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# Development and evaluation of plunger-in-needle liquid-phase microextraction

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ABSTRACT

In this work, a novel, simple and fast one-step liquid-phase microextraction (LPME) approach, termed plunger-in-needle LPME was developed. In this method, the stainless steel plunger wire of a commercially available plunger-in-needle microsyringe was simply etched by immersion in hydrofluoric acid to form a microporous structure, and was used as the extractant solvent holder. The extractant solvent could be easily held within the pores created by the etching. When the plunger wire with the extractant solvent was exposed to the sample solution, analytes directly diffused from the sample solution to the solvent. After extraction, the plunger wire was directly introduced into the injection port of a gas chromatography–mass spectrometry (GC–MS) system for analysis of the analytes after thermal desorption. Polycyclic aromatic hydrocarbons (PAHs) were used as model analytes to evaluate the extraction performance of this new approach to LPME. Parameters affecting the extraction efficiency were investigated in detail. Under the optimized conditions, the method detection limits for 10 PAHs were in the range of 0.003 and 0.136 μg/L (at a signal/noise ratio of 3), with relative standard deviations of between 2.9% and 9.6% on the same etched plunger wire. The linearities of the calibration plots were from 0.05 to 50 or from 1 to 50 μg/L, depending on the PAHs. When this method was applied for the spiked river water sample, the relative recoveries ranged from 70.1% to 106.4%. The proposed method integrates the extraction and extract introduction into one device, without extraneous sorbent needed, which makes the procedure fast and simple. It is also an environmentally friendly approach as the organic solvent consumed is almost negligible.



## 1. Introduction

Recent research activities in sample preparation are oriented toward the development of miniaturized, simple (preferably one-step), efficient, economical, and solvent-minimized (even solvent-free) techniques. In the past decade, miniaturization has developed very rapidly in terms of its technology and applications. These techniques include sorbent and solvent-based procedures such as solid-phase microextraction (SPME) [1] and liquid-phase microextraction (LPME) [2,3].

In 1990, Arthur and Pawliszyn [1] introduced a solventless extraction method, SPME, an important feature of which is that extraction and injection are incorporated in a single step. The technique relies on the equilibration between the analytes and the sorbent phase. There is virtually no sample pretreatment needed before analysis and after extraction. The main drawbacks of SPME are that commercial fibers are expensive and commercial silica-based fibers have a limited lifetime, as they tend to degrade with the number of samplings, particularly in the direct immersion mode.

Cantwell and Jeannot [2] introduced a solvent microextraction technique by which analytes were extracted into a single drop of organic solvent in 1996. He and Lee [3] subsequently introduced the term liquid-phase microextraction for miniaturized solvent-based extraction in general. In its simplest form, LPME is performed by suspending a microliter drop of organic solvent on the surface of either a Teflon rod or the tip of a microsyringe needle immersed in a stirred aqueous solution. This LPME approach is now known as single-drop microextraction (SDME). In SDME, the analytes partition between the bulk aqueous phase and the organic solvent microdrop. The applications of SDME in environmental analysis and drug analysis have been described in several reports [4–10]. Compared to conventional liquid–liquid extraction (LLE) and solid-phase extraction (SPE), SDME gives a comparable and satisfactory sensitivity and usually better enrichment of analytes. In addition, the consumption of solvent is significantly reduced by up to several hundred or several thousand times, and the method is extremely affordable, rapid, and simple to operate, and needs only a common microsyringe to operate.

However, some practical considerations limit the applications of SDME. The major problem of SDME is that the microdrop suspended on the needle of microsyringe is potentially easily dislodged by forces generated by stirring of the aqueous sample. Although the

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selection of a syringe with a beveled needle tip [3], suitable solvent [6], and a very small volume of solvent (~1 μL) can obviate this difficulty, they cannot solve this problem completely.

Another widely used mode of LPME, hollow fiber-protected LPME [11,12], makes use of a polymeric hollow fiber to hold, stabilize and, most importantly, protect the acceptor (organic extractant, 2–3 μL) phase. When the fiber is immersed in or suspended over (for headspace extraction) the donor phase, the target analytes can be extracted into the acceptor phase through the wall pores of the fiber.

Subsequently, Jiang and Lee [13], introduced a novel form of LPME, termed as solvent bar microextraction (SBME). In this method, the organic solvent is held and protected within a short length of a polypropylene hollow fiber with its two ends sealed. This solvent bar can be directly placed into the sample solution for extraction. Due to the tumbling of the solvent bar in the agitated sample solution, mass transfer between the organic phase and aqueous phase is facilitated, thus resulting in higher extraction efficiency. As an extension, a silica monolith was reported as the extractant solvent holder [14] in SBME. Owing to the porous nature of the monolith, the extractant solvent could be easily held in the material; when the monolith containing the extractant solvent was exposed to the sample solution, analytes could directly undergo mass transfer from the sample solution to the extractant solvent. Unfortunately, SBME also suffers from some shortcomings. There is potential loss of organic solvent from the tumbling bar during sample stirring. Also, some manual handling of the hollow fiber is needed (filling it with solvent, heat-sealing it, and trimming it to retrieve the extract). For monolith supported SBME, centrifugation, to force out the extract, and reconstitution of the extract to ensure sufficient volume for analysis are needed. In a recent report, Saraji and Farajmand coated a stainless steel wire with microporous silica, before adsorbing a solvent onto the surface to carry what they described as combined SPME and LPME [15]. The silica acted as a solvent holder in a similar way to that reported in the earlier work by Xu and Lee [14], as mentioned above.

