INFLUENCE OF POLYSTYRENE AND POLYETHYLENE PACKAGING MATERIALS ON FOOD QUALITY

Promotor : Dr. Ir. A.G.J. Voragen
hoogleraar in de Levensmiddelenchemie

Co-promotor: Dr. Ir. J.P. Roozen
universitair hoofddocent, Vakgroep Levensmiddelentechnologie, Landbouwuniversiteit te Wageningen

Jozef P.H. Linssen

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STELLINGEN

1. Het is de moeite waard om het monomeergehalte van polystyreen zodanig te verlagen dat een bredere toepassing mogelijk wordt voor het verpakken van levensmiddelen (Dit proefschrift).

2. Uitkomsten van migratie-experimenten, die zijn verkregen met aanbevolen analysemethoden, moeten met de nodige voorzichtigheid geïnterpreteerd worden (Dit proefschrift).

3. De berekening van diffusiecoëfficienten van styreen monomeer in polystyreen, zoals voorgesteld door Miltz en Rosen-Doody, is niet haalbaar.
(Miltz, J. and Rosen-Doody, V., J. Food. Process. Preserv. 1984, 8, 151 - 161).

4. Het is onmogelijk kwaliteitsaspecten van verpakte levensmiddelen als gevolg van "Food-Packaging-Interactions" te evalueren met "Food Simulants".

5. Polyvinylchloride (PVC) verpakking wordt te vaak onbezonnen vervangen uit angst voor economische tegenslag.

6. De onvermijdelijke interacties tussen verpakking en levensmiddel zijn (nog) geen afspiegeling van de onderzoeksinteracties tussen verpakkings- en levensmiddelenindustrie.

7. Auteurs van wetenschappelijke publicaties dienen in de drukproef formules en tabellen (beter) te controleren op zetfouten.

8. Dankzij het aantrekken van gekwalificeerde derde geldstroomprojecten kunnen vakgroepen van universiteiten hun analytisch instrumentarium up-to-date houden.

9. Frustraties van politie- en opsporingsambtenaren worden vaak veroorzaakt door zogenaamde vormfouten.

10. Ten onrechte wordt de damsport maar al te vaak gezien als niet-volwaardig.

11. Een vereniging met een groot aantal leden is gemakkelijker te besturen dan een vereniging met een klein aantal leden.

12. Bij de toekenning van eerste geldstroom budgetten aan vakgroepen van universiteiten weet men nooit of men met "bedelen" te doen heeft.

Stellingen behorende bij het proefschrift "Influence of polystyrene and polyethylene packaging materials on food quality"

Jozef Linssen, Wageningen, 17 juni 1992

Voor Marlène
mijn moeder
mijn vader zaliger

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VOORWOORD

Het voor u liggende proefschrift is het resultaat van ruim drie jaar onderzoek, dat is uitgevoerd bij de Vakgroep Levensmiddelentechnologie, sectie Levensmiddelenchemie en -microbiologie van de Landbouwuniversiteit te Wageningen. Bij het tot stand komen van dit proefschrift ben ik velen oprecht dank verschuldigd en erkentelijk voor hun bijdragen en interesse. Zonder iemand te kort te willen doen, wil ik een aantal personen met name noemen, die voor mij van bijzondere betekenis zijn geweest.

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Medewerkers van de tekenkamer (Centrale Dienst De Dreijen), die prachtige figuren, soms van onooglijke schetsen, getekend hebben.

Medewerkers van de fotolocatie (Centrale Dienst De Dreijen), die het telkens weer lukte om prima foto's en copy proofs te maken.

Tenslotte, Marlène, ook jij hebt bijgedragen aan het tot stand komen van dit proefschrift door te accepteren, dat jij misschien wel eens te weinig aandacht kreeg.

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Chapter 1 Introduction

In the last decades the use of plastic materials for packaging of food has increased tremendously, because of advantages as low costs, low energy content, low handling weight, wide range of material characteristics and variety of forming techniques (Simmons, 1986). This increase has created the need for more research on interactions between food and package and its effect on product quality. Food packaging interactions can be divided into three main phenomena: migration, permeation and absorption. These phenomena can occur separately or simultaneously (Figure 1).

Migration of packaging components, like residual monomers, additives and polymerisation aids causes an undesirable contamination of food. Migration of such components may adversely effect the quality of the food, e.g. alteration of flavour and sometimes a toxicological risk to human health. A reaction between migrated substances and food components may also occur.

Permeation of gas and vapour, particularly of oxygen, water vapour and aroma components is of considerable interest. In combination with light, a high rate of oxygen permeation can cause oxidation problems. A high water vapour permeation results in physical or physico-chemical alterations as wetting or drying, and can promote microbial spoilage. These reactions lead to an indirect alteration of flavour, while direct flavour alteration can be caused by loss of components from food or by acquiring aspecific odours from the environment through the package (Niebergall and Kutski, 1982; Koszinowski and Piringer, 1987).

Absorption phenomena can influence the quality of the food too. Absorption of aroma components by the package can cause a direct loss of flavour compounds from food. Absorbed fat and essential oils can promote swelling of the package and so disturb its molecular structure.

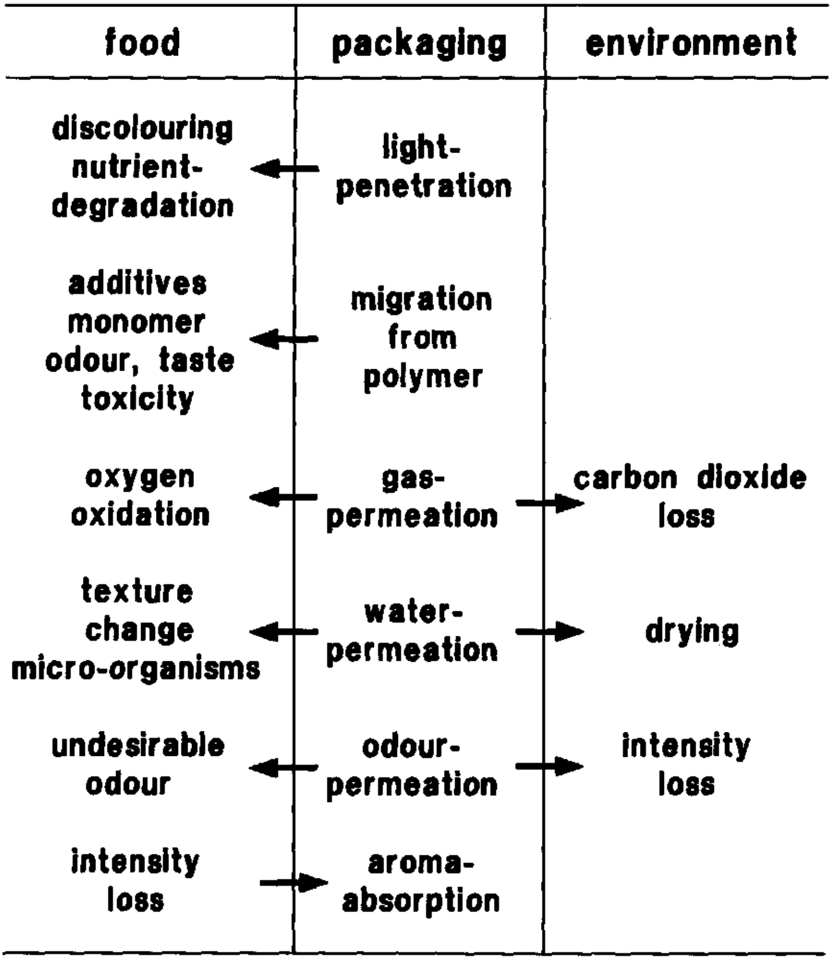

Figure 1: Interactions between food and packaging material. (Adapted from Landois-Garza and Hotchkiss, 1987)

Besides these various phenomena of interactions also the wide variety of foods is a major problem in studying food packaging interactions. Each packed food has its own chemical composition and so its own characteristics related to packaging materials. Therefore Flückiger (1975) has divided food products in several groups as shown in Table 1.

Table 1: Classification of food products on characteristics related to packaging materials

1. Dry foods
   a. with fatty properties
   b. with absorptive properties
   c. without fatty and without absorptive properties

2. Wet foods
   a. with low fat content
      - neutral (pH > 5.0)
      - acid (pH < 5.0)
      - alcoholic
   b. with high fat content
      - neutral (pH > 5.0)
      - acid (pH < 5.0)
      - alcoholic

3. Fat, oil and fatty food without any substantial water content

4. Food products with a high content of essential oils

Hotchkiss (1988) stated that the major problem in studying interactions are the lack of standard methodology and data concerning the actual changes in food quality.

FOOD PACKAGING INTERACTIONS

Migration

Three basic classes of migration can be identified (Figure 2). The first class is the so-called "non-migrating system". This class includes foods packed in relatively inert containers (e.g. glass bottles). The intramolecular linkages between polymer and low molecular weight compounds (monomer) are very strong. The diffusion coefficients approach zero, and only a monolayer of compounds present on the polymer can be transferred into the food.

The second class is an "independently migrating system", in which a compound diffuse through a polymer matrix to the surface and than escape from the surface, independent on the medium, into the food. Diffusion and partition constants are the key parameters and determine the interaction of components of food with components of packaging material. The diffusion constant provides information on the migration velocity, while the partition constant provides information on the quantities which can be transferred from the food to the packaging material and from the packaging material to the food. Both magnitudes are fundamental factors which describe the material interchange of migrating substances between two phases (Koszinowski and Piringer, 1987).

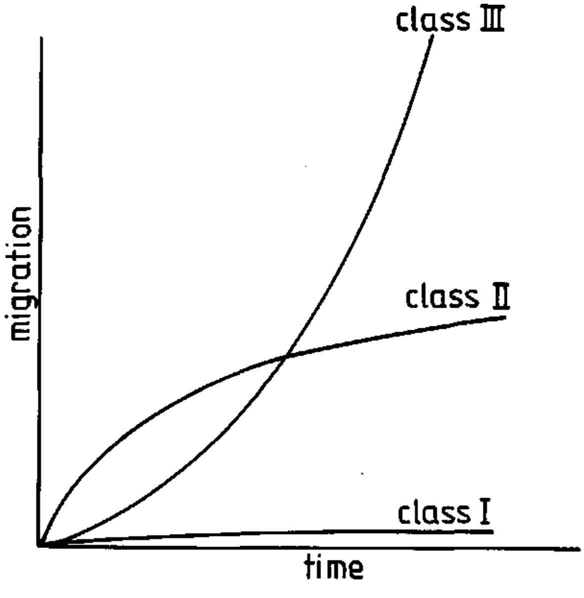

Figure 2: Diagrammatic representation of different types of migration processes
(Adapted from Mannheim and Passy, 1990)

The third class is called "migration controlled by the food". This system is the most difficult one and it occurs frequently. A food component is able to penetrate the polymer, disturbing its physical structure. Swelling may occur, which may result in an accelerated migration. This mechanism is not well understood.

Food simulants

Fazio (1979) stated that it would be almost impossible to use food products for determining migration of packaging components, because the complex matrix of food would disturb the analysis of trace quantities of the migrants. This concept made it necessary to develop models for studying migration of packaging components into foodstuffs. Because of the extensive difficulties inherent to the analysis of migrants in any but the simplest food, food simulants are commonly used. A true simulant will necessarily fulfil two conditions. It must effect migration from the plastic packaging material to the same extent as the food simulated and it must allow relatively simple analysis for the migrant of interest. The following food simulating agents are often used: distilled water, 3 % acetic acid. 10 % and/or 50 % ethanol, heptane and vegetable oils/ HB 307 (Fazio, 1979; Till et al., 1987; Figge, 1982; Risch, 1988).

Distilled water, the ethanol solutions and acetic acid are simulants for respectively wetty, alcoholic and acid food products. Heptane is a simulant for fatty foods. Also vegetable oils, like olive oil, were chosen as simulating agent for products with a high fat content. The composition of vegetable oils is not constant, so Figge et al. (1982) developed an alternative fat simulant (Unilever fat HB 307), which is a mixture of saturated triglycerides (Table 2). It is important to make sure, that simulants reflect adequately the chemical and physical properties of food. However, none of the simulants are completely satisfactory. Schwartz (1985) reported that migration into food simulants exceeded migration into food in 80 % of the tests.

Table 2: Fatty acid composition of Fat Simulant HB 307

No of C-atoms	GC % peak area
6	1.2
8	8.0
10	10.4
12	50.0
14	13.6
16	7.6
18	8.4
other	0.8

Figge (1980) stated that solvents like heptane are totally unsuitable for replacing fatty foods since they cause unrealistically rapid migration. Figge and Baustian (1983) reported that under practical storage conditions milk and milk products interact with packaging materials mainly by their continuous phases and that olive oil and Unilever Fat HB 307 are unsuitable as food simulants for these products (Figure 3).

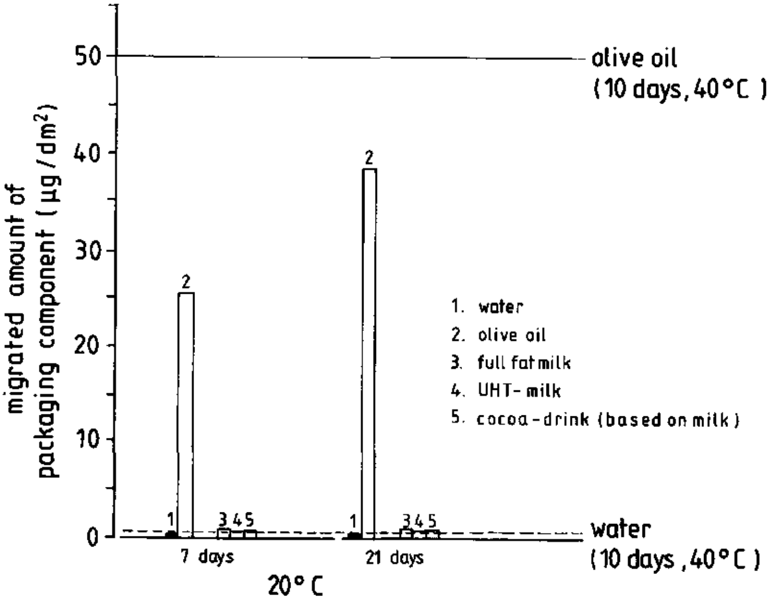

Figure 3: Migration in food and food simulant.
(Adapted from Figge and Baustian, 1983)

Migration tests

Overall migration tests have been developed to avoid time consuming procedures. The migration values obtained are determinations of gravimetric loss of plastic packages before and after exposure to a food simulant (De Kruijf et al, 1983). Overall migration gives an estimation of the potential transfer of packaging substances to food (Sheperd, 1982). No information about specific migrants is provided and so migration tests on specific components are to be preferred. Several test cells are developed for carrying out specific migration tests. Examples are given in figure 4.

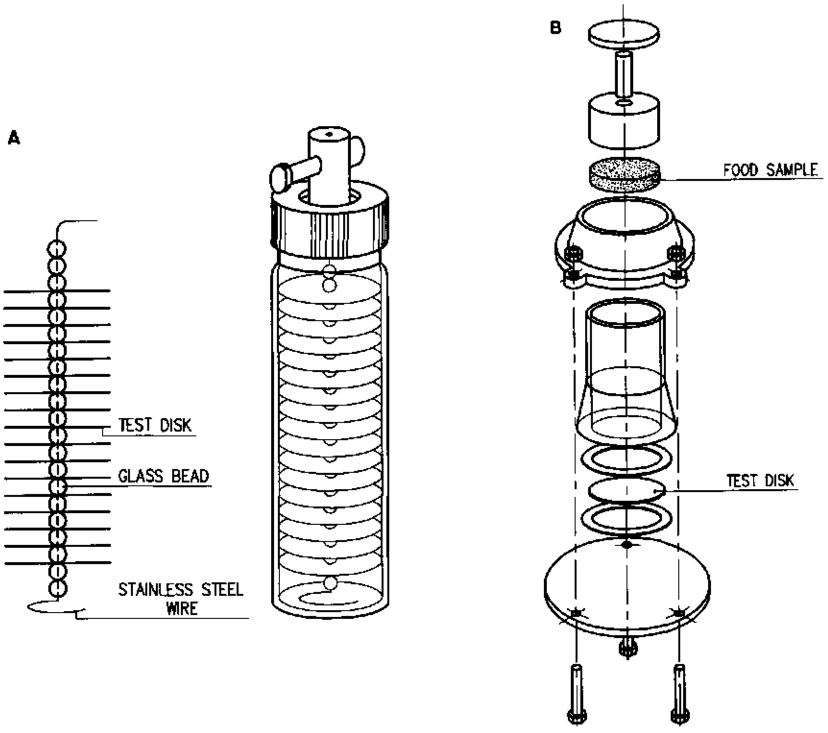

Figure 4: Test cells for migration experiments. Examples for simulants and liquid foods (A) and for solid foods (B) (Adapted from Till et al., 1982)

Migration tests with food simulating agents are suitable for evaluating safety aspects, but not very useful to make firm conclusions about food products themselves. The latter are much more complex, and so a food simulating agent resembles the food product only on a few aspects. Nowadays the necessity for studying foodstuffs themselves is recommended, because working with food simulants alone gives unsatisfactory information about migration values (Risch, 1988; Figge, 1980; Schwartz, 1985). For these reasons Risch (1988) argued that these tests should be conducted with each type of food in a given package under normal conditions of use for an expected shelf life.

Absorption

Absorption of flavour components of foods by packaging material results in a change of flavour characteristics. Loss of flavour compounds is a concern for many products currently being packed aseptically (Harte and Gray, 1987). When foodstuffs are packed in plastic containers, some components of the food are absorbed by the plastic, which can result in a change of taste and/or nutritional value. The significance of absorption may vary considerably, because of the diverse nature of these components in a large variety of foods. The chemical and physical nature of the plastics is also very important, because food components with solubility parameters similar to the plastic tend to be absorbed significantly. Jabarin and Kollen (1988) reported that components like hydrocarbons would be absorbed in hydrocarbon type plastics. Shimoda et al. (1988) found an increase of absorption of flavour components like alcohols, aldehydes and esters with an increase of carbon chain length in polyethylene laminated pouches. When these compounds are selectively removed from the food by the packaging material, they function no longer as flavour components and the perceived quality of the product is changed (Harte and Gray, 1987).

POLYSTYRENE AND POLYETHYLENE AS PACKAGING MATERIAL

Migration of styrene monomer of polystyrene packaging material may be the cause of an characteristic unpleasant plastic-like chemical flavour. Ramshaw (1984) stated that the amount of migrated styrene is higher into products with higher fat content. On the other hand Jenne (1980) found an increased recognition threshold concentration in products with a higher fat content (Table 3). The divergence of the two influences prevent accurate prediction of the strength of off-flavour development in food.

Table 3: Threshold values of styrene in food products.

food product	threshold (ppm)
tea	0.2
nectar	0.2
low fat milk	0.3
yoghurt	0.5
full fat milk	1.2
vanille custard	1.5
cream	6.0

Bojkow et al. (1975, 1979, 1982) studied formation of off-flavour in milk, induced by polyethylene packaging material. Off-flavour transfer into milk can be caused by volatile substances from polyethylene coatings, paper board or printing solvents (Table 4). As the polyethylene coatings are permeable for nearly all substances in question, volatiles of the packaging material may migrate into milk. The formation of off-flavours components seems to be caused by oxidative changes of the polyethylene surface, which may occur by (over)heating of the packaging material when it is moulded. A lot of thermo-oxidative degradation products in low density polyethylene were detected by Hoff and Jacobsson (1981), e.g. aldehydes, ketones and organic acids. All of these degradation products are able to induce an off-flavour. Sometimes an off-flavour in milk induced by plastic packaging material is suggested. However, Bojkow (1982) did not show a significant change in off-flavour intensity in pasteurized milk, packed in polyethylene bottles, during one week storage in a refrigerator. Kiermeyer and Stroh (1969) suggested an ion exchange interaction between the acidic protons of carboxylic acids of polyethylene and metallic cations of milk-salts. The loss of cations might be responsible for the "plastic flavour" sometimes suggested in milk packed in polyethylene. Dürr et al (1987) detected a shift of limonene from orange juice into the polyethylene layer of polyethylene lined cardboard. They considered it as an advantage because limonene is known as a precursor of off-flavour components.

Table 4: Examples of volatiles from PE-lined paper or board responsible for off-flavour.

components	remark
paper	
C_5 - C_{10} aldehydes	autoxidation products from resin
hepten-3-one 3-heptanone	compounds from 2-ethyl-1-hexanol with intensive taste
toluene, terpenes, sesquiterpenes, limonene, alkylbenzenes	components from wood
polyethylene	
isomers of C_8 - C_{18} alkanes and alkenes (also branched) pentamethylheptane C_2 - C_5 aldehydes C_2 - C_5 organic acids acroleine acetone methyl-ethyl-ketone butyrolactone	components with different taste intensities
colour ink	
ethylacetate ethanol ethylglycol	different taste intensities

SCOPE OF THE THESIS

The aim of this study was to obtain a better understanding of food quality influenced by its packaging material. Such a study is quite complex in nature, which makes that literature sources are widespread and scarcely available. It is almost impossible to investigate the whole range of plastic polymers used for packaging of food. Furthermore the interest of the supporting industry led our attention to polystyrene and polyethylene.

Polystyrene

Polystyrene contains detectable amounts of residual monomer, which cannot completely be removed during extrusion of the polymer. Styrene monomer has an unpleasant odour and it could give a taint to the product after migration.

Part I describes the evaluation of several aspects of migration of styrene monomer from different types of polystyrene. Usually a vegetable oil is chosen in these studies. Corn oil was used as a simulant in the present study, because of the presence of natural antioxidants. One of the aspects studied was the possibility of migration of styrene monomer from the polymer into the food through the vapour phase, i.e. direct contact is probably not necessary for migration. Moreover, several aspects related to the polymer were part of the study as there are the residual content of styrene monomer and composition of the polymer. Also other factors, like exposure temperature and composition of food were investigated.

Part II deals with quality aspects as a consequence of styrene migration, evaluated with a food simulant and a food product itself. Chocolate flakes were chosen to study the influence of styrene monomer migration on the development of a taint in the flakes. Because emulsion type food products are very common, oil in water emulsions were used as a model to get more information about taste recognition threshold values of styrene. The dependence of recognition threshold values on the fat content was investigated and these results were compared with emulsion type foods itself, i.e. yoghurts.

Polyethylene

The research on polyethylene and its effect on food quality is even more difficult, because the high volatile monomer cannot be responsible for quality influences on a food product.

