FOOD PACKING – PROBLEMS AND PERSPECTIVES

AMBALAJUL ALIMENTAR – PROBLEME ŞI PERSPECTIVE

Iurie SUBOTIN
Technical University of Moldova
E-mail: iurie.subotin@ftmia.utm.md
ORCID ID: 0000-0002-5570-4713

Artur MACARI
Technical University of Moldova
E-mail: artur.macari@fta.utm.md
ORCID ID: 0000-0003-4163-3771

Raisa DRUŢĂ
Technical University of Moldova
E-mail: raisa.druta@ftmia.utm.md
ORCID ID: 0000-0001-5301-6055

Abstract: *In this paper, the importance of using harmless food packaging, a current problem for the food industry, was analyzed. The regulatory acts of the European Union and their concordance with the national legislation were analyzed. The most important classes of pollutants of food products, detected in food following their migration from the packaging, were analyzed. The necessary instrumental methods were selected for the determination of these compounds both in the food product and in the packaging. The importance of using gas and liquid chromatography, frequently coupled with MS detectors, was highlighted.*

Keywords: *food packaging, contaminants, legislative framework, chromatography*

Rezumat: *În această lucrare a fost analizată importanţa utilizării ambalajelor alimentare inofensive, problemă actuală pentru industria alimentară. Au fost analizate actele reglementatorii ale Uniunii Europene şi concordanţa acestora cu legislaţia naţională. S-au analizat cele mai importante clasele de poluanţi ale produselor alimentare, depistate în alimente în urma migrării acesora din ambalaj. Au fost selectate metodele instrumentale necesare pentru determinarea acestor compuşilor atât în produsul alimentar, cât şi în ambalaj. S-a evidenţiat importanţa utilizării cromatografiei gazoase şi lichide, frecvent cuplate cu detectoare MS.*

Cuvinte cheie:: *ambalajul alimentar, contaminanţi, cadrul legislativ, cromatografia*

Introduction

Packaging, especially for food, is of continuing global interest, with a focus on ensuring the ecological appearance, biodegradability and harmlessness of food. Under the notion of materials, which come into contact with food, various types of materials can be identified, for example, all types of packaging, various containers, equipment, etc. Food packaging is designed to achieve several purposes, such as protecting food from external sources of contamination, convenience of transportation and storage, and of course informing consumers [1, 2]. Food safety is caused by several factors, one of which is caused by the migration of harmful chemicals from packaging materials into food, and as a result adversely affects the health of consumers [3].

In this context, there is a clear need for national and international regulations applicable to all food contact materials. Within the European legislative framework, regulations are implemented through a series of normative acts, such as Regulation (EU) no. Commission Regulation (EC) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food [4]. The Regulation classifies the materials applied for packaging, the manner in which they are placed on the market, the list of authorized substances, the specific requirements and restrictions on the substances applied, the conformity assessment rules, etc.

Discussions

In the Republic of Moldova, the provisions of the various normative acts regulating the European Union regarding the possible damage to food packaging products have been reflected in a number of laws and Government decisions:

• Law no. 306 of 30-11-2018 on food safety [5];

• Law no. 115 of 09.06.2005 regarding the ecological agri-food production [6];

• Law no. 422 of 22.12.2006 on general product safety [7];

• Law no. 235 of 01.12.2011 on accreditation and conformity assessment activities [8];

• GD no. 473 of 03-07-2012 for the approval of the Technical Regulation “Beer and beer-based beverages [9];

• GD for the approval of the Sanitary Regulation regarding the materials and objects destined to come into contact with the food products no. 308 of 29.04.2011 (in force 06.06.2011) Official Gazette no.74-77 art.352 of 06.05.2011 [10];

• GD for the approval of the Sanitary Regulation on active and intelligent materials and objects intended to come into contact with food products no. 945 din 03.10.2018 [11];

• GD for the approval of the Sanitary Regulation regarding the materials and objects that contain the vinyl chloride monomer and that come in contact with food products no. 580 of 20.07.2017 [12];

