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CENTER FOR PHYSICAL SCIENCES AND TECHNOLOGY

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Investigation of Overall and Specific Migration from Food Contact Plastic Materials Made of Polyethylene, Polypropylene and their Composites

DOCTORAL DISSERTATION

Natural Sciences,
Chemistry (N 003)

VILNIUS 2025

This dissertation was written between 2016 and 2025 at the Center for Physical Sciences and Technology.

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VILNIAUS UNIVERSITETAS
FIZINIŲ IR TECHNOLOGIJOS MOKSLŲ CENTRAS

Toma Petrulionienė

Bendrosios ir specifinės migracijos iš polietileno, polipropileno ir jų kompozitų gaminių, skirtų sąlyčiui su maistu, tyrimas

DAKTARO DISERTACIJA

Gamtos mokslai,
Chemija (N 003)

VILNIUS 2025

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Ačiū.

LIST OF ABBREVIATIONS/TRUMPINIŲ SĄRAŠAS

AAS – Atomic absorption spectrophotometry/atominės absorbcijos spektrofotometrija
ATR-FTIR – Attenuated Total Reflectance Fourier-transform infrared spectrometry/visiško vidinio atspindžio Fourier transformacijos infraraudonųjų spindulių spektroskopiją
FCM – food contact materials/plastikai, skirti naudoti sąlyčiui su maistu
HDPE – high-density polyethylene/aukšto tankio polietilenas
IAS – intentionally added substances/tikslingai pridėtos medžiagos
ICP-MS – Inductively coupled plasma mass spectrometry/induktyviai susietos plazmos masės spektrometrija
LDPE – low-density polyethylene/žemo tankio polietilenas
LLDPE – linear low-density polyethylene/linijinis žemo tankio polietilenas
LC-MS/MS – Liquid Chromatography with tandem mass spectrometry/ skysčių chromatografija – masių spektrometrija
LOD – limit of detection/aptikimo riba
LOQ – limit of quantification/kiekybinio nustatymo riba
NIAS – non-intentionally added substances/netikslingai pridėtos medžiagos
PE – polyethylene/polietilenas
PP – polypropylene/polipropilenas
TD-GC/MS – Thermal desorption gas chromatography coupled with mass spectrometry/terminė desorbcija su dujų chromatografija – masių spektrometrija
UV – ultraviolet radiation/ultravioletinė spinduliuotė

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1. INTRODUCTION

Plastics have become an essential component of our daily lives, as they are used in various industries and applications because of their ability to be adapted, resilience, and cost-effectiveness. Among the multitude of uses of plastics, packaging stands out, comprising up to 40 % of all plastic consumption [1]. Plastic packaging provides numerous advantages, including protection against damage from microorganisms, light, and other external factors, while preserving food quality. Moreover, plastic packaging facilitates convenient storage and, transportation.

Because of the advantageous properties and ease of modification, plastics have become the first-choice material for food packaging. However, in their raw form, plastics are rarely used. To modify the raw plastic, various additives are added during the manufacturing process and average non-fiber plastics contain 93 % polymer resin and 7 % additives by mass [2]. Consequently, all the additives, production process residues, and break-down products such as all kinds of derivatives between additives and residues, or additives and monomers, etc. tend to migrate to food.

The adverse effects of intentionally added substances (IAS) to food packages on human health are now well-documented, raising concerns varying from disrupting the thyroid system to causing allergies [3, 4]. Regarding non-intentionally added substances (NIAS), they may pose even more issues than intentionally added substances as NIAS are not investigated enough. Consequently, to protect consumers from the migration of potentially harmful substances (IAS and NIAS) from packaging to food, numerous scientific teams are working on legislation on food packaging materials and public education.

All things considered, the determination of those harmful substances from packaging to food is necessary to fulfil the legal requirements for food packaging as well as to meet the quality-control requirements of food production.

Aim and tasks of the doctoral dissertation

This dissertation aims to understand how the modification of polyethylene and polypropylene food packaging polymers with additives affects the properties of the plastics and their migration to food simulants.

The main tasks for the research:

1. To identify collected polyethylene, polypropylene and their composite samples by Fourier-transform infrared spectrometry (ATR-FTIR);

2. To investigate the samples for overall migration to different food simulants by gravimetry;

3. To investigate the degradation process of polyethylene, polypropylene and their composites by optimized method for determination of possible volatile and semi-volatile organic compounds by thermal desorption gas chromatography coupled with mass spectrometry (TD-GC/MS) and by validated method for determination of cadmium, chromium, lead, and mercury of atomic absorption spectrophotometry (AAS);

4. To investigate the samples for specific migration of metals (cadmium, chromium, and lead) by optimized and validated method of inductively coupled plasma mass spectrometry (ICP-MS);

5. To optimize the conditions and to validate the method for the determination of antioxidants in the composition of food contact materials and their specific migration to food simulants by liquid chromatography with tandem mass spectrometry (LC-MS/MS);

6. To analyse the results finding relations between polymer degradation, overall, and specific migration.

Novelty and actuality of the work

The dissertation includes relevant, comprehensive research on food contact materials made from plastics. Food packaging is a complex chemical material and the challenge is figuring out what is in that mixture and what chemicals are possible migrants. Identifying potential migrants is probably the only way to get knowledge and improve detection, make decisions in manufacturing processes, and assess potential health risks related to the additive and degradation product migration to the food media. Therefore, optimized methods of gravimetry (GA), liquid chromatography with tandem mass spectrometry (LC-MS/MS), thermal desorption gas chromatography coupled with mass spectrometry (TD-GC/MS), atomic absorption spectrophotometry (AAS) and, inductively coupled plasma mass spectrometry (ICP-MS) for degradation of plastics, overall and specific migration testing were described and validated. Unlike most of the published ones in scientific society, all these methods can be easily applied to routine laboratories. This is very important as to assure the safety of consumers, those food contact materials are controlled in routine laboratories.

Statements to be defended

1. Overall migration studies are significantly needed for assessing potential risks associated with plastic packaging.
2. Thermal desorption gas chromatography coupled with mass spectrometry (TD-GC/MS) method that was developed is suitable for investigation of degradation processes of polyethylene and polypropylene food contact materials.
3. Developed and validated methods for determining cadmium, chromium, lead, and mercury by atomic absorption spectrophotometry (AAS) can be effectively applied in studying food contact materials in routine laboratory settings.
4. Developed and validated method for the determination of antioxidants in the composition of food contact materials and their specific migration to food simulants by liquid chromatography with tandem mass spectrometry (LC-MS/MS) is suitable for the study of food contact materials in the routine laboratory.
5. Developed and validated method for the determination of the specific migration of cadmium, chromium, and lead by inductively coupled plasma mass spectrometry (ICP-MS) is suitable for the study of food contact materials in the routine laboratory.

2. LITERATURE REVIEW

2.1. Polyethylene and polypropylene as food contact materials

Thermoplastics, such as polyethylene and polypropylene play a crucial role in the food packaging industry. According to Statista Inc. global plastics production is increasing [5], for example between 2010 and 2020, the global production of plastics has increased by 100 million metric tons, and it is projected that in 2025 the global production of thermoplastics will amount to 445.25 million metric tons [6], constituting an increase of more than 400 %. This trend may be caused by the increasing demand for packaged food in Europe and North America [7]. As purported by MarketsandMarkets Inc. plastics such as polyethylene and polypropylene are mostly used for different types of food packaging [7] because of their noteworthy mechanical

modification (Figure 1 shows the schematic structure of different forms of polyethylene and polypropylene).

Table 1.
Main mechanical and thermal properties of polyethylene and polypropylene [8].
1 lentelė.
Pagrindinės polietileno ir polipropileno mechaninės ir terminės savybės [8].

Properties	**Thermoplastic**		
	PE		**PP**
	Low density	**High density**	
Density, kg/m^3	915 - 925	940 - 960	900 - 930
Working temperature, ˚C, (min/max)	-50/-70	-60/100	-5/150
Melting temperature, ˚C	115	135	176
Tensile strength, MPa	19	860	1400

Even though they are produced at low cost, they are environmentally resistant and because of that, they are characterized by high protection of the content and low environmental impact [9].

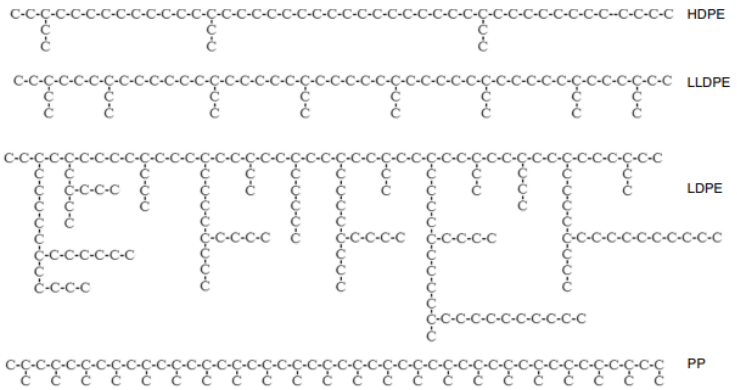


Figure 1. The schematic structure of different forms of polyethylene (high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), low-density polyethylene (LDPE)) and polypropylene (PP) [10].
1 paveikslas. Skirtingų struktūrų polietileno (aukšto tankio polietilenas (HDPE), linijinis žemo tankio polietilenas (LLDPE), žemo tankio polietilenas (LDPE)) ir polipropileno (PP) schemos [10].

Polyethylene and polypropylene, two pivotal polymers in the industry, are produced using ethylene and propylene gas, respectively (see Figure 2a). To produce low-density polyethylene, radical polymerization is employed. In contrast, high-density polyethylene is produced through coordination polymerization, using a specific catalyst shown in Figure 2b. Similarly, the production of polypropylene mainly relies on coordination polymerization but specifically employs $TiCl_4/MgCl_2$ Ziegler–Natta catalysts combined with dialkyl-dialkoxy silane compounds (Figure 2c) [11, 12].

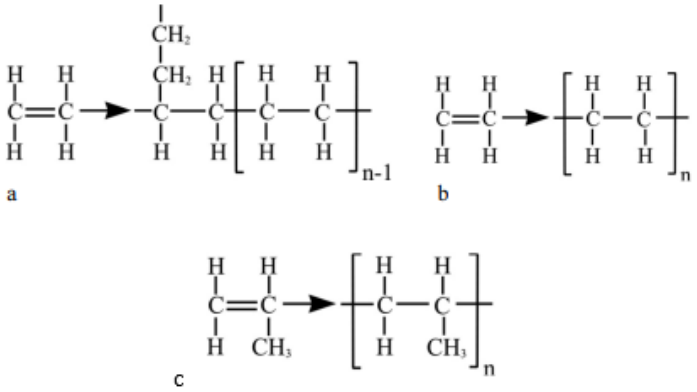


Figure 2. Production of polyethylene from ethylene gas: a – LDPE, obtained by radical polymerization, b – HDPE, obtained by coordination polymerization using catalysts. c – production of PP from propylene by coordination polymerization using $TiCl_4/MgCl_2$ Ziegler and Natta catalysts [8].

2 paveikslas. Polietileno gamyba naudojant etileno dujas: a – LDPE, gaunamas radikalinės polimerizacijos metodu, b – HDPE, gaunamas koordinacinės polimerizacijos metodu naudojant katalizatorių. c – PP gavimas iš propileno koordinacinės polimerizacijos metu naudojant Ziegler ir Natta ($TiCl_4/MgCl_2$) iniciatorius [8].

Polyethylene, as food contact material, is mostly used in the form of films. The largest quantities of film are produced by extrusion blowing (Fig 3a). To produce the wanted package, the polypropylene injection moulding method is mostly used (Fig 3b).

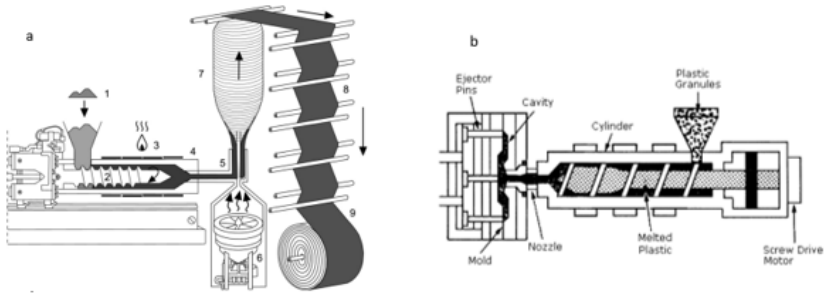


Figure 3. a - principle of polyethylene film production by extrusion blowing method scheme: 1 – plastic granules with additives; 2 – push screw; 3 – heating elements; 4 – the beginning of the extruder forming head; 5 – directional extruder head; 6 – blower; 7 – inflated film bubble; 8 – levelling rollers; 9 - winding device [8], b - injection moulding process of polypropylene [13].

3 paveikslas. a – principinė polietileno plėvelės gamybos ekstrudiniu pūtimo būdu schema: 1 – plastiko granules su priedais; 2 – stūmimo sraigtas; 3 – kaitinimo elementai; 4 – ekstruderio formavimo galvutės pradžia; 5 – kryptingai nukreipta ekstruderio galvutė; 6 – orapūtė; 7 – išpūstas plėvelės burbulas; 8 – išlyginimo volai; 9 – vyniojimo įrenginys [8], b – polipropileno liejimas įpurškimo metodu [13].

2.2. Additives used for packaging materials

The characteristics of the plastic materials are improved by adding a broad array of additives, including lubricants, plasticizers, adhesives, stabilizers, antioxidants, pigments, fillers, polishers, and more, to packing materials [14]. Unfortunately, as most of the additives are low molecular weight, they migrate to food through the functional barrier, therefore plastics that are used for food packaging are not inert [15, 16].

Regarding the growing concern about the potential health effects associated with this migration, countless studies have been conducted to investigate the migration of volatiles, semi-volatiles, additives, monomers, and oligomers from plastic packaging materials into food [16-21]. Nevertheless, significant scientific data uncertainties persist on this subject. Despite the fact, that the migration of additives poses considerable risks, the market continues to expand exponentially. The number of novel additives increases, but the main groups of additives remain unchanged.

Among additives, plasticizers are the most used in plastic materials. Phthalic acid esters, or phthalates, are used as additives to gain the flexibility

and durability of polymer materials. As phthalate additives are not chemically bound to the polymeric matrix, some of them are released slowly to food from the packages [22]. Numerous published studies have described the role of phthalates, such as dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-propyl phthalate (DPrP), diisobutyl phthalate (DIBP), di-n-butyl phthalate (DBP), di-n-pentyl phthalate (DPP), di-n-hexyl phthalate (DHP), butyl benzyl phthalate (BBP), di (2-ethylhexyl) phthalate (DEHP), di (n-octyl) phthalate (DNOP), dinonyl phthalate (DNP), diphenyl phthalate (DPhP) in food packaging materials [16, 19, 22, 23]. But not only phthalic acid esters are used as plasticizers. Also, butyl stearate, acetyl tributyl citrate, alkyl sebacates, and adipates are used as plasticizers because they are assessed as less toxic than phthalates [18], although some previous studies have reported that they might be carcinogenic [11].

Besides plasticizers, thermal stabilizers are commonly added to plastics as they prevent polymer material from thermal degradation. The most investigated stabilizers include different metal soaps like lead, cadmium, barium, calcium, and zinc carboxylates, some di- and mono-alkyltin compounds, e.g., maleates, carboxylates, mercaptides, and epoxy compounds [24-27].

Another significant category of additives is antioxidants, which are used to prevent plastics from oxidation processes. Oxidation can be caused by visible light, heat, ionizing radiation, mechanical effects, or even due to other chemical compounds that are in the plastic material. Recently, so-called hindered-amine light stabilizers (HALS) Irganox 1010 and Irgafos 168 are mostly discussed by the scientific community, as they are primarily used antioxidants in food contact materials [28-31] because of their compatibility, high resistance to extraction, low volatility and, other properties, such as odour and taste. Because of the polymeric structure of HALS, they are of high molecular weight and have restrictive movement. As a result of that, the migration through the functional barrier of plastics might be inconsequential. In most cases, the blends of Irganox 1010 with Irgafos 168 are used, as the manufacturers emphasize noteworthy efficiency. On the other hand, studies by L. Coulier et al. demonstrated that migration into food simulants from commercially available polypropylene and high-density polyethylene samples resulted in concentrations significantly lower than the requirements according to the Directives [29].

To permit the forming process and reduce the adhesion of food components to the packaging, lubricants are used as additives as well. Waxes, paraffin, fats, and oils, acylglycerols, and fatty acid amines are frequently used

as lubricants in the manufacturing processes of food packaging. A study by A. Schaefer et al. confirmed the presence of lubricants in coatings of a commercial epoxy-anhydride coating containing carnauba wax and partial acyl glycerol on tinplate strips [32].

Besides the mentioned additives, stabilizers, antioxidants, UV stabilizers, biocides, and fillers are used as metal additives during the manufacturing processes [33].

To date, numerous researchers have investigated the occurrence of different additives, such as phthalates [16, 19, 22, 34], antioxidants [16, 19, 22, 28, 29, 34-45], volatile organic compounds [3, 46], heat stabilizers [47, 48], lubricants [32], light stabilizers [49], slip agents [50] and others in food and food simulants. Various methods are employed to identify potential migrants in food simulants or extracts of plastic materials including gas chromatography coupled with mass spectrometry, Fourier-transform infrared spectrometry, UV spectroscopy, liquid chromatography, atomic absorption spectrophotometry, inductively coupled plasma optical emission spectroscopy and other methods. Each method and strategy of research has its advantages and drawbacks.

2.3. Legislation of food contact materials

Considering that previous studies have reported that migrated substances may cause harm to humans after exposure [17, 51-53], to protect human health, legal chemical safety requirements for food contact materials are established and must be followed by manufacturers.

According to the European Commission [54], legislation on food contact materials is divided mainly into 4 groups – general legislation, EU legislation on specific materials, other EU legislation, and national legislation. Regarding general legislation, Regulation (EC) No 1935/2004 [55] describes the general principles of safety and inertness for all Food Contact Materials. Concerning EU legislation on specific materials, there are 5 main groups of food contact materials listed – plastic materials, active and intelligent materials, recycled plastic materials, ceramics, and regenerated cellulose film (table 2).

Concerning other EU legislation, there are 3 legislation documents on specific substances - Commission Regulation (EU) 2018/213 [61] for bisphenol A, Commission Regulation 1895/2005/EC [62] for certain epoxy derivatives, and Commission Directive 93/11/EEC [63] for N-nitrosamines and N-nitrosatable substances. What is more, as of 1 July 2011, any

kitchenware made of melamine or polyamide originating or consigned from China or Hong Kong must comply with the import rules of Commission Regulation (EU) No 284/2011 [64]. Also, Commission Recommendation (EU) 2019/794 [65] describes a coordinated control plan for all EU members to establish the prevalence of certain substances migrating from materials and articles intended to come into contact with food.

Table 2.
EU legislation on specific FCM materials [54].
2 lentelė.
EU specifinių plastikų, susiliečiančių su maistu, reglamentavimas [54].

Certain food contact material	**Legislation**
plastic materials	Commission Regulation (EU) No 10/2011 [56]
active and intelligent materials	Commission Regulation (EC) No 450/2009 [57]
recycled plastic materials	Commission Regulation (EU) 2022/1616 [58]
ceramics	Commission Directive 84/500/EEC [59]
regenerated cellulose film	Commission Directive 2007/42/EC [60]

National legislation allows setting out individual rules on different materials and substances that may differ from one EU Member State to another. In Lithuania, there is the only legislation HN 16:2011 [66] which is based on Commission Regulation (EU) No 10/2011 [56]. Commission Regulation (EU) No 10/2011 [56] describes a positive list of almost 900 substances (individual organic substances, mixtures, natural products, resins, monomers, oxides, silicates, and others) from low molecular masses to masses higher than 1000 Da that are allowed to be used in plastic as food contact material. These substances have specific concentration limits or limitations in their application. In efforts to measure these compounds, measurements in real foods seem to show the most realistic data. However, it is very difficult to ensure, that the selected food represents all food types. Therefore, to standardize the testing procedures, official food simulants (ethanol 10%, acetic acid 3%, ethanol 20%, ethanol 50%, vegetable oil, and poly(2,6-diphenyl-p-phenylene oxide)) that mimic the use and properties of real food

and conditions of contact (temperature and test time) are defined in the Regulation. Laboratories must follow the defined specific requirements for testing conditions when performing migration experiments. The availability of validated methods for the simultaneous analysis of regulated substances listed in the Commission Regulation (EU) No 10/2011 [56] would considerably improve the efficiency of compliance testing in the plastic food contact materials field. For the methods to be applied in routine laboratories, the need for limited sample preparation steps is also one of the desired characteristics for the method, together with the possibility of quantification at the legislated migration limits.

2.4. Overall migration

According to Commission Regulation (EU) No 10/2011 [56], 'overall migration limit' (OML) means the maximum permitted amount of non-volatile substances released from a material or article into food simulants. Regarding overall migration experiments, plastic materials and articles shall not transfer their constituents to food simulants in quantities exceeding 10 mg of total constituents released per dm^2 of food contact surface (mg/dm^2), and plastic materials and articles intended to be brought into contact with food intended for infants and young children shall not transfer their constituents to food simulants in quantities exceeding 60 mg of total of constituents released per kg of food simulant. Overall migration testing shall be performed under standardised testing conditions that are related to the intended contact time of food in the material or article and the intended food itself.

Food simulants that represent all food types are used for overall and specific migration evaluation. Foods that have a hydrophilic character and can extract hydrophilic substances are covered by food simulants A, B, and C, while foods that have a lipophilic character and can extract lipophilic substances are covered by food simulants D1 and D2. Dry foods are mimicked by food simulant E (Table 3).

Standardized testing conditions (Table 4) depend on whether the testing material is repeated or a single-use article is used for overall migration. To test repeated use articles, the overall migration test shall be carried out three times on a single sample using another sample of the food simulant on each occasion.

Table 3.
List of food simulants, their abbreviation, and assignment of foods [56].
3 lentelė.
Maisto modelinių tirpalų sąrašas, jų santrumpa ir priskyrimas maisto produktams [56].

Food simulant and abbreviation	**Assignment to foods**
Ethanol 10 % (v/v) – food simulant A	foods that have a hydrophilic character and can extract hydrophilic substance
Acetic acid 3 % (w/v) – food simulant B	foods that have a hydrophilic character and can extract hydrophilic substances; foods that have a pH below 4.5
Ethanol 20 % (v/v) – food simulant C	foods that have a hydrophilic character and can extract hydrophilic substances; alcoholic foods with an alcohol content of up to 20 % and those foods that contain a relevant amount of organic ingredients that render the food more lipophilic
Ethanol 50 % (v/v) – food simulant D1	for foods that have a lipophilic character and can extract lipophilic substances; alcoholic foods with an alcohol content of above 20 % and for oil in water emulsions
Vegetable oil with specific fatty acid distribution – food simulant D2	for foods that have a lipophilic character and can extract lipophilic substances; foods that contain free fats at the surface
Poly(2,6-diphenyl-p-phenylene oxide), particle size 60-80 mesh, pore size 200 nm – food simulant E	specific migration into dry foods

Table 4.
Standardized testing conditions for overall migration [56].
4 lentelė.
Standartizuotos bendrosios migracijos bandymų sąlygos [56].

Contact time in days [d] or hours [h] at Contact temperature in [°C]	**Intended food contact conditions**
10 d at 20 °C	Any food contact at frozen and refrigerated conditions.
10 d at 40 °C	Any long-term storage at room temperature or below, including heating up to 70 °C for up to 2 hours, or heating up to 100 °C for up to 15 minutes.
2 h at 70 °C	Any contact conditions that include heating up to 70 °C for up to 2 hours, or up to 100 °C for up to 15 minutes, which are not followed by long-term room or refrigerated temperature storage.
1 h at 100 °C	High-temperature applications for all food simulants at temperatures up to 100 °C.
2 h at 100 °C or reflux or 1 h at 121 °C	High-temperature applications up to 121 °C.
4 h at 100 °C or reflux	Any food contact conditions with food simulants A, B, or C, at a temperature exceeding 40 °C.
2 h at 175 °C	High-temperature applications with fatty foods exceeding the conditions of high temperature applications up to 121 °C.

2.5. Specific migration

Specific migration or 'specific migration limit' (SML), as regulated by Commission Regulation (EU) No 10/2011 [56], means the maximum permitted amount of a given substance released from a material or article into food or food simulants. Regarding specific migration experiments, plastic materials and articles shall not transfer their constituents to foods in quantities exceeding the specific migration limits (SML), that are expressed in mg of substance per kg of food (mg/kg) and for substances for which no specific migration limit or other restrictions are provided, a generic specific migration limit of 60 mg/kg shall apply.

Migration in general includes two macroscopic mass transfer mechanisms [15]:

1. mass diffusion in and through the different plastic materials as well as the liquid or gas phases separating the primary source from the food;
2. desorption/sorption at the interface between each crossed medium. When it involves fluid phases, migration may also cover an additional transport or mixing effect by advection.

To model mass transfer mechanisms, diffusion coefficient, polymer-specific parameters, and partition coefficient need to be estimated as they are the main input parameters.

Diffusion coefficient (D_p^*, m^2/s) can be estimated by Arrhenius type equation [30, 67]:

$$D_p^* = \exp\left(A_p^* - 0.135M_r^{\frac{2}{3}} + 0.003M_r - \frac{10454}{T}\right) \quad (1)$$

and

$$A_P^* = A_P' - \frac{\tau}{T} \quad (2)$$

Where A_p – a temperature-dependent polymer-specific constant, that describes the basic diffusion behaviour of the polymer matrix with the migrants. The asterisk * indicates an upper bound value and the apostrophe ' indicates the parameter is temperature independent. According to [15, 68], in soft/flexible polymers, such as polyethylene polymer specific constant values are high reflecting high diffusion behaviour and hence high migration through the polymer. M_r – a relative molecular mass of migrant (Da). T – absolute temperature based on empirical relationships and experimental data. τ -

polymer specific "activation temperature" increment (K) and 10454 R – reference activation energy (J mol^{-1}), that contribute to the diffusion activation energy,

$E_A = (10454+\tau)R$. E_A data for a large series of migrants in many polymer matrices, it was concluded that one can take $\tau = 0$ for many polymers [68]. For simplification reasons, it is assumed in this model that the activation energy is the same for all molecules in the applicable molecular mass range. R – gas constant (8.3145 J mol^{-1} K^{-1}). It must be emphasized that $D_p \leq D_p^*$. Therefore, using such a D_p^* for migration estimations leads to overestimated migration values.

Concerning polymer-specific parameters, polyolefins have specific temperature ranges (Table 5) for usage as the food package is generally limited to less than 100 ^{0}C, which is also valid for the applicability of migration modelling.

Table 5.
'Upper-bond' of polymer-specific values for selected polyolefins [15].
5 lentelė.
Pasirinktų poliolefinų polimerui būdingų verčių „viršutinės ribos" [15].

Polymer	**M_r, g/mol**	A'_p	**τ**	**T, ^{0}C**
LDPE	30 – 2000	11,5	0	≤ 80
LLDPE		11,5	0	≤ 100
HDPE		14,5	1577	≤ 90
PP (homo and random)		13,1	1577	≤ 120

The partition coefficient is estimated differently depending on the quantity of layers. When it comes to monolayers, the partition coefficient of the migrant between polymer and food should be taken as K = 1, which means that the migrant is well soluble in food, and, therefore, the migration values are high [15]. As to multi-layers, the partition coefficient must be counted between the layers (plastic vs. food or plastic vs. plastic):

$$K = \frac{c_{plastic}}{c_{food}} \quad (3)$$

or

$$K = \frac{c_{plastic}}{c_{plastic}} \quad (4)$$

where c is the concentration of the migrant in the respective layer of plastic or food at equilibrium.

