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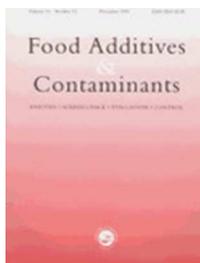
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Time and temperature dependent migration studies of Irganox 1076 from plastics into foods and food simulants

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Methods/Techniques:	Chromatography - GC/MS, Extraction, Clean-up
Additives/Contaminants:	Antioxidants, Food contact materials, Food simulants, Packing migration
Food Types:	Cheese, Cocoa, Animal products – meat, Milk
Abstract:	<p>The present study provides an exhaustive set of migration data for Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (Irganox 1076) from low density polyethylene (LDPE) in several food matrices. Irganox 1076 was used as model migrant because it represents one of the typical substances used as antioxidant in food packaging polymers. Kinetic (time-dependent) migration studies of Irganox 1076 were performed into selected foodstuffs, chosen with different physical-chemical properties and in relation to the actual European food consumption market</p> <p>The effect of the fat content and of the temperature of storage on the migration from plastics packaging was evaluated. The results showed that migration increased with fat content and storage temperature. All data obtained from real foods were also compared with data obtained from simulants tested in the same conditions. In all studied cases, the kinetics in simulants were higher than those in foodstuffs. The work provides data valuable to extend the validation of migration model developed on simulants to foodstuffs themselves.</p>

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Systematic Time and temperature dependent migration studies of investigation of migration kinetics of Irganox 1076 from packaging filmplastics into real foods and food simulants tuffs: a model study in support to food contact material policies developments

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Abstract

The present study provides an exhaustive set of migration data for Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (Irganox 1076) from low density polyethylene (LDPE) in several food matrices. Irganox 1076 was used as model migrant because ~~beyond it~~ represents one of the typical substances used as antioxidant in food packaging polymers. Kinetic (time-dependent) migration studies of Irganox 1076 were performed into selected foodstuffs, chosen with different physical-chemical properties and in relation to the actual European food consumption market

The effect of the fat content and of the temperature of storage on the migration from plastics packaging was evaluated. The results showed that migration increased with fat content and storage temperature ~~and revealed excellent relationships between migration level and fat content confirming the importance of physico-chemical properties of both model migrant and food matrices on migration processes~~. All data obtained from real foods were also compared with data obtained from simulants tested in the same conditions. In all studied cases, the kinetics in simulants were higher than those in foodstuffs. The work ~~contributes to extend existing~~ provides data valuable to extend the validation of migration model developed on simulants suitable for food simulants to foodstuffs themselves.

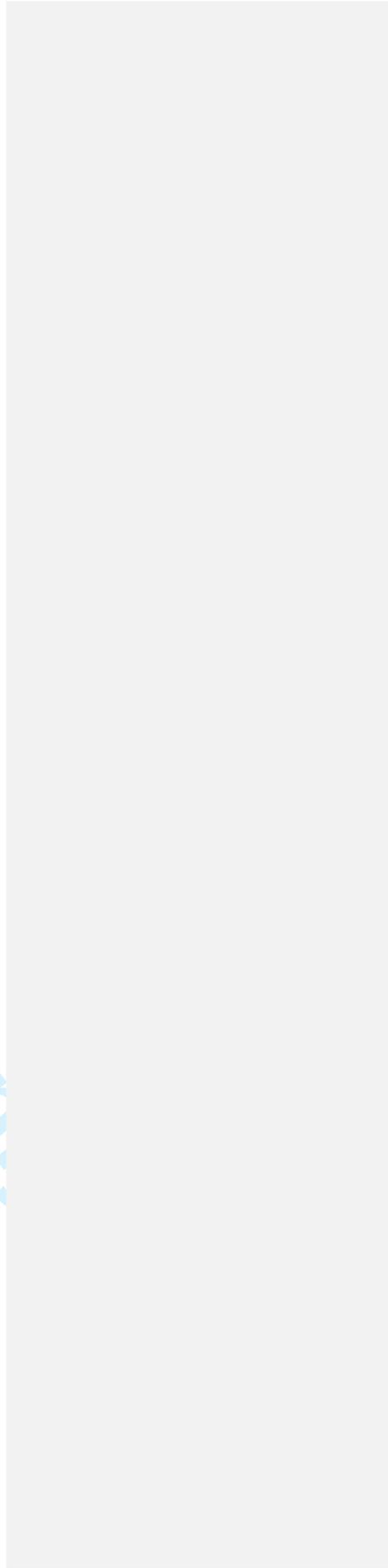
Keywords: Food safety; Food Packaging; Antioxidant; Migration; Food; Simulants

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Introduction

Recent years have seen an increasing interest in issues related to packaging safety. The consumer perception and media interest on migrants from packaging to food has considerably increased as well. Food contact materials can represent a potential risk for food contamination and therefore it is relevant to assess consumer exposure (Pocas and Hogg 2007). The EU regulation covers materials and articles intended to come in contact with foods and lays down general criteria in the framework regulation EC/1935/2004, i.e. they should not transfer their constituents into food in quantities which could endanger human health or bring about unacceptable changes in composition or organoleptic characteristics of foodstuffs (EU, 2004). The transfer of constituents from plastic materials into food (migration) has been regulated by the EU Commission Directive 2002/72/EC now under regulation (EU) 10/2011. The relevant legislation sets in particular Specific Migration Limits (SML), which apply to all individual authorised substances, as well as rules for testing migration where food simulants are specified for different food types and different testing parameters are established. Experimental migration tests are sometimes time consuming and expensive or simply difficult because of lack of available analytical methods to detect migrants especially when they are at low concentration and in complex food matrices with much interferences (Begley et al. 2005, Feigenbaum et al.2002). Yet the determination of exposure in turn relies critically on data of migration into foodstuffs and its correlation with food simulants (Bradley et al. 2010; Franz and Welle 2008). In addition, migration is a process that can be described mathematically (Brandsch, et al. 1998, 2002, O'Brien et al.2001) provided that they are validated by scientific supporting data. The use of such models has been allowed for Regulatory purposes (EU, 2002; EU, 2011), and their potential extension as a tool for exposure assessment relies on supporting data on kinetics of migration of migrants into food matrices (Brandsch et al. 2002; EU, 2003).

The aim of the present study was to generate an extensive set of migration data for Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (Irganox 1076) in several food matrices to better understand the mechanisms and the physical-chemical food properties which might influence the mass transport processes of this substance into foodstuffs (Cruz et al.2008 ; Sanches Silva et al. 2003). Irganox 1076 was used as

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6 model migrant because it is a typical antioxidant in food packaging polymers and was
7 stable (Simoneau and Hannaert 1999; Demertzis et al.1998) and available in a
8 certified reference material (Castle et al. 2000; Specific Migration EU project 2000;
9 Stoffers et al. 2004). Kinetic (time-dependent) migration studies of Irganox 1076 were
10 performed into selected foodstuffs, chosen with different physical-chemical properties
11 and in relation to the actual European food consumption market (Simoneau, 2003).
12 The experimental design was developed to perform kinetics under strictly controlled
13 conditions to obtain migration levels equal or higher than those reached under real
14 storage condition in order to represent the worst case scenario. This paper aims to
15 provide underlying data of migration into foodstuffs vs. simulant. The data can then
16 be used as basis estimate of concentration data over time and end point in foods to
17 validate verify predictive models based on diffusion.

