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Automatic ionic liquid-enhanced membrane microextraction for the determination of melamine in food samples

Nuno Faustino [a], Paula C.A.G. Pinto [b], Marieta L.C. Passos [a, *], M.Lúcia M.F.S. Saraiva [a, **]

[a] LAQV, REQUIMTE, Department of Chemical Sciences, Laboratory of Applied Chemistry, Faculty of Pharmacy, Porto University, Rua de Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal
[b] A3D-Association for Drug Discovery and Development, Rua do Baixeiro, nº 38, Aveiro, Portugal

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ABSTRACT

An innovative miniaturized automatic methodology for the separation of melamine by a hydrophilic microporous membrane and its quantification is proposed. For that an extraction unit containing a hydrophilic microporous membrane was assembled to the system. In the acceptor solution it was used a 10% ionic liquid aqueous solution, instead of an organic hazardous extractant, with an added advantage of the separation process allows the quantification of melamine in liquid samples without any previous treatment. The melamine potentiated the peroxidase catalyzed oxidation of sesamol by hydrogen peroxide with the formation of a fluorescent compound. The effect of physical and chemical parameters in the extraction process and also in the enzymatic reaction used for the quantification of melamine was evaluated. The developed methodology showed detection and quantification limits of 0.07 and 0.22 mg L^{-1}, respectively, and linear range up to 3.00 mg L^{-1}, allowing accurate quantifications of melamine in the concentrations range imposed by food agencies, in a total analysis time of around 5 min (including the extraction process). The novel methodology was applied to milk, powder milk, soy milk and yogurt samples in a precise and accurate fashion. With the sequential injection analysis tool a simple, versatile, rapid, and robust automatic system was implemented avoiding in batch sample pretreatment. Furthermore, the reduction of chemicals consumption and waste generation fulfilled the current recommendations and trends of Green Chemistry.

1. Introduction

In the last years, the control of residues and contaminants has been considered one of the most important problems in food safety. Since they are considered as hazardous to human health, different analytical methods has been developed in order to identify and quantify them (Romero-Gonzalez, 2015). However, the most part of the instruments cannot directly handle the complex food sample matrices. Thus, the sample preparation step commonly involves an extraction, concentration and clean up processes prior to the detection (Hylton & Mitra, 2007). The solvent extraction is one of the most used processes for sample preparation. However, for that, it is required a large amount of high-purity organic solvents, that are expensive and toxic for humans and for the environment. In the last years, ionic liquids (ILs) have been used as an alternative to organic solvents (Ho, Zhang, Hantao, & Anderson, 2014; Vickackaite & Padarauskas, 2012). They are organic salts with melting point at or below 100 °C, that are composed by an organic cation and an organic or an inorganic anion (Ho et al., 2014). They are presented as good alternatives due to their characteristics such as the negligible vapour pressure, high thermal stability, non-inflammability, good dissolving capacity, simple regeneration, low pollutant effect and tunable viscosity and hydrophobicity (Ma & Hong, 2012; Pedersen-Bjergaard & Rasmussen, 2008; Pei et al., 2012; Vidal, Riekkola, & Canals, 2012). Considering this tunability obtained by combining different anions and cations, it is possible to adjust the properties of the ionic liquid to a specific analyte extraction. Bearing in mind the advantages of ionic liquids and the miniaturization of extraction processes (high sample throughput, low costs, easy operation, and low consumption of sample and solvents), the use of ionic liquids in microextraction processes was reported, for the first time, in 2003 by Liu and co-workers (Liu et al., 2003). Since

* Corresponding author.
** Corresponding author.
E-mail addresses: marietapassos@gmail.com (M.L.C. Passos), lsaraiva@ff.up.pt (M.LúciaM.F.S. Saraiva).

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then, the use of ionic liquids in this kind of procedures and in particular in liquid phase microextraction processes has been increased and frequently reported (Aguilera-Herrador, Lucena, Cardenas, & Valcarcel, 2010; Sun, Li et al., 2010; Vickackaite & Padarauskas, 2012; Zhao & Anderson, 2011). In these works the microextraction with ionic liquid exhibited better extraction efficiency and also a higher enrichment factor, when compared with those obtained with conventional organic solvents extractions (Sun, Li et al., 2010). In addition, the miniaturization of the extraction process allows the procedure automation. It can be achieved by implementing the extraction procedure in a flow analysis system (Decastro, 1986). The incorporation of a liquid-liquid extraction in a flow injection system was made for the first time and simultaneously, by Karlberg and Thelander (Karlberg & Thelander, 1978) and Bergamin et al. (Bergamin, Medeiros, Reis, & Zagatto, 1978). The most relevant advantages of this association are to simplify the assemblies, to improve the reproducibility, to decrease the quantities of sample and extractant solvent that in the most part of the cases is an organic solvent, to decrease the operator exposition to the vapours, to promote a higher determination frequency and to decrease the cost per operation (Decastro, 1986). Among the flow analysis systems, the sequential injection analysis (SIA) system (Ruzicka & Marshall, 1990) has shown to be a useful tool for on-line sample handling and pre-treatment (Economou, 2005), including the extraction processes due to its "modus operandi". This system is based on the bi-directional nature of fluid handling, that allow the implementation of forward-backward flow or stopped-flow that can be explored for the improvement of the extraction efficiency of the analyte into the extractant (Miro, Estela, & Cerda, 2005). In addition, it is controlled by a computer that allows the modification of pertinent analytical parameter at run-time and without physical reconfiguration and the reagent consumption is reduced even when compared with flow injection systems. Thus, the robustness and the versatility of operation of a SIA system guarantee a great potential for the integration of an extraction process and the analysis in the same manifold. Therefore, in this work, it was intended to develop, a SIA system that integrate an in-line microextraction process, using an ionic liquid as extractant. For that it was incorporated in the SIA system an extraction unit equipped with a membrane making possible to separate two bulk phases and control the mass transfer between them. It results in an enrichment of the analyte and its removal from the complex sample matrix. One of the advantages of the membrane use is the facility of extraction without the mixing of the two phases avoiding an emulsion formation (Hylton & Mitra, 2007). In addition, the quantities of solvents are reduced and it is allowed the implementation of continuous and real-time processes, since the sample and the extractant are continuously in contact. This can facilitate an on-line connection of the extraction apparatus with other instruments and the procedures automation (Jonsson & Mathiasson, 1999). Thus, after the development of the automatic ionic liquid −enhanced membrane microextraction process it was intended to apply it in the samples pretreatment and in the quantification of melamine in food samples.