Table 6.
Testing conditions of contact time [56].
6 lentelė.
Sąlyčio laiko bandymų sąlygos [56].

Contact time in worst foreseeable use	**Test time**
t ≤ 5 min	5 min
5 min < t ≤ 0,5 hours	0,5 hour
0,5 hours < t ≤ 1 hour	1 hour
1 hour < t ≤ 2 hours	2 hours
2 hours < t ≤ 6 hours	6 hours
6 hours < t ≤ 24 hours	24 hours
1 day < t ≤ 3 days	3 days
3 days < t ≤ 30 days	10 days
Above 30 days	See specific conditions

What is more, other input parameters, such as initial concentration, food, and food simulant, contact time-temperature conditions, contact surface, food volume, and the effective thickness of food, must be estimated by model mass transfer mechanisms [15].

Also, Gregory O. Noonan et al. exclude four nanomaterial release pathways. This is the desorption, diffusion, dissolution, and degradation of the matrix [69]. Desorption likely proceeds because of the weak bonding of migrants to the surface and depends on liquid characteristics (pH, ionic strength, and presence of contaminants that promote bonding), temperature,

fluid velocity, physical abrasion, and vibration. Diffusion mechanisms depend on the concentration gradient, surface treatment, size and shape of migrants, and polymer properties. Regarding the dissolution mechanism of ions release to dissolution, pH, ionic strength, size, shape, and concentration of migrants are the main factors. The last, but likely mechanism is the matrix degradation resulting in the polymer loss. Degradation can be conditioned mainly because of mechanical abrasion, UV exposure, material fatigue, and hydrolysis/selling [69].

Table 7.
Testing conditions of contact temperature [56].
7 lentelė.
Sąlyčio temperatūros bandymo sąlygos [56].

Contact temperature	**Test temperature**
T ≤ 5 °C	5 °C
5 °C < T ≤ 20 °C	20 °C
20 °C < T ≤ 40 °C	40 °C
40 °C < T ≤ 70 °C	70 °C
70 °C < T ≤ 100 °C	100 °C or reflux temperature
100 °C < T ≤ 121 °C	121 °C
121 °C < T ≤ 130 °C	130 °C
130 °C < T ≤ 150 °C	150 °C
150 °C < T < 175 °C	175 °C
T > 175 °C	Adjust the temperature to the real temperature at the interface with the food

As in overall migration, the same food simulants are used for specific migration (Table 3). However, testing conditions (contact time and

temperature) differ. Testing conditions must rely on the intended worst foreseeable use of contact time (Table 6) and temperature (Table 7) of food, also it is preferable to use instructions on the packages.

To assess the repeated use of articles, the migration assessment must be conducted three times using a different food simulant sample each time on a single test sample.

2.5.1. Metals as additives

Metal-based additives are distributed into three forms - insoluble inorganic compounds, partially soluble organic compounds, and organometallic liquids or salts. Different metal concentrations in the final plastic product can be added. It depends on the type of the polymer matrix, the nature of the metal as an additive, and the desired effect (shape, thickness, colour, intended usage, etc. of the final article) [70].

Colourants are a group of metal additives most used in plastic materials. For example, cobalt (II) diacetate is an organic pigment and cadmium, chromium, and lead compounds are used as inorganic pigments [33]. Flame retardants are another group of metal additives. Most are used as inorganic retardants [33]. Apart from flame retardants, thermal stabilizers are also frequently used additive in plastics as they prevent polymer material from thermal degradation. The mostly investigated stabilizers are different metal soaps like lead, cadmium, barium, calcium, and zinc carboxylates, some di- and mono-alkyltin compounds, e.g., maleates, carboxylates, mercaptides, and epoxy compounds [24, 25, 27, 71]. Also, stabilizers, antioxidants, UV stabilizers, biocides, and fillers are used as metal additives during the manufacturing processes [33, 71, 72].

Due to the potential hazard of metals, they are regulated by different legislations. According to European Parliament and Council Directive 94/62/EC of 20 December 1994 on packaging and packaging wastes the sum of concentration levels of Cd, Pb, Cr, and Hg present in packaging or packaging components shall not exceed 100 ppm by weight [73]. Also, as stated in Commission Regulation (EU) No 10/2011 migration of Cd, Pb and Cr from food contact materials to food simulants have to be non-detectable by the limit of detection of 0.01 mg/kg for Pb, Cr and of 0.002 mg/kg for Cd [56].

As stated in the database CPPdb Lists A and B [74] that is designated for plastics, the function of the heavy metals Cd, Cr, Hg and Pb are:

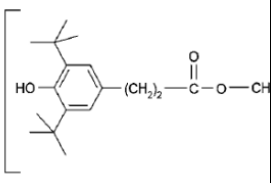
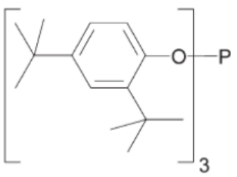
- Cd compounds can be used as catalysts, plastics fillers, hardeners, colourants, adhesives, heat or UV stabilizers or pigments (0.01-1% low e.g., light beige, high e.g., clear war yellow);
- Cr compounds can be used as raw material for plastics production, solvents, hardeners, fillers, colourants, or adhesives;
- Hg compounds can be used as hardeners, fillers, colourants, adhesives, or catalysts;
- Pb or its compounds are used as adhesives, antioxidants, oxidants, raw materials, solvents, stabilisers, paint fillers, hardeners, lubricants, colourants, or adhesives.

What is more, specific migration limits of other elements, such as Al, Sb, As, Ba, Ca, Co, Cu, Eu, Gd, Fe, Ln, Li, Mg, Mn, Ni, K, Na, Tr, and Zn are listed in Commission Regulation (EU) No 10/2011 [56].

2.5.2. Antioxidants as additives

Food packages are affected by heat and light during food transportation, storage, microwave heating, etc. Due to limited stability to high temperatures and UV light of polyethylene and polypropylene, antioxidants need to be added to final packaging materials [18, 41, 75]. Recently investigators have examined mostly the migration of antioxidants such as Irganox 1010 and Irgafos 168 [76-82].

Table 8.
The structure and main properties of Irganox 1010 and Irgafos 168 [86, 87].
8 lentelė.
Irganox 1010 and Irgafos 168 pagrindinės savybės ir struktūra [86, 87].

Properties	**Irganox 1010**	**Irgafos 168**
		
CAS number	6683-19-8	31570-04-4
Appearance	White, free-flowing powder	White powder
Molecular weight	1178 g/mol	647 g/mol

According to [83] the most used antioxidant to ensure the long-term thermal stability of polyolefins is Irganox 1010 (Table 8). Irganox 1010 is regulated for daily intake at 0.115 mg/kg body weight/day by the U.S. [84] and is listed as a possible migrant in Commission Regulation (EU) No 10/2011 and a generic specific migration limit of 60 mg/kg applies [56],

As reported by Xiaowei Wu, the antioxidant Irgafos 168 (Table 8) is the dominant additive of polypropylene food packaging materials [85] and is listed as a possible migrant in Commission Regulation (EU) No 10/2011 and a generic specific migration limit of 60 mg/kg applies [56].

2.6. Degradation of polymers

Apart from the migration of known additives, products of degradation of the article might migrate to the food. Due to different impacts, such as mechanical comminution, temperature, pH, UV/infrared radiation, and others, polymer physicochemical degradation might occur [88]. Zhang et al. [89] illustrated general processes of plastic degradation (Figure 4).

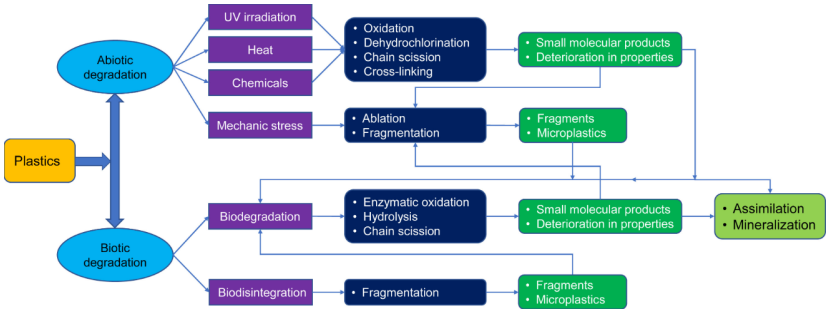


Figure 4. A schematic diagram showing the general processes involved in the degradation of plastics [89].

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4 paveikslas. Scheminė diagrama, vaizduojanti pagrindinius procesus, vykstančius polimero degradacijos metu [89].

The degradation of polymers is adjusted by abiotic and biotic degradation mechanisms. Abiotic degradation of plastics refers to the change of physical or chemical properties that occurs for plastics due to abiotic factors such as light, temperature, air, water, and mechanical forces while biotic degradation of plastics refers to the deterioration of plastics caused by

organisms. The main factors for the abiotic degradation of plastics are UV irradiation, heat, chemicals, and mechanical stress. Due to biodegradation and bio-disintegration, biotic degradation of plastics occurs.

Due to solar irradiation, mainly of high energy ultraviolet (UV) irradiation UV-B (290 – 315 nm) and medium energy UV-A (315 – 400 nm), photodegradation of plastics occurs [90]. Polyethylene would be resistant to photodegradation processes due to the lack of chromophores if there is no presence of impurities or structural defects in polymers during manufacture or weathering, that can act as chromophores [91]. Polyethylene is less stable because of the presence of tertiary carbon, which is more susceptible to oxygen attack [92]. The photodegradation mechanisms of PE and PP are illustrated in Figure 5 [89].

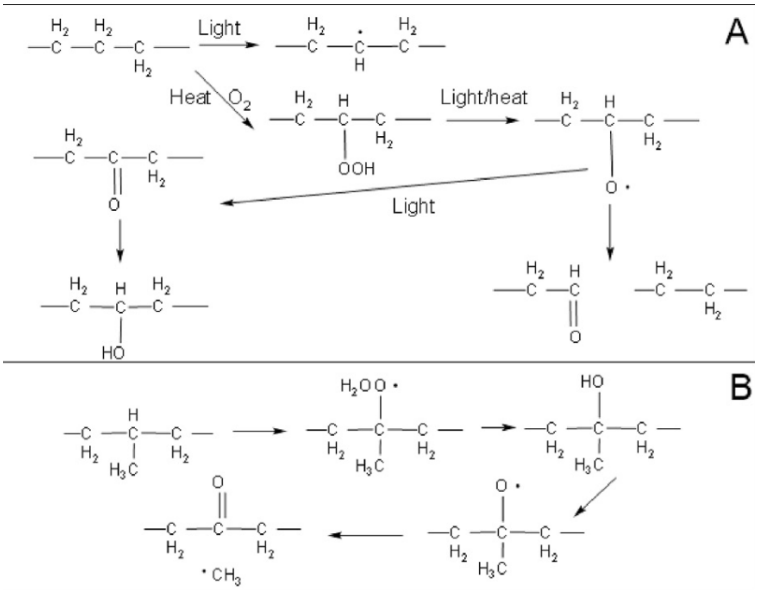

Figure 5. The photodegradation mechanisms of PE (A) and PP (B) [89].

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5 paveikslas. PE (A) ir PP (B) foto-degradacijos proceso mechanizmai [89].

As food is warmed or frozen frequently during storage, regarding food contact materials, the thermal effect is mostly investigated for polymer degradation [93, 94]. During thermal degradation, the long polymer chains can be broken generating radicals when sufficient heat is absorbed by the polymer [95, 96], for thermal degradation initiation temperature and UV light

are required [97]. The General proposed thermo auto-oxidation mechanism for polymers is illustrated in Figure 6 [93].

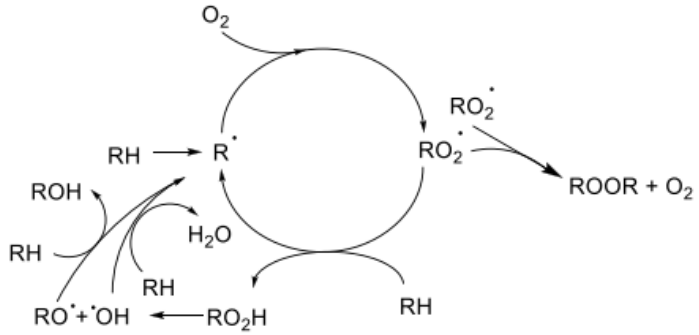

Figure 6. General thermo auto-oxidation mechanism for polymers (R = polymer chain, H = most labile hydrogen) [93].
6 paveikslas. Bendras termo auto-oksidacijos, vykstančios polimeruose, mechanizmas (R = polimerinė grandinė, H = labiliausias vandenilis) [93].

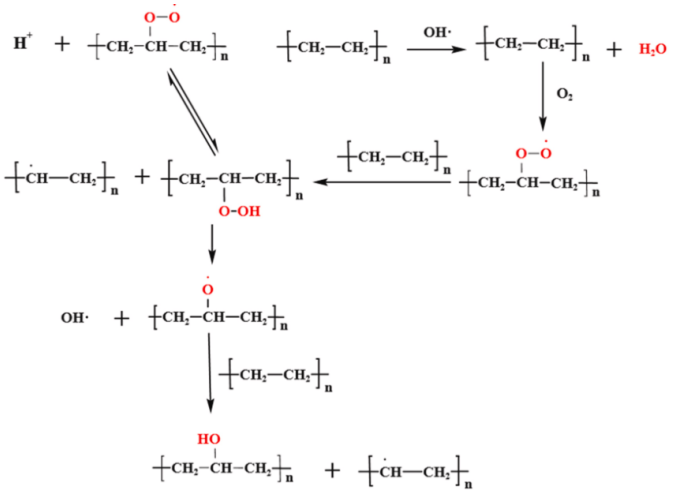

Figure 7. Effect of pH value on PE degradation [88].
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7 paveikslas. pH įtaka PE degradacijos procesams [88].

pH is the most important chemical factor influencing plastic degradation [95]. Previous studies have reported that a lower pH value promoted the degradation of PE, and the degradation mechanism was mainly

affected by the following processes: formation of –COOH or –OH, peroxy radicals, hydroxyl radical, and OH· (Fig. 7.) [88].

Mechanical degradation occurs after mechanical stress and ultrasonic irradiations and leads to polymer chain breakdown [98, 99]. Freezing and thawing of plastics are also factors for the mechanical degradation of plastics [100].

Regarding the biotic degradation of plastics, there are two possible mechanisms, i.e. organisms physically bite, chew, or digest plastics [101, 102] or biochemical processes [103]. Microorganisms that can degrade polyethylene are *Bacillus cereus, Bacillus megaterium, Bacillus subtilis, Bacillus subtilis* [88, 104], *Pseudomonas citronellolis* [88, 105], *Citrobacter sp., Kosakonia sp.* [88, 106, 107], *Streptomyces* sp. [88, 108, 109], *Rhodococcus rhodochrous* [88, 107], *Rhodococcus ruber (C208)* [88, 105-107], *Brevibaccillus borstelensis strain 707* [88, 108], *Bacillus pumilus M27*, *Bacillus subtilis H1584*, *Kocuria palustris M16* [88, 110], *Chryseobacterium gleum EY1* [88, 111], *Rhodococcus sp.* and others [88], while polypropylene can be affected by *Bacillus* sp. *strain 27 and Rhodococcussp. strain 36 micro*organisms [88]. The mechanism of biodegradation of polymers consists of three stages. Firstly, microorganism attaches to the surface of the polymer. Secondly, the polymer is utilized as a source of carbon and thirdly, the polymer degrades [88].

In conclusion, mechanical stress, heat, pH, and other factors are very important factors for the degradation of plastics, but the main factors are UV radiation and biodegradation [88].

2.7. Method validation

The method validation process is used to ensure the method is suitable for its intended analytical purpose. The more complex the method, the more validation procedure is necessary. The main official documents regarding method validation are the guidelines for performance criteria and validation procedures of analytical methods produced by members of the Eurachem Method Validation Working Group [112]. Besides these documents, numerous articles have been published on the topic of analytical method validation [113-120].

To validate the method, method-performance characteristics, such as precision, trueness, selectivity/specificity, working range, the limit of detection (LOD), the limit of quantification (LOQ), sensitivity, and ruggedness/robustness are evaluated. To evaluate all method-performance

characteristics or only the main ones, such as precision, trueness, linearity, limit of detection (LOD) and limit of quantification (LOQ) depends on the method itself and the experience of the specialist who is creating the method. Different ways of evaluating method-performance characteristics are used, but the most frequently used calculations are described in the text below.

Precision is the measure of how close results are to one another and relates to the random error of a measurement system [117, 121, 122]. Depending on the conditions of sample measurement, there can be three types of precision: repeatability [112, 123, 124] intermediate precision [112, 121, 123], and reproducibility [112]. When the samples are measured by the same analyst and equipment, same laboratory, and short timescale, it is called repeatability conditions. Regarding intermediate precision, measurements are made by different analysts and equipment in, the same laboratory, extended timescale. Reproducibility conditions are evaluated when the measurements are carried out by different analysts and equipment, different laboratories, and extended timescales. Precision mostly is expressed as a standard deviation or relative standard deviation of 6 - 15 replicates of reference materials, surplus test samples, or spiked sample blanks at various concentrations across working range measurements [112].

Trueness relates to the systematic error of a measurement system [117, 124] and refers to the agreement between the average of an infinite number of replicates measured values and the true value of the measured quantity [121]. As it is impossible to measure an infinitive number of samples, trueness is evaluated from 10 measurements and the reference values are used instead of the true value of the measured quantity. Trueness is normally expressed quantitatively in terms of 'bias' (b) and can be expressed in absolute terms (equation 5), relative in % (equation 6), or as a relative spike recovery (equation 7) [112]:

$$b = \bar{x} - x_{ref} \tag{5}$$

$$b(\%) = \frac{\bar{x} - x_{ref}}{x_{ref}} \tag{6}$$

$$R'(\%) = \frac{\bar{x}' - \bar{x}}{x_{spike}} \times 100 \tag{7}$$

Where $\bar{x}$ is the mean value of the results, x_{ref} is the reference value, $\bar{x}'$ is the mean value of the spiked sample and x_{spike} is the added concentration.

There are several approaches to the evaluation of trueness. The most accurately evaluated trueness is when the mean value of measured (10 repetitions) reference material concentrations is compared to a reference value. Such a comparison gives a measure of bias considering the effect of both method and laboratory bias. Also, matrix blanks or test samples unspiked and spiked with the analyte of interest over a range of concentrations can be used for trueness evaluation. What is more, measuring concentrations of reference material by alternative methods can be used [112].

In IUPAC recommendations [125], selectivity/specificity is defined as "the extent to which the method can be used to determine particular analytes in mixtures or matrices without interferences from other components of similar behaviour ". The selectivity of the method is investigated by studying the effects of interferences, for example, by proving the lack of response in a blank matrix [117, 126-128]. Also, there is a possibility of the assumption that for merely quantitative procedures, small interferences can be accepted if accuracy (bias) and precision at the lower limit of quantitation remain within certain acceptance limits [114, 117, 129]. According to guidelines for performance criteria and validation procedures of analytical methods produced by members of the Eurachem Method Validation Working Group [112], the selectivity of the method can be determined in two ways. One is to analyze test samples, and RMs by candidate and other independent methods and to use the results from the confirmatory techniques to assess the ability of the method to confirm analyte identity and its ability to measure the analyte in isolation from other interferences. Another is to analyze test samples containing various suspected interferences in the presence of the analytes of interest and examine the effect of interferences.

Regarding the working range of the method, there is a method working range, which relates to the concentration in the laboratory sample (linear relationship between analyte signals and analyte concentrations in samples containing matrix components [120]), and instrument working range, which is defined in terms of the concentration in a processed test sample presented to the instrument for measurement (linear relationship between analyte signals and analyte concentrations in calibration samples [120]). During validation, it is necessary to confirm that the method can be used over the whole working range. To assess the working range, the laboratory needs to consider both the method linearity and the proposed calibration procedure given in the method [112]. According to ICH [123], a minimum of 5 concentration levels of spiked samples must be measured to evaluate linearity and in most of the guides [112, 129, 130] minimum of 6 concentration levels of spiked samples must be

measured and the relationship between concentration and instrument response by examining the regression statistics and residual plot for the chosen model (e.g. linear, quadratic) must be confirmed.

Another method-performance characteristic similar to the working range (linearity) is sensitivity. As stated in the EURACHEM guide [112], sensitivity is defined as "the change in the response of a measuring instrument divided by a corresponding change in the stimulus". Unfortunately, ICH [123, 130] and EMA [130] guides do not even mention this method-performance characteristic. Mostly sensitivity is used for three reasons. Firstly, for method parameters optimization during method development. Secondly, for daily optimization of the instrument parameters. And thirdly, for instrument performance monitoring.

Limit of detection (LOD) and limit of quantification (LOQ) are also very important method-performance characteristics that need to be evaluated. LOD is defined as the lowest amount or lowest concentration of the analyte in a sample which can be reliably detected and identified with the method [112, 129, 131] and LOQ as the lowest concentration of analyte that can be determined with acceptable repeatability and trueness [112]. In addition, as in the evaluation of the working range of the method, LOD and LOQ can be related to the instrument LOD/LOQ and related to the method LOD/LOQ. The difference is that method LOD/LOQ is based on the analysis of samples that have been taken through the whole measurement procedure using results calculated with the same equation as for the test samples and the instrument LOD/LOQ is based on the analysis of a sample, often a reagent blank, presented directly to the instrument (i.e., omitting any sample preparation steps), or on the signal-to-noise ratio in, e.g., a chromatogram [112]. Replicate measurements of blank samples or test samples with low concentrations of analyte are mostly used for LOD and LOQ evaluation. The calculated standard deviation of the results is multiplied by a factor k, which is equal to 3 when LOD is evaluated and 5 in the evaluation of LOQ [112].

Ruggedness/robustness is mostly evaluated method-performance characteristics as it is identified as the ability of an analytical method to remain resistant to variations in method parameters (mobile phase composition, column age, column temperature, etc.) and influential environmental factors (room temperature, air humidity, etc.) [112, 124, 129, 132]. The Plackett–Burmann approach is mostly used for the evaluation of ruggedness/robustness [133, 134]. Kruve et al. [120], for evaluation of ruggedness/robustness during sample preparation recommend testing method parameters such as analyte extraction time, solvent amount, and composition (in liquid/liquid and solid

phase extraction, etc.), injection solvent composition, and matrix effect in a broad sense (sample matrix source). What is more, different method parameters regarding liquid chromatography and mass spectrometry are mentioned in the publication.

Also, another method-performance characteristic called measurement uncertainty is mentioned in the context of method validation. However, though it can be calculated from validation data, trueness, and precision, measurement uncertainty is not a validation parameter. The most frequently used guidelines for uncertainty evaluation are published by NordTest [135].

Specification of acceptance criteria for method-performance characteristics mentioned before is quite difficult as it depends on each specific application. The main rule is that the final validated method should "fit for purpose".

3. INSTRUMENTATION AND METHODOLOGY

3.1. Polyethylene and polypropylene samples and their preparation for analysis

3.1.1. Polymer identification experiments

In order to know which results relates to which FCM, all the samples tested were identified before the analysis. They were cut into small pieces of around 1.0 × 1.0 cm. None of the samples were used for food packaging before the analysis. The identification analysis was carried out by attenuated total reflectance Fourier-transform infrared spectrometry (ATR-FTIR) (clause 3.2.).

3.1.2. Overall migration experiments

A total of different types of 126 samples were chosen to analyse overall migration, 76 of them were made of PE and 50 of PP. Mainly all kinds of films made of PE and candy trays, bottles, and others of PP. None of the samples were used for food packaging before the analysis.

Samples were exposed to different food simulants, such as 3 % acetic acid, 10 % ethanol, 50 % ethanol, 95 % ethanol and isooctane, as they mimic different types of food (Table 3) as stated in Commission Regulation (EU) No 10/2011 [56]. The conditions of exposition were 10 days at 40 °C. According to Commission Regulation (EU) No 10/2011 [56] these conditions mimic

contact times of the sample and food above 30 days (long term) at room temperature and below. Film samples were soldered to make a bag and filled with food simulants (Figure 8). Different containers were filled with food simulants and protected against evaporation by applying a film on the top.

Figure 8. Film samples
8 paveikslas. Plėvelių pavidalo mėginiai.

To be sure, that the samples were exposed to the necessary temperature (40 ± 2 °C), all the samples were kept in the temperature-checked oven, and during the experiment calibrated thermologer was used to log the temperature deviations.

The analysis was done by gravimetry (clause 3.3.).

3.1.3. Polymer degradation experiments

A total of 52 samples were chosen to analyse polymer degradation processes. None of the samples were used for food packaging before the analysis. Regarding the 20 samples of polypropylene (PP), the majority of the light-coloured samples were films for bread, cheese, crisps, etc. packaging, and the dark-coloured packages mostly were candy trays, jars, and bottles, and intended to be used with chocolate, soft drinks, milk products, and others. Considering 20 polyethylene (PE) samples, light-coloured films for packets, food preservation bags, plastic cups, lids, etc. were used for testing. 12 of the PP/PE composite packages consisted mostly of packaging films for bread or

crisps. Different sample preparation techniques were used for packaging testing:

1. to analyse volatile and semi-volatile organic compounds, approximately 0.1 g of polypropylene and polyethylene samples were cut into small pieces of 0.2 cm × 1.0 cm and inserted into glass thermal desorption tubes (Figure 9B and 9C). Plugs of annealed glass wool were inserted into the thermal desorption tubes to hold the sample material in the tube. The tubes were sealed with metal caps lined with Teflon, loaded into an autosampler, and analysed. Two parallels of each sample were tested with the same method. For blank analysis, an empty thermal desorption tube with the plugs of glass wool was tested (Figure 9A).

2. for metals analysis, approximately 0.2 g of PP, PE, and PP/PE samples were cut into small pieces and mineralized in the nitric acid (65 %) and peroxide solution (30 % pure, p.a.) 5:2 (v/v, ml). After the mineralization for 3 hours, the extract was diluted with water to 25 ml. Two parallels of each sample were tested with the same method. For blank analysis, nitric acid, and peroxide solution 5:2 (v/v, ml) diluted with water to 25 ml was tested.

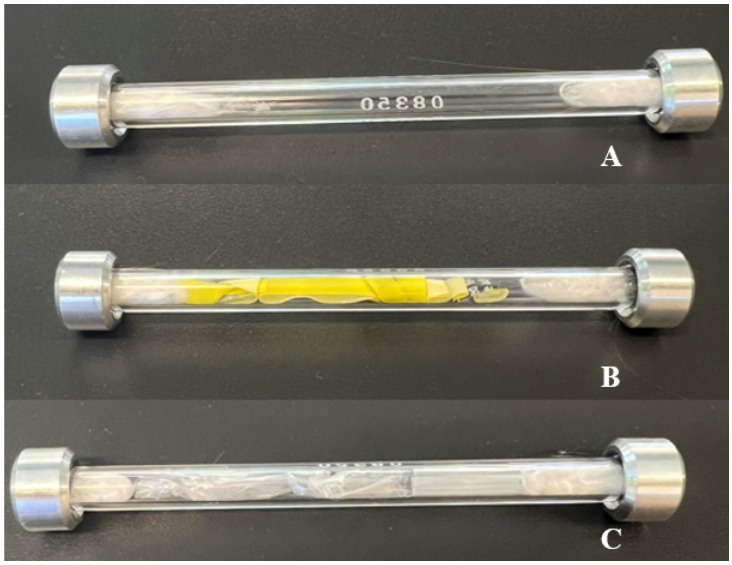


Figure 9. Glass thermal desorption tubes, blank (A), coloured sample (B), transparent sample (C).

