Migration and sensory properties of plastics based nets used as food contacting materials under ambient and high temperature heating conditions

Michael Kontominas, Antonios Goulas, Anastasia Badeka, Alexandra Nerantzaki

Migration and sensory properties of plastics based nets used as food contacting materials under ambient and high temperature heating conditions

Journal:	*Food Additives and Contaminants*
Manuscript ID:	TFAC-2005-312.R1
Manuscript Type:	Original Research Paper
Date Submitted by the Author:	16-Feb-2006
Complete List of Authors:	Kontominas, Michael; University of Ioannina, Department of Chemistry Goulas, Antonios; University of Ioannina, Department of Chemistry Badeka, Anastasia; University of Ioannina, Department of Chemistry Nerantzaki, Alexandra; University of Ioannina, Department of Chemistry
Methods/Techniques:	Sensory analysis, Chromatography - GC/MS, Chromatography - Headspace
Additives/Contaminants:	Food simulants, Food contact materials, Migration
Food Types:	

Migration and sensory properties of plastics based nets used as food contacting materials under ambient and high temperature heating conditions

M.G. Kontominas*, A.E. Goulas, A.V. Badeka and A.Nerantzaki

Lab of Food Chemistry and Technology

Department of Chemistry

University of Ioannina

Ioannina 45110

* Author to whom correspondence should be addressed (e-mail: mkontomi@cc.uoi.gr)

Abstract

Overall migration from a wide range of commercial plastics-based netting materials destined to be used as either meat or vegetable packaging materials into the fatty food simulant isooctane or the aqueous simulant distilled water respectively was studied. In addition sensory tests of representative netting materials were carried out in bottled water in order to investigate possible development of off-odor/taste and discoloration in this food simulant as a result of migration from the netting material. Sensory tests were supplemented by determination of the volatile compounds' profile in table water exposed to the netting materials using SPME-GC/MS. Test conditions for packaging material/food simulant contact and method of overall migration analysis were according to the EU directives 90/128 and 2002/72. The results showed that for both PET and polyethylene based netting materials overall migration into distilled water ranged between 11.5 and 48.5 mg/L, well below the upper limit (60 mg/L) for overall migration from plastics packaging materials set by the EU. The overall migration from netting materials into isooctane ranged between 38.0 and 624.0 mg/L, both below and above the EU upper limit for migration. Sensory tests involving contact of representative samples with table water under refluxing (100^{o}C/4h) conditions showed a number of the netting materials produced both off-odor and/or taste as well as discoloration of the food simulant rendering such materials unfit for the packaging of foodstuffs in applications involving heating at elevated temperatures. GC/MS analysis showed the presence of numerous volatile compounds being produced after netting materials/water contact under refluxing conditions. Even though it is extremely difficult to establish a clear correlation between sensory off-odor development and GC/MS volatile compounds' profile, it may be postulated that plastics oxidation products such as hexanal, heptanal, octanal and 2,6 di-tert-butylquinone may contribute to off-odor development using

commercially bottled table water as a food simulant. Likewise compounds such as carbon disulfide, [1,1' biphenyl]-2-ol and propanoic acid, 2 methyl 1-(1,1 dimethyl)-2-methyl-1,3-propanediyl ester probably originating from cotton and rubber components of netting materials may also contribute to off-odor/taste development.

Key words: plastics based nets, migration, sensory properties

Introduction

Plastics-based threads mainly polyester (polyethylene terephthalate, PET) and polyethylene (PE) are being used for the production of nets or sacks for the packaging of a number of foodstuffs such as processed meats (smoked and/or baked meats, bacon, ham, sausages) and vegetables such as potatoes. While most of vegetable products are peeled before they are consumed (others such as potatoes may be consumed without peeling). National and international authorities such as the US FDA and the EU have set restrictions with regard to the migration behavior of such packaging materials in order to protect consumers from possible migration of low molecular weight compounds from the container into the foodstuff. The situation becomes critical in cases where such plastics nets are used as wrapping materials for meat cuts which are subsequently cooked in conventional ovens for approximately 1 h at temperatures often exceeding 100^{o}C. Meat depending on its fat content (pork, lamb, beef etc.) in contact with such plastics netting materials may result in considerable migration especially under extreme conditions of temperature (Rossi 1993). The European Union (EU) has published a number of Directives setting the basic rules for migration testing of packaging materials intended to come into contact with foodstuffs, laying down the list of simulants, test conditions, and test methods to be used for testing overall migration of constituents from packaging materials (EEC 1982, EEC 1985, EEC 1990).

