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Isolation of the <1000 Dalton Migrants from Food Packaging Materials by Size Exclusion Chromatography (SEC)

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Introduction

Scope: analysis of migrates from food contact materials

The work presented here is part of a project financed by the Swiss Federal Office of Public Health (SFOPH, project 01.00838) for the "Committee of Experts on Materials coming into Contact with Food" of the Council of Europe. It should contribute to the search for a better way to ensure safety of food packaging materials, i.e. making sure with the best possible presently available means that none of the many compounds migrating from packaging materials into foods or beverages are seriously toxic. For the moment the project focuses on coatings, first of all for the internal surface of food cans.

Current European legislation on food packaging materials (national and EU) is based on positive lists authorizing the use of starting materials considered as safe. Originating from the times when comprehensive analysis of the migrate composition was quite impossible, it assumes that the migrate from the finished article into the foods consists of the monomers, oligomers, and additives used as starting materials. It is known for a long time that this is a rather crude assumption, and in the instance of some internal coatings of food cans the shortcomings have become particularly obvious (1). Some migrates contain predictable reaction products, such

as the chlorohydrins from epoxy compounds added to organosols or monomers and oligomers reacted with chain stoppers (epoxy coatings being an example (2)). When not integrated into the polymer, the impurities of the starting materials may also become dominating components in the migrate. Many other migrate components have not even been identified so far. At any rate, migrates are often highly complex mixtures merely containing minor amounts of the starting materials, and the safety achieved through the control of the starting materials is not satisfactory.

The approach proposed to the Council of Europe requires the analysis of the migrate composition within defined limits (3), i.e. components with a molecular weight below a given limit (e.g. 1000 D) and exceeding a specified threshold concentration. Packaging materials can only be considered safe when the safety of these migrants can be documented. In the long run, the analytical threshold concentration should correspond to the threshold of toxicological concern (4, 5), but this may only be achieved stepwise.

Compounds with a molecular weight above 1000 Dalton are commonly considered to be of low toxicological relevance because only some exceptional compounds may enter the metabolism (6). If the analysis of the migrating components can be restricted to those below 1000 D, a method should be available that enables the elimination of all higher molecular weight material from a mixture (extract) or analytically determines whether or not an unknown compound must be identified. As precipitation of the high molecular weight material causes severe problems for the chemical analysis, it is important to perform this separation at an early stage.

Size exclusion chromatography

Size exclusion chromatography (SEC), also called gel permeation chromatography (GPC), is widely used for the determination of the molecular weight distribution of oligomers and polymers. As described in many text books (e.g. (7, 8)), it separates at chromatographic breakthrough conditions (presupposing a strong eluent which suppresses retention on surfaces of the column packing materials) and makes use of the different accessibility of molecules of different size to the pores of the packing. Being excluded from the small pores, the larger molecules are eluted earlier than the small ones. The retention volume corresponds to the sum of the volumes between the particles and of the pores which a compound can enter.

SEC is the method of choice for isolating the fraction of the <1000 D components from migrates, even though it does not enable accurate separation by molecular weight. The retention volume being determined by the exclusion from the pores of the column packing material, SEC separates by molecular size (hydrodynamic volume) rather than molecular weight. For a given molecular weight, a stretched molecule enters less pores (is eluted earlier) than a cyclic or branched molecule of the same weight, and a rigid straight chain enters less pores than a flexible (possibly folded) straight chain.

Rather accurate separation is possible for a series of oligomers of a given fundamental structure, since calibration of the retention time for a given molecular weight can usually be performed with standards of the same structure. The European Commission has adopted a method for the determination of "low molecular weight contents of polymers" (9), which in turn is based on DIN Standard 55672 (10). Retention times are calibrated against molecular weights using polystyrene oligomers or the oligomers of the polymer to be analyzed. This is not possible for the migrate analysis of interest here, since the method starts from the assumption that all possible types of chemicals may be present and should be separated at a molecular weight of 1000 D. With this diversity of components, considerable mixing around the 1000 D limit must be expected: at the retention time corresponding to 1000 D for one type of compound, materials of a substantially higher or lower molecular weight may be eluted if their structure is different.

To ensure that all components of up to 1000 D are included in the fraction, it must be accepted that also higher molecular weight material of substances of smaller molecular size are included (compact structure with a relatively high retention time per molecular weight). Thus calibration of a generally valid 1000 D cut must be performed with the compound with lowest retention per unit molecular weight. Theory suggests that this "worst case" compound will be of linear structure, stiff like a rod. This compound might not have been found in the work presented here and the calibration of the 1000 D cut will, perhaps, require modification in the future.

Another limitation of the method concerns the chromatographic behavior of components of extreme polarity. As SEC presupposes that the solutes move through the column without retention on the surfaces of the packing material, the mobile phase should be such a strong eluent that interactions are suppressed. On the one hand, it should strongly solvate polar substances, i.e. be polar or polarizable. On the other, it must not be that polar that it acts as a reversed phase eluent driving the compounds of low polarity to the packing material. This is achievable for a limited range of polarities only.

