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In-syringe magnetic stirring-assisted dispersive liquid–liquid microextraction for automation and downscaling of methylene blue active substances assay

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ABSTRACT

A simple and rapid method for the determination of the methylene blue active substances assay based on in-syringe automation of magnetic stirring-assisted dispersive liquid–liquid microextraction was developed. The proposed method proved to be valid for the determination of anionic surfactant in waste, pond, well, tap, and drinking water samples.

Sample mixing with reagents, extraction and phase separation were performed within the syringe of an automated syringe pump containing a magnetic stirring bar for homogenization and solvent dispersion. The syringe module was used upside-down to enable the use of chloroform as an extraction solvent of higher density than water.

The calibration was found to be linear up to 0.3 mg/L using only 200 μL of solvent and 4 mL of sample. The limits of detection (3σ) and quantification (10σ) were 7.0 μg/L and 22 μg/L, respectively. The relative standard deviation for 10 replicate determinations of 0.1 mg/L SBDS was below 3%. Concentrations of anionic surfactants in natural water samples were in the range of 0.032–0.213 mg/L and no significant differences towards the standard method were found. Standard additions gave analyte recoveries between 95% and 106% proving the general applicability and adequateness of the system to MBSA index determination. Compared to the tedious standard method requiring up to 50 mL of chloroform, the entire procedure took only 345 s using 250-times less solvent.

1. Introduction

Anionic surfactants (AS) [1] are the most common surfactant group used in industrial detergent formulation, cosmetics, and household cleaners [2] and their consumption of AS is steadily increasing due to the raise of population. Although AS are biodegradable [3] it is well known that high concentrations of anionic surfactants in water can harm aquatic organisms [4,5]. Because of the quantity originated from wastewater treatments plants effluents and untreated urban wastewater discharges [6] is high, many aquatic ecosystems receive large quantities of AS. So that AS can also be found in surface and groundwater endangering the quality of drinking water. Hence, determining AS is of interest for environmental and health studies [7,8] as well as quality and safety control. The European environmental regulations established a maximum tolerated limit of 0.2 mg/L for AS in water supplies for human consumption [9].

The most commonly reference method used to determine AS as sum parameter in water is the methylene blue active substance index (MBAS) [10]. This method consists in the formation of ion-pairs between AS and the cationic dye methylene blue (MB) followed by their extraction into chloroform and determination of the extracted complexes by spectrophotometry. However, the reference method is not only long and tedious but also presents a series of drawbacks such as consumption of large volumes of sample and chloroform being a toxic organic solvent. To address these drawbacks, a number of studies were focused on the development of miniaturized and environmentally benign methods based on liquid–liquid extraction (LLE) automated using analytical flow techniques (FT). In Table 1, an overview and comparison of these methods is given. FT-based LLE was first proposed by Karlberg and Thelander [22] and Bergamin et al. [23] who demonstrated minimization of sample and reagent consumption, risk of sample contamination, and operator's intervention as well as enhanced sampling throughput. The determination of AS based on the coupling of LLE and FT was reported for the first time by Kawase et al. [11] in 1978. Analytical procedures used for the determination of AS are reviewed elsewhere [24]. In 2006, a new

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Table 1
Comparison of various flow methods for determination of MBAS index in water samples with developed method.

Flow technique	Extraction technique	Solvent volume (μL)	Dynamic range (mg/L)	LOD (mg/L)	RSD %	DR (h^{-1})	Refs.
FIA	MLLE	1770	< 360	4	1.5	80	[11]
FIA	LLE	490	0.1–4	–	3.0	50	[12]
FIA	LLE		0.04–3.5	0.04	1.2	20	[13]
FIA	LLE	200	0.1–1	0.07	6.7	20	[14]
FIA	DBALLME	2	< 5.0	0.4	5.0	15	[15]
FIA	MLLE	–	0.02–5	–	–	–	[16]
FIA	–	500	< 6	–	4.6	10	[17]
FIA	MMLLE	–	70–700	35	1.8	50	[18]
SIA	LLE	300	1–10	0.5	5.0	5	[19]
MCFA	MM	700	0.2–1.7	0.008	5.9	20	[1]
FIA	LLME	50	0.03–0.3	0.02	2.4	240	[20]
MCFA	LLME	44	0.05–2.0	0.02	1.5	18	[21]
SIA	MSA-DLLME	220	0.025–0.3	0.007	3	10	This work

Abbreviations: DBALLME, drop-based automated liquid–liquid extraction; DLLME, dispersive liquid–liquid microextraction; DR, determination rate; FIA, flow injection analysis; MCFA, multicommuted flow analysis; LLE, liquid–liquid extraction; LLME, liquid–liquid microextraction; LOD, limit of detection; MLLE, membrane liquid–liquid extraction; MM, multicommutated; MMLLE, microporous membrane liquid–liquid extraction; MSA-DLLME, Magnetic stirring-assisted dispersive liquid–liquid microextraction; RSD, Relative standard deviation; SIA, sequential injection analysis.

