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Automatic pressure-assisted dual-headspace gas-liquid microextraction. Lab-in-syringe platform for membraneless gas separation of ammonia coupled with fluorimetric sequential injection analysis

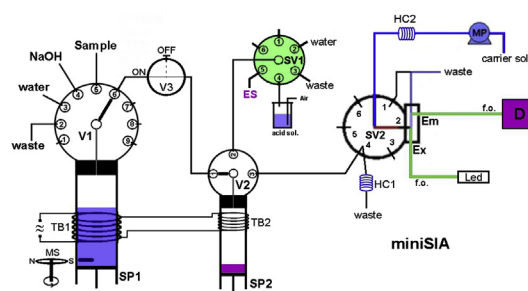
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HIGHLIGHTS

- Automatic pressure-assisted headspace dual-lab-in-syringe microextraction.
- Positive pressure in HS for altering gas solubility in favor of the liquid phase.
- Low pressure environment for achieving increased vapor production in the HS.
- On-line fluorimetric determination of ammonia, used as a model analyte.
- Application in environmental water samples.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel pressure-assisted dual-headspace lab-in-syringe microextraction technique is presented as an alternative approach for automatic on-line membraneless gas separation of volatile compounds. The developed gas-liquid microextraction procedure is based on the lab-in-syringe (LIS) concept by using two independent micro-syringe pumps which are connected to each other for the application of negative and positive pressure inside the common headspace area of the syringe barrels. The adoption of reduced and increased pressure conditions is facilitated by the programmable LIS strategy resulting in increased extraction rates. The analytical process includes the *in-situ* ammonia vapor generation in the headspace of the first microsyringe, under reduced pressure environment, and its subsequent transportation into the headspace of the second microsyringe. Then, positive pressure is applied inside the second microsyringe enabling the ammonia vapor dissolution into the extraction solution to produce a fluorescent product (isoindol-1-sulfonate). The reaction is time and temperature affected, thus after an optimized time of delay inside the thermostated syringe barrel at 60 °C, it is delivered into the flow-cell of the miniSIA system where it is quantified at 425 nm (excitation wavelength, 365 nm). The proposed pre-concentration system has been fully tested and optimized regarding the relevant parameters affecting the generation of gaseous ammonia, its effective transportation into the headspace of the second syringe barrel and its quantitative dissolution and reaction with the extraction solution. For a sample volume of 3000 μL , the sample frequency is 8 h^{-1} , the precision expressed as relative standard deviation (RSD) is 3.6 (at 5.0 $\mu\text{g L}^{-1}$) and a detection limit (3s) of 0.05 $\mu\text{g L}^{-1}$ for ammonium is obtained. The detection is linear in the concentration range of 0.15 and 10.0 $\mu\text{g L}^{-1}$ with a correlation coefficient of 0.9987. The accuracy of the proposed method has been evaluated by analyzing a standard reference material (relative error:

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3.8%) as well as using the Certified Method (relative error < 5.5%) for ammonium determination. The potential of this novel schema has been demonstrated for ammonia determination in natural water samples.

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1. Introduction

The modern trends in analytical chemistry have been focused on the development of multifunctional, versatile and miniaturized analytical tools, in a view of meeting the requirements of Green Analytical Chemistry. Although there is a continuous progress in automated micro-systems based on flow methodologies, the field of analytical techniques still cries for achieving higher sensitivity and interference elimination due to the ultra-trace concentration levels of the analytes and the high complexity of the matrix in different kinds of samples. Sample pretreatment overcomes these problems by preconcentrating or separating the analyte from the matrix; though minimizing the interferences. In this context, a great interest in new extraction methods with lower sample volume requirements, simpler equipment and handling, as well as lower reagent consumption and waste generation, has led to the development of a series of microextraction methods.

The trace analysis of volatile and semi-volatile substances, like ammonia, hydrogen sulfide, mercury or organic solvents (ethanol, benzene, toluene etc) has garnered significant scientific interest due to the difficulties encountered in the steps of sample preparation, volatilization and gas manipulation, prior measurement. Analysis of extremely volatile compounds with large Henry's law constants has been accomplished by direct aspiration of the vapor from the headspace and detection by gas chromatography (GC). In case of semi-volatile compounds, headspace single-drop microextraction (HS-SDME), proposed by Theis et al. [1] and related techniques in green analytical methods [2] have been introduced involving the distribution of the analyte from the aqueous solution into the HS of a closed vial and its subsequent collection on the surface of a solvent droplet. Lately, some attempts have been made with a view to eliminate the drawbacks of batch HS-SDME by automating the technique using the lab-in-syringe (LIS) concept [3].