According to Directive 90/128/EEC the overall migration limit is 10 mg for all transferred substances per dm^2 of the food contact material surface. Alternatively when measuring the surface area of the packaging material is not possible the migration limit is expressed as 60mg/kg of food or mg/L of food stimulant. Testing with aqueous simulants involves evaporating the simulant to dryness and determining the residue gravimetrically. Testing with fatty food simulants (olive oil or approved alternatives: sun flower oil or synthetic triglyceride

HB 307) involves weighing of the plastic before and after simulant contact. The amount absorbed into the plastic is determined by extraction and GC analysis (EEC 1990, CEN 1991).

The use of vegetable oils as food simulants presents a number of difficulties and is a time-consuming procedure (Figge 1996, Van Battum *et al.* 1982). Some alternative fatty food simulants have been proposed – mainly solvents which can be evaporated such as isooctane or heptane and ethanol-water mixtures. Many of the problems encountered in applying fat migration testing can be overcome by using the above alternative solvents because overall migration can been determined directly be weighing a residue after evaporation of the solvent (Baner *et al.* 1992, Baner *et al.* 1994, De Kruijf and Rijk 1996, Hamdani and Feigenbaum, 1996).

Practical Guide N.1 of the Commission of EU (EEC 1993) and Directive 97/48/EC (EC 1997) refer to isooctane as one of the alternative fatty food simulants. De Kruijf and Rijk (1996) reported that isooctane is a suitable alternative food simulant for overall migration testing under various time and temperature conditions. Hamdani and Feigenbaum (1996) found that the affinities of isooctane and sunflower oil to all migrants were similar and isooctane can be considered as an alternative fatty simulant for plasticized PVC.

Migration of low molecular weight compounds (plasticizers, thermal and light stabilizers, antioxidants, residual monomers, solvents etc.) from plastics packaging materials into foodstuffs and food simulants has been the subject of a large number of studies (Badeka and Kontominas 1996, Castle et al. 1988, Castle et al. 1988, Dilettato *et al.* 1991, Gilbert and Startin 1981, Kondyli et al. 1990, Nerin et al. 1998, Perlstein and Orme 1985, Roberts 1988, Zygoura et al. 2006). The migration of such additives or contaminants from polymeric food

packaging materials into food may be separated into three different but interrelated stages. Diffusion within the polymer, dissolution at the polymer-food interface and dispersing into bulk food (Lau and Wong 2000).

Apart from the obvious problem of potential toxicity of such low molecular weight migrating species, another possibility is the development of off-odors/off-tastes as well as discoloration as a result of such migration. In both cases the foodstuff becomes unfit for consumption (Figge 1996, Hodges 1991).

Thus the objectives of the present work were (1) to determine the overall migration from a series of commercial plastics-based netting materials into the food simulants: distilled water and isooctane, (2) to run sensory tests in an effort to evaluate possible deterioration of sensory properties of the food stimulant: bottled table water (odor, taste, color) used as a result of migration and (3) to possibly relate sensory attributes (mainly odor) to GC profile of this food simulant using SPME/GC-MS.

Materials and Methods

Materials

Netting and threat samples were based on PET or PE and were supplied by a local commercial company representing several foreign manufacturing companies. The identity of the materials is listed in Table 1. Analytical grade isooctane was supplied by Merck (Darmstadt, Germany). Water used was double distilled or commercially bottled water.

Migration experiments

Either rectangular strips of net samples (6 g in weight) or plastics threads comprising the raw material for the manufacture of commercial nets (6 g in weight) were immersed in 100 ml of food simulant (distilled water or isooctane) in glass beakers. Beakers were covered with Parafilm® so as to avoid evaporation of simulant during contact period and kept in a thermostatically controlled chamber at 40±0.5°C for ten days (EU directive 2002/72). For isooctane the time/temperature contact conditions were chosen on the basis of EU Directive 97/48 to be 4h/60°C. Following the time/temperature predetermined contact, samples were removed and the simulant was placed in a 250 ml pre-weighed Erlenmeyer flask and evaporated to dryness in a rotary evaporator. The Erlenmeyer flask containing the residue of evaporation was kept in a thermostatically controlled chamber at 105±1.0°C for 1h followed by 1h in a dessicator and then weighed. A Sartorius analytical balance, model BF221S, capable of weighing to 0.1 mg was used. The overall migration was calculated in mg/L of food simulant. For each net or thread sample three determinations were performed and final migration values were the mean of the three determinations.

