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Migration from Plastic Packaging into Meat

Tatiane Melina Guerreiro[1], Diogo Noin de Oliveira[1], Carlos Fernando Odir Rodrigues Melo[1], Estela de Oliveira Lima[1] and Rodrigo Ramos Catharino[1,*]

[1]Innovare Biomarkers Laboratory, School of Pharmaceutical Sciences, University of Campinas – UNICAMP, Campinas, SP, Brazil

[*]Corresponding author:
Prof. Rodrigo Ramos Catharino
rrc@g.unicamp.br

Abstract

Migration is a known phenomenon defined as the partitioning of chemical compounds from the packaging into food, and depends on several factors. Migration assays are generally time-consuming and require specific conditions in order to investigate the behavior of the packaging in different situations. Furthermore, these tests are often performed with food simulants, since the determination of migration under real conditions is highly impaired. Several methodologies have been designed to carry out this study, but an ideal approach should be capable of assessing the migration of compounds in real samples, providing fast and reliable results. Within this context, mass spectrometry can be considered a suitable and versatile technique that shows great potential to accurately characterize several contaminants in food by migration. Thus, in this work we present a mass spectrometry-based application for the detection of several compounds from plastic, directly from vacuum-packed meat samples. This preliminary and simple workflow can be easily applied in routine analyses for either quality control purposes or in the prospection of other potential bioactive contaminants in food.

Keywords: migration, plastic, package, meat, contamination, contaminants.

1. Introduction

The term 'plastic' is used to describe materials based on modified synthetic or natural polymers, which may be molded using heat and/or pressure. Plastic materials used in packaging are very diverse in their chemical structure, presenting variable properties depending on the processing, incorporated additives and combination with other polymers (Robertson, 2006). For the food industry, with the increasing demand for industrialized products, flexible plastic packaging has been widely used due to their versatility and also to increase the product's shelf life (Robertson, 2006).

Flexible plastic packages may be composed of thermoplastic material, which is molded by increasing temperatures, allowing them to be shaped according to the product's size and outline (Jr., Wagner, 2016). The most common example of this class would be vacuum packages, which are usually employed in the packaging of meat products (McMillin, 2017). This type of packaging consists of a multilayer film, aimed at combining the properties of each of the films in its constitution. The main polymer used in the manufacturing process of such package is polyamide, due to its characteristics of high abrasion resistance, thermoformability and resistance up to 200ºC (Robertson, 2006). Additionally, other commonly used polymers are polyethylene terephthalate (PET), polyvinylidene chloride (PVC), and ethylene vinyl alcohol (EVOH). These polymers are more expensive, and some of them are sensitive to moisture or heat sealing. Because of that, low-cost polymers such as polypropylene (PP), polyethylene (PE) and polyethylene copolymers, are mixed in due to their capability of being heat-sealed for lamination or coextrusion (K. H. Lee & Sun, 2016).

More recently, mixing other additives with the polymer base has been a common practice to improve the mechanical behavior of plastic films. Since the technical requirements for many flexible packaging applications are very demanding, they can only be achieved by combining layers with different polymeric materials and additives to form a structure that meets the desired performance needs (K. H. Lee & Sun, 2016). Within the context of the thermoplastic material technology, the term "additive" or "process coadjutant" is used to denote an ingredient capable of enhancing the properties of a polymer without significantly altering its chemical structure, thereby improving polymer resin transformation through changes in physical properties and mechanical properties of the final material. Regarding food packaging, all additives used must be certified by the specific regulatory authority (Robertson, 2006).

Several contributions in the literature show that there is possibility of migration of components from the packaging to the conditioned product (K. T. Lee, 2010; Sanches Silva, Cruz, Sendón García, Franz, & Paseiro Losada, 2007). Migration is defined as the partitioning of chemical compounds by diffusion or absorption from the packaging into the food (Arvanitoyannis & Kotsanopoulos, 2014; Fasano, Bono-Blay, Cirillo, Montuori, & Lacorte, 2012; Lau & Wong, 2000; Tehrany & Desobry, 2004). Contamination of food by migration of monomers or additives is a relevant matter for health legislations due to potential health-related risks. Thus, packaging materials intended for the packaging of foodstuffs must be registered and approved after assessing the absence of toxic effects to the consumer and organoleptic changes to the food (Cherif Lahimer, Ayed, Horriche, & Belgaied, 2017; Mercosul, 2007; Muncke et al., 2017). However, this is still a subject of much debate due to the lack of information and more detailed studies on the safety of exposure to these possible contaminants, as well as assertive determination of the number of allowed compounds and migration limits (Muncke et al., 2017).

