Analysis Method of Trace Compounds by Hollow-fiber Liquid-phase Microextraction with Electric Field Enhancement of Mass Transfer

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A novel electric-field-enhanced liquid-phase microextraction system based on hollow fiber membrane has been developed. By introducing the radially enhancing electric field into this system, it is feasible to accelerate the mass-transfer rate of analyte and shorten the equilibrium time. In the process, the extract time was less than 4 min, which is much less than that of traditional liquid-phase microextraction. Further study is in progress.

Liquid-phase extraction is the most commonly used technique for sample pretreatment. However, this method is tedious, labor-intensive, material-wasting, and time-consuming. In response to the above-mentioned problems, efforts have been directed toward liquid-phase microextraction (LPME).[1–3] A novel LPME called HF-LPME,[4–6] which is based on porous hollow fiber, has emerged as the times have required overcoming the operational instability of traditional LPME. HF-LPME integrates sampling, extraction, analyte enrichment, and stability to form a synergistic whole. It has been widely used in analytical chemistry, pharmaceutical research, food safety, and environmental contamination determination because HF-LPME is accurate, precise, inexpensive, environmentally friendly, reduced solvent consumption, automated, and coupled with other on-line instruments easily.

On the other hand, neither LPME nor HF-LPME can reach liquid–liquid equilibrium in a very short time because there is no effective approach to enhance the mass-transfer efficiency among the liquid phases. Thus, an approach of process intensification is needed in these microextractions. It is well known that substances which are electriferous in solution can migrate in oriented direction under the drive of electric potential difference. Furthermore, electric energy can be directly transformed into liquid–liquid dispersion energy. This mechanism will make the target substances migrate in the required direction more quickly and make a great progress to increase the mass-transfer efficiency among the phases in a microextractor. Therefore, an HF-LPME enhanced by electric fields reported here was developed under the current chemical process intensification.

The aim of this work is to establish an enhanced HF-LPME using electric potential difference as an intensive method. In the proposed technique, a radial electric field, which can avoid the influence of irregular electrical field[7,8] on the mass-transfer efficiency, was introduced into the HF-LPME system to enhance the mass-transfer efficiency among phases. By eliminating irregular electrical field, it is possible to achieve reasonable extraction results and reproducibility.

The electric-field-enhanced HF-LPME system presented here was designed and constructed in-house, the process flow diagram of the microextraction is shown in Figure 1. In the study, the sample compartment was a 5.0 mL of polyethylene tubular container with platinum coating, which could be used as one electrode of the applied voltage, on the inner surface. The other electrode was inserted into a porous hollow fibre membrane, which was located at the center of the tubular container, filled with extraction phase. Thus, a radial electrical field was constructed. The membrane was polysulphone hollow fiber membrane, made by MOTIMO Membrane Technology Ltd (Tianjin, China), with an inner diameter of 1.0 mm, wall thickness of 0.2 mm, pore size of 0.1 µm, and pore ratio of 50%. The direct current power supply, purchased from Dongwen High Voltage Power Supply Plant (Tianjin, China), can be changed within the range of 0–500 V accurately. All chemicals used were of analytical grade or higher unless otherwise stated. The samples were dissolved in deionized water at proper concentrations.

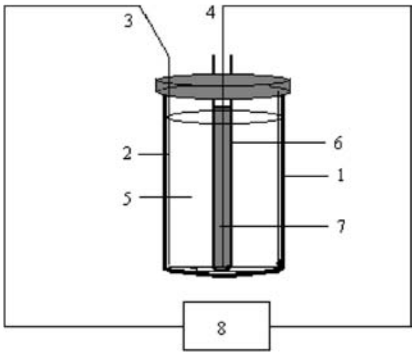

Figure 1. Process flow diagram of the electric-field-enhanced HF-LPME system. (1) tubular container; (2) platinum coating on the inner surface of tubular container; (3), (4) platinum electrode; (5) analyte solution; (6) porous hollow fibre membrane; (7) extraction phase; (8) direct current power supply.

