**Zeitschrift:** Mitteilungen aus Lebensmitteluntersuchungen und Hygiene = Travaux de chimie alimentaire et d'hygiène

**Herausgeber:** Bundesamt für Gesundheit

**Band:** 91 (2000)

**Heft:** 5

**Artikel:** Migration of Novolac glycidyl ether (NOGE) and its chlorohydrins into aqueous canned foods

**Autor:** Brem, Sandra / Grob, Koni

**DOI:** https://doi.org/10.5169/seals-981882

# Migration of Novolac Glycidyl Ether (NOGE) and its Chlorohydrins into Aqueous Canned Foods

Sandra Brem and Koni Grob, Official Food Control Authority of the Canton of Zurich, Zurich

Received 18 April 2000, accepted 14 July 2000

## Introduction

### *Novolac glycidyl ether (NOGE)*

Novolac glycidyl ether (NOGE), also called "epoxy novolac", is a complex mixture of epoxy compounds used for coatings, such as those of food cans and the lids of glass jars. Novolac is the technical name for the mixtures obtained by reaction of phenol with formaldehyde under acidic conditions (for structures, see (1)). Its smallest molecular weight component is called bisphenol F and exists in three isomers. There are seven isomers with three aromatic rings and 27 4-ring components. Novolac is reacted with epichlorohydrin to result in the glycidyl ether (NOGE).

### *NOGE as additive in organosols*

In Europe, NOGE became a problem after 1996, when it was used to substitute bisphenol A diglycidyl ether (BADGE) in organosols. BADGE was under pressure since it widely exceeded national legal limits (2) as well as the limit defined by the Council of Europe. NOGE replaced BADGE as an additive for scavenging hydrogen chloride from the PVC in order to increase the thermostability of the coating during curing (3). Added to the coating at the level of several percents and being largely extracted into some foods, NOGE again reached concentrations in the can content which substantially exceeded 1 mg/kg.

NOGE was not approved as an additive because of lacking data on toxicity. In the US, its use is, nevertheless, legal because it was already applied before legislation requiring testing was introduced. In December 1999, the Scientific Committee for

Food (SCF) of the EU expressed the opinion that the evaluation of the safety of using NOGE is not possible on the basis of the data available and that it should, therefore, not be used as an additive. The EU plans to ban the use of NOGE as additive and to set a specific migration limit (SML) for the products still on the market. The limit might be at 1 mg/kg for the NOGE components with at least one epoxy or chlorohydrin function and a molecular weight below 1000 Dalton. Such a limit calls for analytical control methods.

NOGE with a molecular weight up to 1000 D comprises compounds with up to six aromatic rings, existing in large numbers of isomers. Some of the epoxy groups are converted to chlorohydrins by reaction with hydrochloric acid cleaved from PVC during curing of the coating. In foods with a coherent fat or oil phase in contact with the can coating, these components are almost exclusively located in the oil phase, which protects the epoxy function from hydrolysis. In aqueous foods, the epoxy groups are hydrolyzed or react with food components (4).

### *Subjects of this paper*

This paper describes experimentation on the analysis of NOGE in aqueous foods. The epoxy groups are virtually completely hydrolyzed, i.e. the compounds of interest comprise diol and chlorohydrin functions on the glycidyl moiety. As the fully hydrolyzed components are considered to be of no toxicological concern, the analysis is directed on to the chlorohydrins. Another paper (5) will describe the analysis of NOGE in oily foods, where the components of concern are those containing epoxy and/or chlorohydrin functions. Since the analysis of epoxy compounds requires special attention, the analytical approach differs.

The paper first deals with questions about the extent NOGE components migrate into foods, in particular up to which molecular weight (ring number) migration is significant. Transfer of BADGE from organosol coatings into aqueous, sterilized foods ranged from 16 to more than 96 %, averaging around 50 % (referring to acetonitrile extraction of the coating, which is fairly complete for organosols (6)). For its chlorohydrins, migration is higher, with an average of almost 80 % for BADGE.2HCl. This suggested that also higher molecular weight NOGE and particularly the chlorohydrins might be found in aqueous foods.

Another subject concerns approximations by which the control method could be simplified. The total migration could, for instance, be extrapolated from easily determined components, such as BFDGE. However, previous findings were confirmed that in some can coatings NOGE is almost free of BFDGE. In fact, the percentage of BFDGE in NOGE recovered from coatings varied between 0.05 % (7) and some 10 % (20–30 % being the typical concentration in the NOGE added to the organosol). BFDGE seems to evaporate to a variable extent during curing of the coating, which renders the relationship between BFDGE and NOGE unstable and unsuitable for extrapolations. 3-Ring NOGE is present in a more constant proportion of the 3- to 6-ring components.

*Simal Gandara et al.* (8) were the first to analyze BFDGE, but no method has been described for the analysis of a broader range of NOGE components. Since individual analysis of 2- and 3-ring components in a single separation seemed impossible, size exclusion chromatography (SEC) was used for preseparation (9), followed by reversed phase liquid chromatography (RPLC) with fluorescence detection (FD) as introduced by *Paseiro Losada et al.* (10).

## Methods

### *Preparation of hydrolyzed 2- and 3-ring chlorohydrins as reference materials*

200 mg (in 2 ml dichloromethane/hexane 1:1) of a commercial NOGE (Araldit EPN 1179, Ciba, Basel, CH) was fractionated preparatively using a 16 mm i.d. column packed with 20 g of silica gel Merck 60, 70–230 mesh (Darmstadt, Germany). The first 85 ml of hexane/dichloromethane/propanol 87/10/3 were discarded. The following 10 ml contained the bulk of the BFDGE. The following 30 ml of the same eluent were discarded. Then the 3-ring NOGE was eluted with 25 ml of hexane/dichloromethane/propanol 77/20/3.