Part III describes quality aspects of water in contact with polyethylene packaging material. Water was used as food product in this part of the study, because water is easy to handle, and it is packed commercially in polyethylene lined packages. Moreover water is sensitive to a taint. Migration of polyethylene packaging components could give a taint to water. Therefore, sensory attributes were generated for describing a taint in water, which was in contact with polyethylene lined aluminium pouches. These pouches were produced in such way that a taint could be expected. Commercial mineral water packed in polyethylene lined aluminium/cardboard was stored at several temperatures. Combined gas chromatography and sniffing port analysis was carried out to establish odour impressions of individual compounds. These components were identified with combined gas chromatography and mass spectrometry. It was tried to correlate the sensory and instrumental data.

Part IV deals with some aspects of absorption of flavour components by polystyrene and polyethylene. Flavour components having solubility parameters favourable to the plastic packaging material tend to be absorbed significantly into the plastics. This aspect was investigated on artificially flavoured commercial drink yoghurts and its packages. Also the composition of the food product is an important factor, which is shown by limonene absorption from an imitation juice and from fruit juices with and without addition of pulp.

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PART I. MIGRATION OF STYRENE MONOMER FROM POLYSTYRENE PACKAGING MATERIAL

Polystyrene (PS) packaging material is frequently used for packaging of foods. Homogenous PS is called general purpose polystyrene (GPPS), which is used for foamed trays for meat and crystal clear trays for salads and vegetables. High impact polystyrene (HIPS) consists of a PS matrix with a dispersed rubber phase and is used for packages for desserts and dairy products like yoghurts. Food grade commercial polystyrene has a residual monomer content of less than 500 ppm, which does not mean that no styrene migrates into the packed product.

Chapter 2 presents the migration of styrene monomer into corn oil and emulsions. The latter are chosen because of the emulsion character of many foodstuffs. Styrene is very soluble in apolar solvents like oils. Therefore, the extent of migration of styrene into oils and into emulsions might be different.

Chapter 3 deals with the effect of different sampling methods on the level of styrene monomer migrated from different types of polystyrene into corn oil. Traditionally cut pieces of polymer are immersed in oil using the immersion sampling method. In this way, cut edges come into contact with the oil and might interfere with the migration results. Vapour phase migration effects the level of migrated styrene too. This aspect could be of interest for solid foods, which have only scarcely contact with the packaging material. In a cell sampling method polystyrene sheets are tightened in a special constructed cell. No cut edges have contact with the oil and so, the latter method reflects much better the practical circumstances of food packaging and could be more reliable for the imitation of practical situations.

Chapter 4 presents several aspects which are important for migration of styrene from polystyrene into corn oil. The composition of polystyrene might influence the extent of migration of styrene. Depending on the application different blends of GPPS with HIPS are used for packaging of foods. Also the content of residual styrene monomer could influence the level of migrated styrene, and so the perceived quality of the packed product. Usually foods are stored at certain temperatures before consumption. For that reason, it is valuable to know more about the influence of temperature on the level of migrated styrene.

Chapter 2. Migration of styrene monomer from polystyrene packaging material into food simulants*

ABSTRACT

Migration of residual styrene monomer from polystyrene packaging material (GPPS : HIPS = 1:1) was followed for corn oil, oil (30%) in water- and water in oil (30%) emulsions. The highest level of migration was found for corn oil. The matrix of a simulant influences the amount of styrene migrating from the packaging material. This amount was proportional to the content of residual styrene monomer in the polymer. Only a small part (3%) of the total residual styrene present in the polystyrene samples migrates during 14 days of incubation.

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* Linssen, J.P.H. and Reitsma, J.C.E., Proc. 7th World Conference on Food Packaging. Utrecht, The Netherlands, 0.3.1 - 0.3.6 (1991)

INTRODUCTION

General purpose polystyrene (GPPS) and high impact polystyrene (HIPS) and mixtures of these grades are widely used in food applications. Examples would include crystal clear trays for cookies and candy and foamed trays for meat. Foodstuffs are chemically complex structures and pose too many analytical problems to be readily examined for trace organic contaminants. Also Fazio (1979) stated that it would be almost impossible to use food for determining migration of packaging components. Therefore, several food simulants were recommended. Distilled water, 3% acetic acid, 10% and 50% ethanol solutions in water are often used as simulants for wetty, acid and alcoholic food products. Heptane is used as a food simulant for fatty food, although Figge (1980) stated that solvents like heptane are totally unsuitable for replacing fatty foodstuffs since they cause an unrealistically rapid migration. For that reason vegetable oils like olive oil or corn oil, and an universal fat simulant (Unilever fat HB 307) are used as food simulants for fatty food products (Figge and Freytag, 1978).

In the present study corn oil, an oil in water emulsion (O/W) and a water in oil emulsion (W/O) were used as food simulants for the evaluation of migration of styrene monomer from polystyrene packaging material.

MATERIALS AND METHODS

Materials

GPPS (type "styron* 637") and HIPS (type "styron* 472") were extruded in a 1:1 ratio to sheets of 1 mm thickness at 175 °C (code: PS 175) and 261 °C (code: PS 261) by Dow Benelux NV, Terneuzen, The Netherlands. Corn oil (Mazola) was bought in a local store at Wageningen (Holland). Emulsifiers, sodium

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[*] trademark of the Dow Chemical Company

stearoyl-2-lactylate (Admul SSL 2004) and a mixture of partial esters of polyglycerol with linearly interesterified castor oil fatty acids (Admul WOC 1403) were kindly provided by Quest International, Zwijndrecht (The Netherlands) and used for the preparation of the O/W -and the W/O-emulsion, The emulsions were prepared by mixing oil and emulsifier (1% for the O/W-emulsion and 4% for the W/O-emulsion), then adding water very slowly under continuous stirring with a bladed stirrer and finally homogenising for 1 min with an Ultra Turrax. The W/O-emulsion was prepared at 60 °C.

Styrene analysis

Residual styrene monomer in the polymer was determined by dissolving the polymer in dichloromethane and subsequently precipitation with iso-octane. 1 μl of the clear upperlayer was injected into a gas chromatograph (Carlo Erba, model 4200) equipped with a flame ionisation detector. The analyses were carried out on a 15 m x 0.53 mm (i.d.) wide bore column (DB 225, J & W Scientific). The detector and injector temperature was 250°C. The following temperature program was used: an initial hold for 2 min at 40 °C, then 5 °C/min to 100 °C and a final hold for 2 min (ISO, 1974).

Styrene was determined in corn oil and emulsions by azeotropic distillation with methanol, followed by extraction with pentane. The pentane extract was analyzed with a gas chromatograph (Carlo Erba, model 4160), equipped with a flame ionisation detector and a cold on-column injector. The analysis were carried out on a 30 m x 0.32 mm (i.d.) fused silica capillary column (DB 1701, J & W Scientific). The detector temperature was 280 °C. The following temperature program was used: an initial hold of 4 min at 40 °C, then 5 °C/min. to 90 °C, followed by 15 °C/min to 190 °C and a final hold for 1 min. Calibration curves were prepared by adding different amounts of styrene to the oil and the emulsions (Varner et al, 1983).

Sampling method

1 dm^2 or 2 dm^2 polystyrene sheet were cut with a pair of scissors into 9 or 18 equal pieces, immersed into 50 g oil or emulsion and incubated at 40 °C. At several time intervals samples were analyzed for their amount of migrated styrene. Sample codes are given in table 1.

Table 1: Codes for samples used in this study

sample	code
PS 175/1 dm^2	LE
PS 175/2 dm^2	LD
PS 261/1 dm^2	HE
PS 261/2 dm^2	HD

RESULTS AND DISCUSSION

PS 175 and PS 261 contain 403 ± 13 ppm (n=3) and 339 ± 3 ppm (n=3) residual styrene monomer, respectively. The polystyrene sheets extruded at the lowest temperature (PS 175) have the highest content of styrene monomer. At a higher temperature extrusion seems to promote the loss of styrene. In figure 1, comparison of LE versus LD and HE versus HD shows that a doubling of the surface of the polymer added results in twice the amount of styrene migrated. Comparison of LE versus HE and LD versus HD shows a higher level of styrene migrated from the polymer extruded at a lower temperature.

The ratio for the residual monomer contents of the sheets (PS 175 / PS 261) is 1.2. The same ratio is calculated for styrene migrated into oil and W/O-emulsion (1.2), while the O/W-emulsion has a slightly higher ratio (1.4). The importance of the residual styrene monomer level in the polymer is evident: the lower the styrene monomer content in the polymer, the lower the amount of styrene found in the simulants. Figure 1 demonstrates that the highest level of migration was found in corn oil, followed by the

W/O-emulsion and the O/W-emulsion. So, the matrix of the simulants influences the amount of migrated styrene.

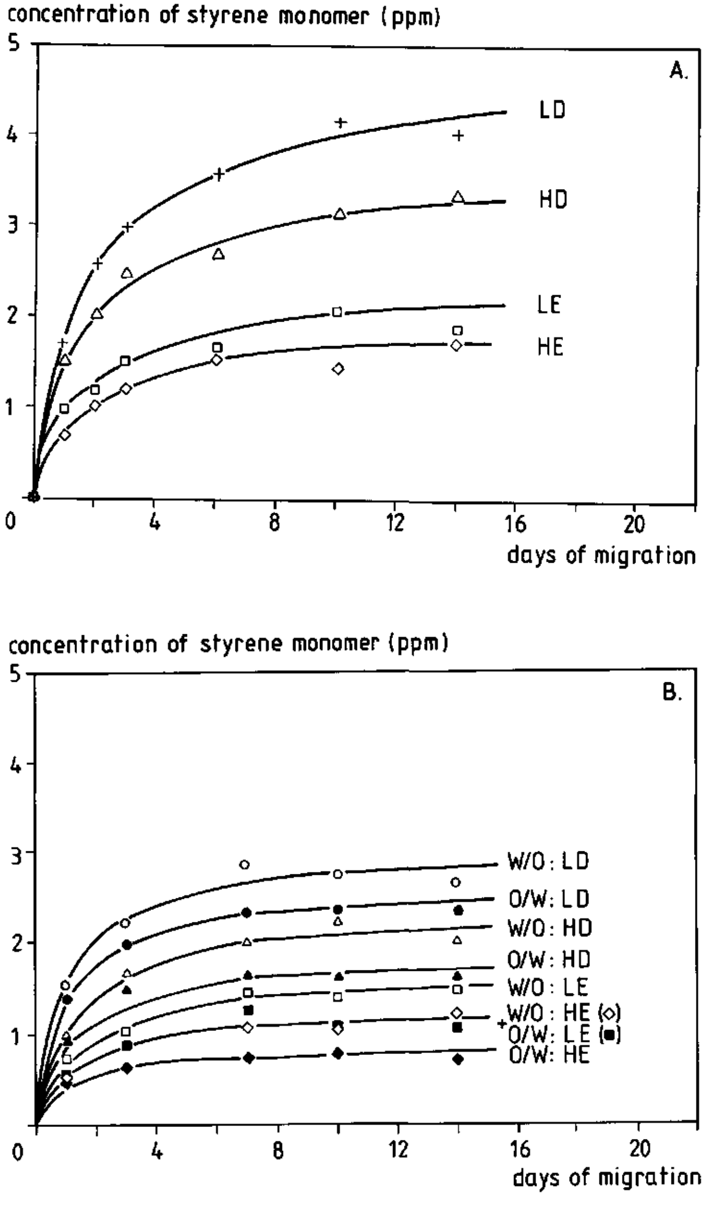

Figure 1: Migration of styrene monomer into corn oil (A) and W/O- and O/W-emulsion containing 30% fat (B)

Table 2: Proportion (%) of residual styrene in the polymer, which has migrated into the simulants after 14 days at 40 °C

simulant	LE	LD	HE	HD	mean
corn oil	2.8	2.8	2.9	2.9	2.9
W/O-emulsion	1.9	1.8	1.9	1.9	1.9
O/W-emulsion	1.4	1.6	1.3	1.4	1.4

Table 2 shows that the proportion of residual styrene in the polymer, which has migrated into the food simulants, is low. The proportion of migrated styrene is similar for each simulant in spite of differences in actual amounts of residual styrene in the polymers. These findings confirm the proportionality of the amount of styrene migrated with the content of residual monomer in the polymer.

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Chapter 3. Effect of sampling method on the level of styrene monomer migrated from polystyrene packaging material*.

ABSTRACT

Different types of polystyrene packaging material were tested on styrene monomer migration in corn oil with three sampling methods: immersion sampling, vapour phase sampling and utilisation of sampling cells. For high impact grade polystyrene immersion sampling resulted in the highest level of migrated styrene. Vapour phase sampling was of considerable interest, because migration was only slightly lower than with immersion sampling. Sampling in cells gave the lowest levels of styrene monomer in oil. However, when crystal clear polystyrene was tested, not much difference was observed for the three sampling methods mentioned.

* Linssen, J.P.H., Reitsma, J.C.E. and Roozen, J.P., Packaging Technology and Science, 4, 171 - 175 (1991).
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INTRODUCTION

Polystyrene is widely used as packaging material for food. Examples are foamed trays for meat or crystal clear trays for candy and cookies. Polystyrene contains detectable amounts of residual styrene monomer, which can be a potential source of off-flavour in food products.

Several methods have been developed for testing the amount of styrene monomer migration. Usually migration studies are carried out using food simulating agents like distilled water, vegetable oils or HB 307[1,2], because it is impractical to use real food products in migration tests[3]. In migration experiments contact of polymer can be established by cutting polymeric material into pieces, immerse them in a food simulating agent and incubate the sample at a given temperature, usually 40 °C[4,5]. Cutting of styrene polymer can disturb its physical structure, which results in an overestimation of migration in food simulants. In test materials of high impact grade polystyrene Figge[6] observed that cut or punched film-like test specimens exhibited much higher additive transfer rates than injection moulded cups under identical test conditions.

The United States Food and Drug Administration in cooperation with Arthur D. Little Inc. developed standard tests with sampling cells for carrying out migration experiments in liquid and solid foods[1,7,8,9,10]. The sampling cell for liquids is a glass vial in which circular test specimens are tacked on a stainless steel wire and immersed in a food simulating liquid or liquid food. Area contact between liquid and polymer can be varied by the number of polymeric disks used. The sampling cell for solids is a specially for this aim constructed apparatus in which a 5 mm thick test plaque of solid matter is brought in contact with a fixed area of 20 cm^2 polymer. Migrant transfer through the vapour phase might also influence the level of migration.

Giacin[11] describes migration from a package as a two steps process: (a) diffusion of the migrant through the polymer bulk phase to the polymer surface and (b) subsequent dissolution or evaporation of the migrant present at the surface. The actual contact between solids and plastic packaging material can range from a few "macro" contacts (e.g. chocolate flakes) to many "mini" contacts (e.g. flour). In both cases, however, it is suggested that transfer at the interface involves a vaporisation step from the plastic package followed by absorption in the solid food[12].

In the present study migration of styrene monomer from different polystyrene test specimens are compared by carrying out different sampling methods: 1) polystyrene pieces immersed in vegetable oil, 2) pieces in its vapour phase and 3) pieces mounted in special constructed sampling cells.

MATERIALS AND METHODS

Materials

General purpose polystyrene (GPPS: type "Styron* 637") and high impact polystyrene (HIPS: type "Styron* 472") were extruded to sheets of 1 mm thickness at approximately 220 °C by Dow Benelux NV, Terneuzen, The Netherlands. Also sheets of a 1:1 mixture of GPPS and HIPS were prepared in the same way.
Corn oil (Mazola) was bought in a local store at Wageningen.

Sample preparation

Both types of high impact grade polystyrene were cut into the pieces necessary for sampling. Crystal polystyrene (GPPS) was scratched with a sharp object and subsequently broken over the scratch.

Styrene analysis

Residual styrene monomer in the polymer was determined by dissolving the polymer in dichloromethane and subsequently

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precipitating with iso-octane. The clear upperlayer was analyzed with a gaschromatograph (Carlo Erba, model 4200) equipped with a flame ionisation detector. The analyses were carried out on a 15 m x 0.53 mm (i.d.) wide bore column (DB 225, J & W Scientific). The detection and injection temperature were 300 °C and 250 °C, respectively. The following temperature program was used: an initial hold for 2 min at 40 °C and then 5 °C/min to 100 °C and a final temperature hold for 2 min[13].

At certain time intervals styrene was determined in corn oil samples by azeotropic distillation with methanol followed by extraction with pentane. The pentane extract was analyzed with a gaschromatograph (Carlo Erba, model 4160), equipped with a flame ionisation detector and a cold on-column injector. The analyses were carried out on a 30 m x 0.32 mm (i.d.) fused silica capillary column (DB 1701, J & W Scientific). The detection temperature was 280 °C. The following temperature program was used: an initial hold of 4 min at 40 °C and then 5 °C/min to 90 °C, followed by 15 °C/min to 190 °C and a final temperature hold for 1 min. A calibration curve was prepared by adding different amounts of styrene to the oil[14].

Sampling methods

For immersion sampling 1 dm^2 polystyrene sheet was cut into 9 equal pieces (12 cut edges), immersed in 50 g corn oil under all-sided contact in a tightly closed jar and incubated at 40 °C.

Vapour phase sampling was carried out by cutting 1 dm^2 polystyrene sheet into 5 equal pieces (12 cut edges). A small hole was drilled at the top of each piece, through which the strips were tacked on to a thread fastened on a wire, which was clenched in an excavated erlenmeyer stop. An erlenmeyer was filled with 50 g corn oil, tightly stoppered with the excavated stop including the pieces of polystyrene sheet and incubated at 40 °C without contact between oil and polymer. In addition this procedure was carried out with polystyrene (HIPS:GPPS 1:1) strips which were left one week in open air at 40 °C before starting the migration experiment.

Cells for sampling were constructed of stainless steel of 5.4 mm thickness in analogy of Figge[15]. Square frames of 100 x 100 mm inner size and 110 x 110 mm outer size were sandwiched by stainless steel plates. Before assembling the cells the edges of the frame were taped with teflon to overcome leakages. 2 sheets of polystyrene were tightened between plate and frame in such way that a different side of each sheet faced the space for containing the corn oil (2 x 1 dm^2 polystyrene in contact with oil). Cells were filled with 50 g corn oil, tightly closed and incubated at 40 °C.

RESULTS AND DISCUSSION

In the polymer sheets used, residual styrene monomer levels were 408 ± 13 ppm (n=3) for GPPS, 325 ± 10 ppm (n=3) for HIPS:GPPS 1:1 and 340 ± 3 ppm (n=3) for HIPS.

Figure 1 shows migration curves for GPPS, HIPS:GPPS 1:1 and HIPS specimens using the three sampling methods described before. Comparison of these sampling methods shows that immersion sampling results in the highest level of migrated residual styrene. This is very clearly shown for pure HIPS and the HIPS:GPPS 1:1 specimens. Vapour phase sampling of the latter two specimens shows a somewhat lower level of migrated styrene than immersion sampling, in which the pieces of polystyrene were in all-sided direct contact with the oil. This falling-off is probably caused by losses of styrene during transfer from polymer into vapour, maybe into open air. Utilisation of sampling cells yields much less migration of residual styrene from the polymer into the oil, except for the GPPS specimen. In case of GPPS the levels of styrene found with the three sampling methods are close to each other.

The differences between GPPS and the other two kinds of specimens are probably caused by the presence of rubber particles in polystyrene of high impact grade. Figure 2 shows a photograph of the cut or broken surface of high impact grade and crystal clear polystyrene, respectively.

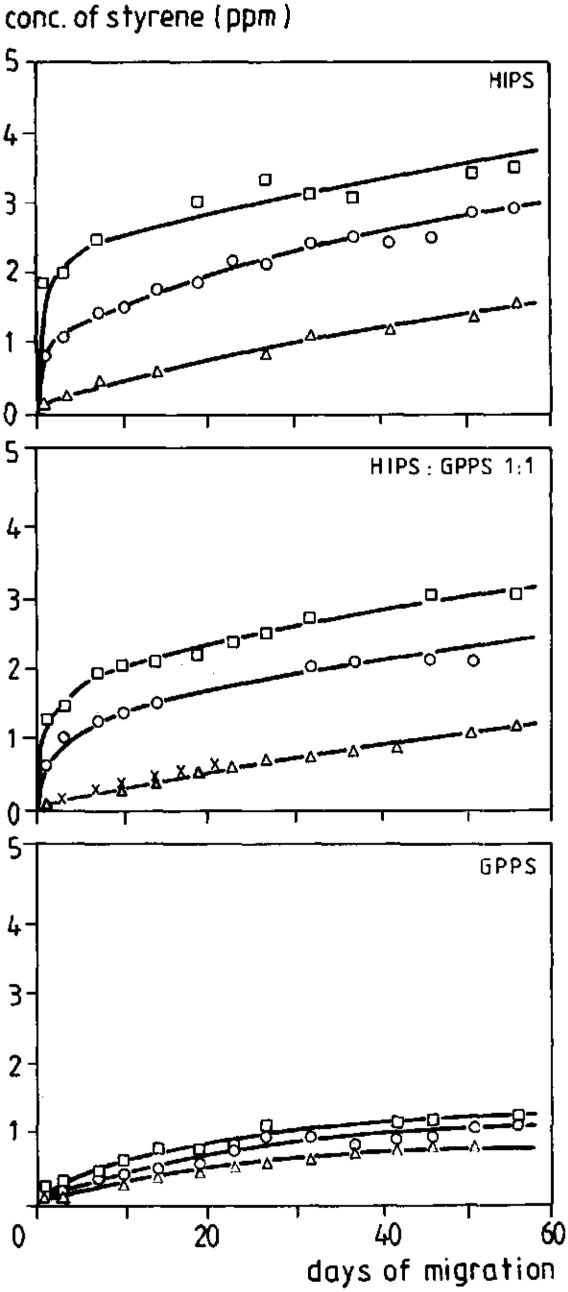

Figure 1: Migration curves of different types of polystyrene obtained by using (Δ) sampling cells; (O) vapour phase sampling; (□) immersion sampling; (x) vapour phase sampling (after leaving the test specimen in open air at 40 °C for one week)

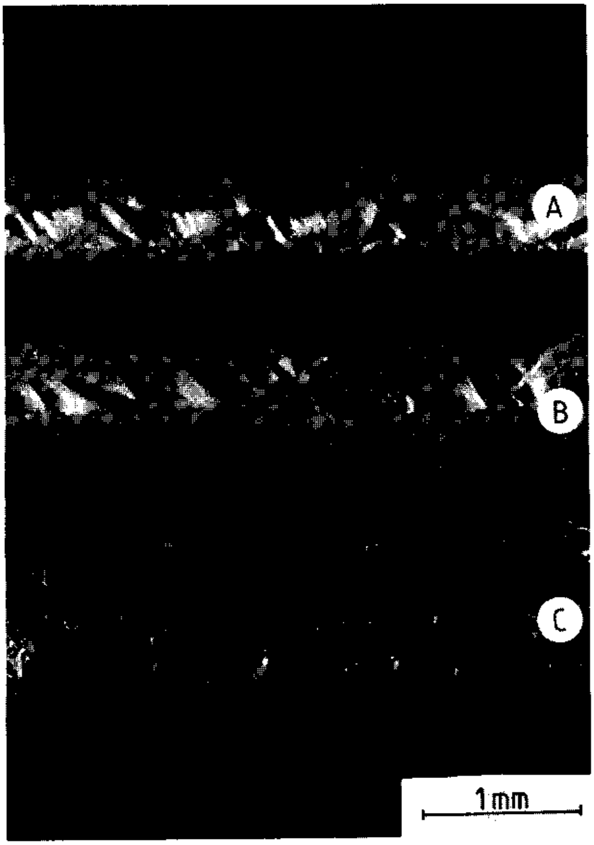

Figure 2: Photograph of the edges of the different types of polystyrene

A: cut HIPS; B: cut HIPS : GPPS; C: broken GPPS

The cut edges of the high impact grade polystyrene types show damages of the surface. In analogy of the model of Klahn et al.[16] cutting of test specimens damages rubber particles at the surface of the polymer. Residual monomer present in the damaged rubber phase might be able to dissolve or evaporate more easily and so migrate faster into the oil. This could be the explanation for the high initial migration rate in both immersion and vapour phase sampling. The low levels of styrene obtained from the experiments using sampling cells can also be explained by this model: no cut-edges are present in direct contact with oil, and thus leakage of styrene from damaged rubber particles is out of question. The existence of leakage is evident from the additional experiment with HIPS:GPPS 1:1 (figure 1), in which the test specimens were left for one week in open air at 40 °C before starting the migration experiment. In that case migration values are about the same as the ones obtained by using sampling cells. Undoubtedly this result can be explained by the loss of styrene from the damaged rubber particles during the aeration period.