9 paveikslas. Stikliniai terminus desorbcijos vamzdeliai, kuriuose tuščias mėginys (A), spalvotas mėginys (B), skaidrus mėginys (C).

The analysis of metals by atomic absorption spectrophotometry (AAS) (clause 3.4.) and of volatile and semi-volatile organic compounds was done by thermal desorption gas chromatography coupled with mass spectrometry (TD-GC/MS) (clause 3.5.).

3.1.4. Specific migration experiments

A total of 23 different food contact materials made of PE were chosen to analyse specific migration. Samples were exposed to different food simulants for determination of antioxidant content, such as 3 % acetic acid, 95 % ethanol and isooctane, as they mimic different types of food (Table 3) as stated in Commission Regulation (EU) No 10/2011 [56]. For metal content determination, 3 % acetic acid as a food simulant was used [56]. None of the samples were used for food packaging before the analysis.

The conditions of exposition to 3 % acetic acid were 10 days at 60 °C. According to Commission Regulation (EU) No. 10/2011, testing for 10 days at 60 °C shall cover long-term storage above 6 months at room temperature and below, including heating up to 70 °C for up to 2 hours or heating up to 100 °C for up to 15 minutes [56]. Regarding migration into isooctane, it was decided to use migration test conditions at 20 ºC for 2 days and 95 % ethanol at 40 ºC for 10 days as it is the standard condition for substitute test of vegetable oil (food simulant D2).

As for overall migration experiments, all the samples were cut into square pieces (1 dm^2; 10 × 10 cm) before the test, soldered in bag form, filled with 100 ml of food simulant, and stored under the required conditions.

Irganox 1010 (CAS: 6683-19-8) and Irgafos 168 (CAS: 31570-04-4) standards were obtained from LGC Standards, HiPerSolv Chromanorm® grade purity methanol (CAS: 67-56-1) and tetrahydrofuran (CAS: 109-99-9) were purchased from VWR Chemicals, toluene (CAS: 108-88-3) and glacial acetic acid (CAS: 64-19-7) were obtained from Supelco, isooctane (CAS: 540-84-1) was obtained from Honeywell, and ethanol 96% (CAS: 64-17-5) from Vilniaus degtinė. LC/MS grade formic acid (CAS: 64-18-6) was obtained from Thermo Fisher Scientific, and LC/MS grade ammonium formate (CAS: 540-69-2) from Honeywell.

The analysis of specific migration of antioxidants was done by liquid chromatography with tandem mass spectrometry (LC-MS/MS) (clause 3.6.) and for migration of metals by inductively coupled plasma mass spectrometry (ICP-MS) (clause 3.7.).

3.1.5. Extraction experiments

The same samples as for specific migration experiments (clause 3.1.4.) were used for the experiments of the extraction of antioxidants.

Samples were cut into small pieces of about 0.1 g and dissolved in 5 ml of toluene by ultrasonic extraction for 10, 20, 30, and 40 min at 60 ºC. After ultrasonic extraction, 20 ml of methanol was added to precipitate the plastic and to isolate only the additives in the solution of toluene and methanol. Sample supernatants were filtered using 0,45 μm nylon membrane filters and injected directly into the column. The analysis was carried out by liquid chromatography with tandem mass spectrometry (LC-MS/MS) (clause 3.6.).

3.2. Attenuated Total Reflectance Fourier-transform infrared spectrometry (ATR-FTIR)

The Attenuated Total Reflectance Fourier-transform infrared spectrometry (ATR-FTIR) (Agilent Technologies Cary 630) was used for polymer identification. Plastic samples of PP, PE and PP/PE were cut into pieces of 1.0 × 1.0 cm. The spectra were identified by comparison to the FTIR spectra database. ATR was performing a total of 4 scans with a 2 cm^{-1} resolution in the 4000 – 600 cm^{-1} spectral range; the background was air (4 scans, 4000 – 600 cm^{-1}).

3.3. Gravimetry

Overall migration from plastics was measured by a gravimetric determination of all non-volatile chemical substances that migrate to the food simulant. For the analysis of overall migrants, all the sample solution was taken in a porcelain crucible and evaporated to dryness. Before the gravimetric analysis, crucibles were thoroughly washed, dried, and placed in desiccators to cool before being weighed three times on the analytical balance (KERN ABS 220-4N). Weighted mass was compared to a reference weight before each experiment. The quantity of overall migration was calculated by comparing the residual amounts of the sample and the blank sample.

Final overall migration (OM) was calculated using the formula:

$$OM = \frac{(m_a - m_b) \times 1000}{V} \quad (5)$$

where OM is the overall migration into the simulant (mg/kg of food), m_a is the mass of the residue from the test specimen after evaporation of the simulant (g), m_b is the mass of residue from the food simulant only (blank) (g) and V is the volume of the food simulant which had filled the article (ml). The results were converted to mg/kg, considering the weight of 1 dm^2 of the sample. The test result for each test specimen was the average of three replicates.

To analyse overall migrants from PP and PE food packages by gravimetry, analytical in-house methods of migration to different food simulants were validated and the main method performance characteristics, such as intermediate precision, repeatability, trueness, limit of quantitation, limit of detection and uncertainty were estimated (Table 9). For method validation certified reference materials (German Reference Office for Proficiency testing and Reference materials (DRRR)) were used with certified values 4.37 ± 0.17 mg/dm^2 for 3 % acetic acid, 3.73 ± 0.12 mg/dm^2 for 10 % ethanol, 4.71 ± 0.09 mg/dm^2 for 50 % ethanol, 5.35 ± 0.22 mg/dm^2 for 95 % ethanol and 1.66 ± 0.14 mg/dm^2 for isooctane.

Table 9.
Method performance characteristics for determination of overall migration by gravimetry.
9 lentelė.
Gravimetrinio metodo veiksmingumo charakteristikos, skirtos bendrajai migracijai nustatyti.

Method performance characteristics regarding food simulants	**3% acetic acid**	**10 % ethanol**	**50 % ethanol**	**95 % ethanol**	**isooctane**
Intermediate precision (mg/dm^2)	0.11	0.11	0.08	0.07	0.11
Repeatability (mg/dm^2)	0.08	0.06	0.06	0.03	0.07

Method performance characteristics regarding food simulants	3% acetic acid	10 % ethanol	50 % ethanol	95 % ethanol	isooctane
Trueness (bias from certified reference material, mg/dm^2)	0.11 < 0.17	0.06 < 0.12	0.02 < 0.09	0.15 < 0.22	0.05 < 0.14
Limit of quantitation (mg/dm^2)	1.0				
Limit of detection (mg/dm^2)	0.5				
Uncertainty (k = 2) (%)	25				

3.4. Atomic absorption spectrophotometry (AAS)

The atomic absorption spectrophotometer AA-6800 with graphite furnace GFA-EX7 and hydride vapour generator HGV-1 (Shimadzu) was used for metals analysis. An Ar gas of 99.95% purity was used at a pressure of 0.35 MPa. A deuterium lamp was used for the correction of the background and the deuterium hollow cathode lamps for analysis. The wavelengths for Pb, Cd, Cr, and Hg were 283.3 nm, 228.8 nm, 357.9 nm, and 253.7 nm respectively.

To analyse Pb, Cd, Cr, and Hg in PP, PE, and PP/PE composite packages, analytical in-house methods were validated and the main method performance characteristics, such as linearity, intermediate precision, repeatability, trueness, limit of quantitation, limit of detection and uncertainty were estimated (Table 10). For method validation, certified reference materials (VWR Chemicals) were used with certified values of 1011.5 ± 4.5 mg/l for Cr, 1016.6 ± 5.0 mg/l for Cd, 991.3 ± 5.5 mg/l for Pb and 1003,3 ± 4,7 mg/l for Hg.

Table 10.
Method performance characteristics of Cd, Pb, Hg, and Cr analytical in-house methods.
10 lentelė.
Cd, Pb, Hg, and Cr nustatymui skirtų namudinių metodų veiksmingumo charakteristikos.

Method performance characteristics regarding metals	**Cd**	**Pb**	**Hg**	**Cr**
Linearity (r^2)	0.9982	0.9972	0.9992	0.9980
Intermediate precision (%)	3.27	3.69	2.63	2.75
Repeatability (%)	3.15	1.76	0.58	2.47
Trueness (bias from certified reference material, mg/l)	0.0001	0.2500	0.0200	0.0244
Limit of quantitation (mg/kg)	0.150	0.150	0.0121	0.025
Limit of detection (mg/kg)	0.025	0.025	0.0072	0.0125
Uncertainty (k = 2) (%)	4.98	7.16	6.42	7.33

3.5. Thermal desorption gas chromatography coupled with mass spectrometry (TD-GC/MS)

The thermal desorption GC/MS using GCMS-QP2010 Plus (Shimadzu) gas chromatography system with mass spectrometer coupled with thermal desorption sampler TD20 (Shimadzu) was used for non-targeted screening analysis of volatile and semi-volatile organic migrants sample analysis. As the non-targeted analysis was employed, no initial standards were used. Potential migrants were identified with a match probability quality higher than 95 % using the NIST MS Search 2.0 mass spectra library. To perform sample thermal desorption, the tubes were heated for 60 min at 80°C and a flow rate of 60 mL/min He carrier gas flow. Gases evolved from the sample were transported to the focusing trap, programmed with adsorption temperature of – 15°C. After 60 min the focusing trap was instantly desorbed by heating it to 240°C. Gases evolved were transported to the GC injection port under 2.7 mL/min He carrier gas flow. For analysis of the samples, capillary column

Restek Rtx®-1 w/Integra-Guard® coated with Crossbond® 100 % dimethylpolysiloxane (60 m, 0.32 mm ID × 1 μm df) was used. The column oven temperature was programmed from 50°C (10 min), then 5°C/min to 125°C and finally 30°C/min to 240°C (5 min). Full scan mode within a 40-400 m/z range and electron ionization (EI) at 70 eV were used.

3.6. Liquid Chromatography with tandem mass spectrometry (LC-MS/MS)

A high-performance liquid chromatography-tandem mass spectrometry system (LCMS-8040, Shimadzu) was used to measure Irganox 1010 and Irgafos 168-ox. Shimadzu LC-40Dxs solvent delivery module, Shimadzu SIL-40Cxs autosampler, and Shimadzu CTO-40S column oven were used, and all operations were performed and recorded by LabSolutions software. A volume of 1 μL of the solution was injected into the EC 100/2 Nucleoshell Biphenyl column (2 by 100 mm, 2.7 μm), which was maintained at 60 ℃. The mobile phase consisted of three eluents: A (85 % methanol), B (10 % acetonitrile), and C (5 % 5 mM formic acid and 5 mM ammonium formate). The flow rate of the mobile phase was 0.6 mL/min.

Shimadzu LCMS-8040 mass spectrometer was used for the detection. The software automatically optimised method optimization consisting of detecting precursor ions, product ions, and the collision energy. A positive ESI ionization mode was used. The nebulizing gas flow rate was set at 2.0 L/min, the drying gas flow rate was 15.0 L/min, the desolvation line temperature was kept at 250℃. Multiple reaction monitoring (MRM) detection mode was used. Mass spectrometry parameters of Irganox 1010 and Irgafos 168-ox are presented in Table 11.

The ion chromatograms of the antioxidants Irgafos 168-ox and Irganox 1010 are shown in Figures 10 and 11 respectively.

Table 11.
Mass spectrometry parameters of Irganox 1010 and Irgafos 168-ox.
11 lentelė.
Irganox 1010 and Irgafos 168-ox parametrai masių spektrometrijai.

	Irgafos 168-ox	**Irganox 1010**
Precursor ions, (m/z)	663.50	1194.80
Product ions, (m/z)	327.10	730.95
$t_{R,}$ (min)	1.45	1.91

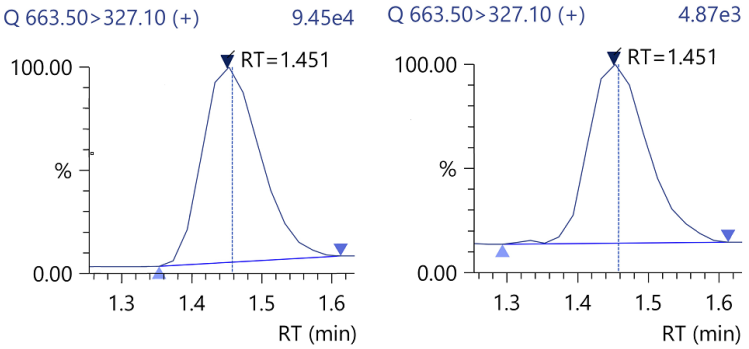


Figure 10. Typical multiple reaction monitoring ion chromatograms of the Irgafos 168-ox standard (left) and Irgafos 168-ox sample (right).

10 paveikslas. Įprastos Irgafos 168-ox standartinės medžiagos (kairėje) and Irgafos 168-ox mėginio (dešinėje) daugialypės reakcijos stebėjimo jonų chromatogramos.

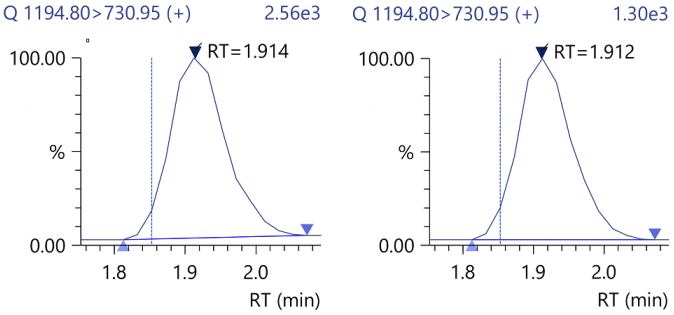


Figure 11. Typical multiple reaction monitoring ion chromatograms of the Irganox 1010 standard (left) and Irganox 1010 sample (right).

11 paveikslas. Įprastos Irganox 1010 standartinės medžiagos (kairėje) and Irganox 1010 mėginio (dešinėje) daugialypės reakcijos stebėjimo jonų chromatogramos.

Regarding method validation, mixed standard solutions with concentrations of 1, 5, 25, 50 and 75 ng/ml were prepared with methanol and tetrahydrofuran (75:25, %v/v). Irgafos 168 was detected in its oxidized form (Irgafos 168-ox) due to the use of THF. The oxidation of Irgafos 168 was similarly reported by Garde et al. [76, 136] where fully oxidized Irgafos 168 was obtained after 24 h of dissolution in tetrahydrofuran. To analyze Irganox 1010 and Irgafos 168-ox in polyethylene packages, the analytical in-house method was validated, and the main method performance characteristics such

as linearity, intermediate precision, repeatability, trueness, the limit of quantitation, limit of detection and uncertainty were estimated (Table 12).

Table 12.
Method performance characteristics for determination of Irganox 1010 and Irgafos 168-ox.
12 lentelė.
Metodo, skirto Irganox 1010 ir Irgafos 168-ox nustatymui, veiksmingumo charakteristikos.

Method performance characteristic	**Irganox 1010**		**Irgafos 168-ox**	
Linearity	$R^2 = 0.9928$		$R^2 = 0.9997$	
Intermediate precision	2.19 %		0.80 %	
Repeatability	1.45 %		0.61 %	
Trueness	98.05 %		96.66 %	
Limit of quantitation	0.0004 mg/dm^2	0.0024 mg/kg	0.0002 mg/dm^2	0.0001 mg/kg
Limit of detection	0.0002 mg/dm^2	0.0012 mg/kg	0.0012 mg/dm^2	0.0006 mg/kg
Uncertainty	13.5 %		10.1 %	

3.7. Inductively coupled plasma mass spectrometry (ICP-MS)

To analyse lead (Pb), cadmium (Cd), and chromium (Cr) in PE packages a Perkin Elmer NexION 2000 ICP mass spectrometer was used. The main instrumental operating conditions for the determination of the elements are following: nebulizer – Meinhard plus concentric; spray chamber – cyclonic; plasma RF generator – Frequency: 10 MHz, Power output 1200 W; plasma Ar flow rate (l/min) – Plasma: 15, auxiliary: 1.2, nebulizer: 1; plasma solution uptake rate – 0.2 ml/min; interface sampler cone – Nickel, i.d.: 1.1 mm; interface Skimmer Nickel, i.d.: 0.9 mm; hyper skimmer – Aluminum; vacuum – Interface:4 torr, quadrupole: 2 105 torr; data acquisition - Peak hopping, replicate time 500 ms, dwell time 25 ms, sweeps/reading 20, readings/replicate 3, number of replicates 3; analytical masses – (52+53)Cr, (111+112+113+114+110)Cd, (206+207+208)Pb.

Analytical in-house methods were validated and the main method performance characteristics, such as linearity, intermediate precision,

repeatability, trueness, limit of quantitation and limit of detection were estimated (Table 13). For method validation certified reference materials (VWR Chemicals) were used with certified values 1011.5 ± 4.5 mg/l for Cr, 1016.6 ± 5.0 mg/l for Cd and 991.3 ± 5.5 mg/l for Pb.

Table 13.
Method performance characteristics of Cd, Pb, and Cr analytical in-house methods.
13 lentelė.
Cd, Pb and Cr nustatymui skirtų namudinių metodų veiksmingumo charakteristikos.

Method performance characteristics regarding metals	**Cd**	**Pb**	**Cr**
Linearity (r^2)	0.9991	0.9962	0.9987
Intermediate precision (%)	4.79	1.95	4.69
Repeatability (%)	3.67	1.80	3.46
Trueness (bias from certified reference material, mg/l)	0.0001	0.2500	0.0244
Limit of quantitation (mg/kg)	0.00006	0.00006	0.00006
Limit of detection (mg/kg)	0.00001	0.00001	0.00001
Uncertainty (k = 2) (%)	6.77	2.76	6.63

4. DISCUSSION ON THE RESULTS

4.1. Polymer identification by attenuated total reflectance Fourier-transform infrared spectrometry (ATR-FTIR)

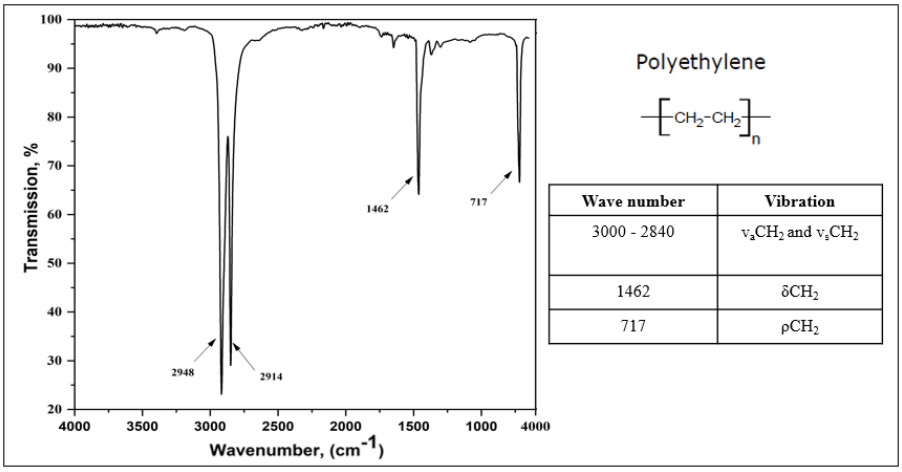
According to the literature, PE, and PP FTIR spectra display distinct and identifiable bands [137-139]. PE is characterized by:

1. antisymmetric and symmetric stretching vibrations of methylene (-CH_2-) groups within the wavenumber range of 3000 - 2840 cm^{-1};
2. in-plane deformations of methylene at 1463 cm^{-1};

3. rocking vibration of methylene at 725 cm^{-1}.

In the case of PP, it is characterized by:

1. antisymmetric and symmetric stretching vibrations of methylene (-CH_2-) and methyl (-CH_3) groups within the wavenumber range of 3000 - 2840 cm^{-1};
2. in-plane deformations of methylene and antisymmetric in-plane deformations of methyl groups at 1459 cm^{-1};
3. in-plane symmetric deformations of methylene at 1376 cm^{-1};
4. rocking vibrations of methyl groups at 1167 cm^{-1};
5. stretching vibrations of (C-C) bonds at 998 and 973 cm^{-1};
6. rocking vibration of methylene at 840 cm^{-1}.



Wave number	Vibration
3000 - 2840	v_aCH_2 and v_sCH_2
1462	δCH_2
717	ρCH_2

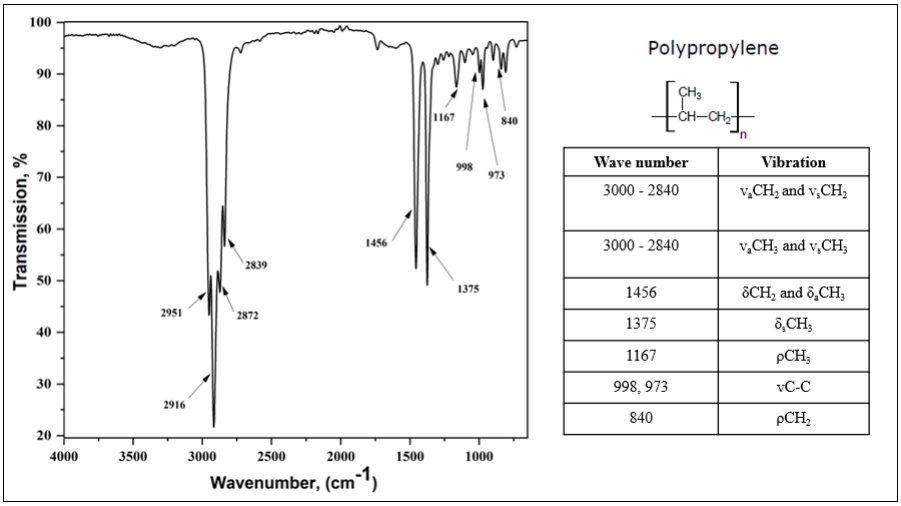
Figure 12. ATR-FTIR spectra of PE. v_aCH_2 and v_sCH_2 correspond to antisymmetric and symmetric stretching vibrations of methylene respectively, δCH_2 to in-plane deformation vibrations of methylene and ρCH_2 to rocking vibration of methylene.

12 paveikslas. PE ATR-FTIR spektras. v_aCH_2 ir v_sCH_2 atitinka antisimetrines ir simetrines metileno tempimo vibracijas, δCH_2 plokštumines metileno tempimo vibracijas ir ρCH_2 siūbuojančias metileno vibracijas.

The present work conducted an FTIR analysis of PE and PP food packages, that were not used for food packaging before the analysis. In Figure 12, the FTIR spectrum of PE revealed four characteristic vibrational absorption bands at 2948, 2914, 1462, and 717 cm^{-1}. These absorption peaks are determinable to the antisymmetric and symmetric stretching vibrations of methylene, along with in-plane deformations and rocking vibrations,

respectively. These findings are in strong concordance with data reported in the literature.

Moreover, the spectra of PP (Figure 13) presented antisymmetric and symmetric stretching vibrations of both methylene (-CH_2-) and methyl (-CH_3) groups within the 3000 - 2840 cm^{-1} range, as well as in-plane deformation of methylene and antisymmetric in-plane deformation of methyl groups at 1459 cm^{-1}. Other characteristic vibrational absorption bands included in-plane symmetric deformations of methylene at 1376 cm^{-1}, rocking vibrations of methyl groups at 1167 cm^{-1}, stretching vibrations of carbon-carbon (C-C) bonds at 998 and 973 cm^{-1}, and a rocking vibration of methylene at 840 cm^{-1}.



Wave number	Vibration
3000 - 2840	v_aCH_2 and v_sCH_2
3000 - 2840	v_aCH_3 and v_sCH_3
1456	δCH_2 and δ_aCH_3
1375	δ_sCH_3
1167	ρCH_3
998, 973	vC-C
840	ρCH_2

Figure 13. ATR-FTIR spectra of PP. v_aCH_2 and v_sCH_2 corresponds to antisymmetric and symmetric stretching vibrations of methylene respectively, v_aCH_3 and v_sCH_3 to antisymmetric and symmetric stretching vibrations of methyl, δCH_2 to in-plane deformation vibrations of methylene, δ_aCH_3 to antisymmetric in-plane deformation vibrations of methyl, ρCH_3 to rocking vibration of methyl, vC-C to stretching vibrations of carbon-carbon and ρCH_2 to rocking vibration of methylene.

13 paveikslas. PP ATR-FTIR spektras. v_aCH_2 ir v_sCH_2 atitinka antisimetrines ir simetrines metileno tempimo vibracijas, δCH_2 plokštumines metileno tempimo vibracijas, δ_aCH_3 antisimetrines plokštumines metilo vibracijas, ρCH_3 siūbuojančias metilo vibracijas, vC-C jungčių tempimo vibracijas ir ρCH_2 siūbuojančias metileno vibracijas.

These characteristics were validated by ATR-FTIR analysis (clause 3.1.1.) of the PP spectrum, which revealed ten distinct vibrational absorption

bands at 2951, 2916, 2872, 2839, 1456, 1375, 1167, 998, 973, and 840 cm^{-1}. These bands align precisely with the spectral characteristics of PP as detailed in existing literature mentioned before, thereby underscoring the reliability of the experimental results.

It must be pointed out that despite the different compositions (especially regarding additives), and forms of the PE and PP samples tested, the spectra presented in Figures 12 and 13 highlight no significant differences between the typical experimental and spectra reported in the literature or spectra database MicroLab FTIR Software.

4.2. Overall migration experiments

The amount of overall migrants for 126 food contact materials manufactured from polyethylene and polypropylene was analyzed using a gravimetric method as described in Sections 3.1.2. and 3.3. The food simulants of 3 % acetic acid, 10 %, 50 %, and 95 % ethanol and isooctane were used to mimic different types of food as stated in Commission Regulation (EU) No 10/2011 [56].

Altogether 76 polyethylene samples were tested (Figure 14). Overall migration to isooctane, 3 % acetic acid, 10 %, and 95 % ethanol were tested in 64, 59, 29, and 61 samples respectively.

For all 29 samples overall migration to 10 % ethanol was under the limit of detection. Overall migration to 95 % ethanol showed that in 24 of 61 food contact materials migration occurred as from 37 of food contact materials migration results were under the limit of detection. Also, overall migration to 3 % acetic acid and isooctane revealed different results. Overall migration to 3 % acetic acid demonstrates that only from 5 of 59 food contact materials migration occurred, but from most of the samples, overall migration was under the limit of detection. Overall migration to isooctane showed that from 21 of 64 food contact materials migration occurred as from 43 of food contact materials migration results were under the limit of detection. But from 5 food contact materials overall migration to isooctane (3 samples) and 3 % acetic acid (2 samples) exceeded the migration limit of 10 mg/dm^2 that is identified by Regulation No 10/2011 [56] (Table 14, lavender coloured).

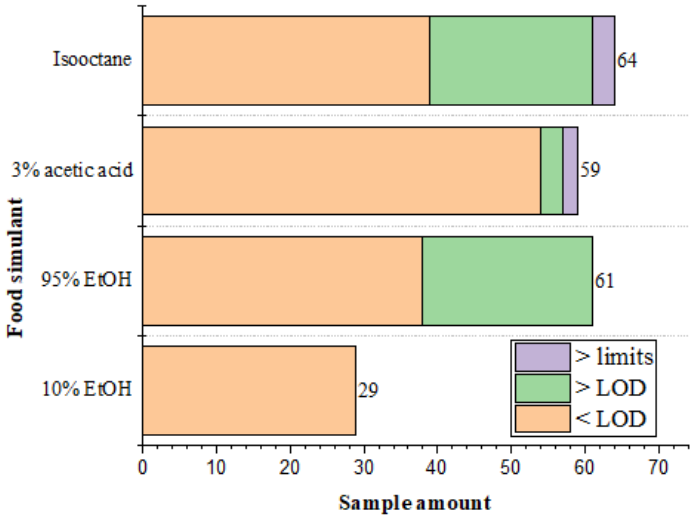


Figure 14. Distribution of PE samples where overall migration occurred below LOD, higher than LOD, and exceeded the Regulation No 10/2011 limit in different food simulants.