The work described here aims at optimizing the technique and establishing a method for the isolation of <1000 D compounds from a complex extract.

Experimental

The SEC columns tested are listed in table 1. They were packed with 5 µm particles, which, except for the OligoPore column, consisted of polystyrene/divinylbenzene polymers. The OligoPore, Phenogel 100 Å, and PLGel columns were equipped with a 50×7.5 mm i.d. guard column. Tetrahydrofuran (THF, puriss, Fluka, Buchs, Switzerland) was used as mobile phase when detection involved a refractive index (RI) detector (Knauer, Berlin Germany), THF free of stabilizer (THF for UV spectroscopy, Fluka) when a UV detector (microUVIS20, Carlo Erba, Milano, Italy) or an Evaporative Light Scattering Detector (ELSD, Sedex 75, Sedere,

Table 1
SEC columns tested (all 5 µm particle size)

	Size (mm)	*Porosity (Å)*
Chrompack (Varian)	25×7.7	50
Phenogel (Phenomenex)	30×7.8	100
Phenogel (Phenomenex)	30×7.8	500
OligoPore (Polymer Laboratories)	30×7.5	100?
PLGel (Polymer Laboratories)	50×7.5	"mixed C"

Table 2
Test components, supplier, and molecular weight(s)

Compound	*Supplier*	*MW*
Doverphos S-9228	Dow	852
BADGE type epoxy resin, Araldit GT 7071	Vernicolor/ Valspar	
cyclic dimer		568
dimer		624
trimer, linear		908
trimer, branched		964
pentamer, linear, branched		1476, 1532, 1588
Irgastab CH 55	Ciba Specialty Chemicals	688
Irganox 1010	Ciba Specialty Chemicals	1177
Novolac glycidyl ether (NOGE), Araldit Py 307	Vernicolor/ Valspar	
4-ring NOGE		636
5-ring NOGE		798
6-ring NOGE		960
Polyethyleneglycol 1000, certified standard	Fluka	970
Polyethyleneglycol 1500	Fluka	1500
Polymethyl methacrylate (PMMA), certified standard	Polymer Laboratories	502, 602, 702, 802, 902, 1002
Polystyrene, certified standard	Fluka	1100
Polystyrene standards	Polymer Laboratories	580, 1320, 3294, 9200
Triarachin (triglyceride tri-20)	Fluka	976

Alfortville, France) was used. For the Phenogel 500 Å column, redistilled dichloromethane was also tested. The flow rates varied between 0.5 and 1 ml/min.

The test components are listed in table 2. They were dissolved in THF (20–30 mg in 10 ml) and injected in 10–100 µl volumes. The systematic names of the antioxidants are the following: Irganox 1010, pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate); Doverphos S-9228, bis (2,4-dicumyl-phenyl)pentaerythritol diphosphite; Irgastab CH55, tris(nonyl phenyl) phosphite.

Results

Figure 1 shows the relevant section of a SEC-RI chromatogram of the epoxy resin Araldit GT 7071 on the OligoPore column: it spans from the high molecular weight material eluted early (with a retention volume corresponding to the volume between the particles of the packing) to bisphenol A diglycidyl ether (BADGE). A low molecular weight material was eluted at the end of the chromatogram (retention volume including all the accessible pores of the packing).

Epoxy resins are usually formed by reaction of BADGE with bisphenol A (advancement process, 11–13). The trimer either consists of bisphenol A with BADGE condensed to the two phenol groups (linear structure of 908 D molecular weight, main component) or of a dimer with BADGE reacted with the center hydroxyl group (964 D). The two molecular weights were averaged. The dimer and the tetramer are minor components because they result from the reaction of BADGE and the trimer, respectively, with bisphenol A monoglycidyl ether.

Above the chromatogram of the epoxy resin is the peak extracted from a chromatogram of triarachin, the triglyceride tri-20 of 976 D molecular weight. Its peak width is indicative of the band broadening process in the column. Its retention time is clearly shorter than that of the trimer of the epoxy resin despite an only slightly higher molecular weight, from which it is concluded that the long straight chains of the fatty acids cause the molecule to occupy a larger volume than the trimer (largely

