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Automated multisyringe stir bar sorptive extraction using robust montmorillonite/epoxy-coated stir bars

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ABSTRACT

Herein we present a simple, rapid and low cost strategy for the preparation of robust stir bar coatings based on the combination of montmorillonite with epoxy resin. The composite stir bar was implemented in a novel automated multisyringe stir bar sorptive extraction system (MS-SBSE), and applied to the extraction of four chlorophenols (4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol and pentachlorophenol) as model compounds, followed by high performance liquid chromatography-diode array detection. The different experimental parameters of the MS-SBSE, such as sample volume, selection of the desorption solvent, desorption volume, desorption time, sample solution pH, salt effect and extraction time were studied. Under the optimum conditions, the detection limits were between 0.02 and 0.34 $\mu g\,L^{-1}$. Relative standard deviations (RSD) of the method for the analytes at 10 $\mu g\,L^{-1}$ concentration level ranged from 3.5% to 4.1% (as intra-day RSD) and from 3.9% to 4.3% (as inter-day RSD at 50 $\mu g\,L^{-1}$ concentration level). Batch-to-batch reproducibility for three different stir bars was 4.6–5.1%. The enrichment factors were between 30 and 49. In order to investigate the capability of the developed technique for real sample analysis, well water, wastewater and leachates from a solid waste treatment plant were satisfactorily analyzed.

1. Introduction

Microextraction techniques, are useful tools for sample pretreatment in the analytical chemistry field [1], minimizing the consumption of chemicals, and obtaining greener and safer analytical methodologies. A popular microextraction technique is the stir bar sorptive extraction (SBSE), which is an environmentally friendly, simple and sensitive extraction technique [2]. SBSE allows the extraction and preconcentration of the target analytes by employing a magnetic bar coated with an active extraction layer typically made of polydimethylsiloxane (PDMS, 0.5–1 mm thick). The extraction process is based on the PDMS–water equilibrium and many analytical applications have been described in several reviews [3–7]. In SBSE, the coated magnetic bar is stirred in the sample medium to extract the analytes, which are later thermally desorbed followed by their quantification using GC [8]. An alternative to thermal desorption, is the liquid desorption using a small amount of organic solvent, followed by HPLC analysis for analyte quantification [9]. In the SBSE technique, the properties of the coating of the stir bar will determine the selectivity and extraction performance.

Although SBSE is a sensitive, non-destructive, reliable, robust and generally fast technique for the preconcentration of organic compounds from water samples, a limitation of the SBSE technique is the scarce availability of commercial coated stir bars. Although a big progress has been made on the synthesis of novel coatings for SBSE, the preparation of SBSE coating involving simple and fast steps, and concomitantly obtaining highly robust and durable coatings is still an active research topic in the field of analytical sample preparation [10–13].

On the one hand, epoxy resins are widely used due to their high mechanical properties and resistance [14]. In addition, epoxy resins are usually used as a surface coating material in the industry because of its toughness, flexibility, adhesion and chemical resistance. Epoxy resins are based on crosslinked polymers in which the crosslinking is derived from reactions involving epoxy groups. On the other hand, the layered silicate montmorillonite received much attention as a reinforcing material for polymers because of its high aspect ratio, surface area, swelling behavior, enhanced mechanical properties, thermal stability and unique

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intercalation/exfoliation characteristics [15,16]. The montmorillonite crystal structure consists of layers made of two silica tetrahedra fused to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide [17]. To the best of our knowledge, the potential of a montmorillonite/epoxy-coated stir bar has not been explored yet for SBSE. The incorporation of the layered structure of the montmorillonite into the epoxy resin would be advantageous for SBSE increasing the surface roughness, thus increasing the effective area for extraction of the stir bar.

Furthermore, the automation of microextraction techniques is highly desirable, in order to fully benefit from their advantages [18–20]. Regarding automation, flow analysis techniques have been a valuable tool for the automation of sample preparation both in solid-phase [21–23] or liquid-phase microextraction approaches [24–26]. Among the different flow analysis techniques, the multisyringe flow injection analysis (MSFIA) technique is one of the most versatile [27], combining the multi-channel operation of flow injection analysis with the ability to select the exact volumes of sample and reagents needed for analysis, as it is carried out in the sequential injection analysis technique [28]. The main advantages of the MSFIA technique are high sampling rates, robustness, versatility and low consumption of reagents and samples [29], making this technique advantageous for automated solid-phase extraction and separations using moderate pressures [30,31].

The aim of this work is to develop a novel strategy for the fast preparation of robust and high performance stir bar coatings, for their implementation to evaluate a novel technique for SBSE that we named as multisyringe stir bar sorptive extraction (MS-SBSE). The coating method is simple, fast and cost-effective, and it is based on the preparation of montmorillonite/epoxy composite-coated stir bars. The advantageous features of the prepared composite stir bar, have been explored using MS-SBSE technique, which includes automatic sample loading, extraction and analyte desorption controlled by a programmable MSFIA system. To investigate the extraction capability of the MS-SBSE, four chlorophenols (4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP) and pentachlorophenol (PCP)) were selected as model compounds. Additionally, the selected compounds were extracted from different water samples using the MS-SBSE prior to their quantification using high performance liquid chromatography-diode array detection (HPLC-DAD). Finally, the optimized method was applied to the determination of the selected analytes in different environmental water samples.

