Zeitschrift: Mitteilungen aus Lebensmitteluntersuchungen und Hygiene = Travaux

de chimie alimentaire et d'hygiène

Herausgeber: Bundesamt für Gesundheit

Band: 91 (2000)

Heft: 2

Artikel: Migration of Novolac glycidyl ether (NOGE) into foods : analytical

problems

Autor: Wagner, Christoph / Grob, Koni / Biedermann, Maurus

DOI: https://doi.org/10.5169/seals-981861

Nutzungsbedingungen

Die ETH-Bibliothek ist die Anbieterin der digitalisierten Zeitschriften auf E-Periodica. Sie besitzt keine Urheberrechte an den Zeitschriften und ist nicht verantwortlich für deren Inhalte. Die Rechte liegen in der Regel bei den Herausgebern beziehungsweise den externen Rechteinhabern. Das Veröffentlichen von Bildern in Print- und Online-Publikationen sowie auf Social Media-Kanälen oder Webseiten ist nur mit vorheriger Genehmigung der Rechteinhaber erlaubt. Mehr erfahren

Conditions d'utilisation

L'ETH Library est le fournisseur des revues numérisées. Elle ne détient aucun droit d'auteur sur les revues et n'est pas responsable de leur contenu. En règle générale, les droits sont détenus par les éditeurs ou les détenteurs de droits externes. La reproduction d'images dans des publications imprimées ou en ligne ainsi que sur des canaux de médias sociaux ou des sites web n'est autorisée qu'avec l'accord préalable des détenteurs des droits. En savoir plus

Terms of use

The ETH Library is the provider of the digitised journals. It does not own any copyrights to the journals and is not responsible for their content. The rights usually lie with the publishers or the external rights holders. Publishing images in print and online publications, as well as on social media channels or websites, is only permitted with the prior consent of the rights holders. Find out more

Download PDF: 20.11.2025

ETH-Bibliothek Zürich, E-Periodica, https://www.e-periodica.ch

Migration of Novolac Glycidyl Ether (NOGE) into Foods: Analytical Problems

Christoph Wagner, Koni Grob and Maurus Biedermann, Official Food Control Authority of the Canton of Zurich, Zurich

Received 9 November 1999, accepted 23 December 1999

Introduction

The analysis of can coatings and the migration from these coatings into foods became a subject of broader interest in food control after bisphenol-A-diglycidyl ether (BADGE) had been detected in oily foods (e.g. fish in oil) at concentrations exceeding some national legal limits by a factor larger than 1000 (1). It triggered broader analysis of the migrants and revealed many more components of possible concern (2–4). It was concluded that migration from coatings is a major source of food contamination. Most of the contaminants have not been identified so far and are, hence, not toxicologically controlled. This is considered as an unsatisfactory situation calling for better regulation (5).

BADGE and novolac glycidyl ether (NOGE) have been used as additives for organosol coatings (6), where they primarily function as a scavenger for hydrogen chloride to increase the thermostability of the PVC. Neither BADGE nor NOGE have been approved for this application. In fact, the toxicity of the resulting BADGE chlorohydrins is checked only now (7) and even less is known about NOGE and its reaction products.

Novolac

Novolac is the technical name for complex mixtures obtained by reaction of phenol with formaldehyde under acidic conditions. It is related to bisphenol A insofar as it is produced from phenol and a carbonyl compound, the latter being formaldehyde instead of acetone. The two ring component in novolac (called bisphenol F) differs from bisphenol A by the missing methyl groups at the bridge head (fig. 1).

Figure 1 Structures of bisphenol F and the 3-ring novolacs

Reaction of phenol with formaldehyde is sterically less hindered than that with acetone, such that substitution is possible also at the two ortho sites. This explains some important differences. Firstly, three isomers of the two-ring structure are obtained: p,p-, o,p- and o,o-bisphenol F (fig. 1). Secondly, two or three phenols can be bonded to a central moiety, enabling further condensation through methylene groups. The resulting three ring components already consists of seven isomers, the 4-ring components of 27. Hence, instead of a well defined substance (bisphenol A), a complex mixture called novolac is obtained.

Novolac glycidyl ether (NOGE)

NOGE, also called epoxy novolac, is produced by reaction of novolac with epichlorohydrin and elimination of HCl. The resulting 2-ring components are called bisphenol-F-diglycidyl ether (BFDGE) and correspond to BADGE without the methyl groups in the center of the molecule.