concept of miniaturization of LLE was proposed by Rezaee et al. [25] denoted dispersive liquid–liquid microextraction (DLLME). A mixture of an extraction solvent and a dispersion solvent with high miscibility in water is rapidly injected into an aqueous sample to form a cloudy component emulsion. By centrifugation, the extraction solvent containing the enriched analytes can be separated and then injected into an appropriated analytical instrument. The advantages of DLLME are its simplicity of operation, rapidity, low cost, high-recovery, high enrichment factor, and minimal waste generation [26]. However, the distribution coefficient of the analyte between organic and aqueous phase could be altered by the dispersion solvent making a comparison with standard protocols based on classical LLE difficult. Besides, method optimization requires finding a suitable dispersion solvent as well as an optimal mixing ratio with the extraction solvent. The alternative to tackle these problems was the replacement of the dispersion solvent by kinetic energy leading to air-assisted [27], vortex-assisted [28], ultrasound-assisted [29], magnetic-stirring-assisted (MSA) dispersion [30]. More recently, the concepts of DLLME and FT automation were combined [31–33]. Here, in-syringe DLLME has demonstrated to be a specially promising technique for automated DLLME, [34–37] with the late report of automated in-syringe MSA-DLLME [38,39] due to its simplicity and versatility. The aim of the present work was to develop a simplification of the MBAS method based on in-syringe MSA-DLLME with the novel modification that the syringe was used upside down in order to use chloroform as extraction solvent to achieve comparability towards the standard procedure for MBSA determination.

2. Material and methods

2.1. Reagents and solutions

All solutions were prepared with analytical grade chemicals from Scharlab SA (Barcelona, Spain) unless otherwise indicated and bi-distilled quality water provided by a Milli-Q Direct-8 purification system (resistivity > 18 MΩ cm, Millipore Iberica S.A.U., Spain) was used throughout. All material were previously soaked for at least 24 h in 10% (v/v) HNO_3 and rinsed with water before used. A stock solution of 10 mg/L sodium dodecyl benzene sulphonate (SDBS) (Sigma Aldrich, Steinheim, Germany) was used as standard solutions of anionic surfactants. For calibration, SDBS standard working solutions were prepared daily by appropriate dilution. A stock solution of 700 mg/L methylene blue (MB) (Panreac SA, Barcelona, Spain) was prepared by dissolution of an appropriate amount of the reagent in Milli-Q water. A solution of 127 mmol/L sodium hydrogen phosphate and 100 mmol/L H_2SO_4 were used for in-syringe buffer preparation. To accelerate phase separation, a 648 mmol/L Na_2SO_4 solution was used as additional reagent. Chloroform was used as extraction solvent without any previous treatment. All reagent solutions were kept in glass bottles at 4 °C.

For the reference procedure, the following solutions were used as recommended [10]: MB solution: 30 mg/L MB in sulfuric acid–sodium phosphate buffer (concentrations 0.123 mol/L and 0.362 mol/L, respectively) and washing solution being the same buffer but without MB.

Solutions used in interference studies were prepared from $CaCl_2$, $MgCl_2 \cdot 2H_2O$, NH_4Cl, $AlCl_3 \cdot 6H_2O$, $Pb(NO_3)_2$, $CuSO_4 \cdot 5H_2O$, $FeCl_3 \cdot H_2O$, $NaNO_3$, $NaNO_2$, NaCl,$NaHCO_3$, Triton X-100, humic acid and CTAB. The substances were chosen in agreement with former interference studies [20,21]. In order to study the influence of water hardness on the extraction process, artificial freshwaters of different hardness grades were prepared according to standard recipes for “very hard water”, “hard water” and “moderately hard water” [10].

2.2. Sample collection and preparation

Different natural water samples were collected and analyzed: drinking water, pond water, well water, and tap water from different places on Mallorca and wastewater from entrance and effluent of a local biological treatment plant. Samples were collected in polyethylene bottles and stored at 4 °C until analysis. Wastewater samples and pond water were paper-filtered to remove suspended particles.

2.3. Manifold configuration

The system used in this work is depicted in Fig. 1 and follows a prior designs [38,39]. It comprised a 5000-step syringe pump (SP) from Crison SL (Alella, Barcelona, Spain) with a 5 mL glass syringe (S) and a rotary 8-port multiposition valve (MPV) from Sciware System SL (Palma de Mallorca, Spain). PTFE tubing of 0.8 mm inner diameter (id) was used for the entire manifold. A short PTFE tube was placed into the syringe inlet to minimize the dead volume. A three-way solenoid head-valve (V) on top of the syringe enabled the connection to either the central port of the MPV (position ON, activated) or to a detection cell and downstream located waste for quantification of the extracted analyte and discharge during syringe cleaning (position OFF, deactivated). Peripheral ports of the MPV were connected to reservoirs of waste (1), water (2), sample (3), MB (4), NaH_2PO_4 (5), chloroform (6), air (7), H_2SO_4 (8), and Na_2SO_4 (9). The connection between the common port of the MPV and the syringe head-valve was done by a holding coil (HC) of 26 cm in length. For sample measurements, a 15-position rotary autosampler from Crison SA was used. For dispersion of the extraction solvent, a magnetic stirring bar (10 mm × 3 mm in diameter) was placed inside the syringe.

In this work, given the fact that the extraction solvent had a higher density than water and thus accumulated at the bottom, the syringe module was used upside-down.