The 2- and 3-ring fractions were converted into mixed diols/chlorohydrins: to 0.5 mg of the material dissolved in 1.5 ml of dioxane, 4 ml of 0.2 % hydrochloric acid was added. The mixture was heated to 120° C in a pressure cooker for 1 h and then neutralized using 10 % sodium hydroxide solution.

### *Opening of the can*

To facilitate the extraction of emptied cans with acetonitrile, lids of filled cans were opened less than half. Three-piece cans with a side stripe over the seam (fig. 1) were opened such that the stripe was outside the opened section, but in reach to get a probe for a Beilstein test. The cans were emptied, rinsed with water containing some detergent, dried at 100° C in an oven and laid on their side. They were filled with acetonitrile to a known proportion of the internal volume, often to 50 %, such

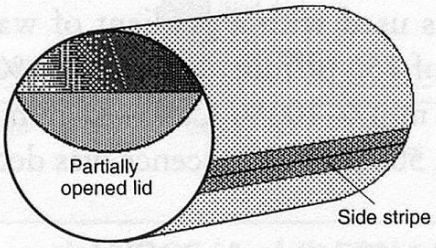


Figure 1 **Opening of cans in order to enable extraction of the coating**

that the solvent was in contact with half of the surfaces of all parts. Extraction was performed for 24 h at 25° C. 10 µl of the extract was injected into RPLC.

For the Beilstein test, a small amount of coating was brought onto a copper wire which was introduced into the tip region of a blue flame. Strong green color was considered as an indication of organically bonded chlorine and organosol ("Beilstein-positive").

### *Analysis of foods*

Foods were analyzed as proposed by *Bas* and *Rijk* (11). The liquid phase was discarded when consumers were assumed to do so (e.g. water from sweet corn). The can content was homogenized by a Polytron blender (Kinematica, Luzern, Switzerland). 4 g of the homogenate (containing 2 g of food) was mixed with 10 ml of acetonitrile, centrifuged, and the liquid phase decanted. The solids were extracted a second time with 10 ml of acetonitrile. The combined liquid phases were defatted by extraction into some 5 ml of pentane and evaporated to dryness after addition of 2 ml of 1-propanol (azeotropic evaporation of water).

### *Size exclusion chromatography*

SEC-FD was performed on a 30 cm × 7.8 mm i.d. Phenomenex (St. Torrance, CA, USA) Phenogel 5 µm, 500 A column, using tetrahydrofurane (THF)/2 % methanol at 400 µl/min as mobile phase (Phoenix SFC syringe pump, Fisons/ThermoQuest, Milan, Italy; Merck F1050 fluorescence detector). FD was performed at 225 (ex)/295 (em) nm. A manual 6-port injection valve (Valco) was used with a 100 µl loop.

Retention windows of the fractions including the hydrolyzed 2- and 3-ring NOGE as well as their chlorohydrins were determined by injection of the reacted 2- and 3-ring fractions obtained as described above. The residue of the evaporated acetonitrile extract from foods was picked up in 400 µl of THF, of which 100 µl were injected. Fractions were collected at the outlet of the detector, brought to dryness, and re-dissolved in 200 µl of acetonitrile. 800 µl of water was added and 500 µl injected into RPLC-FD.

### *Reversed Phase HPLC (RPLC)*

A 25 cm×4.6 mm i.d. column packed with Spherisorb ODS-2, 5 µm (Grom, Herrenberg, Germany) was used with a gradient of water (A), methanol (B), and ethanol (C) at a flow rate of 750 µl/min: 0–5 min: 65 % B; 5–32 min, 65–90 % B; 32–42 min, 90 % B, 42–43 min 0–100 % C; 43–47 min, 100 % C; 47–49 min, back to initial. Injection volume, 500 µl. Fluorescence was detected at 225/295 nm.

## Results

Figure 2 shows an RPLC-FD chromatogram of a mixture of 2- and 3-ring NOGE converted to diols and chlorohydrins. As components are not sufficiently

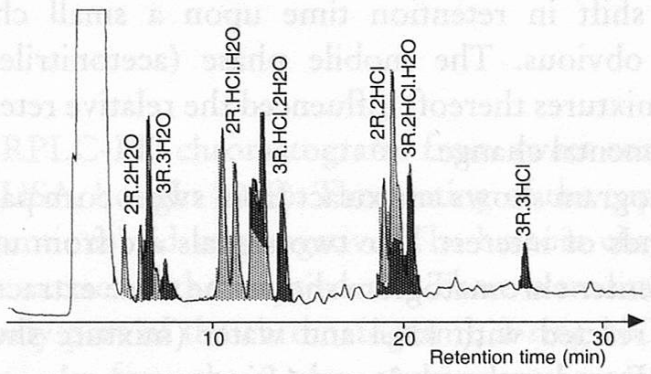


Figure 2 **RPLC-FD of 2- and 3-ring NOGE after conversion of the epoxy groups to diols and chlorohydrins. Abbreviations: number of aromatic rings (2R or 3R) followed by the reactants (.H2O or .HCl)**

well resolved to enable a separate determination of 2- and 3-ring components, preseparation by SEC was introduced.