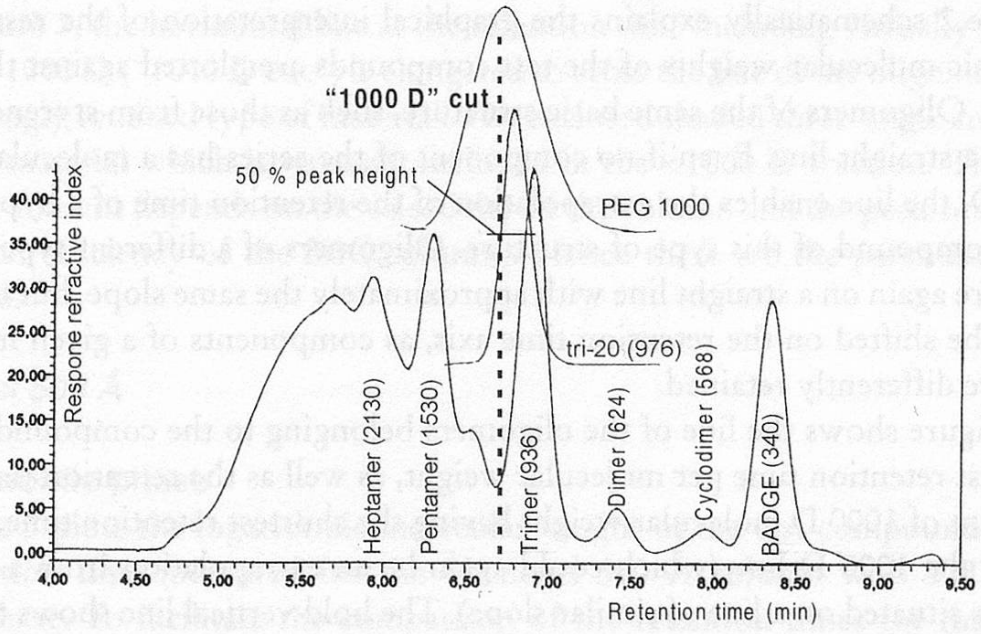

Figure 1 **Relevant section of the SEC-RI chromatogram of an epoxy resin (Araldit GT 7071) with the peaks of triarachin (tri-20) and polyethylene glycol (PEG) 1000 above it. Brackets, molecular weights (averages if present in more than one structures)**

consisting of more compact rings). The standard of polyethylene glycol PEG 1000 (shown on top of the chromatogram) consists of a mixture of oligomers, certified by Fluka to have the peak maximum at 970 D. The signal is broader because of partial separation of the oligomers. It is eluted slightly earlier than tri-20, complying with the rule that a straight chain structure occupies the largest room. However, from all other columns tested, i.e. those packed with polystyrene/divinylbenzene, PEG was eluted after tri-20.

Superposition of the three chromatograms illustrates the two main problems of the task.

1. Selectivity: SEC separates by molecular size, rather than weight, with the consequence that some material exceeding 1000 D is included in the fraction when the cut is determined by the least retained 1000 D material (for this column approximated by the PEG 1000).
2. Peak broadening: the first eluted material of tri-20 is mixed with the center of the tetramers of the epoxy resin with 1192 or 1248 D molecular weight (depending on structure).

Figure 1 also shows the proposed "1000 D cut". It is determined by the commonly least retained peak, tri-20. If the line meets the peak at 50 % height of the upslope (dotted line) and the peak is assumed to be of Gaussian shape, some 15 % of the material is lost. A more complete inclusion of the peak would have primarily introduced more material exceeding 1000 D.

Graphic interpretation

Figure 2 schematically explains the graphical interpretation of the results. The logarithmic molecular weights of the test compounds are plotted against the retention time. Oligomers of the same basic structure, such as those from styrene, are situated on a straight line. Even if no component of the series has a molecular weight of 1000 D, the line enables the extrapolation of the retention time of a hypothetical 1000 D compound of this type of structure. Oligomers of a different type of compounds are again on a straight line with approximately the same slope, but the line is likely to be shifted on the retention time axis, as components of a given molecular weight are differently retained.

The figure shows the line of the oligomers belonging to the compounds having the highest retention time per molecular weight, as well as the retention time of the component of 1000 D molecular weight having the shortest retention time, situated lower on the 1000 D line (which could again be an extrapolation from a series of oligomers situated on a line of similar slope). The bold vertical line shows the range of retention times representing compounds with a molecular weight of 1000 D, related to the (here undesirable) selectivity of the column for compounds of the same molecular weight but different structure.

For preparative isolation, the fraction must contain almost all material of the 1000 D components, i.e. the cut must include most of the peak of the least retained

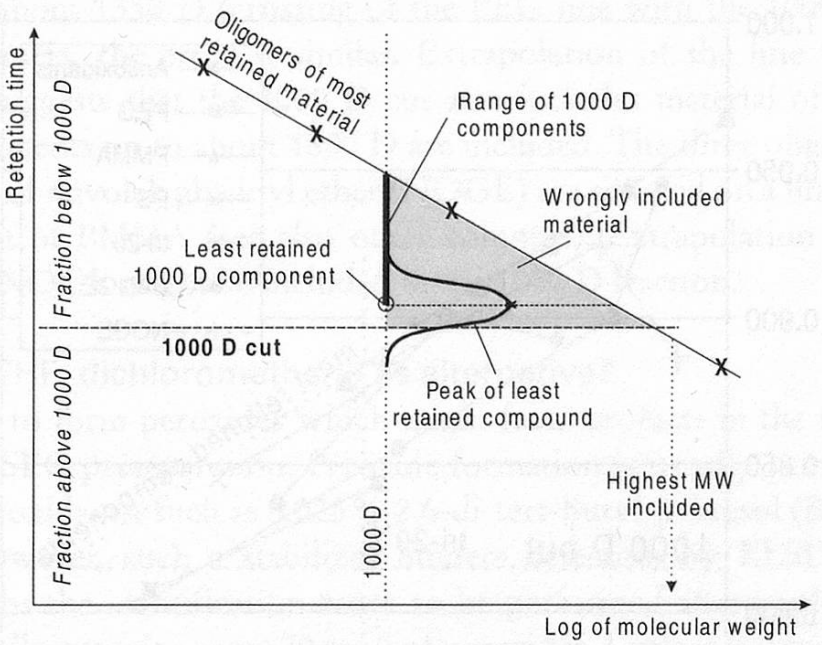

Figure 2 **Drawing for the interpretation of the results**

compound. The peak is schematically drawn into the graphic. Considering that the selection of the least retained compound is already a worst case assumption, it is assumed that it is sufficient to include some 86 % of this material, which means positioning the cut in the up-slope at 50 % peak height.