BFDGE and NOGE are often confused. The technical product used for coatings is NOGE. BFDGE is a component of NOGE. BFDGE cannot be directly produced as a pure compound. NOGE exists with various mean molecular weights.

Migration of NOGE into foodstuffs

When used as an additive, migration of NOGE into foods is a problem. Particularly oil swells the coating and causes a substantial proportion of the added NOGE

to migrate into the food. In 1997, a sample of tuna in oil containing about 20 mg/kg of NOGE with up to six rings was found (8). This NOGE was virtually free of BFDGE (7 µg/kg in the can content), may be because of evaporation of BFDGE during curing of the coating at high temperature. Numerous other samples with more than 1 mg/kg NOGE in the can content were found in the meantime.

Setting a legal limit for NOGE?

A toxicological evaluation of BFDGE seems to be on its way. Supposedly BFDGE is taxed as a material of low toxicity and this conclusion is extended to all NOGE components, the producers might ask for the authorization of its use, coupled with the introduction of a specific migration limit (SML). In analogy to BADGE and its derivatives, this SML could refer to the NOGE-components with a certain range of molecular weights (e.g. up to 1000 Dalton, including the 6-ring compounds with 960 D) as well as its derivatives bearing an epoxy and a chlorohydrin group.

Before setting such a limit, some chromatographic problems should be solved, however, which are illustrated below: the quantitative determination of the large number of components is difficult.

Methods

Analysis of foods

The methods for the analysis of migrates in foods were described in (9). Can contents were diluted 1:1 with water and homogenized. For reversed phase HPLC with fluorescence detection (RPLC-FD), ethanol was admixed before the liquid phase was separated from the solids and analyzed. For normal phase HPLC (NPLC)-FD, the homogenate was extracted with methyl tert. butyl ether (MTBE) and the extract acetylated.

Extraction of used cans

Lids of filled cans were opened less than half. The cans were emptied, rinsed with water containing some detergent and laid on their side. They were filled with acetonitrile to 50 %, such that the solvent was in contact with half of the surfaces of all parts. Extraction was performed for 24 h at 25 °C. For analysis by NPLC-FD, acetonitrile extracts were diluted with water and extracted by 15 % dichloromethane/hexane (v/v) according to (4).

Size exclusion chromatography

Size exclusion chromatography (SEC)-fluorescence detection (FD) was performed as described in (10). Two Chrompack (Middelburg, The Netherlands) 250 x 7 mm i.d. SEC columns were used in series, one packed with Microgel-5 100 Å, the other with Microgel-5 50 Å, using tetrahydrofurane (THF)/2 % methanol at

400 µl/min as mobile phase. FD was performed at 225/295 nm. When used for preparative purposes, emission was detected at 340 nm, i.e. far from the maximum sensitivity, in order to prevent overloading.

Isolation of 3-ring NOGE

For the semipreparative isolation of 3-ring NOGE, 100 μ l of a 1 mg/ml solution of NOGE (Araldit EPN 1179, Ciba, Basel) in THF was separated by SEC and the corresponding fraction (600 μ l, eluted at 29 min) recovered from the detector. Reinjection indicated that the 3-ring material was better than 90 % pure and comprised some 12 μ g.

Reaction products of 3-ring NOGE

NOGE reaction products with water or hydrochloric acid were prepared for the investigation of their chromatographic analysis. 200 µl portions of the 3-ring material isolated by SEC were allowed to react with hydrochloric acid or dilute acetic acid under condition described in (9): 10 ml of the acid defined in table 1 was added (reaction medium). After the time indicated, the products were extracted into 2 ml of MTBE.

Tableau 1

Reaction conditions applied to obtain the 3-ring derivatives

Functional groups	Reaction medium	Duration	Temperature (°C)
Epoxy + chlorohydrin	3 % HCI	1 min	25
Chlorohydrin	18 % HCI	3 min	25
Epoxy + diol	3 % acetic acid	3 d	25
Diol	3 % acetic acid	3 h	90
Chlorohydrin + diol	0,5 % HCI	4 d	25

Normal phase HPLC (NPLC)

NPLC analysis mostly involved acetylation: the MTBE of the extract was evaporated and 50 µl each of pyridine and acetanhydride were added and allowed to react at 35 °C for 30 min. The reagent was evaporated in a stream of nitrogen and the sample picked up by 15 % dichloromethane in hexane.

