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Molecularly imprinted polymer grafted to porous polyethylene frits: A new selective solid-phase extraction format

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ABSTRACT

In this paper, a novel format for selective solid-phase extraction based on a molecularly imprinted polymer (MIP) is described. A small amount of MIP has been synthesized within the pores of commercial polyethylene (PE) frits and attached to its surface using benzophenone (BP), a photo-initiator capable to start the polymerisation from the surface of the support material. Key properties affecting the obtainment of a proper polymeric layer, such as polymerisation time and kind of cross-linker were optimised. The developed imprinted material has been applied as a selective sorbent for cleaning extracts of thiabendazole (TBZ), as model compound, from citrus samples. The use of different solvents for loading the analyte in the imprinted frits was investigated, as well as the binding capacity of the imprinted polymer. Imprinted frits showed good selectivity when loads were performed using toluene and a linear relationship was obtained for the target analyte up to 1000 ng of loaded analyte. Prepared composite material was applied to the SPE of TBZ in real samples extracts, showing an impressive clean-up ability. Calibrations showed good linearity in the concentration range of 0.05–5.00 $\mu g\,g^{-1}$, referred to the original solid sample, and the regression coefficients obtained were greater than 0.996. The calculated detection limit was 0.016 $\mu g\,g^{-1}$, low enough to satisfactory analysis of TBZ in real samples. RSDs at different spiking levels ranged below 15% in all the cases and imprinted frits were reusable without loss in their performance.

1. Introduction

In recent years, great advances in analytical instrumentation have occurred allowing eventually the determination of any compound in environmental, food or bio-samples. Typically, target analytes are determined by chromatographic or electrophoretic techniques coupled to a convenient detector such as UV, fluorescence or, more recently, mass spectrometry (MS) or tandem MS. However, even when using the powerful and selective MS detection, direct injections of crude sample extracts are not recommended since matrix components can inhibit or enhance the analyte ionisation, hampering accurate determination. Thus, a clean sample is generally convenient to improve separation and detection, while a poorly treated sample may invalidate the whole analysis. Another additional and valuable aspect of the use of cleaned samples is the reduction of the time to maintain instruments, therefore reducing associated costs. Therefore, sample preparation is still nowadays considered the bottleneck of the whole analytical process [1] and impacts nearly all the later steps in the analytical process, being hence critical for unequivocal identification, confirmation and quantification of analytes.

In this scenario, molecularly imprinted polymers (MIPs) have gained considerable interest as a powerful tool in analytical chemistry thanks to its ability to improve the selectivity of sample treatment process [2–4]. MIPs are tailor made synthetic materials obtained by copolymerising a monomer with a cross-linker in the presence of a template molecule. After polymerisation, the template is removed from the porous polymeric network providing selective cavities that are complementary in size, shape and functionality to the template. MIPs have higher mechanical and thermal stability, as well as very low cost, compared to receptors of biological origin. These distinct advantages enable MIPs to operate under a wide range of conditions, making them a very suitable tool for several analytical techniques, such as solid-phase extraction (SPE) [5], solid-phase microextraction [6,7], chemical sensing [8] and separation techniques [9,10]. Traditionally, MIPs have been prepared by bulk polymerisation, generating particles irregular in shape, size and distribution of binding sites. The process also involves crushing and sieving of the particles, resulting in a tedious process. These problems were partly solved with the preparation of MIPs by precipitation polymerisation, a simple method that allows controlling the morphology of the MIP particles, as well as some physical and chemical properties. MIP beads synthesized by polymerisation within the pores of preformed spherical silica particles, suspension polymerisation or two-step swelling polymerisation are alternative approaches for the obtainment of MIPs. Each of the

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different strategies has their own advantages and disadvantages and a proper selection is determined for each specific application of the polymer. There is a big number of papers describing the different approaches for their preparation, which have been extensively reviewed [2–4,11,12].

However, there is still a growing interest in alternative routes of MIP preparation, in order to better control the morphology of these materials and thus exploit its potential in new applications. Regarding to this, surface imprinting, which sets in place a thin film of imprinted polymer grafted onto the surfaces of suited supports [13] and MIP composite membranes are of special interest [14–16]. Such methodologies can make use of the properties of the support material, and providing them with selective recognition to the analyte of interest. One added advantage of these approaches is the reduction of the reagents consumption and the potential to produce imprinted materials with minimal or no template bleeding.