25 26 **Materials and methods**

27 28 29 *Reference fortified plastic film*

30 The substance used in the kinetic studies as migrant model was Octadecyl 3-(3,5-di-
31 tert-butyl-4-hydroxyphenyl)propionate (Irganox 1076)(CAS no.2082-79-3 MW =
32 531). A reference low density polyethylene film (thickness $1011 \pm 18 \mu\text{m}$; density
33 $0.916 \pm 0.001 \text{g/cm}^3$) was produced by Fraunhofer IVV (Freising, Germany) according
34 to a established protocol leading to specific characteristics of homogeneity (density
35 and thickness), stability and diffusion (Specific Migration EU project 2000; O'Brien
36 et al. 1997; Stoffers et al. 2004). The initial concentration of the migrant in the
37 polymer ($C_{p,0}$) was $618.5 \text{mg/kg} \pm 9.7\%$, i.e. $5769 \mu\text{g/dm}^2$

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43 44 45 *Food samples and simulants*

46 Food matrices were selected with respect to physical-chemical properties which could
47 be expected to influence the behaviour of food as a sorption matrix for the uptake of
48 Irganox 1076. Foods with different physico-chemical properties were purchased
49 (orange juice, milk, whipping cream, processed cheese, soft cheese, cottage cheese,
50 chocolate, chicken breast, pork neck, fresh salmon, wheat flour, mayonnaise,
51 margarine, cheese sauce, choc spread and pork minced meat). As fat was identified as

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6 key factor to influence migration, pork minced meat with different fat contents was
7 prepared in the laboratory by mixing pork loin with increasing amounts (5%, 10%,
8 20%, 30%, 50%) of pork fat.
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12 The fat content of each food was determined in order to correlate with the migration
13 values. For commercial packed foods having a label (cottage cheese, soft cheese,
14 whipping cream, processed cheese, milk, orange juice, chocolate spread, cheese sauce,
15 margarine and mayonnaise), the declared fat value was used, while for those without a
16 label (chicken breast, chocolate, wheat flour, pork meat, pork neck, salmon) the fat
17 content was measured by the AOAC official method (AOAC International. 1998).

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20 Distilled water, acetic acid 3% and ethanol 10%, rectified olive oil, isooctane and
21 95% ethanol (v/v) were used as recommended food simulants by Directive 82/711/
22 EEC, as amended (European Commission 1982).
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26 27 28 ***Sample preparation and migration tests***

29 30 *Liquid aqueous foods (orange juice, milk and whipping cream) and simulants*

31 10mL of liquid food samples were placed in glass bottles (Schott[®], 100 mL) with a
32 hermetic cup (polytetrafluoroethylene). A disk of the fortified polymer (0.07 dm²
33 surface) was cut to perfectly cover the internal surface of the glass bottle cup used as
34 migration cell. Bottles were incubated at different time and temperature conditions
35 upside down to ensure contact with the plastic film. These cells were used also to
36 perform kinetics in food simulants.
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40 41 42 *Semi-solid or solid food (chocolate, processed cheese, soft cheese, cottage cheese,* 43 *chicken breast, pork minced meat 5%, pork minced meat 24%, fresh salmon, wheat* 44 *flour)*

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46 Food was prepared to have 5-10g portion, Sodium azide 0.1% (w/w) was added at the
47 sampling stage in some cases to prevent microbial spoilage.
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49 Small migration cells were designed and built for the kinetics studies of semi-solid or
50 solid foods. The cell was made up of three parts: a small Petri[®] dish, a glass ring and a
51 lid cover (cell diameter 4.68 cm; glass ring diameter 3.92 cm). The fortified polymer
52 was cut to a dimension of 0.12 dm² surface to cover the internal surface of the cell and
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6 5-10g food was placed in contact with the surface and held in position by a glass ring.
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8 The cell was closed with a glass cover pressed by a weight on the top.
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10 *Kinetics*

11 The cells were incubated at different time-temperature conditions. Kinetics were
12 conducted up to 5 days (chicken, salmon), up to 10 days (cottage cheese, orange juice,
13 pork meat), up to 20 days (fresh cheese, chocolate spread), up to 30 days (cheese
14 sauce, mayonnaise, margarine, whipping cream), up to 90 days (processed cheese
15 type Gouda, chocolate) or up to 180 days (flour). Sampling was done in 4 or 5 time
16 points over the period. For example sampling for the 10 days kinetics was typically
17 done at 1 day, 2 day, 4 days, 10 days. Sampling for the 30 days kinetics was typically
18 done at 1, 2, 4, 10, 20, 30 days.
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24 The kinetics were carried out in 20 different foodstuffs and 3 food simulants at 3
25 different temperatures (5°C, 25°C and 40°C) using the same migration cells,
26 conditions and plastic reference material. Blank samples were also prepared by
27 placing the foods into the cells without the reference film, exposed, and analysed at
28 the same time points. Recovery and stability studies of Irganox 1076 into foodstuffs
29 and food simulants were also performed as for foods and are reported in table 1.
30 Stability studies were performed by fortifying each food or food simulant with 1-5
31 µg/g of Irganox 1076 depending on the food matrix using the same test cells and
32 conditions without film as for the migration tests. Duplicate samples were produced in
33 each case, stored alongside the migration tests, analysed after the maximum contact
34 time of each food kinetic and expressed as percentage of Irganox 1076 recovered at
35 the end. The kinetics were also carried out in ethanol 95%, isooctane and rectified
36 olive oil (10 mL) at 3 different temperatures (5°C, 25°C and 40°C) using the same
37 migration cells, conditions and plastic reference material used to perform the kinetics
38 in actual foodstuffs.
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47 *Extraction*

48 Food samples were taken from different cells at different time points over the entire
49 exposure time. An independent food sample was set up for each time-point. Each food
50 sample taken was analysed entirely to avoid homogeneity problem. The concentration
51 of the model substance Irganox 1076 (expressed as µg/dm² of reference film)
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6 migrated from the plastic film into the food was quantified ~~using analytical methods~~
7 ~~developed and tailored for each specific matrix. Irganox-1076 was extracted from~~
8 ~~each food with hexane~~ and analysed by GC/MS.
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12 *Fatty solid foods (cheese sauce, chocolate, processed cheese, soft cheese, cottage*
13 *cheese margarine, mayonnaise, choc spread, pork minced meat, fresh salmon and*
14 *whipping cream) and olive oil simulant*
15