A 25 cm x 2 mm i.d. column packed with Gromsil 100 cyano 2 PR 5 μm (Stagroma, Reinach, Switzerland) was used with a gradient (400 μl/min) involving 1 % 1-propanol/15 % dichloromethane/pentane (A) and 50 % 1-propanol/dichloromethane (B), programmed as follows: A, 7 min, then 1 %/min B up to 10 %, 3 %/min B up to 22 % and 5 %/min B up to 60 %. Sample volume injected, 80 μl; FD at 225/295 nm.

Reversed phase HPLC (RPLC)

The MTBE was evaporated and the residue picked up in 50 μ l of ethanol to which 200 μ l of water were added after dissolution. A 25 cm x 4.6 mm i.d. column packed with Hypersil MOS (C8), 5 μ m (Macherey-Nagel, Düren, Germany) was used with a gradient of water (A) and 90 % ethanol (B) at a flow rate of 750 μ l/min: 0–6 min: 25–50 % B; 6–20 min: 50–70 % B; 20–30 min: 70–100 % (5 min). Injection volume, 100 μ l.

Results

BFDGE in NOGE

In can coatings or canned foods, usually BFDGE is analyzed, presumably for the determination of NOGE. However, migration of NOGE cannot be extrapolated from the measurement of BFDGE. Figure 2 shows SEC-FD chromatograms of two NOGE samples visualizing the variation of the NOGE compositions found in organosol coatings. The upper chromatogram is from an acetonitrile extract of an unused can intended for tuna in oil. It shows a rather small proportion of BFDGE (7 %) and is dominated by the 3- and 4-ring NOGE. 65 % of the material is of a molecular mass below 1000 Dalton; there is hardly any polymeric material. The peak labelled as 3-ring NOGE also contains some BFDGE reacted with one mole of hydrochloric acid from the organosol to a chlorohydrin (BFDGE.HCl) and that of the 4-ring NOGE some BFDGE.2HCl. However, in this sample both chlorohydrins were minor components as deduced from the analysis by NPLC.

The lower chromatogram is from a NOGE sample (Araldite EPN 1179) containing a high concentration of BFDGE (about 35 %). This product was used to isolate the 3-ring NOGE and perform the experiments discussed below.

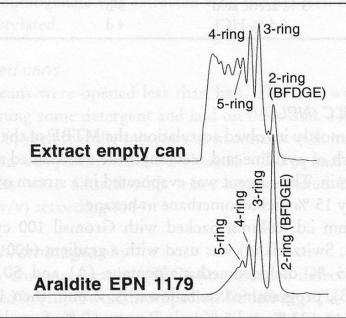


Figure 2 SEC-FD of two NOGE samples

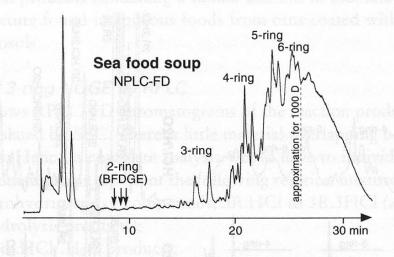


Figure 3 NPLC-FD chromatogram of an etract from a sea food soup

Figure 3 shows the NPLC-FD chromatogram of a non-acetylated extract from a canned sea food soup containing virtually BFDGE-free NOGE (gradient as in (8)). Quantitative analysis is difficult since the material is not resolved for reasons illustrated below. As an approximation, integrating the area of the hump of unresolved material up to a retention time including the 6-ring NOGE (broken line), 7 mg/kg of NOGE with a molecular weight below 1000 D is determined. Comparison with similar samples indicates that at these high attenuations food components do not significantly contribute to the hump.

The chromatogram shown in (8) was more structured and provided a finger print more typical of NOGE. The difference is the result of more reaction with hydrochloric acid from the organosol: the several hundred NOGE isomers partly converted to chlorohydrins form an enormous number of individual components.

There is less than 10 µg/kg of BFDGE, i.e. the analysis of BFDGE alone would have hardly suggested the presence of a large amount of NOGE. In fact, the migration of NOGE cannot be quantitated through the analysis of BFDGE. On the other hand, a more comprehensive determination is difficult because of the extremely high number of NOGE components and their derivatives.

