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Dynamic single-interface hollow fiber liquid phase microextraction of Cr (VI) using ionic liquid containing supported liquid membrane

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ABSTRACT

The concept of dynamic single-interface hollow fiber membrane liquid-phase microextraction (HF-LPME), where the target analyte was extracted on-line and eluted inside the lumen of the HF membrane, was explored. An ionic liquid containing supported liquid membrane was used for the trace determination of Cr(VI) as a model compound. Since the extraction took place on-line inside the hollow fiber membrane, the mass transfer behavior was described and discussed in comparison with the conventional HF-LPME. The extraction efficiency was improved by a recirculation configuration of the sample solution at relatively high sampling flow rates as a result of the increased effective contact area. The positive pressure observed to be built up during extraction was overcome by a flow-balancing pressure design. The dynamic single-interface HF-LPME method with an enrichment factor of 41, a detection limit of 1.2 μg L^{-1} and determination limit of 4.0 μg L^{-1} was successfully applied to the reliable determination of Cr(VI) from environmental water samples. The quantification limit is below the maximum contaminant level in drinking water, set at 10 μg L^{-1} of hexavalent chromium by the California Environmental Protection Agency.

1. Introduction

Liquid-phase microextraction (LPME) involves the extraction of analytes in appropriate chemical form (uncharged species in its simplest configuration) from the aqueous sample into a microvolume of a water-immiscible organic solvent. This approach has been developed to overcome some weaknesses of traditional liquid–liquid extraction (LLE) methods [1–3]. LPME has been reported in various configurations, such as single-drop microextraction (SDME) [4,5], dispersive liquid–liquid microextraction (DLLME) [6,7], and hollow fiber liquid-phase microextraction (HF-LPME) [8,9]. SDME suffers from the low stability and reproducibility of the drop. In DLLME the extract is difficult to collect from the top or the bottom of the sample tube with a syringe [10]. HF-LPME is one attractive alternative since the organic solvent is protected inside the pore of the HF membrane. The advantages of HF-LPME are its low cost, simplicity of operation, use of minute volumes of organic solvent, achievement of high enrichment factors and amenability of automation [11,12].

HF-LPME usually involves the transportation of the analyte from a donor solution across an organic solvent impregnated in the pores of the membrane (supported liquid membrane, SLM) into an acceptor solution filling the lumen of the membrane. Generally, HF-LPME methods are available in two modes: the two-phase mode, where the acceptor solution is the organic solvent, and the three-phase mode, where the acceptor is aqueous. Two-phase HF-LPME is usually applied for the extraction of relatively non-polar organic compounds without acid–base properties. The extraction takes place between two phases, as in conventional LLE. Three-phase HF-LPME is usually applied for the extraction of ionizable or dissociable organic compounds, such as acidic or basic organic compounds. The extraction occurs between three phases in an extraction-back extraction-like process, where the dissociable analytes are first turned into non-dissociated forms, then partitioned into the organic SLM and finally returned in dissociated form into the acceptor solution [13–15].

Several developments in three-phase HF-LPME have been accomplished over the past few years. For examples, several researchers proposed electromembrane assisted extraction in order to enhance the transportation of ionic analytes [16–18], and this has been applied to Cr(VI) [19,20]. Despite the improvement in enrichment factors the use of electric field might accelerate the occurrence of electrolysis causing system instability [20]. Another interesting approach is to assemble on-line/automated three-phase HF-LPME systems for expedient analysis.

HF-LPME has been adapted and incorporated into flow-based analysis systems for on-line/automation configurations [21–23]. Typical on-line HF-LPME systems require feeding configurations in which the donor solution flows outside the membrane and the acceptor

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flows inside the lumen of the membrane. The membrane itself also requires pretreatment steps to allow the organic solvent to fill the pores of the membrane prior to use. The system configuration is more challenging for performing three-phase HF-LPME.

In this work, the concept of dynamic single-interface HF-LPME, similar to in-tube SPME, where the analyte is extracted on-line and eluted into and from the same side inside the lumen of the HF membrane, was explored using an ionic liquid containing supported liquid membrane. Cr(VI) was chosen as a model for our studies because of its toxicity in the environment and its selective detection method with 1,5-diphenylcarbazide (DPC) measured by using UV–Vis spectrophotometer. The extraction performances of the technique for the on-line isolation and enrichment of Cr(VI) were investigated and discussed. Applications of dynamic single-interface HF-LPME to real samples were also investigated.

2. Experimental

2.1. Chemical and reagents

A 100 mg L^{-1} stock standard solution of Cr(VI) was prepared from $K_2Cr_2O_7$ (BDH Chemicals, UK) in Milli-Q water. A 2 mmol L^{-1} 1,5-diphenylcarbazide (DPC) solution (Sigma-Aldrich, USA) containing 80% (v/v) ethanol and 0.05 mol L^{-1} sulfuric acid was prepared daily as the acceptor solution for Cr(VI). The ionic liquid consisted of methyltrialkylammonium chloride (Aliquat 336) and was purchased from Merck (Germany). Kerosene (Carco Chemical Co, Ltd., Thailand), 1-octanol and 1-heptanol (Sigma-Aldrich, USA) were explored as organic co-solvents.