Sensory testing

Sensory testing was carried out using commercially bottled table water packaged in PET as the food simulant. Representative net or thread samples were brought into contact with table water and heated for 4 h at 100°C under refluxing conditions. Heated, under the same conditions, table water (not in contact with plastics nets) was used as the control sample. Evaluation was carried out by a 5-member panel of judges experienced in sensory attributes of water. The judges evaluated taste, odor and color of the aqueous simulant on an intensity scale between 0 and 4 where 0 represented no difference between experimental and control sample, 1 represented a slight difference, 2 represented a moderate difference, 3 represented a

large difference and 4 represented a very large difference. Samples receiving a score larger than 1 were considered to be unacceptable.

Determination of volatile compounds' profile of food simulant using SPME-GC/MS

Heated as described above net samples were placed (10mL) along with a micro-stirring bar in a 20mL glass vial (20×72mm) and 10μL of internal standard solution (20μg/ml of 4-methyl-2-pentanone) which was capped with a PTFE/rubber septum and sealed with an aluminum crimp cap. Solid phase micro-extraction (SPME) was performed with a 50/30 μm divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) fiber mounted to a SPME manual holder assembly (Supelco, Bellefonte, CA, USA). The sample vial was placed in a 40^{o}C water bath and stirred at high speed. After allowing 5 min for the sample to equilibrate at 40^{o}C, the septum piercing needle of the SPME apparatus was pushed down to expose the DVB/CAR/PDMS fiber to the vial headspace. After 30 min of exposure time with constant stirring, the fiber was retracted into the needle assembly, removed from the vial and inserted in the injector of GC/MS instrument.

GC/MS analysis conditions

Gas chromatographic (GC) analysis of volatile compounds adsorbed onto the SPME fiber was carried out on a HP-5MS (5% phenyl methyl siloxane) 30m×0.25mm×0.25μm fused-silica capillary column (J&W Scientific, Folsom, CA, USA). Flow rate of the helium carrier gas was 0.7mL/min. A Hewlett-Packard 6890 series gas chromatograph equipped with a Hewlett-Packard 5973 mass selective detector was used. During the injection phase, the injector was operated in the split mode (2:1 split ration) at a temperature of 260^{o}C. For thermal desorption, the SPME fiber remained in the injector for 5 min. The initial column temperature was 40^{o}C and was maintained at this temperature for 4 min. The column was heated to 280^{o}C at a rate

of 8°C/min and held at 280°C for 5 min. Mass spectrometric (MS) conditions were as follows: source temperature 230°C; quadropole temperature 150°C; acquisition performed in electron impact (E.I.) mode (70eV) by 2.48 scans/s; the mass range m/z: 30-330. The temperature of the transfer line was held constant at 290°C. Peak identification was performed by comparison of mass spectra of eluting peaks to those of the Willey library (Wiley, version 275). Spectral match was based on target and top ten ions as well as relative mass intensity signals.

Results and Discussion

Overall migration

Overall migration values in contact with aqueous or fatty simulant are given in Table 1. Samples #1 and #8 were polyester based materials also containing rubber and cotton threads destined to be used for wrapping boiled meat and salami products respectively, while sample #4 also containing rubber and cotton threads was a polyethylene based material destined to be used for wrapping smoked meat products. Sample #2, 3 and #5-7 were PET based nets also containing rubber destined to be used for wrapping meat cuts to be baked in a conventional oven or boiled. Thus according to EU Directives 85/572 and 97/48 two sets of test contact conditions were chosen for migration testing: (1) 4h/60°C and (2) 4h/100°C under refluxing using isooctane as the fatty food simulant. As shown in Table 1 differences in overall migration values for these samples were not statistically different ($p>0.05$) between the two sets of conditions. Thus all subsequent testing with regard to isooctane was carried out under the former conditions (4h/60°C). All of these samples gave migration values higher than the upper limit of 60mg/L set by the EU. At first, one may attribute such high migration values to constituents such as rubber and cotton threads in plastics based nets in which case Directives 90/128 and 2002/72 do not cover such composite materials. In order to test this hypothesis, manufacturers were asked to provide PET threads used to produce PET based nets (i.e. net

samples # 3, 5 and 6). Such PET threads (i.e. samples #12, 13 and 15 respectively) gave migration values significantly lower than the former. If recorded migration values are divided by a factor of 4 as suggested in EU Directive 85/572 for meat and meat products then resulting migration values between 19 and 55 mg/L are obtained for samples #12, 13 and 15 respectively which are below the above reported upper limit for overall migration. The same rationale holds for samples #4 versus #14 the first giving a very high migration value as compared to the second, consisting solely of PE thread resulting in a migration value within the limit for overall migration (60mg/L). In other cases such as those of samples #1 and 8 the migration value is such that if divided by a factor of 4 falls within the above mentioned migration limit.

