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A novel approach to Lab-In-Syringe Head-Space Single-Drop Microextraction and on-drop sensing of ammonia

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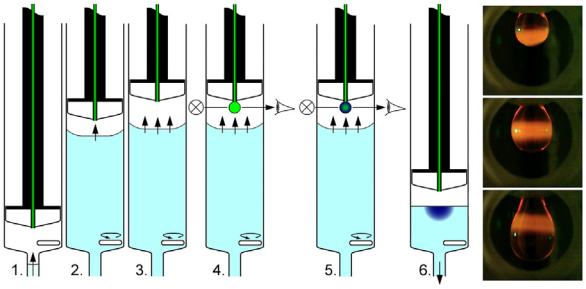
HIGHLIGHTS

- Development of a novel in-syringe head-space single drop microextraction approach.
- Drop formed at the end of a channel drilled through the syringe piston.
- Study of drop formation, size, sphericity, attachment, and optical performance.
- In-drop sensing of analyte enrichment for quantification of ammonium.
- Increased analyte evaporation into the HS by pressure decrease and sample stirring.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel approach to the automation technique Lab-In-Syringe, also known as In-Syringe Analysis, is proposed which utilizes a secondary inlet into the syringe void, used as a size-adaptable reaction chamber, via a channel passing through the syringe piston. This innovative approach allows straightforward automation of head-space single-drop microextraction, involving accurately controlled drop formation and handling, and the possibility of on-drop analyte quantification.

The syringe was used in upside-down orientation and in-syringe magnetic stirring was carried out, which allowed homogenous mixing of solutions, promotion of head-space analyte enrichment, and efficient syringe cleaning.

The superior performance of the newly developed system was illustrated with the development of a sensitive method for total ammonia determination in surface waters. It is based on head-space extraction of ammonia into a single drop of bromothymol blue indicator created inside the syringe at the orifice of the syringe piston channel and on-drop sensing of the color change via fiber optics. The slope of the linear relationship between absorbance and time was used as the analytical signal.

Drop formation and performance of on-drop monitoring was further studied with rhodamine B solution to give a better understanding of the system's performance.

A repeatability of 6% RSD at 10 μmol L^{-1} NH_3, a linear range of up to 25 μmol L^{-1} NH_3, and a limit of detection of 1.8 μmol L^{-1} NH_3 were achieved. Study of interferences proved the high robustness of the method towards humic acids, high sample salinity, and the presence of detergents, thus demonstrating

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the method superiority compared to the state-of-the-art gas-diffusion methods. A mean analyte recovery of 101.8% was found in analyzing spiked environmental water samples.

1. Introduction

About 20 years after its invention [1–4] and numerous applications [5–8], head-space single-drop micro-extraction (HS-SDME) has become a state-of-the-art technique for analyte enrichment and sample matrix removal. Its principal benefits over other liquid phase-based extraction techniques are the strict avoidance of contact between sample and extractant, thus promoting the method selectivity towards volatile and vaporizable analytes.

Since the beginning, automation of HS-SDME was of interest because reproducibility of drop formation, stability, retraction, and transfer to a detection system can be improved by automation e.g. involving the use of autosampler systems [9].

A highly attractive feature of the extraction into a drop approach is the use of the drop as a "windowless optical (detection) cell" [3]. On-drop fiber optic sensing of Cl_2 [2,10], SO_2 [3], or ammonia [11] was demonstrated and detailed theory was provided [2,3]. The unique advantages of the approach are that troublesome transfer of the drop to the detector is not required and selective (by volatility) and sensitive (due to large sample-to-drop volume) analyte enrichment can be achieved. Fluorimetric and spectrophotometric detection are both feasible with this methodology.

The versatility of this approach is also illustrated by the possibility to avoid drop saturation by following the reaction kinetics and to adapt the enrichment time for the required sensitivity for each individual sample. Also, decrease of the analytical error could be achieved by determination of the drop size and compensation of its variation by data regression over the entire extraction time without prolonging the time of analysis [1].

