analyzed by normal phase LC with fluorescence detection (FD) together with BADGE (1): The oil or the food extract with heptane/MTBE 80/20% was injected onto a 25 cm \times 2 mm i.d. column packed with the cyano phase GromsilCN 2 PR 5 μ m (Stagroma, Wallisellen, Switzerland). The mobile phase (400 μ l/min) consisted of pentane/MTBE 80/20%. Fluorescence detection occurred at 225/295 nm.

Positive results were confirmed by LC-LC with heart cutting, adding a silica gel column (25 cm \times 2 mm i.d., packed with Spherisorb Si 5 μ m, Stagroma) and an arrangement enabling the detection of the components of interest first from the cyano, then from the silica gel column. Usually only the BFDGE peak eluted last (p,p-BFDGE) was transferred to the second column. As a further confirmation of peak identity it was taken into consideration that BFDGE is composed of three peaks with an approximate composition as shown below.

For quantitation of BFDGE, the peak areas of the three isomers from the first LC column were added up and compared to an external standard of BFDGE,

Araldit PY306 (Ciba, Basel). The FD response of the summed BFDGE was

practically identical with that of BADGE.

3- and 4-ring NOGE was analyzed using the above cyano LC column and 35% 2-propanol/pentane as mobile phase at 400 µl/min. 100 µl of 10% solutions of oil in heptane or the extract of 1 g of foodstuff in 5 ml of heptane/MTBE 80/20% were injected. Detection again occurred at 225/295 nm. Epoxy Novolac PY 307-1 (Ciba, Basel), consisting of some 54% BFDGE and 23% 3-ring and 10% 4-ring NOGE, was used as a standard material.

GC-MS was performed as described in (3). Triglycerides were removed by LC-LC or LC-backflush-LC. 100 μ l of the LC fractions were injected into GC using concurrent eluent evaporation with the on-column interface. The precolumn system ahead of the early vapor exit consisted of a 1.5 m \times 0.53 mm i.d. uncoated precolumn and a 1.5 m \times 0.32 mm i.d. retaining precolumn coated with PS-255 (a methyl polysiloxane, Fluka) of 0.15 μ m film thickness. An 8 m \times 0.25 mm i.d. capillary column coated with an 0.2 μ m film of SOP-50, a symmetric 50% phenyl polysiloxane obtained from W. Blum (Ciba, Basel, Switzerland), served as separation column.

NOGE with more than 2 aromatic rings were identified by RPLC-MS as described in (3), using a Finnigan MAT SSQ 710C mass spectrometer operated in the Atmospheric Pressure Chemical Ionization (APCI) mode. HPLC separation was performed on a 125 × 2 mm i.d. column packed with Nucleosil 100-5 C₁₈ material and a mobile phase of 15% water in methanol (330 µl/min).

GC-MS analysis of 3-ring NOGE components was performed on a 3 m \times 0.25 mm i.d. fused silica capillary coated with a 20 nm film of PS-255 (prepared in the laboratory). 0.3 μ l of sample was injected on-column. The GC-MS interface was heated to 350 °C, the ion source to 210 °C. Temperature was programmed to

330 °C at 15 °/min.

Results

Bisphenol-F-diglycidyl ether (BFDGE)

Figure 2 shows the LC-FD chromatogram of the extract of a new, empty can releasing an amount of BFDGE which would have corresponded to about 1500 µg/kg related to a hypothetical can content. The cyano phase separated all three BFDGE isomers almost to baseline and isolated them from BADGE. Since steric hindrance favors para-substitution, the p,p- and o,p-isomers should be expected to be predominant. The assumption that the small first peak represents the o,o-isomer, while the last corresponds to the p,p-isomer also fits the expectation that the stretched molecule is most strongly retained.