These findings are of practical interest to the food and packaging industry. Impairment of rubber particles will promote styrene transfer and so migration will be increased. Recommended sampling procedures, in which test specimens with cut-edges are kept in all-sided contact with test media are not appropriate for testing specimens of polystyrene of high impact grade. These procedures will inevitably overestimate migration values concerning commercial usage of HIPS containing packaging materials. Therefore it is important to keep cut-edges of polystyrene test specimens of high impact grade test specimens out of the test medium during sampling.

Also vapour phase migration is important in practical situations, e.g. chocolate flakes[17]. Usually packaging trays for these products are made by thermoforming and cutting in between. The risk of taste deterioration of the packed product is difficult to evaluate with recommended sampling methods because of aging of the cut-edges of the trays. One of the best solutions would be to sample products in HIPS containing packaging materials directly from the production line and conduct the test with the packed product under given time and temperature conditions (Risch, 1988). The limiting factor, however, is then the enormous amount of time involved.

In conclusion: Immersion sampling methods overestimate migration from HIPS containing packaging materials. Exclusion of cut-edges by using sampling cells seems to give more reliable results for evaluation of the levels of migrated substances. Vapour phase migration should be a part of the evaluation of packaging materials.

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Chapter 4. Polystyrene sheet composition and temperature as parameters for migration of styrene monomer into corn oil [*].

ABSTRACT

Different types of polystyrene used in packaging were tested for styrene monomer migration into corn oil. Several blends of general purpose polystyrene with different amounts of high-impact polystyrene demonstrated a linear increase of migration of styrene with increasing amount of high-impact polystyrene in the polymer. Faster migration was found for higher exposure temperatures. Migration depended linearly on the content of residual styrene monomer in the polymer.

[*] Linssen, J.P.H., Reitsma, J.C.E. and Roozen, J.P., to be submitted for publication.

INTRODUCTION

Polystyrene (PS) is frequently used for packaging of foods. Examples for general purpose polystyrene (GPPS) are foamed trays for meat and clear trays for salads and vegetables. Examples for high impact polystyrene (HIPS), which consists of a PS matrix with a dispersed rubber phase, are packages for margarine and dairy products, like yoghurts. Migration from packaging materials is influenced by a number of variables[1]:

- the physical and physico-chemical properties of the polymer (e.g. density, crystallinity, branching, composition, surface roughness).
- the manufacturing process of the packaging material (extrusion, injection-moulding, blowing, deep-drawing).
- the physical and physico-chemical properties of the mobile component (migrant) of the packaging material (e.g. molecular weight, polarity, solubility).
- the composition of the packaged product (e.g. content of fat or water).

A model to predict the migration of components into oil at constant temperatures has been proposed by Reid[2]:

$$M_t = 2C_0\sqrt{\frac{Dt}{\pi}} \qquad (1)$$

in which,

M_t = mass of migrant migrated from polymer in time t
C_0 = original concentration of the migrant in the polymer
t = time
D = diffusion coefficient of the migrant in the polymer

The model was applied to the migration of dioctyladipate from polyvinylchloride[3] and to migration of styrene monomer from PS[4]. Also Figge and coworkers[7-9] proposed a model at constant temperatures. The temperature dependence of diffusion is generally described by an Arrhenius type of correlation[3,5,6]:

$$D = A.e^{-E/RT} \qquad (2)$$

in which,

D = diffusion coefficient of the migrant in the polymer
T = absolute temperature
R = general gas constant
E = activation energy
A = constant

From equation (1) and (2) a more general model for prediction of migration can be derived:

$$M_t = 2C_0\sqrt{\frac{t}{\pi}.Ae^{-E/RT}} \qquad (3)$$

or

$$M_t = KC_0\sqrt{te^{-E/RT}} \qquad (4)$$

in which K is a complex constant.

The present study describes the migration of residual styrene monomer from different types of PS into corn oil. The influence of the amount of HIPS in several blends with GPPS and the effect of reduced contents of monomer in the polymer on migration of styrene was investigated using the immersion as well as the cell sampling method[10]. The influence of temperature on migration of styrene monomer from a 1:1 blend of HIPS and GPPS was evaluated with the cell sampling method only.

MATERIALS AND METHODS

Materials

General purpose polystyrene (GPPS: type "Styron[*] 637"), high impact polystyrene (HIPS: type "Styron[*] 472") and blends of them, containing 3, 5, 10, 25, 50 and 75% HIPS were extruded to sheets of 1 mm thickness at approximately 220 °C by Dow Benelux NV, Terneuzen, The Netherlands. The batch included also a range 1 mm thick sheets of an 1:1 blend of GPPS and HIPS with reduced styrene monomer contents (Table 2). Corn oil (Mazola) was bought in a local store at Wageningen (The Netherlands).

Sample preparation

The high impact grade polystyrene sheets were cut into the pieces necessary for sampling with a pair of scissors. For sampling in GPPS and the blends of HIPS with GPPS containing 3 and 5% HIPS were scratched with a sharp object and subsequently broken over the scratch.

Sampling methods

The influence of both the amount of HIPS in PS and the content of residual monomer in the polymer was evaluated by using the immersion- and cell sampling methods[10]. For immersion sampling 1 dm^2 polystyrene sheet was cut into nine equal pieces, immersed in 50 g corn oil in a tightly closed jar (all-sided contact) and incubated at 40 °C.

Cells for sampling were made of a 10,8 mm thick Teflon ring and an inner diameter of 80,0 mm. The Teflon ring was sandwiched between two stainless steel plates in analogy of Figge[13]. Two sheets of polystyrene were secured between ring and plates in such a way that different sides of each sheet were available for contacting the corn oil. Cells were filled with 50 g corn oil,

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tightly closed and incubated at 40 °C.

Using the cell sampling method sheets of a 1:1 blend of GPPS and HIPS of 1 mm thickness were incubated at 10 °C, 20 °C, 30 °C, 40 °C and 50 °C for evaluation of the effect of temperature on styrene migration.

Styrene analysis

Residual styrene monomer was determined in PS by dissolving the polymer in dichloromethane and subsequently precipitating with iso-octane. The clear upperlayer was analyzed with a gaschromatograph (Carlo Erba, model 4200) equipped with a flame ionisation detector. The analyses were carried out on a 15 m x 0.53 mm (i.d.) wide bore column (DB 225, J & W Scientific). The detection and injection temperature were 300 °C and 250 °C, respectively. The following temperature program was used: an initial hold for 2 min at 40 °C and then 5 °C/min to 100 °C and a final temperature hold for 2 min[11].

In corn oil styrene was determined by azeotropic distillation with methanol followed by extraction with pentane. The pentane extract was analyzed with a gaschromatograph (Carlo Erba, model 4160), equipped with a flame ionisation detector and a cold on-column injector. The analyses were carried out on a 30 m x 0.32 mm (i.d.) fused silica capillary column (DB 1701, J & W Scientific). The detection temperature was 280 °C. The following temperature program was used: an initial hold of 4 min at 40 °C and then 5 °C/min to 90 °C, followed by 15 °C/min to 190 °C and a final temperature hold for 1 min. A calibration curve was prepared by adding different amounts of styrene to the oil[12].

RESULTS AND DISCUSSION

The contents of residual styrene monomer for the different PS samples are 285 ± 6 ppm (n=8), except for those with a reduced monomer content (Table 2).

Influence of different amounts of HIPS

Figure 1 shows the content of migrated styrene in corn oil versus the amount of HIPS in several blends with GPPS.

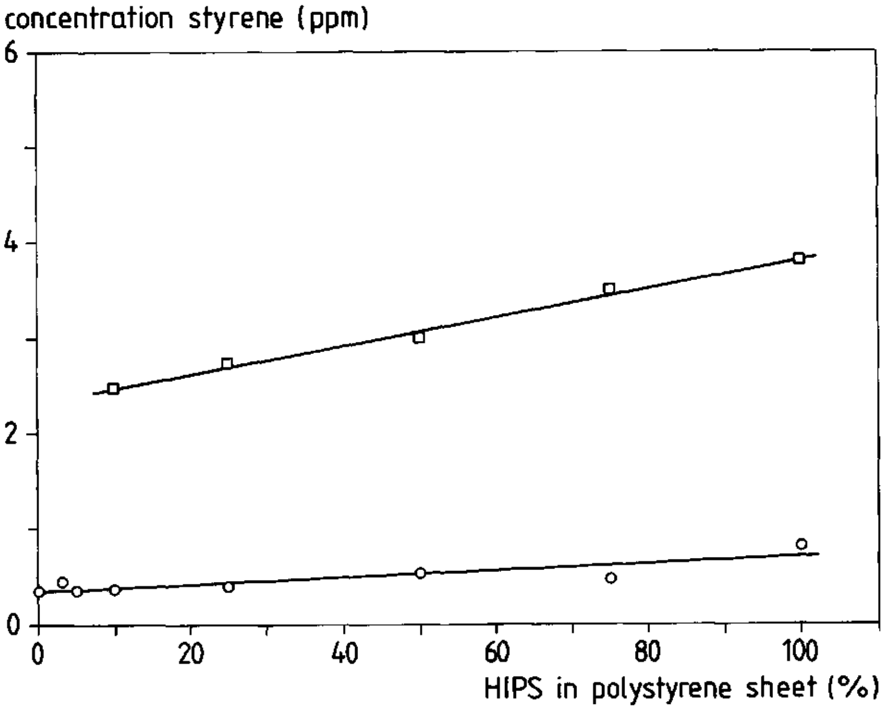

Figure 1: Effect of % HIPS in PS on the level of styrene migrated into corn oil after 21 days at 40 °C using the immersion (□) and the cell (○) sampling method.

Migration increases linearly with increasing amount of HIPS present in the polymer sample in both the immersion sampling method and cell sampling method. Obviously diffusion of styrene monomer in the polymer increases with increasing amounts of rubber particles in the polymer blends of GPPS and HIPS. Immersion sampling results in higher amounts of migrated styrene (level and slope), possibly due to damages of the rubber particles in the cut edges at the surface of the polymer promoting styrene transfer. Therefore sampling cells give a more accurate representation of the migration behaviour in actual packaging applications. These findings confirm previous work[10,14].

Temperature dependence

Table 1 gives the amounts of styrene migrated from 1 mm sheets of an 1:1 blends of GPPS and HIPS into corn oil after 14 days of incubation at different temperatures. The diffusion coefficient D was calculated for each temperature using equation (1).

Table 1: Migrated amounts of styrene monomer and diffusion coefficients (D) for styrene in polystyrene (C_0 = 279 ppm) in contact with corn oil in a cell at different temperatures (T) after 14 days.

T (°C)	migrated amount of styrene ($\mu g/cm^2$)	D (cm^2/s)
10	0.0075	$4.7x10^{-16}$
20	0.0188	$2.8x10^{-15}$
30	0.0333	$0.9x10^{-14}$
40	0.0773	$5.1x10^{-14}$
50	0.1388	$1.5x10^{-13}$

Table 1 demonstrates that the diffusion coefficient increases with increasing temperature from $4.7x10^{-16}$ cm^2/s at 10 °C to $1.5x10^{-13}$ cm^2/s at 50 °C. By comparison, Till et al[4] reported D values of $2\text{-}5x10^{-13}$ cm^2/s for GPPS with a residual styrene monomer content of 800 ppm at 40 °C. Snyder and Breder[15] found D values of $2\text{-}3x10^{-13}$ cm^2/s for GPPS with a monomer content of 4260 ppm at 40 °C. Miltz and Rosen-Doody[16] calculated a D of $5x10^{-10}$ cm^2/s for PS containing 1000 ppm residual monomer at 35 °C. However, the latter value is too high, because their method assumed already an equilibrium of styrene between polymer and contacting phase in an early stage. Using equation (2) ln D versus 1/T can be plotted in which E/R is the slope of the line. Figure 2 shows this relationship obtained from migration of styrene into corn oil. Linear regression results in: $\ln D = 15.61 - 14{,}500\ (1/T)$ ($r = 0.99$). So, E/R = 14,500 and the activation energy calculated is $12.0x10^4$ J/Mol. This is near the activation energy of

7.8×10^4 J/Mol found for styrene migration in cut test coupons made of pressed GPPS[4]. The complex constant K from equation (4) can be calculated from the activation energy found and the results of table 1. A value of $K = 2620 \pm 323$ $cms^{-1/2}$ (n=5) was obtained. Equation (4) represents now a general formula for predicting migration of styrene monomer from polystyrene (GPPS : HIPS = 1:1) into corn oil.

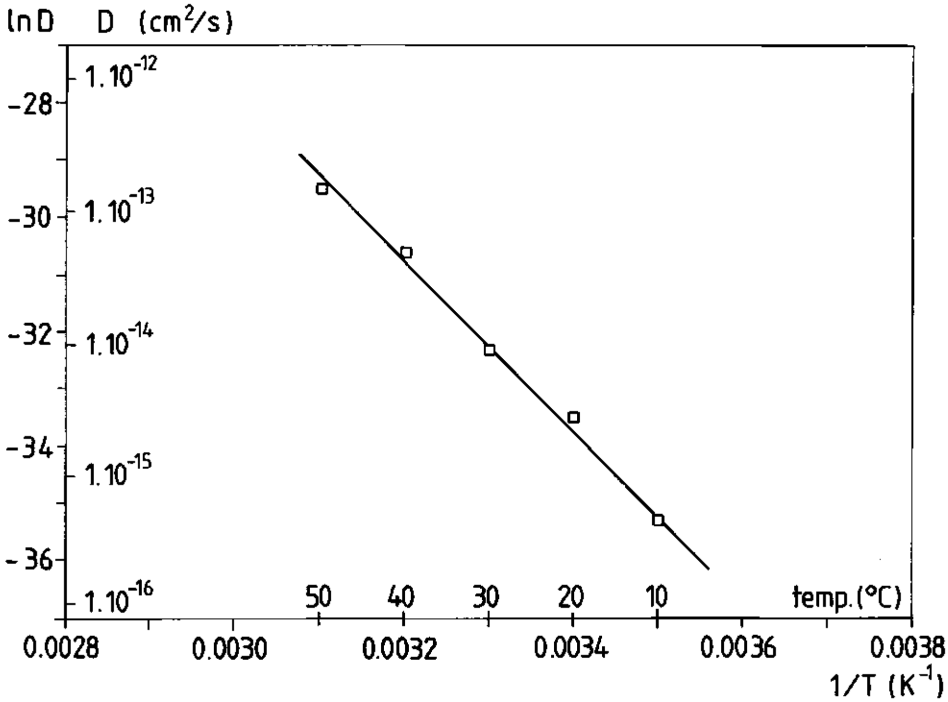

Figure 2: Diffusion coefficient (D) of styrene in PS (HIPS : GPPS 1:1) as a function of temperature as obtained from migration into corn oil.

Effect of content of residual styrene monomer

Table 2 presents the effect of different contents of residual monomer on migration of styrene into corn oil from a sheet of an 1:1 blend of GPPS and HIPS incubated at 40 °C for 21 days. It is demonstrated once more that sampling in migration cells results in much lower levels of migrated styrene than immersion sampling. The cell sampling method shows about the same ratio for all the PS samples, which indicates a linear dependency between the contents of styrene in the polymer and the level of styrene migrated into corn oil. However, in case of immersion sampling this ratio is only similar for the PS samples with the three highest contents of styrene.

Table 2: Contents of styrene in polystyrene samples (GPPS : HIPS 1:1) and contents of styrene in corn oil after 21 days of migration at 40 °C using different sampling methods and the ratio between these contents.

styrene content in polystyrene[1] (ppm)	immersion sampling styrene content in oil (ppb)	ratio	cell sampling styrene content in oil (ppb)	ratio
279 ± 4	2790	100	354	788
191 ± 5	2010	95	246	776
164 ± 4	1590	103	210	781
93 ± 2	660	141	120	775
42 ± 2	120	350	54	778

[1] values are means of triplicates ± SD

The PS samples with the two lowest amounts of styrene in the polymer show increasing ratio's between the contents of styrene in the polymer and the levels of styrene migrated into corn oil. Less styrene seems to be available for migration, especially from the cut edges. At a certain concentration of monomer much less styrene is available for initial leakage from the rubber particles after cutting of the polymer[10].

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PART II. PRODUCT QUALITIES OF FOOD IN CONTACT WITH POLYSTYRENE (MIGRATION)

Polystyrene packaging material contains residual styrene monomer in detectable amounts. Styrene is able to migrate into food products within the reach of the packaging material and may give a taint to the packed product, due to its unpleasant odour and/or taste.

Chapter 5 deals with sensory evaluation of a styrene taint in cocoa powder for drinks, and milk and plain chocolate flakes after exposure to pieces of polystyrene packaging material. A chocolate product was chosen because of the practical use of polystyrene for packing chocolate products like cookies covered with chocolate. Short-cut signal detection measures on differences between control and test samples and on recognition of styrene were carried out in this part of the study.

Chapter 6 treats the question of taste recognition threshold concentrations (TRTC) of styrene in model systems of oil in water emulsions. They were made different in fat content to reflect the range found in foodstuffs. Partition coefficients between vapour and liquid phases were determined and the concentrations of styrene in the continuous phase of the emulsions were calculated at their threshold values. Subsequently, the model was validated by spiking of commercial samples of yoghurts with styrene. A limited survey of the contents of styrene in commercial yoghurts packed in polystyrene beakers was carried out at their expiring date for selling.

Chapter 5. Sensory analysis of polystyrene packaging material taint in cocoa powder for drinks and chocolate flakes[*]

ABSTRACT

Polystyrene packaging material taint was sensorily evaluated in cocoa powder for drinks and chocolate flakes using short-cut signal detection measures on differences between control and test samples and on recognition of styrene. No differences were observed in cocoa powder for drinks and plain chocolate flakes treated with 0.5 dm^2 polystyrene of 1 mm thickness. However, differences were detected in milk chocolate flakes and plain chocolate flakes, which were in contact with a larger area or thicker polystyrene packaging material. The latter results were confirmed by the styrene recognition test, so polystyrene is a potential source of off-flavour for chocolate products. The amount of residual styrene in the polystyrene used was about 320 ppm, while the amounts of styrene ranged 7-132 ppb in cocoa drinks and 414-1447 ppb in chocolate flakes.

[*] Linssen, J.P.H., Janssens, J.L.G.M., Reitsma, J.C.E. and Roozen, J.P., Food Additives and Contaminants, 8, 1-7, (1991) (Reproduced with permission from the publisher)

INTRODUCTION

Packaging materials are potential sources of off-flavour in food products. Polystyrene is frequently used as a packaging material. Probably the use of Polystyrene will be increased because of growing concern having polyvinylchloride in waste disposal. Polystyrene contains residual monomer in detectable amounts. Styrene monomer can only partly be removed from the plastic by extrusion of the packaging material and so it is able to migrate into food products within reach of the packaging material. Styrene may affect product quality due to a characteristic unpleasant plastic-like chemical odour or taste. The intensity of the off-flavour developed depends on the concentration of migrant in the packaging polymer, thickness and type of polymer, type of foodstuff, storage temperature and time of contact. Several authors have reported the presence of styrene in food products, caused by migration of residual styrene from the polymer. Gilbert and Startin (1983) found different levels of styrene in food products, e.g., 180 ppb in chopped peel. Withey and Collins (1978) reported styrene in dairy products at levels up to 245 ppb in sour cream. In hot chocolate and chocolate spread they found 13 ppb and 2 ppb, respectively. Santa Maria et al (1986) reported residual styrene monomer levels in different food products and found levels up to 3590 ppb in mousse. A taste panel (Passy 1984) detected an off-flavour in chocolate and lemon cream cookies packed in polystyrene trays and overwrapped with Cellophane. Analysis of the polystyrene trays showed rather high residual monomer levels of about 0.20%. The amount of styrene in the cookies was not determined.

This study deals with sensory analysis of polystyrene packaging material taint in chocolate flakes and in cocoa powder for drinks.

MATERIALS AND METHODS

Sample preparation

General Purpose PolyStyrene (type "styron* 637") and High Impact PolyStyrene (type "styron* 472) were extruded in a 1:1 ratio to sheets of 1 mm and 2 mm thickness at 223 °C and 210 °C, respectively (Dow Benelux NV, Terneuzen, The Netherlands). 20% fat cocoa powder was provided by Droste BV (Haarlem, The Netherlands) and 10% fat cocoa powder by Gerkens Cacao BV (Zaandam, The Netherlands). Plain and milk chocolate flakes (De Ruyter BV, Baarn, The Netherlands), containing about 15% fat, were bought at a local store in Wageningen, The Netherlands.