Of PET thread samples #16-18 destined for wrapping salami products and samples #19-22 destined for wrapping baked and boiled meat products, samples #18, 21 and 22 meet the above migration criterion, while samples #16, 17, 19 and 20 do not. It is unclear why these four PET samples gave such high migration values given that migrating species from PET packaging materials include mostly PET oligomers responsible for low migration values (Castle *et al.* 1989).

The rest of the net samples namely #9-11 were made solely of polyethylene and were intended for the packaging of unprocessed vegetables such as potatoes, onions and garlic and were thus tested against distilled water as the food simulant. It is clear that overall migration values for all these samples are well below the upper limit of 60mg/L for migration. It should be stressed, at this point that with the exception of potatoes which might be consumed with their skin intact, most vegetables are peeled before consumption and thus even high overall migration values will most probably not pose any kind of health risk for the consumer.

In general migration values in isooctane were significantly higher than corresponding migration values in distilled water. This can be explained by the capability of isooctane to penetrate into the polymer matrix causing swelling of the polymer and thus changes in its structure. The consequence is an increase in the diffusivity of the potential migrants and a resulting increase in both rate and amount of migrating species (Shepherd 1982).

Castle *at al.* (1990) studied overall migration of a series of plastics packaging materials including polyolefins (simulant: water, contact conditions: 100^{o}C/60min) and PET trays (simulant: olive oil, contact conditions: 175^{o}C/120min) in high temperature food-use applications and reported very low migration values < 2 and 4 mg/dm^2 respectively. Czerniawski and Pogorzelska (1997) investigated overall migration of various plastics materials including PET sheets into a number of food simulants including isooctane and reported very low migration values in the order of 0.3mg/dm^2. Castle *et al.* (1989) studied the migration of PET oligomers from PET trays into sausages (contact conditions: 204^{o}C/60min) from PET roasting bags into roasted beef and pork (contact conditions: 204^{o}C/90min) and reported low migration values in the range of 0.4 and 0.8mg/kg respectively. Finally Badeka *et al.* (2003) reported overall migration values for a series of multilayer flexible food packaging materials based on PE containing a layer of recycled PE in distilled water and isooctane in the range of 3.6-10.5 mg/L (0.17-0.52 mg/dm^2) for distilled water and 70.2-102 mg/L (3.5-5.3 mg/dm^2) for isooctane.

To the best of the authors' knowledge these are no reports in the literature involving overall migration values from plastics based netting materials into either food simulants or foodstuffs.

Sensory evaluation

Results of the sensory evaluation are shown in Table 2. Representative samples made of PET and PE were chosen with overall migration values both above and below 60mg/L (samples #1 through 15). Of all the samples tested only seven (#2, 9-12, 14 and 15) received a score lower or equal to 1 (sensory acceptability limit). Usual undesirable sensory attributes recorded, included development of yellowish discoloration, opaque appearance, slight to moderate plastic off-odor and slight to moderate plastic off-taste. At this point it should be mentioned that the migration behavior of present netting materials does not necessarily correlate well with sensory characteristics of the contacting food stimulant, i.e material #1 exhibits an acceptable level of migration while at the same time it significantly deteriorates sensory characteristics of the contacting aqueous simulant. On the other hand material #2 exhibits a high migration value while it does not substantially deteriorate sensory characteristics of the contacting aqueous simulant. Finally a set of netting materials (#9-12, 14 and 15) exhibits migration values below the upper limit for migration and at the same time substantially retains desirable sensory characteristics of the contacting aqueous food simulant. A general trend shown in Table 2 is that netting materials containing rubber or rubber+cotton result in more objectionable sensory attributes as compared to materials consisting solely of plastics (i.e. #1-8 versus # 12-15). An exception to this trend is material #13 consisting of PET thread producing objectionable taste and color. The reason for this is unclear.

