In-syringe-stirring: A novel approach for magnetic stirring-assisted dispersive liquid–liquid microextraction

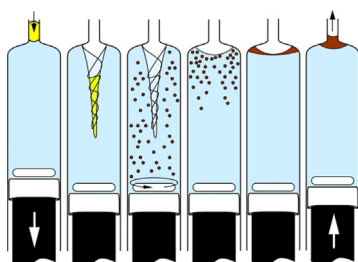Burkhard Horstkotte [a,b], Ruth Suárez [b], Petr Solich [a], Víctor Cerdà [b,*]

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HIGHLIGHTS

- We propose a new automatic magnetic stirring assisted dispersive liquid–liquid microextraction.
- It allows the extraction of aluminum from seawater and freshwater samples within less than 4 min.
- The method was applicable to the natural samples.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

For the first time, the use of a magnetic stirrer within the syringe of an automated syringe pump and the resulting possible analytical applications are described. A simple instrumentation following roughly the one from sequential injection analyzer systems is used in combination with an adaptor, which is placed onto the barrel of a glass syringe. Swirling around the longitudinal axis of the syringe and holding two strong neodymium magnets, it causes a rotating magnetic field and serves as driver for a magnetic stirring bar placed inside of the syringe.

In a first study it was shown that this approach leads to a sealed but also automatically adaptable reaction vessel, the syringe, in which rapid and homogeneous mixing of sample with the required reagents within short time can be carried out.

In a second study in-a-syringe magnetic stirring-assisted dispersive liquid–liquid microextraction (MSA-DLLME) was demonstrated by the application of the analyzer system to fluorimetric determination of aluminum in seawater samples using lumogallion.

A linear working range up to 1.1 μmol L^{-1} and a limit of detection of 6.1 nmol L^{-1} were found. An average recovery of 106.0% was achieved for coastal seawaters with a reproducibility of 4.4%. The procedure lasted 210 s including syringe cleaning and only 150 μL of hexanol and 4.1 mL of sample were required.

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1. Introduction

Dispersive liquid–liquid microextraction (DLLME) has drawn a major interest from scientists from different analytical disciplines since its first description by Rezaee et al. in 2006 [1]. This is most likely due to the possibility of high extraction efficiencies and large enrichment factors with a simple and rapid procedure.

DLLME is based on the dispersion of the extraction solvent into fine droplets, which multiplies enormously its contact surface with the aqueous sample and by this, the extraction efficiency for the analyte of interest.

The original methodology requires a dispersion solvent as major component of the organic phase, which dissolves preferably in the aqueous phase at the rapid injection of the solvent mixture into the aqueous phase. Thus, a very small amount of extraction solvent is

effectively dispersed into droplets, which afterwards are forced to coalesce by a centrifugation step. The organic phase is then transferred into the detector or used for chromatographic separation.

However, the dispersion solvent assisted DLLME has a few inconveniences. The additional solvent leads to increase waste production. The method requires additional optimization effort (dispersion solvent quantity and kind) and, the most important, the dispersion solvent increases the solubility of the analyte in the aqueous phase. Furthermore, the distribution of the dispersion solvent between both phases and by this, the final volume of the organic phase depends on the sample salinity.

Consequently, alternative DLLME methodologies have been developed, where extraction solvent dispersion is achieved by kinetic energy. Depending on the mode of achieving droplet formation or stabilization of the droplets in the aqueous phase, ultrasound-assisted DLLME [2], air-assisted DLLME [3], vortex-assisted DLLME [4], magnetic stirring-assisted DLLME (MSA-DLLME) [5], and surfactant assisted DLLME [6] can be distinguished among others. For details, the reader is referred to recent and extensive review articles on this topic [7–10]).

In spite of the high interest in the development and application of DLLME techniques, the potential of their automation using analytical flow techniques (FT) [11,12] such as Sequential Injection Analysis (SIA) [13–15] has been widely disregarded. Direct coupling with the intended detection technique, higher reproducibility, higher sample throughput, and automated cleaning of the extraction vessel are possible benefits of FT-based automation. These have been demonstrated successfully. However, only by three distinct automation modalities so far:

1. Extraction in flow by confluence of the aqueous sample and an organic solvent mixture with droplet collection on a hydrophobic material and subsequent elution to a detection flow cell requiring additional solvent [16–18].
2. Use of an extraction vessel as a batch approach of automation of the manual DLLME protocol. The solution handling is accomplished by two separate SIA systems [19].
3. In-syringe DLLME by aspiration of the organic solvent mixture followed by sample aspiration at very high flow rate that leads to DLLME. After floating and coalescing of the solvent droplets, the organic phase is expelled into the detection flow cell [20–24].

