Analytica Chimica Acta 907 (2016) 54–59

Contents lists available at ScienceDirect

Analytica Chimica Acta

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

A fully automated effervescence-assisted switchable solvent-based liquid phase microextraction procedure: Liquid chromatographic determination of ofloxacin in human urine samples☆

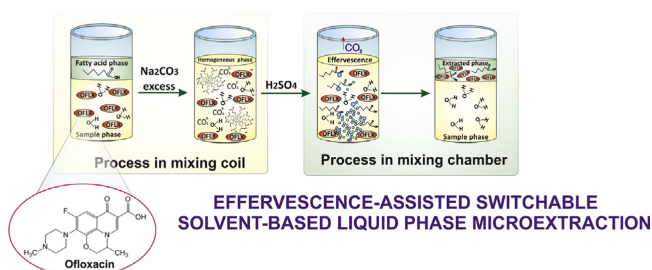
Christina Vakh [a,*], Aleksei Pochivalov [a], Vasil Andruch [b], Leonid Moskvin [a], Andrey Bulatov [a]

[a] Department of Analytical Chemistry, Institute of Chemistry, Saint-Petersburg University St.Petersburg State University, SPbSU, SPbU, 7/9 Universitetskaya nab., St. Petersburg, 199034 Russia
[b] Department of Analytical Chemistry, University of P.J. Šafárik, SK-04154 Košice, Slovakia

HIGHLIGHTS

- Novel effervescence-assisted switchable solvent-based liquid phase microextraction procedure.
- First fully automated EA-SS-LPME coupled with HPLC-FLD.
- The application of fatty acids as switchable hydrophilicity solvents.
- Na_2CO_3 as hydrophilicity modifier, effervescence agent and phase separation intensifier.
- Determination of ofloxacin in human urine samples.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 29 September 2015
Received in revised form
10 December 2015
Accepted 13 December 2015
Available online 17 December 2015

Keywords:
Effervescence-assisted switchable solvent-based liquid phase microextraction
Green analytical chemistry
Flow analysis
Fatty acids
Ofloxacin
Urine

ABSTRACT

A novel fully automated effervescence-assisted switchable solvent-based liquid phase microextraction procedure has been suggested. In this extraction method, medium-chain saturated fatty acids were investigated as switchable hydrophilicity solvents. The conversion of fatty acid into hydrophilic form was carried out in the presence of sodium carbonate. The injection of sulfuric acid into the solution decreased the pH value of the solution, thus, microdroplets of the fatty acid were generated. Carbon dioxide bubbles were generated in-situ, and promoted the extraction process and final phase separation. The performance of the suggested approach was demonstrated by the determination of ofloxacin in human urine samples using high-performance liquid chromatography with fluorescence detection. This analytical task was used as a proof-of-concept example. Under the optimal conditions, the detector response of ofloxacin was linear in the concentration ranges of $3\cdot10^{-8}$–$3\cdot10^{-6}$ mol L^{-1}. The limit of detection, calculated from a blank test based on 3σ, was $1\cdot10^{-8}$ mol L^{-1}. The results demonstrated that the presented approach is highly cost-effective, simple, rapid and environmentally friendly.
© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Green analytical chemistry provides development of various analytical procedures and methods with a minimal impact on operators and the environment. Green sample pretreatment

☆ Selected paper from Flow Analysis XIII Conference, 5-10 July 2015 in Prague, Czech Republic.
* Corresponding author.
E-mail addresses: k.vakh@spbu.ru, kristina-fulmes@mail.ru (C. Vakh).

http://dx.doi.org/10.1016/j.aca.2015.12.004
0003-2670/© 2015 Elsevier B.V. All rights reserved.

approaches, especially microextraction, have attracted great attention as they lead inherently to minimum solvent and reagent consumption, and drastic reduction of laboratory wastes [1]. Liquid-phase microextraction (LPME) has grown increasingly popular due to its simplicity, low cost, adaptability to a wide variety of sample types and analytes, as well as, for all major analytical instrumentation [2]. The most frequently used LPME modes are: single-drop microextraction [3,4], hollow-fiber liquid-phase microextraction [5–7], dispersive liquid–liquid microextraction [8], solidified floating organic drop microextraction [9]. All these modes are well described in numerous reviews where the main benefits and drawbacks are presented [1,6,10–13].

Recently, the group of M. Valcarcel suggested two novel approaches for LPME. The first is so-called effervescence assisted dispersive liquid–liquid microextraction (EA-DLLME), in which the extraction process is encouraged by effervescence effect resulting from in-situ carbon dioxide generation [14]. The second is based on the use of so-called switchable hydrophilicity solvents (SHS) for microextraction [15,16]. These solvents (usually amidines and secondary/tertiary amines) can be switched between hydrophobic and hydrophilic forms, depending on the solution composition [17]. Both procedures were further developed also by other authors [18–20]. Just a few months ago, Jen et al. (2015) presented the application of medium-chain fatty acid as extraction solvent (hydrophobic form) for LPME [21]. This solvent can be switched between hydrophobic and hydrophilic forms by the adjustment of pH of the solution. Thus, in fact, medium-chain fatty acids can also be considered as SHS.

To the best of our knowledge, the above-mentioned procedures were carried out manually, and no automated procedures were reported. Flow analysis can be considered as a superior tool for automation of wide variety of analytical procedures, including microextraction [22–30].