• GD for the approval of the Sanitary Regulation on limiting the use of certain epoxy derivatives in materials and objects intended to come into contact with food products no. 548 of 11.07.2017 [13];

• GD for the approval of the Sanitary Regulation regarding the materials and objects made of regenerated cellulose foil that come in contact with food products no. 493 of 30.06.2017 [14];

• GD for the approval of the Sanitary Regulation regarding the ceramic, glass, porcelain, faience, enameled and vitrified objects that come in contact with food products no. 493 of 11.08.2015 [15];

• GD for the approval of the Sanitary Regulation on recycled plastic materials and objects intended to come into contact with food products no. 492 of 11.08.2015 [16];

• GD for the approval of the Sanitary Regulation regarding the good manufacturing practice of the materials and of the objects destined to come in contact with the food products no. 594 of 17.07.2014 [17].

In accordance with the Sanitary Regulation on plastic materials and articles intended to come into contact with foodstuffs, which implements the provisions of Regulation (EU) no. 10/2011 of the European Commission of 14 January 2011 [10], the specific requirements for the manufacture and placing on the market of plastic materials and articles are proposed:

o Intended to come into contact with food;

o Who are already in contact with food;

o Which may reasonably come into contact with food.

Food packaging materials are categorized according to the material, structure, composition of the packaging:

o Materials, articles and parts thereof made exclusively of plastics;

o Materials and articles consisting of several layers of plastic bonded with adhesives or by other means;

o Layers of plastic and plastic coverings forming cover fittings and fasteners which, together with the respective covers and fasteners, form a set of two or more layers of different types of materials;

o Plastic layers in multimaterial multilayer materials and objects.

It is also identified:

o A list of prohibited packaging materials, such as rubber, silicone, resins, etc.

o A list of permitted materials in the form of monomers (over 900), additives, etc.

The maximum permissible transfer concentrations of the materials from which the packaging is made (plastic) are set - the limit is mg / kg. For substances without a specific migration limit or other restrictions, a migration limit of 60 mg / kg applies.

It has been established that methods of analysis of compounds made from substances which are not included in the list of substances authorized for food packaging are not acceptable if their degree of detection is limited to 0.01 mg / kg.

To verify compliance, the specific migration values are expressed in mg / kg, applying the actual area / volume ratio in actual or intended use. For the migration value expressed in mg / kg, applying a surface / volume ratio of 6 dm^2 / kg of food are:

o Containers and other articles, containing or intended to contain less than 500 milliliters or grams or more than 10 liters;

o Materials and objects for which, due to their shape, it is impracticable to estimate the relationship between the surface of these materials or objects and the amount of food that comes into contact with them;

o Sheets and films that have not yet come into contact with food;

o Sheets and films containing less than 500 milliliters or grams or more than 10 liters.

To demonstrate the conformity of plastic materials and objects that have not yet come into contact with food, the following food simulants are used: 10% ethanol, 3% acetic acid, 20% ethanol, 50% ethanol, vegetable oil. The allocation of food simulants to the appropriate food products - beverages, pastries, fruits, vegetables, meat products, etc. was also established.

The presence of contaminants in food is caused by the migration of polymerization residues or stabilizers on the surface of the package. The diffusion process is considered to be the main phenomenon that causes the presence of pollutants in food. Quite a number of chemicals can migrate into food - plasticizers, antioxidants, heat stabilizers, lubricants, various solvents (adipic acid, toluene, butan-2-ol, ethyl acetate, hexane) [18-21].

Plasticizers (butyl stearate, acetyl tributyl citrate, etc.) are a group of additives used to make plastics to improve the properties of polymers. The toxic properties of these compounds are usually low, but they have a potential mutagenic effect [18]. The migration of plasticizers into foods with a high fat content is usually essential and increases with increasing temperature [22-24].

Thermal stabilizers as well as plasticizers are present in plastic packaging. Their toxicity is caused by purity, because the residual ethylene oxide has a high toxicity [18].

Antioxidants (BHT and Irganox 1010, commonly used) are applied in order to reduce the oxidation processes in plastics used as packaging. Most antioxidants have a non-toxic effect and satisfactory stabilizing action [18].