In figure 2, the horizontal line at the retention time including virtually all material up to 1000 D ("1000 D cut") is elongated to cross the line of the oligomers of the most strongly retained type of material. The enclosed shaded three-angle area represents the material which is wrongly included in the <1000 D fraction. The corresponding amount depends on the selectivity of the column and the peak broadening (separation efficiency of the SEC column). Hence these are the parameters to be optimized.

Phenogel 500 Å

THF as mobile phase

Figure 3 plots the logarithmic molecular weight of the test compounds against the retention time measured for the Phenogel 500 Å column with THF as the mobile phase. To facilitate the comparison of the retention times for the various columns tested, in particular to render results independent of column geometry and flow rate, retention times were divided by that of toluene. Since the resulting values are normalized in terms of time and elution volume, they are called "normalized retention".

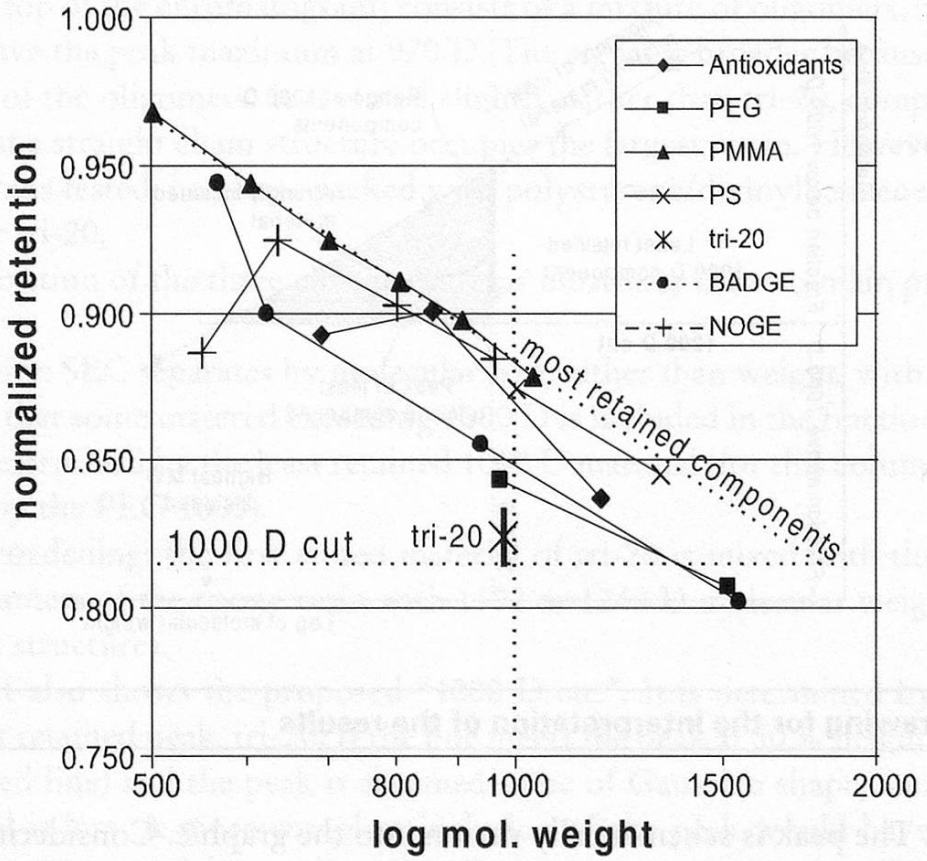

Figure 3 **Normalized retention versus logarithmic molecular weight: results for the Phenogel 500 Å column with THF as mobile phase**

The oligomers of polymethyl methacrylate (PMMA) were the most strongly retained components (dotted line extending to the point where it crosses the 1000 D cut line).

Tri-20 was the earliest eluted compound of about 1000 D – even the linear PEG 1000 was eluted later. Hence it fulfilled the requirement for the calibration of the 1000 D cut at least for the set of test components used. It also offers the advantages of having a molecular weight close to 1000 D (no extrapolation needed) and being a pure substance, such that the peak width is indicative for mixing resulting from the separation process. In figure 3, the peak width at half height of tri-20 is marked by a vertical bar and the normalized retention corresponding to the suggested 1000 D cut is fitted to the bottom of this bar (dotted line).

Comparison of the peak width of tri-20 with the width of the range of 1000 D components shows that the error resulting from the selectivity of the column far exceeded the mixing represented by peak broadening and that the use of a column of higher separation efficiency would only marginally improve the result.