Figure 3 shows gas chromatograms of BADGE and BFDGE together with their chlorohydroxy compounds on the 50% phenyl stationary phase. They were recor-

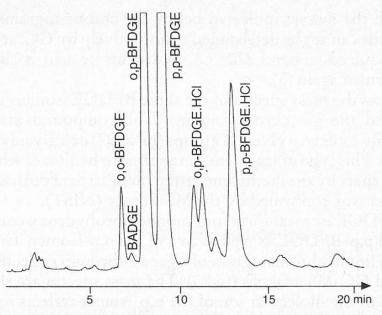


Figure 2. LC-FD chromatogram of an extract of an empty can showing BFDGE (with probable identifications of its isomers), a small amount of BADGE, and the monochlorohydroxy compounds of BFDGE (BFDGE.HCl)

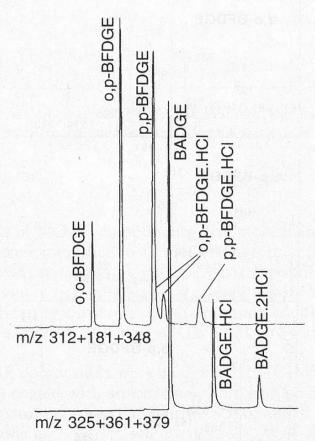


Figure 3. Sections of GC-MS chromatograms of the combined extracts of new, empty cans releasing BADGE (lower trace) and BFDGE (top trace), as well as chlorohydroxy compounds, positioned to equal retention times

ded by MS with the masses indicated below the chromatograms. The chlorohydroxy compounds cannot be determined quantitatively by GC: at the high analysis temperatures required (around 270 °C), hydrochloric acid is eliminated and the epoxy group formed again (3).

Figure 4 shows the mass spectra of the three BFDGE isomers assigned as in the above liquid and the gas chromatograms. The compound assumed to be the 0,0-isomer readily loses two glycidyl groups (m/z 197) or a glycidyl and a glycidoxy group (m/z 181). This type of fragmentation seems to be slower when the glycidoxy groups are kept apart by the methylene group being in para position. The spectrum

of the o,p-isomer was confirmed by the MS-library (NIST).

The three BFDGE isomers form four monochlorohydroxy compounds, i.e. one each of 0,0- and p,p-BFDGE as well as two of the 0,p-isomer. Three of them were identified in the liquid chromatogram of figure 2 through collection of the respective fraction and GC-MS analysis (fig. 3). The mass spectra are shown in figure 5. The large signal of the molecular ion of the p,p-isomer reflects its lower tendency to fragment by loss of the propyl moiety as observed for the p,p-BFDGE. 0,0-BFDGE.HCl might be coeluted with p,p-BFDGE, but is a minor component anyway.

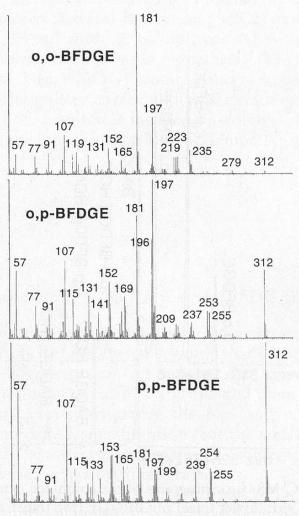


Figure 4. Mass spectra (EI) of the three BFDGE isomers

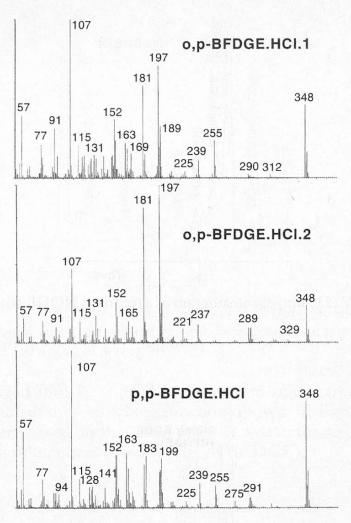


Figure 5. El-Mass spectra of three BFDGE.HCl isomers. o,p-BFDGE.HCl.1 and o,p-BFDGE.HCl.2 were assigned by increasing GC retention time

NOGE

Since no standards of NOGE components with more than two rings (BFDGE) were available, they were identified in an industrial product (Epoxy Novolack PY 307-1). The mixture was separated by RPLC. A corresponding LC-UV (235 nm) chromatogram is shown in figure 6. Peaks were analyzed by LC-MS. BFDGE was recognized by a dominating ion at m/z 330 (ammonium adduct), 3-ring NOGE by ions at m/z 492 and 475 (20%), 4-ring NOGE by m/z 654 and 586 (40%), 5-ring NOGE by m/z 816.