Monomers also actively migrate to food as a result of contact with packaging [25, 26]. As an example, styrene, one of the most widely used monomers for food packaging and as a result of migration, is present in food. The daily exposure of styrene is estimated at 15-55 µg / person, and the annual one - 5-20 mg / person, which presents an essential danger, because it has a toxic effect on the liver and nervous system [27, 28].

It should be noted that the analysis of contaminants is performed both in the materials used for packaging [29, 35] and in food [36-44]. The regulations describe different materials that can come into contact with food - glass, ceramic, rubber, plastics, paper, silicone cardboard, wood [4], but in most works prevail research on food contamination with various plastics. The most used synthetic polymers of a synthetic nature are polyvinyl chloride (PVC), polyvinyl acetate (PVA), polyethylene (PE) and polypropylene (PP).

Hundreds of compounds are known to migrate from food contact materials. In this paper we will try to focus on some relevant classes of organic compounds (aromatic amines, bisphenol A, bisphenol A diglyceride ether, photoinitiators of UV-inks, perfluorides, phthalates, etc. whose content can be determined by gas chromatography (GC) and liquid chromatography (CL).

The selection of instrumental techniques depends on the physico-chemical properties of the analyzed compounds and their concentration. Both CG and CL are applied for the analysis of organic contaminants, frequently coupled to MS detectors. CG is the most suitable technique for non-polar and volatile compounds. CL in turn is usually selected for the analysis of polar compounds with lower volatility or thermal stability.

Gas chromatography (GC)

The high efficiency and low cost of phthalate-containing plastics stimulate their widespread use in various systems, including food. Phthalates are compounds that are basically analyzed by gas chromatography. Using GC-MS, the presence of phthalates was detected in oil [38, 45], milk [46], meat [39], beverages [47], wine [40], vegetables [47], etc. Thus, these compounds have been identified both in the food product (eg oil, fruits, vegetables, meat) and in the material with which it comes into contact (paper, cardboard, plastic). The extraction was performed in different ways - acetonitrile, solid-phase microextraction, ultrasound - assisted dispersive liquid-liquid microextraction, headspace solidphase microextraction; detectors used - especially MS; columns - Supelco SPB-5MS (5% polydiphenylsiloxane, 95% polydimethylsiloxane), DB-XLB column (0.25µmx60mmx0.25mm), HP-5MS Agilent column (0.25µmx30mmx0.25mm), DB5 fused-silica capillary column (0.25µm30)) [38, 39, 42, 45].

Analyzing the bibliographic sources, some measures could be proposed that would lead to the avoidance of phthalate contamination [48]:

o Avoidance of plastic consumables;
o Used organic solvents need to be purified;
o All glassware must be cleaned with pure organic solvents (E.g. acetone, hexane) and dried before use;
o All reagents (including water) must be tested to determine the control value;
o Chromatographic system check (E.g. sampling bottle caps).

Bisphenol A was determined in salt, sugar, carton by gas chromatography [49]. In all determinations the same matrix was used - polysilarylene-95% polydimethylsiloxane column and EI ionization source. Simple mass spectrometry quadrupole (MS) was using providing low detection limits, and a LOQ between 0.05-0.064 mg / l in food and packing material was obtained [50].

Liquid Chromatography (LC)

LC-MC as an analysis technique is applied for the determination of perfluorinated compounds, primary aromatic amines and photoinitiators in plastic packaging [29, 31, 34, 51], plastic utensils [30]. Liquid chromatography is used to determine perfluorinated compounds in food - lead [51], poultry eggs [35], phthalates in dairy products [52], beverages [53, 54]. Typically, columns have dimensions of 100-250 mm, with particle sizes 2-5 µm - C18 (2.6µmx100x2.1mm) water 4.7mM perfluropropanoic acid (PPFPA) / 4.7mM PFPA en methanol; C18 (1.7µmx100x2.1mm) water 0.1% formic / methanol 0.1% formic); C18 1.7µmx50x2.1mm) ACN: water / 0.5mM sodium acetate 8.5mM acetic acid [29, 31, 55]. The possibility of efficient use of ultra-high performance liquid chromatography has been identified, due to the rapid separation of the components and the higher resolution [21]. Acetonitrile and methyl alcohol are applied as solvents.