Moreover, this phenomenon depends on several factors such as chemical composition of the conditioned food, level, time and temperature of contact with the package, and chemical properties of the packaging material (Arvanitoyannis & Kotsanopoulos, 2014). Migration tests generally have a long experimental workflow, and require specific conditions of temperature and humidity in order to mimic conditions of conservation or to generate stress conditions to investigate the behavior of the packaging. Furthermore, since food is a complex matrix both chemically and physically, food simulants are frequently used. These products have defined composition and characteristics that mimic the composition of food classes, facilitating the determination of migration, since working under real conditions is an important methodological challenge (Arvanitoyannis & Kotsanopoulos, 2014; Tehrany & Desobry, 2004).

For this reason, developing an expeditious and accurate methodology, capable of being applied to study the migration of compounds in real samples would represent an important advancement in food analysis. In this context, mass spectrometry has proven to be a great ally for the identification and characterization of compounds in complex samples, from biological fluids to food, exhibiting versatility, sensitivity, and accuracy (Guerreiro et al., 2018; Guerreiro, Oliveira, Ferreira, & Catharino, 2014; Melo et al., 2017; Vivian, Aoyagui, de Oliveira, & Catharino, 2016). High-resolution mass spectrometry (HRMS) is a powerful technique that provides reliable information about the characterization of unknown compounds within any given matrix, with enhanced accuracy and precision (Rubert, Zachariasova, & Hajslova, 2015). In this way, our work presents a preliminary and simple methodology for the identification of several plasticizers migrating from vacuum-packages into meat samples using HRMS as the main detection technique.

2. Materials and Methods

2.1. Sample Preparation

Fifteen pieces of vacuum-packed beef meat from the same batch and brand were purchased from supermarkets in the city of Campinas, São Paulo, Brazil. From each package, triplicates of both beef meat and packaging material were sampled and prepared as described below.

An amount of packaging material equivalent to 2 mg was added to 500 µL of tetrahydrofuran (THF) (242888, Sigma-Aldrich, Saint Louis, USA). The mixture was sonicated at room temperature for 10 minutes, where dissolution of most of the plastic material occurred. To this solution, 500 µL of methanol (34860, Sigma-Aldrich, Saint Louis, USA) was added, and the final resulting solution was homogenized in vortex for 1 minute.

For beef meat samples, a piece of approximately 2 mg was cut from different areas in the surface and 2.5 to 3 cm deep, which underwent the same extraction protocol as that described for the packaging material. In addition, a negative control was performed with fifteen beef meat samples purchased directly from a butcher's shop in the city of Campinas, São Paulo, Brazil, so that these samples were not conditioned in any type of plastic packaging. All purchased meat was from the same type of beef cut (Brazilian rump), with similar fat content, to avoid any potential bias in the results.

Prior to HRMS analyses, 1 µL of formic acid (F0507, Sigma-Aldrich, Saint Louis, USA) was added to 500 µL of the final solution.

2.2. High Resolution Mass Spectrometry (HRMS)

Samples were directly injected into an ESI-LTQ-XL Orbitrap Discovery (Thermo Scientific, USA). Acquisitions were performed in the positive mode, in the mass range of 70-700 *m/z*. Instrument parameters were: flow rate of 10 $\mu L.min^{-1}$, capillary temperature of 280 °C, 5 kV spray voltage and sheath gas at 10 arbitrary units.

HRMS analysis were performed in triplicates for each sample and its replicates (i.e. a total of 540 spectra acquisitions). The online metabolomics database METLIN (www.metlin.scripps.edu) was consulted to provide the candidate molecules during the structure elucidation process, employing the value of the exact experimental mass obtained in comparison with the theoretical mass, so that the error adopted between these two values was < 2 ppm.