50 g of cocoa powder or chocolate flakes were mixed with 1 mm thick polystyrene sheet (0.5 dm^2 or 2 dm^2 cut into 6 or 18 equal pieces) or without polystyrene (standard) in glass jars and incubated for 7 days at 30 °C. For two additional tests with plain chocolate flakes samples, mixed with 2 mm thick polystyrene sheet (0.5 dm^2), as well as control samples were stored in the same way. The cocoa powders and sugar were suspended in water at a 1:1 ratio in order to prepare the cocoa drinks. (Table 1). Earlier investigations (De Graaf et al 1990) showed that sugar had to be added to make an acceptable test medium for tasting cocoa powders.

Table 1: Composition (% w/v) of cocoa drinks for tasting

	cocoa powder		sugar
sample (code)	10% fat	20% fat	
1.5% cocoa 10 drink	1.5	---	1.5
1.5% cocoa 20 drink	---	1.5	1.5
6% cocoa 10 drink	6	---	6
6% cocoa 20 drink	---	6	6

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* trademark of the Dow Chemical Company

Styrene analysis

Residual styrene monomer in the polymer was determined by dissolving the polymer in dichloromethane and subsequently precipitation with iso-octane. 1 µl of the clear upper layer was injected into a gas chromatograph (Carlo Erba, Model 4200), equipped with a flame ionisation detector. The analyses were carried out on a 15 m x 0.53 mm (i.d.) wide bore column (DB 225, J & W Scientific). The detector and injector temperatures were 250 °C. The following temperature programme was used: an initial hold for 2 min at 40 °C, then 5 °C /min to 100 °C and a final hold for 2 min (ISO, 1974).

Styrene in cocoa powders (duplicate) and chocolate flakes (triplicate) was determined by azeotropic distillation with methanol, followed by extraction with pentane. The pentane extract was analyzed with a gas chromatograph (Carlo Erba, Model 4160), equipped with a flame ionisation detector and a cold on-column injector. The analyses were carried out on a 30 m x 0.32 mm (i.d.) fused silica capillary column (DB 1701, J & W Scientific). The detector temperature was 280 °C. The following temperature programme was used: an initial hold of 4 min at 40 °C and then 5 °C/min to 90 °C, followed by 15 °C/min to 190 °C and a final hold for 1 min. Calibration curves were prepared by adding different amounts of styrene to the cocoa products (Varner et al 1983).

Sensory analysis

Untrained panels of 48 - 50 students of the Wageningen Agricultural University, aged 20 -25 years, were used in this experimental part of the study. Flavour difference and styrene recognition tests were carried out in their standard form according to O'Mahony's (1979, 1986) "Short-cut signal detection measures". These methods are chosen because of the one sample presentation. The stickiness and taste lingering of chocolate products makes more than one sample presentation less suitable. The assessors were asked to compare the taste of the samples with the taste of a previously presented standard and then to express their findings in one of the four categories: standard, perhaps standard, perhaps not standard and not standard for the difference test, and styrene recognised, perhaps styrene recognised, perhaps styrene not recognised and styrene not recognised for the recognition test. The results of these tests are expressed as so-called R-indices, which represent the probability values of correctly distinguishing between items or correctly recognizing styrene by the assessors. The chance level for the R-index is 50%. An R-index of 100% indicates perfect distinguishing or recognizing ability. Untreated samples of cocoa powder for drinks and chocolate flakes were used as standards in the flavour difference test, and a standard solution of 200 ppb styrene (BDH Ltd. Poole U.K.) in water was used in the styrene recognition test. Sensory evaluation was carried out in eleven series, divided over five sessions, as shown in table 2.

In any session the standard was presented first to the assessors and after tasting each three samples in order to confirm the standard taste quality. All samples in each series were offered in triplicate and in random order as 15 ml cocoa drinks or as 7 g chocolate flakes in small glass bottles covered with aluminium foil and closed with screw-caps. An unlimited amount of time was allowed for tasting each sample. Seven-up, rinsing water and crackers were freely available for the assessors to recover their taste abilities.

A computer interactive interviewing system (Ci2, Sawtooth Software Inc) was used for composing questionnaires to gather survey information by computer. Portable computers (Toshiba Computer T1000) were placed in sensory evaluation booths. Questions about judging the samples were answered by pushing 1, 2, 3 or 4 on the keyboard for the four categories mentioned before. The SPSS/PC program was used for elaborating the results.

Table 2: Number of samples presented in 11 series for sensory analysis by short-cut signal detection measures.

session	series	samples[1]	(0)	(0.5)	(2)[2]
difference tests					
1	1	1.5% cocoa 10 drink	3	3	3
	2	1.5% cocoa 20 drink	3	3	3
	3	6% cocoa 10 drink	3	3	3
	4	6% cocoa 20 drink	3	3	3
2	1	milk chocolate flakes	3	3	3
3	1	plain chocolate flakes	3	3	3
recognition tests					
4	1	milk chocolate flakes	3	0	3
	2	plain chocolate flakes	3	0	3
5	1	milk chocolate flakes	3	3	3
	2	plain chocolate flakes	3	6[3]	0
	3	plain chocolate flakes	6	0	0

[1] codes of cocoa drinks are explained in Table 1

[2] in parenthesis: area (dm^2) of polystyrene sheet used per 50 g cocoa powder or flakes

[3] 3 samples of 1 mm thickness (0.5) and 3 samples of 2 mm thickness (0.5*) polystyrene sheet are used

RESULTS AND DISCUSSION

Residual styrene monomer levels in the polystyrene sheets used were 320 ppm ± 12 ppm (n=5). After exposure to 2 dm^2 polystyrene the amount of styrene in the cocoa powder (10% fat) and the cocoa powder (20% fat) were 1.8 ppm and 2.2 ppm, respectively.

Most of the amounts of styrene in the cocoa drinks (Table 3) are in between the taste recognition threshold concentrations of styrene in water (22 ppb) and emulsions with 30% fat (2.3 ppm) (Linssen et al. 1990). Ramshaw (1984) stated that the amount of migrated styrene is higher in products with a higher fat content.

Table 3: Amounts of styrene in stimuli for sensory analysis, which were calculated for the drinks from their contents in cocoa powders exposed to 2 dm^2 polystyrene.

samples[1]	styrene (ppb)
drinks	
1.5% cocoa 10 drink (0.5)	7[2]
1.5% cocoa 10 drink (2)	27
1.5% cocoa 20 drink (0.5)	8[2]
1.5% cocoa 20 drink (2)	33
6% cocoa 10 drink (0.5)	27[2]
6% cocoa 10 drink (2)	108
6% cocoa 20 drink (0.5)	33[2]
6% cocoa 20 drink (2)	132
flakes	
milk chocolate flakes (0.5	414±17[3]
milk chocolate flakes (2)	1245±10[3]
plain chocolate flakes (0.5)	407±20[3]
plain chocolate flakes (2)	1254±31[3]
plain chocolate flakes (0.5*)	1447±50[3]

[1] sample codes as explained in Table 2

[2] values are calculated on the assumption of proportional migration

[3] values are means of triplicates ± SD

The amounts of styrene found in the cocoa powders and calculated for the cocoa drinks confirm this statement. Styrene migrates from 0.5 dm^2 polystyrene sheet of 1 mm thickness into chocolate flakes to give a level of approximately 410 ppb. A four fold increase of added sheet results in a three times greater amount of styrene in the chocolate flakes. When the thickness of the sheet is doubled the amount of styrene in the chocolate flakes is much more than doubled. An explanation of this effect could be the influence of cut-edges on migration as described by Figge (1988). In the standard and control samples no styrene was detected.

The mean R-indices of the samples of cocoa drinks and chocolate flakes were calculated from the individual R-indices of the assessors (Table 4).

Table 4: Mean R-indices (%) of cocoa drinks and chocolate flakes determined by short-cut signal detection measures

samples[1]	mean R-index ± SD
Difference tests of drinks	
1.5% cocoa 10 drink (0.5)	52 ± 23
1.5% cocoa 10 drink (2)	49 ± 23
1.5% cocoa 20 drink (0.5)	47 ± 24
1.5% cocoa 20 drink (2)	55 ± 25
6% cocoa 10 drink (0.5)	51 ± 21
6% cocoa 10 drink (2)	55 ± 22
6% cocoa 20 drink (0.5)	53 ± 25
6% cocoa 20 drink (2)	55 ± 24
Difference tests of flakes	
milk chocolate flakes (0.5)	60 ± 26
milk chocolate flakes (2)	72 ± 24
plain chocolate flakes (0.5)	49 ± 28
plain chocolate flakes (2)	64 ± 29
Recognition tests of flakes	
milk chocolate flakes (0.5)	73 ± 25
milk chocolate flakes (2)	83 ± 18
plain chocolate flakes (0.5)	62 ± 27
plain chocolate flakes (2)	87 ± 23
plain chocolate flakes (0.5*)	88 ± 22
plain chocolate flakes (0)	52 ± 20

[1] sample codes as in Table 2

In the difference test, mean R-indices for all the cocoa drinks and chocolate flakes in contact with 0.5 dm^2 polystyrene sheet are near 50%, which indicates that there is no difference in taste between test samples and the standard. The other two chocolate flakes samples, however, show higher mean R-indices: 64% and 72% for the plain- and milk-chocolate flakes, respectively. Milk chocolate flakes show higher mean R-indices than plain chocolate flakes, indicating that milk chocolate flakes are more sensitive to styrene off-flavour, probably because of the low bitter taste intensity. A standard deviation (SD) of approximately 20% was also found by O'Mahony

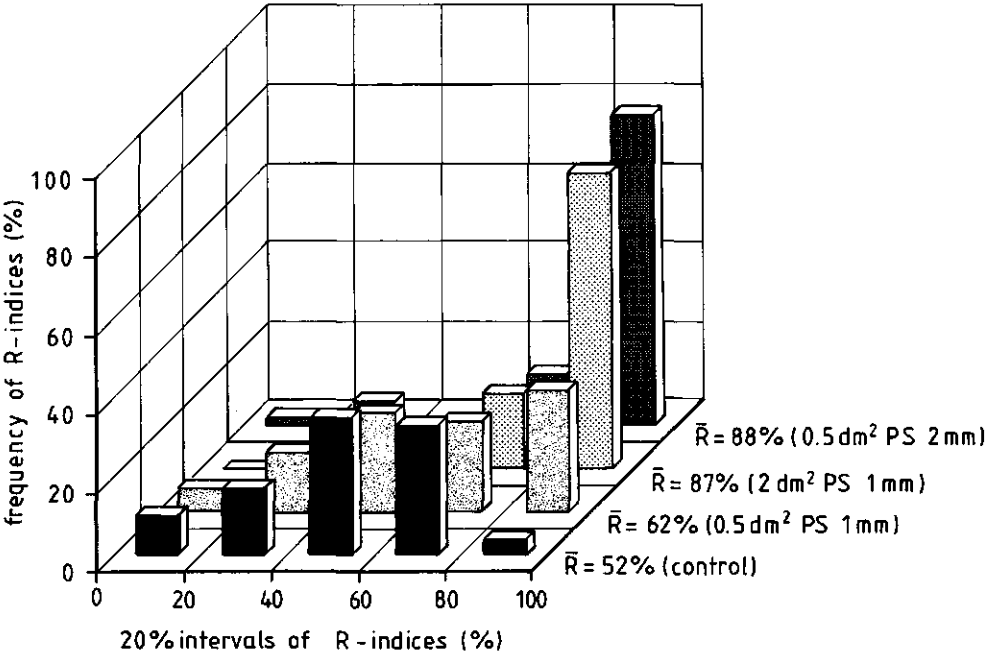

Figure 1: Frequencies of R-indices for recognition of styrene in plain chocolate flakes. A solution of 200 ppb styrene in water was used as standard for short-cut signal detection measures.

et al (1980).

An important question is whether the differences tasted can be recognised as styrene. For this reason, a styrene recognition test was carried out with a 200 ppb solution of styrene in water as standard for each series. As can be seen in Table 4, the R-indices are much higher in that case. It seems to be that styrene is more easily recognised (after knowing the kind of taste of styrene) than detected (amongst the complex taste impressions of chocolate products, without knowing the kind of taste of styrene) as a taint in chocolate flavour. In Figure 1, an almost gaussian distribution of the R-indices was found for the control test. An increased amount of styrene monomer in chocolate flakes caused a shift of the frequencies of R-indices to higher values.

In our experimental design no attempt was made to determine threshold values: nor detection, nor recognition. The samples just represent practical product exposition to packaging materials. There might be a learning effect to the assessors during the difference test. This effect has been neglected in the recognition test, because of the overwhelming taint impression by the 200 ppb styrene standard.

CONCLUSION

Polystyrene packaging material can be a latent source of off-flavour when used for packaging of cocoa products. A taint was not detected in the cocoa powder for drinks. Milk chocolate flakes are more sensitive to an off-flavour caused by migration of residual styrene monomer than plain chocolate flakes. Increasing contact area and increasing thickness (i.e. surface of cut-edges) of polystyrene result in higher levels of styrene migrated and thus in more chance of a taint.

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Chapter 6. Taste recognition threshold concentrations of styrene in oil in water emulsions and yoghurts[*]

ABSTRACT

Taste recognition threshold concentrations (TRTC) of styrene were determined in samples of oil in water emulsions (3 - 30% fat) and yoghurts (0.1 - 3% fat), spiked with styrene. The TRTC's obtained increase linearly with increasing fat content and ranged from 0.3 - 2.1 ppm for the emulsions and from 36 - 171 ppb for the yoghurts. Styrene equilibrium partition coefficients between emulsions and their respective vapour phases were determined. The concentrations of styrene in the continuous aqueous phase of the emulsions and yoghurts were calculated. At the TRTC values these concentrations have constant values of about 15 ppb, which indicates that perception of styrene for oil in water emulsions is determined by the aqueous phase of the emulsion. Also the concentrations of styrene in the vapour phases of the emulsions and yoghurts were calculated. They were constant at their TRTC levels, which was probably caused by an equilibrium of styrene between the respective phases. Commercial yoghurts packed in polystyrene beakers contained styrene levels in the range of 2 - 11 ppb: much lower then their TRTC values mentioned.

[*] Linssen, J.P.H., Reitsma, J.C.E., Janssens, J.G.L.M. and Roozen, J.P., to be submitted for publication

INTRODUCTION

Polystyrene (PS) is frequently used as a polymer for the packaging of foods. Typical examples include yoghurt and dessert packaging, foamed trays for meat and crystal clear trays for salads and vegetables. PS contains traces of residual styrene monomer. When the concentration in the PS matrix is too high, styrene monomer can impart an off-flavour to the packaged product. Several authors found styrene in food products present in very low amounts (Withey and Collins, 1978; Gilbert and Startin, 1983; Flanjak and Sharrad, 1986). A taste panel used by Passy (1983) detected an off-flavour in chocolate and lemon cookies packed in PS trays. The intensity of off-flavour depended on the level of residual styrene in the polymer package, type of food matrix and contact time.

Threshold values are important parameters for flavour perception and it is desirable to know more about the mechanism of release of flavours from a food product. Flavour perception is determined by the nature and quantity of the flavour compound and the availability of such a compound to the sensory system as a function of time. As many food products are emulsions, it is valuable to develop a model for flavour release in emulsions. McNulty and Karel (1973a, 1973b, 1973c) considered flavour release in oil in water (O/W) emulsions. In their concept the driving force for release is the difference between the flavour concentration in the saliva immediately after instantaneous mixing of the product with the saliva and the concentration in the saliva after reaching a certain equilibrium between oil and saliva. The concentration in the aqueous phase was supposed to be crucial for perception. However, Overbosch et al (1991) suggested that also the partitioning with the vapour phase has to be taken into account. The driving force for flavour release is then the deflection from thermodynamic equilibrium between the product phase and the vapour phase. On these principles the authors developed a model for emulsions and proposed the following relation:

$$K_{ve}=\frac{K_{vd}\cdot K_{dc}}{1+(K_{dc}-1)\,\Phi_d} \qquad (1)$$

in which K_{ve}, K_{vd} and K_{dc} are the equilibrium partition coefficients between vapour- and emulsion phase, between vapour- and dispersed phase and between dispersed- and continuous phase, respectively. Φ_d represents the volume fraction of the dispersed phase. In case of an O/W - emulsion the enumerator of equation (1) can be replaced by the equilibrium partition coefficient between vapour phase and water ($K_{vw} = C_v/C_w$), which results in:

$$K_{ve}=\frac{K_{vw}}{1+(K_{ow}-1)\,\Phi_d} \qquad (2)$$

in which K_{ow} (= C_o/C_w) is the equilibrium partition coefficient between the oily and aqueous phase in the O/W - emulsion. Furthermore C_e is defined as:

$$C_e = (1 - \Phi_d)C_w + \Phi_d C_o \qquad (3)$$

in which C_e, C_o and C_w represent the concentration in the emulsion phase, the oily phase and the aqueous phase, respectively.

The present study deals with the taste recognition threshold concentrations of styrene in O/W - emulsions and yoghurts with different amounts of dispersed phase (i.e. oil). Partition coefficients between vapour phase and emulsions, between vapour phase and yoghurts and between vapour phase and water have been determined. C_w can be calculated from equations (2) and (3) and the equation (1) for the release of styrene from O/W - emulsions was verified. The concentrations of styrene were calculated for the vapour phases of emulsions, yoghurts and water with styrene contents at their taste recognition threshold concentrations (TRTC's). Moreover actual styrene concentrations were analysed in several commercial yoghurts.

EXPERIMENTAL

Materials

Styrene was provided by BDH limited, Poole (Great Britain). Corn oil (Mazola) and yoghurts containing about 0.1%, 1.5% and 3% fat, freshly packed in polyethylene laminated cartons and in polystyrene beakers, were bought at a local store in Wageningen (The Netherlands). The polyethylene packed yoghurts were spiked with styrene and used in the sensory part of the study. The polystyrene packed yoghurts were stored in a refrigerator at 5 °C and analysed for their actual styrene content on their expiring date. Emulsifier, sodium stearoyl-2-lactylate (Admul SSL 2004) was kindly provided by Quest International, Zwijndrecht (The Netherlands). O/W - emulsions, containing 3, 10, 15, 20, 25 and 30% corn oil were prepared by mixing oil and 1% emulsifier, then adding water very slowly under continuous stirring with a bladed stirrer and finally homogenising the mixture for 1 min with an Ultra Turrax.

Sample preparation

Aliquot amounts of styrene (2.2 - 66 μl) were added with a 10 or 100 μl syringe to the O/W - emulsions in 2 l measuring flasks. For the lower concentrations styrene was added from stock solutions (50 ppm) of styrene in the respective emulsions. Each test series of O/W - emulsions consists of 9 solutions (Table I), which were offered as 15 ml samples in small glass bottles covered with aluminium folium and tightly closed with screw caps. The upper limits of the series and standards solutions have been established by informal tasting with colleagues in a preliminary test.

Table I: Concentrations (ppm) of styrene in standards and test sample series used for determining taste recognition threshold concentrations in O/W - emulsions with different amounts of fat.

fat content (%)	3	10	15	20	25	30
sample series	0	0	0	0	0	0
	0.06	0.2	0.25	0.25	0.25	1
	0.09	0.4	0.5	0.5	0.5	2.5
	0.12	0.8	0.75	1	1	5
	0.15	1.4	1	1.5	2	7.5
	0.2	2.2	2	2.5	3	10
	0.5	3.2	3	3.5	5	15
	0.7	4.4	5	5	10	20
	1	5.6	10	10	20	30
standard	4	25	40	40	40	40

Test series for yoghurts were prepared by spiking the yoghurts with different amounts of styrene vapour. A tightly closed 100 ml flask with 20 ml styrene was incubated at 50 °C. Different quantities of styrene vapour were taken through a septum with a 10 ml syringe and added to the yoghurts. The actual concentrations of styrene in the yoghurts were analysed immediately before tasting of the samples.

Sensory evaluation

TRTC 's of styrene in O/W -emulsions and in yoghurts were determined by using two different untrained panels of respectively 48 - 53 assessors and 24 assessors, aged 20 - 25 years old. In a session an emulsion without styrene and a standard emulsion (Table I) were presented first to the assessors for assuring recognition of the taste quality of styrene. Water containing 300 ppb styrene was used as standard for the yoghurt experiments. The 9 samples of a series were presented in random order. The assessors were asked to keep the sample 20 seconds in the mouth or shorter until styrene was recognized. The time interval between tasting of samples was 1 min. During that time the assessors were asked to rinse their mouths with Seven-up and water and to eat crackers for recovering their taste abilities.

A computer interactive interviewing system for composing questionnaires was used to gather survey information (Ci2 system, Sawtooth Software inc.). Portable computers (Toshiba Personal Computer T1000) with field disks were placed in sensory evaluation booths. Each assessor entered her/his personal code, after which detailed instructions about evaluation of the samples were displayed on the screen. Samples were offered in randomized order and questions about recognizing styrene in the O/W - emulsions were answered with a simple push on 1 (yes) or 2 (no). Data from the field disks were accumulated onto a hard disk (HP Vectra ES/computer), sorted with a Pascal programme and converted into the SPSS/PC$^+$ data file, with which the proportions of assessors recognizing styrene were determined.

The TRTC of styrene was defined as the concentration of styrene for which 50% of the answers of the assessors were positive in the recognition test. The proportions obtained were converted into Z - values using a conversion table (Amarine, 1965) and subsequently plotted versus the logarithm of the stimulus concentration. The 50% TRTC values are then the concentrations at the Z = 0 values of the best fitting linear regressions.

Styrene analysis

Styrene contents in emulsions, yoghurts and water were determined by azeotropic distillation with methanol, followed by extraction with hexane. The hexane extracts were analysed with a gas chromatograph (Carlo Erba, Model 4160), equipped with a flame ionisation detector and a cold on-column injector. The analyses were carried out on a 30 m x 0.32 mm (i.d.) fused silica capillary column (DB 1701, J & W Scientific). The detector temperature was 280 °C. The following oven temperature programme was used: an initial hold of 4 min at 40 °C and then 5 °C/min to 90 °C, followed by 15 °C/min to 190 °C and a final hold for 1 min. Calibration

curves were prepared by adding different amounts of styrene to emulsions, yoghurts and water (Varner et al 1983).
Amounts of styrene in a vapour phase were analysed by taking a 10 ml headspace sample, inject it onto a tube, which contains Tenax TA 35/60 mesh (Alltech Nederland BV, Zwijndrecht, The Netherlands). Styrene was analysed with a gas chromatograph (Carlo Erba, Model HRGC 5300), equipped with a flame ionisation detector and a thermal desorption/cold trap device (Carlo Erba, TDAS 5000) for transferring styrene from the Tenax onto a 60 m x 0.25 mm (i.d.) fused silica capillary column (Supelcowax 10, Supelchem BV, Leusden, The Netherlands). The detector temperature was 280 °C. The following temperature programme was used: an initial hold of 4 min at 40 °C, and then 2 °C/min to 92 °C, followed by 6 °C/min to 270 °C and a final hold for 4 min (Badings et al, 1985). A calibration curve was prepared by adsorbing different amounts of styrene on Tenax TA.