Conclusions

In this paper, the legislative acts of the Republic of Moldova regarding the possible damage of food products with the compounds present in the packaging were analyzed. The need to continuously harmonize and improve the national legislative framework in the field analyzed with the normative acts of the European Union was identified.

The classes of compounds (primary aromatic amines, phthalates, bisphenols and their derivatives, perfluorinated compounds, etc.) that may affect food as a result of contact with the appropriate packaging were analyzed and the importance of harmonization, possible automation of the sample preparation process and of analytical methods for determining contaminants.

Acknowledgments: The research was funded by State Project 20.80009.5107.09 “Improving of food quality and safety through biotechnology and food engineering”, running at Technical University of Moldova.

Bibliography:

1. Muniandy P., Shori A.B., Baba A.S. Influence of green, white and black tea addition on the antioxidant activity of probiotic yogurt during refrigerated storage, Food packaging and shelf life, 8, 2016, p. 1-8.
2. Koutsimanis G., Getter K., Behe B., Harte J., Almenar E. Influences of packaging attributes on consumer purchase decisions for fresh produce, Appetite 59, 2012. p. 270-280.
3. Gallart-Ayala H., Nunez O., Lucci P. Recent advances in LC-MS análisis of food packaging contaminants, Trends in Analytical Chemistry, 42, 2013. p. 99-124.
4. http://eur-lex.europa.eu/legal-content/RO/TXT/PDF/?uri=CELEX:32011R0010&from=RO
5. https://www.legis.md/cautare/getResults?doc_id=122838&lang=ro
6. https://www.legis.md/cautare/getResults?doc_id=115169&lang=ro
7. https://www.legis.md/cautare/getResults?doc_id=95869&lang=ro
8. https://www.legis.md/cautare/getResults?doc_id=100065&lang=ro
9. https://www.legis.md/cautare/getResults?doc_id=114371&lang=ro
10. https://www.legis.md/cautare/getResults?doc_id=114330&lang=ro
11. https://www.legis.md/cautare/getResults?doc_id=109123&lang=ro
12. https://www.legis.md/cautare/getResults?doc_id=101165&lang=ru
13. https://www.legis.md/cautare/getResults?doc_id=100964&lang=ro