*Preseparation by SEC*

SEC well separated the 2- to 4-ring NOGE, i.e. the epoxy compounds (fig. 3, bottom). Reaction of the epoxy groups of BFDGE with HCl or water shortened the retention time by more than a phenyl glycidyl moiety, whereby the 2R.2HCl and

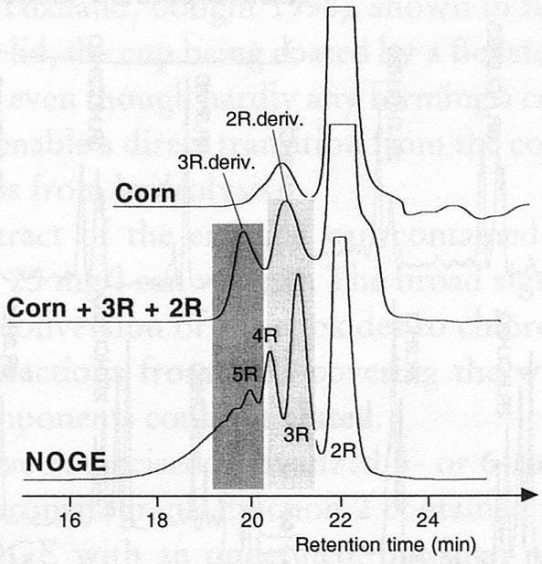


Figure 3 **SEC-FD of a commercial NOGE (Araldit EPN 1179) as well as of an extract of sweet corn with and without admixture of 2- and 3-ring NOGE reacted with HCl and water. The fractions analyzed by RPLC are shaded**

the 2R.2H2O had a similar retention time (the chlorohydrins being eluted slightly later). This strong shift in retention time upon a small change in molecular weight/size is not obvious. The mobile phase (acetonitrile, dichloromethane, methanol, THF, or mixtures thereof) influenced the relative retention times, but did not result in a fundamental change.

The top chromatogram shows an extract from sweet corn packed in a pouch, i.e. free of the compounds of interest. The two signals are from unidentified endogenous material. The center chromatogram shows the same extract after addition of 2- and 3-ring NOGE reacted with HCl and water (mixture shown in fig. 2). The reacted 2-ring NOGE coeluted with 3- and 4-ring epoxy compounds, the reacted 3-ring NOGE with 5- to 7-ring NOGE. The fractions collected for RPLC are shaded.

Preseparation by SEC was tested with the reacted 2- and 3-ring standards (diols and chlorohydrins) shown in figure 2. The chromatograms at the left in figure 4 show the standards before mixing. They were combined, picked up in THF/2% methanol, chromatographed through the SEC system and brought back to the initial volume before being injected into RPLC-FD. Fraction 1, the window from 18 to 19 min, did not contain material of interest. Fraction 2 (19–20.25 min) comprised the 3-ring components with the worst recovery exceeding 85% for the 3R.3H2O. Fraction 3 (20.25–21.75 min) contained the 2-ring components, again with a maximum loss for the 2R.2H2O (less than 20%). Fraction 4 (21.75–22.75 min) merely contained unidentified by-products. This experiment,

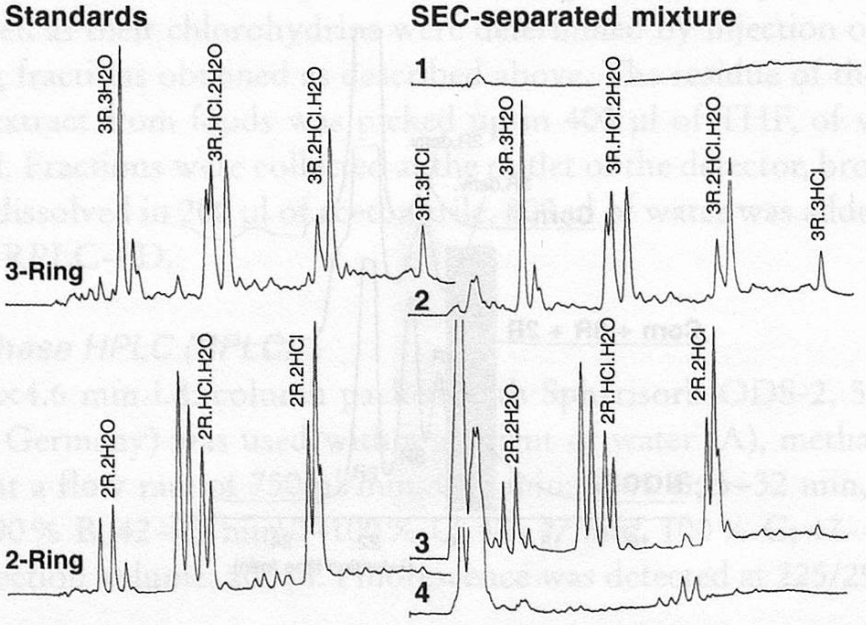


Figure 4 **Standards of reacted 2- and 3-ring NOGE (left) and the same products after being combined and re-separated by SEC (fractions 1–4)**

performed three times, confirmed that preparative SEC was sufficiently quantitative for the application.

### *Sweet corn*

Figure 5 shows RPLC-FD chromatograms from sweet corn packed in a deep-drawn 2-piece can (USA, bought 1998). The coating of the cup was Beilstein-positive, while the conventional lid was negative. The bottom chromatogram resulted from the acetonitrile extract of the emptied can. There were little hydrolyzed material (eluted in the early part of the chromatogram), 2-ring NOGE (BFDGE), and 2-ring chlorohydrins. In fact, the 2-ring components were almost completely extracted into the food (see below). The broad peaks of the 3- to 6-ring components contain the many isomers with epoxy and chlorohydrin functions, the epoxy compounds being eluted in the early part of the signals. It is concluded that epoxy groups have retention characteristics similar to the chloro hydroxy groups. The large amounts of 3- to 6-ring components recovered from the used can suggests that little had migrated into the food.