2.2. Apparatus

The polypropylene hollow fiber membrane (Accurel Q3/2, 600 μm ID, 200 μm thickness, 0.2 μm pore size) was purchased from Membrana, Wuppertal, Germany. A syringe pump (Prosense B.V., USA) with a 5.0 mL medical syringe and a peristaltic pump furnished with 0.8 mm id Tygon tubing (Masterflex, USA) were used to deliver the acceptor and donor solutions in the flow system. A fiber-optic UV–Vis spectrophotometer (Avantes BV, the Netherlands) and a quartz ultra-micro cuvette (50 μL; 10 mm light path, Hellma, Germany) were used for the detection of Cr–DPC.

2.3. Dynamic single-interface HF-LPME procedure

A 12.5 cm piece of hollow fiber membrane was sonicated with acetone for 10 min to remove any contaminants and dried prior to use. The membrane was immersed into the organic solvent for 1 h to ensure that the pores were completely filled. The excess solvent in the lumen was removed with air blow pushed by a medical syringe. Then, the membrane was inserted into a glass tube (5.0 mm od×3.0 mm id×140 mm length). Both ends of the membrane were sealed to syringe needles attached to Tygon tubing that connected with the sample solution reservoir as shown in Fig. 1. A 30 mL aliquot of sample solution was fed into the lumen of the membrane in continuous-flow recirculation mode at 10 mL min^{-1} for 15 min using a peristaltic pump as a liquid driver.

After extraction, the sample solution remaining in the lumen of the HF membrane was flushed out with air blow pushed by a medical syringe. Then, the membrane was removed and reattached by one end to a six-port injection valve (V-451, Upchurch Scientific, USA) (position 5) and by the other end to a multi-position selection valve (V-1241-DC, Upchurch Scientific, USA) (position 3) as shown in Fig. 2. A DPC solution as the eluent was filled in a 65 μL sample loop (0.75 mm id×150 mm length) using a medical syringe at the loading position (position 2 of the six-port valve). At the inject position, the DPC solution was pulled into the lumen of the membrane by the syringe pump in aspiration mode at 50 μL min^{-1}. The eluent was drawn into a holding coil (position 6 of the selection valve) and then pushed to an insert vial (position 2 of the selection valve) at 1.5 mL min^{-1} for collection and further analysis. In this study, the hollow fiber membrane was discarded after each use to avoid sample carryover; it could be reused, nonetheless.

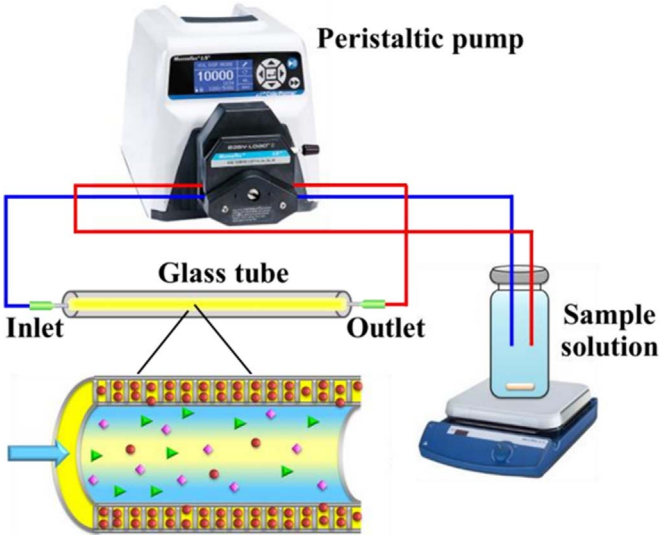

Fig. 1. Schematic diagram of extraction step in dynamic single-interface HF-LPME.

2.4. Determination of Cr(VI)

Cr(VI) was determined by the standard Cr–DPC colorimetric method. A violet solution of Cr–DPC complex was formed in the elution step, collected in a microvial and detected by a fiber-optic UV–Visible spectrophotometer at 544 nm.

2.5. Real samples

Several kinds of water samples were selected for the determination of Cr(VI). Drinking water samples were purchased from local markets in Bangkok, Thailand. Surface water samples were collected from the Chaopraya River and Chulalongkorn University pond. Tap water was analyzed as well. The water samples were filtered through a membrane filter (nylon membrane filter, 47 mm, 0.45 μm, Munktell Germany) to remove particulate matter. After that, the samples were extracted by the described method.

3. Results and discussion

Since the extraction was not exhaustive as in SPME procedures, the extraction performance was evaluated using the enrichment factor (EF), which is the ratio of the final concentration of the analytes in the acceptor solution after the elution to the initial concentration of the analytes in the aqueous donor solution.

3.1. Dynamic single-interface HF-LPME system

3.1.1. Mass transfer behavior and recirculation configuration

In the dynamic single-interface HF-LPME format, the donor is fed inside the lumen of the membrane. The extraction takes place at the interface of the donor phase with the thin layer of the extracting SLM at the wall of the membrane. Unlike conventional three-phase HF-LPME, there are no driving forces from the acceptor phase to continually draw the mass of the analyte from the donor solution. Therefore, the mass transfer of the analyte being extracted depends on the contact time and