16 5-10g of fatty food was weighted in a 100 mL glass bottle. 70-100 mL of hexane was
17 added and immediately shaken by vortex mixing for 3 minutes. 4 mL of NaCl
18 saturated solution was added, samples were then homogenised by ultraturrax for 2
19 minutes and centrifuged at 1500 rpm for 10 minutes. Samples were stored for at least
20 3 hours at -18°C . The hexane phase was collected, filtered through a $0.20\ \mu\text{m}$ PTFE
21 filter and analysed by GC-MS. The amount of sample and the hexane volume used for
22 the extraction was tailored for different food matrices.
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28 *Non Fatty solid foods (chicken breast, wheat flour)*
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30 10 g of non fatty solid food was weighted in a glass centrifuge tube of 40 mL. 5 mL of
31 acetonitrile was added and immediately shaken by vortex mixing for 3 minutes. 20
32 mL of hexane were added, samples were then homogenised by ultraturrax for 2
33 minutes and centrifuged at 3000 rpm for 5 minutes. The hexane phase was collected,
34 filtered through a $0.20\ \mu\text{m}$ PTFE filter and analysed by GC-MS.
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39 *Liquid foods (orange juice, milk)*
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41 10 mL of liquid food were put in a 40 mL centrifuge tube. 10 mL of hexane were
42 added, immediately shaken by vortex mixing for 3 minutes and centrifuged at 2500
43 rpm for 10 min. The hexane phase was filtered through a $0.45\ \mu\text{m}$ PTFE filter and
44 analysed by GC-MS.
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47 *Simulants*
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49 10 mL of Ethanol 95% after the migration exposure were evaporated to dryness. 10
50 mL of hexane were added to the samples and then immediately shaken and analysed
51 by GC-MS. Isooctane samples were analysed directly without any preparation by GC-
52 MS. Olive oil was treated as a fatty food.
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Analysis by Gas Chromatography coupled to mass spectrometry (GC-MS).

The extraction solutions of all the samples were analysed by GC-MS (Hewlett Packard 5890 GC) coupled with a Hewlett-Packard mass selective detector (HP 5973 MSD) under the following conditions:

GC unit: Carrier gas, Helium; flow, 1.2 mL/min, Splitless. Column, 30 m x 0.25 mm i.d. 0.15µm thickness DB-17HT phase. Injection volume: 1µL. Injector block: 280°C.

Oven program: 70°C (0 min), 20°C/min to 250°C, 10°C/min to 350°C (20 min).

Depending on the composition of the samples injected, the final step at 350°C can be adapted or shortened. The GC column was cleaned with hexane in between successive injections to avoid memory effect. Under the conditions given above the typical retention time obtained from standard solutions was 15.5 ± 0.1 min.

Mass Detector: (Electronic Ionisation Mode): SIM mode (target ion 530, qualifier ion 515).

GC/MS peak identification was also performed by the Hewlett-Packard Enhanced ChemStation Software Rev. B.00.00.

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Results and discussion

Selection of model migrant, experiment design and analytical method

Irganox 1076 was selected as model migrant for migration studies due to his chemical-physical properties. This sterically hindered phenolic antioxidant protects plastics materials against thermo-oxidative degradation. It has low volatility and high resistance to extraction. Irganox 1076 is commonly used by the industry in food contact materials and it is not present in food naturally or as food additive.

A polyolefin was used as reference film for fortification due to its relatively high diffusion coefficient in plastic (D_p). ~~The kinetic measurements were carried out in a situation by which the diffusion coefficient in plastic (D_p) was higher than the diffusion in food (D_f) as it was known to be the kinetic rate limiting step (Franz 2005).~~

The very thick and rigid film in which the substance was embedded did not allow testing by pouch as normally done for a number of other films. A special migration cell was designed to avoid leakage of the food matrix and contamination with the outer surface as

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6 it could occur with a more classical sandwich technique when using semi-solid foods at
7 room temperature such as margarine, choc spread and some processed or fresh cheeses.
8 The slight pressure applied to the ring-film contact surface ensured that the food matrix
9 was in any case not constrained. The whole system was protected from outside
10 contamination by the glass cover and the food matrix was restrained from leaking by
11 capillary action around the film. Another advantage using this ad-hoc cell was that all
12 cell parts could be weighed making the determination of the food quantity available on
13 an exact weight basis.
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18 Migration of Irganox 1076 from fortified plastic films was performed in 20 different
19 food matrices and three simulants at several time and temperature exposure conditions in
20 order to compare the different kinetic curves obtained. Amongst the standardised
21 simulants distilled water, acetic acid 3% and ethanol 10% were excluded after some
22 preliminary tests since no measurable migration of Irganox 1076 was observed due to
23 the hydrophobic behaviour of Irganox 1076. Hence, olive oil, isooctane and 95% ethanol
24 (v/v) in aqueous solution were used as simulants, as described by the Directive 82/711/
25 EEC because their greater affinity to Irganox 1076.
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28 Preliminary analytical trials were carried out to optimise the analytical method for the
29 determination and the extraction of Irganox 1076 (Sendon Garcia et al, 2003). The
30 solubility of Irganox 1076 was checked in different solvents hexane was chosen as
31 solvent to prepare standard solutions. As foods are complex matrices, different protocols
32 (solvent, solvent to food ratio, extraction time, extraction mode, extraction temperature)
33 were tailored for each. Chromatographic methods were compared for the various
34 foodstuffs. The simplest approach consisted in dilution/extraction with hexane followed
35 by direct analysis by gas chromatography coupled to mass spectrometry (GC-MS).
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38 In the case of fatty foods, the amount of hexane for extraction was increased (100mL)
39 and the fat was separated by crystallization to avoid interferences with Irganox 1076. In
40 same cases (meat, fish, cheeses), acetonitrile was added to foods to increase sample
41 homogenisation. For dairy products a sodium chloride saturated solution was used to
42 avoid emulsion after hexane extraction. Laboratory experiments were first conducted to
43 assess the absence of possible interferences for the food matrices with Irganox 1076, and
44 to check the general acceptability of chromatograms. For that purpose blank
45 chromatograms of each food matrix were compared with the same spiked food matrices.
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47 After checking the absence of interferences between food matrices and Irganox 1076 by
48 GC-MS in a scan mode, the single-selected ion monitoring mode (530,515) method was
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used for GC-MS analysis to increase the sensitivity of the method. The LOD was of about 0.1 mg/kg for the different foods.

Recovery and Stability test in food and simulants

A recovery study was performed fortifying each foodstuff with the model compound (table 1) the average recovery over six replicates for each food was > 83.5% regardless of the concentration of the model migrant. Table 1 also shows the spiked concentrations used to carry out the stability test and the results obtained.