3. Results and Discussion

The analyses of all resulting survey spectra showed that HRMS was capable of identifying 5 contaminants in all pieces of beef meat that were in contact with the vacuum-plastic packaging, as presented in Table 1. The replicates analysis showed that the methodology maintained the same spectral profile for each of the sample types analyzed (negative control meat, packed meat and packaging material), which demonstrates the reproducibility of the method. Their spectral profiles are presented at Figure 1. Observing and comparing the spectra, no signals related to these compounds are found in the spectrum from the butcher's shop beef meat (negative control, Figure 1A); instead, they are present at the profile for packaging material spectrum (Figure 1B) and for packed beef meat spectrum (Figure 1C). In addition, for the spectrum of the packaging material (Figure 1B) the signal intensity of the identified components is greater than in the packaged beef meat spectrum (Figure 1C), which corroborates the fact that these components belong to the analyzed material, and they were able to migrate into meat. The profiles presented for the samples from superficial and deeper cuts showed no differences.

Regarding the elucidated compounds of interest, three are related to the manufacturing of polymers, providing strong evidence that they came from plastic packaging, namely phthalic anhydride (149.0235 *m/z*), which is used in the manufacturing process of organic polymers (European Commission, 2011); stearamide (284.2952 *m/z*), an additive that is incorporated into the polymeric substrate to provide enhanced stability and performance of the final product (Jr., Wagner, 2016) and polyethylene glycol (PEG) (415.2542, 437.2349 and 453.2088 *m/z*), which is used in combination with other polymers to provide hardness and ductility to the structure of the material (Chieng, Ibrahim, Then, & Loo, 2016). Complementary with plastic manufacture, the last compound is the diisooctyl phthalate (DIOP) (391.2850 and 454.2921 *m/z*), which has plasticizer function.

The migration phenomenon may lead to the contamination of the conditioned product, due to direct and indirect interactions that may occur with the food product. In the case of packaging-environment interactions, the interface between food and the environment may be allowed according to the permeability level of the packaging, and in the case of packaging-food interaction, the migration of monomers, oligomers and/or food additives may occur due to the direct contact with the food (Lau & Wong, 2000). Currently, two migration tests are required to release the use of chemicals in food packaging: "Quantity in Material", for carrying out the quantity of a substance which may be present in the packaging material, and "Specific Migration", for assessing the quantity of a determinate substance that may possibly migrate to the food product (Arvanitoyannis & Bosnea, 2004).

Currently, the majority of tests to identify migrating packaging components to food are carried out using food simulants. These are needed because of the difficulty of analyzing the wide range of food matrices and also the actual conditions or stress during storage (Sanches Silva et al., 2007). Some analytical methods are already standardized, but official methods are often long, complicated and impractical in a daily routine of quality control. Releasing or restricting the use of substances in food packaging involves the analyses of the risks and benefits, and the quality control of packaging materials is heavily impaired. It is on account of the existence of more than 1,000 additives and monomers that are listed as potential migrants in the regulatory list of positive substances, many of which are authorized with specific migration restrictions or limits, and the general objective of the legislation is to ensure consumer safety (Arvanitoyannis & Bosnea, 2004; Gillet, Vitrac, & Desobry, 2010).

In an attempt to control and harmonize the legislation on food packaging, the EU (European Union) and the FDA (Food and Drugs Administration) created a list of positive substances, which have their permitted use, and restricted substances, as they have a potential toxic effect (Simoneau & Hannaert, 1999). However, problems about this list involve mainly the lack of information on the toxicity of the substances, especially the absence of studies related to the toxicity of the final product, and not just of a specific compound, as currently evaluated. Moreover, studies on a mixture of substances to ascertain potential synergistic effects are required, as well as studies on the cumulative effects of exposure to these substances (Muncke et al., 2017).

In this context, fast screening methods such as HRMS refer to the agile identification of possible agents coming from plastic packaging that can lead to potential health risks to consumers. Research in this area should be guided by improvements in the current analytical methods for food packaging control, aiming at minimal prepare os samples, using a minimal quantity of solvents, and the rapid and effective determination of potential migrants in food. At this work we presented a preliminary methodology for screening possible migrants from plastic into beef meat using only HRMS technique, and the results showed the potential of the use of this technique at food industries for identification of compounds from packaging material.

4. Conclusions

Through the results obtained it was possible to develop a new, simple and effective methodology, capable of identifying the phenomenon of migration of packaging components to the conditioned food, without the need to use food simulants, since the application was carried out in real samples. HRMS proved to be a reliable tool in this context, due to its speed and sensitivity, showing an even broader potential for application in the analysis of food contaminants.