Analysis of volatile substances by automation techniques such as flow injection analysis (FIA) [12], sequential injection analysis (SIA) [13], and related techniques mainly relies on membrane-based gas diffusion (GD) [14] or pervaporation [15–18] on one hand, or membraneless gas diffusion (ML-GD) [19–21] on the other. GD shows the highest sensitivity among these approaches thanks to the short diffusion length involved. However, it also bears the risk of membrane stretching [21] or clogging by particles or biofouling [18], thus requiring periodic membrane replacement or cleaning [22]. Moreover, membranes, especially if in contact with a sample containing organic solvents [14], surfactants [17] or high salt content (exhibiting osmotic pressure) [22] are susceptible to pore-leaking.

This disadvantage is overcome in pervaporation (PV) technique [16] by using an additional air gap separating the sample and the membrane. However, the presence of headspace leads to a dilution effect of the gaseous analyte [19] and condensation on the membrane surface being in contact with the headspace can affect the sensitivity [16,18]. Pore leaking from the upper acceptor chamber caused by gravity, sensitivity decrease resulting from the use of ticker membranes than those used in GD, and problems with sealing of the upper compartment of the pervaporation cell can be named as additional shortcomings of this technique [15,17,19].

In ML-GD the analyte diffuses from the donor to the acceptor chamber, both encapsulated into one flow-through [19,20] or batch unit [21] through its headspace.

Both ML-GD and PV techniques require chamber cleaning, careful solution levelling, and pressure equilibration to avoid chamber overflowing (ML-GD) or membrane-failure (PV). Therefore, complex flow systems composed of several valves and pumps are often required. Moreover, volume and surface ratio between the donor and acceptor chambers is less favorable than in HS-SDME.

HS-SDME, proposed by Theis et al. (2001) [23], presents a much simpler approach: the acceptor drop is accessible (and observable) from all sides, surface contact is minimal, the drop can be positioned closely over a large surface of sample to increase the sensitivity, and – in contrast to membrane based methods – both organic and aqueous donor and acceptor phases can be employed. Despite these advantages and the high interest from scientists, reflected in several reviews [24–26], there have been hardly any reports on flow automation of HS-SDME [10] while most employ autosampler systems [9].

Lately, we reported on an automation approach, where the void of a syringe was used as a reaction and extraction chamber also known as Lab-In-Syringe (LIS) [28–30]. The main advantage of using this configuration, based on a classic SIA assembly, was that solution mixing is not performed by solution dispersion but by homogenization in the syringe void using a magnetic stirring bar inside it [31]. This makes the technique less prone to difficulties related to sample viscosity or gas content and ideally suited for the automation of sample pretreatment procedures benefitting from mixing a large volume of a sample with small volumes of reagents such as dispersive liquid-liquid microextraction (DLLME). Different modes of stirring and operations have been developed using the syringe either in normal position [31] or in an up-side down orientation [32].

Recently, we described the first application of in-syringe HS-SDME [33] with formation of a drop at the inlet of the syringe above the prior aspirated sample. Later, a second syringe pump was used to bypass the holding coil via an additional head valve (HV) port [34].

In both studies, decreased pressure was applied to increase HS enrichment with analyte vapors, which, in contrast to GD or PV, was achieved easily because the syringe provides a closed yet size-adaptable void. However, the risk of carry-over was still present because of the wetting of the same internal surfaces (syringe inlet, valve manifold, holding coil) by sample and drop reagent. Also, reliable delivery of the minute drop to the detector was a matter of concern.

The current paper describes a new approach to the Lab-in-syringe technique using for the first time a modified piston with an axially drilled channel. This permits a direct access to the syringe void, i.e. bypassing the syringe's HV. In an upside-down positioned syringe pump, a drop can now be formed inside the syringe void at the piston channel outlet. This new automated configuration, allows (i) the reagent drop to be visually observed for on-drop sensing, (ii) complete separation of sample and reagent drop (i.e. no contact of the same surfaces and independent handling), (iii) applicability of decreased pressure.

To the best of our knowledge, this is the first report on the use of a double-orifice syringe for the automation of HS-SDME and on in-syringe on-drop measurement. The system was applied to the determination of total ammonia ($NH_3 + NH_4^+$) by observation of the color change of an acid-base-indicator drop [17,19,20,22,27,35–40].