The error of the method, i.e. the inclusion of higher molecular weight material, can be estimated as follows. From figure 3 it is extrapolated that for the polyethyl-

ene glycols the 1000 D cut drawn on the basis of the tri-20 peak includes half of a compound of about 1350 D (crossing of the PEG line with the 1000 D cut). For BADGE oligomers, the error is similar. Extrapolation of the line for the polystyrenes (PS) suggests that the 1000 D cut also includes material of 1700 D. For PMMA, components up to about 1800 D are included. The three oligomers of 636, 798, and 960 D of novolak glycidyl ether (NOGE) are situated on a line with a slope lower than that of PMMA (see also other columns). Extrapolation suggests that even a 2000 D NOGE might be included in the 1000 D fraction.

Peroxides in THF; dichloromethane as alternative?

THF tends to form peroxides which might form artifacts in the fraction to be analyzed after SEC preseparation. Peroxide formation is usually prevented by the addition of antioxidants, such as 0.025 % 2,6-di-tert-butyl-p-kresol (BHT). For our application, however, such a stabilizer hinders detection by ELSD or UV and severely disturbs the identification work to be performed afterwards. Non-stabilized THF rapidly contains some 20 mg/l of peroxides. Little is known about possible artifact formation under such conditions.

Dichloromethane, the alternative tested, must be free of hydrogen chloride (reaction with epoxides), which is more easily achieved than removal of peroxides.

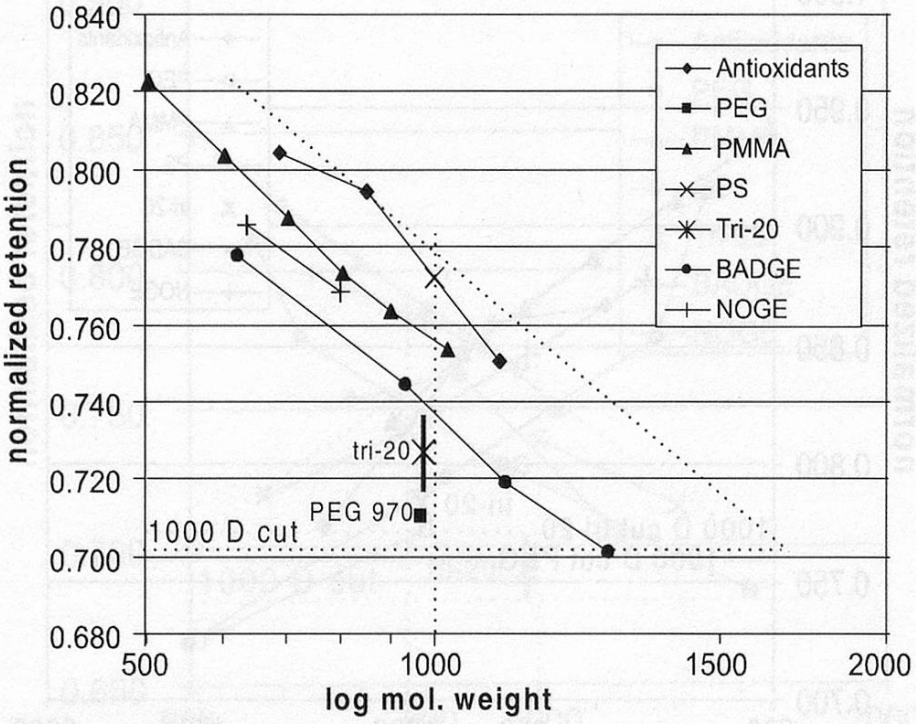

Figure 4 **Normalized retention versus logarithmic molecular weight: results for the Phenogel 500 Å column with dichloromethane instead of THF as mobile phase**

Results with dichloromethane for the same Phenogel 500 Å column and the same set of test components are shown in figure 4. Retention is remarkably shifted: the 1000 D compounds were eluted with relative retention varying between 0.71 and 0.78, instead of between 0.825 and 0.882 as observed with THF, suggesting that swelling reduced the pore size. There were, furthermore, substantial differences in selectivity: polyethylene glycol 1000 was eluted clearly before tri-20 (as observed for the OligoPore column) and the three antioxidants after the PMMA. These differences in selectivity are probably due to different solvation and, hence, a different conformation of the molecules. Despite these significant differences, general performance was similar: using PEG 1000 for the calibration of the 1000 D cut, the amount of >1000 D material included in the fraction was similar.

Dichloromethane was rejected as mobile phase because it turned out to be too weak an eluent: hydrolyzed BADGE (BADGE.2H2O) was eluted with strong chromatographic extra retention and formed a seriously distorted peak. The addition of 2% methanol, 10% acetone, or 10% acetonitrile improved on this, but could not prevent substantial tailing of the peak. It was thus concluded that THF should be used as mobile phase. A method will be needed to minimize peroxide concentrations, and possible artifact formation should be tested for some labile compounds.