The corn contained 1.8 mg/kg of 2-ring components (top chromatogram, fraction 3 from SEC). Some 60 % of the functions were reacted with chloride primarily from degraded PVC, while the remaining epoxy groups were hydrolyzed. The chromatogram of the 3-ring compounds is four times less attenuated and represents a total of 110 µg/kg in the corn. The mixed 3R.HCl.2H2O and 3R.2HCl.H2O predominate. No traces of 4-ring components were detected in this or the previous SEC fraction (less than 20 µg/kg).

### *Tuna in water*

The tuna in water (Thailand, bought 1998), shown in figure 6, was in a 2-piece can with a conventional lid, the cup being coated by a Beilstein-positive lacquer. The fish contained some fat, even though hardly any forming a coherent phase in contact with the can surface to enable a direct transition from the coating to the oil and protecting the epoxy groups from hydrolysis.

The acetonitrile extract of the emptied can contained an amount of NOGE which corresponded to 25 mg/l can volume. The broad signals of the 3- and 4-ring NOGE suggest a high conversion of the epoxides to chlorohydrins (5). The upper chromatograms show fractions from SEC covering the whole range of retention times some NOGE components could be eluted.

Fraction 1 could have comprised derivatized 5- or 6-ring NOGE, but nothing alike is visible in the chromatogram. Fraction 2 contained a small amount of non-hydrolyzed 4-ring NOGE with an undefined, but high number of chlorohydrin functions (4R.xHCl). The larger part of this material, with a lower number of chloro hydroxy groups, was found in fraction 3. The unreacted 4-ring NOGE (exclusively epoxy groups) would have been eluted in fraction 4, but is not observed. The material eluted earlier in fraction 2 (with a retention time similar to

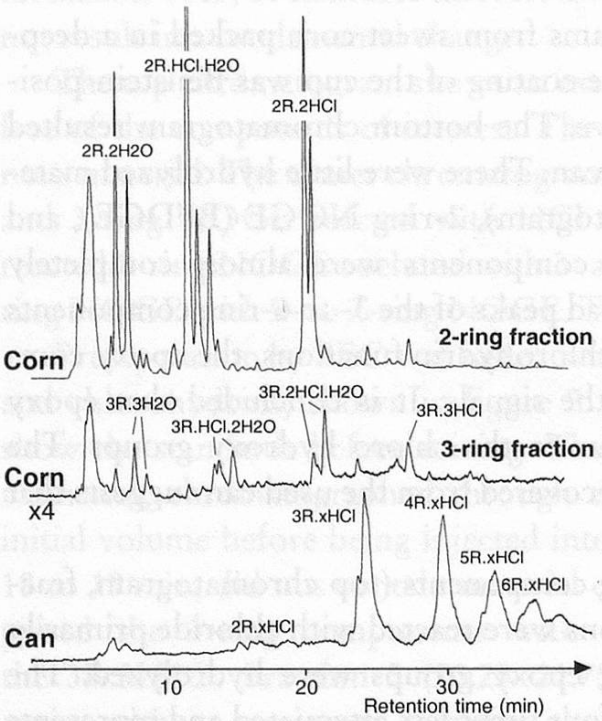


Figure 5 **RPLC-FD chromatograms from sweet corn (top and center, the latter being four times less attenuated) and an acetonitrile extract of the emptied, deep-drawn can (bottom). The peaks of the can extract comprise components with a number of chlorohydrin functions equal to zero up to the number of rings ("x")**

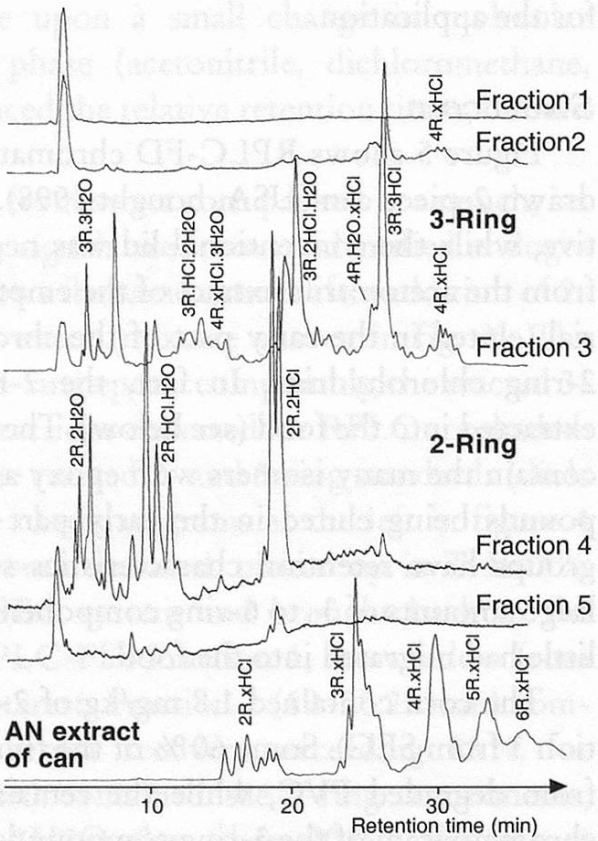


Figure 6 **Tuna in water with fully hydrolyzed 2- and 3-ring NOGE and its chlorohydrins, as well as partially hydrolyzed 4-ring compounds. Bottom, acetonitrile extract of the emptied can**

3R.3HCl) was probably mono-hydrolyzed 4R.xHCl (3R.3HCl was eluted near the end of fraction 3, slightly reaching into fraction 4).