2. Experimental

2.1. Chemicals and standard solutions

Methanol (HPLC, ≥99.8%), ethanol (≥99.8%), acetone (≥99.5%), 2,4-dichlorophenol (2,4-DCP, 99%), 2,4,6-trichlorophenol (2,4,6-TCP, >98%), pentachlorophenol (PCP, 97%) and montmorillonite were obtained from Sigma-Aldrich (St. Louis, USA). Other reagents and solvents were also obtained from Sigma-Aldrich and all of them were of analytical grade. 4-Chlorophenol (4-CP, 98%) was obtained from Fluka (Buchs, Switzerland). Commercially available epoxy glue with the trademark of Araldite® was purchased from a local hardware store. The epoxy glue consists of two components (part A: bisphenol *A*-epichlorohydrin epoxy resin (MW < 700), part B: hardener including triethylenetetramine, C18-unsatd, dimmers and polymers with oleic acid).

A stock standard solution of each analyte at a concentration of 1000 mg L^{-1} was prepared in methanol and stored at 4 °C. An intermediate stock solution containing the four chlorophenols at a concentration of 10 mg L^{-1} was prepared by diluting the stock standard solutions in methanol. A working standard solution at a concentration of 1 mg L^{-1} was prepared by diluting the intermediate stock standard solution in water. More diluted working solutions were prepared daily by diluting the working stock standard solution with water. Ultrapure quality water (resistivity >18 MΩ cm) was obtained using a Direct-8 purification system (Millipore, Millipore Iberica S.A.U., Spain). Nitrogen was purchased from Carburos Metalicos S.A. (99.9997% N_2 BIP, Seville, Spain), and it was used to evaporate the extracted analytes prior to analysis by HPLC.

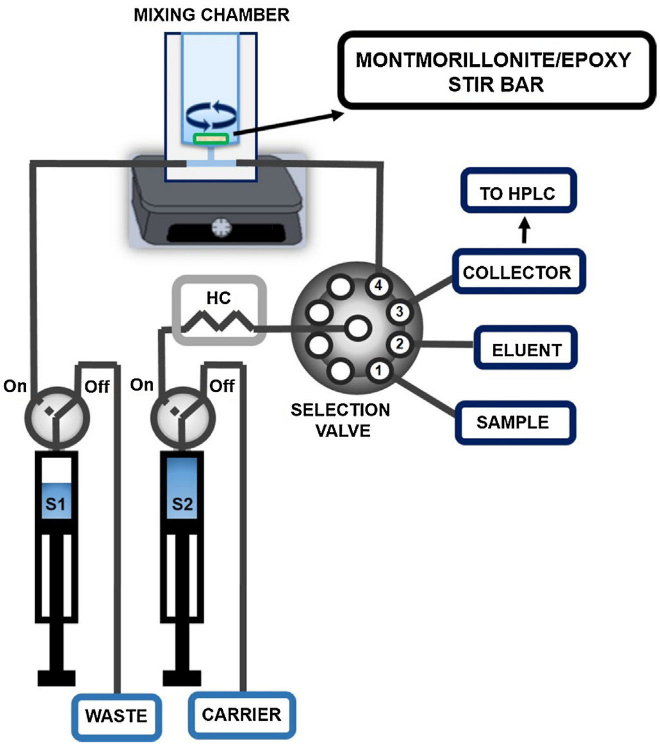

Fig. 1. Schematic diagram of the automated SB-MSFIA system. S1 and S2, 5 mL glass syringes. HC, holding coil.

2.2. Instrumentation

The developed MSFIA set-up consists of a multisyringe pump module (BU4S, Crison Instruments, S.A., Alella, Barcelona, Spain) and an 8-port multiposition selection valve (Sciware Systems S.L., Palma de Mallorca, Spain). The multisyringe burette module was equipped with two 5.0 mL glass syringes (S_1, S_2. Hamilton, Switzerland) driven simultaneously by the same step-by-step motor redirecting the liquid depending on the position of the solenoid valve located at the head of each syringe. S_1 is empty and it is connected (On position) to the mixing chamber with the purpose of quickly drain the sample when the extraction is finished, and subsequently pumps it to a waste reservoir (Off position). S_2 is connected to a water carrier reservoir (Off position) and to central port of the selection valve (On position). The manifold is composed of polytetrafluoroethylene (PTFE) tubes of 0.8 mm of internal diameter (i.d.). The different ports of the selection valve are connected to the sample and eluent reservoirs, the extraction chamber, and a small vial for the collection of the extractant. The S_1 and the selection valve are connected using a holding coil made of PTFE 1.6 mm id, with a volume of 4 mL.

The mixing chamber used for the solid-phase extraction exploiting the MS-SBSE was made of poly(methyl methacrylate). The homemade cell consists of a hollow cylinder with an inner diameter of 1.40 cm and a height of 2.80 cm with a volume of 3.7 mL.