The 3-ring NOGE compounds were analyzed by GC-MS (EI). Using a 3 m \times 0.25 mm i.d. column coated with an extremely thin film of PS-255, the Total Ion Current (TIC) chromatogram shown in figure 7 was obtained. The EI-mass spectra are summarized in table 1.

Since the analysis of the samples (oils and food extracts) was performed on a normal phase LC (NPLC) column, peak identification had to be transferred from RPLC-MS. Fractions from the RPLC chromatogram were collected, 1:1 diluted

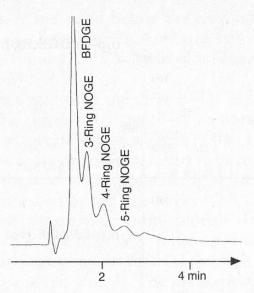


Figure 6. RPLC-UV (235 nm) chromatogram of a technical NOGE with peaks identified by LC-MS

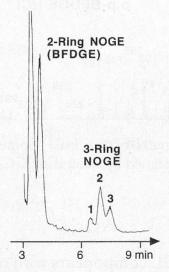


Figure 7. GC-MS (TIC) chromatogram of NOGE components

Table 1. Mass spectra (EI) of the three main 3-ring NOGE isomers. Peak numbers refer to figure 7. Moleculare mass, 474

| Peak nr. | Mass signal (relative abundance in %) | | | | | | | | | |
|----------|---|--|--|--|--|--|--|--|--|--|
| 1 | 107 (100), 105 (95), 253 (65), 57 (65), 197 (60), 343 (55), 91 (60), 133 (55); 474 (25) | | | | | | | | | |
| 2 | 107 (100), 105 (95), 253 (65), 57 (65), 197 (60), 343 (55), 91 (60), 133 (55); 474 (25) 107 (100), 57 (65), 343 (40), 253 (35), 163 (35), 197 (30), 105 (30), 91 (25), 131 (25), 133 (25), 311 (20), 474 (20) | | | | | | | | | |
| 3 | 107 (100), 57 (70), 474 (30), 163 (30), 359 (25), 343 (20), 91 (20), 165 (20), 311 (15), 133 (15) | | | | | | | | | |

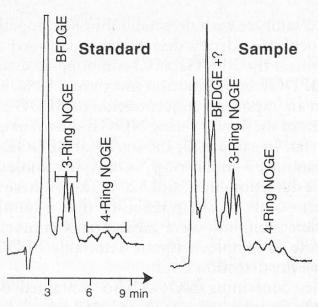


Figure 8. NPLC-FD (225/295 nm) chromatograms of the Epoxy Novolack PY 307-1 and the extract from a sample of canned octopus in vegetable oil (containing 600 μg/kg of 3-ring and 150 μg/kg of 4-ring NOGE)

with water, extracted into 20% MTBE in pentane and analyzed on the NPLC column. This enabled the peak identification shown in figure 8. Quantitative determinations were based on the assumption of a detector response equal to that of BFDGE (which in turn was equal to that of BADGE).

BFDGE and NOGE in canned foods

BFDGE was analyzed together with BADGE in 227 samples of oily canned foods (\geq 5% oil or fat), 209 of which were taken from the Swiss market between November 1996 and February 1997. For most samples, the detection limit was at or below 20 µg/kg (sum of the 3 isomers), whereas for a few others interfering material increased it to about 50 µg/kg.

As shown in table 2, 207 samples (91%) did not contain BFDGE above the detection limit. Since there had been no previous action against the use of BFDGE and NOGE, it shows that this kind of food contamination was clearly less frequent than that by BADGE. Since BFDGE and NOGE have not been analyzed before, no trend can be documented, but from the information of some producers we know of cans where BADGE has been replaced by NOGE.