[Table 1 about here]

The amount of Irganox 1076 added was different from sample to sample, depending on the food matrix and the detection limit of the method for that particular food. Matrices with a high fat content had a higher spiked concentration (5 µg/g), due to the difficulty to extract Irganox 1076 from fatty food. In this case, the average value between 2 replicates was reported. A target value of at least 80% was considered satisfactory as indicator of adequate stability. In very few food matrices such as pork meat, pork neck and in particular mayonnaise, this target value could not be reached. However, considering the whole set of data from the stability study, Irganox 1076 in all food matrices tested showed a good stability even when exposed to more drastic conditions. Table 1 also reported the spiked concentrations used to carry out the stability test on food simulants. The Irganox 1076 spiked was higher in rectified oil, because of the difficulty to extract Irganox 1076 from this fatty simulant. The results showed a good stability of Irganox 1076 along side all kinetics experiments at all temperatures tested.

Kinetics in foods and simulants

The maximum migration levels of Irganox 1076 obtained at different time-temperatures in various foodstuffs are summarised in table 2.

[Table 2 about here]

High migration levels of Irganox 1076 were generally detected into foods with high fat content, low water content, ~~food physical state and~~ i.e. where a chemical affinity between

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6 | this lipophilic model migrant and fatty compounds fatty food matrices was present. The
7 highest migration value (1413 μgdm^{-2}) for Irganox 1076 was obtained for chocolate at
8 40°C. Chocolate represents, from a physical stand point, a highly concentrated
9 suspension of solid components (e.g. sugar particles, cocoa solid) dispersed in a
10 continuous fatty phase from cocoa butter (Soeters 1970). This high migration value
11 could be also related to its liquid physical state at 40°C. In fact at 25°C, when chocolate
12 is solid, Irganox 1076 encounters boundary resistance and no migration was observed,
13 not even after 90 days. Chocolate spread at 25°C over 20 days also had a high migration
14 level (682 μgdm^{-2}), probably due to the high concentration of oils and emulsifiers into
15 the food matrix that helped the migration process.

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21 | A relevant-significant migration level (511 $\mu\text{g}/\text{dm}^2$ and 563 $\mu\text{g}/\text{dm}^2$) were determined in
22 margarine and processed cheese. The migration in margarine at 25°C over 20 days was
23 in a certain way predictable having a very high fat content (80%), in processed cheese at
24 25°C over 30 days could be explained by the ability for the oil to move to the surface
25 (oiling off) in contact with the reference plastic film, thus helping the migration of this
26 substance.

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31 | An unexpected low migration was observed in cheese sauce despite the fat content
32 (19%), probably because this rubbery-viscous food where the fat is dispersed in a fine
33 state, was less prone to promote a migration process. The migration in cheese sauce was
34 performed also at 90°C for a maximum exposure time of 120 minutes, but even in this
35 case a low migration was observed. The kinetics at 5°C carried out in all pork minced
36 meat samples at different level of fat content (Figure 1) confirmed the affinity of Irganox
37 1076 for fatty food. It is possible to better see this trend at 25°C (Figure 2) where the
38 increase of temperature also accounts in reaching a higher migration value. Although
39 whipping cream and processed cheese have similar fat content as shown in table 2 the
40 last one achieved higher migration level, probably because the oiling off process taking
41 place in the processed cheese. Milk, that is a dispersion of lipoprotein particles, proteins,
42 casein micelles but with only a 3.8% of fat was not able to extract Irganox 1076 and any
43 migration was obtained.
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6 The physical state of the foodstuff is an important factor in migration process of the
7 model migrant as confirmed by wheat flour. This food in fact contains starch and protein
8 as two major components and lipids only as minor components(less than 1%) but
9 reached ~~relevant-significant~~ migration level probably due to its small particle size that
10 brings to have a high contact surface hence a good extraction power. In the case of soft
11 cheese although several factors (fat content, physical state) could lead ~~to foresee one to~~
12 ~~anticipate~~ -high migration level of Irganox 1076, no migration at 25°C was detected.
13 Kinetics carried out in chicken breast, pork neck, salmon, cottage cheese and orange
14 juice ~~also did not show anyno~~ migration of Irganox 1076 occurred.
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21 The same considerations made for the kinetics in foodstuffs were confirmed when using
22 simulants. The kinetics of the three simulants at the three different temperatures 5°C,
23 25°C and 40°C are reported in figure 3, 4, 5. Kinetics obtained in Ethanol 95% and
24 Olive Oil showed a comparable migration level at all temperatures. Migration level of
25 Irganox 1076 in Isooctane, was always the highest at all temperatures and times.
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30 [Figure 3, 4, 5 about here]
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34 The food showing the highest migration level was chosen to perform a comparison with
35 kinetics carried out in simulants at 5°C, 25°C, and 40°C (Figure 6, 7, 8). Applying the
36 same time and temperature conditions, the maximum migration level reached for each
37 foodstuff was in all cases lower than that obtained with the correspondent simulants.
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43 [Figure 6, 7, 8 about here]
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48 ***Correlation between foods fat content and migration***

49 Considering the lypophilic behaviour that Irganox 1076 showed during the kinetic
50 studies, a possible correlation between the fat content and the migration level was
51 investigated. Practically, the maximum migration values obtained from the different
52 kinetics at 5°C (Figure 9) and 25°C (Figure 10) were plotted against the fat content
53 expressed as %.
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[Figure 9 about here]

One important aspect that seemed to be relevant, was the physical characteristic of the fat itself, whether it was an emulsion of fat in water matrix (such as whipping cream or milk) resulting in a lower affinity with Irganox 1076, or an emulsion where the fat is the continuous phase (such as chocolate) was resulting in an higher affinity. Even if a correlation was observed, there were several cases where the trend was not clearly confirmed, maybe due to other factors not considered, such as the presence of particular additives as emulsifier. For what it concerns chocolate spread and processed cheese and their very high migration, it was above the trend line. The gap between margarine and mayonnaise seemed to increase when raising the temperature. Soft cheese and salmon, even if a somewhat fatty, did not show any migration.

Conclusions

Different protocols were carried out to develop adequate analytical methods for the detection of Irganox 1076 in each food matrix. While interference problems between matrix and analyte were more easily resolved, and stability during time-temperature experiments was adequate, the extraction yield and sensitivity were interdependent and gave the greatest challenge. The GC-MS (SIM mode) method was suitable to achieve the detection limit of ~~10 ppb~~ 0.1 mg/kg and recoveries average over six replicates were higher than 83.5% for each foodstuff.

The present study provided an exhaustive set of data concerning the migration of a model compound into real foodstuff. The comparison between migration in food and simulants contributed to fill the lack of information concerning real foods and to extend existing migration model suitable for food simulants to foodstuffs themselves.