Melamine is a chemical compound commonly used for the fabrication of laminates, filters, adhesives, coating and plastics (Desmarchelier, Cuadra, Delatour, & Mottier, 2009). However, melamine has been unethically added to food products as protein substitute (Attia, Bakir, Abdel-aziz, & Abdel-mottaleb, 2011; Mauer, Chernyshova, Hiatt, Deering, & Davis, 2009). It happens since melamine contains 66% nitrogen by mass (Attia et al., 2011), and standard methods for protein quantification such as Kjeldahl and Dumas tests (Newton & Utley, 1978) are not specific, estimating the protein level by measuring the nitrogen content. Unfortunately, this improper use of melamine was linked with serious illnesses and deaths of Chinese babies that ingested melamine-tinted milk formulas (Li, Qi, & Shi, 2009; Tyan, Yang, Jong, Wang, & Shiea, 2009). It happed since melamine accumulates in the body and cause bladder or kidney stones lead to a renal failure and ultimately to death (F. Sun, Ma et al., 2010). These problems showed the necessity to regulate the maximum residue limits for melamine in various everyday products. The US Food and Drug Administration (FDA) and the European Union established the values of 0.25 mg L^{-1} for milk and dairy products and 2.5 mg L^{-1} for dairy products and high-protein food, respectively. Many other countries, such as Australia and Canada, introduced melamine standard limits of 1 mg L^{-1} for infant formulas and 2.5 mg L^{-1} for other milk products (Sun, Ma et al., 2010). In consequence of this, it became essential to develop new, sensitive, rapid and reliable ways for the quantification of melamine in food samples. In the last years, different methods have been developed using different kinds of detections and sample pretreatments (Broszat, Bramer, & Spangenberg, 2008; Goscinny, Hanot, Halbardier, Michelet, & Van Loco, 2011; Huang, Zheng, & Cooks, 2009; Wang, Jiang, Chu, & Ye, 2010; Wu et al., 2009; Yang et al., 2009; Zhu, Gamez, Chen, Chingin, & Zenobi, 2009), most of them complicated time-consuming procedures and use very expensive instruments. Thus, in this work it was intended to develop an automatic system that incorporate a microextraction process using an ionic liquid as extractant and to apply it, simultaneously, in the samples pretreatment and in the melamine determinations in food. For that, it was intended to introduce the food samples in the SIA system without any kind of pre-treatment. The insertion of the sample should be performed through the extraction unit, where it would be placed a membrane. Thus, the melamine would be extracted from the samples to the acceptor solution using a porous membrane to physically separate the phases. As in another liquid-liquid membrane extractions, the efficiency would be dependent on the concentration gradient of the analyte and would be limited by the partition coefficient (Hylton & Mitra, 2007). Melamine extractions from food samples are commonly carried-out in neutral conditions using acetonitrile-water or methanol-water mixtures (Filigenzi, Puschner, Aston, & Poppenga, 2008; Sun, Ma et al., 2010), but in this work it was intended to replace this organic solvents by an ionic liquid, in order to emphasize its previously described advantages. In addition, the ionic liquid used as acceptor solution, could also improve the enzymatic reaction used for the quantification of the analyte.

Therefore, this system should associate the advantages of the miniaturization, automation, integration of pretreatment and determination procedures and the replacement of organic solvents by ionic liquids, being in agreement with the Green Chemistry demands.

2. Experimental

2.1. Reagents and solutions

All solutions were prepared with analytical reagent grade and high purity water (milipore RG) with a specific conductivity <0.1 μS cm^{-1}.

A 0.1 mol L^{-1} Palitzsch buffer solution with a pH of 8.0 was prepared using the appropriate amount of boric acid (Merck) sodium borate decahydrate (Panreac) and sodium chloride (Riedel-de-Hagën). This buffer solution was used as carrier and to prepare the ionic liquid solution.

The ionic liquid used in this work was 1-butyl-3-metylimidazolium tetrafluoroborate (bmim [BF_4]). A 10% solution was prepared by dilution of the appropriate volume in buffer solution.

The 0.037 mol L^{-1} H_2O_2 solution was daily obtained by dilution in water, of a commercial 30% (w/w) solution (Panreac). The