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Comparison of a disposable sorptive sampler with thermal desorption in a gas chromatographic inlet, or in a dedicated thermal desorber, to conventional stir bar sorptive extraction-thermal desorption for the determination of micropollutants in water

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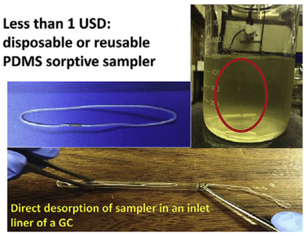
HIGHLIGHTS

- Low cost (less than 1 USD) disposable/reusable PDMS sorptive loop sampler.
- Direct thermal desorption of sampler in GC inlet of 2DGC-TOFMS, cryogenics not required.
- Comparison of the loop sampler to commercial stir bar sorptive extraction.
- Comparison of thermal desorption in a GC inlet to a dedicated thermal desorber.

GRAPHICAL ABSTRACT



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ABSTRACT

The presence of micropollutants in the aquatic environment is a worldwide environmental concern. The diversity of micropollutants and the low concentration levels at which they may occur in the aquatic environment have greatly complicated the analysis and detection of these chemicals. Two sorptive extraction samplers and two thermal desorption methods for the detection of micropollutants in water were compared. A low-cost, disposable, in-house made sorptive extraction sampler was compared to SBSE using a commercial Twister sorptive sampler. Both samplers consisted of polydimethylsiloxane (PDMS) as a sorptive medium to concentrate micropollutants. Direct thermal desorption of the disposable samplers in the inlet of a GC was compared to conventional thermal desorption using a commercial thermal desorber system (TDS). Comprehensive gas chromatography coupled to time-of-flight mass spectrometry (GC × GC-TOFMS) was used for compound separation and identification. Ten micropollutants, representing a range of heterogeneous compounds, were selected to evaluate the performance of the methods. The in-house constructed sampler, with its associated benefits of low-cost and disposability, gave results comparable to commercial SBSE. Direct thermal desorption of the disposable sampler in the inlet of a GC eliminated the need for expensive consumable cryogenics and total analysis time was greatly reduced as a lengthy desorption temperature programme was not required. Limits of detection for the methods ranged from 0.0010 ng L^{-1} to 0.19 ng L^{-1}. For most compounds, the mean ($n = 3$) recoveries ranged from 85% to 129% and the % relative standard deviation (% RSD) ranged from 1% to 58% with the majority of the analytes having a %RSD of less than 30%.

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1. Introduction

Micropollutants, also referred to as emerging contaminants, comprise of an ever expanding range of anthropogenic and natural substances [1]. The presence of micropollutants, such as pharmaceuticals, personal care products (PCPs), steroid hormones, industrial chemicals, pesticides and endocrine disrupting chemicals (EDCs), in the aquatic environment is a worldwide environmental concern [1,2]. Long- and short-term toxicity of drinking water, endocrine disrupting effects and antibiotic resistance of microorganisms are some of the examples of the adverse effects associated with emerging contaminants in the aquatic environment [2]. The diversity of micropollutants and the low concentrations ($\mu g\ L^{-1}$ to $ng\ L^{-1}$) at which they occur in aquatic systems have significantly complicated analyses of these chemicals [1,2]. Water quality standards and contaminant guidelines do not exist for the majority of micropollutants, due to the challenges posed by the analysis and detection thereof [1]. However, recent advances in analytical chemistry and instrumentation have enabled the detection of vast ranges of micropollutants at trace level, resulting in increased public awareness and facilitation of the legislation process [2].

