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Study of the effect of the presence of silver nanoparticles on migration of bisphenol A from polycarbonate glasses into food simulants

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ABSTRACT

The impact that the presence of nanoparticles in food can have on the migration from food contact materials (FCMs) of substances, which occurrence in foodstuffs is regulated, is posed in this paper through a case-study. Migration of bisphenol A (BPA) from polycarbonate glasses into aqueous food simulant B (3% acetic acid, w/v) and simulant D1 (50% ethanol, v/v), both in the absence and presence of silver nanoparticles is tested. The analysis of the amount of BPA released into the food simulants is conducted by comparing population results instead of using the classical location and scatter estimates. β-content tolerance intervals are used to model the statistical distribution of BPA migrated from the polycarbonate glasses. Experimental measurements are performed by HPLC-FLD, and partial least squares regression models are then fitted to determine the concentration of BPA. The analytical procedure fulfils the trueness property. The capability of detection of the method is between 1.7 and 2.3 $\mu g\,L^{-1}$ when the probabilities of false positive and false negative are fixed at 0.05. Using β-content tolerance intervals, in 90% of the specimens of a population of polycarbonate glasses, the amount of BPA migrated into simulant B in the presence of AgNPs is 13.34 $\mu g\,L^{-1}$, at least twice the quantity that migrated in the absence of them.

1. Introduction

Nanotechnology in food industry concerns with, among other things, developing food products and packaging materials with new and improved properties. Many naturally food occurring substances exist at the nanoscale, but new food products with prolonged shelf-life, novel tastes and textures, health benefits, etc., are being developed and engineered in this field [1–3]. The high surface area to mass ratio of nano-sized substances can lead, for example, to a reduction in the use of additives since small amounts may provide a high level of functionality or because of their ability to be disperse uniformly in foodstuffs.

On the other hand, substances may be added in food contact materials (FCMs) in the form of nanoparticles to increase the functionality of such materials, which includes improved barrier properties and better temperature performance [4–6]. The antimicrobial and antifungal food packaging properties of silver nanoparticles (AgNPs), for example, are well known [5,7]. For this reason, AgNPs have been used to prepare packaging containing antimicrobial agents in order to extend the product life, despite the possible health risk of exposure to nanoparticles [8,9]. The use of AgNPs in food plastic containers is not allowed in the European Union (except for certain silver zeolites and rubber seals) [10], but it is usual in markets outside Europe; AgNPs are the most widely inorganic nanoparticles employed for antimicrobial packaging [5]. Nanoparticles may reach the food contact surface and release into the food [11]; several studies on the migration of silver from FCMs can be found in the literature where silver speciation and quantification of the fraction migrated in the silver nanoform are performed [12–14]. However, it seems that the overall conclusion from the analysis performed so far is that consumer exposure is negligible [14] because the concentrations of AgNPs found are very low.

Nanoparticles may be present in foods as a consequence of the manufacture and processing of food or because they are transferred from the FCMs. The presence of nanoparticles in food that comes into contact with FCMs might have effect on the migration of other substances such as non-intentionally added substances (NIAS) that may be present in the FCM as a result of reaction or degradation processes that take place in that material [15]. In fact, the reactivity of many nanoparticles (metallic and magnetic nanoparticles, carbonaceous and silicon nanomaterials and polymer-based nanosorbents) has led to their increasing use as sorbents in sample preparation [16–18].

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Table 1
Conditions of the migration tests and characteristics of the PLS models fitted (number of latent variables and explained variance in X and Y blocks).

Migration test					PLS models			
Simulant	Temperature (ºC)	Time (h)	AgNPs	Experiment	Model	Latent variables	X-block explained variance (%)	Y-block explained variance (%)
D1	74	24	No	*Experiment_1*	1	1	82.59	98.98
			Yes	*Experiment_1NP*	2	1	83.18	98.41
B	100	24	No	*Experiment_2*	3	1	79.26	99.25
			Yes	*Experiment_2NP*	4	1	84.83	99.28
D1	70	10	No	*Experiment_3*	5	2	75.28	99.32
			Yes	*Experiment_3NP*	6	2	71.71	99.47
B	100	10	No	*Experiment_4*	7	2	77.18	99.61
			Yes	*Experiment_4NP*	8	2	66.84	99.24

The aim of this work is to study the impact that the presence of nanoparticles in food could have on the migration behaviour (from FCMs) of substances such as bisphenol A, formaldehyde, aromatic amines or phthalates, the occurrence of which in foodstuffs is regulated [10]. As an example to illustrate the procedure, the issue is addressed through a case-study, to assess if the release of bisphenol A (PBA) from polycarbonate (PC) tableware into food simulants [19] is different in the presence and in the absence of AgNPs.

