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Sensitivity enhancement in membrane separation flow injection analysis by ultrasound

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Abstract

The effect of ultrasound on gas-diffusion and pervaporation flow injection separation was investigated. Ammonia and three aliphatic amines (propylamine, tri-ethylamine and di-*n*-butylamine) with different volatility and surface activity were used as model analytes. Under the experimental conditions used, sonication did not enhance gas-diffusion separation efficiency and resulted in up to 62% improvement in pervaporation mass transfer. Based on these findings and taking into account the surface activity of the analytes studied which decreased with their molecular mass it was postulated that ultrasound-induced surface rippling was primarily responsible for the enhanced evaporation in the donor chamber of the pervaporation cell. The results reported in this paper suggest that ultrasonic pervaporation separation could extend the applicability of this on-line flow injection separation technique to the direct determination of higher molecular mass volatile and semi-volatile analytes in 'dirty' samples.

Keywords: Surface rippling; Gas-diffusion flow injection analysis; Pervaporation flow injection; Ammonia; Aliphatic amines

1. Introduction

Flow injection (FI) analysis, which is a powerful flow-through technique for solution manipulation prior to detection, allows the construction of portable semi-automated or automated chemical analysers [1]. In a typical basic FI analyser the sample is injected into a carrier stream where it may react with a reagent present or additionally introduced to produce a chemical species that can be sensed by a flow-through detector positioned downstream of the injection device. A peak shaped signal is recorded as the sample zone passes through the flow-through detector and the peak height or peak area can be related to the analyte concentration in the original samples or standards.

The majority of flow injection analysers currently in use incorporate spectrophotometric or electrochemical flow-through detectors because of the relatively low cost of these two types of detectors. However, such detectors often experience serious interference problems with samples containing suspensions, emulsions, macromolecules or coloured compounds. For this reason on-line separation steps should be introduced in the FI procedure. Very often such separation steps involve processes such as solvent extraction, adsorption, precipitation or membrane based separation. Depending on the hydrophobicity of the membrane different types of analytes can be targeted. If the membranes are hydrophilic in nature, ionic or neutral water-soluble chemical species can be separated from the sample matrix by various forms of dialysis (e.g. passive, Donnan or electrodialysis). Hydrophobic membranes, often referred to as gas-diffusion membranes, are suitable for the separation of volatile or semi-volatile analytes or analytes, which can be converted chemically to volatile

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chemical species [1]. In a typical gas-diffusion flow injection (GD–FI) system the sample is injected into a donor stream separated from a co-currently flowing acceptor stream by a suitable hydrophobic porous membrane (Fig. 1a). The volatile species evaporates into the pores of the membrane, diffuses through it, and is absorbed into the acceptor stream, where the detection takes place. The membrane prevents other non-volatile species from passing through; thus, matrix interferences are effectively eliminated to a great extent. The selectivity of the GD method leads to the possibility of using cheaper non-selective detectors.

However, very often environmental and industrial samples contain emulsions, suspensions, macromolecules, surfactants and corrosive compounds. Such samples are normally difficult to analyse by GD–FI analysers because the direct contact between the sample and the membrane results in deterioration of the membrane performance as a result of blockage of the membrane pores or damage of the membrane surface. A more recently introduced membrane separation technique called pervaporation-flow injection (PFI) allows the direct quantitative determination of volatile and semi-volatile analytes in such complex liquid samples [2]. In PFI, the analytes evaporate into the headspace of the pervaporation cell's donor chamber (Fig. 1b) and diffuse through a hydrophobic porous membrane into the acceptor stream where detection takes place. Since there is no direct contact between the sample and the membrane, deterioration of the latter is avoided. A substantial drawback of PFI, compared to GD–FI, is the slower mass transfer process, resulting in higher detection limits and lower sampling rates. For example, the sampling rate of a PFI system for cyanide developed in our laboratory was found be 6 times lower than that of the corresponding GD–FI system employing the same chemistry [3,4]. One of the main reasons for this drawback is the relatively thicker membranes used in PFI systems to support the weight of the acceptor stream. Another factor slowing down the overall mass transfer process in PFI systems is the diffusion of the analyte through the headspace. The analytical performance of PFI systems can be improved by applying a stopped flow approach [5] though this further reduces the sampling rate.

The use of ultrasound as a technical/technological tool has been realized in the fields of chemistry, physics, engineering, medicine and industrial processes. Ultrasound has been used to accelerate chemical reactions and to remove chemical or biological contamination from surfaces and liquids. High-powered ultrasound has a wide range of possible applications, including catalysis, dentistry, electroplating, mixing and food processing, cleaning and plastic welding [6–10]. Ultrasound achieves its chemical and physical effects by generating bubbles within the liquid (reaction) medium – a process called cavitation [6].

A number of physical effects resulting from the application of ultrasound include agitation, microstreaming, turbulence, surface rippling and mass transport. Microstreaming and surface rippling are described as the flow of fluid induced by the action of a sound field. This fluid flow occurs either in a free non-uniform sound field or near various types of obstacles immersed in a sound field or near oscillatory bodies [11]. When the bubbles undergo oscillations within a sound field, the frictional forces generated at the air/liquid interface induce a bulk fluid flow around the air bubble, called cavitation microstreaming or acoustic microstreaming.

Microspace chemistry, taking place in microreactors and micro total analysis systems, has been recognized as an innovative technology which enables combinatorial approaches with the acceleration of the reactions and measurements involved. A novel way of utilizing cavitation within microspace has been reported by Iida et al. [12]. By using a transducer operating at a frequency of 162 kHz in 200×200 μm cross section microchannels, these researchers observed the generation of small bubbles with diameter of a few μm which moved around and grew up rapidly to a few tens of μm. The bubble oscillations were found to enhance the mixing process within these microchannels. It was expected that similar ultrasonic effects could be implemented in membrane separation units of FI systems in order to enhance the chemical reactions and mass transfer processes taking place.

This paper reports on the effect of ultrasound on the mass transfer of amines with different volatility and surface tension in GD–FI and PFI systems.

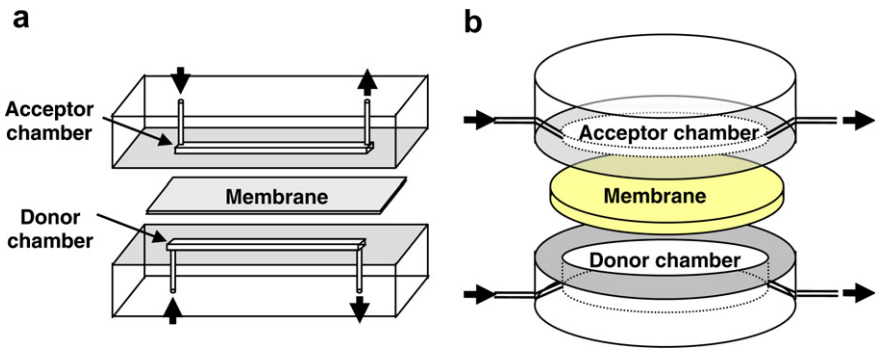

Fig. 1. Schematic of a GD (a) and a PFI (b) cell.