Currently, the most common extraction technique used for monitoring micropollutants in environmental water samples is solid phase extraction (SPE) employed together with gas chromatography (GC) or liquid chromatography (LC) coupled to mass spectrometry (MS) or tandem mass spectrometry (MS/MS) [2,3]. However, new, efficient and inexpensive analytical methods are necessary for on-going environmental monitoring and evaluation [4]. Several research groups have shifted their focus from adsorbents, such as SPE, to another class of materials, namely sorption materials [5]. Combining sample extraction, purification, and enrichment, using approaches such as solid phase microextraction (SPME) and stir bar sorptive extraction (SBSE), has moved sample preparation towards a more “green”, i.e. solvent free, approach [6]. SPME and SBSE are commercial solvent free sorptive extraction techniques. SPME was introduced in 1990 by Arthur and Pawliszyn [7] to address the need for rapid sample preparation in the laboratory and on-site [8]. The potential sensitivity drawback due to low sorptive volumes of SPME samplers was overcome with the introduction of SBSE (developed by Baltussen and Sandra in 1999) [9]. Polydimethylsiloxane (PDMS) is currently the most popular sorbent material. It is an apolar 100% methyl substituted siloxane polymer [5]. The popularity of PDMS is due to its: (1) inertness, therefore reducing analyte loss due to irreversible adsorption or catalytic (surface) reactions, (2) retention data for many compounds are widely available, (3) PDMS synthesis is moderately simple leading to reproducible properties and consistency between manufacturers, and (4) the degradation products are well known and can easily be identified by mass spectrometry [5]. Various researchers have employed the advantages of PDMS to develop new samplers. Triñanes, Pena, Casais and Mejuto (2015) developed disposable silicone disks for the detection of polyaromatic hydrocarbons (PAHs) in water samples [10]. Naudé and co-workers developed a PDMS loop sampler for solvent free extraction of soil [11,12]. The same sampler was also used by Naudé et al. (2015) as a passive sampler to concentrate pollutants from surface water [13]. Recently, the loop sampler was used to quantitatively extract endocrine disrupting compounds (EDCs) from surface water [14]. When developing customized samplers the use of bulk, relatively inexpensive, PDMS gives the user control over the choice of sorbent volume and preparation of application specific sorptive samplers. The low cost of the sorbent material allows the employment of a new sampler for each extraction thereby avoiding difficulties with carry-over and cross contamination [10]. The hydrophobicity of PDMS enables high recovery of hydrophobic compounds. In order to increase the recovery for polar compounds, Ochiai et al. (2008) developed a sequential salting out extraction procedure for multi-residue analysis [15].

In order to overcome sensitivity shortcomings of liquid extraction techniques, due to the injection of only an aliquot of the extract into the analytical instrument, sorptive sampling techniques coupled to thermal desorption (TD), in combination with GC, are more often being used [5,16]. During TD volatile and semi-volatile organic compounds are desorbed from the sorptive material, either directly in a heated capillary GC injection port liner [17], or in a stainless-steel or glass tube in a thermal desorber system [18,19]. Heat is applied followed by direct introduction of the compounds into the GC injection port via a heated transfer line (in the case of a thermal desorber system). The technique is solvent free and can be automated [20]. Comprehensive two-dimensional gas chromatography (GC × GC) is a powerful tool that aids in the determination of a vast number of compounds in a complex matrix during a single analysis [21]. It realizes better resolution (increased selectivity), higher sensitivity and larger peak capacity compared to the conventional one-dimensional GC [22,23]. The increased resolving power and enhanced sensitivity make GC × GC extremely useful in detecting targeted and non-targeted trace-level components in complex samples [24].

We report a comparison of conventional SBSE-thermal desorption to extraction using an in-house developed, disposable PDMS loop sorptive sampler with thermal desorption thereof directly in the inlet liner of a GC (an approach used by Bicchi, Iori, Rubiolo and Sandra (2002) with SBSE [17]), or in a dedicated themal desorber, followed by analysis with comprehensive two-dimensional gas chromatography and time-of-flight mass spectrometry (GC × GC-TOFMS) for the detection of micropollutants in surface water. Ten micropollutants representing diverse classes, including pesticides, personal care products and pharmaceuticals commonly occurring in surface water were selected to evaluate the performance of the methods in terms of linearity, limits of detection (LODs), limits of quantification (LOQs), accuracy and precision.

2. Materials and methods

2.1. Chemicals

Methanol (MeOH), *n*-hexane, toluene, de-ionised water, acetonitrile (ACN), acetone and sodium chloride (NaCl) were all purchased from Merck, South Africa. Certified reference standards were used. Caffeine solution ($1.0\ mg\ mL^{-1}$ in MeOH), atrazine (PESTANAL, analytical standard, purity 98.8%), chlorpyrifos (PESTANAL, analytical standard, purity 99.7%), musk ketone solution ($100\ ng\ \mu L^{-1}$ in acetonitrile, analytical standard, $95\ ng\ \mu L^{-1} \pm 5\%$), lindane (PESTANAL, analytical standard, purity 99.8%), metolachlor (PESTANAL, analytical standard, purity 97.6%), terbuthylazine (PESTANAL, analytical standard, purity 99.4%) and bifenthrin (PESTANAL, analytical standard, purity 98.8%) were all purchased from Fluka Analytical, Sigma-Aldrich, South Africa. Terbutryn (purity 98.1%) was purchased from Supelco Analytical, Sigma-Aldrich, South Africa. 4-tert-Amylphenol (purity 99.5%) was purchased from Dr. Ehrenstorfer, Augsburg, Germany.

Structures of target analytes and corresponding molecular formulas, nominal masses and log K_{ow} values are given in Fig. 1.

2.2. Standard solutions

Individual stock solutions of $100\ ng\ \mu L^{-1}$ were prepared by dissolving 5 mg powder in 50 mL (or 2.5 mg powder in 25 mL) of methanol or toluene depending on their solubility. All the stock solutions were stored in glass vials and kept at 4 °C. Working