Determination of the partition coefficient for styrene between vapour- and liquid phases.

40 ml emulsion, yoghurt or water containing certain amounts of styrene were filled in 120 ml flasks, which were tightly closed and left for 6 hours at 25 ± 1 °C for equilibration. The partition coefficient for styrene can be calculated from the concentrations of styrene in the vapour phases and in the liquid phases.

RESULTS

The concentrations of styrene determined in the sample series for yoghurts are given in table II. Table III shows the linear regression equations of Z-values versus log (conc styrene) for O/W - emulsions and yoghurts and the 50% TRTC values at the Z = 0 value.

Table II: Concentrations (ppb) of styrene determined in test sample series used for determining TRTC of styrene in yoghurts with different fat content.

fat content (%)	0.1	1.5	3
sample series	0	0	0
	20	31	57
	38	54	123
	43	65	285
	58	80	452
	91	88	461
	96	157	503
	122	250	516
	170	496	571

Table III: Linear regression equations of Z - values versus log (conc styrene) for O/W - emulsions and yoghurts with different fat contents and the 50% TRTC values calculated at the Z = 0 value.

% oil	linear regression line		50% TRTC ppb
emulsions			
3	z = 1.38 + 1.95 log(C)	r=0.99	196
10	z = 0.24 + 1.30 log(C)	r=0.98	654
15	z = -0.11 + 1.52 log(C)	r=0.91	1181
20	z = -0.21 + 1.45 log(C)	r=0.94	1396
25	z = -0.27 + 1.40 log(C)	r=0.94	1559
30	z = -0.47 + 1.48 log(C)	r=0.95	2078
yoghurts			
0.1	z = -3.58 + 2.76 log(C)	r=0.91	36
1.5	z = -4.05 + 2.03 log(C)	r=0.97	99
3	z = -4.58 + 2.05 log(C)	r=0.95	171

Figure 1 shows the linear regression of the amount of oil in an O/W - emulsion versus 50 % TRTC value. The linear regression equation calculated is: 50% TRTC (ppm) = 0.068 (% oil) + 0.035 (r=0.99). Additionally, the 50% TRTC values for water (Linssen et al, 1991) and yoghurts are presented in figure 1 to show their positions in respect to the regression line. Table IV gives the partition coefficients of styrene between vapour phase and respectively emulsions and yoghurts with different amounts of fat (K_{ve}). C_e measured and C_e calculated from figure 1 represent the TRTC values of styrene for each emulsion or yoghurt. Using equations (2) and (3), and K_{vw} (= 0.027 ± 0.001 (n=3)), C_w is calculated at the TRTC values. Also the concentrations of styrene in the vapour phases (C_v) are given for emulsions and yoghurts containing styrene at their TRTC values.

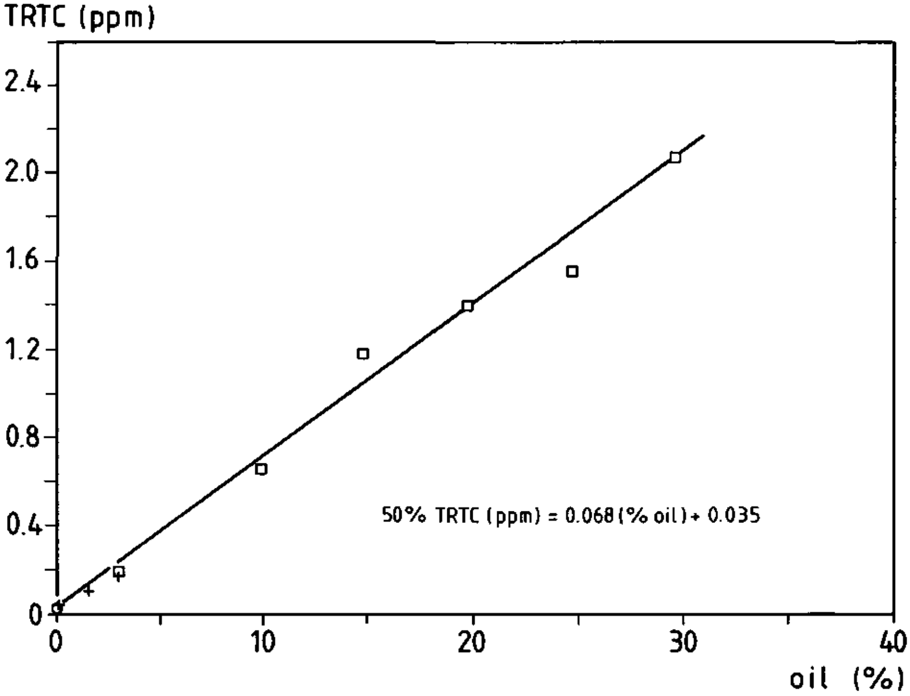

Figure 1: Recognition threshold concentrations of styrene in water (○), O/W - emulsions (□) and yoghurts (+) with different amounts of fat.

Table IV: Partition coefficients between vapour phase and emulsions or yoghurts (K_{ve}). Concentrations of styrene in the aqueous phase of the O/W - emulsions and yoghurts (C_w); and in the vapour phase of emulsions and yoghurts (C_v). All styrene contents are at their TRTC values (C_e).

fraction oil	K_{ve}[1] x 10^{-3}	C_e[2] ppb	C_w[3] ppb	C_e[4] ppb	C_w[5] ppb	C_v[6] ppb
emulsions						
0.03	1.70 ± 0.10	239	15	196	12	0.41
0.10	0.55 ± 0.02	715	15	654	13	0.39
0.15	0.39 ± 0.02	1055	15	1181	17	0.41
0.20	0.29 ± 0.01	1395	15	1396	15	0.40
0.25	0.24 ± 0.02	1735	15	1559	14	0.42
0.30	0.21 ± 0.02	2075	16	2078	16	0.44
yoghurts						
0.001	19.1 ± 1.6			36	25	0.69
0.015	3.7 ± 0.2			99	15	0.37
0.03	2.4 ± 0.2			171	15	0.41

[1] values are means of 6 replicates ± SD

[2] calculated from the curve in figure 1 (yoghurts excluded, because data are not available)

[3] calculated from equations (2) and (3) using C_e calculated

[4] C_e measured

[5] calculated from equations (2) and (3) using C_e measured

[6] calculated from $K_{ve} = C_v/C_e$, using C_e calculated; C_e measured is used for the yoghurts

DISCUSSION

The present study shows that the TRTC's for yoghurts with 0.1%, 1.5% and 3% fat are respectively 36 ppb, 99 ppb and 171 ppb. The latter is in good agreement with a TRTC value for yoghurt of 0.2 ppm found by Jensen (1972). TRTC values of 0.5 ppm for yoghurt, 1.2 ppm for whole milk and 6.0 ppm for cream were reported by Jenne (1980). These results imply that the TRTC is higher in products with higher fat content, and so making styrene less noticeable in high fat products. The results presented in Table III confirm the observation that the TRTC values increase with increasing fat contents. Both in the model systems of emulsions and in the yoghurts the increase of the TRTC is linearly with the fat content of the O/W-emulsions and yoghurts (Figure 1). However, the amount of styrene migrated from polystyrene is higher into products with a higher fat content (Ramshaw, 1984; Linssen and Reitsma, 1991). These two diverging influences hinder accurate calculation of the probability of off-flavour development.

Partition coefficients could be important for estimating the chances of an off-flavour. Table IV shows that the concentrations calculated for styrene in the aqueous phases of emulsions or yoghurts (C_w) are similar at about 15 ppb at their TRTC levels. This is in agreement with the assumption of McNulty and Karel (1973a) that the aqueous phase of an emulsion or an emulsion type of foodstuff determines the flavour perception. Moreover, the uniform concentration of styrene in the aqueous phase of the different emulsions and yoghurts is close to the 50% TRTC value of 22 ppb found for water (Linssen et al, 1990). So, a fixed concentration of styrene is needed in the aqueous phase of an emulsion for recognizing styrene in O/W-emulsions and in yoghurts. As can be seen from Table IV only a minor part of the styrene dissolved in the emulsion or yoghurt, is present in the aqueous phase; the major part is hidden in the oily phase. Because of the very good solubility of styrene in the fat fractions, the TRTC's of the emulsions will increase with increasing fat contents of the emulsions. More styrene is needed then to reach the equilibrium at which the concentration of styrene is about 15 ppb in the aqueous phase. It was also found that the concentrations of styrene in the vapour phases (C_v) of the emulsions and most of the yoghurts at their TRTC's are similar at about 0.41 ppb (Table IV). This can be explained by the following equilibrium:

$$C_o \rightleftharpoons C_w \rightleftharpoons C_v \qquad (4)$$

As already discussed C_w is constant at the TRTC's of styrene in O/W-emulsions and yoghurts. Water is the continuous phase in an O/W-emulsion and thus in a closed system an equilibrium exists between continuous phase and vapour phase. So, C_v is also constant at the TRTC's of styrene. However, C_v's calculated for low fat yoghurt and water are higher than the constant value of 0.41 ppb, namely 0.69 and 0.59 ppb, respectively. The method of tasting allows styrene is to evaporate very quickly from these samples and a firm part of it has already escaped before reaching the mouth. Therefore, higher concentrations of styrene could be necessary in water and low fat yoghurt for meeting its concentration in the mouth vapour phase at TRTC level.

The present findings could be important for practical situations. If the concentration of styrene in the vapour phase exceeds 0.41 ppb one could expect an off-flavour of styrene in O/W - emulsions and emulsion type of foods. Analysis of the styrene content in the vapour phase can be predictive then for an off-flavour caused by styrene. At the TRTC's a number of variables in equation (2) are known: C_v is at a constant level of 0.41 ppb, C_o/C_w is 462 and C_v/C_w is 0.027. Using these data in equation (2) and $K_{ve} = C_v/C_e$ results in a simple linear relationship between TRTC (C_e) and the dispersed (oily) phase in an O/W - emulsion: C_e (ppm) = 0.070 (% oil) + 0.015. A calculation of the TRTC's for the yoghurts, containing 0.1%, 1.5% and 3% fat estimates at 22, 120 and 225 ppb, respectively. These estimates are in good agreement with the values found experimentally. Moreover, the latter relationship is similar to the linear regression equation of figure 1, which validates equation (1) for this particular type of system.

In a survey of commercial yoghurts packed in polystyrene beakers, none of them reached their TRTC levels: 8 samples of low fat yoghurt (0.1 - 0.5% fat) have styrene levels in the range of 3 - 4 ppb with a mean of 3 ppb; 16 samples of medium fat yoghurt (1.5% fat) showed a styrene content in the range of 5 - 11 ppb with a mean of 7 ppb; and 16 samples of high fat yoghurt (3 - 3.5% fat) contained styrene in the range of 2 - 5 ppb with a mean value of 3 ppb. The amounts of styrene in the medium fat yoghurts are slightly higher, because these yoghurts are thick yoghurts while the others are of the stirring type. These values indicate that polystyrene is an acceptable material for packaging yoghurts in the context of their TRTC's for styrene.

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PART III. PRODUCT QUALITIES OF FOOD IN CONTACT WITH POLYETHYLENE (MIGRATION)

Polyethylene (PE) packaging material is widely used in the food packaging industry as mono- and multilayer system as well as lined on carton and aluminium. Oxygen and peroxides are often used as initiators for free radical polymerisation of PE and as a consequence it is possible that carbonyl groups are present. Additional carbonyl groups can be formed during high temperature processing of PE in the presence of oxygen, e.g. extrusion coating. Short chain compounds containing such groups are able to migrate into the PE packed product and might influence product quality. Also several hydrocarbons, like alkanes or aromatic hydrocarbons might influence the quality of a PE packed product. These compounds arise probably from a C_{12} mineral oil fraction used as a solvent for the production of PE. Therefore, sensory evaluation can give some guidance to instrumental analysis. Water was chosen as a test medium because it is rather sensitive for acquiring a taint.

Chapter 7 demonstrates the generation of descriptive sensory attributes for a taint in water packed in test pouches made of PE lined aluminium. Dynamic headspace samples of water were analysed on combined gas chromatography and mass spectrometry to identify the compounds probably responsible for the taint described.

Chapter 8 presents dynamic headspace sampling of volatile compounds from commercial mineral water packed in PE lined aluminium/paper board packages. Combined gas chromatography and sniffing port analysis was carried out in order to get odour impressions of individual peaks of the gas chromatogram by 10 assessors. Combined gas chromatography and mass spectrometry analysis was performed to identify these compounds which could be responsible for the odour impressions given by the assessors.

Chapter 7. Sensory descriptors for a taint in water packed in pouches made of polyethylene lined aluminium*

ABSTRACT

A panel of 48 assessors evaluated a taint in water, packed in test pouches made of low density polyethylene (LDPE) lined aluminium. This panel agreed upon eight descriptive attributes (in dutch): metallic (metaal), synthetic (synthetisch), dry (droog), rough (stroef), astringent (wrang), musty (muf), sickly (wee) and penetrating (doordringend). 14 assessors, selected with a standard triangle test, were asked to judge intensities for these attributes on a visual analogue scale. Factor analysis reduced the original data-matrix to a six dimensional one losing only 6.4 % of the original variance. Synthetic and penetrating loaded high on one factor as well as rough and astringent on another one. Musty, sickly, metallic and dry loaded high on separate factors.

Direct dynamic headspace analysis of the LDPE-lined test pouches gave mainly peaks of branched alkanes of 12 carbon atoms. However, dynamic headspace analysis of water in contact with the LDPE layer of the test pouches showed no alkanes but (C_4 - C_{11}) aldehydes and ketones.

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* Linssen, J.P.H., Janssens, J.L.G.M, Roozen, J.P. and Posthumus, M.A., Journal of Plastic Film & Sheeting, 7, 294-305 (1991)
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INTRODUCTION

In the food industry polyethylene (PE) is an often used packaging material as mono- and multilayer systems as well as lined on cartons and aluminium. PE molecules have short and/or long chain branching, which controls the level of crystallinity and so the density. Low density polyethylene (LDPE) is in the range 0.910 - 0.935 g/cc and contains both long and short chain branching. Oxygen or peroxides are used as initiators for the free radical polymerisation and as a consequence it is possible to have carbonyl groups present (1). Additional carbonyl groups can be formed during high temperature processing in the presence of oxygen, e.g. extrusion coating (2). Short chain compounds containing such groups are able to migrate into PE packed products and maybe responsible for a taint. However, besides sensoric intensity and concentration of the migrating substances taste perception depends on flavour intensity of the product (3). Kiermeyer and Stroh (4) suggest an ion exchange interaction between the acidic proton of carboxylic acids of PE and metallic cations of milk-salts as responsible for a "plastic flavour" sometimes found in milk packed in PE. Berg (5) reported that products like spring water, milk and fruit juices have frequently an unfavourable off-taste after being stored in bottles of PE or coated PE cartons. In this kind of tests consumer-like panels use terms as "unpleasant plastic", which are hedonic in nature. Peled and Mannheim (6) carried out instrumental analysis of off-flavour caused by PE, but conclude that sensory tests are more reliable for determination of off-flavour originated from the packages.

However, descriptive attributes are hardly found in literature. Koszinowsky and Piringer (7) reported that the taste and odour of water, packed in PE, was described as candle-grease, musty, rancid or soapy, although PE itself was almost odourless. Solin et al (8) compared four types of plastics, polyvinylchloride (PVC), high-density polyethylene (HDPE), polycarbonate (PC) and polyethylene terephthalate

(PET) to evaluate their effect on the taste and odour of mineral water versus a glass control. PVC had the lowest contribution to taste and odour, followed by PET and then PC and HDPE. However, the growing concern about PVC in waste disposal makes the applications of PVC in the packaging of food products uncertain. For that reason it is worthwhile to search for alternatives.

Because of the scarcely available data describing taste and odour of water packed in PE, the main purpose of the present study was to generate attributes for the taint of water in contact with the LDPE layer of aluminium lined test pouches. Additionally, combined gas chromatography and mass spectrometry analysis was carried out to get an idea of which components could be responsible for the off-taste detected by the assessors.

EXPERIMENTAL

Sample preparation

Low density polyethylene (LDPE) lined aluminium was prepared at 310 °C by DOW EUROPE (Horgen, Switzerland) on an extrusion coating line and immediately fold and sealed into test pouches to prevent evaporation of volatile compounds. The test pouches were filled with 250 ml water and incubated at 40 °C for 24 hours. The dimensions of the test pouches were chosen proportional to commercial 1 l packages, which is 8 dm^2. The water was used for the following experimental procedures.

Sensory evaluation

A panel of 48 assessors, all of them were students of the Wageningen Agricultural University (The Netherlands) and aged 20 - 25 years, was presented with samples of LDPE incubated water (code: LDPE). The assessors were asked to characterize the taste/odour impression of the water by their own expressions and afterwards to choose from given terms, which were mentioned several times in preliminary investigations. In a separate session 1:3 diluted samples of LDPE incubated water (code: LDPE dil) was presented to the assessors asking them the same questions. From these experiments attributes were chosen for intensity studies with a trained panel (Table 1). 17 assessors from the former panel were selected with a standard triangle test in duplicate (9) and trained to use a 180 mm visual analogue scale on a portable personal computer screen (Toshiba Personal Computer T 1000). 14 of them were available to participate in the trained panel.

A computer interactive interviewing system for composing questionnaires was used to gather survey information (Ci 2 system, Sawtooth Software Inc). The portable computers with field disks were placed in sensory evaluation booths. Each assessor entered his/her personal code after which detailed information about evaluation of the samples were displayed on the screen. Data from the field disks were accumulated with the Ci 2 program onto a hard disk (HP vectra ES/12 computer) and converted with the Ci 2 program into a SPSS "include File". The SPSS program was used for evaluating the dataset by factor analysis *(See Appendix of this chapter)*.

Instrumental analysis

Additionally to the sensory evaluation qualitative instrumental analysis was carried out by dynamic headspace sampling. LDPE lined aluminium test pouches were opened and topped with a tube containing Tenax TA 35/60 mesh, Alltech Europe (Brussels), and sampled directly by flushing the test pouch with purified nitrogen at a flow rate of 30 ml/min for 90 minutes. Water, which had been incubated (24 h, 40 °C) in the test pouches, was purged at room temperature with purified nitrogen at a flow rate of 30 ml/min for 4 hours. A cold trap (- 10 °C) was used for freezing out water vapour, while the volatiles were trapped on a Tenax TA tube. The same water packed in glass was treated in the same way and used as control sample. The trapped volatiles were identified on a combined gaschromatograph (Pye 204) and mass spectrograph (VG MM 7070 F). A thermal desorption/ cold trap device (Chrompack TCT injector 16200) was used for transferring the volatile compounds onto a fused silica column (Supelcowax 10 length 60 m, inner diam. 0.25 mm). The carrier gas was helium at 18 psi. An initial oven temperature of 40 °C for 4 min was used, followed by a rate of 2 °C/min to 92 °C and 6 °C/min to 270 °C and a final hold for 4 min. Mass spectra were recorded in the electron impact mode at a ionisation voltage of 70 eV and scanned for $m/z = 300 - 25$ with a cycle time of 1.8 s (10, 11)

RESULTS AND DISCUSSION

The 48 assessors of the panel generated similar expressions for the taste of the samples LDPE and LDPE dil, which were also mentioned in the preliminary investigations. This means that dilution did not influence the nature of the taste and/or odour of the samples tested. From the list obtained similar expressions were combined and those suggested by more than 50 % of the assessors were used for the intensity studies (table 1).

Table 2 shows the intensity scores of the trained panel for each attribute, which scores were higher for LDPE dil. and LDPE samples than for control. Paired Student t-tests were carried out on these: metallic, synthetic, dry, penetrating and musty for the samples LDPE dil. and LDPE were significantly different from the control sample ($p < 0.05$). Scores on rough and sickly showed only a significant difference between the control and LDPE sample ($p < 0.05$). Astringent showed no significant difference at all ($p > 0.05$). The mean scores were intercorrelated and factor analysis was applied to the correlation matrix obtained . Frijters (12) extracted the factors having Eigenvalues greater than one and explained 85.3 % of variance.

Table 1: Sensory attributes of water which was incubated in LDPE lined aluminium test pouches (24 h, 40 °C)

attributes presented*	attributes used for intensity studies
metallic (metaal) tin (blik) silver paper (zilverpapier) rusty (roestig)	metaal
synthetic (synthetisch) plastic (plastic) synthetic material (kunststof) chemicals (chemisch)	synthetisch
dry (droog)	droog
rough (stroef)	stroef
astringent (wrang)	wrang
bitter (bitter)	
earthy taste (grondsmaak)	
candle grease (kaarsvet)	
musty (muf)	muf
sickly (wee)	wee
penetrating (doordringend)	doordringend

* in parenthesis: Original Dutch words used by the assessors; they may not be exactly synonymous with the English translation.

In our case, however, only two factors have Eigenvalues > 1, which explain 62.7% of variance, so factor extraction was proceeded up to 6 factors (Table 3). This reduction of an eight dimensional space into a six dimensional one involves a loss of only 6.4% of the original variation, as can be seen from table 3. The loadings on the factors indicate the attributes very clearly. Synthetic and penetrating load high

Table 2: Mean score (± S.D.) of intensity (%) for each attribute on a visual analogue scale of 180 mm.

attribute	intensity (%) reported with sample of water control		LDPE dil		LDPE	
	mean	SD	mean	SD	mean	SD
metallic	11	(13)	46	(36)*	54	(33)*
synthetic	18	(24)	62	(28)*	77	(16)*
dry	32	(25)	59	(28)*	65	(24)*
rough	30	(32)	56	(29)	55	(23)*
astringent	25	(29)	42	(32)	41	(35)
penetrating	14	(25)	48	(28)*	70	(29)*
musty	20	(22)	61	(29)*	63	(24)*
sickly	30	(28)	38	(27)	55	(24)*

* significantly different from control ($p < 0.05$)

Table 3: Rotated factor matrix showing factor loadings of eight variables on six factors.

	factor					
variables	1	2	3	4	5	6
metallic	0.24	0.23	0.13	0.18	0.89	0.20
synthetic	0.83	0.15	0.23	0.24	0.25	-0.11
dry	0.14	0.36	0.14	0.03	0.20	0.87
rough	0.25	0.83	0.25	-0.01	0.16	0.14
astringent	0.03	0.86	-0.02	0.20	0.12	0.25
penetrating	0.90	0.12	0.10	0.08	0.08	0.28
musty	0.21	0.14	0.93	0.16	0.11	0.12
sickly	0.20	0.13	0.16	0.94	0.15	0.03
Eigenvalue	3.75	1.26	0.78	0.66	0.57	0.45
Cumulative % total variance	46.9	62.7	72.4	80.7	87.8	93.6

on one factor and rough and astringent on another one. The magnitude of these loadings is sufficient to conclude that in both cases the two attributes share the same underlying perceptual continuum. Rough and astringent seem to be less important attributes for describing LDPE tainted water, because they are only significantly different from the control in one case (Table 2). The other attributes have sufficient high loadings on different factors, making these factors unique for each attribute.

