Analytical Chemistry Research 10 (2016) 28–32

Contents lists available at ScienceDirect

Analytical Chemistry Research

journal homepage: www.elsevier.com/locate/ancr

Towards coupling dispersive liquid-liquid microextraction with hollow fibre liquid phase microextraction for extraction of organic pollutants of agricultural origin

Thabiso Letseka, Mosotho J. George*

Department of Chemistry and Chemical Technology, National University of Lesotho, P.O. Roma 180, Lesotho

ARTICLE INFO

Article history:
Received 14 September 2016
Received in revised form
3 November 2016
Accepted 3 November 2016
Available online 9 November 2016

Keywords:
Dispersive liquid-liquid microextraction
Liquid phase microextraction
Coupling
Mixed-solvents
Agro-chemicals
River water

ABSTRACT

Liquid-based miniaturized techniques have received a lot of attention recently resulting in the development of the liquid phase microextraction (LPME) and dispersive liquid-liquid microextraction (DLLME) techniques each offering unique benefits over the other technique. Herein we report a combination of the two techniques for the extraction of hexestrol and atrazine from aqueous systems. The method sets off with the DLLME thereafter a hollow fibre filled with the organic solvent is introduced for the extraction of the pre-extracted analytes in the dispersed organic solvent. The method was modified further by introducing a second extracting solvent in place of the disperser solvent. Under the optimum conditions, namely, toluene in the acceptor phase, 1:1 chloroform:toluene (v/v) as a dispersed solvent, 15% NaCl, with the 15 min extraction time, the method achieved satisfactory enrichment factors (87- and 62-fold); sufficiently low detection limits of 0.018 μg/mL and 0.016 μg/mL using the flame ionization detector, while 0.072 and 0.063 ng/mL were obtained using single ion monitoring mass spectrometry detector, for atrazine and hexestrol, respectively; with sufficient linearity ($R^2 \geq 0.9959$). Although the compounds were not detected in the river water sample, satisfactory recoveries (111–115%) were achieved indicating the method did not suffer any negative matrix effect.

1. Introduction

As the search for ways of improving the quality of life in general, new chemicals enter the fore. The most common among these chemicals are agro-chemicals, such as pesticides and fertilizers that are used to improve agricultural production. However, these chemicals end up in places that they were not intended to be where they pose a challenge to environmentalists, public health practitioners and analytical chemists [1,2]. Since some of these chemicals have a potential to bio-accumulate [3], it is important for environmentalists to keep up with the pace at which these chemicals are being produced, so that they can be detected even in the ultra-trace level concentrations to help mitigate their build-up in the eco-system. Sadly, the adoption of the newly developed techniques into the official methods is reportedly very slow, thus worsening the state of pollution from these chemicals [4].

The role of analytical chemists in this conundrum is to develop new efficient, robust and affordable methods that can be applied for the analysis of these important chemicals. Of the two main aspects, namely, instrumental development and sample preparation, the latter is the most feasible to the poorly resourced economies where technological advancement is not at its best. Sample preparation techniques have a capacity to improve the detectability of the otherwise, non-detectable compounds through either converting them to analysable derivatives or pre-concentration to the detectable levels. To this effect, there are mainly two classes based on the physical states of the materials used, namely, solid-based and liquid-based techniques.

In an effort to replace the copious amounts of the hazardous organic solvents used in liquid-based techniques, a solid-based technique commonly known as solidphase extraction was developed which later gave rise to its miniaturised form - solidphase micro-extraction [5]. Similar strides have been made in the liquid-based techniques leading to the establishment of the three main classes of miniaturised liquid-based techniques: drop-based techniques [6], membrane-supported [7] techniques and lately the dispersed solvent-assisted techniques [8]. Each of these techniques

* Corresponding author. Fax: +266 2234 0000.
E-mail addresses: letsekathabby@gmail.com (T. Letseka), jm.george@nul.ls, maluti2005@gmail.com (M.J. George).

http://dx.doi.org/10.1016/j.ancr.2016.11.001

has been a focus of studies resulting in the birth and evolution of different formats. The drop-based techniques have arguably seen more evolution resulting in the following different formats: drop-to-drop variants [9], freely suspended droplet [10], film-based extraction [11] and the bubble-assisted variants [12,13]. Despite this evolution, the drop-based techniques have not yet been officially accepted for broad application for routine analysis arguably due to its manual intensity requiring good hand-eye coordination to carefully pipette immiscible layers of similar appearance [14].

