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Attenuated total reflectance-mid infrared spectroscopy (ATR-MIR) coupled with independent components analysis (ICA): A fast method to determine plasticizers in polylactide (PLA)

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ABSTRACT

Compliance of plastic food contact materials (FCMs) with regulatory specifications in force, requires a better knowledge of their interaction phenomena with food or food simulants in contact. However these migration tests could be very complex, expensive and time-consuming. Therefore, alternative procedures were introduced based on the determination of potential migrants in the initial material, allowing the use of mathematical modeling, worst case scenarios and other alternative approaches, for simple and fast compliance testing. In this work, polylactide (PLA), plasticized with four different plasticizers, was considered as a model plastic formulation. An innovative analytical approach was developed, based on the extraction of qualitative and quantitative information from attenuated total reflectance (ATR) mid-infrared (MIR) spectral fingerprints, using independent components analysis (ICA). Two novel chemometric methods, Random_ICA and ICA_corr_y, were used to determine the optimal number of independent components (ICs). Both qualitative and quantitative information, related to the identity and the quantity of plasticizers in PLA, were retrieved through a direct and fast analytical method, without any prior sample preparations. Through a single qualitative model with 11 ICs, a clear and clean classification of PLA samples was obtained, according to the identity of plasticizers incorporated in their formulations. Moreover, a quantitative model was established for each formulation, correlating proportions estimated by ICA and known concentrations of plasticizers in PLA. High coefficients of determination (higher than 0.96) and recoveries (higher than 95%) proved the good predictability of the proposed models.

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1. Introduction

In food contact applications, plastic food contact materials (FCMs) such as packaging, cups, containers, kitchen- and tableware etc., come in direct contact with food. Plastic FCMs are however not inert and may transfer their constituents to food, raising serious concerns about its safety. Migrating compounds are intentionally added substances (IAS) such as monomers, pre-polymers, antioxidants, plasticizers etc. intentionally used along the production process of plastics. In addition to IAS of known origins, plastic FCMs may contain substances, mainly of unknown origins, that are non-intentionally added (NIAS) such as impurities, contaminants and by-products introduced or created during the manufacturing process of plastics.

In order to ensure that the use of FCMs is safe, general requirements are set up by the European Union (EU). For plastic FCMs, EU regulations 1935/2004/EC [1] and EU 10/2011 [2] specify that migration tests should be carried out using foodstuffs or food simulants under defined conditions of temperature and storage

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duration. However, these kinds of tests could be very complex, expensive and time-consuming for several reasons, among which one could mention the low concentration of migrants in food simulant or foodstuff, the complexity of the studied food matrix and the incompatibility between simulants and tested materials [3]. Therefore, alternative procedures have been introduced, based on the identification of potential migrants and their quantification in the initial material. In fact, knowing the identities and the concentrations of substances that may migrate from FCMs could help to understand the kind of approaches to be undertaken in order to evaluate their migration as well as their toxicological potency [4]. Moreover, worst case scenario strategies could be applied considering the extreme assumption of a 100% transfer, as well as mathematical modeling which can eventually provide maximum acceptable concentrations in the formulations, avoiding the complexity of migration tests [5,6]. These kinds of information could also help to supplement databases allowing a more efficient quality management system for the selection of starting substances, the control of manufacturing processes as well as for the monitoring of final products [7,8].

Common analytical strategies applied to determine potential migrants in plastic materials, particularly plasticizers, often combine solvent extraction/clean-up steps followed by chromatographic separations and mass spectrometric detections [9–14]. However, these solvent extraction-based approaches are complex, use up solvents, require laborious sample preparation and are, in some cases, inconvenient for labile analytes [15]. Moreover, unavoidable clean-up steps are generally necessary in order to overcome problems that may be caused by the presence of large molecules such as oligomers in the extracts [16]. These approaches can be effective, but they are usually time consuming, to the same degree as the migration tests, making them of limited interest.

Therefore, instrumental approaches are gaining more and more attention, as they may allow a direct determination of analytes without prior preparation steps. In this context, Fourier transform infrared spectroscopy (FTIR) has the advantage of being a direct, rapid and non-destructive method that can be applied for the determination of additives in polymeric matrices. Moreover, it is one of the best established analytical methods because of its low cost and accessibility to industrial and regulatory laboratories [8]. The attenuated total reflectance (ATR) spectral acquisition mode in the mid-infrared (MIR) range has been commonly used for the determination of several additives in polymers [17–21], through a simple and direct analysis of the solid sample. Transmission mode spectral acquisition has also been used [22]. However, in the majority of cases, it requires some sample preparation steps since it is limited to thin films due to the high absorptivities of mid-IR bands [23]. Moreover, another approach could be found in the literature, where MIR spectra of polymer extracts are acquired [7,8,24,25]. This approach includes an extraction step which makes it, once again, of limited interest.