Table 2. BFDGE in 217 samples

| Concentration | Number of samples | | | | |
|--------------------------|-------------------|--|--|--|--|
| > 1000 µg/kg | 3 (1.3%) | | | | |
| 100–1000 μg/kg | 10 (4.4%) | | | | |
| 20–100 μg/kg | 7 (3.1%) | | | | |
| n.d. (< 20 – < 50 μg/kg) | 207 (91%) | | | | |

Table 3 lists the 20 samples with detectable BFDGE together with the concentrations of the monochlorohydroxy derivatives mentioned above. Results show that the concentrations of the BFDGE.HCl components usually corresponded to around 30% of the BFDGE concentration (maximum 54%, sample 2). No sample was found to contain an important concentration of BFDGE.2HCl.

The concentrations of the 3- and 4-ring NOGE shown in table 3 often exceeded those of BFDGE by far. In sample 12, 150 µg/kg of BFDGE came along together with 1650 µg/kg of summed 3- and 4-ring NOGE. In sample 20, with a concentration of BFDGE at the detection limit, still 520 µg/kg of these NOGE components were detected, which points to the possibility that a number of samples with BFDGE below the detection limit were substantially contaminated with NOGE. On the other hand, the 10 samples without detectable BFDGE analyzed did not contain NOGE above the detection limit.

Almost all samples containing NOGE also contained BADGE. Of the 209 canned foods from the Swiss market analyzed, 167 samples contained detectable amounts neither of BFDGE nor BADGE. Of the 42 samples rejected, 40 contained more than 20 μ g/kg BADGE in the can content, 19 of them also more than 20 μ g/kg of NOGE. A single sample was rejected solely because of an excessive concentration of NOGE. However, in a number of samples recently obtained from manufacturers for testing, BADGE was totally replaced by NOGE.

Table 3. Concentrations (μg/kg) of BFDGE.HCl as well as 3- and 4-ring NOGE in the 20 samples containing detectable amounts of BFDGE

| Sample | BFDGE | BFDGE.HCl | 3-Ring NOGE | 4-Ring NOGE | | |
|--------|-------|-----------|--|-------------------|--|--|
| 1 | 1350 | 450 | | 2007 | | |
| 2 | 1300 | 700 | 930 | 400 | | |
| 2 3 | 1020 | 350 | | | | |
| 4 | 900 | <50 | Experience of the control of the con | | | |
| 5 | 750 | 110 | TERRES SELL FOREILE | SA GRANA MAR | | |
| 6 | 650 | 180 | 480 | 150 | | |
| 6 7 | 320 | 100 | | at a ready spirit | | |
| 8 | 300 | 200 | 460 | 150 | | |
| 9 | 300 | 100 | day and sept and | on Highligh | | |
| 10 | 200 | 70 | 700 | 500 | | |
| 11 | 180 | <50 | Arra Janderson Vac | ead reaching the | | |
| 12 | 150 | <50 | 1150 | 500 | | |
| 13 | 120 | <50 | | | | |
| 14 | 80 | <50 | <20 | <20 | | |
| 15 | 70 | <50 | <20 | <20 | | |
| 16 | 60 | <50 | La Companya (1975) | | | |
| 17 | 60 | <50 | 360 | 120 | | |
| 18 | 50 | <50 | 110 | 30 | | |
| 19 | 30 | <50 | <50 | | | |
| 20 | 20 | <50 | 220 | 300 | | |

Accumulated contaminants

Data from the 42 products rejected is given in table 4. Cans are characterized by whether they were made of two or three pieces and whether or not they had an easy open lid. As shown by the third column, a majority of the rejected samples were canned sea foods. 26 samples were in oil, while 16 were in a primarily aqueous liquid. Concentrations of BADGE, NOGE and their derivatives illustrate how contaminants tend to be accumulated. In sample 1, for instance, a high concentration of BADGE was accompanied by a substantial concentration of BADGE. HCl and BADGE dimer, as well as by 2000 µg/kg of 3- and 4-ring NOGE. The analysis of BADGE alone thus yields an incomplete evaluation of the contamination. In fact, many canned foods containing less than 100 µg/kg BADGE were strongly contaminated by chlorohydroxy compounds or oligomers as well as by NOGE or the corresponding chlorohydroxy derivatives.