14 paveikslas. PE mėginių paskirstymas, įvertinant mėginius, kuriuose bendroji migracija identifikuota kaip mažesnė už metodo aptikimo ribą, kai identifikuota kaip didesnė nei metodo kiekybinio nustatymo riba ir kai bendrosios migracijos rezultatai viršijo Reglamento Nr. 10/2010 nustatytą ribinę koncentraciją.

The average amount of overall migration when using 95 % ethanol, isooctane, and 3 % acetic acid was 1.4 ± 0.3 mg/dm^2, 3.4 ± 0.7 mg/dm^2, and 0.9 ± 0.2 mg/dm^2 respectively. The results of migration to isooctane and 3 % acetic acid that exceeded the migration limit of 10 mg/dm^2 were omitted from the average calculation.

Table 14.

Concentrations of overall migration levels to different food simulants obtained by gravimetry in different packaging materials of PE.

14 lentelė.

Bendrosios migracijos į skirtingus maistinius modelinius tirpalus koncentracijos, gautos gravimetrijos metodu, iš skirtingų maisto pakavimui skirtų pakuočių, pagamintų iš PE.

PE sample No.	Overall migration in 95 % ethanol, mg/dm^2	PE sample No.	Overall migration in 95 % ethanol, mg/dm^2
1	0.8 ± 0.2	58	2.2 ± 0.4
5	1.6 ± 0.3	59	0.8 ± 0.2
8	0.8 ± 0.2	60	1.1 ± 0.2
10	1.5 ± 0.3	62	3.0 ± 0.6
11	3.6 ± 0.7	64	0.7 ± 0.1
12	1.3 ± 0.3	69	0.9 ± 0.2
13	0.7 ± 0.1	71	1.4 ± 0.3
21	0.8 ± 0.2	72	2.2 ± 0.4
30	2.2 ± 0.4	74	1.6 ± 0.3
32	1.0 ± 0.2	75	0.9 ± 0.2
51	1.1 ± 0.2	76	1.1 ± 0.2
57	0.9 ± 0.2		
PE sample No.	**Overall migration in 3 % acetic acid, mg/dm^2**	**PE sample No.**	**Overall migration in 3 % acetic acid, mg/dm^2**
11	1.1 ± 0.2	70	40.0 ± 8.0
12	0.9 ± 0.2	71	60.1 ± 12.0
36	0.8 ± 0.2		
PE sample No.	**Overall migration in isooctane, mg/dm^2**	**PE sample No.**	**Overall migration in isooctane, mg/dm^2**
1	0.7 ± 0.1	38	37.0 ± 7.4
5	4.3 ± 0.9	39	12.4 ± 2.5
6	1.6 ± 0.3	40	5.1 ± 1.0
8	3.6 ± 0.7	41	51.2 ± 10.2
9	1.3 ± 0.3	51	5.3 ± 1.1
10	1.3 ± 0.3	52	4.1 ± 0.8
11	9.3 ± 1.9	57	0.9 ± 0.2
21	6.5 ± 1.3	60	3.6 ± 0.7
22	4.7 ± 0.9	62	2.1 ± 0.4
27	1.1 ± 0.2	63	1.4 ± 0.3
35	6.9 ± 1.4		

Totally 50 polypropylene samples were tested for overall migration (Fig. 15). Overall migration to isooctane, 3 % acetic acid, 95 %, 50 %, and 10 % ethanol were tested in 22, 24, 22, 8, and 18 samples respectively.

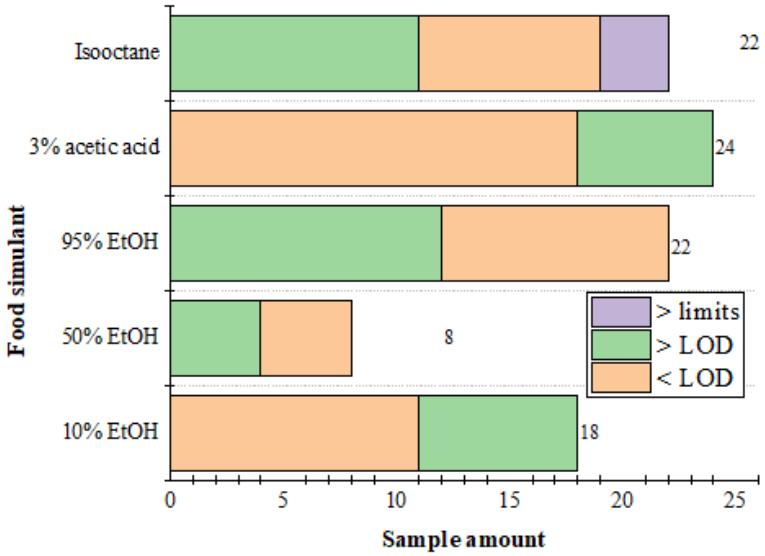


Figure 15. Distribution of PP samples where overall migration occurred below LOD, higher than LOD, and exceeded the Regulation No 10/2011 limit in different food simulants.

15 paveikslas. PP mėginių paskirstymas, įvertinant mėginius, kuriuose bendroji migracija identifikuota kaip mažesnė už metodo aptikimo ribą, kai identifikuota kaip didesnė nei metodo kiekybinio nustatymo riba ir kai bendrosios migracijos rezultatai viršijo Reglamento Nr. 10/2010 nustatytą ribinę koncentraciją.

Overall migration to isooctane showed that from 12 of 22 food contact materials migration occurred as from 10 of food contact materials migration results were under the limit of detection. Unfortunately, from 4 food contact materials overall migration to isooctane exceeded the migration limit of 10 mg/dm^2 according to Regulation No 10/2011 [56] (Table 18, lavender coloured). Overall migration to 3 % acetic acid demonstrates that only 6 of 24 food contact materials migration occurred, but from most of the samples, overall migration was under the limit of detection. Regarding overall migration to 95 % ethanol, from 12 of 22 food contact materials migration occurred as from 10 of food contact materials migration results were under the limit of detection. Overall migration to 50 % and 10 % of ethanol showed that from 4 and 7 of 8 and 18 food contact materials migration occurred as from 4

and 11 of food contact materials respectively migration results were under the limit of detection.

The average amounts of overall migration when using 10, 50 and 95 % ethanol, isooctane and 3 % acetic acid were 2.2 ± 0.4 mg/dm^2, 3.2 ± 0.6 mg/dm^2, 3.5 ± 0.7 mg/dm^2, 6.6 ± 1.3 mg/dm^2 and 4.4 ± 0.9 mg/dm^2 respectively. The results of overall migration to isooctane that exceeded the migration limit of 10 mg/dm^2 were omitted from the average calculation.

Table 18.
Concentrations of overall migration levels to different food simulants obtained by gravimetry in different packaging materials of PP.
18 lentelė.
Bendrosios migracijos į skirtingus maistinius modelinius tirpalus koncentracijos, gautos gravimetrijos metodu, iš skirtingų maisto pakavimui skirtų pakuočių, pagamintų iš PP.

PP sample No.	**Overall migration in 10 % ethanol, mg/dm^2**	**PP sample No.**	**Overall migration in 95 % ethanol, mg/dm^2**
1	1.6 ± 0.3	9	2.0 ± 0.4
5	0.6 ± 0.1	12	1.3 ± 0.3
6	0.8 ± 0.2	13	4.7 ± 0.9
21	2.3 ± 0.4	14	4.3 ± 0.9
22	1.9 ± 0.4	15	1.1 ± 0.2
23	7.4 ± 1.4	16	1.0 ± 0.2
39	1.1 ± 0.2	28	6.2 ± 1.2
		31	3.8 ± 0.8
PP sample No.	**Overall migration in 50 % ethanol, mg/dm^2**	32	2.4 ± 0.5
17	1.3 ± 0.3	33	5.8 ± 1.2
19	2.2 ± 0.4	34	0.7 ± 0.1
36	6.6 ± 1.3	35	8.3 ± 1.7
38	2.8 ± 0.6		

PP sample No.	Overall migration in isooctane, mg/dm^2	PP sample No.	Overall migration in isooctane, mg/dm^2
2	1.5 ± 0.3	16	7.1 ± 1.4
11	2.5 ± 0.5	24	1.5 ± 0.3
12	2.0 ± 0.4	32	12.5 ± 2.5
13	12.8 ± 2.6	33	13.6 ± 2.7
14	12.0 ± 2.4	34	9.3 ± 1.9
15	8.4 ± 1.7	35	4.9 ± 1.0
PP sample No.	**Overall migration in 3 % acetic acid, mg/dm^2**	**PP sample No.**	**Overall migration in 3 % acetic acid, mg/dm^2**
3	0.6 ± 0.1	25	9.1 ± 1.8
9	1.6 ± 0.3	28	6.7 ± 1.3
19	3.3 ± 0.7	38	5.2 ± 1.0

All things concluded isooctane seems to be the most aggressive food simulant as overall migration from PE or PP to isooctane is higher than from other food simulants (3 % acetic acid, 10 %, 50 % and 95 % ethanol). What is more, PE might be safer than PP as the overall migration of non-volatile chemical substances is higher in some cases even twice. On the other hand, if there is a case of exceeding the limits of Regulation No 10/2011, PP samples exceed limits by 30 % and PE by 300 %. Also, as the samples in which overall migration exceeded limits set by Regulation No 10/2011 do not differ from the others, these results confirm that the number of migrants does not depend on the product's appearance – its shape or colour.

4.3. Analysis of polymer degradation

4.3.1. Thermal desorption gas chromatography coupled with mass spectrometry (TD-GC/MS)

A non-targeted screening analysis by thermal desorption gas chromatography coupled with mass spectrometry (clause 3.1.3. and 3.5.) was

carried out to find out what potential volatile and semi-volatile organic migrants could be present in different compositions of PE and PP packages.

Firstly, the difference between GC-MS chromatograms of different coloured – dark and light – PP packages was investigated. Figure 16 shows an example of typical chromatograms of detected substances (undesignated peaks) of dark and light-coloured PP samples. As shown in Figure 16 a) dark-coloured PP packages release more migrants than light-coloured PP packages (Figure 16 b), but the main groups of migrants are the same (Table 19).

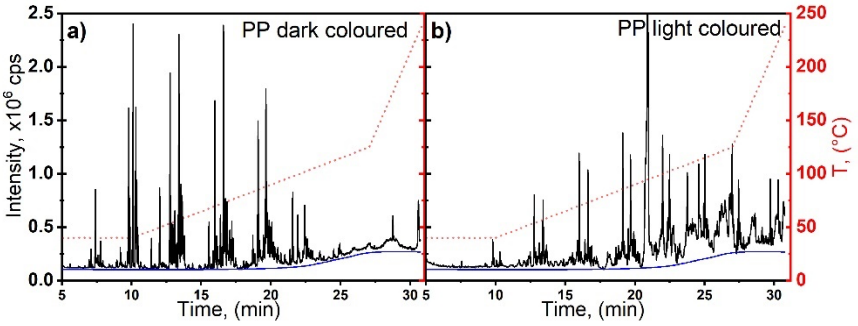


Figure 16. TD-GC/MS total ion chromatogram of dark-colored (a) and light (b) PP packages. The blue line represents background signals. Dotted red lines mark temperature during sample analysis.

16 paveikslas. Tamsios spalvos (a) ir šviesios spalvos (b) pakuočių, pagamintų iš PP, mėginių TD-GC/MS suminė jonų chromatograma. Mėlyna linija žymi foninius signalus. Taškinės raudonos linijos žymi temperatūrą mėginio analizės metu.

The definite reason for this observation is not clear. However, this might result from higher concentrations of degraded oligomers in coloured plastics. Also, it could be because of the considerable number of additives, such as colourants, used during the manufacturing process of dark plastic packages. Table 19 illustrates the groups/compounds of potential migrants that were identified using the NIST MS Search 2.0 spectra library with a match probability higher than 95 % in PP samples.

Table 19.
Possible origin of only PP samples emitted compounds, according to Groh et al., 2018 [74].
19 lentelė.
Galima tik iš PP mėginių išsiskyrusių junginių kilmė, remiantis Groh ir bendraautoriais, 2018 [74].

No.	Groups of compounds	Identified compounds	Possible origin
1	Esters	1,2,4-Benzenetricarboxylic acid, 1,2-dimethyl ester; 1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester; 1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester; 1,3-Cyclohexadiene-1-carboxylic acid, 2,6,6-trimethyl-, ethyl ester; 1,4-Benzenedicarboxylic acid, bis(4-butylphenyl) ester; 2-Propenoic acid, 3-(4-methoxyphenyl)-, 2-ethylhexyl ester; Arsenous acid, tris(trimethylsilyl) ester; Benzoic acid, 3-methyl-2-trimethylsilyloxy-, trimethylsilyl ester; Benzoic acid, 4-methyl-2-trimethylsilyloxy-, trimethylsilyl ester; Benzoic acid, heptyl ester; Dichloroacetic acid, decyl ester; Oxalic acid, 6-ethyloct-3-yl propyl ester; Oxalic acid, bis(6-ethyloct-3-yl) ester; Sulfurous acid, 2-ethylhexyl isohexyl ester;	Plasticizers

		Sulfurous acid, hexyl pentadecyl ester; 1,3-Bis-t-butylperoxy-phthalan; Hexanoic acid, 2-ethyl-, hexadecyl ester	
2	Compounds of octane	1-chlorooctance; 2,3,6,7-tetramethyloctane; 2,4,6-trimethyloctane; 2,7-dimethyloctane; 3,3-dimethyloctane; 4-methyloctane; 2,2,4,4-Tetramethyloctane; 4,4-Dimethyloctane; 1-Methoxy-3-hydroxymethyloctane	Solvents, lubricants, colourant dyes, adhesives
3	Compounds of dodecane and hexadecane	Dodecane, 2,5-dimethyl-	Solvents, lubricants
4	1-tetradecene and compounds of heptadecane, nonane, and undecane	2,5-Dimethylnonane; 3-Methylnonane; 5-Butylnonane; 2,4-Dimethylundecane; 2,5-Dimethylundecane; 2-Methylundecane; 3,7-Dimethylundecane; 3-Methylundecane; 4,6-Dimethylundecane	Lubricants
5	Compounds of tridecane	1-Iodo Tridecane; 2,5-dimethyl tridecane; 2-methyltridecane	Solvents
6	Mixed	4,4-Dimethyl-1,3-dioxane	Filler, colourant and adhesive

Secondly, the difference between GC-MS chromatograms of different plastics – PP and PE – of different compositions was determined. A typical GC/MS total ion chromatogram of detected substances (undesignated peaks) of the PE sample is presented in Figure 17.

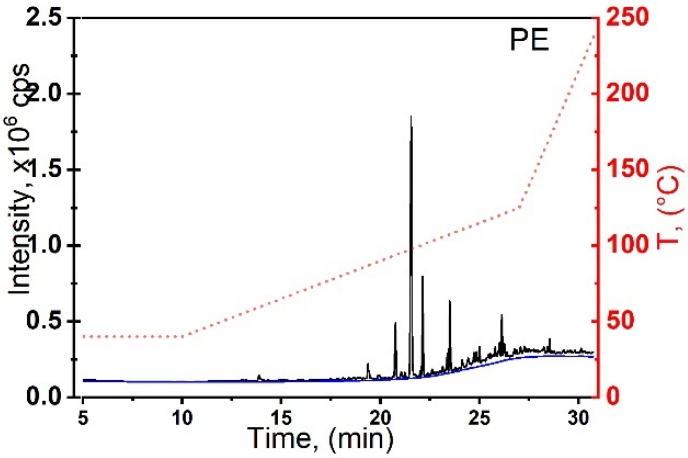


Figure 17. TD-GC/MS total ion chromatogram of PE packages. The blue line represents background signals. Dotted red lines mark temperature during sample analysis.

17 paveikslas. Pakuočių, pagamintų iš PE, mėginių TD-GC/MS suminė jonų chromatograma. Mėlyna linija žymi foninius signalus. Taškinės raudonos linijos žymi temperatūrą mėginio analizės metu.

Comparing the results of GC/MS total ion chromatograms (undesignated peaks) of PP samples (Figure 16) and PE samples (Figure 17) it is noticeable that PE samples release far fewer potential migrants than PP samples, but the origin of the main groups of migrants or degradation products are the same, for example plasticizers, solvents, lubricants, etc. (Table 20). The reason why the number of potential migrants released from PE samples is smaller is not clear, but it might be related to the difference in the structure, as PP, due to its rigidity, demands a greater amount of modification agent compared to PE. PP's melting point is also higher than PE's, which restricts its use in temperatures above 0 °C. Also, PP displays less chemical resistance than PE. These properties of PE, including its flexibility, lower melting point, and superior resistance, enable the manufacture of packaging materials with fewer additives.

Table 20 illustrates the groups/compounds of potential migrants that were identified using the NIST MS Search 2.0 spectra library with a match probability higher than 95 % in PE samples.

Table 20.
Possible origin of only PE samples emitted compounds, according to Groh et al., 2018 [74].
20 lentelė.
Galima tik iš PE mėginių išsiskyrusių junginių kilmė, remiantis Groh ir bendraautoriais, 2018 [74].

No.	Groups of compounds	Identified compounds	Possible origin
1	Esters	Hexanoic acid, 2-ethyl-, hexadecyl ester; Hydracrylic acid, monoanhydride with 1-butaneboronic acid, cyclic ester; Cyclopentaneacetic acid, 3-oxo-2-pentyl-, methyl ester; Oxalic acid, cyclohexylmethyl isohexyl ester; Phosphonic acid, bis(1-methylethyl) ester; Phthalic acid, butyl 3-fluorophenyl ester; Phthalic acid, bis(7-methyloctyl) ester; Phthalic acid, butyl hexyl ester; Phthalic acid, cis-hex-3-enyl tetradecyl ester; Phthalic acid, ethyl 3-methylbutyl ester; Dibutyl phthalate; Diethyl Phthalate; Diisooctyl phthalate; Sulfurous acid, hexyl octyl ester;	Plasticizers

		1-Propene-1,2,3-tricarboxylic acid, tributyl ester; 1,4-di-iso-propylnaphthalene; 1,7-di-iso-propylnaphthalene; Bis-(3,5,5-trimethylhexyl) phthalate	
2	Compounds of dodecane and hexadecane	Hexadecane, 2,6,10,14-tetramethyl-	Solvents, lubricants
3	1-tetradecene and compounds of heptadecane, nonane, and undecane	5,5-Diethylheptadecane; 7,7-Diethylheptadecane	Lubricants
4	Compounds of heneicosane	3-Methyl-heneicosane	Stabilizers
5	Compounds of tridecane	5,5-dimethyl tridecane	Solvents

Table 21 illustrates the groups/compounds of potential migrants that were identified using the NIST MS Search 2.0 spectra library with a match probability higher than 95 % in both, PE, and PP samples. The identified compounds in different PP and PE samples were grouped into 8 compound groups regarding the functional groups and possible origin, according to Groh et al. 2018 published database of CPPdb Lists A and B [74]. These compound groups were comprised of esters, compounds of octane, dodecane and hexadecane, 1-tetradecene and compounds of heptadecane, nonane and undecane, pentane, heneicosane, tridecane, mixed group as it consists of single compounds of different origin (Table 21).

Table 21.
Possible origin of emitted compounds from both PE and PP, according to Groh et al., 2018 [74].
21 lentelė.
Galima ir iš PP, ir iš PE mėginių išsiskyrusių junginių kilmė, remiantis Groh ir bendraautoriais, 2018 [74].

No.	Groups of compounds	Identified compounds	Possible origin
1	Esters	1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester; Dodecanoic acid, 1-methylethyl ester; Silicic acid, diethyl bis(trimethylsilyl) ester; Sulfurous acid, octadecyl 2-propyl ester; 7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione; Bis(2-ethylhexyl) phthalate; Bis(tridecyl) phthalate; Di-n-octyl phthalate	Plasticizers
2	Compounds of octane	1,1'-oxybisoctane; 5-ethyl-2-methyloctane	Solvents, lubricants, colourant dyes, adhesives
3	Compounds of dodecane and hexadecane	Dodecane; 3,5-Dimethyldodecane; 2-Bromo dodecane;	Solvents, lubricants

		Dodecane, 2,6,10-trimethyl-; Dodecane, 4,6-dimethyl-; Dodecane, 4-methyl-; Hexadecane; Hexadecane, 1-iodo-; Hexadecane, 2-methyl-	
4	1-tetradecene and compounds of heptadecane, nonane, and undecane	1-Tetradecene; 5-(2-methylpropyl)-nonane; 5-Methyl-5-propyl-nonane; Undecane; 3-Methyl-undecane; Heptadecane; 2,6,10,15-Tetramethyl-heptadecane	Lubricants
5	Compounds of pentane	Pentane; 2,2-Dimethylpentane; 2-Methylpentane; 3-Methylpentane	Solvents, lubricants, colourants, adhesives
6	Compounds of heneicosane	Heneicosane	Stabilizers
7	Compounds of tridecane	1-Tridecene; Tridecane; 3-Methyl Tridecane	Solvents
8	Mixed	Di-n-decylsulfone	Antimicrobials, adhesives, and curing agents
		2-Hexyl-1-decanol	Dispersion agents, plasticizers, lubricants and monomers
		D-Limonene	Plastic polishers, hardeners, lubricants, fillers, colourants and adhesives

		Acetone	Adhesion promoters, antistatics, catalysts, polishers, seal materials, solvents, stabilizers, lubricants, hardeners
		Tetrahydrofuran	Adhesives, dispersion agents and solvents
		Nonanal	Plastic polishers and, lubricants
		Decanal	Plastic polisher
		Nonanoic acid	Antimicrobial, lubricant, colourant and adhesive
			Filler, colourant and adhesive

As seen in Table 21, different plasticizers [16, 19, 22, 23, 74], such as bis(2-ethylhexyl) phthalate, bis(tridecyl) phthalate, di-n-octyl phthalate and other esters were identified in all PP and PE samples tested. What is more, not only plasticizers were identified, but also the non-intentionally added substances such as 7,9-Di-tert-butyl-1-oxaspiro-(4,5)-deca-6,9-diene-2,8-dione which is the product of well-known antioxidant Irganox 1010 degradation reactions [74, 140-142].

As expected, alkanes and alkenes were detected among the major compounds (Tables 19 – 21). Linear alkanes and iso-alkanes originate from the so-called paraffin wax used for external lubricant. Alkanes are also used as a solvent. Alkenes are used as starting compounds for several additives and polymers. Besides that, alkenes are formed as a by-product in the olefin polymerization [143, 144]. According to the database of CPPdb Lists A and B [74]:

- compounds of octane are used as solvents, lubricants, colourant dyes and adhesives. In all samples tested octane, 1,1'-oxybis-octane, and 5-ethyl-2-methyl-octane were identified. No different compounds of octane were identified in PE samples.
- compounds of dodecane and hexadecane are used as solvents and lubricants. Differently, methylated dodecane, such as 4-methyl-dodecane, 4,6-

dimethyl-dodecane, and hexadecane compounds, such as 2-methyl-hexadecane were identified in the samples tested.

- 1-tetradecene, heptadecane, 3-methyl-nonane, 3-methyl-undecane, and others are used as lubricants and were also identified during the analysis.
- compounds of pentane, such as 2-methyl-pentane, 2,2-dimethyl-pentane, and 3-methyl-pentane are used as solvents, lubricants, colourants and adhesives. All these additives were identified in all PP and PE samples tested and no different compounds of pentane were identified only in PE or PP.
- compounds of tridecane, such as 1-tridecane, and 3-methyl-tridecane are used as solvents and they were identified in all samples tested. 5,5-dimethyl-tridecane was identified only in PE samples, while 1-iodo-tridecane, 2-methyl-tridecane and 2,5-dimethyl-tridecane were identified only in PP samples.
- stabilizer heneicosane was identified in all samples tested and 3-methyl-heneicosane was identified only in PE samples.
- di-n-decylsulfone, 2-hexyl-1-decanol, d-limonene, acetone, tetrahydrofuran, nonanal, decanal and nonanoic acid were identified in all PP and PE samples tested. 4,4-dimethyl-1,3-dioxane was identified only in PP samples and it is used as filler, colorant and adhesive.

Also, more possible migrants or degradation products, such as compounds of decane, heptane, cyclohexane, and 2-propanol were identified in different samples (Table 22). All the migrants are listed in the database of CPPdb Lists A and B [74] as additives for food contact or other plastic materials but there is no information of possible origin provided.

Table 22.
The list of identified compounds that were listed as additives for food contact or other plastic materials but the function was not determined according to Groh et al., 2018 [74].
22 lentelė.
Identifikuotų junginių, kurie yra įvardinti kaip priedai, naudojami su maistu besiliečiančių plastikinių gaminių gamyboje, bet jų kilmė neįvardinta remiantis Groh ir bendraautoriais, 2018 [74], sąrašas.

Identified compounds			**Plastic composition**
Eicosane	Heptanal	Tetracosane	PP and PE
2,2-dimethylpropanoic acid	3-Ethyl-3-methylheptane	Decane	
1-iododecane	Decane, 3,7-dimethyl-	Decane, 3,8-dimethyl-decane	
Pentadecane	Dodecanal	2-hexyl-1-dodecanol	
Heptane	2,2,3,3,5,6,6-Heptamethylheptane	2,4,6-trimethylheptane	PP
2,3-dimethylheptane	2,4-dimethyl-heptane	2,5,5-trimethylheptane	
4-methylheptane	2,3,4-trimethylhexane	2,3,5-trimethylhexane	
2,4-dimethylhexane	2,5-dimethylhexane	n-Hexane	
Cyclohexane	1-Ethyl-2-propylcyclohexane	2,6,7-trimethyldecane	
4-Methyldecane	5,6-dimethyldecane	2,6,10,14-tetramethylpentadecane	
1-Cyclopentyleicosane	2,2,4,6,6-pentamethylheptane	Pentylcyclohexane	PE

1-(2-methoxy-1-methylethoxy)-2-propanol	1-(isooctyloxy)-2-methyl-2-propanol	1-ethoxy-2-propanol	
1-methoxy-2-propanol	5,6-dipropyldecane	5-methyl-6-methylenedecane	

Most of the migrants identified (Tables 19 – 22) are not regulated in the EU and, therefore, have no legal limits in place. The exact origin of the volatile and semi-volatile potential migrants or degradation products is not clear but it is possible to draw the tendencies based on the literature [74], as it was done in this thesis.

4.3.2. Atomic absorption spectrophotometry (AAS)

The amount of extracted Pb, Cr, Cd and Hg from 52 different food contact materials manufactured from polyethylene, polypropylene and their composites were analyzed using an AAS method as described in Sections 3.1.3. and 3.4.

Under the analysis results, Pb and Cd were not detected in PP packages (Figure 18) as the concentrations were below the limit of detection. Hg and Cr were detected in 25 % and 15 % of the samples respectively (Table 22).