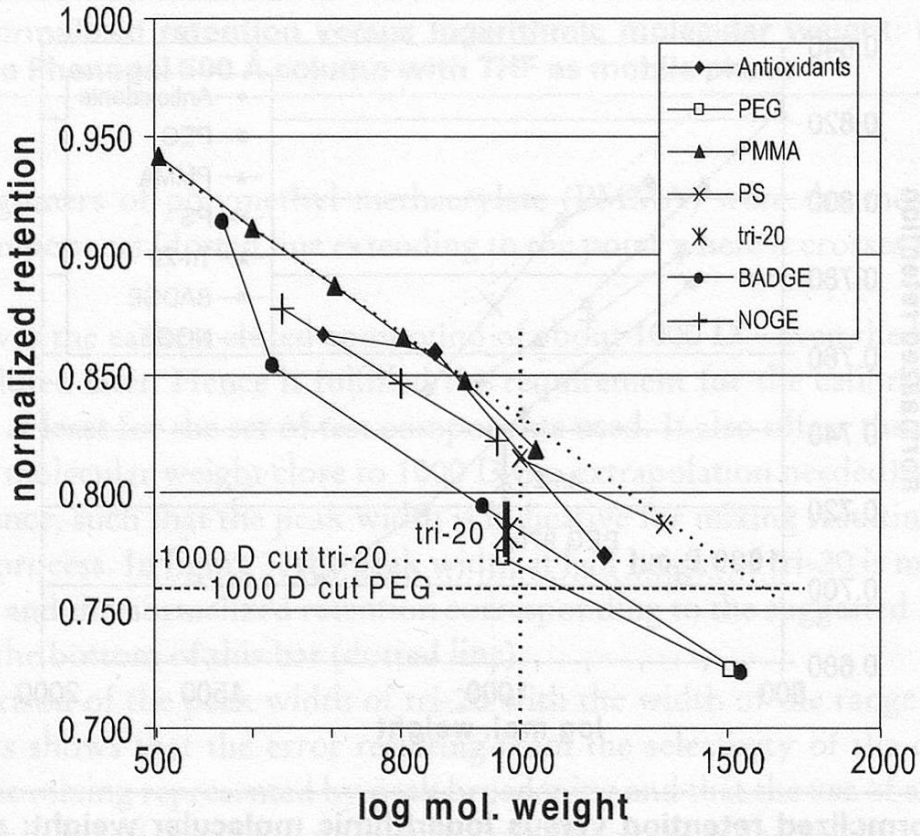

Figure 5 **Results for the OligoPore column**

OligoPore

Figure 5 shows analogous results for the OligoPore column (some sections of chromatograms were shown in figure 1). As relative retention was shorter than on the Phenogel 500 Å column (using THF, figure 3), the average pore size of this packing must be smaller. The manufacturer specified it at 100 Å, but our results suggest it to be larger than that (compare with figure 6). PEG 1000 was eluted before tri-20, perhaps because the packing material does not seem to be a polystyrene/divinylbenzene polymer. If this column would be selected, calibration of the 1000 D cut had to be based on this type of solute. Also the BADGE components were eluted earlier. Performance regarding inclusion of more strongly retained higher molecular weight material is similar to the Phenogel 500 Å column.

Phenogel 100 Å

For a separation at 1000 D, usually a packing of 100 Å pore size is recommended, since 1000 D is in the center of the useful working range (logarithmic scale), i.e. provides the best selectivity. The results in figure 6 show a clearly lower relative retention than for Phenogel 500 Å and also the OligoPore column. Tri-20 is eluted long before the other materials of 1000 D, with the effect that the BADGE pentamer and PEG 1500 would largely be included in the 1000 D fraction. It

