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Selective extraction of triazine herbicides based on a combination of membrane assisted solvent extraction and molecularly imprinted solid phase extraction

Luke Chimuka [a], Manuela van Pinxteren [b], Johan Billing [c], Ecevit Yilmaz [c], Jan Åke Jönsson [d,*]

[a] School of Chemistry, University of the Witwatersrand, Private Bag 3, WITS, 2050 Johannesburg, South Africa
[b] Department of Analytical Chemistry, Helmholtz Centre for Environmental Research-UFZ, Permoserstrase 15, 04318 Leipzig, Germany
[c] MIP Technologies AB, P.O. Box 737, S-22007 Lund, Sweden
[d] Center of Analysis and Synthesis, Department of Chemistry, University of Lund, P.O. Box 124, S-22100 Lund, Sweden

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ABSTRACT

A selective extraction technique based on the combination of membrane assisted solvent extraction and molecularly imprinted solid phase extraction for triazine herbicides in food samples was developed. Simazine, atrazine, prometon, terbumeton, terbuthylazine and prometryn were extracted from aqueous food samples into a hydrophobic polypropylene membrane bag containing 1000 μL of toluene as the acceptor phase along with 100 mg of MIP particles. In the acceptor phase, the compounds were re-extracted onto MIP particles. The extraction technique was optimised for the type of organic acceptor solvent, amount of molecularly imprinted polymers particles in the organic acceptor phase, extraction time and addition of salt. Toluene as the acceptor phase was found to give higher triazine binding onto MIP particles compared to hexane and cyclohexane. Extraction time of 120 min and 100 mg of MIP were found to be optimum parameters. Addition of salt increased the extraction efficiency for more polar triazines. The selectivity of the technique was demonstrated by extracting spiked cow pea and corn extracts where clean chromatograms were obtained compared to only membrane assisted solvent extraction or only molecularly imprinted solid phase extraction. The study revealed that this combination may be a simple way of selectively extracting compounds in complex samples.

1. Introduction

Sample preparation and clean up steps are of paramount importance prior to analysis of triazines in plant materials because of the many interferences found in such samples. One such technique for sample preparation is liquid–liquid extraction (LLE) which is now less popular because of its drawbacks of being time consuming, not easy to automate and consuming large quantities of organic solvents [1]. Other alternative sample preparation techniques for aqueous samples are solid-phase extraction (SPE) [2], solid-phase microextraction (SPME) [3], stir bar sorptive extraction [4] and membrane extraction [5–7].

Membrane based extraction [5–7] techniques and techniques using selective sorbents such as molecularly imprinted polymers (MIPs) [8,9] in solid-phase extraction are attractive for plant samples for a number of reasons. In membrane extraction, because the membrane is nonpolar, any polar or charged matrices are prevented from diffusing to the acceptor side. Further, neutral macromolecules have slow mass transfer across membrane and in somes cases, depending on the pore size, may be excluded altogether. Membrane based extractions also use very little organic solvents and are in most cases cheap and simple to use.

MIPs are known to be much more selective than other SPE media since analyte extraction is based on the size, shape and structure [8,9]. A number of researchers have therefore used MIP based sorbents for selective extraction of organic compounds from various complex samples giving desired selectivity [9–12]. In some cases, the use of MIP sorbents [13] alone may not give the desired selectivity for plant materials because of the complexity of such samples. Thus, a two step extraction approach was reported by Cacho et al. [13], in which the plant materials were first extracted on the non-imprinted polymer (NISPE) followed by on a molecularly imprinted polymer sorbent (MISPE).

A combination of supported liquid membrane extraction (SLM) and molecularly imprinted polymers has been reported by Mhaka et al. [14], in trying to increase the selectivity in extracting plant materials. In the work of Mhaka et al. [14], MIPs were incorporated as part of the acceptor phase that contained toluene as a solvent. The solvent was also impregnated in the pores of a hydrophobic flat sheet membrane that separated the acceptor and donor phases. The combination resulted into good selectivity compared to SLM extraction alone or SLM-NIP combination. However, no comparison

* Corresponding author. Tel.: +46 46 222 8169.
E-mail address: Jan_Ake.Jonsson@organic.lu.se (J.Å. Jönsson).

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between the MISPE and SLM-MIP combination was made. Further, the set-up was designed in such a way that only the bottom part of the membrane was in contact with the stirred sample. This limited the mass transfer of the compounds from the sample into the acceptor side. After extraction, the separation of the MIP particles from the rest of organic solvent was performed by passing the entire extract into a 0.1 μm syringe filter where the particles were retained. This was followed by subsequent washing and elution of the trapped analytes. This procedure of separating the MIP particles from the bulk acceptor solvent was found to be not very efficient.

In order to minimise some of the problems experienced in SLM-MIP combination, instead a combination of membrane assisted solvent extraction (MASE) and molecularly imprinted polymers is proposed. The MASE technique [7,15–19] which involves a dense polypropylene bag is ideal for incorporating MIP particles as part of the acceptor solution. Since it is in the form of a bag, the mass transfer of analytes from the sample is not limited to only one direction. Instead of passing MIP particles and bulk acceptor solvent through a 0.1 μm syringe filter in order to separate the two as reported by Mhaka et al. [14], a convenient way using empty cartridges and solid phase extraction unit was used. The MASE–MISPE combination was tested by extracting cowpea and baby corn plant materials.