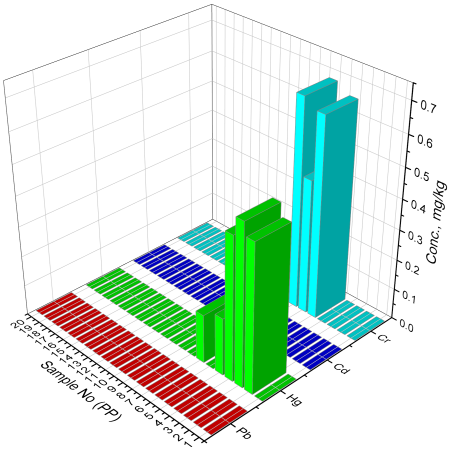


Figure 18. Concentrations of Cr, Cd, Hg, and Pb obtained by AAS in different packaging materials of PP.
18 paveikslas. Cr, Cd, Hg ir Pb koncentracijos, identifikuotos AAS metodu skirtingose maisto pakuotėse, pagamintose iš PP.

Table 22.
Concentrations of Hg obtained by AAS in different packaging materials of PP.
22 lentelė.
Hg koncentracijos, identifikuotos AAS metodu skirtingose maisto pakuotėse, pagamintose iš PP.

Sample No.	**Hg, mg/kg**
2	0.485 ± 0.031
3	0.527 ± 0.034
4	0.469 ± 0.030
5	0.189 ± 0.012
7	0.160 ± 0.010
Sample No.	**Cr, mg/kg**
5	0.659 ± 0.048
6	0.443 ± 0.032
7	0.687 ± 0.050

Also, almost in all PE packages (Figure 19) concentrations of Cd, Pb, and Cr were under the limit of detection and only in 5 %, 10 % and 15 % respectively of the samples Cd, Pb and Cr were detected (Table 23). Hg was detected in 70 % of the PE samples (Table 24).

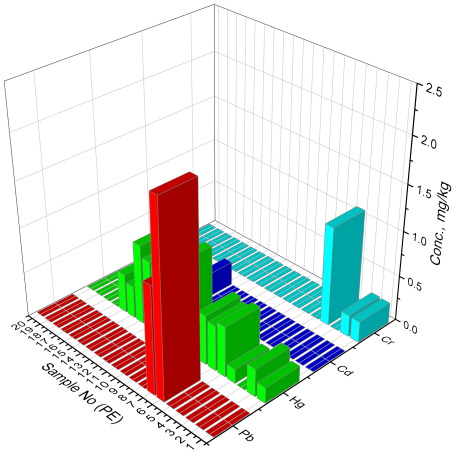


Figure 19. Concentrations of Cr, Cd, Hg, and Pb obtained by AAS in different packaging materials of PE.
19 paveikslas. Cr, Cd, Hg ir Pb koncentracijos, identifikuotos AAS metodu skirtingose maisto pakuotėse, pagamintose iš PE.

Table 23.
Concentrations of Cd, Pb and Cr obtained by AAS in different packaging materials of PE.
23 lentelė.
Cd, Pb ir Cr koncentracijos, identifikuotos AAS metodu skirtingose maisto pakuotėse, pagamintose iš PE.

Sample No.	**Cd, mg/kg**
33	0.264 ± 0.013
Sample No.	**Pb, mg/kg**
26	2.113 ± 0.151
27	1.184 ± 0.085
Sample No.	**Cr, mg/kg**
21	0.232 ± 0.017
22	0.239 ± 0.018
24	1.097 ± 0.080

Table 24.
Concentrations of Hg obtained by AAS in different packaging materials of PE.
24 lentelė.
Hg koncentracijos, identifikuotos AAS metodu skirtingose maisto pakuotėse, pagamintose iš PE.

Sample No.	Hg, mg/kg	Sample No.	Hg, mg/kg
21	0.173 ± 0.011	30	0.917 ± 0.059
22	0.306 ± 0.020	31	0.340 ± 0.022
24	0.158 ± 0.010	32	0.727 ± 0.047
25	0.558 ± 0.036	33	0.758 ± 0.049
26	0.500 ± 0.032	34	0.881 ± 0.057
27	0.547 ± 0.035	35	0.356 ± 0.023
28	0.218 ± 0.014	36	0.431 ± 0.028

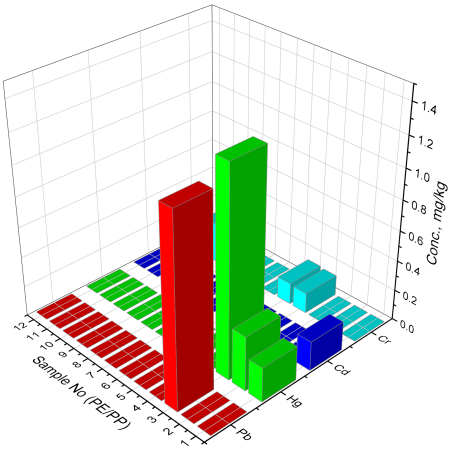


Figure 20. Concentrations of Cr, Cd, Hg, and Pb obtained by AAS in different packaging materials of PP/PE composites.
20 paveikslas. Cr, Cd, Hg ir Pb koncentracijos, identifikuotos AAS metodu skirtingose maisto pakuotėse, pagamintose iš PP/PE kompozitų.

Furthermore, in 8 % of PP/PE composite samples (Figure 20), the detected concentrations of Pb and Cd were above the limit of detection, and in 25 % of the samples Hg and Cr were detected (Table 25).

Table 25.
Concentrations of Cd, Pb and Cr obtained by AAS in different packaging materials of PP/PE composites.
25 lentelė.
Cd, Pb ir Cr koncentracijos, identifikuotos AAS metodu skirtingose maisto pakuotėse, pagamintose iš PP/PE kompozitų.

Sample No.	**Pb, mg/kg**
43	1.247 ± 0.089
Sample No.	**Cd, mg/kg**
41	0.194 ± 0.010
Sample No.	**Hg, mg/kg**
41	0.227 ± 0.015
42	0.359 ± 0.023
43	1.353 ± 0.087
Sample No.	**Cr, mg/kg**
44	0.135 ± 0.010
45	0.142 ± 0.010
50	0.271 ± 0.010

There were no samples where more than two metals were identified and only in 6, 2 and 2 samples of PE, PP and PP/PE respectively, two metals were identified in the same sample (Table 26). What is more, in all samples where two metals were identified, Hg was detected.

Table 26.
Concentrations of Cd, Pb and Cr obtained by AAS in different packaging materials of PE, PP and PP/PE composites.
26 lentelė.
Cd, Pb ir Cr koncentracijos, identifikuotos AAS metodu skirtingose maisto pakuotėse, pagamintose iš PP/PE kompozitų.

Plastic composition	**Sample No.**	**Cd, mg/kg**	**Pb, mg/kg**	**Cr, mg/kg**	**Hg, mg/kg**
PE	21	-	-	0.232 ± 0.017	0.173 ± 0.011
	22	-	-	0.239 ± 0.018	0.306 ± 0.020
	24	-	-	1.097 ± 0.080	0.158 ± 0.010
	26	-	2.113 ± 0.151	-	0.500 ± 0.032
	27	-	1.184 ± 0.085	-	0.547 ± 0.035
	33	0.264 ± 0.013	-	-	0.758 ± 0.049
PP	5	-	-	0.659 ± 0.048	0.189 ± 0.012
	7	-	-	0.687 ± 0.050	0.160 ± 0.010
PP/PE	41	0.194 ± 0.010	-	-	0.227 ± 0.015
	43	-	1.247 ± 0.089	-	1.353 ± 0.087

According to European Parliament and Council Directive 94/62/EC of 20 December 1994 on packaging and packaging wastes the sum of concentration levels of Cd, Pb, Cr, and Hg present in packaging or packaging components shall not exceed 100 mg/kg by weight [73]. There were no samples tested where the sum of concentration levels of Cd, Pb, Cr, and Hg exceeded 100 mg/kg by weight.

4.4. Extraction and specific migration experiments

4.4.1. Experiments of antioxidants extraction

The extraction of antioxidants – Irgafos 168-ox and Irganox 1010 – experiments in 23 food contact materials manufactured from polyethylene was analyzed using an LC-MS/MS method as described in Sections 3.1.4., 3.1.5. and 3.6.

Irgafos 168-ox was detected in all the samples. As shown in Table 27, in 52 % of the samples (12 samples) extracted concentration did not exceed 1 mg/dm^2 (green), in 39 % of the samples (9 samples) extracted concentration was between 1 and 2 mg/dm^2 (yellow) and in 9 % of the samples (2 samples) extracted concentration did exceed 2 mg/dm^2 (red).

Table 27.
Extraction of Irgafos 168-ox concentration data.
27 lentelė.
Išekstrahuoto Irgafos 168-ox koncentracijos.

Concentration range	**< 1 mg/dm^2**	**1 – 2 mg/dm^2**		**> 2 mg/dm^2**
Sample No	**Concentration mg/dm² using different ultrasonic extraction durations**			
	t = 10 min	**t = 20 min**	**t = 30 min**	**t = 40 min**
1	0.8425 ± 0.0851	1.1881 ± 0.1200	1.9869 ± 0.2007	1.9871 ± 0.2007
2	1.2775 ± 0.1290	2.0046 ± 0.2025	2.7694 ± 0.2797	2.7696 ± 0.2797
3	0.4519 ±0.0456	0.8542 ± 0.0863	0.9732 ± 0.0983	0.9800 ± 0.0990
4	0.3585 ± 0.0362	0.3956 ± 0.0399	0.4185 ± 0.0423	0.4286 ± 0.0433
5	0.3385 ± 0.0342	0.3805 ± 0.0384	0.8060 ± 0.0814	0.8091 ± 0.0817
6	0.4329 ± 0.0437	0.9873 ± 0.0997	1.0951 ± 0.1106	1.0952 ± 0.1106
7	0.0050 ± 0.0005	0.3120 ± 0.0315	0.3560 ± 0.0360	0.3561 ± 0.0360

Concentration range	< 1 mg/dm²	1 – 2 mg/dm²	> 2 mg/dm²	
Sample No	Concentration mg/dm² using different ultrasonic extraction durations			
	t = 10 min	t = 20 min	t = 30 min	t = 40 min
8	0.7496 ± 0.0757	1.3042 ± 0.1317	1.7359 ± 0.1753	1.7359 ± 0.1753
9	0.5592 ± 0.0565	0.5600 ± 0.0566	0.5696 ± 0.0575	0.5697 ± 0.0575
10	0.5120 ± 0.0517	0.6346 ± 0.0641	1.5260 ± 0.1541	1.5270 ± 0.1542
11	0.6418 ± 0.0648	0.7049 ± 0.0712	1.1641 ± 0.1176	1.1661 ± 0.1178
12	0.7009 ± 0.0708	0.7515 ± 0.0759	0.9850 ± 0.0995	0.9870 ± 0.0997
13	0.7213 ± 0.0729	1.3856 ± 0.1399	1.6257 ± 0.1642	1.6260 ± 0.1642
14	0.6085 ± 0.0615	0.7074 ± 0.0715	0.7788 ± 0.0787	0.7792 ± 0.0787
15	2.5053 ± 0.2530	3.1279 ± 0.3159	4.2630 ± 0.4306	4.2631 ± 0.4306
16	0.5007 ± 0.0506	0.6558 ± 0.0662	0.9798 ±0.0990	0.9799 ± 0.0990
17	0.5757 ± 0.0581	0.5912 ± 0.0597	1.0945 ± 0.1105	1.0947 ± 0.1106
18	0.2422 ± 0.0245	0.5548 ± 0.0560	0.6344 ± 0.0641	0.6412 ± 0.0648
19	0.2434 ± 0.0246	0.4348 ± 0.0439	0.5377 ± 0.0543	0.5378 ± 0.0543
20	0.3460 ± 0.0350	1.0507 ± 0.1061	1.1496 ± 0.1161	1.1496 ± 0.1161
21	0.0804 ± 0.0081	0.1092 ± 0.0110	0.3093 ± 0.0312	0.3094 ± 0.0313
22	0.3185 ± 0.0322	0.3499 ± 0.0353	0.5131 ± 0.0518	0.5121 ± 0.0517
23	0.4933 ± 0.0498	1.0088 ± 0.1019	1.1542 ± 0.1166	1.1542 ± 0.1166

Extraction studies of Irgafos 168-ox were conducted by extracting four analogous pieces of the same sample for 10, 20, 30, and 40 min (Figure 21). The results of concentration differences obtained in each extraction duration showed that the optimal ultrasonic extraction time was 30 min as the concentrations obtained after 40 min of extraction differed within the uncertainty limits, and after 40 min they increased insignificantly.

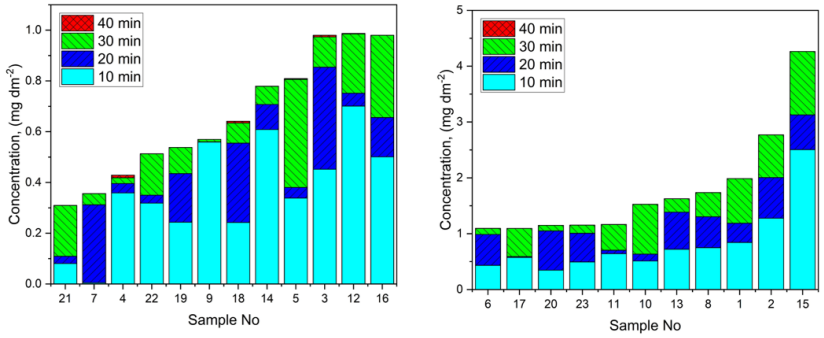


Figure 21. The extraction kinetics of Irgafos 168-ox from PE samples were extracted for 10, 20, 30, and 40 minutes, with the left and right bar charts representing groups of samples with lower (left) and higher (right) concentrations, respectively. The samples are organized in ascending order of concentration.

21 paveikslas. Irgafos 168-ox ekstrakcijos iš PE mėginių kinetika, ekstrahuojant 10, 20, 30 ir 40 minučių. Diagramoje kairėje pusėje pavaizduota mažesnių koncentracijų mėginių grupė, dešinėje – didesnių. Mėginiai diagramose vaizduojami koncentracijos didėjimo tvarka.

Irganox 1010 is often used with Irgafos 168-ox to enhance the antioxidant capacity of plastic products as reported by Liu et al. [146]. In the present study, Irganox 1010 was not detected only in 1 sample (Sample No. 23), in which the measured concentration was above the limit of quantitation (Table 28). Also, further analysis has shown, that in 22 polyethylene samples both, Irgafos 168-ox and Irganox 1010 were detected. The measured concentrations of Irganox 1010 are given in Table 22. In 61 % of the samples (14 samples) extracted concentration did not exceed 0.1 mg/dm^2 (green), in 26 % of the samples (6 samples) extracted concentration was between 0.1 and 0.3 mg/dm^2 (yellow), and in three samples extracted concentration was higher than 0.3 mg/dm^2 (red) while only in one sample extracted concentration of Irganox 1010 was 1.3329 ± 0.1800 mg/dm^2 (Sample No 1).

Table 28.
Extraction of Irganox 1010 concentration data.
28 lentelė.
Išekstrahuoto Irganox 1010 koncentracijos.

Concentration range	**< 0.1 mg/dm²**	**0.1 – 0.3 mg/dm²**		**> 0.3 mg/dm²**
Sample No	**Concentration mg/dm² using different ultrasonic extraction durations**			
	t = 10 min	**t = 20 min**	**t = 30 min**	**t = 40 min**
1	0.4227 ±0.0571	0.5639 ± 0.0761	1.3328 ± 0.1799	1.3329 ± 0.1800
2	< 0.0004	0.0011 ± 0.0001	0.0017 ± 0.0002	0.0017 ± 0.0002
3	< 0.0004	< 0.0004	0.0284 ± 0.0038	0.0284 ± 0.0038
4	0.0532 ± 0.0072	0.0931 ± 0.0126	0.1053 ± 0.0142	0.1054 ± 0.0142
5	< 0.0004	< 0.0004	0.0846 ± 0.0114	0.0910 ± 0.0123
6	0.0043 ± 0.0006	0.0057 ± 0.0008	0.2471 ± 0.0334	0.2471 ± 0.0333
7	< 0.0004	0.0078 ± 0.001	0.0376 ±0.0051	0.0377 ± 0.0051
8	< 0.0004	0.0027 ± 0.0004	0.0398 ± 0.0054	0.0399 ± 0.0054
9	0.0049 ± 0.0007	0.0167 ± 0.0023	0.1670 ± 0.0225	0.1671 ± 0.0226
10	< 0.0004	< 0.0004	0.2660 ± 0.0359	0.2660 ± 0.0305
11	0.0975 ± 0.0132	0.1716 ± 0.0232	0.1716 ± 0.0232	0.1716 ± 0.0232
12	< 0.0004	< 0.0004	0.0061 ± 0.0008	0.0061 ± 0.0008
13	< 0.0004	< 0.0004	0.0091 ± 0.0012	0.0098 ± 0.0013

Concentration range	< 0.1 mg/dm²	0.1 – 0.3 mg/dm²		> 0.3 mg/dm²
Sample No	Concentration mg/dm² using different ultrasonic extraction durations			
	t = 10 min	t = 20 min	t = 30 min	t = 40 min
14	0.7914 ± 0.1068	0.7989 ± 0.1079	0.8111 ± 0.1095	0.8112 ± 0.1095
15	< 0.0004	< 0.0004	0.0429 ± 0.0058	0.0431 ± 0.0058
16	0.9784 ± 0.1321	0.9918 ± 0.1339	0.9919 ± 0.1339	0.9919 ± 0.1339
17	< 0.0004	< 0.0004	0.0616 ± 0.0083	0.0618 ± 0.0083
18	< 0.0004	< 0.0004	0.0089 ± 0.0012	0.0090 ± 0.0012
19	< 0.0004	0.0179 ± 0.0024	0.0391 ± 0.0053	0.0393 ± 0.0053
20	0.0089 ± 0.0012	0.0109 ± 0.0015	0.0191 ± 0.0026	0.0196 ± 0.0026
21	< 0.0004	0.0111 ± 0.0015	0.0115 ± 0.0016	0.0119 ± 0.0016
22	< 0.0004	< 0.0004	0.0361 ± 0.0049	0.0361 ± 0.0049
23	< 0.0004	< 0.0004	< 0.0004	< 0.0004

The same type of experiment as with Irgafos 168-ox was conducted for Irganox 1010 using extraction times of 10, 20, 30, and 40 min. In Figure 22 clear trend of the most significant increase of Irganox 1010 concentration at 30 min of extraction can be seen. Similarly, to Irgafos 168-ox extraction experiments, the optimal ultrasonic extraction time of 30 min was determined for Irganox 1010 as the concentrations obtained after 40 min of extraction did not increase distinctly.

Further analysis showed, that in 52 % of the samples (12 samples) the ratio of Irgafos 168-ox and Irganox 1010 was 9:1 demonstrating a much higher fraction of Irgafos 168-ox. Approximately a third of the samples (7 samples) consisted of 10 – 30 % of Irganox 1010 and 70 – 90 % of Irgafos 168-ox. In

one sample (Sample No. 1), 67 % of the composition consisted of Irganox 1010, and in 13 % of the samples (3 samples) higher amount of Irganox 1010 was present than Irgafos 168-ox.

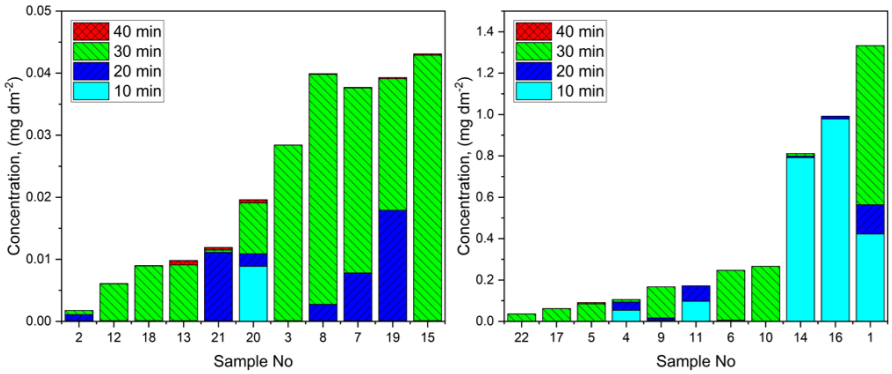


Figure 22. The extraction kinetics of Irganox 1010 from PE samples were extracted for 10, 20, 30, and 40 minutes, with the left and right bar charts representing groups of samples with lower (left) and higher (right) concentrations, respectively. The samples are organized in ascending order of concentration.

22 paveikslas. Irganox 1010 ekstrakcijos iš PE mėginių kinetika, ekstrahuojant 10, 20, 30 ir 40 minučių. Diagramoje kairėje pusėje pavaizduota mažesnių koncentracijų mėginių grupė, dešinėje – didesnių. Mėginiai diagramose vaizduojami koncentracijos didėjimo tvarka.

Unfortunately, no clear correlation was observed between the concentration range of Irgafos 168-ox or Irganox 1010 and the appearance of the intended usage of the samples. From this, it could be concluded that the amount of antioxidants does not depend on the product's appearance – its shape or colour.

4.4.2. Specific migration of antioxidants

The specific migration of antioxidants – Irgafos 168-ox and Irganox 1010 – experiments in 23 food contact materials manufactured from polyethylene was analyzed using an LC-MS/MS method as described in Sections 3.1.4. and 3.6.

Irgafos 168-ox is hydrolyzed over time in the water-based migration system to 2,4-ditert-butylphenol and bis(2,4-ditert-butylphenyl) hydrogen

phosphate degradation products [147]. Therefore, during the migration experiments in acetic acid 3% at 60 ºC for 10 days, no migration levels of Irgafos 168-ox were detected. What is more, previous studies have reported that Irgafos 168 leached out of food packaging in contact with oil and consequently it was decided to carry out migration studies with a substitute for vegetable oil – 95 % ethanol and isooctane [39, 136, 147]. As expected, unlike the migration of Irgafos 168-ox to 3% acetic acid, migration to isooctane (Table 29) and 95 % ethanol (Table 30) did occur in all the samples tested. The dimensions of the results have been chosen based on the conversion that 1 kg of food is packaged with 6 dm^2 of food contact material [56].

Table 29.
Migration of Irgafos 168-ox to isooctane concentration data.
29 lentelė.
Irgafos 168-ox migracijos į izooktaną koncentracijos.

Group	**< 1 mg/kg**	**1 – 2 mg/kg**	**> 3 mg/kg**
Sample No	**Migration to isooctane, mg/kg**	**Sample No**	**Migration to isooctane, mg/kg**
1	0.7762 ± 0.0784	13	0.9240 ± 0.0933
2	1.1673 ± 0.1179	14	0.9555 ± 0.0965
3	3.1216 ± 0.3152	15	0.0329 ± 0.0033
4	1.5582 ± 0.1574	16	0.2592 ± 0.0262
5	1.7200 ± 0.1737	17	0.4807 ± 0.0485
6	1.1836 ± 0.1195	18	1.6295 ± 0.1646
7	0.5337 ± 0.0539	19	0.9426 ± 0.0952
8	0.7814 ± 0.0789	20	4.0596 ± 0.4100
9	0.3324 ± 0.0336	21	1.7227 ± 0.1740
10	1.3981 ± 0.1412	22	1.8548 ± 0.1873
11	1.3533 ± 0.1367	23	0.3408 ± 0.0344
12	0.4145 ± 0.0419		

As no specific migration limits are set for Irgafos 168 or Irgafos 168-ox under Commission Regulation (EU) No 10/2011, a generic specific migration limit of 60 mg/kg applies [56]. It can be seen from the data in Tables 23 and 24 that there were no samples from which the migration levels exceeded 60 mg/kg. What is more, the migration concentrations were

significantly lower than the limit of 60 mg/kg. In 52 % of the samples (12 samples), migration levels to isooctane did not exceed 1 mg/kg (green), and in 39 % of the samples (9 samples) migration levels to isooctane did not exceed 2 mg/kg (yellow). Only in two samples (samples No 3 and 20) did migration level reach 3.1216 ± 0.3152 mg/kg and 4.0596 ± 0.4100 mg/kg respectively (red).

Regarding the migration to 95 % ethanol, there were no samples where the migration level exceeded 1 mg/kg (Table 30).

Table 30.
Migration of Irgafos 168-ox to 95 % ethanol concentration data.
30 lentelė.
Irgafos 168-ox migracijos į 95 % etanolį koncentracijos.

Sample No	**Migration to 95 % ethanol, mg/kg**	**Sample No**	**Migration to 95 % ethanol, mg/kg**
1	0.5922 ± 0.0598	13	0.7548 ± 0.0762
2	0.8748 ± 0.0884	14	0.2509 ± 0.0253
3	0.6575 ± 0.0664	15	0.1475 ± 0.0149
4	0.7903 ± 0.0798	16	0.4252 ± 0.0429
5	0.0698 ± 0.0071	17	0.6633 ± 0.0670
6	0.0125 ± 0.0013	18	0.6633 ± 0.0670
7	0.0850 ± 0.0086	19	0.4106 ± 0.0415
8	0.7330 ± 0.0740	20	0.2246 ± 0.0227
9	0.4415 ± 0.0446	21	0.7429 ± 0.0750
10	0.4417 ± 0.0446	22	0.0119 ± 0.0012
11	0.2090 ± 0.0211	23	0.1962 ± 0.0198
12	0.8036 ± 0.4145		

The results of the determined percentages of migrated Irgafos 168-ox to food simulants from the samples are shown in Tables 31 and 32. It can be observed that from 43 % of the samples (10 samples) less than 10 % of Irgafos 168-ox migrated to isooctane (yellow), from 35 % of the samples (8 samples) 10 – 50 % of the Irgafos 168-ox migrated to isooctane (green), and in 22 % of the samples (5 samples) more than 50 % of the additive migrated to isooctane (red) (Table 31).

Table 31.
Percentage of Irgafos 168-ox additive migration from plastic to isooctane.
31 lentelė.
Irgafos 168-ox migracijos iš plastiko į izooktaną procentinis kiekis.

Groups	**< 10 %**	**10 – 20 %**	**> 36 %**
Sample No	**Migration to isooctane, %**	**Sample No**	**Migration to isooctane, %**
1	6.5	13	9.5
2	7.0	14	20.4
3	53.1	15	0.1
4	72.4	16	4.4
5	35.4	17	7.3
6	18.0	18	42.4
7	25.0	19	29.2
8	7.5	20	58.9
9	9.7	21	92.8
10	15.3	22	60.4
11	19.3	23	4.9
12	7.0		

In the case of the migration to 95 % ethanol (Table 32), out of 65 % of the samples (15 samples) less than 10 % of Irgafos 168-ox migrated to 95 % ethanol (green), and out of 26 % of the samples (6 samples), 10 – 20 % of the Irgafos 168-ox migrated to 95 % ethanol (yellow). There were two samples from which 36,7 % (sample No. 4) and 40 % (sample No. 21) of the additive migrated to food simulant (red).

These results show that the migration of Irgafos 168-ox to isooctane is higher than to 95 % ethanol, as from 22 % of the samples about 50 % of added Irgafos 168-ox migrated to isooctane and only from 2 samples (9 %) migration of Irgafos 168-ox was higher than 35 % of added additive. Also, from the data shown in Figure 23 (left), it is seen that migration to isooctane is, in most cases, greater than 95 % ethanol. Unfortunately, there were no possibilities to carry migration tests with vegetable oil (food simulant D2), so it cannot be concluded that isooctane represents vegetable oil better. But as in 72 % of the samples (18 samples), migration of Irgafos 168-ox to isooctane is greater than in 95 % ethanol, it is clear, that isooctane is a more aggressive food simulant

than 95 % ethanol.

Table 32.
Percentage of Irgafos 168-ox additive migration from plastic to 95 % ethanol.
32 lentelė.
Irgafos 168-ox migracijos iš plastiko į 95 % etanolį procentinis kiekis.