Separation of NOGE by NPLC

The complexity of the material and the difficulty encountered in quantitative analysis are further illustrated in figure 4, showing gradient NPLC-FD chromatograms from a NOGE (EPN 1179) and its derivatives after acetylation. BFDGE and its reaction products have been identified by GC-MS, the 3-ring components through their preparation from the isolated 3-ring NOGE and co-chromatography. Other identifications are tentative. Peaks are named by number of rings (e.g. 3R) and a specification of the side chain either as epoxy (.E), diol (.H₂O), or chlorohydrin (.HCl). The composition may not be typical for extracts from coatings and oily

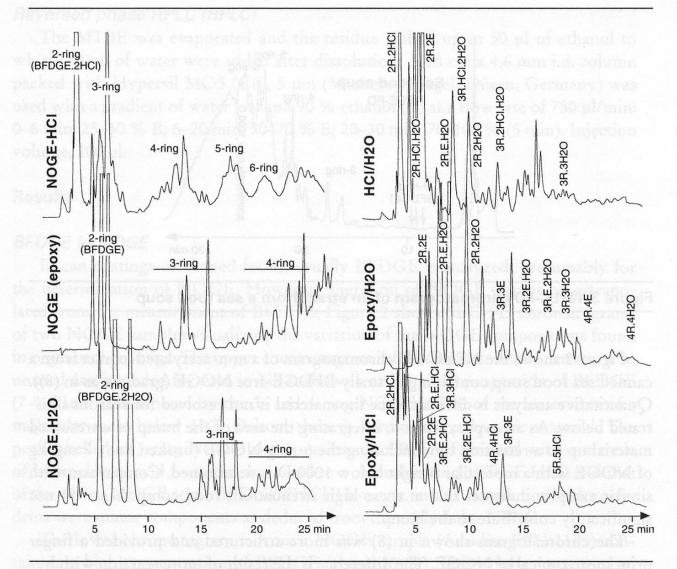


Figure 4 NPLC-FD chromatograms from NOGE EPN 1179 as well as its .HCl and H₂O derivatives after acetylation. Peak assignments: e.g. 3R.2E.HCl, 3-ring NOGE with two epoxy (.E) and a chlorohydroxy (.HCl) group

foods because the low molecular mass material predominates to an unusual extent (compare with fig. 3).

Chromatograms at the left show compounds with one type of functional group only.

- Center: NOGE (epoxy compounds) with up to four rings. There are seven components with three rings and 27 with four rings.
- Top: NOGE after complete conversion to the chlorohydrins.
- Bottom: fully hydrolyzed NOGE.
 Chromatograms at the right show compounds with mixed functional groups.
- Bottom: NOGE reacted such that part of the epoxides were converted to chlorohydroxy groups. Mixture typically found in oily foods from cans with NOGE-stabilized organosols.
- Center: partially hydrolyzed NOGE, i.e. with epoxy and diol groups.

 Top: reaction products containing a similar amount of diol and chlorohydroxy groups. Mixture found in aqueous foods from cans coated with NOGE-stabilized organosols.

Separation of 3-ring NOGE by RPLC

Figure 5 shows RPLC-FD chromatograms of the reaction products from the 3-ring NOGE isolated by SEC. There is little material overlapping between the four chromatograms. Hence, a complete analysis would have to individualize all major peaks. The chromatograms represent the following reaction mixtures:

- 1 the 45 chlorohydrin/epoxy compounds, 3R.HCl to 3R.3HCl (and some minor peaks of hydrolysis products);
- 2 the 38 mixed .HCl/.H₂O products;
- 3 the 7 fully hydrolyzed 3-ring NOGE (and some minor peaks of 4-ring components);
- 4 the 38 partially hydrolyzed compounds.

In total there are 135 different 3-ring NOGE components resulting from the seven positional isomers. Complexity is, of course, far worse for the 27 isomers of 4-ring NOGE and the many more 5- and 6-ring NOGE constituents.