Determination of volatile compounds

Volatile compounds' profiles of representative netting materials (i.e. #2, 8 and 12) including control samples are given in Table 3. Samples were chosen on one hand to represent composite materials made of PET + rubber (#2), of PET + rubber + cotton (#8), of PE + rubber + cotton (#4) and of PET thread (i.e. #12) and on the other hand on the basis of

increasing off-odor development in the food simulant: commercially bottled table mineral water after refluxing (100^{o}C/4h). Semi-quantitative determination of volatiles was achieved using 4-methyl-2pentanone as internal standard**.** Comparison for example between control sample and samples #2 and #8 leads to the suggestion that either a number of compounds show up in the aqueous simulant after contact with the netting material which do not exist in the control sample or the concentration of other compounds significantly increases in the aqueous simulant after contact with the netting material. Examples of the former case are: hexanal, heptanal, octanal, benzaldehyde, butylated hydroxytoluene and 2,6 di(t-butyl)-2,5 cyclohexadien-1-one while an example of the latter case is: 1,2 benzenedicarboxylic acid, bis (2-methyl propyl) ester and butylated hydroxytoluene (BHT).

What should be stressed at this point is that numerous volatile compounds show up in the control sample which was table water packaged in PET. Thus their presence is largely justified. What we were interested in seeing were differences in volatiles produced as a result of heating either plastics based nets or plastics threads. It is also apparent that numerous compounds identified in composite netting materials absent from both the PET thread (sample #12) and the control such as carbon disulfide; [1,1' biphenyl]-2-ol; propanoic acid-2-methyl 1-(1,1 dimethyl)-2-methyl-1,3-propanediyl ester etc. are most probably related to specific treatments applied to the rubber and/or cotton component of the netting materials.

Even though it is extremely difficult to establish a clear correlation between volatile compounds' profile and sensory (odor) evaluation it may be postulated that oxidation products of plastics materials such as 2-ethyl hexanal, heptanal, octanal and 2,6-di-tert butyl quinone probably contribute to off-odor development in heated plastics based netting materials. Riganakos *et al.* (1999) determined the volatile compounds' profile of a series of

plastics packaging films including LDPE and PET/PE laminates and reported a large number of volatile compounds samples, most of which were found in the present study. Ezquerro *et al.* (2003) quantified volatile organic compounds in a composite flexible packaging material based on polyethylene using HS-SPME and reported a series of compounds among which hexanal, heptanal, decanal, nonanal, decane, toluene and 2-ethyl hexanal were also found in the present study. Similar compounds were also identified by Bravo *et al.* (1992) as odor-active species resulting from thermal oxidation of polyethylene.

Rose (1991) determined volatile extractives from microwave susceptor PET based materials (conditions: Temp=125^{o}C, time=3-4 min) and reported the production of 72 compounds including many of the compounds determined in the present study**.**

Conclusions

Based on data of the present study it is concluded that PE netting materials used for the packaging of vegetable products (i.e. potatoes) are absolutely safe as packaging materials. Netting materials based on PET used for packaging of meat products should be carefully selected especially for applications involving heat treatment at high temperatures (i.e. baked and boiled products) in which case they can produce off-odor/taste as well as discoloration problems.

Acknowledgements

The authors would like to thank the Unit of Food Standardization of the University of Ioannina for providing access to the GC/MS instrument.

References

BADEKA, A., GOULAS, A.E., ADAMANTIADI, A., and KONTOMINAS, M.G., 2003, Physicochemical and mechanical properties of experimental coextruded food-packaging films containing a buried layer of recycled low density polyethylene. *Journal of Agriculture and Food Chemistry*, **51**, 2426-2461.

BADEKA, A., and KONTOMINAS, M.G., 1996, Effect of microwave heating on the migration of dioctyladipate and acetyltributylcitrate plasticizers from food-grade PVC and PVDC/PVC films into olive oil and water, *Z Lebensm Unters Forsch*, **202**, 313-317.

BANER, A., BIEBER, W., FIGGE, K., FRANZ, R., and PIRINGER, O., 1992, Alternative fatty food simulants for migration testing of polymeric food contact materials. *Food Additives and Contaminants*, **9**, 137-148.

BANER, A.L, FRANZ, R., and PIRINGER, O., 1994, Alternative fatty food simulants for polymer migration testing. In: Mahtlouthi, M., editor. Food packaging and preservation. Blackie Academic and Professional, London, p. 23.

BRAVO, A., HOTCHKISS, J.H., ACREE, T.E., 1992, Identification of odour-active compounds resulting from thermal oxidation of polyethylene. *Journal of Agricultural and Food Chemistry*, **10**, 1881-1885.