Liquid-phase microextraction (LPME) is a good candidate for the application in complex matrices like environmental samples given that the membrane already acts as a selective sampler by providing some degree of size exclusion depending on the pore size irrespective of the affinity of the acceptor/extracting phase for the analytes, thereof. On the other hand, dispersive liquid-liquid microextraction (DLLME) offers the unbeatably quick extraction rates although sadly this is accompanied by extensive human manipulation leading to extra steps that could be a gateway for inadvertent contamination, sample loss and poor automation. Interestingly, there are no reports where any of these somewhat seemingly complementary variants have been combined safe for an approach where a somewhat modified dispersive liquid-liquid microextraction was coupled to headspace SPME extraction, using the pre-dispersed solvent to drive the analytes into the headspace for eventual sampling with the SPME fibre [15], and another one where the pre-dispersed solvent was separated into a different vial and evaporated completely and sampled with the SPME for eventual analysis [16]. Herein we report the attempt to couple LPME with the DLLME where the hollow fibre is directly immersed in to the aqueous solution containing hexestrol and atrazine as model analytes whose introduction into the environment is linked to agricultural practices. The modification takes advantage of the fast extraction kinetics of the DLLME while eliminating the extra steps required in DLLME such as precipitating the solvent after the extraction.

2. Experimental

2.1. Chemical and standard solutions

Atrazine (1-Chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine, CAS 1912-24-9) was purchased from (Chem Service, Pennsylvania, USA), hexestrol (4,4′-(1,2-diethylethylene) diphenol, CAS 84-16-2) was obtained from Dr Ehrenstorfer GmbH (Augsburg, Germany), diphenylamine was obtained from Sigma Aldrich (Johannesburg, South Africa) while all the HPLC grade solvents: methanol, toluene, chloroform were obtained from Riedel-de Haën (Seelze, Germany). NaCl was obtained from ACE (Johannesburg, South Africa). The distilled water was prepared in-house. The Accruel Q3/2 PP polypropylene hollow fibre membrane with the dimensions of 600 μm (internal diameter) × 200 μm (wall thickness) × 0.2 μm pore size was obtained from Membrana GmbH (Wuppertal, Germany) and cut in 1-cm strips using a measuring ruler and a pair of scissors.

The standard solution of the concentration 10 mg/mL was prepared by dissolving the pre-weighed amounts of the standards in 1-mL ethanol. This solution was diluted serially to achieve lower concentrations as necessary using the same ethanol or water. All the solutions were stored in the refrigerator at temperature below 5 °C when not in use.

2.2. Instrumentation

Most of the development work was carried out using a Varian 3800 Gas Chromatograph (California, USA) equipped with a flame ionization detector and a 30 m × 1 μm × 0.53 mm SGE-BP5 (5% phenyl-95%dimethyl-polysiloxane) capillary column (Texas, USA). Nitrogen gas (5.0 Grade) was used as a carrier gas and maintained at 5 mL/min while hydrogen and air were used for the detector. The injector and detector temperature were set at 250 °C and 200 °C respectively. The column was held at 100 °C for 2 min, then ramped at 20 °C/min to 300 °C and held for 3 min to achieve a total run time of 15 min.

For the low level concentrations and validation experiments, a Shimadzu QP2010 GC-MS (Kyoto, Japan) fitted with an Rtx-5ms capillary column of 30 m × 0.25 mm × 0.25 μm dimensions was used with the same gas chromatograph settings as above. The mass spectrometer settings included the electron impact voltage of 70 eV with acquisition carried out relative to the tune file, the ion source temperature set 200 °C and the interface set 240 °C. Initially the acquisition was set on full scan with the *m/z* values in the range 50–350 for identification, followed by selected ion monitoring using the *m/z* values 135 (207,107) for hexestrol and 200 (205) for atrazine, the values in the parentheses representing the qualifying ions.

2.3. Water samples

Two water samples were collected in 50-ml Schott bottles from Liphiring River running about 3–4 km North West of the Roma campus few meters upstream of the road bridge to avoid potential pollution from the traffic. These samples were stored in a refrigerator at 5 °C. There was no sample preparation steps undertaken to the water samples except employing the optimized conditions are set out in the prior sections: addition the ideal amount of NaCl, chloroform and toluene to obtain optimum extraction conditions. Thereafter these samples were spiked with the analytes and the recovery was determined thereof.

2.4. Extraction procedure

For the extraction, firstly the aqueous sample of the mixture of the analytes was spiked with an organic solvent (toluene) and shaken vigorously to achieve homogeneity. Thereafter it was allowed to stand as the 1 cm long hollow fibre membrane filled with the extracting solvent (pre-spiked with the diphenylamine internal standard) fitted at the tip of the Hamilton® syringe was introduced carefully into the solution. After the extraction time had elapsed, 3 μL was withdrawn and injected into the gas chromatograph for analysis. Different parameters, namely, effect of the dispersed organic solvent, effect of changing disperser solvent with the second extracting solvent, effect of ionic strength, extraction time were assessed for their effect on the extraction in a univariate fashion.

The optimized method was further assessed for repeatability (both inter- and intra-vial), linearity, limits of detection as well as its applicability to field samples using a river water sample. All the analyses were carried out in triplicate unless otherwise stated under the relevant section of the results and discussions.

3. Results and discussions

3.1. Optimization of extraction conditions

3.1.1. Determination of the effective organic solvent volume

From the chemical structures of the compounds toluene was deemed the most suitable of the available solvents owing to the aromatic ring in the analytes, together with its water immiscibility. The task was then to determine the optimum volume of toluene that would effectively extract and preconcentrate the analytes.