This experimental design allowed obtaining a large amount of useful data to generate a better understanding of the mechanisms and physical-chemical food properties which influence mass transport processes of Irganox 1076 into and within foodstuffs. The kinetic migration experiments confirmed the importance of physico-chemical properties of both model migrant and food matrices. The physical state of the samples seems also to influence the mass transport processes. In all the kinetics performed on foods, the

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6 combination of a high temperature and a high fat content concentration was helping the
7 migration of Irganox 1076. The migration was increasing when raising the temperature
8 and the fat content showed to be also a determinant parameter for the migration into fatty
9 food. The results have demonstrated the strong influence of food chemistry on migration
10 of substances from food contact materials.
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13 To complete the study, kinetics in food simulants were also performed. Migration levels
14 of Irganox 1076 in simulants were higher than those in foodstuffs at all temperature
15 checked. These results confirm in the cases studied that using simulants in migration
16 studies, gives a good safety margin.
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20 21 22 23 24 25 Acknowledgements

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32 33 References

- 34
35
36
37 AOAC International. 1998. AOAC 960.39, AOAC 920.85, AOAC 948.16, AOAC
38 963.15, AOAC 960.39, AOAC 970.20. Cunniff P editor. 16 edition, 4th revision,
39 vol 1. Maryland, USA.
- 40
41 Begley T, Castle L, Feigenbaum A, Franz R, Hinrichs K, Licky T et al. 2005.
42 Evaluation of migration models that might be used in support of regulation for
43 food-contact plastics. Food Add Contam. 22(1):73-90.
- 44
45 Bradley, EL, Castle L, Day JS, Ebner I, Ehlert K, Helling R, Koster S, Leak J and
46 Pfaff K. 2010. Comparison of the migration of melamine from melamine-
47 formaldehyde plastics ('melaware') into various food simulants and foods
48 themselves. Food Add Contam Part A. 27 (12):1755 — 1764.
- 49
50 Brandsch J, Mercea P, Piringer O. 1998. Modelling of additive diffusion coefficients
51 in polyolefins, in New Development in Chemistry of Packaging. American
52 Chemical Society Symposium, Dallas; March April 1998; TX USA.
53
54
55
56
57
58
59
60

- 1
2
3
4
5
6 Brandsch J, Mercea P, Rüter M, Tosa V, Piringer O. 2002. Migration modeling as a
7 tool for quantity assurance of food packaging. *Food Add Contam.* 19(Suppl): 29-
8 41.
9
- 10 Castle L, Honeybone CA, Irvine A, Read WA and Boenke A. 2000. The certification
11 of a polymer film for its mass fraction of a fat soluble additive related to migration
12 into foodstuffs and for its film thickness. Establishment of a migration test method
13 for fatty contact. European Project Final Report Contract No. MAT1-CT94-
14 0044 Report BCR-CRM 593.
15
- 16 Cruz, J. M., Sanches Silva, A., Sendón García, R., Franz, R., & Paseiro Losada, P.
17 2008. Studies of mass transport of model chemicals from packaging into and
18 within cheeses. *Journal of Food Engineering*, 87(1), 107-115
19
- 20 Demertzis PG, Franz R. 1998. Development of an HPLC method for measurements of
21 the stability of Irganox-type polymer antioxidants in fatty food simulants. *Z*
22 *Lebensm Unters Forsh A.* 206: 193-198.
23
- 24 EU Project “SPECIFIC MIGRATION” Certified reference materials for specific
25 migration testing of plastics for food packaging needed by industry and
26 enforcement laboratories. European Commission Project Contract No. (G6RD-
27 CT-2000-00411).
28
- 29 European Commission. 1982. EU Council Directive 82/711/EEC of 18 October 1982
30 laying down the basic rules necessary for testing migration of the constituents of
31 plastic materials and articles intended to come into contact with foodstuffs.
32 (Plastics: Basic rules for testing migration – Unofficial consolidated version
33 including 82/711/EC, 93/8/EEC and 97/48/EC).
34
- 35 European Commission. 2004. EU Regulation (EC) No 1935/2004 of the European
36 Parliament and of the Council of 27 October 2004 on materials and articles
37 intended to come into contact with food and repealing Directives 80/590/EEC and
38 89/109/EEC.
39
- 40 European Commission. 2002. EU Commission Directive 2002/72/EC of 6 August
41 2002 relating to plastic materials and articles intended to come into contact with
42 foodstuffs. (Plastics: Unofficial consolidated version including 2002/72/EC,
43 2004/1/EC, 2004/19/EC, 2005/79/EC, 2007/19/EC, 2008/39/EC).
44
- 45 Feigenbaum A, Scholler D, Bouquant J, Brigot G, Ferrier D, Franz R et al. 2002.
46 Safety and quality of food contact materials. Part 1: Evaluation of analytical
47 strategies to introduce migration testing into good manufacturing practice. *Food*
48 *Add Contam.* 19(2):184–201.
49
- 50 FOODMIGROSURE (Modelling migration from plastics into foodstuffs as a novel
51 and cost efficient tool for estimation of consumer (plastic food) for estimation of
52 exposure from food contact materials). Project supported by European
53 Commission (re. QLK1-CT2002-2390) <http://www.foodmigrosure.com>.
54
55
56
57
58
59
60

~~Franz R. 2005. Migration modeling from food contact plastics into foodstuffs as a new tool for the consumer exposure estimation. Food Add Contam. 22(10): 920-937.~~

Franz R and Welle F. 2008. Migration measurement and modelling from poly(ethylene terephthalate)(PET) into soft drinks and fruit juices in comparison with food simulants. Food Add Contam: Part A. 25(8): 1033 — 1046.

O'Brien I, Cooper I. 2001. Polymer additive migration to foods-a direct comparison of experimental data and values calculated from migration models for polypropylene. Food Add Contam. 18 (4):343-355.

Pocas M and Hogg T. 2007. Exposure assessment of chemicals from packaging materials in foods: a review. Trends in Food Sci & Tech (18): 219-230.

Sanches Silva, A., Cruz, J. M., Sendón García, R., Franz, R., & Paseiro Losada, P. 2007. Kinetic migration studies from packaging films into meat products. Meat Science, 77(2), 238-245.

Simoneau C. 2003. Relating migration to consumption: in consideration of consumer protection. List of most relevant foodstuffs/groups from a consumption stand point. Report FOODMIGROSURE QLRT-2002-02390.

Simoneau C and Hannaert P. 1999. Stability testing of selected plastics additives for food contact in EU aqueous, fatty and alternative simulants. Food Add Contam: Part A. 16(5):197 — 206.

Soeters CJ. 1970. Physical behavior and chemical composition of chocolate, cocoa butter and some cocoa butter substitutes. Fette, Seifen, Anstrichmittel 72(8):711-718

Stoffers N, Stormer A, Brandley E, Brandsch R, Cooper I, Linssen J P H et al. 2004. Feasibility study for development of certified reference materials for specific migration testing. Part 1: initial migrant concentration and specific migration. Food Add Contam. 21(12):1203-1216.

