Analytica Chimica Acta 1006 (2018) 33–41

Contents lists available at ScienceDirect

Analytica Chimica Acta

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

A fully automated analytical platform integrating water sampling-miniscale-liquid-liquid extraction-full evaporation dynamic headspace concentration-gas chromatography-mass spectrometry for the analysis of ultraviolet filters

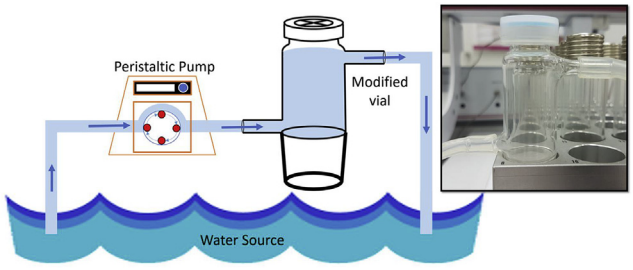
Christina Shu Min Liew [a, b], Xiao Li [c], Hong Zhang [b], Hian Kee Lee [a, b, d, *]

[a] NUS Graduate School for Integrative Sciences and Engineering, National University of Singapore, Centre for Life Sciences #05-01, 28 Medical Drive, Singapore 117456, Singapore
[b] Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore
[c] Gerstel LLP, The Alpha #02-18, 10 Science Park Road, Singapore 117684, Singapore
[d] National University of Singapore Environmental Research Institute, T-Lab Building #02-01, 5A Engineering Drive 1, Singapore 117411, Singapore

HIGHLIGHTS

- A fully automated sampling-sample preparation-analysis platform was developed.
- Automated water sampling was setup using a modified vial and a peristaltic pump.
- Miniscale-LLE and full evaporation DHS extraction was combined with GC-MS.
- Derivatization step could even be included in the sample preparation step.
- High recoveries of test analytes UV filters were achieved.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 October 2017
Received in revised form
7 December 2017
Accepted 24 December 2017
Available online 5 January 2018

Keywords:
Miniscale liquid-liquid extraction
Full evaporation dynamic headspace
Online water sampling
Automation
Sample preparation
UV filters

ABSTRACT

A fully automated analytical platform that seamlessly integrates online water sampling-sample preparation-gas chromatography-mass spectrometry (GC-MS) was developed for ultraviolet (UV) filters in this work. The online water sampling system consisted of a conventional sample vial (slightly modified to have both inlet and outlet ports), two tubings and a peristaltic pump, which controlled the water flow into and out of the vial. The sample preparation segment consists of miniscale liquid-liquid extraction (msLLE), coupled to full evaporation dynamic headspace concentration (FEDHS) on a commercial dual-arm autosampler. The extract from the msLLE step was subjected to a derivatization step, before being passed through a Tenax TA sorbent tube at the FEDHS stage. UV filters were used as model compounds in this work due to their potential endocrine and developmental toxicities, including benzhydrol, 2-ethylhexyl salicylate, homosalate, 2-hydroxy-4-methoxybenzophenone, 3-(4′-methylbenzylidene) camphor and benzophenone. The analytes (of which the first four underwent derivatization, by virtue of them possessing hydroxyl groups, but not the last two) were concentrated on the sorbent, and were thermally desorbed before being introduced to the GC-MS system for analysis. An orthogonal array design (OAD) strategy was employed to facilitate the optimization of the msLLE and derivatization factors

* Corresponding author. Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore.
E-mail address: chmleehk@nus.edu.sg (H.K. Lee).

https://doi.org/10.1016/j.aca.2017.12.035
0003-2670/

while univariate optimization was performed for FEDHS. The optimized settings achieved low limits of detection (0.6–9.7 ng L^{-1}) with good linearity ($r^2 \geq 0.9926$), and satisfactory absolute extraction recoveries (62.0%–80.7%) were obtained. The fully automated online water sampling-extraction/concentration-detection approach was demonstrated by applying it to the analysis of swimming pool water. Relative recoveries of the analytes in the pool water ranged from 85.4% to 118.2%. The described procedure has the potential to be a fully automated online water sampling-msLLE-FEDHS-GC-MS platform for the purpose of conducting routine onsite water analysis.

1. Introduction

In environmental water analysis where conventional sample preparation methods such as liquid-liquid extraction and solid-phase extraction are used, large volumes (>500 mL) of sample are usually required to be transported from the field to the laboratory [1,2]. This can incur significant cost and logistical issues, including manpower, which is undesirable. There has been some research done in the area of continuous sampling in order to minimize the manual labor involved in collecting samples, particularly for microextraction procedures. For instance, Eisert and Levsen developed a quasi-continuous sampling of aqueous samples through the use of a self-constructed flow-through cell and an automated solid-phase microextraction (SPME) unit coupled to gas chromatography (GC) [3]. The setup involved continuous pumping of the sample through the flow-through cell, mounted on a GC autosampler carousel via a peristaltic pump. The SPME fiber was dipped into the flowing sample at regular intervals for sampling, and then withdrawn and introduced automatically into the GC injector. This setup was stated to have great potential for on-site continuous monitoring of organics of interest, in various aqueous systems such as rivers, lakes or even wastewater effluents. This flow-through cell system was found to have similar extraction efficiency when compared to magnetic stirring and fiber vibration agitation mode [4].