Fraction 3 contained 1.4 mg/kg of 3-ring components with a high proportion of HCl derivatives (small 3R.3H2O *versus* a large 3R.3HCl). It also contained 4-ring components at a roughly estimated concentration of 600 µg/kg. They probably contained an epoxy group (as they would have been in fraction 2 otherwise). 4R.xHCl.2H2O was co-eluted with 3R.2HCl.H2O.

Fraction 4 predominantly contained HCl-reacted 2-ring components at a concentration of 2.3 mg/kg. It comprised as little 3-ring components with epoxy func-

tions as fraction 5 contained epoxy 2-ring structures. The small signals in fraction 5 belong to 2R.HCl.H2O and 2R.2HCl, but the composition is different and suggests some unusual isomers (abnormal substitution?).

Apart from some signals in the early part, all relevant peaks in the chromatograms belonged to NOGE derivatives from the can coating; there was hardly any interference by the tuna. Hence, summing up all areas of the peaks eluted after 3R.3H2O provided a good estimate of the chlorohydrins present in the food. It must, however, be considered that the total concentration exceeded 4 mg/kg. At a ten times lower migration, distinction from endogenous components would become difficult. Furthermore, the lid did not release relevant amounts of material, which may also complicate the analysis if its coating is different.

### *Salmon in water*

Figure 7 reports RPLC-FD chromatograms from canned salmon in water with a fairly high fat content in the fish (Canada, bought in 2000). Both parts of the deep-drawn two-piece can with easy open lid were Beilstein-positive. The acetonitrile extract of the emptied can shows little 2-ring NOGE, but 3- to 6-ring NOGE and chlorohydrins corresponding to 15 mg/l can volume. Adding the 2-ring components transferred to the can content, there were 0.8 mg/l of 2-ring components in the original can coating. Compared to 5 mg/l of 3-ring compounds and taking into

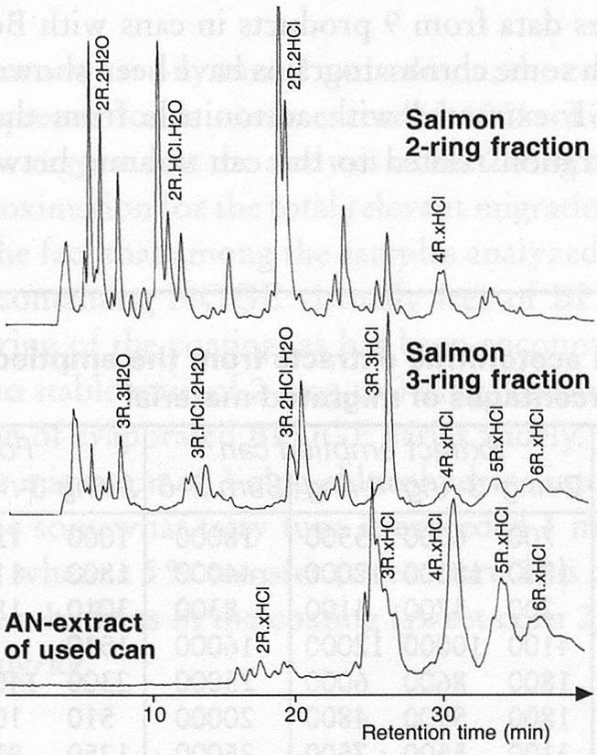


Figure 7 **RPLC-FD chromatograms from canned salmon in water**

account that commercial NOGE typically contains clearly more BFDGE than 3-ring NOGE, over 90 % of the BFDGE must have evaporated during curing of the coating.

The 2-ring fraction from SEC contained 300 µg/kg of virtually completely hydrolyzed 2-ring components (no epoxy compounds detected, as confirmed by normal phase LC-FD). Hence there was not enough fish oil to protect the epoxy groups. Some 75 % of the original epoxy groups were converted to chlorohydrins (strong predominance of 2R.2HCl over 2R.2H2O). The peak following 2R.2H2O probably represents BADGE.2H2O. In the rear of the chromatogram, there are unidentified peaks, perhaps representing partially or non-hydrolyzed 3- and 4-ring components (the epoxy groups being responsible for a relatively late elution from SEC).

The sum of the 3-ring components was 140 µg/kg and again shows a high degree of reaction with chloride. In addition, the 3-ring fraction contained higher molecular weight epoxy and chlorohydroxy derivatives. As already observed for the tuna sample, the higher molecular weight compounds seem not to be hydrolyzed, presumably because of low solubility in water.

The fish contained enough oil to extract some higher molecular weight NOGE (in contrast to sweet corn). The oil protected the poorly soluble NOGE components from hydrolysis, but not the 2- and 3-ring constituents. Hence salmon in water should be considered border line between aqueous and oily foods.