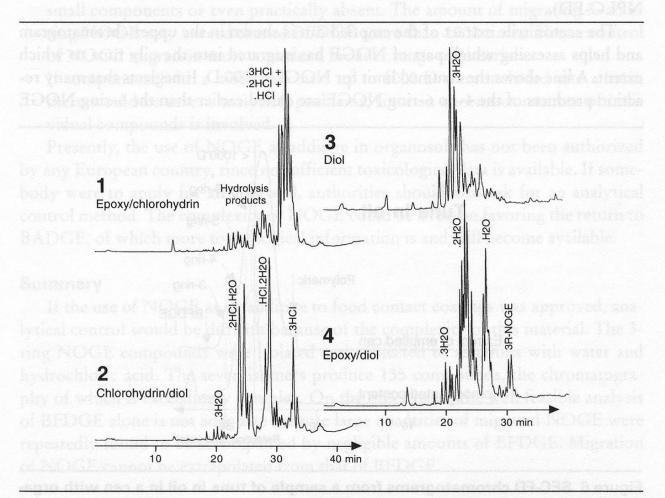


Figure 5 RPLC-FD chromatograms of the reaction products from 3-ring NOGE with water and hydrochloric acid

Migration of NOGE

Migration of BFDGE and its reaction products into sterilized aqueous foods (involving heating to 120 °C) varied between about 20 and over 95 % (compared to the acetonitrile extract, which is assumed to be fairly complete) (6). Thus it is not much lower than that into foods containing a liquid oil phase (droplets or oil present as a component). Migration of NOGE components with more than two rings, however, is substantially lower for aqueous foods (difficult to quantitate because all the reaction products would have to be summed up) and that of 4-ring NOGE certainly below 10 %. It may still be significant when these components predominate the mixture as strongly as they often do.

Figure 6 indicates that migration into oily foods remains high up to far higher molecular masses. It shows SEC-FD chromatograms from a sample of canned tuna in oil. SEC (lower chromatogram) and NPLC-FD (not shown) from the homogenized can content indicate a concentration of NOGE components with up to 6 rings of between 5.5 and 6 mg/kg. BFDGE was not detectable (< 5 μ g/kg). The small peak at the position of BFDGE as well as the larger peak eluted just afterwards belong to food components. The concentration of 3-ring NOGE in the food was about 220 μ g/kg, that of 4-ring NOGE around 500 μ g/kg (fair agreement with NPLC-FD).

The acetonitrile extract of the emptied can is shown in the upper chromatogram and helps assessing which part of NOGE has migrated into the oily tuna to which extent. A line shows the assumed limit for NOGE <1000 D. It neglects that many reaction products of the 4- to 6-ring NOGE are eluted earlier than the 6-ring NOGE

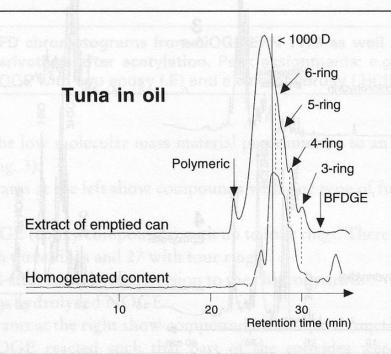


Figure 6 SEC-FD chromatograms from a sample of tuna in oil in a can with organosol coating: extract from the homogenated can content (20 %) and acetonitrile extract of the emptied can

(as mentioned above, addition of H₂O or HCl shifts about as much as adding a ring). 40-45 % of the 3- to 6-ring NOGE was transferred to the food. NPLC confirmed this for the 3- to 4-ring NOGE. Hence transfer occurred at similar rates for the 3- to 6-ring NOGE, but sharply dropped off behind the 8-ring compounds.

It should be emphasized that quantitative estimations for this and similar examples were possible because of extremely high NOGE concentrations. Once sensitivity of the analysis must be increased by a factor of 5-10, as would be required for checking a 1 mg/kg limit, food components interfered and the assumption were no longer appropriate that all the FD response observed is related to components from the can coating.

Conclusions

For BADGE and some of its reaction products, the EU-Scientific Committee for Foods (SCF) has introduced a limit of 1 ppm. BFDGE and the corresponding reaction products might have a similar toxicological profile, which would suggest to include them into the same limit. Before such a decision is taken, the following two points should be taken into consideration:

- In the migrating NOGE, BFDGE and its reaction products are often merely small components or even practically absent. The amount of migrating 3- to 6ring NOGE may exceed that of BFDGE more than 1000 times. Hence control of NOGE migration must consider a broader range of materials.
- If components with a molecular mass up to 1000 D were included into a limit, there would be severe analytical problems, since an enormous number of individual compounds is involved.