Recently, the use of bare stainless steel wire etched by hydrofluoric acid (HF) as an SPME fiber was developed by Xu and co-workers [16] and applied to the extraction of several polycyclic aromatic hydrocarbons (PAHs), pyrethroid insecticides [17] and polybrominated diphenyl ethers [18]. The purpose of the present study was to develop a novel concept of LPME combined with a commercially available plunger-in-needle microsyringe. The plunger wire was initially etched using HF by simply immersing it in the acid, and it served as the holder for organic solvent, which penetrated the pores created by the etching. The HF-etched wire possessed a rough and porous structure, that conceivably increased the interfacial area between solvent and aqueous sample, thus increasing the extraction efficiency. Several PAHs were selected as model analytes to evaluate the procedure, termed plunger-in-needle LPME (PIN-LPME). Extraction parameters influencing PIN-LPME were investigated and optimized. The procedure was compared with SDME, hollow fiber LPME, and plunger-in-needle SPME. Finally, PIN-LPME was applied to process genuine environmental water samples.

## 2. Experimental

### 2.1. Chemicals and reagents

HPLC-grade methanol and toluene were obtained from Tedia Co. (Fairfield, OH, USA). 1-Octanol was purchased from Sigma–Aldrich (St. Louis, MO, USA). The PAH standards (fluoranthene (Flt), pyrene (Pyr), chrysene (Chr), benz[*a*]anthracene (BaA), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[*1,2,3-cd*]pyrene (InP), dibenz[*a,h*]anthracene (DBA) and benzo[*g,h,i*]perylene (BPe)) were bought from Supelco (Bellefonte, PA, USA). Fluka Analytical (Buchs, Switzerland) was the supplier of the hydrofluoric acid (HF) (47–51%). Sodium chloride (NaCl) was acquired from Goodrich Chemical Enterprise (Singapore). Ultrapure water was obtained from ELGA Purelab Option-Q (High Wycombe, UK).

The Accurel Q 3/2 polypropylene hollow fiber membrane purchased from Membrana GmbH (Wuppertal, Germany), has the following dimensions: inner diameter, 600 μm; wall thickness, 200 μm; pore size, 0.2 μm.

### 2.2. Apparatus and instrumentation

The plunger-in-needle (with replaceable 26-gauge, 70 mm long needle, 0.47 mm internal diameter (I.D.)) microsyringe (1-μL capacity) was purchased from SGE (Ringwood, VIC, Australia). For LPME applications, a replacement needle (23-gauge, 50 mm long needle, 0.63 mm I.D.) (SGE) was necessary. The latter shorter needle allowed the plunger, particularly the solvent-impregnated tip (of ca. 2.0 cm length), to be withdrawn into it for protection, during PIN-LPME operations, and introduction of the extract into the gas chromatography–mass spectrometry (GC–MS) system for analysis.

In order to impregnate solvent onto the HF-etched plunger wire thoroughly, an ultrasonic cleaner (Soniclean 160HT, Thebarton, S.A., Australia) was used. A Vibramax 100 (Heidolph, Kelheim, Germany) magnetic stirrer was employed for stirring the sample during extraction. A JSM-6701F Field Emission Scanning Electron Microscope (JEOL, Tokyo, Japan) was used for the investigation of the surface morphology of the stainless steel plunger wire before and after etching. The wire was fixed on the stub by a double-sided sticky tape and then coated with platinum by a JFC-1600 Auto Fine Coater (JEOL) for 30 s.

GC–MS analysis was carried out using a Shimadzu (Kyoto, Japan) QP2010 system equipped with a Shimadzu AOC-20i auto sampler and a ZB-5 MS GUARDIAN$^{TM}$ fused silica capillary column (30 m × 0.25 mm I.D., film thickness 0.25 μm) (Phenomenex, Torrance, CA, USA). Helium was used as carrier gas at a flow rate of 1.7 mL/min. For PAH analysis, the GC conditions were as follows: initial oven temperature 70 °C for 2 min, increased to 230 °C at a rate of 25 °C/min and held for 1 min, and then increased to 260 °C at a rate of 10 °C/min, and then further increased to 285 °C at a rate of 5 °C/min, and held for 7 min. The injector temperature was set at 295 °C. Injections were in splitless mode. The GC–MS interface was maintained at 300 °C. Solvent cut time was 5 min. For toluene analysis, the GC conditions were set as: initial temperature 70 °C for 1 min and increased to 100 °C at a rate of 7 °C/min and held for 5 min. The injector temperature was 295 °C. Split injection (split ratio of 20) mode was used. The GC–MS interface temperature was set as 150 °C. Solvent cut time was 1 min. All standard and samples were analyzed in selective ion monitoring (SIM) mode at least in triplicate.

### 2.3. Sample preparation

Stock PAH solutions (10 μg/mL each of analyte) were prepared in methanol and stored in the dark at 4 °C. Water samples were prepared by spiking ultrapure water with the analytes at known concentrations (generally 50 μg/L) to study extraction performance under different conditions.

Genuine water samples were collected from the Singapore River and stored in aluminum-wrapped glass bottles in the dark at 4 °C. They were processed and analyzed directly or after being spiked with PAHs at a concentration of 5 μg/L of each compound. Samples were used directly (unfiltered) for extraction.