The additional qualitative GC-MS analysis of the dynamic headspace samples of the LDPE test pouches showed only a group of volatiles, which are mainly branched alkanes of 12 carbon atoms (figure 1A). They form presumably the C_{12} fraction of a mineral oil used as a solvent for the production of LDPE. One of these compounds, 2,2,4,6,6,- pentamethylheptane was suggested to be the cause of an off-taste sometimes found in products packed in PE (13). Figure 1B gives the chromatogram obtained from the dynamic headspace sample of water, which was incubated in the LDPE lined aluminium test pouches. The peaks were identified mainly as aldehydes and ketones with a chain length from C_4 to C_{11}. These carbonyls could be the cause of the off-flavour attributes detected by our assessors, because the control sample contained hardly carbonyls. Further attempts for making a correlation between sensory and instrumental analysis will be investigated by using sniffing-port gas chromatography. The carbonyl compounds have been described as thermo-oxidative degradation products, which are formed during the process of coating LDPE on aluminium (14). The alkanes found in the dynamic headspace of the test pouches are absent in the water, probably because of the very low solubility of such compounds in water. From these experiments might be concluded, that the C_{12} mineral oil fraction is not responsible for the off-taste in watery food products. However, vom Bruck and Hammerschmidt (13) suggested that this fraction was the reason for an off-taste found in commercial water, packed in LDPE. In this case, however, the contact period is much longer than the 24 hours chosen for our experiment using the LDPE

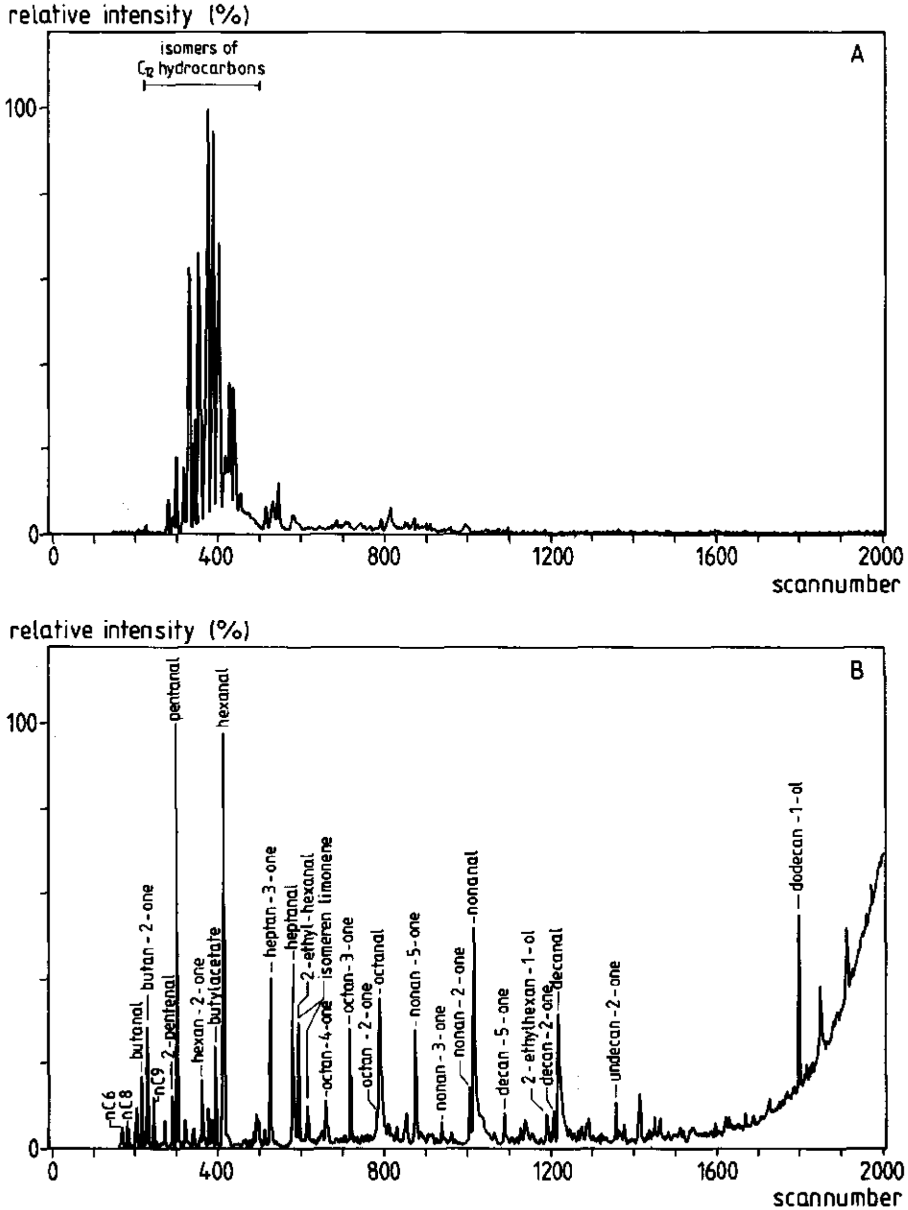

Figure 1: Reconstructed total ion current chromatograms of volatile compounds from LDPE (A) and from water packed in LDPE (B) obtained by a dynamic headspace technique.

test pouches. It is imaginable that during the distribution period of water, alkanes migrate in such amounts into the product that they become detectable by GC-MS as compounds, which are likely to influence the taste of water.

CONCLUSION

Taint in water packed in LDPE lined aluminium test pouches has been described by a six dimensional sensory structure. The six variables are: synthetic (penetrating), rough (astringent), musty, sickly, metallic and dry. However, rough (astringent) seems to be a less important attribute, because its insignificancy with the control. Qualitative instrumental analysis showed the presence of carbonyl compounds in the water, which could be the reason for the taint as described by the assessors.

APPENDIX

The basic assumption of factor analysis is that underlying dimensions, or factors, can be used to explain complex phenomena. It is a statistical technique to identify a relatively small numbers of factors that can be used to explain correlations between sets of many interrelated variables. Factors are patterns of relationships among the variables. The factor analysis used proceeds in three steps:
1) The correlation matrix for all variables is computed (Table 4); 2) Factor extraction, which determines the number of factors necessary to represent the data, and 3) rotation, which focuses on transformation of the factors for making them more interpretable. Factor extraction from table 4 results in the factor matrix of table 5. For simplicity all variables and factors are expressed in standardized form with a mean of 0 and a standard deviation of 1. So, the total variance is 8 in the present case.

Table 4: Correlation matrix of descriptive variables of a polyethylene taint in water.

variables	metallic	synthetic	dry	rough	astringent	penetrating	musty	sickly
metallic	1.00							
synthetic	0.48	1.00						
dry	0.47	0.22	1.00					
rough	0.44	0.40	0.56	1.00				
astringent	0.41	0.19	0.52	0.64	1.00			
penetrating	0.41	0.71	0.39	0.37	0.26	1.00		
musty	0.36	0.45	0.32	0.39	0.23	0.38	1.00	
sickly	0.41	0.48	0.19	0.26	0.28	0.31	0.38	1.00

The first factor is the combination of variables that accounts for the largest amount of variance in the sample. The second one accounts for the next largest amount of variance and does not correlate with the first factor. Successive factors explain progressively smaller portions of the total sample variance. The total variance explained by each factor is labelled Eigenvalue, which is calculated for factor 1 as follows: $(0.74)^2 + (0.73)^2 + (0.67)^2 + (0.75)^2 + (0.64)^2 + (0.71)^2 + (0.63)^2 + (0.58)^2 = 3.75$. Eigenvalue of 3.75 means 46.9 % of the total variance of 8. The number of factors needed to represent the data is chosen by 1) examining the total cumulative amount of variance explained by these factors, and 2) factors that account for Eigenvalues bigger than 1. The latter criterion, however, delivers 2 factors, which explain only 62.7 % of the cumulative total variance. It was decided to proceed factor extraction up to 6 factors, because then, after rotation, on each factor at least one variable shows a high factor loading, explaining 93.6 % of the total cumulative variance.

Table 5: Factor matrix of 6 extracted factors

	factor					
variables	1	2	3	4	5	6
metallic	0.74	-0.01	0.11	-0.25	-0.51	-0.31
synthetic	0.73	0.53	-0.19	-0.13	0.16	-0.13
dry	0.67	-0.47	-0.19	0.09	-0.31	0.39
rough	0.75	-0.40	-0.45	0.08	0.30	-0.22
astringent	0.64	-0.57	-0.17	-0.14	0.28	-0.02
penetrating	0.71	0.34	-0.49	-0.13	0.10	0.19
musty	0.63	0.23	0.14	0.70	-0.61	-0.06
sickly	0.58	0.35	0.64	-0.18	0.07	0.28
Eigenvalue	3.75	1.26	0.78	0.66	0.57	0.45
Cumulative % total variance	46.9	62.7	72.4	80.7	87.8	93.6

The coefficients presented in table 5 are called factor loadings, since they indicate how much weight is assigned to each factor. Variables with large coefficients for a factor are closely related to that factor and to each other. Although the factor matrix obtained indicates the relationship between the factors and the individual variables, it is difficult to identify meaningful factors. The factors are correlated with many variables. The third step, rotation, attempts to minimize the number of variables that have high factor loadings on a factor. Table 3 shows the rotated factor matrix. The variables with high factor loadings indicate the attributes for a taint in water, which was in contact with polyethylene lined aluminium. In this table the factor loadings indicate the attributes very clearly. Synthetic and penetrating (0.83 and 0.90) load high on factor 1, while rough and astringent (0.83 and 0.86) load high on factor 2. The other attributes have sufficient high loadings on different factors making these factors unique for each attribute. Musty, sickly, metallic and dry load high on respectively factor 3, factor 4, factor 5 and factor 6 with factor loadings of respectively 0.93, 0.94, 0.89 and 0.87.

Further reading about factor analysis in Kim, J.O and Mueller, C.W., (1982). Introduction to factor analysis (What It Is and How To Do It). Series: Quantitative Applications in the Social Sciences, no 13. SAGE Publications Ltd, London and in Kim. J.O. and Mueller, C.W., (1983). Factor analysis (Statistical Methods and Practical Issues). Series: Quantitative Applications in the Social Sciences, no 14. SAGE Publications Ltd, London.

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Chapter 8 Combined gas chromatography and sniffing port analysis of volatile compounds of mineral water packed in polyethylene laminated packages[*]

ABSTRACT

Commercial mineral water packed in polyethylene lined aluminium/cardboard packages was sensory evaluated for intensities of the descriptors: synthetic, musty, sickly, metallic, astringent and dry. Tasting the samples with the use of nose clips diminishes the intensities of the descriptors significantly, except for dry. Combined gas chromatography and sniffing port analysis of volatile compounds of the mineral water provided similar descriptors as mentioned. The components detected by sniffing were identified by combined gas chromatography and mass spectrometry as being mainly aromatic hydrocarbons and carbonyls. Semi-quantitative analysis showed that the concentrations of the compounds migrated into the mineral water ranged between 10-15 ppb.

[*] Linssen, J.P.H., Janssens, J.L.G.M., Roozen, J.P. and Posthumus, M.A., to be submitted for publication.

INTRODUCTION.

The rapid substitution of relatively inert material as glass and metal with more interactive synthetic polymers for packaging materials has created new problems concerning interactions between foods and their packages. Migration of low molecular weight components from these polymers to a packed product can result in a change of flavour, and so affect the perceived quality of the product (Harte and Gray, 1987). Polyethylene (PE) packaging material is widely used by the food packaging industry, because of its low costs and outstanding service properties (Giacin, 1980). It is used in mono- and multilayer systems as well as in lined cardboard and aluminium packages. Oxygen and peroxides are added to initiate radical polymerisation reactions and consequently, it is possible to have carbonyl and carboxyl groups present in PE (Shorten, 1982). Additional oxidation products can be formed during high temperature processing in the presence of oxygen, e.g. extrusion coating (Hoff and Jacobsson, 1981; Hoff et al, 1982). Extrusion conditions of low density polyethylene (LDPE) can affect the flavour of the packed product: higher melt temperatures were responsible for increased off-taste intensity of drinking water in contact with PE (Potts et al, 1990).

There is hardly any information about the nature of the off-flavour, which can be caused by interactions between food and PE. Kiermeier and Stroh (1969) suggested an exchange of ions between the cations of milk-salts and the acidic proton of carboxyl groups of PE as responsible for a "plastic flavour" sometimes found in milk. Bojkow et al (1976) have not found significant changes in off-flavour intensity of milk packed in PE-lined cardboard after one week of storage. Berg (1980) reported that products like spring water, milk and fruit juices have frequently an unfavourable off-taste after being stored in bottles of PE or PE-lined cartons. In PE granulate he found volatile compounds like saturated and unsaturated hydrocarbons, aromatic hydrocarbons and aromatic hydrocarbons with an unsaturated side chain. An intense plastic off-flavour was ascribed to C_3- and C_4-alkyl benzenes. Also C_2 - C_5 carbonyl and carboxyl compounds can influence taste and odour of a packed product (Bojkow, 1982). Carbonyls like 2-nonenal and 1-hepten-3-one were identified as a source of off-odour in water packed in LDPE lined cardboard by Koszinowski and Piringer (1983). The off-flavour was described as candle-grease, musty, rancid and soapy. Degradation products formed during extrusion lamination of an ionomer, in which PE was the major component, were studied by Fernandes et al (1986). Mainly carbonyl compounds like pentanal, 2-hexanone and 3-heptanone were identified. Performing combined gas chromatography and sniffing port analysis the aldehyde was described as pungent and the ketones as acrid. In our former study the taint of water packed in PE lined aluminium test pouches was described as musty, sickly, astringent, synthetic, metallic and dry. Additional Instrumental analysis showed that C_4 - C_{11} carbonyls could be responsible for the taint. (Linssen et al, 1991)

The aim of the present study was to describe and identify volatile compounds in commercial mineral water packed in PE lined aluminium/cardboard packages. Techniques used were combined gas chromatography and respectively sniffing port analysis and mass spectrometry.

MATERIALS AND METHODS

Sample preparation

Commercial mineral water packed in 2 l packages of LDPE lined aluminium/cardboard (test samples) were bought at a local store in Wageningen (The Netherlands). Reference mineral water packed in glass bottles was kindly provided by the manufacturer and used as a control. Test samples were incubated at 20 °C and 40 °C for 24 hours. These samples and the control were used for flavour intensity studies and for preparation of dynamic headspace samples for combined gas chromatography and respectively sniffing port analysis and mass spectrometry. Dynamic headspace samples were prepared by purging 2 l of water at 40 °C for 1 hour with purified nitrogen at a flow rate of 100 ml/min. A cold trap (- 10 °C) was used for retention of water vapour and volatile compounds were trapped on Tenax TA (35/60 mesh, Alltech Nederland BV, Zwijndrecht, The Netherlands).

Sensory evaluation

In our former study the PE taint of water packed in LDPE lined aluminium test pouches was described by 6 attributes: metallic, synthetic, dry, astringent, musty and sickly (Linssen et al, 1991). These attributes were now used for a flavour intensity study of commercial mineral water packed in LDPE aluminium/cardboard packages. A panel of 11 assessors was selected and trained. All of them were students of the Wageningen Agricultural University and aged 20 - 25 years. Part of the training was utilisation of a 180 mm visual analogue scale on a portable computer screen (Toshiba personal computer T1000) for scoring perceived flavour intensities.

A computer interactive interviewing system for composing questionnaires was used to gather survey information (Ci2 system, Sawtooth, Software. Inc.). The portable computers with field disks were placed in sensory evaluation booths. Each assessor entered her/his personal code after which detailed information about evaluation of the samples was displayed on the screen. Data from the field disks were accumulated with the Ci2 program onto a hard disk (HP Vectra ES/12 computer) and converted into a SPSS "include File". The SPSS program was used for statistical evaluations. Samples were tasted with and without the use of nose clips (Jaeger Nederland BV, Breda).

Gas chromatography

Combined gas chromatography and sniffing port analysis was performed with a Carlo Erba gas chromatograph, type 6000 VEGA series. A thermal desorption/cold trap device (Chrompack TCT injector 16200) was used for transferring the volatile compounds from the Tenax onto a fused silica capillary column (DB 1; 30 m x 0.32 mm, film thickness 1,0 µm; J & W Scientific). An initial oven temperature of 60 °C for 4 min was used, followed by a rate of 2 °C/min to 140 °C and 10 °C/min to 250 °C and a final hold for 5 min. The detector temperature was kept at 275 °C. The gas chromatograph was equipped with a flame ionisation detector (FID) and 2 sniffing ports (SGE, Milton Keynes, Great Britain), one at each side of the instrument. At the end of the capillary column the effluent was split 1:2:2 for FID, sniffing port 1 and sniffing port 2, respectively. 10 assessors, 20 - 25 years of age, were selected on their availability, sensitivity, memory and ability to recognize odours. Prior to exit port sniffing of samples the assessors were trained on the technique of sniffing with a standard mixture. The instrument was placed in a room made free from distracting odours and noise to create an ideal environment for the assessors. The maxima 820 system (Dynamic solutions, Ventura, California, USA) recorded the FID chromatogram outside the room of the assessors. Supplementary air was bubbled through distilled water in a gas-scrubbing bottle, which runs through stainless steel tubing to the exit port in order to prevent drying out of assessors nasal membranes during sniffing for approximately 40 min. Assessors used portable computers (Toshiba T1000) with a program in Pascal for data collection. They kept a button pushed on the keyboard during the time that they got an odour impression. Using a Pascal program the data were converted from the field disks into the Lotus 123 program for manipulating of the raw data.

A listing of 14 descriptors was obtained from a preliminary session of combined gas chromatography and sniffing port analysis for describing the volatile compounds obtained from water packed in LDPE lined aluminium/cardboard packages (Table 1). Besides "other" these descriptors had to be used for each component detected by the 10 assessors at the sniffing port.

Dummy samples were used for determining the signal-noise level of the group of assessors. FID calibration curves for pentanal, heptanal, decanal, 2-nonanone and ethylbenzene were prepared to estimate the concentrations of migrants in the mineral water.

The volatile compounds trapped on Tenax TA were identified by combined gas chromatography (Pye 204) and mass spectrometry (VG MM 7070 F), using the thermal desorption device, the capillary column and the temperature conditions described before (GC/MS). Mass spectra were recorded in the electron impact mode at an ionisation voltage of 70 eV and scanned from $m/z = 300$ to 25 with a cycle time of 1.8 s (Olafsdottir, 1985; Badings, 1985).

Table 1: Odour descriptors used for sniffing port analysis

Dutch expression*	English translation
champignon geur	mushroom like
cacao	cocoa
fris	fresh
fruitig	fruity
gras	green
kunstmatig	artificially
lijm	glue like
metaal	metallic
muf	musty
plastic	synthetic
prikkelend	astringent
wee	sickly
zoetig	sweet
zuurtjes	candy like

* Original Dutch words used by the assessors; they may be not an exact synonym of the English translation.

RESULTS AND DISCUSSION

The use of nose clips by the assessors in the flavour intensity studies diminishes significantly ($p<0.05$) the flavour intensities of the commercial sample incubated at 40 °C for 24 hours for each descriptor except for the descriptor "dry". The latter appears to be a kind of mouthfeel (Table 2).

These findings indicate that most of the descriptors are related to volatile substances. Therefore, combined gas chromatography and sniffing port analysis is appropriate for further studies.

Table 2: Mean score (± SD) of intensity (%) obtained for each descriptor on a visual analogue scale of 180 mm with (N) and without (WN) the use of nose clips (n=11).

	mineral water					
	reference		20 °C/24 hr[*]		40 °C/24 hr[*]	
descriptors	N	WN	N	WN	N	WN
metallic	28±24	34±25	20±19	20±18	23±21	51±23
synthetic	20±18	39±32	15±18	27±23	18±22	79±21
dry	41±28	34±22	45±24	41±22	35±31	55±26
astringent	34±25	31±18	30±23	28±21	28±25	48±22
musty	13±10	30±23	14±11	31±28	18±16	58±23
sickly	21±18	34±24	18±23	24±17	23±18	58±20

[*] temperature/time conditions for incubation of commercial mineral water samples "as is".

Figure 1A presents the average FID chromatograms (n=5) of control (REF) and commercial LDPE packed water samples, which were incubated at 20 °C (BD 20) and 40 °C (BD 40). Reconstructed chromatograms of the components detected at the sniffing port by more than 4 assessors at the same time, are shown in figure 1B. Sniffing port analysis of dummy samples revealed, that detection of a smell at the sniffing port by less than 5 out of 10 assessors, can be considered as "noise". Table 3 presents the compounds identified by GC/MS, and the odour described by the assessors at the sniffing port. Glue-like is a new descriptor, while synthetic, metallic, musty, astringent and sickly were also generated in our previous study (Linssen et al, 1991). The test pouches used then were made of aluminium and LDPE coated at a relatively high temperature of 310 °C, so they are not directly comparable with a commercial LDPE lined package. Moreover, the pouches were immediately folded and sealed after LDPE lining to prevent evaporation of volatile compounds. In that case,carbonyls were identified to be responsible for the taint described. However, as can be seen in table 3, mainly aromatic hydrocarbons, like toluene, xylenes, n-propylbenzene, C_3- and C_4-alkyl benzenes, and some unknowns, were found to be the compounds corresponding with the descriptors given by the assessors. Berg (1980) reported similar compounds in PE granulate and indicated that C_3- and C_4-alkyl benzenes have an intense plastic smell. In figure 1A differences between test samples and control mineral water were notably found for three groups of compounds: isomers of C_3-alkyl benzenes with retention times 33-34 min (peaks 12-16) and two groups of unknown isomers with retention times 41-43 min (peaks 22-26) and 46-47 min (peaks 27-29). At the same retention times sniffing port assessors agreed upon the detection of volatile compounds from the LDPE packed water samples (Figure 1B). The absence of a descriptor for 2,2,4,6,6,- pentamethylheptane is remarkable, because this compound has been suggested for the off-flavour sometimes found in LDPE packed products (Vom Bruck and Hammerschmidt, 1977). In table 3 pentanal, hexanal and octanal were found to be present in the LDPE packed mineral water sample, which was incubated at 40 °C. Also the unknown compounds are (probably branched) carbonyl compounds. The latter are hardly present in the control sample, but appear as higher peaks in the FID chromatograms of the LDPE packed mineral water samples after incubation.