The last column in table 4 sums all the concentrations determined. This combines, of course, components with strongly different characteristics. They have in common, however, that at present there is no satisfactory evidence to ensure that they are harmless to the consumer. The sum demonstrates that the total amount of contaminants frequently exceeds 1 mg/kg. It should be noted that blank fields mean that a component was not analyzed, i.e. the sums of many lines could still be

substantially too low.

Discussion and conclusion

This investigation into the analysis of NOGE was undertaken because it seemed that NOGE would be increasingly used for replacing BADGE. However, as mentioned in the introduction, the Swiss authorities do not accepted such a substitution as a solution of the problem.

The results show that the analysis of BFDGE does not provide a realistic evaluation of the contamination, because the products applied in reality usually contain substantial amounts of NOGE compounds with 3 and more rings. Just considering the 3- and 4-ring NOGE, the total contamination may be more than

ten times higher.

When used as a stabilizer for organosol coatings, some NOGE is hydrolyzed, forming chlorohydroxy compounds. These have an analogous structure component to chloropropanols which are considered cancerogenic (5). BFDGE.HCl concentrations usually corresponded to around 30% of the BFDGE concentration. We did not analyze the chlorohydroxy derivatives of the NOGE components with more than 2 aromatic rings (also because they consist of exceedingly many isomers). If it is assumed that all epoxy groups have the same probability of being hydrolyzed, the proportion of the chlorohydroxy compounds increases with the number of epoxy groups and easily exceeds 50% for 3- and 4-ring structures. Hence sample nr. 10 in table 3 or nr. 34 in table 4 with 200 µg/kg of BFDGE and 1200 µg/kg of 3-

Table 4. The 42 rejected samples. 2p, 3p, 2 or 3 piece can; ea, easy open lid. Concentrations referring to can content (µg/kg)

| Nr. | Type | Food | Liquid | BADGE | | | | | NOGE | | | | Sum |
|-----|--------|-----------|--------|-------|------|-------|--------|---------|-------|------|---------|----------|------|
| | of can | | | BADGE | .HCl | .2HCl | dimers | trimers | BFDGE | .HCl | 3 rings | 4 rings | |
| 1 | 2p, ea | octopus | oil | 1700 | 370 | | 500 | ≤100 | 150 | | 1500 | 500 | 4720 |
| 2 | 3p, ea | tuna | oil | 730 | 175 | ≤30 | 970 | 70 | <20 | | | | 1945 |
| 3 | 2p, ea | mussels | sauce | 500 | 100 | | | | 1350 | 450 | | | 2400 |
| 4 | 2p, ea | sardines | oil | 450 | 80 | 40 | | | <50 | | | | 570 |
| 5 | 2p, ea | sardines | oil | 390 | 90 | | 150 | <20 | <50 | | 110 | 30 | 770 |
| 6 | 2p, ea | tuna | oil | 360 | 25 | 600 | | | <20 | | 215 | 300 | 1500 |
| 7 | 3p, ea | soup | | 220 | 30 | | | | <50 | | | | 250 |
| 8 | 2p, ea | sardines | oil | 220 | 40 | | 540 | 500 | <50 | | | 护业等 | 1300 |
| 9 | 3p | meat loaf | | 210 | <10 | 57 | | | <50 | | | | 210 |
| 10 | 3p, ea | tuna | oil | 200 | 100 | 30 | | | <20 | 100 | | | 330 |
| 11 | 2p, ea | sardines | oil | 200 | <20 | | 250 | 280 | 80 | | <20 | <20 | 810 |
| 12 | 2p, ea | sardines | oil | 170 | | | 215 | 230 | 70 | | <20 | <20 | 685 |
| 13 | 3p, ea | soup | | 160 | 50 | | <5 | <5 | <20 | | | | 210 |
| 14 | 2p, ea | anchovies | oil | 160 | 100 | | | | 1300 | 700 | 930 | 400 | 3590 |
| 15 | 3p, ea | soup | | 115 | | | | | <20 | | | | 115 |
| 16 | 2p, ea | sardines | oil | 90 | | | | | <20 | | | | 90 |
| 17 | 2p, ea | sardines | oil | 90 | | | | | <20 | | | | 90 |
| 18 | 3p, ea | rice | water | 80 | | | 20 | 55 | <20 | | | | 155 |
| 19 | 3p, ea | olives | water | 80 | | | 320 | 400 | <20 | | | | 800 |
| 20 | 2p, ea | sardines | oil | 80 | | | 1600 | 1800 | <50 | | | | 3480 |
| 21 | 3p, ea | tuna | oil | 80 | <20 | | 800 | 500 | <50 | | | | 1380 |
| 22 | 2p, ea | tuna | oil | 75 | | | | | <20 | | | | 75 |
| 23 | 2p, ea | sardines | oil | 70 | <20 | | 100 | 90 | <20 | | | | 260 |
| 24 | 2p, ea | sardines | oil | 70 | 200 | | 60 | 80 | 30 | | <50 | | 240 |
| 25 | 2p, ea | hering | sauce | 65 | | | | | <20 | | | 7 A 12 - | 65 |
| 26 | 3p, ea | peas | oil | 60 | | | | | <20 | | | | 60 |
| 27 | 3p, ea | tuna | oil | 60 | | | | | <20 | | | | 60 |
| 28 | 3p, ea | tuna | oil | 60 | | | | | 750 | 110 | | | 920 |