2. Experimental

2.1. Chemicals

Simazine, atrazine, prometon, terbumeton, terbuthylazine and prometryn were purchased from Sigma–Aldrich (Darmstadt, Germany). Organic solvents were also from Sigma–Aldrich. All other chemicals used were of analytical grade.

2.2. HPLC of triazines

The HPLC system used was from Hewlett Packard (model 1050, Palo Alto, CA, USA). It incorporated an autosampler set to an injection volume of 5 μL and a UV detector set to 230 nm for detection of triazines. Agilent Chemstation software was used for acquiring of the data. A C_{18} Hypersil column (2.1 mm × 150 mm, 5 μm) from Supelco (Darmstadt, Germany) was used. The mobile phase was composed of 30% acetonitrile and 70% water pumped with a flow rate of 0.2 mL min^{-1}. A stock solution of each triazine was prepared in acetonitrile at a concentration of 1 g L^{-1}. From this a working stock solution consisting of 300 mg L^{-1} of each triazine as mixture was prepared. External calibration was made with samples of 100, 250, 500 and 2000 μg L^{-1} of each triazine mixture.

2.3. MIPs, membrane bags and other accessories

MIP particles for triazines were supplied by MIP Technologies AB (Lund, Sweden) along with NIP particles (both are part of the ExploraSep™ screening library, the MIP is designated A31 and the NIP is designated A32). Empty 3 mL cartridges with frits 10 μm, were from Sorbent AB (Frölunda, Sweden). Membrane bags and their accessories were supplied by Gerstel (Mülheim, Germany).

2.4. MASE preparation

The MASE device has been described in previous publications [15–19]. The membrane extraction cell consisted of a 20 mL headspace vial filled with 18 mL of aqueous sample. The membrane bag (4 cm long, 0.03 mm wall thickness, 6 mm internal diameter) was attached to a metal funnel and fixed with a PTFE ring. The material of the membrane bag is dense polypropylene. Before extraction, the membrane bags with their metal cylinders were preconditioned in 40 mL cyclohexane by shaking overnight at 160 rpm. After 3 h, the cyclohexane was replaced with fresh cyclohexane. The extraction cell caps were preconditioned by shaking them in cyclohexane for 3 h. Thereafter, both the caps and membrane bags were dried at room temperature. The membrane bags were dried by putting them upside down through clean Pasteur pipettes. The same glass tubes were used to make sure that the membrane bags were filled with cyclohexane during the preconditioning stage. When cyclohexane was not used as the organic acceptor solvent in the extraction, the dried membrane bags were soaked in the respective solvent for about 2 h and dried again before extraction. The assembled membrane bag was tested for any leakages at the joints by pipetting inside 1000 μL of extraction solvent. The membrane bag with organic solvent was placed inside the extraction cell containing the aqueous sample and stirrer (MASE only) or MIP particles added into the organic acceptor solvent (MASE–MISPE combination). Any organic solvent on the outside of the bag was wiped with a tissue before putting the bag in the sample.

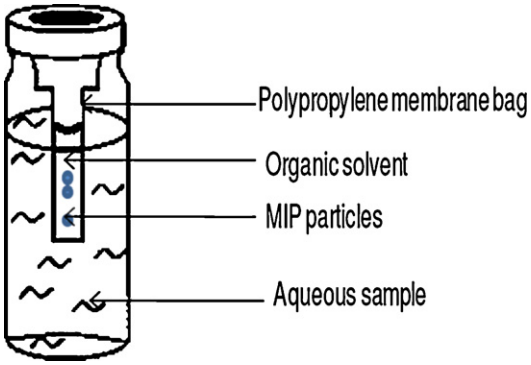

Fig. 1. Schematic representation of a MASE-MIP combination.

2.5. Extraction procedure with MASE–MISPE technique

100 mg of MIP particles was placed inside the membrane bag filling about two thirds of the volume followed by 1000 μL of toluene. The membrane bag was then compressed with clean gloves so as to mix the organic solvent with MIP particles. The membrane bag was placed in the extraction cell containing 18 mL of aqueous sample saturated with sodium chloride and stirrer (Fig. 1). The extraction proceeded for 120 min. At least three parallel extractions were performed simultaneously.

After extraction, the acceptor content was transferred into a 3 mL empty cartridge with a filter at the bottom and mounted onto solid phase extraction unit. As the bags are quite stiff, they can easily be handled manually and easily be rinsed with fresh 1000 μL toluene for quantitative transfer of MIP particles onto the cartridge. The outside of the membrane bag was rinsed with deionised water to remove any salts while wet. Toluene was separated from MIP particles by opening the SPE valve slowly and allowing it to flow out by gravity at about 0.5 mL min^{-1}. The membrane bag was then washed with 1000 μL of dichloromethane which was also passed into the cartridge containing the MIP particles. Thereafter, a full vacuum was applied for 2 min. The trapped analytes were eluted with 3× 1000 μL fractions of methanol. The first two portions of methanol were also used to rinse the membrane bag for any remaining MIP particles and then transferred into the cartridge. Between elutions, methanol portions were allowed to pass completely through the cartridge. The combined extracts were either analysed directly or reduced to almost dryness with gentle stream of nitrogen and then made up with 500 μL of methanol.

The used membrane bags, still attached to the metal funnels were then soaked into about 40 mL of acetonitrile or in combi-