### *Extent of the migration*

Table 1 summarizes data from 9 products in cans with Beilstein-positive coatings, for three of which some chromatograms have been shown above. The amounts of 2- to 6-ring NOGE extracted with acetonitrile from the emptied can corresponded to a concentration related to the can volume between 8.3 and 44 mg/l

Table 1
**NOGE components in acetonitrile extracts from the emptied can (µl/l) and foods (µg/kg), as well as percentages of migrated material**

| *Product* | *Can size* | *Extract emptied can* | | | | *Food* | | | *% Migration* | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | *2-ring* | *3-ring* | *4-ring* | *Sum 2–6* | *2-ring* | *3-ring* | *4-ring* | *2-ring* | *3-ring* |
| Sweet corn 1 | 340 g | 700 | 6000 | 5500 | 18000 | 1000 | 120 | | 59 | 2 |
| Sweet corn 2 | 340 g | 1800 | 18000 | 12000 | 44000 | 1800 | 110 | | 50 | 0.6 |
| Sweet corn 3 | 340 g | 200 | 3700 | 3100 | 8300 | 3010 | 180 | | 94 | 5 |
| Tuna in water 1 | 200 g | 4100 | 10000 | 12000 | 16000 | 1530 | | | 27 | <1 |
| Tuna in water 2 | 200 g | 1800 | 8600 | 6000 | 25000 | 2300 | 1400 | 750 | 56 | 14 |
| Tuna in water 3 | 200 g | 1800 | 5900 | 4800 | 20000 | 510 | 100 | | 22 | 2 |
| Tuna in water 4 | 195 g | 3100 | 5500 | 7500 | 25000 | 1250 | 230 | | 30 | 4 |
| Asparagus | 460 g | <10 | <10 | <10 | <50 | 550 | 35 | | >95 | >80 |
| Salmon | 200 g | 500 | 5000 | 4000 | 15000 | 300 | 140 | | 38 | 3 |

(extracts from organosols are fairly complete). The canned asparagus was an exception since merely the side stripe of this 3-piece can contained NOGE.

From the three cans from the same producer of sweet corn and of apparently identical make, acetonitrile extracted between 8.3 and 44 mg/l of NOGE or 2.7–15 mg per can, suggesting that migration may vary strongly within different samples of the same product. The surface coated by an organosol (cup) comprised 2.5 $dm^2$ and the NOGE migration 1–5.7 $mg/dm^2$.

The amount of NOGE material transferred to the can content was between 3 and 6 % for corn and salmon, but reached 18 % for tuna 2. This low migration results from low transfer of high molecular weight components: migration averaged about 50 % for the 2-ring components, dropped into the range of a few percents for the 3-ring derivatives, and was negligible for higher molecular weight components. Tuna 2 is an exception, because it contained enough fat to enhance migration. The other exception concerned the canned asparagus: migration of the low molecular weight NOGE must have been almost complete.

## Conclusions

### *Only 2- and 3-ring NOGE migrate*

In aqueous foods, no NOGE components with epoxy groups are to be expected. The migration of chlorohydrins seems to be restricted to 2- and 3-ring components. Components with 4–6 rings, often with preserved epoxy groups, are only found in foods containing a few percents of fat at least (such as fish in water).

Disregarding the somewhat oily tuna 2 and salmon, the concentrations of 3-ring components in the aqueous foods never exceeded 12 % of those of the BFDGE derivatives. This might suggest that the analysis of the 2-ring compounds alone provides a sufficient approximation for the total relevant migration. However, this conclusion results from the fact that among the samples analyzed there happened to be none with a coating containing NOGE virtually free of BFDGE (BFDGE being evaporated during curing of the coating, as has been encountered fairly frequently other times). Hence no stable ratio of 2-ring to 3-ring components can be expected because the proportion of evaporated BFDGE varies widely.

It remains that the migration of 3-ring chlorohydrins into aqueous foods tends to be low. Only in the somewhat fatty tuna it exceeded 1 mg/kg. However, in an unfortunate situation, where a 5 % transfer (sweet corn 3) is combined with a large amount of 3-ring chlorohydrins in the coating (sweet corn 2), the migration could reach as much as 900 µg/kg.

### *Analytical procedure*

The procedure shown in figure 8 is designed to focus on the critical products.

1. The can is partially opened and emptied as described in the experimental part.

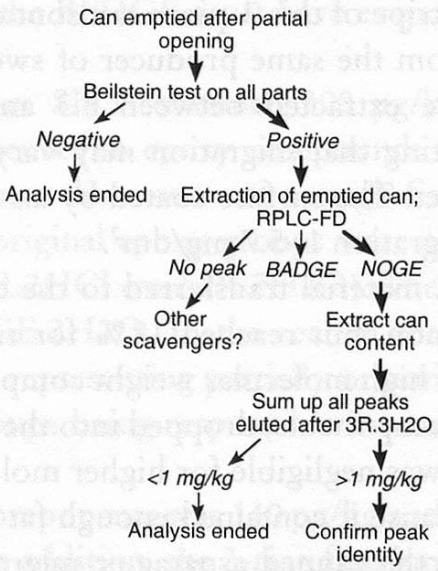


Figure 8 **Screening aqueous foods on relevant NOGE components, assuming an SML of 1 mg/kg for the chlorohydrins <1000 D**

2. All parts, including the side stripe (3-piece cans) are checked for organosols using the Beilstein test. If the result is negative, the coatings are likely to consist of polyesters or epoxies and the analysis is ended. When epoxy coatings release BADGE, it is present as BADGE.2H2O which is considered untoxic.
3. Cans with Beilstein-positive parts are extracted with acetonitrile. 1 h at 25° C is sufficient to determine the presence of BADGE or NOGE. If both are absent, the analysis is again stopped, but the question arises by what other material the organosol was stabilized.
4. If the extract shows the presence of BADGE, the three chlorohydrins are analyzed, e.g. according to (12).
5. If NOGE is detected, the can content is extracted with acetonitrile, followed by RPLC-FD.
6. All peaks eluted after 3R.3H2O are summed up (all chlorohydrins are eluted later) and quantitated through an external standard, such as BFDGE or BADGE. If this concentration corresponds to less than 1 mg/kg, the analysis is ended.
7. If it exceeds 1 mg/kg, the peaks are identified by co-chromatography, eliminating those which are not belonging to NOGE chlorohydrins. Work is ended as soon as a sufficient amount of interfering material, such as from the food or an epoxy coating from another part of the can, has been identified to reduce the sum below 1 mg/kg.
8. If the identified NOGE material exceeds 1 mg/kg, peak identity must be confirmed. Often the peak pattern is sufficiently characteristic (qualitative and

quantitative composition, considering a variable proportion of reaction with hydrochloric acid). 2-ring components can be confirmed by NPLC-FD after acetylation and/or GC-MS (12). SEC preseparation helps a better understanding of peak patterns. A broader range of compounds can be confirmed by LC-MS (13, 14). Hydrolysis, as proposed by *Bas and Rijk* (11), is another elegant method for confirmation.