14. https://www.legis.md/cautare/getResults?doc_id=99900&lang=ru
15. https://www.legis.md/cautare/getResults?doc_id=84028&lang=ro
16. https://cancelaria.gov.md/sites/default/files/hg_nr._492_din_11.08.2015.pdf
17. https://www.legis.md/cautare/getResults?doc_id=102933&lang=ro
18. Lau O, Wong, S. Contamination in food from packaging material. Journal of Chromatography A, 2000. 882: p. 225-270.
19. Begley T.H. Migration from food packaging: Regulatory considerations for estimating exposure. In Plastic Packaging Materials for Food, 2000. Piringer, O.G. and Baner, A.L., Eds.Willey-VCH, Germany, p. 359-391.
20. O' Brien A., Goodson A., Cooper I. Polymer additive migration to foods - A direct comparison of experimental data and values calculated from migration models for high density polyethylene (HDPE). Food Additives and Contaminants, 1999. 16(9): p. 367–380.
21. Vam Deventer D., Mallikarjunan P. Optimizing an electronic nose for analysis of volatiles from printing inks on assorted plastic films. Innovative Food Science and Emerging Technologies, 2002.
22. Castle L., Sharman M., Gilbert J. Gas chromatographic-mass spectrometric determination of epoxidized Soya bean oil contamination of food by migration from plastic packaging. Journal of the Assosiation of Official Analytical Chemists, 1988. 71: p. 1183–1186.
23. Page, B.D., Lacroix G.M. The occurrence of phthalate ester and bi-2-ethylhexyl adipate plasticizers in Canadian packaging and food sampled in 1985–1989: Asurvey. Food Additives and Contaminants, 1995. 12(1): p. 129–151.
24. Losada P., Lamela C., Fabal M., Fenollera P., Lozano J. Two RP-HPLC sensitive methods to quantify and identify Bisphenol A diglycidyl ether and its hydrolysis products. European union aqueous food simulants. J. Agric. Food Chem., 1997. 45(9): p. 3493–3500.
25. Bush J., Gilbert J., Goenaga X. Spectra for the identification of monomers in food packaging. Kluwer Academic Publishers. Dordrecht, Netherlands. 1994.
26. UK. Ministry of Agriculture. Fisheries and Foods. 1997. Survey of Bisphenol a diglycidyl ether (badge) epoxy monomer in canned foods. Food Surveillance Information Sheet, 125:12.
27. Tang W., Hemm I., Eisenbrand G. Estimation of human exposure to styrene and ethylbenzene. Toxicology, 2000. 144: p. 39–50.
28. Nerin C., Rubio C., Cacho J., Salafranc, J. Parts-per-trillion determination of styrene in yogurt by purge-and-trap gas chromatography with mass spectrometry detection. Food Additives and Contaminants, 1998. 15(3): p. 346–354.
29. Mattarozzi M., Lambertini F, Suman M., Careri M. Liquid chromatography – full scan-high resolution massspectrometry - based method towards the comprehensive analysis of migration of primary aromatic amines from food packaging, Journal of Chromatography A, 1320,2013. p. 96-102.
30. Sanchis Y., Coscollà C., Roca M., Yusà V. Target analysis of primary aromatic amines combined with a comprehensive screening of migrating substances in kitchen utensils by liquid chromatography-high resolution mass spectrometry, Tal. 114, 2015. p. 290-297.
31. Nerin C., Alfaro P., Aznar M., Domeno C. The challenge of identifying non-intentionally added substances from food packaging materials: A review, Analytica Chimica Acta, 2013. p. 14– 24.
32. Aznar M., Domeno C., Nerín C., Bosetti O. Set-off of non volatile compounds from printing inks in food packaging materials and the role of lacquers to avoid migration, Dyes and Pigments. 114, 2015. p. 85-92.
33. Castillo M. Biedermann A., Riquet K. Comprehensive on-line HPLC GC for screening potential migrants from polypropylene into food: The effect of pulsed Light decontamination as an example, Polymer Degradation and Stability, 98, 2013. p. 1679-1687.
34. Vavrous L., Vapenka J., Sosnovcov K., Kejlov K., Vrbík D. Method for analysis of organic contaminants in food contact paper using gas and liquid chromatography coupled with tandem mass spectrometry, Food Control. 60, 2016, p. 221-229.
35. Zafeiraki E., Costopoulou D., Vassiliadou I., Bakeas E., Leondiadis L. Determination of perfluorinated compounds (PFCs) in various foodstuff packaging materials used in the Greek market, Chemosphere. 144, 2016, p. 2106-2112.
36. Alabi A., Caballero-Casero N., Rubio S. Quick and simple sample treatment for multiresidue analysis ofbisphenols, bisphenol diglycidyl ethers and their derivatives in cannedfood prior to liquid chromatography and fluorescence detection, Journal of Chromatography A, 1336, 2014, p. 23-33.