Presently, the use of NOGE as additive in organosols has not been authorized by any European country, since no sufficient toxicological data is available. If some-body were to apply for an approval, authorities should also ask for an analytical control method. The complexity of NOGE could be a reason favoring the return to BADGE, of which more toxicological information is and will become available.

Summary

If the use of NOGE as an additive to food contact coatings was approved, analytical control would be difficult because of the complexity of this material. The 3-ring NOGE compounds were isolated and subjected to reactions with water and hydrochloric acid. The seven isomers produce 135 compounds, the chromatography of which is exceedingly complex. On the other hand, the well feasible analysis of BFDGE alone is not adequate because large quantities of migrated NOGE were repeatedly found to be accompanied by negligible amounts of BFDGE. Migration of NOGE cannot be extrapolated from that of BFDGE.

Zusammenfassung

Falls die Verwendung von NOGE als Additiv für Lacke mit Lebensmittelkontakt bewilligt würde, wären Schwierigkeiten bei der analytischen Kontrolle absehbar, da das Material aus sehr vielen Komponenten besteht. Die 3-Ring Verbindungen von NOGE wurden isoliert und mit Wasser oder Chlorwasserstoff umgesetzt. Allein diese sieben Positionsisomere ergeben 135 Produkte, deren Chromatographie entsprechend komplex ist. Auf der anderen Seite genügt die (gut machbare) Bestimmung allein von BFDGE nicht, da in manchen Dosenkonserven hohe Mengen von NOGE praktisch ohne BFDGE gefunden wurden. Aus dem BFDGE-Gehalt lässt sich also nicht auf die Migration von NOGE schliessen.

Résumé

Si l'utilisation de NOGE comme additif pour des vernis en contact avec des aliments était légalisée, le contrôle analytique s'avérerait difficile en raison du grand nombre de composés inclus dans ce matériel. Les composés à trois anneaux ont été isolés et mis à réagir avec de l'eau et de l'acide chlorhydrique. Ces sept isomères produisent 135 composés, dont la chromatographie est extrèmement complexe. D'un autre côté, l'analyse unique du BFDGE (qui est facilement praticable) n'est pas suffisante, car dans de nombreuse boîtes de conserve on trouve une forte concentration de NOGE presque sans BFDGE. De la teneur en BFDGE on ne peut donc pas extrapoler la migration du NOGE.

Key words

Canned foods, Organosol coatings, Novolac glycidyl ether (NOGE), Size exclusion chromatography (SEC).

References

- 1 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).
- 2 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).
- 3 Cottier, S., Feigenbaum, A., Morteuil, P., Reynier, A., Dole, P. and Riquet, A. M.: Interaction of a vinylic organosol used as a can coating with solvents and food simulants. J. Agric. Food Chem. 46, 5254–5261 (1998).
- 4 Biedermann, M., Grob, K., Böhler, P. and Widmer H.R.: Identification of migrants from coatings of food cans and tubes: reaction products of BADGE with phenols and solvents. Mitt. Gebiete Lebensm. Hyg. 89, 529–547 (1998).
- 5 Grob, K., Spinner, Ch., Brunner, M. and Etter, R.: The migration from the internal coatings of food cans; summary of the findings and call for more effective regulation of polymers in contact with foods. Food Add. Contam. 579–590 (1999).
- 6 Biedermann, M., Wagner, Ch., Grob, K., Imhof, D. and Beuggert, H.: BADGE and NOGE as additives in can coatings. Mitt. Gebiete Lebensm. Hyg. (in press).

- 7 Scientific Committee for Foods (SCF), Opinion on bisphenol A diglycidyl ether (BADGE). Expressed on March 24, 1999.
- 8 *Biedermann*, *M.* and *Grob*, *K.:* Food contamination from epoxy resins and organosols used as can coatings; analysis by gradient NPLC. Food Add. Contam. 15, 609–618 (1998).
- 9 Biedermann, M., Bronz, M., Bürchler, B., Grob, K., Keller, F., Neukom, H.-P., Richard N. and Spinner Ch.: Reaction products of BADGE and BFDGE with hydrochloric acid and water in canned foods with aqueous matrix: 1. Analytical methods. Mitt. Gebiete Lebensm. Hyg. 90, 195–210 (1999).
- 10 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).

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