A key step of the procedure is illustrated in figure 9 for the salmon sample, the more detailed analysis of which was reported in figure 7. The identified 2- and 3-ring components had summed up to 440 µg/kg, 340 µg/kg belonging to chlorohydrins, the rest to 2R.2H2O and 3R.3H2O (which are not of concern). Summing up the area of all peaks eluted after 3R.3H2O in figure 9 resulted in 410 µg/kg. With an SML of 1 mg/kg, the analysis would be ended. Otherwise it must be determined which non-identified material represents further NOGE chlorohydrins.

The samples available for this investigation turned out relatively easy: none of them contained important amounts of migrants from epoxy coatings (cans containing different types of coatings), nor was there a food with strongly interfering material, such as sauces. While the determination in the salmon at a level of 440 µg/kg was far above the detection limit, severe problems may arise for samples with high background.

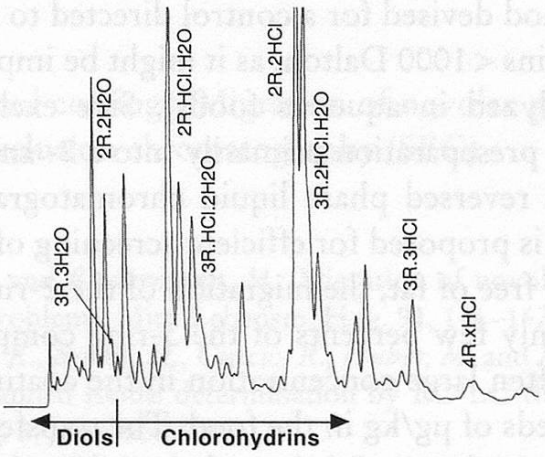


Figure 9 **Salmon sample as in figure 7, but without SEC preseparation**

### *Quantitative analysis*

Regarding quantitative performance, the method includes the following risk points.

1. *Extraction from the sample into acetonitrile.* The most critical partitioning concerns the epoxy compounds and an oily or waxy food: as shown in (5), complete extraction is only achieved when the acetonitrile contains not more than 20 %

water. This is why the extraction is performed twice: in the first step, the water concentration is too high.

2. *Defatting with pentane* (or another hydrocarbon). Again, the epoxy compounds are most critical. They remain in the acetonitrile provided the water content does not exceed 20 % (5).
3. *Solvent evaporation* is a critical step since epoxy groups easily react with food components (they are no longer protected by an oil or fat phase), resulting in losses of corresponding NOGE components. This is why epoxy compounds, present in oily foods, are analyzed by a modified procedure (5).
4. *Preseparation by SEC.* This step was checked by the experiment reported above.
5. *RPLC-FD.* As far as not checked by the above experiment, the main problems concern recognition of the peaks and of possible interference.

The accuracy of the results is largely determined by the last step and the composition of the sample. With careful peak identification it is assumed that at a 1 mg/kg level the results will be reliable at ± 25 %. When NOGE migrants are present at concentration of 100 µg/kg only, interfering material often render the analysis extremely difficult. For routine analysis, a limit for quantitating NOGE chlorohydrins should be assumed to be around 500 µg/kg.


## Summary

Migration of NOGE derivatives into aqueous samples (such as sweet corn) was investigated and a method devised for a control directed to an SML of 1 mg/kg for the NOGE chlorohydrins < 1000 Dalton, as it might be imposed by the EU (epoxy compounds are hydrolyzed in aqueous foods). Size exclusion chromatography (SEC) was used for the preseparation primarily into a 2- and a 3-ring fraction. The main analysis involved reversed phase liquid chromatography with fluorescence detection. A procedure is proposed for efficient screening of samples.

Even in foods fairly free of fat, the migration of the 2-ring NOGE components easily exceeds 50 %. Only few percents of the 3-ring components are transferred, but considering their often large concentration in the coating, this may still correspond to several hundreds of µg/kg in the food. The transfer of 4-ring components is negligible unless the sample contains some fat or oil (such as tuna in water).



## Zusammenfassung

Die Migration von NOGE-Derivaten in wässerige Lebensmittel (z.B. Süssmais) wurde untersucht und eine Methode für die Kontrolle von Lebensmitteln entwickelt im Hinblick auf eine mögliche Einführung einer EU-Limite von 1 mg/kg für NOGE-Chlorhydrine < 1000 Dalton (in wässerigen Produkten werden Epoxyverbindungen hydrolysiert). Size Exclusion-Chromatographie (SEC) diente der Vortrennung vor allem in eine 2- und eine 3-Ring-Fraktion. Die Hauptanalyse erfolgte mittels Reversed phase-Flüssigchromatographie und Fluoreszenzdetektion. Ein Analysenverfahren für ein schnelles Screening von Proben wird vorgeschlagen.