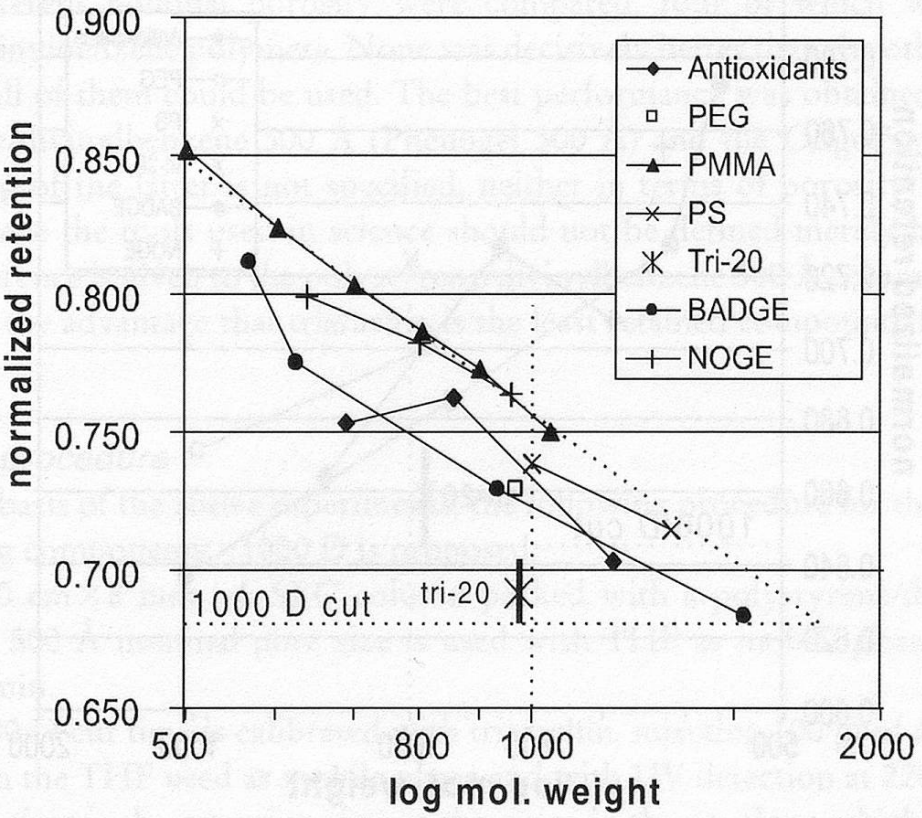

Figure 6 **Performance of the Phenogel 100 Å column (THF as mobile phase)**

appears that the high selectivity is rather of disadvantage regarding the performance for our purpose.

Chrompack 50 Å

Figure 7 shows some results for the Chrompack 50 Å column. Relative retention is again substantially lower, which corresponds to the expectations for the packing with smaller pores: 0.658 for tri-20 compared to 824, 784, and 690 for the Phenogel 500 Å, OligoPore, and Phenogel 100 Å column, respectively. As the column was old and its separation efficiency reduced (see broader tri-20 peak), the oligomer mixtures of PMMA and NOGE were no longer satisfactorily resolved.

The results do not suggest a simple interpretation. The retention of PEG is further increased, and an extrapolated material of 2000 D is included in the 1000 D fraction. This is a continuation of the undesirable changes observed from the 500 to the 100 Å column. On the other hand, retention of the epoxy resin (BADGE oligomers) was more similar to tri-20 again than on the 100 Å column, reversing the trend from the 500 to the 100 Å column. The same is observed for the antioxidant Irganox 1010, which showed lower retention compared to tri-20 than on the 100 Å column.

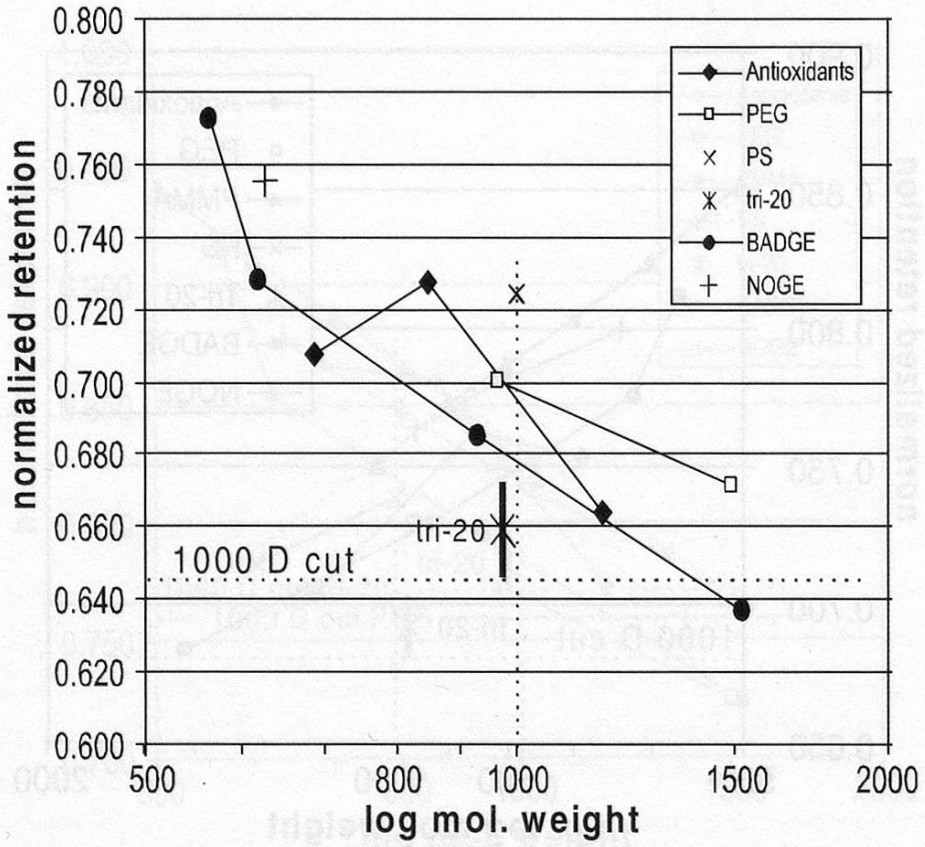

Figure 7 **Results for the Chrompack 50 Å column**

Plgel

From the Plgel column, tri-20 was eluted with a relative retention of 904, indicating average pore sizes beyond 500 Å. Selectivity did not significantly differ from the other polystyrene divinylbenzene columns, but separation efficiency around 1000 D was substantially lower, which was the reason for not further considering this column.

