Identification of Volatile Compounds coming from Starch-Base Biopolymer intended to Food Contact by GC-MS

Jazmín Osorio, Alejandro López, Margarita Aznar, Cristina Nerín

Grupo Universitario de Investigación Analítica (GUIA)
Instituto de Investigación en Ingeniería de Aragón (I3A)
Universidad de Zaragoza, Mariano Esquillor s/n, 50018, Zaragoza, España.
Tel. +34-976761873, e-mail: *jazminosorio@unizar.es*

Abstract

Starch-base biopolymers are commonly used as food contact materials. In this work, the volatile compounds of a starch-base material and its migration to ethanol 95% food simulant were determined by GC-MS. A total of 35 compounds were detected in the material, 5 of them were also detected in migration.

Introduction

In recent years the use of biopolymers for food packaging has increased, because they are abundant, renewable, inexpensive, environmentally friendly, biodegradable, and biocompatible [1]. Starch-base biopolymers have been one of the most used for the manufacturing of bio-films, because starch is low cost, safe and abundant [2]. Nevertheless, the materials used to manufacture food packaging must be evaluated to confirm their acceptability. Migration tests of materials are used to study the transference of specific migrants to food and assess consumers' safety. It is important to check their presence in the positive list of Commission Regulation (EU) No 10/2011 [3] and their specific migration limits. The migration tests require specific conditions of temperature, time and simulants that are established according to the use of the material. In this work, the extraction process of volatile compounds of starch-base biopolymer was optimized. The compounds of pellet were identified by GC-MS and their migration to ethanol 95% was tested on market samples.

Materials and methods

Samples

Starch-base biopolymer samples were supplied by a Packaging Company. They were provided in two different forms: pellets and market samples (glasses and plates). Additional information cannot be provided due to confidential reasons.

Solvent extraction of pellet samples

Methanol was selected as extraction solvent. The other solvents tested such as dichloromethane, hexane, toluene or dimethyl sulfoxide formed a precipitate. Extraction was tested in three different forms of the pellet samples: pellets without any modification (spheric), pellets smashed under high pressure (lentil) and pellets ground in a mill (dust). Two extraction times were evaluated: 30 min and 60 min. (Fig 1). ***Final protocol****: 500 grams of sample as lentils are sonicated with 2.5 mL of methanol during 60 minutes at 40ºC. Three consecutive extractions of each sample are performed. The three extracts are combined and concentrated to 1 mL under a gentle N_2. current. This solution was analysed by GC-MS.*

Migration assays

The migration assays were carried out in accordance with the legislation for food contact materials EU/10/2011. Market samples were filled with ethanol 95%. The migration assays conditions were as follows: 6 hours at 70 ºC. Since the samples were intended to be for repeated use, the migration tests were performed three consecutive times. Experiments were carried out in a thermostatic oven. All the analyses were performed in triplicate and blank samples were also analysed by GC-MS.

Analysis by GC-MS

Analyses were carried out in a Gas Chromatograph 7890N with mass spectrometry detector 5977D (Agilent Technologies). HP-5MS column was used (30m x 25mm x 0.25µm film thickness). Injection volume was 1 µL and it was carried out in splitless mode. Acquisition was performed in SCAN mode.

The temperature ramp was as follows: initially 50ºC for 5 min, 10ºC/min to 300 ºC and held for 5 min.

Results and discussion

Identification

The compounds were identified by comparing their mass spectra with the NIST electronic Mass Spectral Database. In Fig. 2a a pellet sample chromatogram can be observed. A total of 35 compounds were detected and 28 were tentatively identified, as esters, acids, alcohols and amides. Glycerin, a common plasticizer, 1,6-dioxacyclododecane-7,12-dione a lactone coming from the esterification of adipic acid, isopropyl palmitate, hexadecanamide, 9-octadecenamide, (z), myristyl myristate, phthalic acid and nonyl oct-3-yl ester compounds had the highest intensity.

Migration study

In the migration test, five compounds were identified, 1,6-dioxacyclododecane-7,12-dione, octadecanoic acid, ethyl ester, tetradecanoic acid, dodecyl ester, myristyl myristate and tetradecanoic acid, hexadecyl ester. All these compounds were previously detected in the pellet sample. Fig 2b shows a chromatogram of the migration solution. Three compounds migrated mostly, tetradecanoic acid, dodecyl ester, myristyl myristate and tetradecanoic acid, hexadecyl ester, in the first day of migration. The intensity of these compounds decreased in the second migration test below 57%, 53% and 59%, respectively. In the third migration test, their intensity decreased below 70%, 65% and 71%, respectively. This fact suggested that the migration decreased on the repeated used. All the compounds that migrated are present in the positive list of Commission Regulation (EU) No 10/2011.

Conclusions

The results obtained in this study establish that solvent extraction allows the identification of the compounds present in starch-base materials. Esters, alcohols, acids, and amides can migrate to food during food storage. The results show also that the migration of these compounds decreased with the repeated used.

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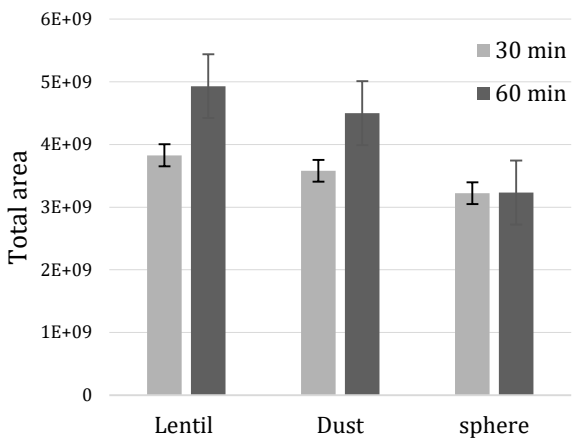

Fig 1. Results of optimization in the solvent extraction process for 30 min and 60 min with three pellet different form: lentil, dust and sphere.

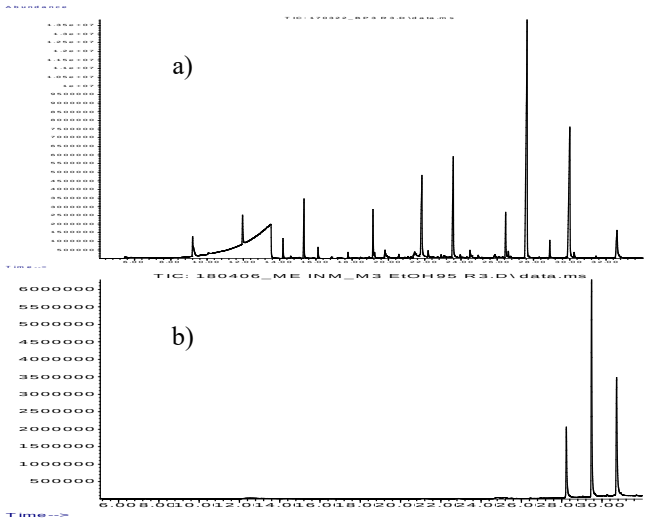

Fig 2. Chromatogram of **a)** solvent extraction of the film sample and **b)** day one migration of the market sample.