As far as liquid-phase microextraction (LPME) is concerned, continuous-flow microextraction (CFME) was developed in 2000 as the first semi-automated LPME approach, by Liu and Lee [5]. In this setup, the aqueous sample was pumped continuously, using a high-performance liquid chromatographic (HPLC) solvent delivery system, into a glass extraction chamber via a polyether ether ketone (PEEK) tubing. This is then followed by the introduction of an organic extraction drop at the outlet of the PEEK tubing stationed in the chamber, via an HPLC injection valve. This enabled the sample solution to be continuously pumped “around” the drop, allowing efficient extraction [6]. A microsyringe needle was then manually introduced into the chamber to collect some of the extract for analysis. Following its introduction, CFME has been applied to a wide range of analytes (i.e. polycyclic aromatic hydrocarbons [7], pesticides [8,9], phenolic compounds [10], volatile halohydrocarbons [11], phoxim [12], trace metals [13] and aluminum [14]) in various types of samples (i.e. water [7,8,10–12,14], vegetables [9](after microwave-assisted extraction), and biological samples [13]). Subsequently, Es'haghi developed another method that was similar to CFME, where hollow-fiber LPME was performed in a continuous sampling setup to determine non-steroidal anti-inflammatory drugs in wastewater [15].

In order to improve the CFME concept, Moinfar et al. developed a method named continuous sample drop flow-based microextraction (CSDF-ME) [16], where 20–30 μL of organic solvent was used instead of a single drop, as in CFME. On top of that, instead of having a continuous contact between the flowing aqueous sample and the outer surface of the solvent droplet in CFME, a series of fine droplets of the aqueous sample were passed through the extraction solvent, contained in a conical bottom test tube. A peristaltic pump was used to supply a continuous flow of aqueous sample through the denser and immiscible organic solvent. This allowed the extraction solvent to be easily transferred for subsequent instrumental analysis, addressing the droplet instability problem faced in CFME.

Previously, a new partially automated extraction/concentration sample preparation approach was developed by us to use with a commercial autosampler, named miniscale liquid-liquid extraction coupled to full evaporation dynamic headspace concentration (msLLE-FEDHS), integrated with gas chromatography-mass spectrometry (GC-MS) [17]. This approach retained the advantages of conventional liquid-liquid extraction, such as low matrix effects, without the limitations of LPME (*e.g.* repeatability issues and lack of true across-sample automation). However, the msLLE step had to be done manually using a vortex mixer, before the sample-extract mixture was loaded onto the autosampler tray for subsequent automated transferring of the extract to the autosampler's DHS module for FEDHS, followed by a GC-MS analysis.

Growing concerns over the effects of UV radiation on the skin (e.g., premature skin ageing, skin cancer, etc.) have led to greater use of sunscreen products containing UV filters by the public [18,19]. Due to the lipophilic nature and poor biodegradability of UV filters [20], their widespread use and subsequent discharge can lead to environmental build-up. Thus, these compounds pose a threat to living organisms due to their potential endocrine and developmental toxicities [21]. In particular, 3-(4′-methylbenzylidene) camphor has been reported to demonstrate comparatively high estrogenic activity among the UV filters as well as significant adverse effects on the reproductive, brain and central nervous systems of the offspring of rats exposed to it [21]. Hence, UV filters are recently being labelled as contaminants of emerging concern [22].

The aim of present study was to develop an approach to combine automated online water sampling and automated msLLE-FEDHS on a widely accessible commercial autosampler, seamlessly coupled with GC-MS for the analysis of UV filters. This includes an online derivatization step for four of the compounds, which is also conducted automatically. A conventional 20 mL autosampler vial, which was easily modified to have inlet and outlet ports, was connected to a water source via an independently operated and controlled peristaltic pump to manage the water flow. A flow-through water sampling system was thus set up from which water could be sampled as and when needed by the autosampler syringe. This way, aliquots of water could be automatically collected and transferred to another vial for subsequent automated msLLE-FEDHS, followed by GC-MS analysis. msLLE parameters and derivatization conditions were optimized using orthogonal array design (OAD) [23–25]. FEDHS settings were optimized using a univariant approach. Finally, the optimized fully automated water sampling-