Conclusions

Optimization of separation

The analysis of migrates from food packaging materials calls for a preseparation such that all compounds with a molecular weight up to 1000 D are included in the fraction for further analysis and as many other components as possible are eliminated. As SEC separates by molecular size rather than weight, some overlapping is inevitable. For a method designed to be applicable comprehensively for all substances, the 1000 D cut must be calibrated for the worst case, i.e. the 1000 D compound with the shortest retention time. Among the test compounds used, the triglyceride triarachin (tri-20) was usually the least retained. The price to be paid for this worst case assumption is that for all other types of substances some larger molecular weight material will be included in the <1000 D fraction.

The first aim of this work was the optimization of the SEC column. Five packings of different nominal porosity were compared, four of which were polystyrene/divinylbenzene polymers. None was decisively better than the others and, if necessary, all of them could be used. The best performance was obtained from the polystyrene/divinylbenzene 500 Å (Phenogel 500 Å) and the OligoPore column. The packing of the latter is not specified, neither in terms of porosity nor of the material. Since the tools used in science should not be defined merely by a brand name, preference is given to the polystyrene/divinylbenzene 500 Å column. The latter also has the advantage that triarachin is the least retained compound, facilitating calibration.

Proposed procedure

On the basis of the above experiments, the following procedure for the isolation of migrating components <1000 D is proposed:

1. A ca. 30 cm × 8 mm i.d. SEC column packed with a polystyrene/divinylbenzene of 500 Å nominal pore size is used with THF as mobile phase at about 700 µl/min.
2. The 1000 D cut time is calibrated with triarachin, injecting 100 µl of a 0.1 % solution in the THF used as mobile phase and with UV detection at 220–225 nm. The cut time is the retention time at the point in the up-slope which is at 50 % peak height.

3. The other end of the fraction must be positioned such that the small molecular weight migrants are included. It can be determined injecting toluene (about 1 mg/ml in THF) and measuring the retention time at the end of this peak.
4. The extract from a packing material (obtained using a food simulant or an exhaustively extracting solvent) is evaporated to dryness. The residue is re-dissolved in THF.
5. If SEC preseparation is followed by further analysis, it is usually of interest to inject an amount of migrate close to the capacity limit of the SEC column (for a 8 mm i.d. column about 1 mg). Overloading may be detected by injection of 10 and 100 µl of the same extract. Usually retention times are prolonged and peaks broadened. If UV-detection is used, a wavelength higher than the absorption maximum must often be chosen to avoid saturation of the detector.
6. 100 µl of a solution of about 10 mg/ml (around 1 mg of migrate) is injected and the eluate recovered between the 1000 D cut and the end of the toluene peak.

Summary

The method enables the isolation of components of up to 1000 D molecular weight from extracts of food packaging materials. It is proposed to use a polystyrene/divinylbenzene packing with an average nominal pore size of 500 Å and tetrahydrofuran as mobile phase. The 1000 D cut is calibrated with triarachin, since this was the component of lowest retention per unit of molecular weight. As size exclusion chromatography (SEC) actually separates by molecular size rather than weight, some overlapping with components of higher molecular weights must be accepted. In the worst case the resulting fraction may include components of up to almost 2000 D molecular weight.

Zusammenfassung

Die Methode erlaubt die Isolierung von Komponenten mit bis zu 1000 D Molekulargewicht aus Extrakten von Lebensmittelverpackungsmaterialien. Es wird vorgeschlagen, ein Polystyrol/Divinylbenzol mit einer durchschnittlichen nominellen Porosität von 500 Å und Tetrahydrofuran als Laufmittel zu verwenden. Der Schnitt der <1000 D Fraktion wird mit Triarachin kalibriert, weil dieses die geringste Retention pro Molekulargewicht aufwies. Da Ausschlusschromatographie (SEC) in Wirklichkeit nach Molekulargrösse und nicht nach Molekulargewicht trennt, ist eine Überlappung verschiedener Molekulargewichte unvermeidlich. Im ungünstigsten Fall schliesst die so gewonnene Fraktion noch Materialien von bis zu nahezu 2000 D Molekulargewicht ein.

Résumé

La méthode discutée permet l'isolation des composés provenant d'extraits d'emballages alimentaires ayant un poids moléculaire inférieur ou égal à 1000 D. Il est proposé d'utiliser un substrat de type polystyrène/divinylbenzène avec une porosité moyenne nominale de 500 Å et du tetrahydrofurane comme phase mobile. La limite de fractionnement <1000 D est étalonnée avec la triarachine car ce composé montre une rétention minimale par poids moléculaire. Comme la SEC (size exclusion chromatography = chromatographie d'exclusion) sépare en réalité par taille plutôt que par poids moléculaire, une certaine coélution de composés ayant des poids moléculaires différents reste inévitable. Dans les cas limites, la fraction obtenue peut inclure des matériaux ayant des poids moléculaires de presque 2000 D.

Key words

Size exclusion chromatography (SEC), GPC (gel permeation chromatography), Food packaging materials, Migration from packing materials into foodstuffs, Preseparation at 1000 D molecular weight

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