The first lab-in-syringe system for automatic HS-SDME has been presented for inorganic mercury determination [4]. Low-pressure environment has been applied to facilitate the transportation of mercury vapor from the aqueous phase to the formed drop in the headspace area. In this context, some other relative experimental designs have been proposed and applied in the determination of organic and inorganic compounds [5,6].

Among the volatile, ammonia determination has always been a matter of interest for the scientists due to its recognized toxicity. Several flow methodologies based on flow injection analysis (FIA), sequential injection analysis (SIA) and related techniques for spectrophotometric, conductimetric and fluorimetric assays [7–10] have been developed for ammonia determination. In the pursuit of suppressing matrix effects and enhancing the selectivity of a method, membrane-based apparatus such as a gas-diffusion (GD) unit [9–11] is integrated in the flow configuration for on-line gas separation. In this technique, the gaseous compound diffuses across a hydrophobic membrane from a donor to an acceptor stream offering selective separation and collection of the analyte. However, this approach appears some significant problems focused on the clogging and cracking of the GD membrane from suspended particles existed in real samples. This results in frequent membrane

replacement.

To avoid membrane-related problems, an on-line pervaporation (PV) unit [12,13] or a membraneless gas-diffusion (MGD) one [14] have been introduced as an alternative approach for matrix isolation. The proposed MGD unit contains two parallel channels inside a closed module in which the diffusion of gas takes place between both open channels. Lately, an interesting design has been presented using two cone-shaped reservoirs, with a common HS area, as the membraneless vaporization (MBL-VP) unit for ammonia determination [15]. Although the MGD unit provides a greater mass transfer than the flow membrane-based units, it requires thorough cleaning and careful solution manipulation inside the used chamber to avoid overflowing [16].

The present work reports on the development of a fully automated pressure-assisted dual-headspace lab-in-syringe (PA-D-HS-LIS) platform for membraneless gas separation and determination of volatile and semi-volatile compounds. Ammonia has been chosen as the vapor forming compound for the optimization and implementation of the proposed system. The developed method is based on the *in-situ* ammonia vapor generation in the headspace of a micro-syringe, under low pressure conditions, and its subsequent on-line transportation into the headspace of another micro-syringe, where positive pressure is then applied to facilitate the gaseous ammonia dissolution into the extraction solution. On the basis of LIS strategy for automatic manipulation, pressure inside the common headspace area of the sealed syringe barrels appropriately alters to allow the conversion of aqueous to gaseous ammonia and vice versa. To the best of our knowledge, this is the first reported work utilizing two micro-syringe pumps, connected to each other, in a view to implement reduced and increased pressure inside the common headspace area of the two syringe barrels. Through a process of optimization of main factors affecting the PA-D-HS-LIS efficiency, the proposed method has been applied in environmental water samples analysis.

2. Experimental

2.1. Apparatus

The developed PA-D-HS-LIS platform is schematically presented in Fig. 1. It consists of two high precision bi-directional micro-syringe pumps (MicroCSP-3000, FIALab Instruments, Bellevue, WA), SP1 and SP2, with overall dimensions 12 × 5 × 12 cm (H × D × W) each, a two-position (ON/OFF) valve, V3, and a six-port selection valve, SV1, which are parts of a FIALab[®]-3000 (Alitea FIALab, USA) sequential injection, SI, system. SP1 is equipped with a 5000 μL glass barrel and a nine-position Teflon/Kel-F selection valve, V1, directly connected on the top of it, while SP2 consists of a glass syringe barrel with a capacity of 2500 μL and a three-position Teflon/Kel-F selection valve, V2, on it for fluidic manipulation. Each syringe pump is interfaced with the FIALab[®]-3000 system and controlled by a personal computer and the FIALab application software for windows v. 5.9.245 (<http://www.flowinjection.com>).

A minimum length of PTFE tubing (20 cm, 0.3 mm i.d.) has been used for the connection of the two headspaces of the syringe pumps. The connection tubing between V2 (port 3) and SV2 (port

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