CASTLE, L., GILBERT, J., JICKELLS, S.M., and GRAMSHAW, 1988, Analysis of the plasticizer acetyltributyl citrate in foods by stable isotope-dilution gas-chromatography mass-spectrometry. *Journal of Chromatography,* **437**, 281-286

CASTLE, L., JICKELLS, S.M., GILBERT, J., and HARRISON, N., 1990, Migration testing of plastics and microwave-active materials for high temperature food-use applications. *Food Additives and Contaminants*, **7**, 779-796.

CASTLE, L, MAYO, A, CREWS, C., and GILBERT, J., 1989, Migration of PET oligomers from PET plastics into foods during microwave and conventional cooking and into bottled beverages. *Journal of Food Protection*, **52**, 337-342.

CASTLE, L., SHARMAN, M., and GILBERT, J., 1988, Gas-chromatographic mass-spectrometric determination of epoxidized soybean oil contamination of foods by migration from plastic packaging. *Journal of the Association of Official Analytical Chemists*, **71**, 1183-1186.

CEN, 1991, Methods of test for materials and articles in contact with foodstuffs. In: CEN Guide to selection of conditions and methods to test. Part I. Cen draft standard TC194 N11, Brussels.

CZERNIAWSKI, B., and POGORZELSKA, Z., 1997, Investigations on overall migration of various plastics materials and articles used in contact with foodstuffs. *Packaging Food and Science*, **10**, 261-270.

DE KRUIJF, N., and RIJK, M., 1996, The suitability of alternative fatty food simulants of overall migration testing under both low and high-temperature test conditions. In: International Life Science Institute (ILSI) (ed), Food Packaging Ensuring the Quality and Safety of Foods. Proceeding of the International Symposium on Food Packaging, Sept. 11-13, Budapest, Hungary; ILSI, Brussels, Belgium, p. 27.

DILETTATO, D., ARPINO, P.J., NGUYEN, K., and BRUCHET, A., 1991, Investigation of low mass oligomers and polymer additives from plastics. Part II: Application to polyolefin soxhlet extracts. *Journal of High Resolution Chromatography*, **14**, 335-342

EC, 1997, Commission Directive No. 97/48/EC of 29 July 1997 amending Council Directive 82/711/EEC laying down the basic rules necessary for testing migration of constituents of plastic materials and articles intended to come into contact with foodstuffs. *Official Journal of the European Communities*, **L 222**, 12 August 1997, pp. 10-15.

EEC, 1982, Council Directive No. 82/711/EEC of 19 December 1985 laying down the basic rules necessary for testing migration of constituents of plastic materials and articles intended to come into contact with foodstuffs. *Official Journal of the European Communities*, **L 297**, pp. 26-30.

EEC, 1985, Council Directive No. 85/572/EEC of 19 December 1985 laying down the basic rules necessary for testing migration of constituents of plastic materials and articles intended to come into contact with foodstuffs. *Official Journal of the European Communities*, **L 372**, 31 December 1985, pp. 14-21.

EEC, 1990, Council Directive No. 90/128/EEC of 23 February 1990 relating to plastic materials and articles intended to come into contact with foodstuffs. *Official Journal of the European Communities*, **L 75**, 21 March 1990, pp. 19-39.

EEC, 1993, *Practical Guide No.1. A Practical Guide for Users of EEC Directives on Materials and Articles Intended to Come into Contact with Foodstuffs*. Commission of the European Communities. Documents CS/PM/2024, 2 April 1993.

EEC, 2002, Commission Directive 2002/72/EEC of 6 August 2002 relating to plastic materials and articles intended to come into contact with foodstuffs, *Official Journal of the European Communities*, **L 220**, 15/08/05, pp. 18-58.

EZQUERRO, O., PONS, B., and TENA, M.T., 2003, Direct quantification of volatile organic compounds in packaging materials by HS – SPME - gas chromatography - mass spectroscopy. *Journal of Chromatography A*, **985**, 247-257.

FIGGE, K., 1996, Plastics. In: Katan, L.L., editor. Migration from the food contact materials. Blackie Academic and Professional, London, UK, p.77.

GILBERT, J., and STARTIN, J.R., 1981, Single-ion monitoring of styrene in foods by coupled mass-spectrometry automatic headspace gas-chromatography. *Journal of Chromatography*, **205**, 434-437.

HODGES, K., 1991, Sensory directed analytical concentration techniques for aroma-flavor characterization and quantitation. In: Risch S.J. and Hotchkiss J.H., editors, Food and Packaging Interactions II, ACS Symposium Series, **473**, 174-186.