Up to date, there are hardly any works on FT-based automation of DLLME, in which the dispersion solvent was omitted leaving alone an automation approach of air-assisted DLLME [25]. To the best of our knowledge, the present work reports the first FT-based automation of MSA-DLLME. It is based on a novel approach using a magnetic stirring bar within the syringe pump of a SIA system. Hence, a sealed but adaptable reaction vessel is obtained, in which all solutions can be aspirated with high precision and mixed homogeneously and nearly instantaneous. If air and an extraction solvent lighter than water are used, vortex formation will allow the contact of the extraction solvent with the turning stirring bar and hereby, the dispersion of the solvent into fine droplets. Stopping the stirring allows then droplet floatation, coalescence, and expulsion of the extraction solvent into a detection flow cell.

The system was used for the extraction of aluminum (Al^{3+}) as lumogallion (LMG) complex from seawater samples. This also allowed a critical comparison with a similar application but based on in-syringe dispersion solvent-assisted DLLME, which was reported recently [23]. In both works, LMG was chosen as a very selective fluorescence reagent for aluminum [26]. In contrast to the often-used morin, the LMG-Al complex is extractable into moderately hydrophobic organic solvents. It further shows low interference from sample matrix or other cations and has

therefore been successfully used in oceanographic research over about three decades [27–32].

Although aluminum is a non-essential element, its determination in seawater is of interest as concentration data allow the calculation of atmospheric deposition of dust particles on the ocean surface due to its presence in numerous minerals. Then, these calculations allow the estimation of the entry of essential trace nutrients such as iron originating from the dissolution of the dust particles and which are limitation factors for growth of algae.

Herein, in-syringe MSA-DLLME is presented. The improvement of existing analyzer systems for aluminum as well as the demonstration and application of a novel extraction technique was intended with the critical discussion of its shortcomings and potential benefits for future works.

2. Methods and materials

2.1. Reagents

All chemicals were of reagent grade for analysis and ultrapure water (resistivity >18 MΩ cm Millipore Iberica S.A.U., Madrid, Spain) was used throughout. All glassware and polyethylene bottles were previously soaked in 10% (v/v) HNO_3 and rinsed with ultrapure water prior to use. All working solutions were stored in polyethylene bottles at 4 °C in the dark when not used.

An aluminum stock solution of 13.5 mg L^{-1} was prepared by diluting a commercial 1000 mg L^{-1} $Al(NO_3)_3 \cdot 9H_2O$ atomic absorption standard (Scharlab, Barcelona, Spain) in 0.5 mol L^{-1} HNO_3. Synthetic seawater (SSW) prepared according to standard recipe as given elsewhere [33] was used for most optimization experiments and for standard preparation. To eliminate aluminum contamination of the SSW, the formed $Al(OH)_3$ at the slightly alkaline pH of the SSW (pH 8) was removed by filtration through a 0.45 μm membrane filter.

Acidification was done to avoid Al^{3+} hydrolysis and loss of Al^{3+} availability for the complex formation with LMG. Adjustment to a lower pH was impractical due to the later required adjustment to the optimal reaction pH of 5.0.

A reagent solution of 1.5 mmol L^{-1} lumogallion (4-chloro-6-(2,4-dihydroxyphenylazo)-1 phenol-2-sulfonic acid) and a buffer solution of 5 mol L^{-1} of ammonium acetate (NH_4Ac) buffer, adjusted with glacial acetic acid to pH 5.4, were prepared. For extraction, n-hexanol was used throughout.

For measurement of aluminum in seawater, the interference of fluoride anion has to be taken into consideration since aluminum fluoride formation competes with the formation of the LMG-complex. In a previous work, this interference was considerably reduced at the addition of beryllium. Therefore, 25 mmol L^{-1} of beryllium nitrate were added to the LMG reagent solution to yield a final concentration of 350 μmol L^{-1} Be^{2+}, which had been found to be the optimal value in our previous work [23].

A 1 mg L^{-1} rhodamine B solution was used for studies of in-syringe homogenization by stirred-assisted mixing.

2.2. Sample collection and preparation

Coastal seawater samples were collected at different bays of the island Mallorca to evaluate the methods applicability to surface seawater analysis. The samples were acidified to pH 3 at the time of collection. The samples were measured with the proposed analyzer system without any other previous treatment but allowing only the grouse particles to sediment. Likewise, two pond water samples were collected on different places on the Mallorca Island, acidified to pH 3, and measured under the same conditions. After acidification and before measurement, the samples were allowed