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Development of a total analytical system by interfacing membrane extraction, pervaporation and high-performance liquid chromatography

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Abstract

This paper discusses the interfacing of continuous membrane extraction, pervaporation and on-line HPLC–UV detection into a total analytical system (TAS). Organics from a water sample were extracted into an organic solvent, and then concentrated via pervaporation prior to HPLC–UV detection. Factors affecting the system performance were studied. With optimized experimental parameters enrichment factors as high as 192 were obtained, the method detection limits were at low ng/mL levels, and the precisions were better than 5%.

Keywords: Membrane extraction; Pervaporation; HPLC–UV detection; Total analytical system; Continuous on-line analysis

1. Introduction

There has been much interest in integrating different analytical functions onto a single platform. The efforts have been mainly confined to the bio-analytical arena, where procedures, such as, cell lysis, extraction, PCR and electrophoresis have been integrated in a micro total analytical system (μ-TAS) [1,2]. These ideas are equally valid for conventional laboratory techniques. Typical approach for inorganic, organic, metals and biological analysis involves extraction and concentration followed by analytical detection. The development of total analytical system (TAS) requires the hyphenation of these steps so that continuous, on-line analysis can be carried out without manual intervention.

Let us take the example of the analysis of semi-volatile organics in water. Liquid–liquid extraction (LLE), solid-phase extraction (SPE) and solid-phase microextraction (SPME) [3–9] are the conventional extraction procedures. Although they have some excellent merits, there exist limitations when it comes to direct interfacing with instruments. Classical LLE is labor intensive, uses large amounts of solvents and is difficult to couple directly to an analytical instrument. LLE coupled with flow injection (FI) analysis was reported first time in the late 1970s [10] and since then it has been developed quickly [11–13]. It minimizes the reagent consumption, and can be carried out continuously followed by on-line or off-line detection. In SPE the analytes are extracted from an aqueous sample onto a solid sorbent, and then eluted with a suitable solvent. It has been automated on-line involving multiple batch processes such as conditioning, washing, and elution [14,15]. SPME, where the analytes are adsorbed onto a fused-silica coated fiber and then desorbed at a high temperature prior to analysis, it is simpler, but only suitable for high concentration analysis due to its low sensitivity. The extracts, especially those from SPE and LLE may need further concentration. Conventional methods for this include nitrogen blowing, rotary evaporator, or Kuderna–Danish concentrators. It is evident that both the extraction and concentration procedures involve several discreet batch operations, and are either time-consuming or labor intensive. Thus automated continuous sampling systems are needed.

In the realm of continuous, on-line extraction procedures, membrane extraction is one of the most promising techniques. It is simple, inexpensive, requires small solvent volumes and offers high enrichment. It allows on-line extraction, and has been coupled to gas chromatography (GC) [16–18], high performance liquid chromatography

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(HPLC) [19,20], mass spectrometry (MS) [21], GC–MS [22] and other analytical instruments [23]. Liquid phase membrane extraction can be classified into supported liquid membrane extraction (SLME) and liquid–liquid membrane extraction (LLME) [24]. SLME is a three-phase system in which the analytes are extracted from an aqueous sample into an acceptor phase via an organic extractant held in the pores of the membrane by capillary force. It is suitable for analyzing highly polar and ionizable compounds. LLME is a two-phase system where the analytes are extracted from an aqueous sample to an organic acceptor. The extraction occurs across a membrane, so that the two phases contact through the membrane pores without direct mixing. LLME can be used in any application as long as the compounds can be extracted into an organic solvent [20,25,26]. The driving force in LLME is the partition of analytes between the aqueous phase and the organic acceptor. The presence of membrane in LLME prevents emulsion formation, and other complex phenomena due to the physicochemical instability of the organic-aqueous interface, which occurs when the two phases are directly contacted, such as LLE.

In membrane pervaporation, a liquid mixture contacts a membrane, the volatile species selectively permeate through, and are removed by a vacuum or an inert stripping gas. It has been used in the analysis of volatile organics by selectively stripping from an aqueous medium [27], and for solvent removal in various industrial applications [28]. In this paper analytical-scale membrane pervaporation was carried out continuously for the removal of solvent from the membrane extraction step. The extract is passed through the lumens of hollow fiber membranes while a counter-current inert gas selectively removes the solvent, resulting in the enrichment of the analytes in the lumens. Temperature is one of the important variables in membrane pervaporation and the effect has been studied in previous research [29], thus it was not investigated in this study.

The objective of this study is to develop an automated and simple TAS by interfacing LLME, membrane pervaporation and HPLC–UV detection. These steps will perform extraction, concentration and detection respectively. The automated TAS will have the capability of continuous on-line monitoring of trace analytes in water.

2. Experimental

2.1. Experimental system

The experimental system is shown in Fig. 1. It included two hollow fiber membrane modules, two pumps (Hewlett-Packard 1050 HPLC pump) and a HPLC system (Hewlett-Packard 1050). The first pump was used for the delivery of the organic extractant, and the other for the water sample. An automatic six-port injection valve (Valco Instruments, Houston, TX, USA) was used to make repeat injections into the HPLC. The two membrane modules were structurally similar. Hollow fiber membranes were selected because they provided higher surface area per unit volume. The modules were made in the shell and tube format [16,30–37]. The first one served as the extraction module, and the latter as the pervaporation module. Water sample flowed through the shell side of the extraction module while the organic extractant flowed inside the hollow fiber lumens. The target analytes from the aqueous sample were extracted into the organic solvent in the membrane pores and then into the acceptor phase in the lumens. The extract continued to flow through the membrane lumen of the pervaporation module, where the nitrogen stripping gas flowed counter-current on the shell side. The evaporation of the solvent into the nitrogen flow concentrated the extract. The enriched extract was injected directly into the HPLC for analysis. The injection volume was 20 μL, and the injections were made automatically by a timer controlled six-port injection valve every 5 min.

2.2. Membrane module construction

The hollow fiber membrane modules were made with six pieces of composite membrane fibers packed in a Teflon tube. The length of the membrane used in the extraction and pervaporation modules were 128 and 144 cm, respectively. These

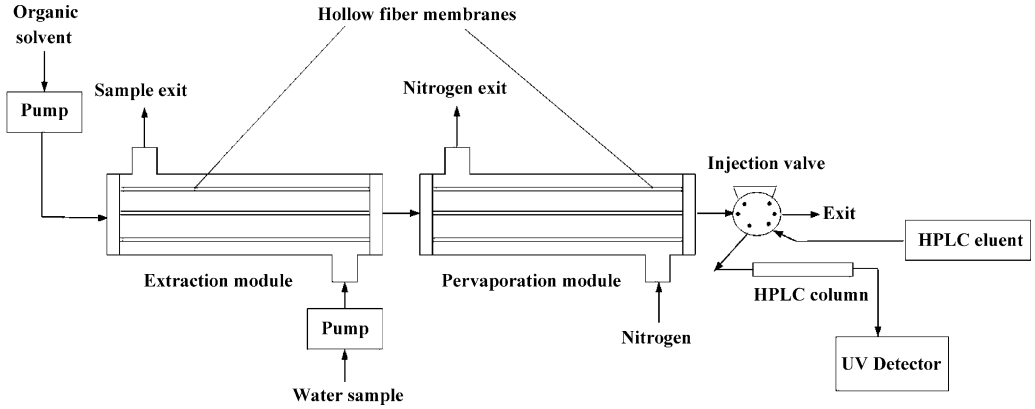

Fig. 1. On-line interfacing membrane extraction, pervaporation and HPLC–UV detection into a TAS.