Groups	**< 10 %**	**10 – 20 %**	**> 36 %**
Sample No	**Migration to 95 % ethanol, %**	**Sample No**	**Migration to 95 % ethanol, %**
1	5.0	13	7.7
2	5.3	14	5.4
3	11.2	15	0.6
4	36.7	16	7.2
5	1.4	17	10.1
6	0.2	18	17.2
7	4.0	19	12.7
8	7.0	20	3.3
9	12.9	21	40.0
10	4.8	22	0.4
11	3.0	23	2.8
12	13.6		

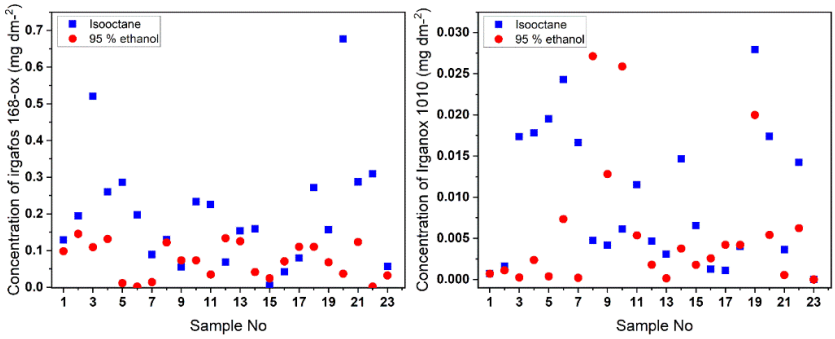


Figure 23. Migration of Irgafos 168-ox (left) and Irganox 1010 (right) to isooctane and 95 % ethanol data.
23 paveikslas. Irgafos 168-ox (kairėje) ir Irganox 1010 (dešinėje) migracijos į izooktaną ir 95 % etanolį koncentracijos.

Unlike Irgafos 168-ox, the migration of Irganox 1010 to 3% acetic acid was observed, but the concentrations were lower than the quantitation limit. As for Irgafos 168-ox determination, it was decided to carry out migration studies with 95 % ethanol and isooctane and the dimensions of the results have been chosen based on the convention that 1 kg of food is packaged with 6 dm^2 of food contact material [56].

As for Irgafos 168-ox, no specific migration limits are set for Irganox 1010 under Commission Regulation (EU) No 10/2011, consequently, a generic specific migration limit of 60 mg/kg applies [56]. Comparing Irgafos 168-ox and Irganox 1010, the migrated concentrations of Irganox 1010 were even lower than those of Irgafos 168-ox and significantly lower than the limit of 60 mg/kg. It can be seen from the data in Tables 33 and 34 that in 22 % of the samples (5 samples) and 35 % of the samples (8 samples), migration levels did not exceed 0.01 mg/kg (green) to isooctane and 95 % ethanol respectively.

Table 33.
Migration of Irganox 1010 to isooctane concentration data.
33 lentelė.
Irganox 1010 migracijos iš plastiko į izooktaną koncentracijos.

Groups	**< 0.01 mg/kg**	**0.01 – 0.10 mg/kg**	**> 0.1 mg/kg**
Sample No	**Migration to isooctane, mg/kg**	**Sample No**	**Migration to isooctane, mg/kg**
1	0.0044 ± 0.0006	13	0.0185 ± 0.0025
2	0.0097 ± 0.0013	14	0.0880 ± 0.0119
3	0.1041 ± 0.0141	15	0.0393 ± 0.0053
4	0.1068 ± 0.0144	16	0.0076 ± 0.0010
5	0.1171 ± 0.0158	17	0.0066 ± 0.0009
6	0.1458 ± 0.0197	18	0.0243 ± 0.0033
7	0.0997 ± 0.0135	19	0.1676 ± 0.0226
8	0.0283 ± 0.0038	20	0.1044 ± 0.0141
9	0.0249 ± 0.0034	21	0.0217 ± 0.0029
10	0.0367 ± 0.0050	22	0.0853 ± 0.0115
11	0.0691 ± 0.0093	23	< 0.0024
12	0.0279 ± 0.0038		

Also, in 52 % of the samples (12 samples) migration levels of Irganox 1010 were between 0.01 and 0.1 mg/kg (yellow) to both isooctane and 95 %

ethanol, and in 26 % of the samples (6 samples) and 13 % of the samples (3 samples), migration levels exceeded 0.1 mg/kg (red) to isooctane and 95 % ethanol respectively, but there were no samples were migration levels to isooctane or 95 % ethanol exceeded 0.2 mg/kg.

Table 34.
Migration of Irganox 1010 to 95 % ethanol concentration data.
34 lentelė.
Irganox 1010 migracijos iš plastiko į 95 % etanolį koncentracijos.

Groups	**< 0.01 mg/kg**	**0.01 – 0.10 mg/kg**	**> 0.1 mg/kg**
Sample No	**Migration to 95 % ethanol, mg/kg**	**Sample No**	**Migration to 95 % ethanol, mg/kg**
1	0.0043 ± 0.0006	13	0.0009 ± 0.0001
2	0.0067 ± 0.0009	14	0.0225 ± 0.0030
3	0.0015 ± 0.0002	15	0.0107 ± 0.0014
4	0.0142 ± 0.0019	16	0.0154 ± 0.0021
5	0.0022 ± 0.0003	17	0.0253 ± 0.0034
6	0.0440 ± 0.0059	18	0.0253 ± 0.0034
7	0.0013 ± 0.0002	19	0.1200 ± 0.0162
8	0.1628 ± 0.0220	20	0.0325 ± 0.0044
9	0.0768 ± 0.0104	21	0.0033 ± 0.0004
10	0.1553 ± 0.0210	22	0.0374 ± 0.0051
11	0.0321 ± 0.0043	23	< 0.0024
12	0.0108 ± 0.0108		

The results of percentages of the amount migrated Irganox 1010 to food simulants from the samples are shown in Tables 35 and 36.

It is apparent from Table 35 that from 36 % of the samples (8 samples) less than 10 % of Irganox 1010 migrated to isooctane (green), from 41 % of the samples (9 samples) 10 – 50 % of the additive migrated to isooctane (yellow), from 23 % of the samples (5 samples) more than 50 % of the additive migrated to isooctane (red).

Table 35.
Percentage of migrated Irganox 1010 additive from the plastic to isooctane.
35 lentelė.
Irganox 1010 migracijos iš plastiko į izooktaną procentinis kiekis.

Groups	**< 10 %**	**10 – 50 %**	**> 50 %**
Sample No	**Migration to isooctane, %**	**Sample No**	**Migration to isooctane, %**
1	0.1	13	33.9
2	92.5	14	1.8
3	61.1	15	15.2
4	16.9	16	0.1
5	23.1	17	1.8
6	9.8	18	45.1
7	44.1	19	71.1
8	11.8	20	91.1
9	2.5	21	30.4
10	2.3	22	39.4
11	6.7	23	-
12	76.4		

Regarding migration to 95 % ethanol, 65 % of the samples (15 samples) less than 10 % of Irganox 1010 migrated to 95 % ethanol (green), from 18 % samples (4 samples) 10 – 50 % of the additive migrated to 95 % ethanol (yellow) and from 14 % of the samples (3 samples) more than 50 % of the additive migrated to 95 % ethanol (red) (Table 36).

As in the case with Irgafos 168-ox, the results show that migration of Irganox 1010 to isooctane is higher than to 95 % ethanol, as from 23 % of the samples more than 50 % of added Irganox 1010 migrated to isooctane and regarding the migration to 95 % ethanol, only from 14 % of the samples more than 50 % of Irganox 1010 migrated to ethanol.

Comparing migration percentages amounts of Irgafos 168-ox and Irganox 1010, migration amounts of Irganox 1010 are higher as the average migrated Irgafos 168-ox to isooctane is 27 % and 9 % to 95 % ethanol, while migration of Irganox 1010 is 29 % and 15 % respectively. Even though the molecular mass of Irganox 1010 is higher than Irgafos 168 and because of the structure Irganox 1010 molecule occupies a greater matrix volume, Irganox

1010 tend to migrate more than Irgafos 168-ox. This might be because during the ultrasonic extraction the polyethylene begins to degrade and, as a result, the secondary antioxidant begins to work. As a consequence, the amount of Irgafos 168 available in the matrix diminishes. Unfortunately, no correlation between the concentration range of antioxidants and the appearance of the intended usage of the samples was observed.

Table 36.
Percentage of migrated Irganox 1010 additive from the plastic to 95 % ethanol.
36 lentelė.
Irganox 1010 migracijos iš plastiko į 95 % etanolį procentinis kiekis.

Groups	**< 10 %**	**10 – 50 %**	**> 50 %**
Sample No	**Migration to 95 % ethanol, %**	**Sample No**	**Migration to 95 % ethanol, %**
1	0.1	13	1.7
2	63.3	14	0.5
3	0.9	15	4.1
4	2.2	16	0.3
5	0.4	17	6.8
6	3.0	18	46.9
7	0.6	19	50.9
8	68.0	20	28.4
9	7.7	21	4.5
10	9.7	22	17.3
11	3.1	23	-
12	29.6		

Also, from the data shown in Figure 23 (right), as well as for Irgafos 168-ox, migration of Irganox 1010 to isooctane in 74 % of the samples is greater than in 95 % ethanol. This leads to the same conclusion as for Irgafos 168-ox, that isooctane is a more aggressive food simulant than 95 % ethanol.

4.4.3. Specific migration of metals

The amount of migrated Pb, Cr and Cd for 23 food contact materials manufactured from polyethylene was analyzed using an ICP-MS method as described in Section 3.1.4. and 3.7. The food simulant of 3% acetic acid was used for metal migration as stated in Commission Regulation (EU) No 10/2011 [56].

Following the analysis results, only in 2 PE samples Pb and Cr, and in 14 samples Cd were not detected (Figure 24) as the concentrations were below the limit of detection. What is more, there were only 2 samples (Sample No. 2 and 17), where none of the metals were determined. Also, there was only one sample (Sample No. 11) in which the specific migration of Pb significantly differed from the other samples. As these 3 samples mentioned above did not significantly differ from others, no clear correlation was observed between the concentrations of Pb, Cr and Cd and the appearance of the intended usage of the samples. From this, it could be concluded that the amount of metals, as well as antioxidants, does not depend on the product's appearance – its shape or colour.

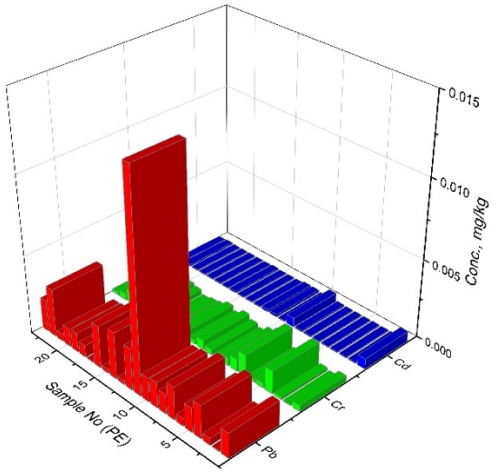


Figure 24. Concentrations of Cd, Cr and Pb obtained by ICP-MS in different packaging materials of PE.
24 paveikslas. Cd, Cr ir Pb koncentracijos, identifikuotos ICP-MS metodu skirtingose maisto pakuotėse, pagamintose iš PE.

As stated in Commission Regulation (EU) No 10/2011 migration of Cd, Pb, and Cr from food contact materials to food simulants have to be non-detectable by the limit of detection of 0.01 mg/kg for Pb, Cr and 0.002 mg/kg

for Cd [56]. From the data shown in Table 37, there were no samples where the specific migration of metals exceeded 0.01 and 0.002 mg/kg for Pb and Cr, and for Cd respectively.

Even keeping in mind that the PE samples that were tested during extraction and migration experiments were different, comparing the extraction (Table 23) and migration (Table 37) of Pb, Cr and Cd migration from PE samples, there is a clear tendency that extracted concentrations are higher in thousands. Also, regarding the comparison results and the migration limits set by Commission Regulation (EU) No 10/2011 [56], there is a high possibility, that only a small amount (< 0.001 %) of added metals to the final product of food contact material might migrate to food simulants and therefore to food.

Table 37. Migration of Pb, Cr and Cd concentration data.
37 lentelė. Pb, Cr ir Cd migracijos koncentracijos.

	Pb, mg/kg	**Cr, mg/kg**	**Cd, mg/kg**
1	0.00158 ± 0.00011	0.00039 ± 0.00003	0.00066 ± 0.00002
2	< 0.00006	< 0.00006	< 0.00006
3	0.00045 ± 0.00003	0.00017 ± 0.00001	< 0.00006
4	0.00211 ± 0.00014	0.00147 ± 0.00010	0.00007
5	0.00155 ± 0.00011	0.00032 ± 0.00002	< 0.00006
6	0.00049 ± 0.00003	0.00018 ± 0.00001	< 0.00006
7	0.00210 ± 0.00014	0.00141 ± 0.00009	0.00007
8	0.00125 ± 0.00008	0.00078 ± 0.00005	0.00009
9	0.00164 ± 0.00011	0.00050 ± 0.00003	0.00058 ± 0.00002
10	0.00154 ± 0.00010	0.00015 ± 0.00001	< 0.00006
11	0.01370 ± 0.00093	0.00034 ± 0.00002	0.00015
12	0.00266 ± 0.00018	0.00061 ± 0.00004	0.00016
13	0.00026 ± 0.00002	0.00027 ± 0.00002	< 0.00006
14	0.00299 ± 0.00020	0.00055 ± 0.00004	< 0.00006
15	0.00026 ± 0.00002	0.00027 ± 0.00002	< 0.00006
16	0.00271 ± 0.00018	0.00019 ± 0.00001	0.00010
17	< 0.00006	< 0.00006	< 0.00006
18	0.00077 ± 0.00005	0.00033 ± 0.00002	< 0.00006
19	0.00123 ± 0.00008	0.00046 ± 0.00003	< 0.00006
20	0.00117 ± 0.00008	0.00100 ± 0.00007	< 0.00006
21	0.00046 ± 0.00003	0.00083 ± 0.00005	< 0.00006
22	0.00307 ± 0.00021	0.00042 ± 0.00003	0.00011
23	0.00198 ± 0.00013	0.00020 ± 0.00001	< 0.00006

5. CONCLUSIONS

1. The overall migration from PP packages to food simulants is higher than from PE, and this confirms that migration studies are needed to assess the potential risks associated with plastic additive migration to food simulants and, therefore, to food.

2. The developed thermal desorption gas chromatography coupled with mass spectrometry (TD-GC/MS) method was very efficient in performing non-targeted screening analysis of solid plastic samples. This method proved effective in identifying migrants and degradation products in PE and PP samples and the results obtained showed that there is a discernible difference in the migrant composition of PE, PP, and PP/PE composite packages.

3. Analysis done by developed and validated method of the atomic absorption spectrophotometry (AAS) revealed that plastics contained Cr, Cd, Hg, and Pb but their mass concentration in PE, PP, and PP/PE composite plastic samples did not exceed 100 mg/kg.

4. The developed and validated liquid chromatography with tandem mass spectrometry (LC-MS/MS) method is suitable for the study of Irgafos 168-ox and Irganox 1010 antioxidants in the composition of food contact materials and their specific migration to food simulants. The results proved that both Irgafos 168 and Irganox 1010 are added to the polymer matrix, and they tend to migrate to food simulants and therefore to food.

5. The Developed and validated inductively coupled plasma mass spectrometry (ICP-MS) method is suitable for the determination of cadmium, chromium, and lead in food contact materials. The analysis demonstrates, that there is a high possibility that only a small amount of added metals to food contact materials might migrate to food.

6. Regarding the results obtained by overall migration and specific migration of antioxidants, it is clear that plastics may not be safe for oily food packaging as the migration to food simulant isooctane, which represents oily food, is higher than to any other food simulants, that represents other foods.

7. Even though there were not so many samples tested that exceeded limits set by different regulations (considered safe for consumers), it must be noted how many different migrants migrate to food and for which the consequences for human health are not clear yet.

SANTRAUKA

ĮVADAS

Plastikai dėl savo fizikinių ir cheminių savybių gali būti pritaikomi įvairiose pramonės srityse, todėl tapo svarbia mūsų kasdienio gyvenimo sudedamąja dalimi. Plastikai gali būti naudojami daug kur, bet iki 40 % viso plastiko sunaudojama maisto pakuočių gamybai [1]. Maisto pakuočių gamybai plastikas labai tinka, kadangi apsaugo nuo mikroorganizmų, šviesos ir kitų išorinių veiksnių padarytos žalos, kartu išsaugant maisto kokybę, yra lengvai transportuojamas.

Dėl naudingų savybių ir lengvo modifikavimo plastikai tapo pirmu pasirinkimu maisto produktų pakavimui, tačiau neapdorotas plastikas naudojamas retai. Norint modifikuoti žaliavinį plastiką, gamybos proceso metu pridedami įvairūs priedai, o vidutiniuose nepluoštiniuose plastikuose yra 93 % polimerinės dervos ir 7 % masės priedų [2]. Todėl visi priedai, gamybos proceso likučiai ir skilimo produktai, taip pat junginiai, susidarantys tarp priedų ir likučių, arba priedų ir monomerų, vien monomerai ar mažos masės polimerai ir t.t. yra linkę migruoti į maistą.

Tikslingai į plastiko matricą pridedamų medžiagų poveikis žmonių sveikatai šiai dienai yra jau gan gerai dokumentuotas, vis keliant klausimus dėl iškylančių sveikatos problemų, tokių kaip skydliaukės sutrikimai, alergijos [3, 4], kurios kelia didelį susirūpinimą. Kalbant apie netikslingai į plastikus pridedamas medžiagas, daugelio jų poveikis nėra ištirtas ir apskritai nežinomas. Todėl, siekdamos apsaugoti vartotojus nuo potencialiai kenksmingų medžiagų (tikslingai ir netikslingai pridedamų cheminių medžiagų) migracijos iš pakuočių į maistą, daugybė mokslinių grupių rengia teisės aktus dėl maisto pakuočių sudėties reglamentavimo ir visuomenės švietimo.

Apibendrinus, visų iš maisto pakuočių į maistą išsiskiriančių, nesvarbu, tikslingai ar netikslingai pridėtų, kenksmingų cheminių medžiagų tikslus identifikavimas yra būtinas, kad būtų tinkamai įvertintas atitikimas teisės aktams, susijusiems su maisto pakuočių priedais ir maisto gamybos kokybės kontrolės reikalavimais.

Darbo tikslas ir uždaviniai

Šios disertacijos tikslas – suprasti kaip maisto pakavimui skirtų polietileno ir polipropileno pakuočių polimerų modifikavimas įvairiais priedais įtakoja plastikų savybes bei ištirti tų priedų migraciją į maistinius modelinius tirpalus.

Pagrindinės tyrimo užduotys:

1. Analizei atrinktus polietileno, polipropileno ir jų kompozitų mėginius ištirti pažeistojo visiškojo vidaus atspindžio Furjė transformacijos infraraudonosios spektroskopijos metodu;
2. Atlikti bendrosios migracijos tyrimus į maistinius modelinius tirpalus gravimetrijos metodu;
3. Optimizuotu terminės desorbcijos dujų chromatografijos masių spektrometrijos (TD-GC/MS) tyrimo metodu, skirtu lakių ir vidutiniškai lakių organinių junginių detekcijai, ir validuotu atominės absorbcijos spektrometrijos (AAS) tyrimo metodu, skirtu metalų (kadmio, chromo, švino ir gyvsidabrio) analizei, ištirti polietileno, polipropileno ir jų kompozitinių mėginių degradacijos procesus;
4. Optimizuotu ir validuotu induktyviai susietos plazmos masės spektrometrijos (ICP-MS) tyrimo metodu atlikti kadmio, chromo ir švino specifinės migracijos tyrimus į maistinius modelinius tirpalus;
5. Optimizuoti skysčių chromatografijos masių spektrometrijos (LC-MS/MS) tyrimo metodą ir jį validuoti antioksidantų ekstrakcijos ir specifinės migracijos į maisto modelinius tirpalus analizei;
6. Išanalizuoti gautus rezultatus, nustatant ryšius tarp polimero degradacijos, bendrosios ir specifinės migracijos į maistinius modelinius tirpalus.

Darbo naujumas ir aktualumas

Disertacijoje aprašyti atlikti aktualūs, išsamūs su maistu besiliečiančių medžiagų, pagamintų iš plastikų, tyrimai. Maisto pakuotės yra sudėtingas cheminių medžiagų mišinys, todėl yra iššūkis išsiaiškinti, kas yra tame mišinyje ir kokios cheminės medžiagos gali migruoti į maistą. Galimų migrantų nustatymas, yra vienintelis būdas sužinoti apie migraciją ir pagerinti migrantų identifikavimą, priimti sprendimus gamybos procesuose bei įvertinti galimą pavojų, susijusį su priedų ir jų skilimo produktų migracija į maistą, žmonių sveikatai. Todėl šioje disertacijoje aprašyti ir validuoti optimizuoti gravimetrijos (GA), skysčių chromatografijos masių spektrometrijos (LC-

MS/MS), terminės desorbcijos dujų chromatografijos masių spektrometrijos (TD-GC/MS), atominės absorbcijos spektrometrijos (AAS) ir induktyviai susietos plazmos masės spektrometrijos (ICP-MS) tyrimų metodai, skirti polimerų degradacijos, bendrosios ir specifinės migracijos tyrimų atlikimui. Visi šie metodai, skirtingai nei dauguma mokslo visuomenėje paskelbtų metodų, gali būti lengvai pritaikomi įprastose rutininėse su maistu besiliečiančių gaminių kontrolės funkciją atliekančioms laboratorijose.

Ginamieji teiginiai

1. Bendrosios migracijos į maistinius modelinius tirpalus tyrimai yra labai reikšmingi, siekiant įvertinti maisto pakuočių keliamas rizikas žmonių sveikatai.
2. Dujų chromatografijos masių spektrometrijos su termine desorbcija (TD-GC/MS) tyrimo metodas, optimizuotas disertacijos metu, yra tinkamas polietileno, polipropileno ir jų kompozitų degradacijos procesams tirti.
3. Optimizuotas ir validuotas atominės absorbcijos spektrometrijos (AAS) tyrimo metodas yra tinkamas atlikti kadmio, chromo, švino ir gyvsidabrio kiekio nustatymo plastiko sudėtyje tyrimus rutininėse laboratorijose.
4. Optimizuotas ir validuotas skysčių chromatografijos masių spektrometrijos (LC-MS/MS) tyrimo metodas yra tinkamas atlikti antioksidantų kiekio nustatymo plastikuose ir maisto modelinėse terpėse tyrimus rutininėse laboratorijose.
5. Optimizuotas ir validuotas induktyviai susietos plazmos masės spektrometrijos (ICP-MS) metodas yra tinkamas atlikti kadmio, chromo ir švino kiekio nustatymo maisto modelinėse terpėse tyrimus rutininėse laboratorijose.

6. MATAVIMAI, REZULTATAI IR JŲ APTARIMAS

6.1. Polimerų identifikavimas naudojant pažeistojo visiškojo vidaus atspindžio Furjė transformacijos infraraudonosios spektroskopijos (ATR-FTIR) metodą

Polimerų identifikavimui naudotas pažeistojo visiškojo vidaus atspindžio Furjė transformacijos infraraudonųjų spindulių (ATR-FTIR) spektrometras Agilent Technologies Cary 630. PP, PE ir PP/PE kompozitų

mėginiai, kurie nebuvo naudojami maisto pakavimui, buvo sukarpyti mažais maždaug 1,0 × 1,0 cm dydžio gabalėliais. Spektrai matuoti atliekant 4 skanavimus su 2 cm^{-1} rezoliucija 4000 – 600 cm^{-1} spektro dalyje. Fonui naudotas oras (4 skanavimai, 4000 – 600 cm^{-1} spektro dalyje). Išmatuoti plastiko spektrai buvo lyginami su spektrų duomenų baze.

12 paveiksle (Figure 12) pavaizduotas tipinis PE spektras, kuriame matomos keturios charakteringos vibracijos sugerties juostos ties 2948, 2914, 1462 ir 717 cm^{-1} bangos skaičiais. Sugerties juostos ties 3000 – 2840 cm^{-1} rodo simetrines ir antisimetrines metileno ir metilo grupių tempimo vibracijas, ties 1462 ir 717 cm^{-1} – atitinkamai metileno plokštumos deformacijas ir siūbavimo vibracijas. 13 paveiksle (Figure 13) pavaizduotas tipinis PP spektras, kuriame matoma dešimt charakteringų vibracijos sugerties juostų ties 2951, 2916, 2872, 2839, 1456, 1375, 1167, 998, 973 ir 840 cm^{-1}. Kaip ir PE atveju, sugerties juostos ties 3000 – 2840 cm^{-1} rodo simetrines ir antisimetrines metileno ir metilo grupių tempimo vibracijas. Ties 1459 cm^{-1} spektre matomos metileno deformacijos ir antisimetrinės metilo grupių deformacijos plokštumoje. Taip pat, stebimos plokštuminės simetrinės metileno deformacijos sugerties juostos ties 1376 cm^{-1}, metilo grupių virpesiai ties 1167 cm^{-1}, C-C jungčių tempimo virpesiai ties 998 ir 973 cm^{-1} ir svyruojanti metileno vibracija ties 840 cm^{-1}.

Nepaisant skirtingų tirtų PE ir PP mėginių sudėties (ypač atsižvelgiant į tai, kad gamyboje naudojami skirtingi priedai) ir formų, 12 ir 13 paveiksluose pateikti spektrai neparodo reikšmingų skirtumų tarp šiame darbe išmatuotų, [137-139] pavyzdinių literatūroje pateiktų ar FTIR duomenų bazėje saugomų spektrų.

6.2. Bendrosios migracijos tyrimai naudojant gravimetrijos metodą

Bendrosios migracijos tyrimams atlikti buvo atrinkti 126 skirtingų tipų mėginiai, iš kurių 76 pagaminti iš PE ir 50 iš PP. PE mėginiai įvairių rūšių plėvelės, o PP – saldainių padėklai, buteliai, plėvelės. Prieš analizę nė vienas mėginys nebuvo naudojamas maisto pakavimui.

PE ir PP mėginiai buvo skirtingų maistinių modelinių tirpalų, tokių kaip 3 % acto rūgštis, 10 % etanolis, 50 % etanolis, 95 % etanolis ir izooktanas, imituojančių įvairių rūšių maistą (3 lentelė/Table 3), kaip nurodyta Komisijos reglamente (ES) Nr. 10/2011 [56], ekspozicijoje. Ekspozicijos sąlygos – 10 parų 40 °C temperatūroje. Pagal Komisijos reglamentą (ES) Nr. 10/2011 [56], šios sąlygos imituoja mėginio ir maisto sąlyčio ilgesnę nei 30 dienų trukmę kambario ir žemesnėje temperatūroje. Siekiant užtikrinti, kad mėginiai su

maistiniais modeliniais tirpalais laikomi reikiamoje temperatūroje (40 ± 2 °C), buvo naudojamos atestuotos krosnys, o eksperimento metu krosnyse buvo laikomas kalibruotas termologeris, skirtas temperatūros nuokrypiams užregistruoti, jei tokių būtų. Plėvelių mėginiai buvo lituojami siekiant pagaminti maišelį ir užpildyti maistiniais modeliniais tirpalais (8 pav./Figure 8). Įvairūs tūriniai indai buvo užpildyti maistiniais modeliniais tirpalais ir apsaugoti nuo išgaravimo, ant viršaus uždedant plėvelę.