The process of microextractions was carried out according to the following: In order to eliminate the contamination disturbance from membrane, the hollow fiber membrane tubes were washed with methanol at least three times after being cut in 5 cm pieces and sealed at one end on a flame. Then, 5 mL of sample solution was filled into the tubular container, and 20 µL of *n*-octanol as extraction solution was implanted into the hollow fiber membrane tube. Enhancing voltage was then applied between sample solution and extraction phase for several minutes after the equipment was assembled as in Figure 1. In the process, analyte can migrate quickly through the thin layer of the wall of porous hollow fiber membrane, from the sample solution into the extraction solution present inside the lumen of the hollow fiber membrane by the drive of a radial voltage. After extraction completed, the extraction phase was collected with a microsyringe and analyzed by gas chromatography directly. Then, the enrichment factor[9] and the logarithm of the partition coeffi-

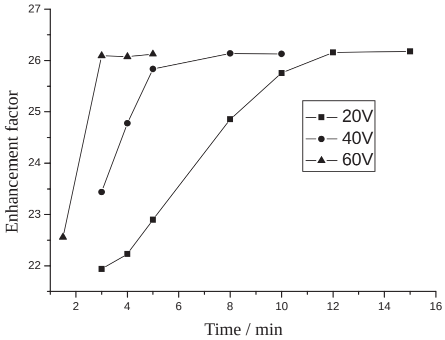

Figure 2. Influence of voltage on the HF-LPME of phenol.

cient between *n*-octanol and water values ($\log P$)[10] of organic compounds can be calculated through these experimental data.

To evaluate the efficiency of enhancing mass transfer by the electrical field, 7.8×10^{-5} g/mL phenol solution was taken as a model compound, and the microextractions were monitored with different applied voltage. The plots of enrichment factor and time of these extractions are shown in Figure 2. It is illustrated in Figure 2 that the efficiency of enrichment increased sharply with the time at the beginning of each process while the parameter remained almost constant even experiment time was prolonged after the extraction reached equilibrium state. It is also indicated from Figure 2 that the applied voltage has a distinct influence on the equilibrium time. The microextraction reached equilibrium within 4 min under 60 V extraction voltage. This time was much shorter than that of 40 and 20 V while the equilibrium time was more than 20 min if the enhancing method was magnetic stirring at 600 rpm instead of electric field.[10] Furthermore, it has been found experimentally that Joule heat, which was generated during electrophoresis, could have some negative effects on the properties of hollow fibre membrane and made microextraction operation unstable if the operation voltage was over 80 V. Therefore, the optimal operation conditions were compromises of enhancing efficiency and operation stability. So the following series of experiments were all done under 60 V extraction voltage.

Also, phenol was taken as a model compound to determine the application scope of the electric-field-enhanced HF-LPME. In these experiments, the phenol solution was diluted into seven concentrations from 1.0×10^{-5}–1.0×10^{-3} g/mL. Then, microextractions were processed under 60 V drive voltage. The experiment results indicated that the $\log P$ values were constant throughout the range of low concentrations.

In order to evaluate the service performance of the proposed method roundly, some model compounds were analyzed within 4 min on this system. The experimental and literature data of $\log P$ are shown in Table 1. It was shown from comparison of the results that the data obtained by the proposed method are in good agreement with the literature values, which are regarded as credible. The novel experimental apparatus and procedure are, therefore, speedy and reliable.

Table 1. Comparison of experimental $\log P$ data with documented values

Compound	Experimental values	Literature values
Nitrobenzene	1.77	1.83[11]
Aniline	0.93	0.92[12]
Phenol	1.47	1.46[13]

The electric-field-enhanced HF-LPME analysis presented here can be performed under the driving force of radial electrical field effectively. The experimental results indicated that the polysulphone porous hollow fiber has excellent permeability and that organic compounds can be commendably enriched under the electric drive. Thus, the electric-field-enhanced HF-LPME system can be an effective and prompt approach to trace organic analysis. Further work on the technique and its applications is undergoing in our group. The novel technique should be applied widely to research on phase equilibrium, trace chemical analysis, environmental analytical chemistry, physical properties of drugs, pesticides, and other chemicals.

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