5. Authors Contributions

TG performed sample collection, experiments and wrote the manuscript. CM, DO and EL performed manuscript review. RC idealized all experiments and managed the research group.

6. Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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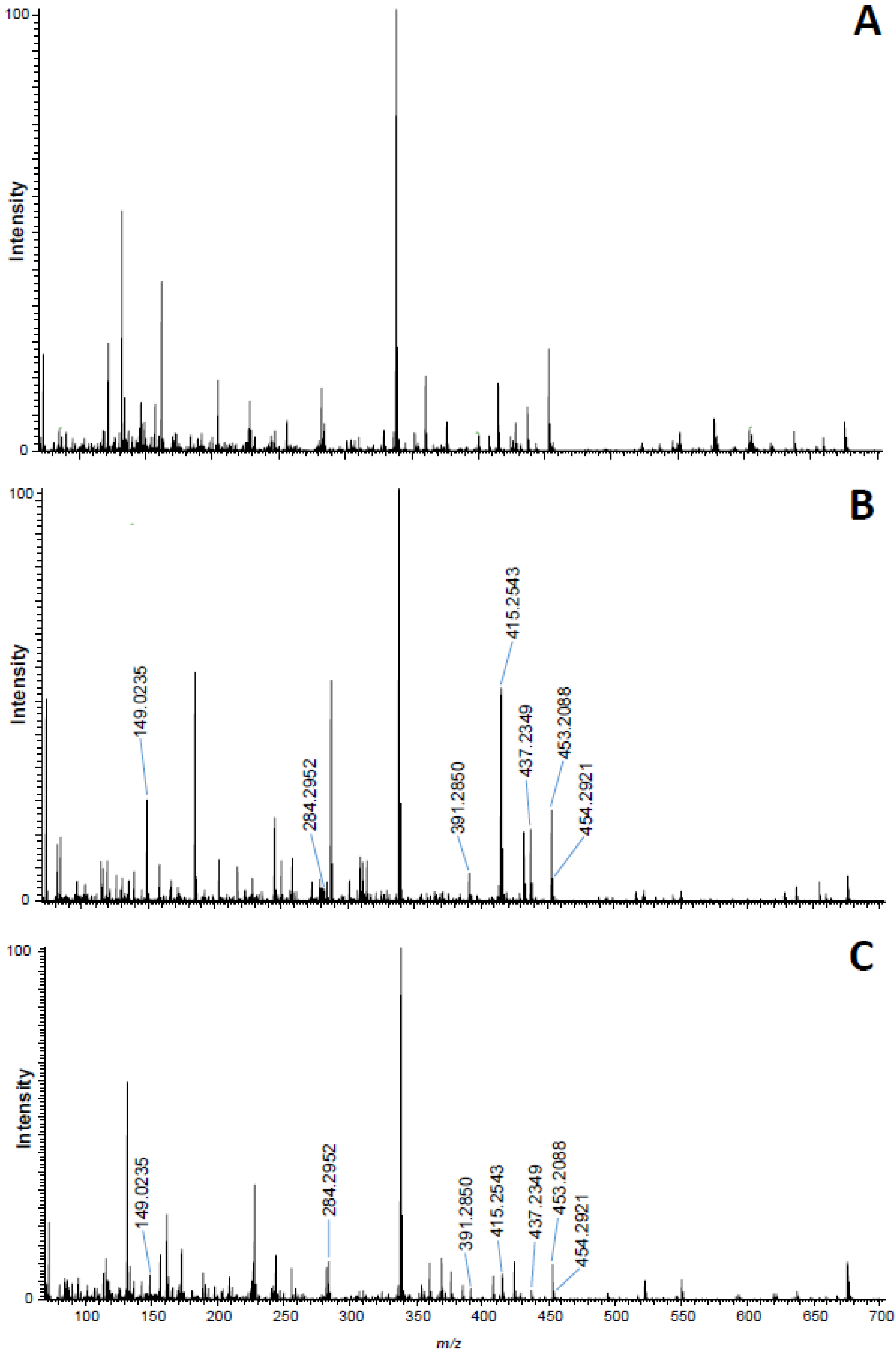
Figure Captions