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Figure captions

Figure 1. Kinetics at 5°C of pork minced meat 5% (Δ), 10% (\square), 20% (+), 30% (\diamond) and 50% (\bullet) fat content

Figure 2. Kinetics at 25°C of pork minced meat 5% (Δ), 10% (\square), 20% (+), 30% (\diamond) and 50% (\bullet) fat content

Figure 3. Comparison among kinetics of ethanol 95 % (X), olive oil (\circ) and isooctane (\blacksquare) at 5°C

Figure 4. Comparison among kinetics of olive oil (\circ), ethanol 95% (X) and isooctane (\blacksquare) at 25°C

Figure 5. Comparison among kinetics of ethanol 95% (X), olive oil (\circ) and isooctane (\blacksquare) at 40°C

Figure 6. (a) Comparison among kinetics of processed cheese (\bullet), ethanol 95% (X) and olive oil (\circ) at 5°C

Figure 7. Comparison among kinetics of processed cheese (\bullet), ethanol 95% (X), olive oil (\circ) and isooctane (\blacksquare) at 25°C

Figure 8. Comparison among kinetics of chocolate (\blacktriangle), ethanol 95% (X), olive oil (\circ) and isooctane (\blacksquare) at 40°C

Figure 9. Correlation between Irganox 1076 migration level and foods percentage of fat content at 5°C

Figure 10. Correlation between Irganox 1076 migration level and foods percentage of fat content at 25°C

Table 1. Recovery and stability tests of foodstuffs and food simulants.

Food/Simulants	Temperature (°C)	Fortification (mg kg ⁻¹)	Recovery (%) (n=6)	Stability (%) (n=2)
Chicken Breast	25	1	98.0	102.9
Orange juice	25	1	102.0	96.4
Wheat Flour	25	1	98.2	109.72
Wheat Flour	40	1	98.2	91.6
Wheat Flour	70	1	98.2	86.7
Milk	25	5	84.1	97.0
Whipping cream	5	5	87.2	93.6
Whipping cream	25	5	87.2	88.0
Cottage Cheese	25	5	87.3	83.66
Soft cheese	25	5	93.7	107.0
Processed Cheese	5	5	83.3	81.8
Processed Cheese	25	5	83.3	84.2
Cheese sauce	5	2	84.0	101.8
Cheese sauce	90	2	84.0	90.28
Margarine	5	5	95.0	80.5
Margarine	25	5	95.0	105.6
Mayonnaise	5	5	88.0	60.7
Mayonnaise	25	5	88.0	72.4
Salmon	25	5	92.4	89.7
Pork meat 5%	5	5	97.7	82.8
Pork meat 5%	25	5	97.7	89.3
Pork meat 10%	5	5	104.4	100.7
Pork meat 10%	25	5	104.4	95.4
Pork meat 20%	5	5	91.60	86.4
Pork meat 20%	25	5	91.60	67.8
Pork meat 30%	5	5	104.5	104.3
Pork meat 30%	25	5	104.5	93.2
Pork meat 50%	5	5	89.7	62.7
Pork meat 50%	25	5	89.7	83.7
Pork neck	5	5	101.6	71.47
Pork neck	25	5	101.6	83.77
Choc spread	25	5	95.0	101.3
Chocolate	25	5	83.50	101.2
Chocolate	40	5	83.50	97.5
Ethanol 95%	5	1	100.0	85.8
Ethanol 95%	25	1	100.0	80.2
Ethanol 95%	40	1	100.0	81.4
Rectified oil	5	5	92.0	89.3
Rectified oil	25	5	92.0	88.1
Rectified oil	40	5	92.0	79.9
Isooctane	5	1	100.0	110.97
Isooctane	25	1	100.0	108.78
Isooctane	40	1	100.0	102.81

Table 2. Kinetics in foods and food simulants.

Food/Simulants	Fat content (%)	Time (days) (* minutes)	Temperature (°C)	Maximum migration level (μgdm^{-2})
Cheese sauce	19	30	5	45
Cheese sauce	19	120*	90	19
Chicken breast	1.1	2	25	<LOD
Chocolate	32.1	90	25	<LOD
Chocolate	32.1	30	40	1413
Cottage cheese	4.6	10	25	<LOD
Processed cheese	28.6	90	5	139
Processed cheese	28.6	30	25	563
Margarine	80	30	5	101
Margarine	80	20	25	511
Mayonnaise	82	30	5	70
Mayonnaise	82	20	25	170
Milk	3.6	10	40	<LOD
Choc spread	31	20	25	682
Orange juice	0	10	40	<LOD
Soft cheese	27.5	20	25	<LOD
Pork minced meat 5%	5.1	10	5	41
Pork minced meat 5%	5.1	10	25	76
Pork minced meat 10%	14.6	10	5	40
Pork minced meat 10%	14.6	10	25	137
Pork minced meat 20%	24.1	10	5	36
Pork minced meat 20%	24.1	10	25	168
Pork minced meat 30%	33.6	10	5	51
Pork minced meat 30%	33.6	10	25	226
Pork minced meat 50%	52.6	10	5	92
Pork minced meat 50%	52.6	10	25	262
Pork neck	9	10	25	<LOD
Salmon	14.7	5	5	<LOD
Wheat flour	0.8	180	25	100
Wheat flour	0.8	10	40	26
Wheat flour	0.8	10	70	53
Whipping cream	33	30	5	65
Whipping cream	33	20	25	205
Ethanol 95%	-	30	5	129
Ethanol 95%	-	30	25	1300
Ethanol 95%	-	30	40	3510
Rectified oil	100	30	5	230
Rectified oil	100	30	25	978
Rectified oil	100	30	40	3335
Isooctane	-	30	5	2603
Isooctane	-	30	25	4522
Isooctane	-	30	40	7139

Figure 1. Kinetics at 5°C of pork minced meat 5% (Δ), 10% (\square), 20% (+), 30% (\diamond) and 50% (\bullet) fat content

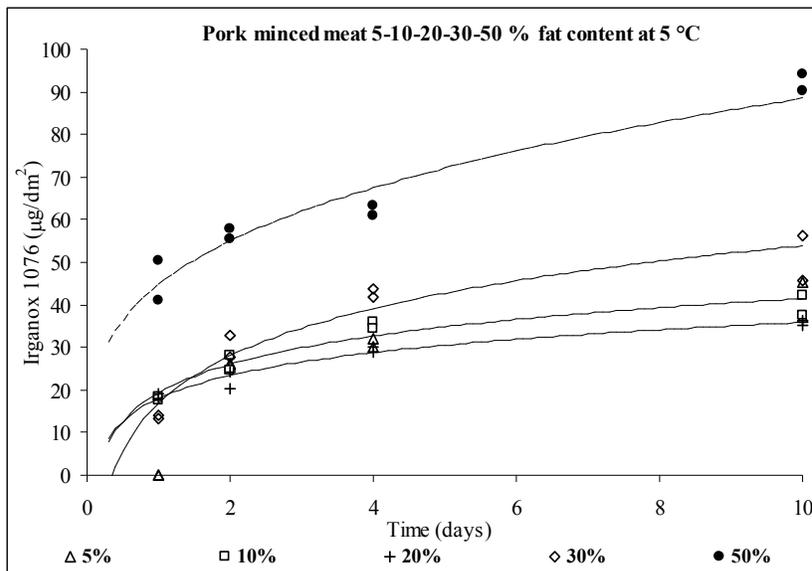


Figure 2. Kinetics at 25°C of pork minced meat 5% (Δ), 10% (\square), 20% (+), 30% (\diamond) and 50% (\bullet) fat content