37. Zafeiraki E., Costopoulou D., Irene V., Leondiadis L. Perfluoroalkylated substances (PFASs) in home and commercially produced chicken eggs from the Netherlands and Greece, Chemosphere, 144, 2016. p. 2106-2112.
38. Dugo G., Fotia V., Turco V., Maisano R., Potorti A. Phthalate, adipate and sebacate residues by HRGC-MS in olive oils from Sicily and Molise (Italy), Food Control, 22, 2011, p. 982-988.
39. Fierens T., Servaes K., Van Holderbek M., Geerts L., De Henauw S., Sioen I., Vanermen G. Analysis of phthalates in food products and packaging materials sold on the Belgian market, Food and Chemical Toxicology, 50, 2012, p. 2575–2583.
40. Cinell i G., Avino P., Notardonato I., Centola A. Rapid analysis of six phthalate esters in wine by ultrasound-vortex-assisted dispersive liquid-liquid microextraction coupled with gas chromatography-flame ionization detector or gas chromatography-ion trap mass spectrometry, Analytica Chimica Acta, 769, 2013. p. 72-78.
41. He J., Lu K. Selective solid-phase extraction of dibutyl phthalate from soybean milk using molecular imprinted polymers, Anal. Chim. Acta, 661, 2010, p. 215-221.
42. Moreira M., Coelho L. Analysis of plasticiser migration to meat roasted in plastic bags by SPME–GC/MS, Food Chemistry, 178, 2015. p. 195–200.
43. Makkliang F., Kanatharana P., Thavarungkul P., Thammakhet C. Development of magnetic micro-solid phase extraction for analysis of phthalate esters in packaged food, Food Chemistry, 166, 2015. p. 275-282.
44. Bignardi C., Cavazza A., Corradini C., Salvadeo P. Targeted and untargeted data dependent experiments for characterization of polycarbonate food-contact plastics by ultra high performance chromatography coupled to quadrupole orbitrap tandem mass spectrometry, Journal of Chromatography A, 2014, p. 133–144.
45. Rios J., Morales A., Marquez-Ruiz G. Headspace solid-phase microextraction of oil matrices heated at high temperature and phthalate esters determination by gas chromatography multistage mass spectrometry, Talanta, 80, 2010. p. 2076-2082.
46. Yan H., Cheng X., Liu B. Simultaneous determination of six phthalate esters in bottled milks using ultrasound-assisted dispersive liquid-liquid microextraction coupled with gas chromatography, Journal of Chromatography. B. 879, 2011. p. 2507-2512.
47. Zhu L., Zhu T., Ma Y., Ni Y. Rapid determination of 15 kinds of phthalate esters in vegetable juice hollow fiber-liquid phase microextraction coupled with gas chromatography-Mass spectrometry, Anal. Chem., 41, 2013, p. 1019-1024.
48. Yang J., Wang Y., Ruan J., Zhang J., Sun C. Recent advances in analysis of phthalate esters in foods, TrAC 72, 2015. p. 10-26.
49. Aznar M., Rodriguez-Lafuente A., Alfaro P., Nerin C., UPLC-Q-TOF-MS analysis of non-volatile migrants from new active packaging materials, Anal. Bioanal. Chem., 404, 2012. p. 1945-1957.
50. Franz, R., Huber, M., and Piringer, O. 1997. Presentation and experimental verification of a physico-mathematical model describing the migration across functional barrier layers into foodstuffs. Food Additives and Contaminants, 14(6–7): p. 627–640.
51. C. Moreta, MT. Tena, Determination of perfluorinated alkyl acids in corn, popcorn and popcorn bags before and after cooking by focused ultrasoundsolid–liquid extraction, liquid chromatography and quadrupole-time of flight mass spectrometry, Journal of Chromatography A (2014) 211–218.
52. W. Jia, X.Chu,Y. Ling, J. Huang, J. Chang, Analysis of phthalates 854 in milk and milk products by liquid chromatography coupled to quadrupole Orbitrap high-resolutionmass spectrometry, Journal of Chromatography A (2014) 110–118.
53. D.M. Xu, X.J. Deng, E.H. Fang, X.H. Zheng, Y. Zhou, 1157 L.Y. Lin, et al., Determination of 53 phthalic acid esters in food by liquid chromatography tandem mass spectrometry, Journal of Chromatography A (2014) 49–56.
54. Y. Havasaka, Analysis of phthalates in wine using liquid chromatography tandem mass spectrometry combined with a hold-back column: Chromatographic strategy to avoid the influence of pre-existing phthalate contamination in a liquid chromatography system, Journal of Chromatography A (2014) 120-127.
55. D. Perez-Palacios, MA. Fernandez-Recio, C. Moreta, MT Tena, Determination of bisphenol-type endocrine disrupting compounds in food-contact recycled-paper materials by focused ultrasonic solid–liquid extraction and ultra performance liquid chromatography-high resolution mass spectrometry, Talanta 99 (2012) 167–174.