Bendroji migracija iš plastikų buvo matuojama gravimetriškai nustatant visas nelakias chemines medžiagas, kurios migruoja į maistinį modelinį tirpalą. Bendrų migrantų analizei visas mėginio tirpalas buvo pilamas į porcelianinį tiglį ir išgarintas iki sausumo. Prieš atliekant gravimetrinę analizę, tigliai kruopščiai plaunami, džiovinami eksikatoriuose iki pastovios masės, sveriant tris kartus analitinėmis svarstyklėmis (KERN ABS 220-4N). Bendras migracijos kiekis buvo apskaičiuotas lyginant mėginio sausą liekaną ir modelinio tirpalo (tuščio mėginio) masę. Bendroji migracija (OM) apskaičiuojama naudojant 5 formulę, kur OM yra bendroji migracija (mg/kg iš maisto), m_a – mėginio sausos liekanos masė (g), m_b – tik maistinio modelinio tirpalo (tuščiojo mėginio) sausoji liekana (g) ir V – maistinio modelinio tirpalo tūris (ml). Rezultatai buvo konvertuoti į mg/kg, atsižvelgiant į 1 dm^2 mėginio masę. Kiekvieno bandinio tyrimo rezultatas buvo trijų pakartojimų vidurkis.

Siekiant atlikti bendrosios migracijos matavimus iš PP ir PE maisto pakuočių gravimetrijos metodu, buvo validuoti migracijos į skirtingus maistinius modelinius tirpalus namudiniai metodai ir įvertintos pagrindinės metodo veiksmingumo charakteristikos, tokios kaip vidinis atkuriamumas, pakartojamumas, teisingumas, kiekybinio nustatymo riba, aptikimo riba ir neapibrėžtis (9 lentelė/Table 9). Metodo validavimui buvo naudojamos sertifikuotos pamatinės medžiagos (Vokietijos kvalifikacijos tikrinimo ir etaloninių medžiagų biuras (DRRR)), kurių sertifikuotos vertės 4,37 ± 0,17 mg/dm^2 3 % acto rūgštyje, 3,73 ± 0,12 mg/dm^2 10 % etanolyje, 4,7 0,09 mg/dm^2 50 % etanolyje, 5,35 ± 0,22 mg/dm^2 95 % etanolyje ir 1,66 ± 0,14 mg/dm^2 izooktane.

Bendrosios migracijos tyrimai su izooktanu, 3 % acto rūgštimi, 10 % ir 95 % etanoliu buvo atlikti su 64, 59, 29 ir 61 PE mėginiais atitinkamai.

Visuose 29 PE mėginiuose bendra migracija į 10 % etanolį buvo mažesnė už metodo aptikimo ribą. Migracija į 95 % etanolį parodė, kad 24 iš 61 su maistu besiliečiančių gaminių migracija įvyko, nes 37 iš 61 su maistu besiliečiančių gaminių migracijos rezultatai buvo mažesni už metodo aptikimo ribą.

Bendros migracijos į 3 % acto rūgštį ir izooktaną rezultatai kitokie nei migracijos į etanolio modelinius tirpalus. Bendra migracija į 3 % acto rūgštį rodo, kad migracija įvyko tik iš 5 iš 59 PE su maistu besiliečiančių gaminių, tačiau iš daugumos mėginių bendra migracija buvo mažesnė už metodo aptikimo ribą. Bendra migracija į izooktaną parodė, kad iš 21 iš 64 su maistu besiliečiančių PE gaminių bendroji migracija įvyko, nes 43 su maistu besiliečiančių gaminių migracijos rezultatai buvo mažesni už metodo aptikimo ribą. Tačiau iš 5 su maistu besiliečiančių gaminių, pagamintų iš PE, bendra migracija į izooktaną (3 mėginiai) ir 3 % acto rūgštį (2 mėginiai) viršijo 10 mg/dm^2 išsiskyrimo ribą, nustatytą Reglamente Nr. 10/2011 [56] (14 lentelė, levandų spalva/Table 14, lavender coloured).

Vidutinis bendros migracijos kiekis iš PE gaminių naudojant 95 % etanolio, izooktano ir 3 % acto rūgšties maistinius modelinius tirpalus buvo atitinkamai 1,4 ± 0,3 mg/dm^2, 3,4 ± 0,7 mg/dm^2 ir 0,9 ± 0,2 mg/dm^2. Migracijos į izooktaną ir 3 % acto rūgštį, viršijančios migracijos ribą 10 mg/dm^2, rezultatai į vidurkio skaičiavimus nebuvo įtraukti.

Iš viso bendrosios migracijos tyrimams buvo ištirta 50 PP mėginių (15 paveikslas/Figure 15). Bendra migracija į izooktaną, 3 % acto rūgštį, 95 %, 50 % ir 10 % etanolį buvo tiriama atitinkamai 22, 24, 22, 8 ir 18 PP mėginiuose.

Bendros migracijos į izooktaną tyrimai parodė, kad iš 12 iš 22 su maistu besiliečiančių gaminių migracija įvyko, nes iš 10 su maistu besiliečiančių gaminių migracijos rezultatai buvo mažesni nei metodo aptikimo riba. Iš 4 su maistu besiliečiančių gaminių bendra migracija į izooktaną viršijo 10 mg/dm^2 išsiskyrimo ribą pagal Reglamentą Nr. 10/2011 [56] (18 lentelė, levandų spalva/Table 18, lavender coloured). Bendra migracija į 3 % acto rūgšties modelinį tirpalą rodo, kad migracija įvyko tik iš 6 iš 24 su maistu besiliečiančių PP gaminių, tačiau iš daugumos mėginių bendra migracija buvo mažesnė nei metodo aptikimo riba. Kalbant apie bendrą migraciją į 95 % etanolį, iš 12 iš 22 su maistu besiliečiančių PP gaminių migracija vyko, nes iš 10 su maistu besiliečiančių gaminių migracijos rezultatai buvo mažesni už metodo aptikimo ribą. Bendra migracija į 50 % ir 10 % etanolio maistinius modelinius tirpalus parodė, kad iš 4 ir iš 7 iš 8 ir iš 18 su maistu besiliečiančių PP gaminių migracija vyko, nes atitinkamai iš 4 ir 11 su maistu besiliečiančių gaminių migracijos rezultatai buvo žemiau metodo aptikimo ribos.

Vidutinės bendrosios migracijos vertės į 10, 50 ir 95 % etanolį, izooktaną ir 3 % acto rūgštį buvo 2,2 ± 0,4 mg/dm^2, 3,2 ± 0,6 mg/dm^2, 3,5 ± 0,7 mg/dm^2, 6,6 ± 1,3 mg/dm^2 ir atitinkamai 4,4 ± 0,9 mg/dm^2. Skaičiuojant vidurkį, bendros migracijos į izooktaną, viršijančios 10 mg/dm^2 migracijos ribą, rezultatai neįskaičiuoti.

Apibendrinus bendrosios migracijos iš PE ir PP gaminių į maistinius modelinius tirpalus rezultatus, galima daryti išvadą, kad izooktanas yra agresyviausias maistinis modelinis tirpalas, nes bendra migracija iš PE arba PP į izooktaną yra didesnė nei į kitus maistinius modelinius tirpalus (3 % acto rūgštį, 10 %, 50 % ir 95 % etanolį). Be to, PE gali būti saugesnis už PP, nes bendra nelakių cheminių medžiagų migracija iš PP gaminių kai kuriais atvejais yra didesnė net dvigubai. Kita vertus, jei viršijamos Reglamento Nr. 10/2011 [56] ribos, bendroji migracija iš PP gaminių viršija ribas 30 %, o PE – 300 %. Kadangi mėginiai, iš kurių bendroji migracija viršijo Reglamente Nr. 10/2011 [56] nustatytas ribas, nesiskiria nuo kitų, šie rezultatai patvirtina, kad migruojančių medžiagų skaičius nepriklauso nuo gaminio išvaizdos – formos ar spalvos.

6.3. PE ir PP gaminių degradacijos tyrimai

Iš viso polimerinių gaminių, pagamintų iš PE, PP ir jų kompozitų degradacijos procesams tirti buvo atrinkti 52 mėginiai. Prieš analizę nė vienas mėginys nebuvo naudojamas maisto pakavimui. Iš 20 PP mėginių, didžioji dalis buvo šviesių spalvų duonos, sūrio, traškučių ir kt. pakavimo plėvelės, o tamsios spalvos pakuotės dažniausiai buvo saldainių padėklai, skirti naudoti šokolado pakavimui, gaiviesiems gėrimams, pieno produktams ir kt. Tyrimams naudoti 20 PE mėginių buvo šviesios plėvelės, maisto konservavimo maišeliai, plastikiniai puodeliai, dangteliai ir kt. Beveik visi 12 PP/PE kompozito pakuočių mėginių buvo plėvelės duonai ar traškučiams.

Pakuočių tyrimams buvo naudojami įvairūs mėginių paruošimo būdai:

1. lakiųjų ir pusiau lakiųjų organinių junginių analizei apytiksliai 0,1 g PE ir PP mėginių buvo supjaustyta į mažus 0,2 cm × 1,0 cm gabalėlius ir įterpta į stiklinius terminės desorbcijos vamzdelius (9B ir 9C paveikslai/Figure 9B and 9C). Į terminės desorbcijos vamzdelius įkišti atkaitintos stiklo vatos kamščiai, kad mėginys neiškristų iš sorbcinio stiklinio vamzdelio. Vamzdeliai užsandarinti metaliniais dangteliais, išklotais teflonu, įkeliami į automatinį mėginių ėmiklį ir analizuojami. Kiekvienos analizės metu buvo tirtos dvi kiekvieno mėginio paralelės. Atliekant tuščiojo mėginio analizę, tirtas tuščias terminės desorbcijos vamzdelis su stiklo vatos kamščiais ir metaliniais dangteliais (9A paveikslas/Figure 9A).

2. metalų analizei maždaug 0,2 g PP, PE ir PP/PE mėginių buvo supjaustyti smulkiais gabalėliais ir mineralizuoti azoto rūgšties (65 %) ir peroksido tirpale (30 % grynumo, p.a.) 5:2 (v/v, ml). Po mineralizacijos ekstraktas praskiedžiamas vandeniu iki 25 ml. Kiekvienos analizės metu buvo

tirtos dvi kiekvieno mėginio paralelės. Atliekant tuščiojo mėginio analizę, tiriama azoto rūgštis ir peroksido tirpalas santykiu 5:2 (v/v, ml), praskiestas vandeniu.

Lakiųjų bei pusiau lakiųjų organinių junginių analizė atlikta termodesorbcinės dujų chromatografijos būdu kartu su masės spektrometrija (TD-GC/MS) (žr. skyrių 6.3.1.), o metalų analizė atlikta atominės absorbcijos spektrofotometrijos (AAS) metodu (žr. skyrių 6.3.2.).

6.3.1. PE ir PP gaminių degradacijos tyrimai naudojant terminę desorbciją su dujų chromatografija – masių spektrometrija (TD-GC/MS)

Netikslinei lakiųjų ir pusiau lakiųjų organinių junginių, potencialių migrantų, analizei naudota terminės desorbcijos dujų chromatografijos sistema su masės spektrometru GCMS-QP2010 Plus (Shimadzu), kartu su terminės desorbcijos mėginių ėmikliu TD20 (Shimadzu). Kadangi buvo naudojama netikslinė analizė, pamatinės medžiagos nebuvo naudojamos. Naudojant NIST MS Search 2.0 masės spektrų biblioteką, buvo nustatyti potencialūs migrantai, kurių atitikties tikimybė buvo aukštesnė nei 95 %. Atliekant mėginio terminės desorbcijos analizę, vamzdeliai su mėginiu buvo kaitinami 60 minučių 80 °C temperatūroje, kai He nešiklio dujų srauto greitis 60 ml/min. Dujos, išsiskyrusios iš mėginio, transportuojamos į – 15°C temperatūros šaldomą koncentravimo vamzdelį. Po 60 min vamzdelis užkaitinamas iki 240°C ir desorbuojamos dujos transportuojamos į GC įpurškimo angą esant 2,7 ml/min He nešiklio dujų srautui. Mėginių analizei buvo naudojama kapiliarinė kolonėlė Restek Rtx®-1 w/Integra-Guard®, padengta Crossbond® 100 % dimetilpolisiloksanu (60 m, 0,32 mm ID × 1 µm df). Kolonėlės krosnies temperatūra buvo užprogramuota nuo 50 °C (10 min.), tada temperatūrą keliant kas 5 °C/min iki 125 °C ir galiausiai temperatūrą keliant kas 30 °C/min iki 240 °C (5 min.). Buvo naudojamas viso skenavimo režimas 40–400 m/z diapazone esant 70 eV elektronų jonizacijai (EI).

Visų pirma buvo tiriami skirtingų spalvų – tamsių ir šviesių – PP gaminiai ir lyginamos GC-MS chromatogramos. 16 paveiksle (Figure 16) pavaizduotas tipiškų tamsių ir šviesių PP gaminių chromatogramų pavyzdys. Kaip parodyta 16 a paveiksle (Figure 16a), tamsios spalvos PP pakuotės išskiria daugiau potencialių migrantų nei šviesios PP pakuotės (16 b paveikslas/Figure 16 b), tačiau pagrindinės migrantų grupės yra tos pačios (19 lentelė/Table 19). Didesnio kiekio potencialių migrantų išsiskyrimo iš tamsios spalvos PP pakuočių priežastis nėra aiški. Tačiau taip gali būti dėl keletos priežaščių, t.y. dėl didesnės suskaidytų oligomerų koncentracijos spalvotuose

plastikuose arba daugybės priedų, tokių kaip dažikliai, naudojamų tamsaus plastiko pakuočių gamybos procese išsiskyrimo. 19 lentelėje (Table 19) pateiktos potencialių migrantų grupės/junginiai, kurie buvo identifikuoti naudojant NIST MS Search 2.0 spektrų biblioteką, kurių atitikimo tikimybė didesnė nei 95 % PP mėginiuose.

Sekančiu etapu, buvo siekiama išsiaiškinti skirtumus tarp skirtingos sudėties skirtingų plastikų – PP ir PE – GC-MS chromatogramų. Tipinė PE mėginio potencialių migrantų GC/MS suminė jonų chromatograma pavaizduota 17 paveiksle (Figure 17). Lyginant PP mėginių (16 paveikslas/Figure 16) ir PE mėginių (17 paveikslas/Figure 17) GC/MS suminių jonų chromatogramų rezultatus, pastebėta, kad PE mėginiai išskiria daug mažiau potencialių migruojančių medžiagų nei PP mėginiai, tačiau PP mėginių kilmė, pagrindinės migrantų ar skilimo produktų grupės yra tos pačios, pavyzdžiui, plastifikatoriai, tirpikliai, tepalai ir kt. (žr. 20 lentelę/Table 20). Priežastis, kodėl potencialių migrantų išsiskiria mažiau iš PE mėginių, nėra aiški, tačiau tai gali būti susiję su struktūros skirtumais, nes PP dėl savo standumo reikalauja didesnio modifikavimo priedų kiekio nei PE. Taip pat, PP lydymosi temperatūra yra aukštesnė nei PE, o tai riboja jo naudojimą aukštesnėje nei 0 °C temperatūroje. PP pasižymi mažesniu cheminiu atsparumu nei PE. Šios PE savybės, įskaitant jo lankstumą, žemesnę lydymosi temperatūrą ir didesnį atsparumą, leidžia pakuočių gamybos procese naudoti mažiau priedų. 20 lentelėje (Table 20) pateiktos potencialių migrantų grupės/junginiai, kurie buvo identifikuoti naudojant NIST MS Search 2.0 spektrų biblioteką, kurių atitikimo tikimybė PE mėginiuose yra didesnė nei 95 %.

21 lentelėje (Table 21) pateiktos potencialių migrantų grupės/junginiai, kurie buvo identifikuoti naudojant NIST MS Search 2.0 spektrų biblioteką, kurių atitikties tikimybė PE ir PP mėginiuose yra didesnė nei 95 %. Nustatyti junginiai skirtinguose PP ir PE mėginiuose buvo suskirstyti į 8 junginių grupes pagal funkcines grupes ir galimą kilmę, remiantis 2018 metais paskelbta CPPdb A ir B sąrašų duomenų baze [74]. Šias junginių grupes sudaro esteriai, oktano, dodekano ir heksadekano junginiai, 1-tetradecenas ir heptadekano, nonano ir undekano, pentano, heneikozano, tridekano junginiai, mišri grupė, sudaryta iš pavienių skirtingos kilmės junginių (21 lentelė/Table 21).

Kaip matyti iš 21 lentelės (Table 21), visuose PP ir PE mėginiuose buvo nustatyti skirtingi plastifikatoriai [16, 19, 22, 23, 74], tokie kaip bis(2-etilheksil)ftalatas, bis(tridecil)ftalatas, di-n-oktilftalatas ir kiti esteriai. Nustatyti ne tik plastifikatoriai, bet ir netyčia pridėtos medžiagos, tokios kaip 7,9-di-tret-butil-1-oksaspiro-(4,5)-deka-6,9-dienas-2,8-dionas, kuris yra gerai

žinomų antioksidantų Irganox 1010 skilimo reakcijų produktas [74, 140-142]. Kaip ir tikėtasi, tarp pagrindinių junginių buvo aptikti alkanai ir alkenai (19 – 21 lentelės/Tables 19 – 21). Linijiniai alkanai ir izoalkanai yra kilę iš vadinamojo parafino vaško, naudojamo išoriniam pakuotės lubrikavimui. Alkanai taip pat naudojami kaip tirpiklis. Alkenai naudojami įvairių priedų ir polimerų gamyboje. Be to, alkenai susidaro kaip šalutinis olefino polimerizacijos produktas [143, 144]. Remiantis CPPdb A ir B sąrašų duomenų baze [74]:

- oktano junginiai naudojami kaip tirpikliai, tepalai, dažikliai ir klijai. Visuose tirtuose mėginiuose buvo nustatytas oktanas, 1,1'-oksibis-oktanas ir 5-etil-2-metil-oktanas. PE mėginiuose jokių kitokių oktano junginių neidentifikuota.
- dodekano ir heksadekano junginiai naudojami kaip tirpikliai ir lubrikantai. Tirtuose mėginiuose buvo identifikuoti metilinto dodekano junginiai, pvz., 4-metil-dodekanas, 4,6-dimetil-dodekanas, ir heksadekano junginiai, tokie kaip 2-metil-heksadekanas.
- analizės metu identifikuoti 1-tetradecenas, heptadekanas, 3-metil-nonanas, 3-metil-undekanas ir kiti junginiai naudojami kaip lubrikantai.
- pentano junginiai, tokie kaip 2-metil-pentanas, 2,2-dimetil-pentanas ir 3-metil-pentanas, naudojami kaip tirpikliai, lubrikantai, dažikliai ir klijai. Visi šie priedai buvo nustatyti visuose tirtuose PP ir PE mėginiuose, jokie kiti pentano junginiai nebuvo identifikuoti.
- tridekano junginiai, tokie kaip 1-tridekanas ir 3-metil-tridekanas yra naudojami kaip tirpikliai. Šie junginiai nustatyti visuose tirtuose mėginiuose. 5,5-dimetil-tridekanas buvo identifikuotas tik PE mėginiuose, o 1-jodo-tridekanas, 2-metil-tridekanas ir 2,5-dimetil-tridekanas buvo identifikuoti tik PP mėginiuose.
- stabilizatorius heneikozanas buvo nustatytas visuose tirtuose mėginiuose, o 3-metil-heneikozanas – tik PE mėginiuose.
- visuose tirtuose PP ir PE mėginiuose buvo nustatyti di-n-decilsulfonas, 2-heksil-1-dekanolis, d-limonenas, acetonas, tetrahidrofuranas, nonanalas, dekanalas ir nonano rūgštis. 4,4-dimetil-1,3-dioksanas, naudojamas kaip užpildas, dažiklis ir klijai, buvo identifikuotas tik PP mėginiuose.

Skirtinguose mėginiuose buvo nustatyta ir daugiau potencialių migracijos ir skilimo produktų, tokių kaip dekanas, heptanas, cikloheksanas ir 2-propanolio junginiai (22 lentelė/Table 22). Visi minėti migrantai yra įtraukti į CPPdb A ir B sąrašų [74] duomenų bazę kaip maisto priedai ar kitos plastikų

gamyboje naudojamos medžiagos, tačiau informacijos apie galimą tų medžiagų kilmę nepateikta.

Dauguma identifikuotų potencialių migrantų (19–22 lentelės/Tables 19 – 21) nėra reglamentuojami ES, todėl neturi teisinių apribojimų ar nustatytų ribinių verčių. Tiksli lakių ir vidutiniškai lakių potencialių migrantų ar skilimo produktų kilmė nėra aiški, tačiau remiantis literatūroje pateiktais duomenimis [74] galima įvertinti tendencijas, kaip tai buvo padaryta šioje disertacijoje.

6.3.2. PE ir PP gaminių degradacijos tyrimai naudojant atominės absorbcijos spektrofotometriją (AAS)

Metalų analizė buvo atlikta naudojant atominės absorbcijos spektrofotometrą AA-6800 su grafito krosnele GFA-EX7 ir hidrido garų generatoriumi HGV-1 (Shimadzu). Naudotos 99,95 % grynumo Ar dujos, kurių slėgis 0,35 MPa. Fono korekcijai naudota deuterio lempa, analizei – tuščiavidurio katodo lempa. Pb, Cd, Cr ir Hg bangos ilgiai buvo atitinkamai 283,3 nm, 228,8 nm, 357,9 nm ir 253,7 nm.

Siekiant ištirti Pb, Cd, Cr ir Hg PP, PE ir PP/PE kompozitiniuose gaminiuose, buvo validuoti namudiniai analitiniai metodai ir įvertintos pagrindinės metodo veiksmingumo charakteristikos, tokios kaip tiesiškumas, vidinis atkartojamumas, pakartojamumas, teisingumas, kiekybinio nustatymo riba, aptikimo riba ir neapibrėžtis (10 lentelė/Table 10). Metodo validavimui buvo naudojamos sertifikuotos pamatinės medžiagos (VWR Chemicals), kurių sertifikuotos vertės buvo 1011,5 ± 4,5 mg/l Cr, 1016,6 ± 5,0 mg/l Cd, 991,3 ± 5,5 mg/l Pb ir 1003,3 ± 4, 7 mg/l Hg.

Remiantis analizės rezultatais, Pb ir Cd PP pakuotėse nebuvo aptikta (18 paveikslas/Figure 18), nes koncentracijos buvo mažesnės už aptikimo ribą. Hg ir Cr buvo aptikta atitinkamai 25 % ir 15 % mėginių (22 lentelė/Table 22). Beveik visose PE pakuotėse (19 paveikslas/Figure 19) Cd, Pb ir Cr koncentracijos buvo mažesnės už aptikimo ribą ir tik atitinkamai 5 %, 10 % ir 15 % mėginių Cd, Pb ir Cr buvo aptikta (23 lentelė/Table 23). Hg buvo aptikta 70 % PE mėginių (24 lentelė/Table 24). 8 % PP/PE kompozitiniuose mėginiuose (20 paveikslas/Figure 20) aptiktos Pb ir Cd koncentracijos viršijo aptikimo ribą, o 25 % mėginių buvo aptikta Hg ir Cr (25 lentelė/Table 25). Mėginių, kuriuose būtų identifikuoti daugiau nei du metalai, nebuvo ir tik atitinkamai 6 PE, 2 PP ir 2 PP/PE kompozitiniuose mėginiuose tame pačiame mėginyje buvo nustatyti du metalai (26 lentelė/Table 26). Be to, visuose mėginiuose, kuriuose buvo nustatyti 2 metalai, buvo aptikta Hg.

Remiantis 1994 m. gruodžio 20 d. Europos Parlamento ir Tarybos direktyva 94/62/EB dėl pakuočių ir pakuočių atliekų, Cd, Pb, Cr ir Hg koncentracija pakuotėse arba pakuotės komponentuose neturi viršyti 100 mg/kg svorio [73]. Nebuvo tokių tirtų mėginių, kuriuose Cd, Pb, Cr ir Hg koncentracijos lygių suma viršytų 100 mg/kg svorio.

6.4. Ekstrakcijos ir specifinės migracijos tyrimai

Irganox 1010 ir Irgafos 168-ox matavimams buvo naudojama didelio efektyvumo skysčių chromatografijos – masių spektrometrijos sistema (LCMS-8040, Shimadzu). Buvo naudojami Shimadzu LC-40Dxs tirpiklio tiekimo modulis, Shimadzu SIL-40Cxs automatinė mėginių paėmimo sistema ir Shimadzu CTO-40S kolonėlės krosnelė, o visos operacijos atliekamos LabSolutions programine įranga. 1 µl mėginio tirpalo tūris buvo įšvirkščiamas į EC 100/2 Nucleoshell Biphenyl kolonėlę (2 x 100 mm, 2,7 µm), kuri buvo laikoma 60 °C. Mobiliąją fazę sudarė trys eliuentai: A (85 % metanolis), B (10 % acetonitrilas) ir C (5 % 5 mM skruzdžių rūgšties ir 5 mM amonio formiato). Judančios fazės srautas – 0,6 ml/min. Detekcijai buvo naudojamas Shimadzu LCMS-8040 masės spektrometras. Programinė įranga automatiškai atlieka metodo optimizavimą, kurį sudaro pirmtakų jonų, produkto jonų ir susidūrimo energijos aptikimas. Buvo naudojamas teigiamas ESI jonizacijos režimas. Purškimo dujų srautas – 2,0 l/min., džiovinimo dujų srautas 15,0 l/min., o desolvatavimo linijos temperatūra palaikoma 250 °C. Buvo naudojamas kelių reakcijų stebėjimo (MRM) aptikimo režimas. Irganox 1010 ir Irgafos 168-ox masių spektrometriniai parametrai pateikti 11 lentelėje (Table 11). Antioksidantų Irgafos 168-ox ir Irganox 1010 jonų chromatogramos parodytos atitinkamai 10 ir 11 paveiksluose (Figure 10, Figure 11). Metodo validavimui metanolio ir tetrahidrofurano (75:25, % v/v) tirpale ruošti mišrūs etaloniniai tirpalai, kurių koncentracija yra 1, 5, 25, 50 ir 75 ng/ml. Irgafos 168 buvo aptiktas oksiduota forma (Irgafos 168-ox), kadangi po 24 valandų THF Irgafos 168 pilnai oksiduojasi [76, 136]. Norint nustatyti Irganox 1010 ir Irgafos 168-ox kiekį polietileno pakuotėse, buvo sukurtas ir validuotas namudinis analitinis metodas ir nustatytos pagrindinės metodo veikimo charakteristikos, tokios kaip tiesiškumas, vidutinis atkuriamumas, pakartojamumas, teisingumas, kiekybinio nustatymo riba, aptikimo riba ir neapibrėžtis (12 lentelė/Table 12).

Pb, Cd ir Cr PE pakuotėse analizei buvo naudojamas Perkin Elmer NexION 2000 induktyviai susietos plazmos masės spektrometras. Pagrindinės instrumentinės darbo sąlygos elementams nustatyti yra šios:

purkštuvas – Meinhard plus koncentrinis; purškimo kamera - ciklonin ė; plazminis RF generatorius – Dažnis: 10 MHz, Galia 1200 W; plazmos Ar srauto greitis (l/min) – Plazma: 15, pagalbinis: 1,2, purkštuvas: 1; plazmos tirpalo įsisavinimo greitis – 0,2 ml/min.; sąsajos mėginių ėmimo kūgis – Nikelis, i.d.: 1,1 mm; sąsaja Skimmer Nickel, i.d.: 0,9 mm; hiper skimeris – aliuminis; vakuumas – sąsaja:4 torr, kvadrupolis: 2 105 torr; duomenų gavimas – didžiausias šuolis, pakartojimo laikas 500 ms, išlikimo laikas 25 ms, nuskaitymas/nuskaitymas 20, rodmenys/pakartojimas 3, pakartojimų skaičius 3; analitinės masės – (52+53)Cr, (111+112+113+114+110)Cd, (206+207+208)Pb. Analitiniai namudiniai metodai buvo sukurti ir validuoti, įvertintos pagrindinės metodo veikimo charakteristikos, tokios kaip tiesiškumas, vidutinis atkuriamumas, pakartojamumas, teisingumas, kiekybinio nustatymo riba ir aptikimo riba (13 lentelė/Table 13). Metodo validavimui buvo naudojamos sertifikuotos pamatinės medžiagos (VWR Chemicals), kurių sertifikuotos vertės 1011,5 ± 4,5 mg/l Cr, 1016,6 ± 5,0 mg/l Cd ir 991,3 ± 5,5 mg/l Pb.