HAMDANI, M., and FEIGENBAUM, A., 1996, Migration from plasticized poly(vinyl chloride) into fatty media: Importance of simulant selectivity for the choice of volatile fatty simulants. *Food Additives and Contaminants*, **13**, 717-729.

KONDYLI, E., DEMERTZIS, P.G., and KONTOMINAS, M.G., 1992, Migration of dioctylphthalate and dioctyladipate plasticizers from food-grade PVC films into ground-meat producst. *Food Chemistry*, **45**, 163-168.

LAU, O.W., and WONG, S.K., 2001, Contamination in food from packaging material. *Journal of Chromatography A*, **882**, 255-270.

NERIN, C., RUBIO, C., CACHO, J., and SALFRANCA, J., 1998, Parts-per-trillion determination of styrene in yoghurt by purge-and-trap gas chromatography with mass spectrometry detection. *Food Additives and Contaminants*, **15**, 346-354.

PERLSTEIN, P., and ORME, P., 1985, Determination of polymeric hindered-amine light stabilizers in plastics by pyrolysis-gas chromatography. *Journal of Chromatography*, **325**, 87-93.

ROBERTS, D.C.E., 1988, Enforcement of regulations governing plastics, materials and articles in contact with food in the UK. *Food Additives and Contaminants*, **5**, 509-512.

RIGANAKOS, K.A., KOLLER, W.D., EHLERMANN, D.A.E., BAUER, B., and KONTOMINAS, M.G., 1999, Effects of ionizing radiation on properties of monolayer and multilayer flexible food packaging materials. *Radiation Physics and Chemistry*, **54**, 527-540.

ROSE, W.P., 1991. Determining volatile extractives from microwave susceptor food packaging. In: Risch, S.J., and Jotchkiss J.H., editors, Food Packaging Interactions II, ACS Series, **473**, 67-78

ROSSI, L., 1993, European Community controls for high temperature testing of food contact materials. *Food Additives and Contaminants*, **10**, 615-620.

SHEPHERD, M.J., 1982, Trace contamination of foods by migration from plastics packaging - A review. *Food Chemistry*, **8**, 129-145.

VAN BATTUM, D., RIJK, M.A.H., VERPOOR, R., and ROSSI, L., 1982, Draft EEC method for the determination of the global migration of plastics constituents into fatty-food simulants - applicability to lacquers, plastics and laminates. *Food Chemical Toxicology*, **20**, 955-959.

ZYGOURA, P.D., GOULAS, A.E., RIGANAKOS, K.A., and KONTOMINAS, M.G., 2006, Determination of di-(2-ethylhexyl)adipate and acetyltributyl citrate plasticizers from food-grade PVC film into isooctane: Effect of gamma radiation. *Journal of Food Engineering*. In press.

Table 1. Identity and overall migration values (mg/L) of plastics netting materials into aqueous (distilled water) and fatty (isooctane) food simulants.

Sample #	Sample ID	Application	Overall migration (mg/L)		
			Distilled water 10d/40°C	Isooctane 4h/60°C	Isooctane 4h/100°C (reflux)
1	PET+rubber+cotton net	boiled meat products		120.0±4.8	131±7.2
2	PET+rubber net	boiled meat products		377±13.2	382±22.9
3	PET+rubber net	baked + boiled meat products		357.0±7.1	359±19.7
4	PE+rubber+cotton net	smoked meat products		624±21.8	645±28.4
5	PET+rubber net	ham		317±19.1	338±16.9
6	PET+rubber net	baked + boiled meat products		320±6.4	349±19.2
7	PET+rubber net	baked + boiled meat products		423±12.7	452±18.1
8	PET+rubber+cotton net	salami products		153±7.6	162±11.3
9	PE net	potatoes	13.0±0.5		
10	PE net	potatoes	36.2±1.8		
11	PE net	potatoes	33±1.9		
12	PET thread	baked and boiled meat products		75.0±4.5	
13	PET thread	baked and boiled meat products		114±5.0	
14	PE thread	potatoes		38±1.1	
15	PET thread	baked and boiled meat products		228.6±13.7	
16	PET thread	salami products		312.5±18.8	
17	PET thread	salami products		531.5±15.9	
18	PET thread	salami products		42.5±1.7	
19	PET thread	baked and boiled meat		287.0±8.6	
20	PET thread	baked and boiled meat		554.0±27.7	
21	PET thread	baked and boiled meat		74.0±3.0	
22	PET thread	baked and boiled meat		64.5±3.2	

PET = poly ethylene terephthalate
PE= polyethylene

Table 2. Sensory evaluation of plastic nets and threads materials subjected to refluxing (100°C/4h) in contact with distilled water.