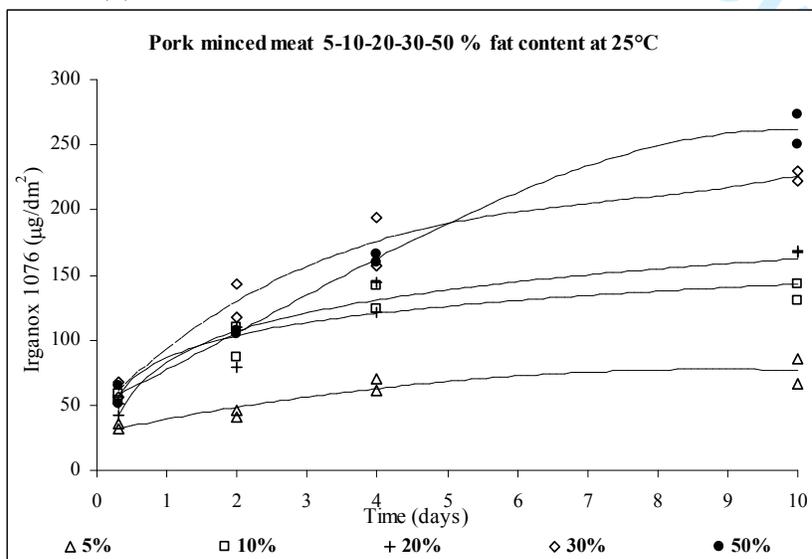


Figure 3. Comparison among kinetics of ethanol 95 % (X), olive oil (○) and isooctane (■) at 5°C

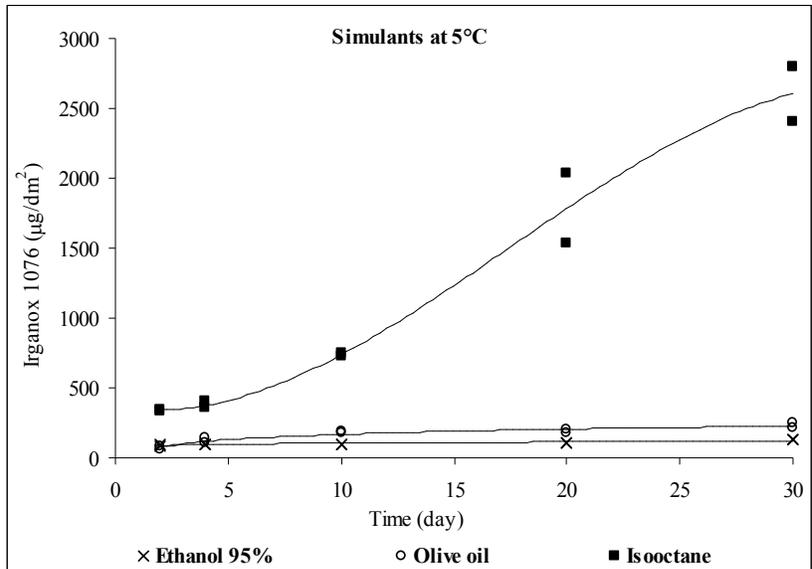


Figure 4. Comparison among kinetics of olive oil (○), ethanol 95% (X) and isooctane (■) at 25°C

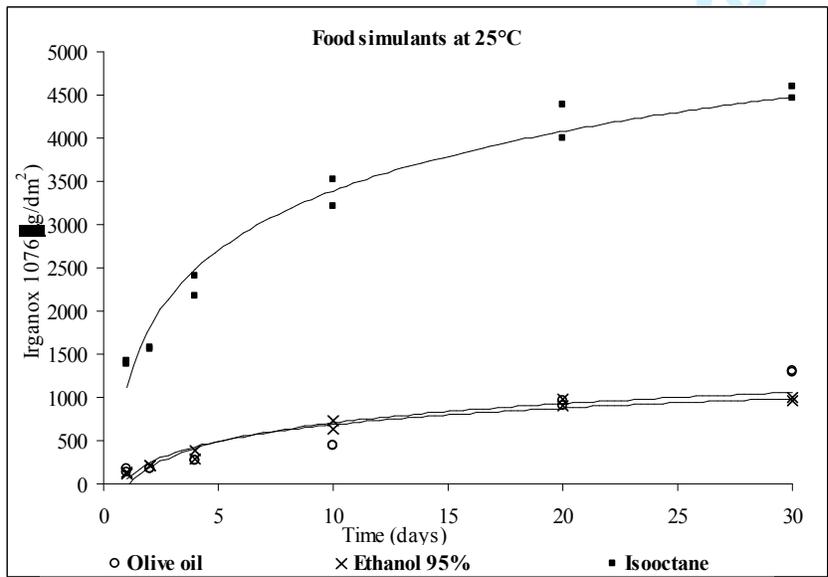


Figure 5. Comparison among kinetics of ethanol 95% (X), olive oil (o) and isooctane (■) at 40°C

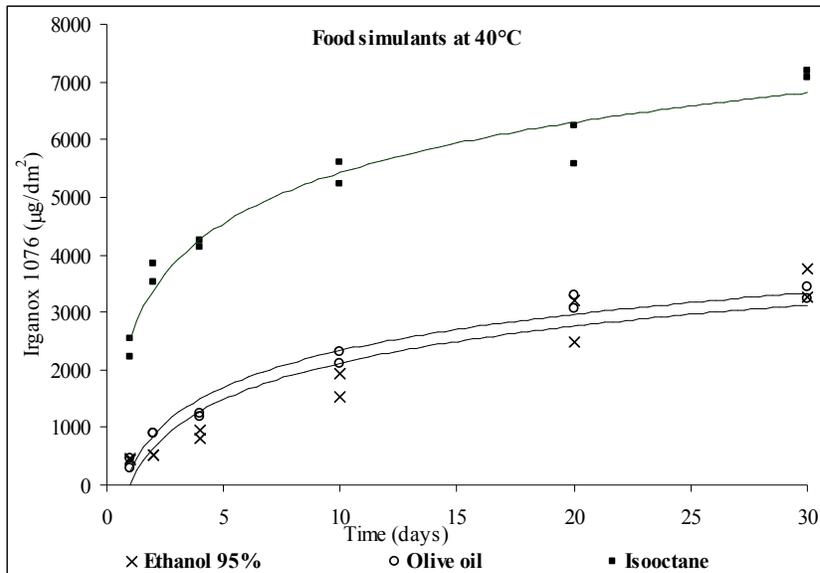


Figure 6. (a) Comparison among kinetics of processed cheese (●), ethanol 95% (X) and olive oil (o) at 5°C