6.4.1. Antioksidantų ekstrakcijos tyrimai

Antioksidantų ekstrahavimo eksperimentams buvo pasirinktos 23 skirtingos maisto pakavimui naudojamos pakuotės, pagamintos iš PE. Mėginiai buvo sukarpyti mažais maždaug 0,1 g gabalėliais ir ištirpinti 5 ml tolueno ekstrahuojant ultragarsu 10, 20, 30 ir 40 minučių 60 ºC temperatūroje. Po ultragarsinio ekstrahavimo įpilta 20 ml metanolio, kad nusėstų plastikas ir tolueno ir metanolio tirpale būtų išskirti tik į plastikus pridėti priedai. Mėginių supernatantai buvo filtruojami naudojant 0,45 μm nailono membraninius filtrus. Analizė atlikta LC-MS/MS metodu.

Irgafos 168-ox identifikuotas visuose tirtuose mėginiuose. Kaip parodyta 27 lentelėje (Table 27), 52 % mėginių (12 mėginių) išekstrahuota koncentracija neviršijo 1 mg/dm^2 (lentelėje pažymėta žalia spalva), 39 % mėginių (9 mėginiai) išekstrahuota koncentracija buvo nuo 1 iki 2 mg/dm^2 (lentelėje pažymėta geltona spalva), o 9 % mėginių (2 mėginiai) išekstrahuota koncentracija viršijo 2 mg/dm^2 (lentelėje pažymėta raudona spalva). Irgafos 168-ox ekstrahavimo tyrimai buvo atlikti 10, 20, 30 ir 40 minučių ekstrahuojant keturis paralelinius mėginius (21 paveikslas/Figure 21). Koncentracijų skirtumų rezultatai, gauti per kiekvieną ekstrahavimo trukmę, parodė, kad optimalus ultragarso ekstrahavimo laikas yra 30 min., nes po 40 min ekstrahavimo gautos koncentracijos skyrėsi neapibrėžties ribose, t.y. po 40 min ekstrakcijos padidėjo nežymiai.

Irganox 1010 dažnai naudojamas kartu su Irgafos 168, siekiant padidinti plastikinių gaminių antioksidacinį pajėgumą [146]. Atliekant matavimus, Irganox 1010 nebuvo identifikuotas tik 1 mėginyje (mėginys Nr. 23), kuriame išmatuota koncentracija buvo mažesnė už kiekybinio nustatymo ribą (28 lentelė / Table 28). Be to, tolesnė analizė parodė, kad likusiuose 22 PE mėginiuose buvo aptikta ir Irgafos 168-ox, ir Irganox 1010. Išmatuotos Irganox 1010 koncentracijos pateiktos 22 lentelėje (Table 22). 61 % mėginių (14 mėginių) išekstrahuota koncentracija neviršijo 0,1 mg/dm^2 (lentelėje pažymėta žalia spalva), 26 % mėginių (6 mėginiai) koncentracija buvo tarp 0,1 ir 0,3 mg/dm^2 (lentelėje pažymėta geltona spalva), o trijuose mėginiuose išekstrahuota koncentracija buvo didesnė nei 0,3 mg/dm^2 (lentelėje pažymėta raudona spalva), ir tik viename mėginyje išekstrahuota Irganox 1010 koncentracija buvo 1,3329 ± 0,1800 mg/dm^2 (mėginys Nr. 1). Tokie pat ekstrahavimo eksperimentai, kaip ir su Irgafos 168-ox, buvo atlikti naudojant Irganox 1010, ekstrahuojant 10, 20, 30 ir 40 min. 22 paveiksle (Figure 22) matoma aiški Irganox 1010 koncentracijos reikšmingo padidėjimo po 30 min. tendencija. Panašiai, kaip ir atliekant Irgafos 168-ox ekstrakcijos eksperimentus, optimalus 30 min. ultragarso ekstrahavimo laikas buvo nustatytas ir Irganox 1010, nes po 40 min ekstrahavimo gautos koncentracijos reikšmingai nepadidėjo.

Tolesnė analizė parodė, kad 52 % mėginių (12 mėginių) Irgafos 168-ox ir Irganox 1010 koncentracijų santykis buvo 9:1, o tai rodo daug didesnę Irgafos 168-ox frakciją. Maždaug trečdalį mėginių (7 mėginiai) sudarė 10 –30 % Irganox 1010 ir 70 – 90 % Irgafos 168-ox. Viename mėginyje (mėginys Nr. 1) 67 % kompozicijos sudarė Irganox 1010, o 13 % mėginių (3 mėginiai) didesnis Irganox 1010 kiekis lyginant su Irgafos 168-ox.

Deja, nebuvo pastebėta aiški koreliacija tarp Irgafos 168-ox arba Irganox 1010 identifikuotos koncentracijos diapazono ir numatytos gaminių paskirties ir jų išvaizdos. Iš to būtų galima daryti išvadą, kad antioksidantų kiekis nepriklauso nuo produkto išvaizdos – formos ar spalvos.

6.4.2. Specifinės migracijos tyrimai

Antioksidantų specifinės migracijos tyrimams buvo naudojami tie patys 23 PE maisto pakavimui skirti gaminiai kaip ir antioksidantų ekstrakcijos eksperimentams. Mėginiai buvo veikiami skirtingais maistiniais modeliniais tirpalais – 3 % acto rūgštimi, 95 % etanoliu ir izooktanu, nes jie imituoja skirtingus maisto produktus (3 lentelė / Table 3), kaip nurodyta Komisijos reglamente (ES) Nr. 10/2011 [56]. Metalų kiekiui nustatyti buvo naudojamas

3 % acto rūgšties maistinis modelinis tirpalas [56]. Prieš analizę nė vienas mėginys nebuvo naudojamas maisto pakavimui.

Specifinės migracijos į 3 % acto rūgštį sąlygos buvo 10 dienų 60 °C temperatūroje, į 95 % etanolį – 2 dienos 20 °C temperatūroje ir į izooktaną 10 dienų 40 °C temperatūroje. Pagal Komisijos reglamentą (ES) Nr. 10/2011 [56] 10 dienų bandymai 60 °C temperatūroje apima ilgalaikį laikymą ilgiau nei 6 mėnesius kambario temperatūroje ir žemesnėje temperatūroje, įskaitant kaitinimą iki 70 °C iki 2 valandų arba kaitinimą iki 100 °C iki 15 minučių [56]. Atliekant migracijos į izooktaną tyrimus, nuspręsta naudoti 20 °C temperatūros 2 dienų migracijos bandymų sąlygas, o į 95 % etanolį 40 °C temperatūros 10 dienų sąlygas, kadangi tai yra standartinės sąlygos, norint 95 % etanolio tirpalą laikyti kaip augalinio aliejaus pakaitalą (maisto modelinis tirpalas D2).

Visi mėginiai prieš bandymus buvo supjaustyti kvadratiniais gabalėliais (1 dm^2; 10 × 10 cm), lituojami maišelio pavidalu, pripildomi 100 ml maistinio modelinio tirpalo ir laikomi reikiamomis sąlygomis.

Antioksidantų specifinės migracijos analizė atlikta LC-MS/MS, o metalų migracija ICP-MS metodu.

6.4.2.1. Antioksidantų specifinės migracijos tyrimai

Irgafos 168-ox laikui bėgant hidrolizuojamas vandens pagrindu veikiančioje migracijos sistemoje iki 2,4-ditret-butilfenolio ir bis(2,4-ditert-butilfenil) vandenilio fosfato skilimo produktų [147]. Todėl atliekant migracijos eksperimentus su 3% acto rūgštimi 60 ºC temperatūroje 10 dienų Irgafos 168-ox migracija nebuvo aptikta. Be to, ankstesniuose moksliniuose tyrimuose traktuojama, kad Irgafos 168 iš maisto pakuočių migruoja į aliejines modelines terpes, todėl buvo nuspręsta atlikti migracijos tyrimus su augalinio aliejaus pakaitalais – 95 % etanoliu ir izooktanu [39, 136, 147]. Kaip ir tikėtąsi, skirtingai nei Irgafos 168-ox migracija į 3 % acto rūgštį, visuose tirtuose mėginiuose migracija į izooktaną (29 lentelė/Table 29) ir į 95 % etanolį (30 lentelė/Table 30) vyko. Rezultatai buvo skaičiuojami remiantis konversija, kad 1 kg maisto supakuota su 6 dm^2 su maistu besiliečiančios medžiagos [56].

Atsižvelgiant į tai, kad pagal Komisijos reglamentą (ES) Nr. 10/2011 Irgafos 168 arba Irgafos 168-ox specifinės išsiskyrimo ribos (normos) nenustatytos, taikoma bendroji specifinė išsiskyrimo riba – 60 mg/kg [56]. Iš 23 ir 24 lentelių (Table 23 and 24) duomenų matyti, kad mėginių, iš kurių

migracijos lygis viršytų 60 mg/kg, nebuvo. Svarbu ir tai, kad migracijos koncentracijos buvo žymiai mažesnės už 60 mg/kg ribą.

52 % mėginių (12 mėginių) Irgafos 168-ox migracijos į izooktaną lygiai neviršijo 1 mg/kg (lentelėje pažymėta žalia spalva), o 39 % mėginių (9 mėginiai) migracijos į izooktaną lygiai neviršijo 2 mg/kg (lentelėje pažymėta geltona spalva). Tik dviejuose mėginiuose (3 ir 20 mėginiai) Irgafos 168-ox migracijos lygis siekė atitinkamai 3,1216 ± 0,3152 mg/kg ir 4,0596 ± 0,4100 mg/kg (lentelėje pažymėta raudona spalva).

Vertinant Irgafos 168-ox migracijos į 95 % etanolį rezultatus paaiškėjo, kad nebuvo mėginių, kuriuose migracijos lygis viršytų 1 mg/kg (24 lentelė/Table 24). Iš mėginių į maistinius modelinius tirpalus išmigravusio Irgafos 168-ox procentiniai kiekiai pateikti 31 ir 32 lentelėse (Table 31 and 32). Galima pastebėti, kad iš 43 % mėginių (10 mėginių) mažiau nei 10 % Irgafos 168-ox išmigravo į izooktaną (lentelėje pažymėta geltona spalva), iš 35 % mėginių (8 mėginiai) 10 – 50 % migravo į izooktaną (lentelėje pažymėta žalia spalva), o iš 22 % mėginių (5 mėginiai) daugiau nei 50 % priedo išmigravo į izooktaną (lentelėje pažymėta raudona spalva) (31 lentelė).

Vertinant migracijos į 95 % etanolį (32 lentelė / Table 32) rezultatus, iš 65 % mėginių (15 mėginių) mažiau nei 10 % Irgafos 168-ox išmigravo į 95 % etanolį (lentelėje pažymėta žalia spalva), o iš 26 % mėginių (6 mėginiai), 10 – 20 % (lentelėje pažymėta geltona spalva). Buvo du mėginiai, iš kurių 36,7 % (mėginys Nr. 4) ir 40 % (mėginys Nr. 21) priedo išmigravo į maistinį modelinį tirpalą (lentelėje pažymėta raudona spalva).

Gauti rezultatai rodo, kad Irgafos 168-ox migracija į izooktaną yra didesnė nei į 95 % etanolį, nes iš 22 % mėginių apie 50 % pridėto Irgafos 168-ox išmigravo į izooktaną ir tik iš 2 mėginių (9 %) pridėto Irgafos 168-ox migracija buvo didesnė nei 35 %. Be to, iš duomenų, pateiktų 23 paveiksle (kairėje) (Figure 23, left), matome, kad migracija į izooktaną daugeliu atvejų buvo didesnė nei į 95 % etanolį. Deja, nebuvo galimybių atlikti migracijos tyrimų su augaliniu aliejumi (maisto modeliniu tirpalu D2), todėl negalima daryti išvados, kad izooktanas geriau reprezentuoja augalinį aliejų nei 95 % etanolis. Tačiau, atsižvelgiant į tai, kad iš 72 % mėginių (18 mėginių), Irgafos 168-ox migracija į izooktaną yra didesnė nei į 95 % etanolį, akivaizdu, kad izooktanas yra agresyvesnis maistinis modelinis tirpalas nei 95 % etanolis.

Skirtingai nei Irgafos 168-ox, Irganox 1010 migracija į 3% acto rūgšties vyko, tačiau koncentracijos buvo mažesnės už metodo kiekybinę nustatymo ribą. Nuspręsta atlikti Irgafos 168-ox migracijos tyrimus į 95 % etanolį ir izooktaną, Rezultatai buvo skaičiuojami remiantis konversija, kad 1 kg maisto supakuota su 6 dm^2 su maistu besiliečiančios medžiagos [56].

Kaip ir Irgafos 168-ox atveju, vadovaujantis Komisijos reglamentu (ES) Nr. 10/2011 Irganox 1010 specifinės išsiskyrimo ribos nenustatytos, todėl taikoma bendroji specifinė išsiskyrimo riba – 60 mg/kg [56]. Lyginant Irgafos 168-ox ir Irganox 1010, Irganox 1010 migracijos koncentracijos identifikuotos mažesnės nei Irgafos 168-ox ir žymiai mažesnės už 60 mg/kg ribą. Iš 33 ir 34 lentelių (Table 33, Table 34) duomenų matyti, kad 22 % mėginių (5 mėginiai) ir 35 % mėginių (8 mėginiai) migracijos lygis neviršijo 0,01 mg/kg (lentelėje pažymėta žalia spalva) į izooktaną ir į 95 % etanolį. 52 % mėginių (12 mėginių) Irganox 1010 migracijos lygis buvo nuo 0,01 iki 0,1 mg/kg (lentelėje pažymėta geltona spalva) ir į izooktaną, ir į 95 % etanolį, o 26 % mėginių (6 mėginiai) ir 13 % mėginių (3 mėginiai) migracijos lygis atitinkamai viršijo 0,1 mg/kg (lentelėje pažymėta raudona spalva) atitinkamai į izooktaną ir į 95 % etanolį, tačiau nebuvo mėginių, kurių migracijos lygis į izooktaną arba 95 % etanolį viršytų 0,2 mg/kg.

Iš mėginių į maistinius modelinius tirpalus migruojančių Irganox 1010 procentinio kiekio rezultatai pateikti 35 ir 36 lentelėse (Table 35 and 36). Iš 35 lentelės (Table 35) matyti, kad iš 36 % mėginių (8 mėginiai) mažiau nei 10 % Irganox 1010 migravo į izooktaną (lentelėje pažymėta žalia spalva), iš 41 % mėginių (9 mėginiai) 10 – 50 % priedo migravo į izooktaną (lentelėje pažymėta geltona spalva), iš 23 % mėginių (5 mėginiai) daugiau kaip 50 % priedo migravo į izooktaną (lentelėje pažymėta raudona spalva).

Vertinant Irganox 1010 migraciją į 95 % etanolį, iš 65 % mėginių (15 mėginių) mažiau nei 10 % migravo į 95 % etanolį (lentelėje pažymėta žalia spalva), iš 18 % mėginių (4 mėginiai) 10 – 50 % priedo migravo į 95 % etanolį (lentelėje pažymėta geltona spalva) ir iš 14 % mėginių (3 mėginiai) daugiau kaip 50 % priedo migravo į 95 % etanolio (lentelėje pažymėta raudona spalva) (36 lentelė/Table 36).

Kaip ir Irgafos 168-ox atveju, rezultatai rodo, kad Irganox 1010 migracija į izooktaną yra didesnė nei į 95 % etanolį, kadangi iš 23 % mėginių daugiau nei 50 % pridėto Irganox 1010 migravo į izooktaną ir tik iš 14 % mėginių daugiau nei 50 % Irganox 1010 migravo į 95 % etanolį. Lyginant Irgafos 168-ox ir Irganox 1010 migracijos procentinį kiekį, Irganox 1010 migracijos kiekiai yra didesni, nes vidutinis Irgafos 168-ox migracijos į izooktaną kiekis yra 27 % ir 9 % į 95 % etanolį, o Irganox 1010 migracija yra atitinkamai 29 % ir 15 %. Nors Irganox 1010 molekulinė masė yra didesnė nei Irgafos 168 ir dėl struktūros Irganox 1010 molekulė užima didesnį matricos tūrį, Irganox 1010 linkęs migruoti daugiau nei Irgafos 168-ox. Taip gali būti dėl to, kad ekstrahuojant polietilenas pradeda irti ir dėl to pradeda veikti antrinis antioksidantas (Irgafos 168). Dėl to matricoje sumažėja Irgafos 168

kiekis. Deja, nebuvo pastebėta jokios koreliacijos tarp produkto išvaizdos – formos ar spalvos.

Taip pat, remiantis 23 paveiksle (dešinėje) (Figure 23 (right)) pateiktais duomenimis, taip pat kaip ir Irgafos 168-ox atveju, Irganox 1010 migracija į izooktaną 74 % mėginių yra didesnė nei į 95 % etanolį. Tai leidžia daryti tą pačią išvadą, kaip ir Irgafos 168-ox atveju, kad izooktanas yra agresyvesnis maistinis modelinis tirpalas nei 95 % etanolis.

6.4.2.2. Metalų specifinės migracijos tyrimai

Remiantis analizės rezultatais, tik dvejuose PE mėginiuose Pb ir Cr ir 14 mėginių Cd neaptikta (24 paveikslas/Figure 24), nes koncentracijos buvo mažesnės už metodo aptikimo ribą. Be to, buvo tik 2 mėginiai (gaminiai Nr. 2 ir 17), kuriuose nebuvo identifikuotas nė vienas metalas. Taip pat buvo tik vienas mėginys (gaminys Nr. 11), kuriame specifinė Pb migracija reikšmingai skyrėsi nuo kitų mėginių. Kadangi šių trijų aukščiau minėtų pakuočių išvaizda reikšmingai nesiskyrė nuo kitų, aiškios koreliacijos tarp Pb, Cr ir Cd koncentracijų ir numatytos gaminių naudojimo paskirties nepastebėta. Iš to būtų galima daryti išvadą, kad metalų, kaip ir antioksidantų, kiekis nepriklauso nuo gaminio išvaizdos – formos ar spalvos.

Kaip nurodyta Komisijos reglamente (ES) Nr. 10/2011, Cd, Pb ir Cr išsiskyrimas iš su maistu besiliečiančių medžiagų į maistinius modelinius tirpalus turi būti neaptinkamas, apibrėžiant metodo aptikimo ribą 0,01 mg/kg Pb, Cr ir 0,002 mg/kg Cd [56]. Remiantis 37 lentelėje (Table 37) pateiktais duomenimis, nebuvo mėginių, kuriuose specifinė metalų migracija būtų didesnė nei 0,01 ir 0,002 mg/kg atitinkamai Pb, Cr ir Cd.

Net ir turint omenyje, kad PE mėginiai, kurie buvo tirti ekstrahavimo ir migracijos eksperimentų metu, buvo skirtingi, lyginant Pb, Cr ir Cd migracijos iš PE mėginių ekstrakciją (23 lentelė/Table 23) ir specifinę migraciją (37 lentelė/Table 37), pastebima aiški tendencija, kad ekstrahuojant identifikuojamos metalų koncentracijos yra didesnės tūkstančiais. Taip pat, lyginant specifinės migracijos rezultatus su Komisijos reglamente (ES) Nr. 10/2011 [56] nustatytomis išsiskyrimo ribomis, yra didelė tikimybė, kad į galutinį maisto produktą, ir į maistą, migruoja tik nedidelis kiekis (< 0,001 %) pridėtų metalų.

7. IŠVADOS

1. Bendroji migracija iš PP pakuočių į maistinius modelinius tirpalus yra didesnė nei iš PE ir tai patvirtina, kad norint įvertinti galimą riziką, susijusią su plastiko priedų migracija į maistinius modelinius tirpalus, taip pat ir į maistą, reikalingi migracijos tyrimai.

2. Sukurtas terminės desorbcijos su dujų chromatografija – masių spektrometrija (TD-GC/MS) metodas pasirodė esąs labai efektyvus atliekant netikslinę plastiko mėginių analizę, nustatant migruojančius cheminius junginius ir pačio plastiko skilimo produktus PE ir PP mėginiuose, gauti rezultatai rodo, kad iš PE, PP ir PP/PE kompozitinių mėginių migruoja skirtingi migrantai.

3. Analizė, atlikta sukurtu ir validuotu atominės absorbcijos spektrofotometrijos (AAS) metodu parodė, kad plastikuose buvo Cr, Cd, Hg ir Pb, tačiau jų masės koncentracija PE, PP ir PP/PE sudėtiniuose plastiko mėginiuose neviršija 100 mg/kg.

4. Sukurtas ir validuotas skysčių chromatografijos su tandeminės masės spektrometrija (LC-MS/MS) metodas tinkamas Irgafos 168-ox ir Irganox 1010 antioksidantų ekstrakcijos iš su maistu besiliečiančių gaminių ir specifinės migracijos į maisto modelinius tirpalus tyrimams. Gauti rezultatai rodo, kad tiek Irgafos 168, tiek Irganox 1010 yra pridedami į polimero matricą ir gali migruoti į maistinius modelinius tirpalus, o tuo pačiu ir į maistą.

5. Sukurtas ir validuotas induktyviai susietos plazmos masės spektrometrijos (ICP-MS) metodas tinka kadmio, chromo ir švino kiekiui su maistu besiliečiančiose medžiagose nustatyti. Analizė rodo, kad yra didelė tikimybė, kad tik nedidelis metalų kiekis, pridėtas gamybos metu į su maistu besiliečiančias medžiagas, gali migruoti į maistą.

6. Lyginant antioksidantų bendrosios ir specifinės migracijos rezultatus, aišku, kad PE, PP ir PP/PE kompozitiniai plastikai gali būti nesaugūs riebių maisto produktų pakavimui, nes migracija į maistinį modelinį tirpalą izooktaną, kuris imituoja riebaus maisto matricą, yra didesnė nei į bet kurį kitą maistinį modelinį tirpalą, o tai reiškia, ir į maistą.

7. Nors tirtų mėginių, viršijančių įvairiuose reglamentuose nustatytas ribas (laikomų saugiais vartotojui) nebuvo tiek daug, reikia atkreipti dėmesį, kiek skirtingų migrantų vienu metu migruoja į maistą ir kurių sumos pasekmės žmonių sveikatai kol kas nėra aiškios.

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Relevant work experience	
2024 - present	**Head of the Chemical Testing Department** **Chief specialist of the Quality Management Department**
	Also: • International project lead in Lithuania – PARC. • National representative at EURL-FCM JRC. • National representative at EDQM. • National project coordinator "Improving chemical threat management". • National project coordinator "Development and implementation of a biological monitoring model".
2021 – 2024	**Deputy Head of the Chemical Testing Department and Chief specialist of the Quality Management Department**
	Also: • International project lead in Lithuania – PARC. • National representative at EURL-FCM JRC. • National representative at EDQM.

	• National project coordinator “Improving chemical threat management”. • National project coordinator “Development and implementation of a biological monitoring model”.
2021 – 2024	**Analytical methods validation lead** at RDA SPOT
2017 - 2021	**Head of Instrumental Testing subdepartment of Chemical Testing department**
	Also: • International project lead in Lithuania - HBM4EU and JATC. • National project participant “Žmogaus biologinės stebėsenos Mechanizmo kūrimas Lietuvoje”. • National representative at EURL-FCM JRC.
2013 – 2017	**Chemist at the Instrumental testing subdepartment of the Chemistry department in the National Public Health Surveillance Laboratory**
	• HPLC-UV/DAD/FL, IES, GC-FID, GC-ECD, GC/MS chromatography expert and method developer: (food, food contact materials, cosmetics, water, building materials, air, plastics, etc.) • Auditor. Well-acquainted with various document management and quality assurance procedures. Experience in the development and implementation of various procedures according to higher quality assurance institutions like Eurachem, Nordtest, and others. • One of few client consultants for chemical processes and possible analysis methods for industrial and other types of samples.
Additional skills: Experienced operator of Shimadzu software for chromatography. Proficiency in applying and adapting various external legislations, standards, and other documents in working practice, such as ISO/IEC 17025, 15189. Driver’s license (B category).	

PUBLICATIONS

1. Petrulionienė Toma, Murauskas Tomas, Norkus Mantas, Naujalis Evaldas. Emission of additives and degradation products from commercial polypropylene, polyethylene, and their composite packages. Chemija, 34(2), 99–111 (2023) https://doi.org/10.6001/chemija.2023.34.2.4.

2. Petrulionienė Toma, Murauskas Tomas, Naujalis Evaldas. Validation and Application of an LC–MS/MS Method for the Determination of Antioxidants Originating from Commercial Polyethylene Packages and their Migration into Food Simulants. Food Analytical methods (2024) https://doi.org/10.1007/s12161-024-02631-8.

CONFERENCES ATTENDED

1. Toma Petrulionienė, Mantas Norkus (2024). Verification of the method for overall migration from food contact materials to food simulants. Eurachem 2024: Quality Assurance in Chemical, Medical and Microbiological Laboratories, May 13 – 14, 2024, Vilnius. Poster presentation at international conference (Vilnius).

2. Petrulionienė, Toma, Murauskas Tomas (2024). Antioxidant content of food packages made from polyethylene. Open readings 2024: 67th international conference for students of physics and natural sciences, April 23-23, 2024, Vilnius, Lithuania: abstract book. Vilnius: Vilnius University, 2024. Poster presentation at international conference (Vilnius).

3. Toma Petrulionienė, Tomas Murauskas (2024). Determination of potential migrants in food contact polyethylene. Chemija ir geomokslai, March 22, 2024, Vilnius, Lithuania: abstract book. Vilnius: Vilnius University, eISSN: 3030-0312, p. 74. Poster presentation at national conference (Vilnius).
https://www.chgf.vu.lt/files/doc/chemija_ir_geomokslai_2024_tezes.pdf

4. Petrulionienė, Toma, Grakauskaitė, Grėta, & Naujalis, Evaldas. (2019). Overall and specific migration from commercial polyethylene

packages. Open readings 2019: 62nd international conference for students of physics and natural sciences, March 19-22, 2019, Vilnius, Lithuania: abstract book. Vilnius: Vilnius University, 2019. P1-74, p. 152. Poster presentation at international conference (Vilnius).
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5. Petrulionienė, Toma, & Naujalis, Evaldas. (2018). Migration of additives from commercial polypropylene packages. Open readings 2018: 61st international conference for students of physics and natural sciences, March 20-23, 2018, Vilnius, Lithuania: program and abstracts. Vilnius: [s.n.]. 2018. p. 275. Poster presentation at international conference (Vilnius).
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6. Toma Petrulionienė, Evaldas Naujalis. Polietileno ir polipropileno gaminių specifinės migracijos tyrimai. 8-toji Doktorantų ir jaunųjų mokslininkų konferencija FizTech 2018. Presentation at a local conference (Vilnius).

7. Toma Petrulionienė, Evaldas Naujalis. Specifinės migracijos iš polipropileno tyrimas, naudojant dujų chromatografiją. 7-toji Doktorantų ir jaunųjų mokslininkų konferencija FizTech 2017. Presentation at local conference (Vilnius).

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