	Sensory attributes			
Sample #	**Taste**	**Odor**	**Color**	**Comments**
Control	0	0	0	clear, no taste or odor
1	2	1	2	yellowish color, dispersion development, moderate plastic taste, slight odor
2	1	0	1	opaque, slight plastic taste
3	1.5	1	1	opaque, slight plastic odor and taste
4	1.5	1	1	opaque, slight yellowish color, slight plastic odor and taste
5	2.5	1.5	0.5	slightly opaque, slight plastic odor, moderate plastic taste
6	2	1.5	1	opaque, slight odor, moderate plastic taste
7	2.5	1	0.5	slightly opaque, slight plastic odor, moderate plastic taste
8	4	2	2.5	clear, yellow color, moderate plastic odor, very strong plastic taste
9	1	0	0	slight off-taste
10	1	1	0	slight off-taste and odor
11	1	1	0	slight off-taste and odor
12	1	1	1	opaque, slight off-odor/taste
13	2	1	2	yellowish color, dispersion development, slight plastic odor, moderate plastic taste
14	1	1	0	slight off-odor/taste
15	1	0	1	opaque, slight off-taste

Scoring scale:

0 – no difference with control sample
1 – slight difference with control sample
2 – moderate difference with control sample
3 – large difference with control sample
4 – very large difference with control sample

Table 3. Tentative identification and amounts (μg/mL) of volatile compounds of selected plastics netting materials using SPME-GC/MS.

RT*	Compound	control	sample #2	sample #4	sample #8	sample #12
1.66	2-Propanone		30.6	48.3	11.2	
1.83	Carbon disulfide		65.5	39.7	31.0	
2.10	Hexane	6.58	5.13	6.59	9.99	9.6
2.90	Butane, 2,2,3,3-tetramethyl	10.6	12.0	17.2	1.62	
3.18	pentanal				1.48	
3.70	4-methyl-2-pentanone (i.s.)	20	20	20	20	20
4.65	toluene		9.06	2.00	3.00	3.06
5.54	3-penten-2-one, 4-methyl-		4.50	5.47		
5.52	hexanal				1.00	
7.15	Benzene, ethyl-	8.37	3.57	3.97	4.93	5.88
7.38	Benzene, 1,3-dimethyl	15.5	15.6	18.6	19.8	19.6
7.98	Benzene, 1,4-dimethyl	11.1	6.19	5.76	12.6	7.43
8.26	n-heptanal				0.76	
9.70	Benzaldehyde		6.16	5.77	12.6	
10.37	6-methyl-5-hepten-2-one					2.22
10.71	Octanal		3.38		2.69	
11.28	2-ethyl hexanal		1.12	1.29	2.43	8.26
12.88	Nonanal	1.27	7.73	2.20	10.2	3.10
14.64	2-decanone				0.95	
14.84	Decanal	2.63	11.2	2.30	10.8	3.56
19.10	Geranyl acetone	0.84	1.92	1.71	2.77	1.30
19.39	2,6 di(t-butyl)-2,5-cyclohexadien-1-one		1.77	3.11	6.75	
19.81	pentadecane		1.80			
20.01	phenol, 2,4-bis(1,1-dimethylethyl) or *2,6-di-tert-butylquinone*			1.16	1.41	2.19
20.09	Butylated hydroxytoluene (BHT)	1.51	6.16	4.37	1.76	
20.14	[1,1'-biphenyl]-2-ol		1.50	1.79	1.38	
21.29	hexadecane		0.87	1.15		
21.33	Propanoic acid, 2 methyl, 1-(1,1 dimethyl)-2-methyl-1,3-propanediyl ester		1.31	1.39	0.97	
21.46	Phenol, 4(1,1,3,3-tetramethyl butyl)	2.12	0.93	0.90	0.74	2.14
22.71	heptadecane		1.50			
23.15	Benzenemethanamine, N-(phenylmethyl)		8.60	7.72	13.2	7.85
23.46	Benzenemethanamine, N-(phenylmethylene)		2.13	2.16	2.72	
24.06	octadecane			1.20		
25.01	1,2-benzenedicarboxylic acid, bis(2-methyl propyl) ester	2.16	33.5	40.6	42.8	9.30
28.70	phenol, 4,4'-(1-methyl-ethylidene) bis or *Bisphenol A*		3.83	2.64		

* Retention time

i.s. = internal standard