Keeping these concepts in mind, a novel format of MIP is described. A small amount of MIP has been synthesized within the pores of commercial polyethylene (PE) frits and attached to its surface using benzophenone (BP), a photo-initiator capable to start the polymerisation from the surface of the support material [17]. Parameters affecting the obtainment of the MIP have been properly optimised. The developed new imprinted material has been applied to the extraction of thiabendazole (TBZ) as model compound, in citrus samples. TBZ is a post-harvest systemic fungicide very commonly used to prevent vegetables and fruits, particularly citrus fruits, from deteriorating during storing and transportation. It has been reported the presence of residual TBZ in fruits, even in the edible part [18–20], as well as in other processed fruits, such as orange juices [21,22] and fruit-based soft drinks [23]. Authorities have established the maximum residue levels (MRLs) for TBZ in fruits in the range from 0.05 to 15 mg kg^{-1}, depending upon the type of crop [24]. In the case of citrus fruits, the permitted levels have been established in 5 mg kg^{-1} for TBZ. Only in the last years, several papers have been published reporting analytical methods for the determination of TBZ in citrus samples. Most of them used conventional extraction techniques like liquid-phase extraction [25–27], SPE [28,29], matrix solid phase dispersion [30] or a combination of them, in the so-called method QuEChERS [31,32] (referring to *quick*, *easy*, *cheap*, *effective*, *rugged* and *safe*). The determination of TBZ in aqueous samples by molecularly imprinted-SPE (MISPE) [10,33–35], and in citrus samples by preparing molecularly imprinted stationary phases for HPLC [35,36] and CEC [37] has also been reported. In this paper, a very simple method for the preparation of frits modified with a thin film of MIP, providing them selective recognition properties, is proposed.

2. Experimental

2.1. Chemicals and materials

Thiabendazole (TBZ), methacrylic acid (MAA), ethylene glycol dimethylacrylate (EGDMA), divinylbenzene-80 (DVB), trimethylolpropane trimethacrylate (TRIM) and benzophenone (BP) were obtained from Sigma–Aldrich (Madrid, Spain). MAA was purified by distillation under reduced pressure. EGDMA and TRIM were freed from impurities using an inhibitor remover disposable column from Sigma–Aldrich, and DVB were freed from stabilizers by passing through a small column filled with alumina (Aldrich). HPLC-grade toluene, water, acetonitrile (ACN) and methanol (MeOH) were purchased from Scharlab (Barcelona, Spain). Acetic acid (HOAc) was obtained from Panreac (Barcelona, Spain).

Polyethylene frits (20 μm porosity) for use with 6 mL SPE glass tubes were purchased from Supelco (Bellefonte, PA, USA).

2.2. Polymerisation procedure

The polymerisation procedure is schematically depicted in Fig. 1A. First, a 100 mM solution of BP in MeOH was prepared. PE frits, which had been previously weighted, were connected to a medical needle and immersed in the solution of BP for 30 min. Next, the frits hanging from the needle, with the pores still wetted by this solution, were dipped for 15 s in a vessel containing the polymerisation mixture whose composition is shown in Table 1. Polymerisation was carried out by UV-irradiation at 15 °C for 30 min. The temperature was controlled by a thermostatic laboratory fridge, and irradiation was by means of a UV lamp VL-6-L (Vilbert Lourmat, Marnee La Valle, France) placed at 5 cm from the frits. After irradiation, the template was removed from the imprinted frit (frit-MIP) by Soxhlet extraction for 6 h using a

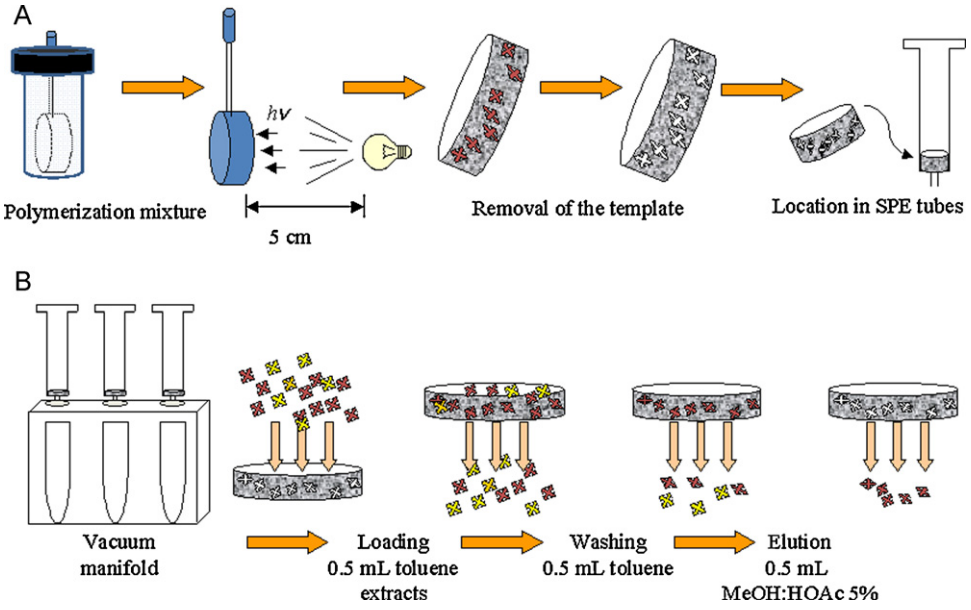

Fig. 1. Scheme of: (A) polymerisation procedure; and (B) selective SPE procedure using imprinted frits.