| Nr. | Туре | 2 - | | Food Liquid | | BADGE | | | | | NOGE | | | | Sum |
|-----|--------|------------|-------|-------------|------|--------|--------|---------|-------|------|---------|---------|------|--|-----|
| | of can | | | BADGE | .HCl | .2HCl | dimers | trimers | BFDGE | .HCl | 3 rings | 4 rings | | | |
| 29 | 2p, ea | sardines | sauce | 55 | | | | | 15 | | <20 | <20 | 70 | | |
| 30 | 2p, ea | mackerels | oil | 50 | 150 | 1100 | 55 | <20 | <20 | | | | 1355 | | |
| 31 | 3p | goose-fat | | 50 | | 19-2-5 | | | 900 | <50 | | | 950 | | |
| 32 | 2p, ea | tuna | sauce | 50 | 150 | 350 | | | <20 | | | | 550 | | |
| 33 | 2p | tuna | oil | 50 | 100 | 2700 | | | <20 | | | | 2850 | | |
| 34 | 2p, ea | anchovies | oil | 50 | | | | | 200 | | 700 | 500 | 1450 | | |
| 35 | 2p, ea | sardines | oil | ≤40 | | | 100 | 70 | 120 | | | | 290 | | |
| 36 | 2p, ea | sardines | sauce | 40 | | | 10 | 10 | <20 | | | | 60 | | |
| 37 | 2p, ea | octopus | oil | 35 | | | | | 300 | <200 | 460 | 150 | 945 | | |
| 38 | 3p | cocos milk | | 35 | | | | | <20 | | | | 35 | | |
| 39 | 2p, ea | calamares | water | 30 | | | 50 | 100 | 60 | | 360 | 120 | 720 | | |
| 40 | 2p, ea | sardines | oil | 30 | | | | | <20 | | | | 30 | | |
| 41 | 2p, ea | octopus | water | <20 | | | | | 650 | | 480 | 150 | 1280 | | |
| 42 | 2p, ea | mussels | water | <20 | 25 | 900 | | | <20 | | | | 925 | | |

and 4-ring NOGE is likely to contain additional 700 µg/kg of NOGE.HCl,

increasing the sum of the concentrations above 2 mg/kg.

Table 4 not only neglects the chlorohydroxy compounds of NOGE, but also its oligomers, i.e. NOGE moieties connected to each other over the oxygen of a phenol and an epoxy group. As shown for BADGE, such oligomers may well far exceed the concentration of the monomers. Again, their analysis is likely to be extremely demanding because of the number of possible isomers.

Repeatedly cans have been obtained which were declared «BADGE-free». An extract and RPLC-FD revealed a «forest» of peaks and it seemed pure coincidence that there was no peak at the retention time of BADGE. These cans are BADGE-free, indeed, but the selectivity through fluorescence detection suggests the presence of massive amounts of material of similar nature. We know by now that in many instances, these cans released NOGE and the related components.