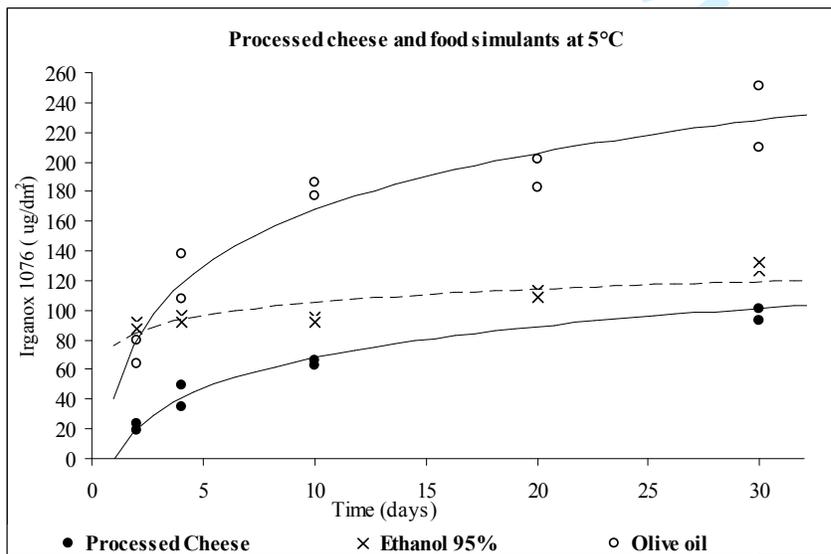


Figure 7. Comparison among kinetics of processed cheese (●), ethanol 95% (X), olive oil (○) and isooctane (■) at 25°C

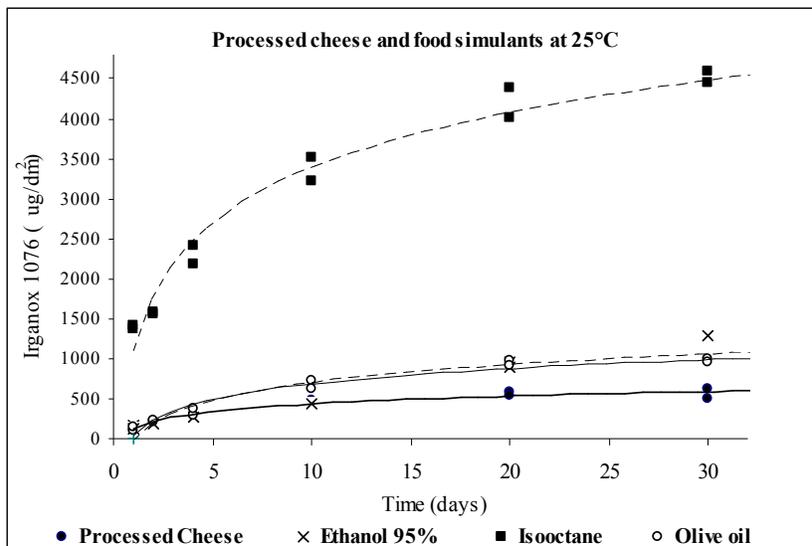


Figure 8. Comparison among kinetics of chocolate (▲), ethanol 95% (X), olive oil (○) and isooctane (■) at 40°C

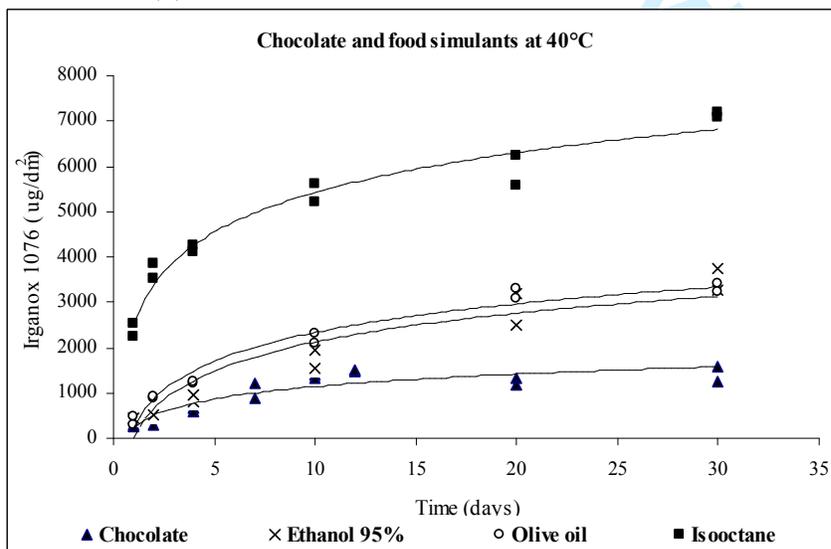


Figure 9. Correlation between Irganox 1076 migration level and foods percentage of fat content at 5°C

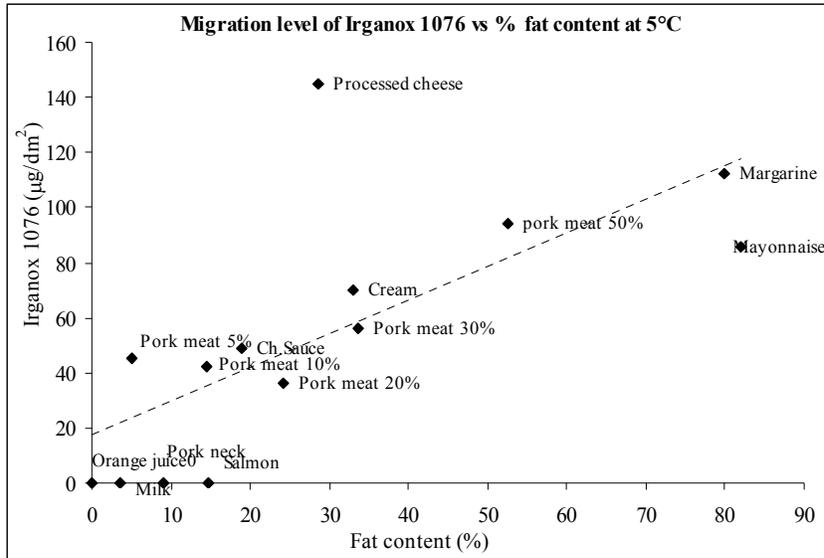


Figure 10. Correlation between Irganox 1076 migration level and foods percentage of fat content at 25°C