Semi-quantitative analysis showed that the concentrations of the compounds identified by GC/MS are in the very low ppb range. Ethylbenzene, pentanal, heptanal, decanal and 2-nonanone are below a level of 2 ppb; it can be expected that none of the compounds exceed a level of 10-15 ppb.

In conclusion: The main descriptors for volatile compounds (separated by gas chromatography) in commercial mineral water packed in LDPE lined aluminium/cardboard, are: synthetic, astringent, musty, sickly, glue-like and metallic. Isomers of C_3-alkyl benzenes and isomers of unknown carbonyls appear to be responsible for these descriptors. The concentrations of these

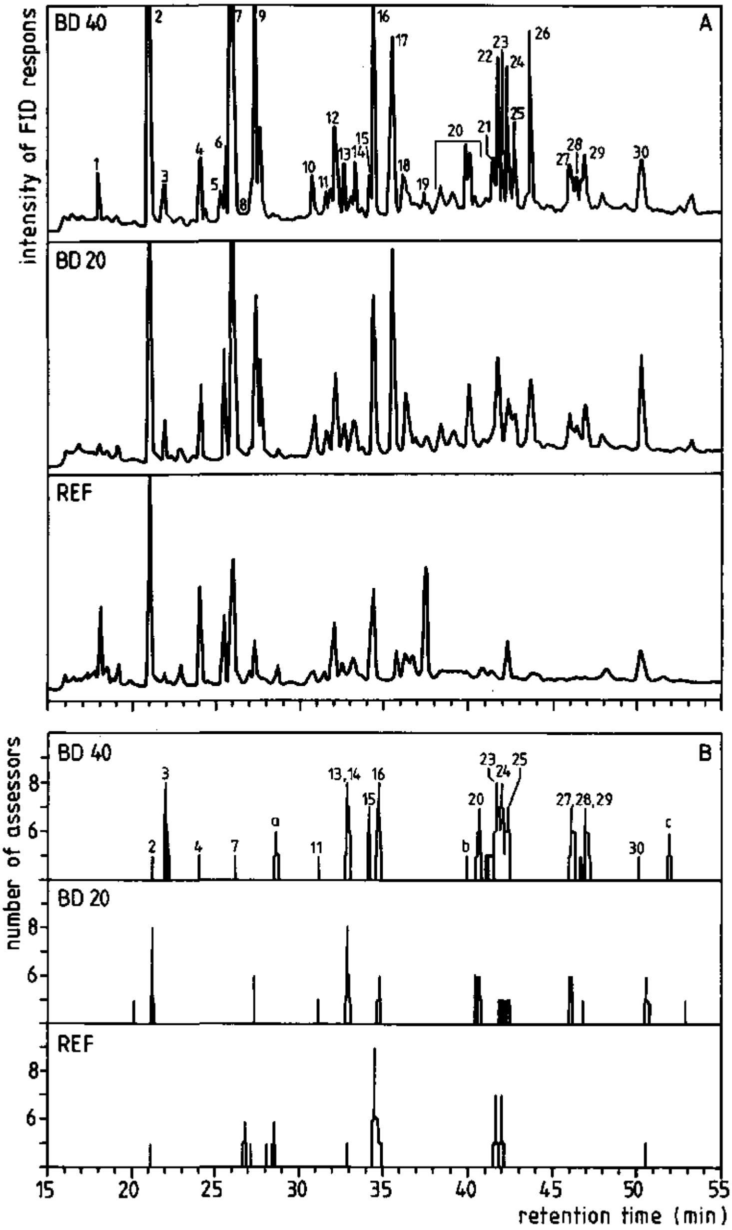

Figure 1: Reconstructed chromatograms of dynamic headspace samples. Average of 5 replicates (A) and the number of assessors out of 10, who had a smell impression at the sniffing port at the same time (B). Corresponding responses have the same symbol. REF: control; BD 20 and BD 40: LDPE packed water samples incubated at 20 °C and 40 °C, respectively.

Table 3: Volatile compounds of mineral water incubated at 40 °C in LDPE lined aluminium/cardboard packages and their odour description

Peakno[*]	compound	odour description
1	pentanal	
2	toluene	synthetic, astringent, glue-like, "other"
3	hexanal	green, artificially, mushroom fruity, musty, "other"
4	4-OH-4Me-2-pentanone	musty, fruity, "other"
5	isopropylacetate	
6	ethylbenzene	
7	p-, m-xylene	synthetic, musty, astringent,
a		astringent, artificially, metallic, mushroom, "other"
8	heptanal	
9	o-xylene	
10	α-pinene	
11	n-propylbenzene	fruity, sweety, "other"
12	C_3-alkyl benzene	
13	C_3-alkyl benzene	synthetic, astringent, glue-like
14	C_3-alkyl benzene	musty, astringent, metallic
15	octanal	sickly, musty, candy-like, "other"
16	C_3-alkyl benzene	astringent, fresh, sweet, candy-like, fruity
b		fresh, green, mushroom, sweet
17	2,2,4,6,6, pentamethylheptane	
18	C_3-alkyl benzene	
19	limonene	
20	C_4-alkyl benzene + branched alkanes	artificially, fresh, mushroom, musty, metallic, sweet, sickly
21	2-nonanone	
22	unknown	
23	nonanal	astringent, cocoa, mushroom, "other"
24	unknown	synthetic, glue-like, metallic, artificially, musty
25	unknown	synthetic, glue-like, metallic
26	unknown	
27	unknown	synthetic, astringent, sickly metallic, artificially
28	unknown	
29	unknown	synthetic, glue-like, metallic musty, artificially
30	decanal	artificially, synthetic, metallic
c		synthetic, sweet, glue-like, "other"

[*] Peakno corresponds with the peak symbols in figure 1

compounds are in the very low ppb range. Storage at higher temperatures for a longer time can imply a risk for flavour deterioration.

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PART IV. PRODUCT QUALITIES OF FOOD IN CONTACT WITH POLYSTYRENE AND POLYETHYLENE (ABSORPTION)

Absorption is one of the main phenomena of the interactions between food and packaging. Absorption of flavour components from the food matrix by the packaging material can result in an alteration of flavour characteristics, which has a detrimental effect on product quality. Important parameters for absorption are both the chemical and physical nature of packaging material and the composition of food.

Chapter 9 deals with the absorption of flavour compounds from artificially flavoured commercial drink yoghurts by polyethylene packaging material. The investigation has been made under practical conditions of use. Absorption of flavour compounds is of considerable interest because: (1) absorbed flavours cannot contribute to the aroma of a product and (2) the balance of flavour compounds in the packed product is disturbed due to differential sorption of volatiles.

Chapter 10 demonstrates the importance of juice composition, e.g. with and without addition of pulp particles, for the absorption of limonene by polystyrene and polyethylene from imitation juice and juices . Nowadays fruit juices, like orange juice with added pulp particles, become more and more popular. Most of these juices are currently packed in polyethylene laminated aluminium/paper board packages.

Chapter 9. Absorption of flavour compounds by packaging material: Drink yoghurts in polyethylene bottles[*]

ABSTRACT

Artificially flavoured commercial drink yoghurts with different flavours and their packaging material high density polyethylene (HDPE) were studied for absorption of volatile compounds using a dynamic headspace technique. Volatiles were identified by combined gas chromatography and mass-spectrometry. Short chain carbon compounds seemed to remain preferably in the yoghurt, while compounds of medium chain length were present both in the drink yoghurt and the packaging material. In general, compounds with more than 8 carbon atoms and highly branched components tended to be absorbed by the polyethylene packaging material. So, they would contribute less to the flavour of the products. Apolar alkanes from HDPE stayed in the plastic material because of the polar nature of a watery product like drink yoghurt.

[*] Linssen, J.P.H., Verheul, A., Roozen, J.P., and Posthumus, M.A., International Dairy Journal, 2, 33 - 40, (1992).
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INTRODUCTION

The food industry is introducing aseptic processing systems for the production of shelf-stable foods. Aseptically packed fruit juices in polyethylene (PE) lined cartons are well known. The packaged product is in direct contact with the interior PE lining just like ultra high temperature (UHT)-sterilized flavoured drink yoghurts in PE blow-moulded bottles. In such containers sorption of flavour compounds by the packaging material is liable to occur. The compounds removed can no longer function as flavour compounds and thus the perceived sensory quality of the product may be changed.

Mannheim et al (1987) showed that the concentration of limonene is substantially reduced in an aseptic brick style package in only a few days storage at 25 °C. Dürr et al (1981) reported significant losses of D-limonene, neral, geranial, octanal and decanal from orange juice stored in PE lined packages. Also Hirose et al (1988) found a rapid loss of limonene into PE packaging material at 24 °C and 35 °C storage. Shimoda et al (1988) described in model studies that sorption of flavour components increased with increasing carbon chain length.

In the present study, sorption of volatiles from artificially flavoured commercial drink yoghurts into PE packaging material was investigated under practical conditions of use.

MATERIALS AND METHODS

Materials

Three different types of commercial flavoured drink yoghurts were bought in a local store in Wageningen (The Netherlands). Trade names of the samples were: Yovol drink yoghurt-1-vrucht (raspberry); Yovol drink yoghurt-2-vrucht (strawberry/apple) and Yovol drink yoghurt-3-vrucht (peach/apricot/pear). The yoghurts contain less than 0.1% fat and are a blend of 89.7% yoghurt (made from defatted milk), 8.9% sugars, 1.0% fruit juice(s), 0.4% stabilizer, artificial flavouring and colouring agents. The yoghurts were packed in high density polyethylene (HDPE) bottles, of which empty control bottles were kindly provided by the manufacturer (Coberco Zuivel Nijkerk, The Netherlands). The plastic bottles were prepared from ELTEX B 4020 LG or B 2020 LG HDPE (Solvay, Brussels, Belgium) and produced by the blow-moulding process. The wall of the bottles was composed of three layers: a PE layer with 2% carbon sandwiched by PE layers with 5% TiO_2 to create white coloured inner- and outer layer (Van der Kort, 1988).

Methods

Dynamic headspace sampling was used to prepare the samples. Drink yoghurt (50 ml) was diluted with 200 ml distilled water and purged at 37 °C with a stream of purified nitrogen stream at a flow rate of 30 ml/min for 30 min. A cold trap, cooled with ethanol at - 10 °C, was used to freeze out the water vapour, and afterwards the volatiles were trapped on Tenax TA 35/60 mesh (Alltech Nederland BV, Zwijndrecht, The Netherlands). Emptied bottles were rinsed carefully with distilled water and dried overnight at room temperature. Emptied bottles and control bottles were topped with a tube containing Tenax TA and sampled directly by flushing the bottle with purified nitrogen at a flow rate of 30 ml/min for 90 min (Olafsdottir et al, 1985). The trapped volatiles were identified on a coupled gas chromatograph (Pye 204) and mass-spectrograph (VG MM 7070 F). A thermal desorption/cold trap device (Chrompack T.C.T. Injector 16200) was used to transfer the volatile compounds from the Tenax on to a fused silica capillary column (Supelcowax 10; length 60 m, i.d. 0.25 mm). The carrier gas was helium at 18 psi (120 kPa) . An initial oven temperature of 40 °C for 4 min was used, followed by heating at a rate of 2 °C /min up to 92 °C and then at 6 °C/min up to 270 °C and finally a temperature hold at 270 °C for 4 min (Badings et al, 1985). Mass spectra were recorded in the electron impact mode at an ionization voltage of 70 eV and scanned from m/z = 300 to 25 with a cycle time of 1.8 sec.

RESULTS AND DISCUSSION

Figure 1 shows the chromatograms of the drink yoghurt and the emptied bottle of Yovol-3. It indicates that flavour compounds with higher retention times and higher molecular weights were likely to be absorbed by the packaging material. Besides flavour compounds, the chromatogram of the bottle (Fig. 1b) shows n-alkanes, branched alkanes and siloxane, which were found by analysis of the volatiles of the control bottles also. Vom Bruck and Hammerschmidt (1977) and Berg (1980) also identified such compounds as volatiles from PE, which probably arise from a C_{12} mineral oil fraction used as a solvent in the production of PE. Interestingly, these compounds remained in the plastic and are not likely to migrate into an aqueous product like drink yoghurt (absent in Fig. 1a). Other compounds present in the chromatograms of Fig. 1, as styrene, benzaldehyde and acetophenone, are reported to be always present, when one uses dynamic headspace techniques with Tenax as adsorbent (Schaeffer, 1989; Lewis and Williams, 1980).

Table 1 presents the major volatile compounds in the yoghurts Yovol 1 (raspberry), Yovol 2 (strawberry/apple) and Yovol 3 (peach/apricot/pear) and Table 2 presents the major volatile compounds of the HDPE bottles corresponding to the yoghurts. All the volatiles listed in these tables are reported by Maarse and Visscher (1989) as volatiles of the fruits labelled on the Yovol drink yoghurts. However, some flavour compounds, e.g. lactones, were not found, because of the very low content of fruit juices in the drink yoghurts. Tables 1 and 2 also show that certain volatiles preferentially remained in the drink yoghurts while others are easily absorbed by the packaging material. Compounds with short

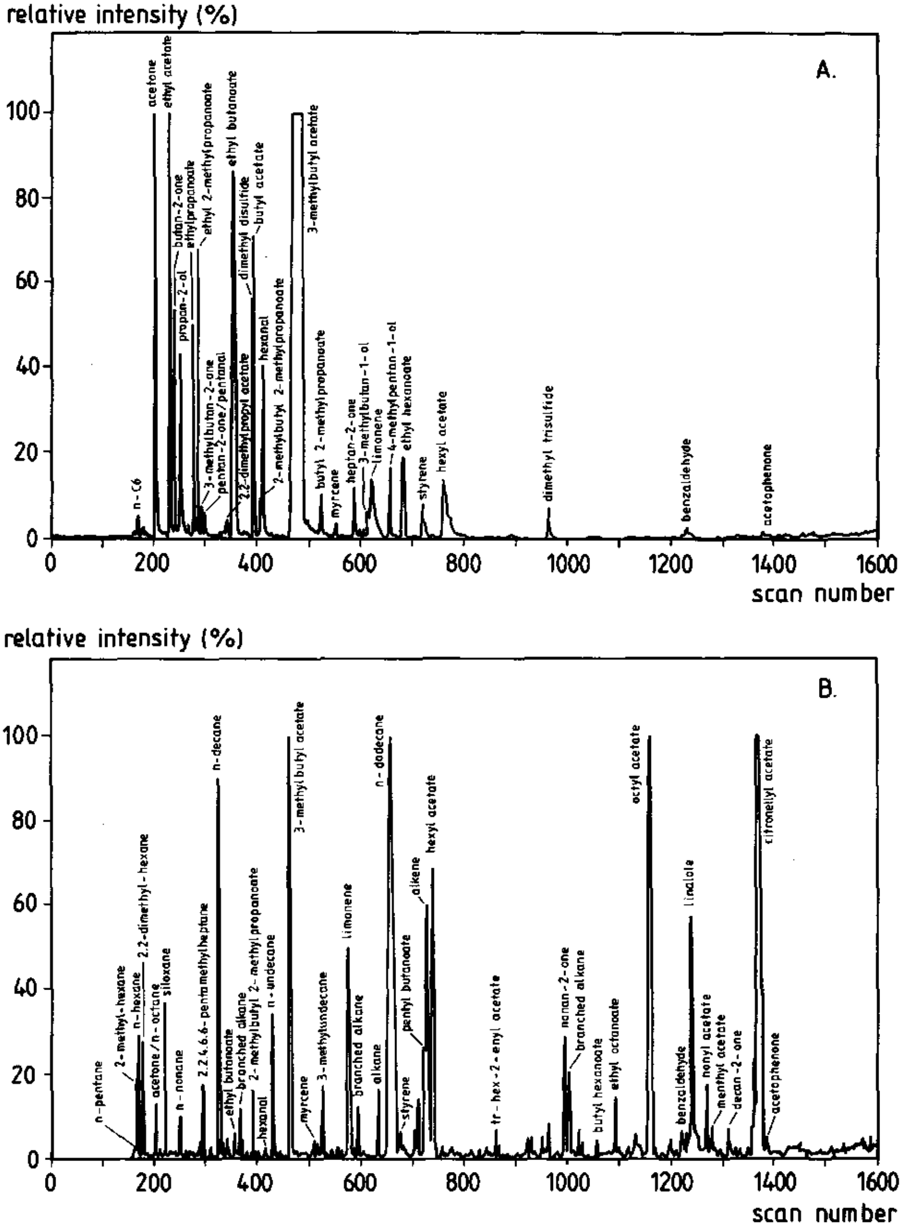

Figure 1: Reconstructed total ion current chromatograms of volatile compounds from drink yoghurt Yovol-3 (A) and its HDPE bottle (B) obtained by dynamic headspace technique

carbon chains and sulphides remained in the aqueous phase of th drink yoghurt while compounds with medium carbon chain length (u to eight carbon atoms) were found in the drink yoghurts as well a in the packaging material. Compounds with longer carbon chains an highly branched chains, and compounds with more complex structur seem to be absorbed by the packaging material. The contribution o these compounds to the flavour of the products might be reduced.

A PE distribution ratio was defined by Shimoda et al (1988) a the ratio of the components in PE and in solution. This rati increased from n-alcohols to n-aldehydes to aliphatic esters an benzoates. Thus, esters are very susceptible to absorption into P packaging materials. These findings were confirmed under th practical circumstances of the present case study. Mainly, th higher molecular weight esters were absorbed by the HDPE bottles As a consequence of differential sorption of volatiles, th balance of flavour compounds in the packed yoghurts might b disturbed. It does not seem worthwhile to use these volatiles fo the enrichment of flavour when food products are packed in contac with PE packaging materials, because they will not reach th consumers as was intended by the manufacturer.

CONCLUSION

Polyethylene packaging material is able to absorb volatil compounds from artificially flavoured drink yoghurts. Esters wit more than eight carbon atoms and also highly branched component are very susceptible to absorption by PE. These compounds will no contribute to the flavour of foodstuffs when they are absorbed b the packaging material.

Table 1: Major volatile compounds found in drink yoghurts identified by GC/MS

	area (computer counts of total ion current (TIC chromatograms)		
compounds	Yovol-1	Yovol-2	Yovol-3
alcohols			
propan-2-ol	1413	228	1609
butan-1-ol	-	574	-
3-methylbutan-1-ol	-	1061	500
4-methylpentan-1-ol	-	-	722
carbonyl compounds			
hexanal	137	1622	1634
hexen-2-al	-	1499	-
butan-2-one	1000	1200	1468
3-methylbutan-2-one	-	-	289
pentan-2-one/pentanal	18	-	270
heptan-2-one	651	533	686
esters			
ethyl acetate	10588	612	5090
2-methylpropyl acetate	3238	-	-
ethyl propanoate	-	417	1400
ethyl 2-methylpropanoate	-	-	1900
2,2-dimethylpropyl acetate	-	-	189
methyl 2-methylbutanoate	-	15972	-
methyl 3-methylbutanoate	-	821	-
ethyl butanoate	3066	14590	3575
ethyl 2-methylbutanoate	2489	35535	-
butyl acetate	-	-	2902
2-methylbutyl 2-methylpropanoate	-	1100	422
ethyl 3-methylbutanoate	-	2720	-
3-methylbutyl acetate	2983	38565	50906
butyl 2-methylpropanoate	-	-	484
ethyl hexanoate	-	18143	1084
hexyl acetate	1063	565	1891
cis-hex-3-enyl acetate	1662	-	-
sulphur compounds			
dimethyl sulphide	500	690	-
dimethyl disulphide	-	-	460
dimethyl trisulphide	182	182	471
hydrocarbons			
α-pinene	193	-	-
myrcene	101	-	151
limonene	7044	-	1911

- not detected

Table 2: Major volatile compounds identified by GC/MS in HDPE bottle which had contained drink yoghurts

	area (computer counts of total ion current (TIC chromatograms)		
compounds	Yovol-1	Yovol-2	Yovol-3
alcohols			
3-methylbutan-1-ol	-	190	-
hexan-1-ol	-	1073	-
linalole	-	-	2492
carbonyl compounds			
hexanal	155	227	74
hexen-2-al	-	270	-
nonanal	-	126	-
heptan-2-one	-	301	-
nona-2-one	1790	701	1016
decan-2-one	-	-	181
γ-damascone	104	-	-
α-ionone	288	-	-
β-ionone	400	-	-
esters			
ethyl acetate	720	-	-
2-methylpropyl acetate	313	-	-
ethyl butanoate	583	837	131
ethyl 2-methylbutanoate	1126	2148	-
2-methylbutyl 2-methylpropanoate	-	706	300
3-methylbutyl acetate	1126	4463	4670
pentyl butanoate	-	-	900
ethyl hexanoate	-	15256	-
3-methylbutyl 2-methylpropanoate	-	878	-
3-methylbutyl 3-methylbutanoate	-	420	-
hexyl acetate	3955	941	3042
3-methylbutyl 3-methylbutanoate	-	1535	-
cis-hex-3-enyl acetate	4774	1073	-
tr-hex-3-enyl acetate	95	-	233
butyl hexanoate	-	-	116
ethyl octanoate	-	-	452
octyl acetate	347	1119	7384
2-methylpropyl octanoate	-	461	-
nonyl acetate	-	-	571
benzyl acetate	484	-	-
menthyl acetate	-	-	487
citronellyl acetate	-	-	10063
hydrocarbons			
myrcene	220	-	96
limonene	14756	579	2111
naphtalene	368	-	-

- not detected

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Chapter 10. Influence of pulp particles on limonene absorption into plastic packaging materials*

ABSTRACT

Limonene can be rapidly absorbed by packaging materials polystyrene and polyethylene. About 75% of the limonene present in an imitation juice is absorbed by both type of plastics within 2 days. Absorption of limonene from an orange juice with and without an extra addition of pulp was 20% and 40%, respectively, after holding for 3 weeks. It appears to be that the presence of pulp particles diminishes absorption of limonene by packaging materials.

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*Linssen, J.P.H., Reitsma, J.C.E. and Roozen, J.P., Proceedings "Food Packaging: A Burden or an Achievement ?, Reims, 5-7 juni 1991, vol 2, 24.18 - 24.20 (1991).