Bisphenol A was chosen because it is a compound released from FCMs that may be present in food [20]. This substance is authorized [10] for use as a monomer in plastic FCMs, with a specific migration limit in food of 0.6 mg kg^{-1}, although the European Union maintains the ban of BPA in PC infant feeding bottles [21]. It is used as a monomer in the manufacture of polycarbonates, which in turn are used in FCMs such as tableware, storage containers or microwave ovenware. BPA displays estrogenic properties and acts as an endocrine-disrupting agent, which constitutes a risk to human health; in fact, its epigenetic properties have been confirmed [22,23].

The determination of BPA in food and food simulants released from FCMs has been reviewed in many papers [20,24–26]; analytical methods used include liquid or gas chromatography coupled to mass spectrometry [27], excitation-emission fluorescence spectroscopy [28], etc. European standard EN 13130-13 [29] specifies a method for the determination of BPA in some food simulants by HPLC-UV, which is applicable at a minimum level of 200 μg per kilogram of food simulant.

In the present work, to study the effect of AgNPs on migration of BPA, clear PC glasses are subjected to different test conditions under which the residual monomer in the polycarbonate could migrate into simulant, thereby releasing BPA. Two food simulants, simulant B (3% acetic acid, w/v) and simulant D1 (50% ethanol, v/v), are used to carry out the migration tests; these food simulants represent acidic (with pH 4.5 or less) and fatty (amphiphilic and milk) foods, respectively [19].

The concentration of BPA released into the simulants is analysed on a population basis rather than on sample measurements because, in practice, it is impossible to carry out a migration test on the same glass in the presence and absence of nanoparticles; the validity of classical location and scatter estimates may be not clear in this case. β-content tolerance intervals [30–32] are used to model the statistical distribution of BPA migrated from the PC glasses into the food simulants. The authors in Ref. [33] already has stated that the migration can be very different from one glass to another.

Experimental measurements are performed by HPLC-FLD, analytical method that makes it possible to reach around 1–2 μg L^{-1} of BPA, well below the specific migration limit in food simulants indicated above, levels necessary in this work given the low released quantities. The determination of BPA is carried out by multivariate calibration through partial least squares (PLS) regression.

2. Experimental

2.1. Reagents and samples

2,2-bis(4-hydroxyphenyl)propane or BPA (CAS no. 80-05-7; 99% minimum purity) is supplied by Aldrich (Saint Quentin Fallavier, France). Silver nanoparticles (CAS no. 7440-22-4; 20 nm, 0.02 mg/mL in 0.002 M sodium citrate) are purchased from Alfa Aesar (Karlsrue, Germany).

Ethanol (96% vol, HiPerSolv Chromanorm) and glacial acetic acid (HiPerSolv Chromanorm) are purchased from VWR (Fontenay-sous-Bois, France). Methanol (LiChrosolv® for liquid chromatography) is supplied by Merck (Darmstadt, Germany). Deionised water is obtained by using the Milli-Q gradient A10 water purification system from Millipore (Bedford, MA, USA).

A stock BPA solution of 1000 mg L^{-1} is prepared in methanol for further dilution. Standards are prepared, from the stock solution, in the appropriate simulant. When appropriate, AgNPs are added to standard solutions to get 33.33 μg L^{-1} of nanoparticles. All these solutions are stored at 4 °C and protected from light.

Clear PC glasses are purchased from a local food store and first analysed by means of Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC) to confirm what material they are made of.

2.2. Instrumental

Analyses are carried out on an Agilent 1260 Infinity HPLC system (Agilent Technologies, Santa Clara, CA, USA) that consists of a quaternary pump VL (G1311C), standard autosampler (G1329B), thermostated column compartment (G1316A) and fluorescence detector (G1321B). The chromatographic column used is a Kinetex® C18 100A (150 mm length × 4.6 mm i.d. 5.0 μm particle diameter) column (Phenomenex, Torrance, CA, USA). A P-Selecta model 210 thermostatically controlled oven is used to incubate the test samples.

2.3. Migration tests

Migration tests are carried out using two aqueous food simulants, simulant B (3% acetic acid, w/v) and simulant D1 (50% ethanol, v/v). Different temperatures and contact times are assessed for the two food simulants, both in the presence and absence of AgNPs (see Table 1). Migration experiments are performed by glass filling with simulant D1 at 74 °C for 24 h (*Experiment_1* and *Experiment_1NP*, in the absence and presence of AgNPs, respectively), with food simulant B at 100 °C for 24 h (*Experiment_2* and *Experiment_2NP*), with simulant D1 at 70 °C for 10 h (*Experiment_3* and *Experiment_3NP*), and with simulant B at 100 °C for 10 h (*Experiment_4* and *Experiment_4NP*). That is, a total of eight migration experiments are carried out, four of them in the presence of AgNPs (those labelled *Experiment_*NP*) and the other four in the absence of them.

A population of 30 PC glasses is considered for each experiment. In most cases, glasses filled with simulant containing AgNPs and with just simulant are intermingled in the oven under the same migration conditions.

Each migration test is performed by filling the PC glasses to within 0.5 cm from the top with food simulant (a volume of 180 mL) and putting them inside the oven in the darkness at a certain temperature during a