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Summary

Epoxy novolacs (NOGE) seem to find increasing use in coatings for cans, partly to replace Bisphenol-A-diglycidyl ether (BADGE). Bisphenol-F-diglycidyl ether (BFDGE), the 2-ring NOGE, was analyzed by LC and LC-LC with fluorescence detection (FD) or GC-MS. 3- and 4-ring NOGEs were identified by LC-MS and determined in foods by LC-FD.

NOGE was less frequently found in canned foods than BADGE and was almost always accompanied by BADGE. In 9% of 227 samples, BFDGE concentrations exceeded 20 µg/kg, in 6% also the 100 µg/kg above which products were confiscated. 3- and 4-ring NOGE frequently reached concentrations exceeding that of BFDGE by a factor of 5. When also including the chlorohydroxy-NOGE and the oligomers into consideration, the number of components to be analyzed becomes exceedingly high.

Zusammenfassung

Epoxy-Novolac (NOGE) scheint vermehrt für die Innenbeschichtung von Konservendosen eingesetzt zu werden, teilweise als Ersatz von Bisphenol-A-Diglycidyl Ether (BAD-GE). Bisphenol-F-Diglycidyl Ether (BFDGE), der 2-Ring NOGE, wurde über LC und LC-LC mit Fluoreszenzdetektion (FD) oder GC-MS analysiert. 3- und 4-Ring NOGE-Komponenten wurden mit LC-MS identifiziert und mit LC-FD in Lebensmitteln nachgewiesen.

NOGE wurde in Lebensmitteln aus Dosen seltener gefunden als BADGE und war fast immer ein Begleiter von BADGE. In 9% aller Proben überschritt die BFDGE-Konzentration 20 µg/kg und in 6% auch jene 100 µg/kg, über der die Proben beschlagnahmt wurden. Die Konzentrationen von 3- und 4-Ring NOGE überschritten jene von BFDGE leicht um einen Faktor 5. Wenn auch die NOGE-Chlorhydroxyverbindungen und die Oligomere

berücksichtigt werden sollen, wird die Anzahl der zu analysierenden Komponenten extrem hoch.

Résumé

Il paraît que époxy-novolac (NOGE) est utilisé de plus en plus comme composante de vernis pour l'interieur des boîtes de conserves, en partie comme replaçement de bisphenol-A-diglycidyl ether (BADGE). Bisphenol-F-diglycidyl ether (BFDGE), le NOGE avec deux anneaux, a été analysé par LC et LC-LC avec détection fluorimétrique (FD) ou GC-MS. Les composantes de NOGE avec 3 ou 4 anneaux ont été identifiées par LC-MS et analysées dans les aliments par LC-FD.

NOGE se trouve dans les aliments moins souvent que BADGE et presque toujours ensemble avec BADGE. Dans 9% des échantillons, BFDGE dépassait 20 µg/kg et dans 6% 100 µg/kg, limite au-delà de laquelle les produits ont été confisqués. Les concentrations de NOGE avec 2 ou 3 anneaux dépassaient ceux de BFDGE facilement d'un facteur de 5. Si les composés chlorohydroxy et les oligomères de NOGE sont aussi pris en considération, le nombre de composantes à analyser devient extrêmement élevé.

Literature

- 1. Biedermann, M., Grob, K., Bronz, M., Curcio, R., Huber, M. and Lopez-Fabal, F.: Bisphenol-A-diglycidyl ether (BADGE) in edible-oil-containing canned foods: determination by LC-LC-fluorescence detection. Mitt. Gebiete Lebensm. Hyg. 87, 547–558 (1996).
- 2. Oldring, P. (Ed.): Waterborne and Solvent Based Epoxies and their End User Applications, SITA Technology Ltd, Wimbledon, UK, 1996.
- 3. Biedermann, M., Bronz, M., Grob, K., Gfeller, H. and Schmid, J.P.: BADGE and its accompanying compounds in canned oily foods: Further results. Mitt. Gebiete Lebensm. Hyg. 88, 277–292 (1997).
- 4. Schönenberger, B.: Fluka, Buchs, Switzerland, see addendum ref. 3.
- 5. Rodman, L.E. and Ross, R.D.: GLC of 3-Chloropropanediol. J. Chromatogr. 369, 97-103 (1986).

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