Figure 1. HRMS **s**pectra of the beef meat samples showing the presence of five contaminants in all pieces of beef meat that were in contact with the vacuum-plastic packaging. A: negative control butcher's shop beef meat; B: packaging spectrum; C: packed beef meat spectrum



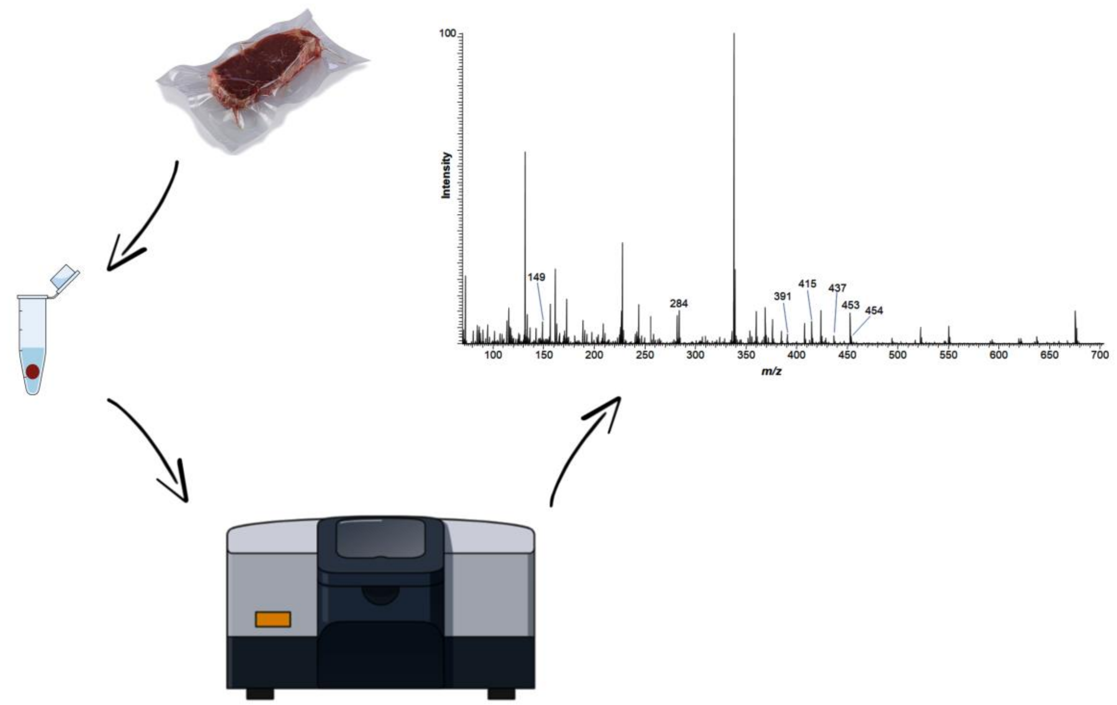
A
B
C
Intensity
100
0
149.0235
284.2952
391.2850
415.2543
437.2349
453.2088
454.2921
100
150
200
250
300
350
400
450
500
550
600
650
700
m/z

Fig. 1

Table 1. Contaminants found in meat samples from plastic package.

Compound	Adduct[a]	Exact Mass	Experimental Mass	Error (ppm)	CAS No.
Phthalic Anhydride	$[M+H]^+$	149.0233	149.0235	1.34207	85-44-9
Stearamide	$[M+H]^+$	284.2947	284.2952	1.75874	124-26-5
Diisooctyl phthalate	$[M+H]^+$	391,2843	391.2850	1.82476	84-69-5
	$[M+CH_3CN+Na]^+$	454.2927	454.2921	1.32073	
Polyethylene glycol (PEG)	$[A_9B+H]^+$	415.2537	415.2543	1.44490	25322-68-3
	$[A_9B+Na]^+$	437.2357	437.2349	1.82968	
	$[A_9B+K]^+$	453.2096	453.2088	1.76519	

([a]The adducts presented are in accordance with Keller *et al*, 2008 (Keller, Sui, Young, & Whittal, 2008))



Graphical abstract

Highlights

- Food contamination by packaging must be known to avoid consequences to health.
- Contaminants' migration from packaging to meat was detected in real samples.
- Mass spectrometry provided accurate and faster results, in a simpler workflow.