The qualitative and quantitative information contained in MIR spectra reside in band positions, shapes and intensities [26]. However, in order to extract pertinent information, well resolved bands are needed, which is not the case for polymer matrices, where highly overlapped polymer/additives bands are usually found. In order to overcome this problem, chemometric tools have become a fundamental part of infrared spectroscopic approaches and proved their efficiency in many fields, mainly for the analysis of complex matrices such as food [26,27], pharmaceutical products [28], for polymer composition and classification [29] etc. A wide range of chemometric techniques has been applied to infrared data, mainly for classification and regression purposes. Without being exhaustive, these include principal components analysis (PCA), common components and specific weights analysis (CCSWA), soft independent modeling of class analogy (SIMCA), hierarchical cluster analysis (HCA) and factorial discriminant analysis (FDA), which could be considered among the most common methods to have been combined with infrared spectral data for exploratory or discriminant analysis [26,29–31]. Partial least squares (PLS) regression and principal components regression (PCR) have been commonly used for quantitative purposes [26,28,31,32]. Independent components analysis (ICA), a relatively new method, is increasingly applied to infrared spectral data, mainly as a discrimination tools, but also, in several cases, as a multivariate regression method [33–36].

Although IR analysis lacks of sensitivity, it could be a valuable tool for analyzing plastic formulations with high additive contents. Typically, plasticizers are incorporated at concentrations up to 30 wt% in plastic materials, in order to sufficiently increase polymer ductility. Furthermore, plasticizers lower the glass transition temperature (T_g). The low T_g of the polymer as well as the high concentrations of plasticizers in the plastic formulation both increase migration risk. Therefore, the determination of plasticizers in plastic formulations is of high interest for the safety assessment of plastic FCMs.

In the aim of decreasing environmental impact of the plastic industry, novel bioplastics have been developed. Polylactide (PLA), an aliphatic polyester, is one of the most produced resins in this class and is considered as a sustainable alternative to petroleum-based plastics, since it is a biodegradable polymer derived from renewable resources mainly carbohydrate-rich substances [37,38]. Various end-user markets are concerned, such as packaging, textile, biomedical and automotive industries, especially since polymerization technologies have significantly reduced production costs and thus made PLA economically cost-effective [39]. PLA has many advantages such as ease of processing and conversion, glass transition temperature above room temperature, reasonably good optical, physical, mechanical and barrier properties, ability for heat sealing, high transparency, good printability etc. [37,40,41]. Moreover, its compostability can be an important asset regarding solid waste disposal problems, especially in applications that are difficult to recycle [42].

Despite its numerous advantages, the inherent brittleness of PLA has been a major drawback preventing its wide-scale commercialization, especially for applications in the packaging sector [38,40,43]. Plasticization is one of the main approaches used in order to overcome this problem and improve the processability, the flexibility and the ductility of PLA [44,45]. Therefore, a wide range of plasticizers have been investigated and have been found to be efficient for use with PLA such as: citrate esters: among which acetyl tributyl citrate (ATBC) [43,44,46] and tributyl citrate (TBC) [47,48] could be considered the best candidates and poly (ethylene glycol) (PEG) [42–44,49,50]. More recently, adipate esters: mainly dioctyl adipate (DOA) [46,51], and Polysorb ID37™, a bio-based isosorbide diester used, were tested successfully as a plasticizer for PLA [52].

In the majority of the studies dealing with PLA plasticization, concentrations up to 15–30 wt% of plasticizers are used [39,45], in order to sufficiently lower the glass transition (T_g) and thereby enhance the ductility of the material. However, these significant quantities could induce serious problems regarding the compliance of PLA when used for food contact applications. In fact, besides good compatibility and enhanced mechanical properties, several safety requirements need to be fulfilled in a plasticized PLA in order to meet international regulatory requirements. The contamination of foodstuffs in contact with PLA by plasticizer migration is an important topic in this field [47,48,51]. Furthermore, and due to its polyester structure, PLA showed an incompatibility risk with some food simulants of the European regulation, in particular the water/ethanol mixtures, due to polymer swelling. These two issues: high concentrations of plasticizers and

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