Therefore, the aim of this study was to hyphenate the effervescence-assisted microextraction with switchable hydrophilicity solvents microextraction, and automate the hyphenated procedure. The combined method, effervescence-assisted switchable solvent-based liquid phase microextraction (EA-SS-LPME), assumes using medium-chain fatty acids as extractant. Furthermore, sodium carbonate was used on one hand, to induce conversion of fatty acid from water-immiscible to water-miscible form, and on the other hand, to provide effervescence, while its excess reacts with a mineral acid. In this case, the effervescence increases the efficiency of extraction and phase separation. To demonstrate the efficiency of the suggested approach, the automated EA-SS-LPME procedure was applied to determine fluoroquinolone antibacterial agent, ofloxacin (OFLX) as a proof-of-concept analyte in human urine samples, using HPLC with fluorescence detection (HPLC-FLD).

2. Experimental

2.1. Reagents and solutions

All chemicals and reagents were of analytical grade. Ultra pure water from Millipore Milli-Q RG (Millipore, USA) was used. Fatty acids (nonanoic, hexanoic and pivalic acids), ofloxacin and methanol were purchased from Sigma–Aldrich. Stock solution of $3 \cdot 10^{-3}$ mol L^{-1} of OFLX was prepared by dissolving the reagent in 1 mol L^{-1} NaOH. The solution was stored in a dark place at 5 °C and used within 2 months. The solutions of sulfuric (2.5 mol L^{-1}), phosphoric (2.5 mol L^{-1}) and hydrochloric (4 mol L^{-1}) acids were prepared by dilution of the concentrated acids with water. 2 mol L^{-1} solution of Na_2CO_3 was prepared by dissolving the reagent in water. Phosphate buffer solution (pH 6.4) was prepared by mixing 0.05 mol L^{-1} Na_2HPO_4 and 0.05 mol L^{-1} NaH_2PO_4 (1:3, v/v) and adjusted by 1 mol L^{-1} NaOH. Britton–Robinson buffer (pH 4.0) was prepared by mixing 0.12 mol L^{-1} H_3BO_3, 0.12 mol L^{-1} H_3PO_4 and 0.12 mol L^{-1} CH_3COOH (1:1:1, v/v) and adjusted by 1 mol L^{-1} NaOH.

2.2. Manifold and apparatus

The manifold for automated EA-SS-LPME procedure (Fig. 1) consists of two eight-port selection valves (Sciware Systems SL, Spain), a 2.5 mL syringe pump (Sciware Systems SL, Spain), a peristaltic pump MasterFlex L/S (Cole-Parmer, USA), ensuring reverse flow (0.5–5 mL min^{-1}), a mixing coil (80 cm length) and a 3 mL conical tube as a mixing chamber (8 mm in i.d.). A three-way solenoid head valve on-top of the syringe (valve 3) enabled the connection to the mixing coil (position ON, activated) or to the waste (position OFF, deactivated). The PTFE tubs of 0.8 mm in i.d. were used for the entire manifold.

The flow system was coupled with LC-20 Prominence liquid chromatograph (Shimadzu, Japan) with fluorescence detection.

An RF-5301 PC spectrofluorometer (Shimadzu, Japan) equipped with 10 mm quartz cell was used for the preliminary studies and for the spectrofluorimetric determination of OFLX.

2.3. Samples and sample preparation

Human urine samples were collected from fasting and healthy three volunteers in the morning. Before analysis, the urine samples were filtered through a 0.45 μm membrane filter. Spiked samples were prepared by addition of calculated volumes of working solutions of OFLX to filtrated blank urine samples so that the volume of resulting solutions was 1 mL. The samples were left to stand for 30 min, to allow interaction between the analyte and the urine matrix. Before analysis, the samples were diluted ten-fold three times, and appropriate aliquot of this solution was used for the analysis.

2.4. The procedure for automated determination of ofloxacin in human urine samples

At the first stage, 350 μL of 2 mol L^{-1} Na_2CO_3 (port 1, valve 1), 1 mL of diluted urine sample (port 2, valve 1) and 50 μL of hexanoic acid (port 3, valve 1) were sequentially aspirated to the mixing coil by the syringe pump. While reagents were passing through the mixing coil, formation of homogeneous solution of sodium hexanoate, OFLX and excess carbonate ions took place. Afterwards, the resulting mixture was delivered (port 4, valve 1) into the mixing chamber using the syringe pump. In order to clean the mixing coil from sodium carbonate residues, it was washed out by water (port 5, valve 1) twice.

260 μL of 2.5 mol L^{-1} H_2SO_4 (port 6, valve 1) was aspirated to the mixing coil and delivered into the mixing chamber. Addition of sulfuric acid solution led to conversion of the water-miscible hexanoate ions into hydrophobic hexanoic acid, effervescence-assisted microextraction of OFLX and phase separation.

Afterwards, the aqueous phase was moved to waste (port 7, valve 1), while organic phase remained in the mixing chamber. Then, 450 μL of phosphate buffer (pH 6.4) and methanol mixture (1:1, v/v) (port 11, valve 2) was delivered into the mixing chamber by the peristaltic pump for dissolving hexanoic acid, containing the extracted analyte for HPLC analysis. The mixture was mixed by air bubbles (port 12, valve 2) for 20 s.

The obtained solution was aspirated (port 14, valve 2) to chromatographic vial using peristaltic pump and analyzed by HPLC-FLD. The fluorescence excitation and emission wavelengths were 293

Download English Version:

https://daneshyari.com/en/article/1163104

Download Persian Version:

https://daneshyari.com/article/1163104

Daneshyari.com