Auch in ziemlich fettfreien Lebensmitteln überschreitet die Migration von 2-Ring-NOGE-Komponenten oft 50%. Andererseits werden nur wenige Prozente der 3-Ring-Verbindungen übertragen. Da aber deren Gehalte in den Lacken oft hoch sind, muss im Lebensmittel trotzdem mit Konzentrationen von einigen 100 µg/kg gerechnet werden. Der Transfer von 4-Ring-Verbindungen ist vernachlässigbar, ausser die Probe enthält etwas Fett oder Öl (z.B. Thunfisch in Wasser).


## Résumé

La migration des dérivés du NOGE dans des aliments aqueux a été étudiée et une méthode dévelopée pour le contrôle des produits en vue d'une introductions possible d'une limite de 1 mg/kg pour les chlorhydrines de NOGE <1000 Dalton par la CE (dans les aliments aqueux, les composées epoxy sont hydrolysées). La size exclusion chromatography (SEC) était utilisée pour préséparer surtout les composées de deux ou trois anneaux. L'analyse principale était fait par chromatographie liquide en phase inverse et avec détection fluorimétrique.

Même pour les aliments sans graisse, la migration des composées de NOGE de deux anneaux souvent exige 50%. Celle des chlorhydrines à trois anneaux reste sur peu de pourcents, mais comme le teneur dans les vernis est souvent haut, les concentrations dans l'aliments peuvent quandmême arriver à plusieurs 100 µg/kg. Le transfer des composées a quatres anneaux est négligeable sauf l'échantillon contient un peu de graisse ou huile (comme le thon dans l'eau).



## Key words

Canned foods, Organosol coatings, Migration of novolac glycidyl ether (NOGE), Preseparation by size exclusion chromatography (SEC)


## References


1 *Wagner, Ch., Grob, K.* and *Biedermann, M.:* Migration of novolac glycidyl ether (NOGE) into foods: analytical problems. Mitt. Lebensm. Hyg. **91,** 146–157 (2000).

2 *Biedermann, M., Grob, K., Bronz, M., Curcio, R., Huber, M.* and *Lopez-Fabal, F.:* BADGE in edible-oil-containing canned foods: determination by LC-LC-fluorescence detection. Mitt. Gebiete Lebensm. Hyg. **87,** 547–558 (1996).

3 *Biedermann, M., Wagner, Ch., Grob, K., Imhof, D.* and *Beuggert, H.:* Bisphenol-A-diglycidyl ether (BADGE) and novolac glycidyl ether (NOGE) as additives in can coatings. Mitt. Lebensm. Hyg. **91,** 274–286 (2000).

4 *Richard, N., Biedermann, M.* and *Grob, K.:* Reaction of bisphenol A diglycidyl ether (BADGE) from can coatings with food components. Mitt. Lebensm. Hyg. **90** (1999) 532–545.

5 *Brem, S.* and *Grob, K.:* Migration of novolac glycidyl ether (NOGE) and its chlorohydrins into oily canned foods. (submitted to Food Addit. Contam.)

6 *Biedermann, M., Bronz, M., Bürchler, B., Grob, K., Keller, F., Neukom, H.-P., Richard N.* and *Spinner Ch.:* 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. 2. results from a survey of the Swiss market. Mitt. Gebiete Lebensm. Hyg. **90,** 177–194 (1999).

7 *Biedermann, M.* and *Grob, K.:* Food contamination from epoxy resins and organosols used as can coatings; analysis by gradient NPLC. Food Addit. Contam. **15,** 609–618 (1998).
8 *Simal Gandara, J., Paz Abuin, S., Lopez Mahia, P., Paseiro Losada, P.* and *Simal Lozano, J.:* Identification of RP-HPLC peaks of bisphenol F and of bisphenol F diglycidyl ether and its hydrolysis products by thermospray MS and GC-MS. Chromatographia **34,** 67–72 (1992).
9 *Bronz, M., Biedermann, M.* and *Grob, K.:* Characterization of migrates from can coatings by size exclusion chromatography; total amounts of phenolics with molecular weight below 1000 D. Mitt. Gebiete Lebensm. Hyg. **89,** 327–338 (1998).
10 *Paseiro Losada, P., Paz Abuin, S., Vazquez Oderiz, L., Simal Lozano, J.* and *Simal Gandara, J.:* Quality control of cured epoxy resins. Determination of residual free monomers (m-xylylenediamine and BADGE) in the finished products. J. Chromatogr. **585,** 75–81 (1991).
11 *Bas, R.C.* and *Rijk, R.:* TNO Voeding, NL, draft method provided to EU on Jan. 21, 2000.
12 *Biedermann, M., Bronz, M., Bürchler, B., Grob, K., Keller, F., Neukom, H.-P., Richard, N.* and *Spinner, Ch.:* Reaction products of BADGE and bisphenol-F-diglycidyl ether (BFDGE) with hydrochloric aid and water in canned foods with aqueous matrix. 1. Analytical methods. Mitt. Lebensm. Hyg. **90,** 177–194 (1999).
13 *Roubtsova, S., Hollaender, J.* and *Franz, R.:* A rapid and convenient method for the quantitative determination of BADGE in foodstuffs. Dtsch. Lebensm.-Rundsch. **93,** 273–276 (1997).
14 *Berger, U.* and *Oehme, M.:* Identification of derivatives of BADGE and NOGE in can coatings by HPLC/ion trap MS. J. AOAC (submitted).

Corresponding author: Koni Grob, Official Food Control Authority of the Canton of Zurich, P.O. Box, CH-8030 Zurich