INTRODUCTION

The fruit juice industry has widely accepted aseptic filling for fruit juices. Most aseptically filled juices are packed into carton packs, in which polyethylene used as an interior lining, is in direct contact with the packed juices. When packaging juices in such containers an absorption of flavour compounds into the plastic film is liable to occur, resulting in a change of taste or odour. When these compounds are selectively removed by the packaging material they no longer function as flavour components and thus the perceived quality of the product is diminished.

Several researchers have demonstrated that packaging materials absorb flavour components. Mannheim et al (1987) reported that the concentration of limonene is substantially reduced in only a few days at 25 °C storage in a brick style aseptic package. Dürr et al (1981) reported significantly losses of d-limonene, neral, geranial, octanal and decanal from orange juice stored in polyethylene lined packages. Shimoda et al (1988) found that the sorption of flavour compounds increased with carbon chain length. Hirose et al (1988) reported a rapid loss of limonene into polyethylene at 24 °C and 35 °C, respectively.

Nowadays fruit juices, as orange juice and grapefruit juice, with addition of pulp particles become more and more popular. Although limonene is not the most important contributor to flavour in citrus products, it is an important indicator of overall flavour presence in this food category (Delassus and Hilker, 1987).

In the present study the effect of pulp particles in orange juice on limonene absorption into polyethylene and polystyrene was investigated.

MATERIALS AND METHODS

Materials

0.3 mm thick Low density polyethylene (LDPE) film, extruded at 280 °C and 1 mm thick polystyrene sheet, extruded at 223 °C was kindly provided by DOW Benelux NV, Terneuzen (The Netherlands).

The following samples were prepared: a model solution consisted of 10% sucrose, 0.5% citric acid, 0.035% orange juice essence on water base, 0.015% orange peel oil and 10% isopropanol; orange juice was prepared by reconstituting concentrate of 50 °Brix to a juice of 12 °Brix; orange juice with pulp was prepared in the same way, followed by and addition of 8.7% pulp. 0.1% Potassium sorbate was added to prevent microbial spoilage.

Sample preparation

The interaction between the plastics and samples was investigated by immersing polyethylene (8 pieces; 1.5 x 1.25 cm) and polystyrene (5 pieces; 1 x 3 cm) double sided in 50 ml liquid in a conical flask. The surface/volume ratio was 6 dm^2/l, which is common in practical applications. The flask was stoppered, the content mixed and stored in the dark at room temperature. Once a day each sample was mixed and the amount of absorbed limonene was determined at certain time intervals.

Methods

The plastics were extracted five times with 10 ml pentane and combined in a 50 ml measuring flask. 1 ml internal standard (62.5 µl butylbenzene in 100 ml pentane) was added and the measuring flasks was filled up with pentane. Approximately 4 ml solution was poured into small glass vials and water free sodium sulphate was added.

The amounts of limonene in the extracts were analyzed by injection of approximately 1 μl into a gas chromatograph, Carlo Erba, model 4160, equipped with a flame ionisation detector (FID) and a cold on-column injector. The analysis were carried out on a 25 m x 0.32 mm i.d. fused silica capillary column, CP sil 5 CB. The detector temperature was 280°C. The following temperature programme was used: an initial hold for 3 min at 65 °C and then 20 °C/min to 105 °C. The same procedure was carried out for determination of the initial amount of limonene in the solutions.

RESULTS AND DISCUSSION

Figure 1 shows the absorption of limonene by the plastics. The figure shows clearly that both types of plastic absorb limonene very quickly. 70 - 80% of the limonene present in the model solution is already absorbed after 2 days. This confirms the statement of Jabarin and Kollen (1988) that components with solubility parameters similar to the plastic tend to sorb significantly. Absorption of a hydrocarbon type component, like limonene, is high in hydrocarbon type of plastics, like polyethylene and polystyrene. Within three weeks approximately 40% limonene present in the orange juice and 20% limonene present in the juice with added pulp particles is absorbed by the plastics.

Similar results were found by Hirose et al (1988) who reported a loss of limonene into LDPE of 20% from orange juice within 3 days at 24 °C and 29% at 35 °C at a surface/volume ration of 9 dm^2/l. After 11 days the loss of limonene was respectively 56% at 24 °C and 62% at 35 °C. Mannheim et al (1988) found a 58% loss of limonene from aseptically filled orange juice stored at 25 °C during 15 days. Dürr et al (1981) reported a 40% loss of limonene from orange juice into PE within 6 days. Although the initial rate for absorption is higher for PE the amounts absorbed by polyethylene and polystyrene are similar after 3 weeks.

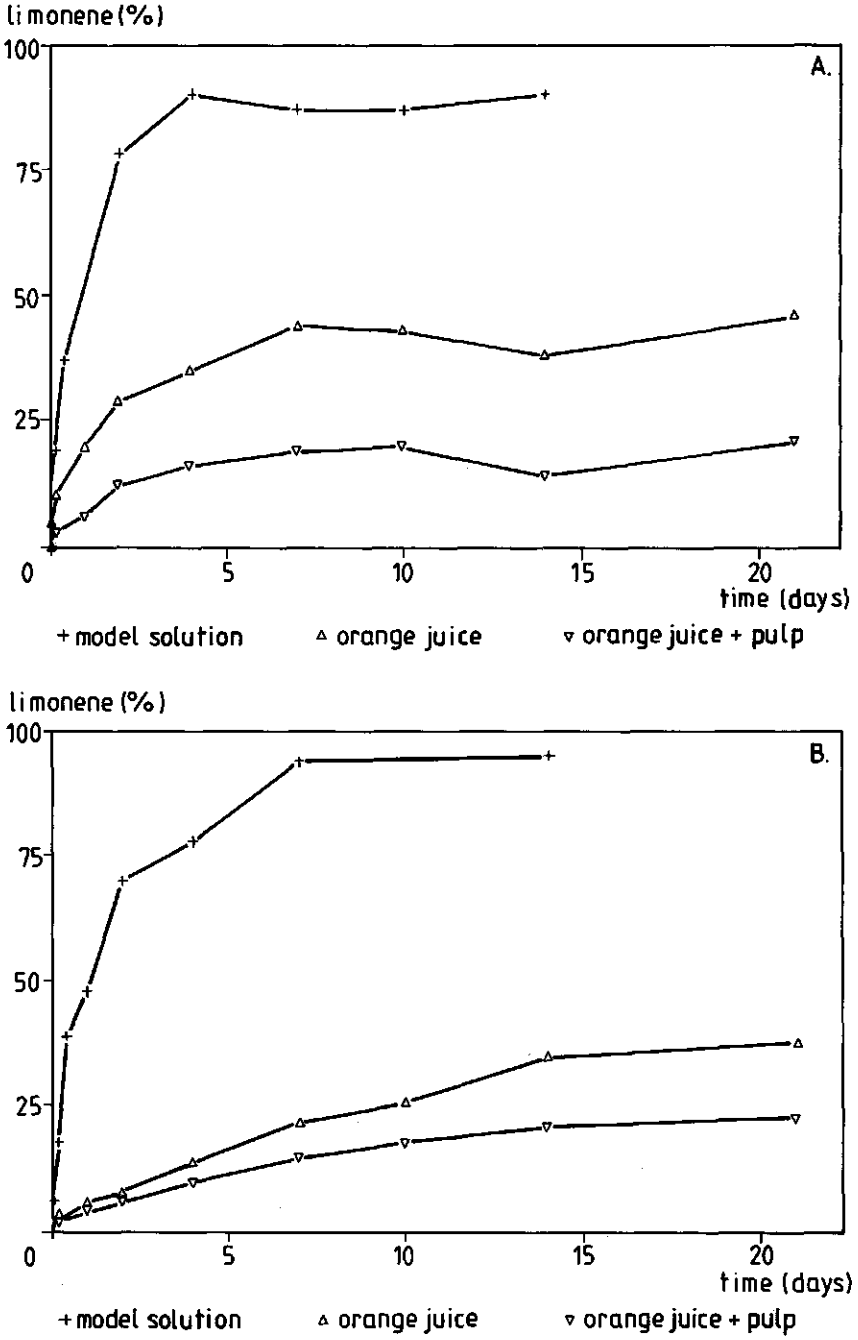

Figure 1: Absorption of limonene into polyethylene (A) and polystyrene (B)

The presence of pulp particles results in a decreased absorption of limonene. This suggests that pulp particles are holding limonene in equilibrium with the watery phase, which subsequently decreases the absorption by the plastics.

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Chapter 11 Concluding remarks

Migration of styrene monomer from polystyrene depends on the matrix of the food: a high fat content results in increased migration. On the other hand sensory recognition thresholds of styrene increase also in products with higher fat contents. The divergence of these two influences hinders accurate estimation of the intensity of off-flavour in foodstuffs caused by migration of styrene. Storage conditions like temperature, have a big effect on the level of migration of styrene: Migration is much faster at higher temperatures. Polymer composition has also an influence on the level of migrated styrene: a higher content of high impact polystyrene in blends with general purpose polystyrene increases the migration of styrene.

High impact grade polystyrene types have to be analyzed with care, because cutting of this type of polymer results in damages of rubber particles ("cut-edges"). Due to leakage of styrene from the rubber particles, the level of migrated styrene is increased considerably. Reduction of the content of styrene in the polymer decreases the level of migrated styrene linearly. This may give a broader application of polystyrene in the food packaging industry, because of the diminished risk of taste deterioration of the packed product.

Vapour phase migration should not be ignored in the study of migration of styrene to solid foods. The cell sampling method is recommended for migration tests, because other sampling methods overestimate the migration of styrene from samples of high impact grade polystyrene types. The best choice for the evaluation of migration is to sample products in their package directly from the production line and conduct the test with the packed product under given time and temperature conditions.

Food products can acquire a taint due to migrants from the packaging material. The perceived intensity of a taint depends on the flavour characteristics of the product itself. For instance, milk chocolate flakes are more sensitive to styrene off-flavour than plain chocolate flakes, probably caused by a lower bitter intensity. Taste recognition threshold concentrations of styrene increase linearly with increasing fat content for O/W emulsions and yoghurts. At their threshold levels the concentrations of styrene were constant in both the aqueous phases and the vapour phases of the emulsions. The latter finding could be of interest for practical use. Analysis of styrene in the vapour phase of a product would be predictive for an off-flavour caused by styrene, without doing time consuming sensory analysis.

Studies on migration of components from polyethylene packaging materials is much more difficult, because several components can migrate in the product and be responsible for the development of an off-flavour. Water tainted by contact with polyethylene packaging material has been described by 6 attributes: synthetic, astringent, musty, sickly, metallic and dry. In a study with mineral water packed in polyethylene laminated aluminium/cardboard packages mainly hydrocarbons like C_3- and C_4-alkyl benzenes were found and described at the sniffing port by the attributes mentioned above. Probably these hydrocarbons find their origin in a C_{12} mineral oil fraction used for the production of polyethylene. Also carbonyl compounds were found, and they could be responsible for a taint in polyethylene packed products. Carbonyl compounds are often formed during polymerisation and subsequent extrusion coating. Migration of the compounds mentioned is faster at higher temperatures and consequently the chance for taste deterioration was found to be increased in that case.

Polyethylene packaging material is able to absorb volatile compounds. Absorption depends on the chemical composition of the packed food. In aqueous products like drink yoghurts the compounds with more than 8 carbon atoms and highly branched components tend to be absorbed by polyethylene. Differential sorption of flavour compounds from the packed product disturbs its flavour balance. Such compounds are not worthwhile to add, because they do not reach the consumer as was intended by the manufacturer. A practical solution sometimes used is adding an excess of absorbing flavour compounds.

Interactions between food and packaging materials have to be studied thoroughly before a polymer is accepted as a food packaging application. Evaluation of these interactions with food simulants is important for considering legal and safety aspects. However, food simulants alone give insufficient information about the interaction of the food itself and the package, because food simulants resemble food products only on physical properties, and are thus not very useful to make firm conclusions about the food product. Although simulants can provide information about quality aspects in some cases (Chapter 6), prediction of the effect of packaging materials on food quality from model systems is limited. Therefore, the use of the food itself is highly recommended for studying food packaging interactions in relation to food quality aspects. Sensory as well as instrumental analysis are essential tools for gathering the information needed to deduce about the suitability of a package for a foodstuff.

SUMMARY

Polystyrene (PS) and polyethylene (PE) used for packaging of food were studied on their effect on product quality. Different types of PS were tested: General purpose polystyrene (GPPS), high impact polystyrene (HIPS, which contains a dispersed rubber phase) and several blends of these types. PS contains detectable amounts of residual monomer, which has an unpleasant odour and/or taste. When the concentration in the polymer is too high, it could give a taint to the packed product after migration. Several aspects of migration of styrene monomer were evaluated. Migration of styrene increases with increasing fat content in a product, but the styrene migrated was only a small part (3% after incubation during 14 days at 40 °C) of the total amount of residual styrene present in the polymer.

The sampling method used influences the level of migrated styrene in corn oil. Immersion sampling of cut pieces of high impact grade PS types showed a much higher level of migrated styrene than utilisation of sampling cells. Cut edges of the samples cause a high initial leakage of styrene from cut rubber particles. Also vapour phase migration exists and is of considerable interest for solid foods. In that case integral contact between the surface of the packed product and PS is not possible. For GPPS only little differences were found between the sampling methods. The composition of PS influences the level of migrated styrene. Migration increases linearly with increasing amount of HIPS in blends with GPPS. Migration is faster at higher temperatures and is linearly dependent on the content of residual styrene monomer in the polymer.

Some food products were also studied on a taint caused by styrene migration. Cocoa powders for drinks and chocolate flakes were exposed to pieces of PS and sensorily evaluated using short-cut signal detection measures on differences

between control and test samples and on recognition of styrene. Compared to control samples significant differences were detected in milk -and plain chocolate flakes, but not in the cocoa powders for drinks. Styrene was clearly recognized in the flakes at contents of approximately 1.2 ppm. Recognition threshold values of styrene were sensorily determined in oil in water emulsions with different fat contents (3 - 30%). The recognition threshold concentrations of styrene increase linearly with increasing fat content in the emulsions and ranged between 0.3 - 2.1 ppm. Recognition thresholds of styrene in yoghurts (0.1 - 3% fat) were found in the range 36 - 171 ppb. At their threshold levels the concentrations of styrene in the aqueous phases and the vapour phases of the emulsions were similar at 15 and 0.41 ppb, respectively. In commercial yoghurts packed in PS the actual styrene contents ranged between 2 - 11 ppb at their expiring date. These results indicate that PS is an acceptable packaging material for yoghurts.

PE is widely used in the food packaging industry as mono -or multilayer system as well as laminated with carton and aluminium. A sensory descriptive analysis was carried out for a taint in water packed in test pouches made of PE lined aluminium. The taint could be described by 6 attributes: synthetic, astringent, musty, sickly, metallic and dry. Dynamic headspace analysis of water in contact with the PE layer of the test pouches showed (C_4 - C_{11}) carbonyl compounds, which could be responsible for the taint described. Commercial mineral water packed in PE laminated aluminium/cardboard was evaluated by combined gas chromatography and sniffing port analysis after incubation at different temperatures. Similar descriptors as mentioned were found for individual components, which were migrated into mineral water. These components were identified as mainly aromatic hydrocarbons, while also carbonyls were detected. The concentrations of these migrants in the mineral water were in the low ppb range (10-15 ppb).

Finally, some aspects of absorption of aroma compounds from artificially flavoured commercial drink yoghurts into PE bottles were studied. Short chain compounds appeared to remain preferably in the yoghurts, while compounds of medium chain length were present in both the drink yoghurts and the packaging material. Compounds with more than 8 carbon atoms and highly branched components tend to be absorbed by the PE packaging material and could, therefore, contribute less to the flavour of the product. The influence of juice composition on the absorption of flavour components was illustrated for limonene absorption from an imitation juice and from juices with and without addition of pulp. The presence of pulp particles diminishes the extent of absorption of limonene by the packaging materials.

SAMENVATTING

De kwaliteit van levensmiddelen verandert als gevolg van interacties met verpakkingen. Dit fenomeen werd bestudeerd voor de materialen polystyreen (PS) en polyethyleen (PE). Verschillende typen PS waren onderwerp van studie: General purpose polystyreen (GPPS), high impact polystyreen (HIPS: bevat rubber, gedispergeerd in de PS matrix) en diverse mengsels van deze typen. Polystyreen bevat aantoonbare hoeveelheden van het monomeer, dat een onaangename geur en/of smaak heeft. Na migratie kan het verpakte produkt een smaak - en/of geurafwijking aannemen. Verschillende aspecten met betrekking tot migratie van dit monomeer (styreen) werden onder de loep genomen. Wanneer een produkt meer vet bevat, is de migratie van styreen hoger; hoewel de hoeveelheid gemigreerd styreen slechts een klein gedeelte (3% na 14 dagen incubatie bij 40 °C) is van de totale hoeveelheid styreen, dat in het polymeer aanwezig is.

De gebruikte methode van bemonstering beïnvloedt de migratie waarden zeer sterk. Wanneer bij een bemonstering de geknipte randen van HIPS in contact komen met olie, is de migratie aanzienlijk hoger dan bij een bemonstering in de zogenaamde cellen. Deze, vooral initieel, verhoogde migratie van styreen wordt veroorzaakt door versneld uittreden van styreen uit beschadigde rubberdeeltjes op de geknipte randen. Ook werd migratie via de gasfase vastgesteld. Dit is van belang voor vaste levensmiddelen. Immers in dat geval is volledig contact tussen oppervlak van het produkt en verpakking niet mogelijk. Bij GPPS werden slechts geringe verschillen geconstateerd bij het gebruik van verschillende methoden van bemonstering. De samenstelling van PS beïnvloedt ook de migratie van styreen. Migratie neemt lineair toe met een hoger gehalte aan HIPS in mengsels met GPPS. Migratie is sneller bij een hogere temperatuur en lineair afhankelijk van het gehalte aan styreen

in het polymeer.

De verandering van smaak van levensmiddelen door migratie van styreen werd sensorisch onderzocht in cacaopoeders, die worden gebruikt voor de bereiding van cacaodranken, en in chocoladevlokken. Deze produkten werden blootgesteld aan in stukken geknipt polystyreen en vervolgens sensorisch geëvalueerd. Ten opzichte van onbehandelde monsters werden verschillen waargenomen in melk -en pure chocolade vlokken, maar niet in de dranken, die waren bereid met de aan PS blootgestelde cacaopoeders. Styreen werd duidelijk herkend bij concentraties van ongeveer 1,2 ppm in de vlokken.

Herkenningsdrempels van styreen werden bepaald in olie in water emulsies met verschillende vetgehalten (3 - 30%). De hierbij behorende herkenningsdrempels stijgen lineair met de vetgehalten in de range 0,3 - 2,1 ppm. Als herkenningsdrempels van styreen in yoghurts (0,1% - 3% vet) werd 36 - 171 ppb gevonden. Bij deze drempels werden voor de concentraties aan styreen in de continue (water) fase en de gasfase van de emulsies en de yoghurts telkens dezelfde waarden gevonden, nl. respectievelijk 15 en 0,41 ppb. In polystyreen verpakte yoghurts uit de handel bedroeg het styreengehalte 2 - 11 ppb, dus ver beneden hun herkenningsdrempels. Dit houdt in dat polystyreen een acceptabele verpakking is voor yoghurt en dat een risico op smaakafwijking nauwelijks aanwezig is.

Polyethyleen (PE) wordt veel toegepast in de verpakkingsindustrie als een -of meerlagig systeem al dan niet met karton en/of aluminium. Een beschrijvende sensorische analyse werd uitgevoerd met water, dat in contact was geweest met PE, dat bij een relatief hoge temperatuur was aangebracht op aluminium. Er werden 6 attributen geselecteerd: kunstmatig, prikkelend, muf, droog, wee en metaal-achtig. Bemonstering van het water door doorleiden van stikstof leverde C_4 - C_{11} aldehyden en ketonen op, die verantwoordelijk zouden kunnen zijn voor de gevonden beschrijvingen. Mineraal water uit de handel, dat verpakt was in PE/aluminium/karton, werd in de verpakking geïncubeerd bij verschillende temperaturen en op geur onderzocht met behulp van proefpersonen, die roken aan een snuffelpoort gekoppeld aan een gaschromatograaf. Deze personen gebruikten dezelfde beschrijvingen als boven genoemd. De vluchtige verbindingen werden geïdentificeerd met GC/MS. Er werden hoofdzakelijk aromatische koolwaterstoffen aangetroffen, hoewel ook aldehyden aanwezig waren. De concentraties van de migranten in het water liggen in het lage ppb bereik (10-15 ppb).

Tenslotte werden enkele aspecten onderzocht van de absorptie van aromastoffen aan de wand van PE flessen van commerciële drinkyoghurts met toegevoegde kunstmatige geurstoffen. Verbindingen met korte ketens blijven voornamelijk in de yoghurts, terwijl componenten met middellange ketens zowel in de yoghurt als in de PE verpakking verblijven. Componenten met ketens langer dan 8 koolstofatomen en hoog vertakte verbindingen absorberen bij voorkeur aan het verpakkingsmateriaal. Geabsorbeerde verbindingen kunnen niet meer bijdragen aan de smaak van een produkt. De invloed van de samenstelling van een produkt op de absorptie van aromacomponenten aan PE wordt geïllustreerd door vergelijking van de absorptie van limoneen vanuit een imitatiesap en vanuit sinaasappelsappen met en zonder toegevoegde pulp. Pulpbestanddelen verminderen de mate van absorptie van limoneen aan het verpakkingsmateriaal.

CURRICULUM VITAE

Jozef Linssen werd geboren op 24 augustus 1954 te Roermond. In 1974 behaalde hij het Gymnasium β diploma aan het Bisschoppelijk College te Roermond. In datzelfde jaar begon hij met de studie Levensmiddelentechnologie aan de Landbouwhogeschool te Wageningen, alwaar hij in 1981 zijn studie met het predicaat "met lof" afrondde. Vanaf 1 mei 1981 tot 1 januari 1986 was hij werkzaam aan het Laboratorium van het Ministerie van Financiën te Amsterdam, alwaar hij sectiehoofd was van een van de laboratoria. Per 1 januari 1986 trad hij in dienst van de Landbouwuniversiteit als universitair docent bij de Vakgroep Levensmiddelentechnologie, sectie Levensmiddelenchemie en -microbologie. Hij schreef op verzoek van DOW Benelux NV een onderzoeksvoorstel met als thema "Invloed van verpakkingsmateriaal op de kwaliteit van levensmiddelen".