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The Use of a Beveled Porous-Polypropylene Hollow Fiber for Liquid-Liquid Microextraction in Paper Spray- Mass Spectrometry

Jian-Siang Wang, Pei-Hua Lai, Yea-Wenn Liou, Chien-Chung Chen and Cheng-Huang Lin*

Department of Chemistry, National Taiwan Normal University, 88 Sec. 4, Tingchow Road, Taipei, Taiwan

Abstract

The use of a porous, hollow polypropylene fiber for sample microextraction in paper spray-mass spectrometry is described. After the microextraction process, one of the end of the hollow fiber was cut into a bevel-shaped, and then used directly for electrospray ionization. Since analytes can be extracted from a very dilute solution using this liquid-liquid extraction process, the limit of detection can be dramatically improved, compared to an ordinary paper-spray mass spectrometry in which a triangular shaped piece of chromatography paper is used. Detailed information and the use the technique in the analysis of a urine sample are reported.

Keywords: Paper spray-mass spectrometry; *p*-chloroamphetamine; Porosity-polypropylene; Hollow fiber; Liquid-liquid extraction

Introduction

By using a triangular shaped section of chromatography paper, so-called paper spray-mass spectrometry (paper-spray MS) has opened new insights in the field of mass spectrometric analysis. This method is simple, economical and rapid, since its debut in 2010 [1], and as a result, it has now become a quite popular and important method for use in mass spectrometry. The method has recently been applied successfully in many areas of research, including food science [2-5], biofluid sample [6], protein complexes [7], rapid discrimination of bacteria [8], online chemical monitoring of cell cultures [9], and drugs of abuse in whole blood [10], and even in an ambient inorganic analysis [11]. Some novel alternate techniques based on paper-spray MS have also been reported, including a 3D-printed paper spray ionization cartridge/continuous solvent supply [12] and the rapid detection of cocaine residues by paper spray ionization coupled with ion mobility spectrometry [13], etc. Although various types of paper have been evaluated for use in this area [1,14], chromatography paper continues to be the most commonly used material. In our previous study [15], we compared the normal chromatography paper that is used in paper-spray MS with a series of papers (natural fibers and *synthetic* fibers), and the findings showed that the limit of detection could be measurably improved when either gampi paper or a poly-L-lactic acid (PLLA) nanofiber sheet was used. This is because gampi paper or a PLLA nanofiber sheet is very tough and extremely thin, which permits sample molecules to be instantly transported and evaporated. Since ionization occurs within a very short period, an abundance of ions is formed, leading to a dramatic improvement in the limit of detection. However, all of these methods have limitations, especially they are difficult to combined with any extraction method. In this paper we report on a combination of the paper-spray technique and an efficient microextraction process [16]. A commercial porosity-polypropylene (PP) hollow fiber [17-24] was used for the microextraction, and, after the microextraction was complete then one of the ends of the PP hollow fiber was cut into a beveled shape and then directly used for electrospray ionization. A series of designer drugs, including *p*-chloroamphetamine were used model analytes, which permitted the data obtained in this study to be compared to previously acquired data collected in our laboratory, using the same mass spectrometer. Details of the procedures for conducting the *microextraction and p*aper-spray mass spectrometric analysis are also reported in detail.

Experimental

Materials

p-Chloroamphetamine, ketamine, 3,4-methylenedioxymethylamphetamine (3,4-MDMA) were generously donated previously by the Military Police Command, Forensic Science Center, Taiwan. Analytical-grade *n*-dodecane was purchased from Sigma-Aldrich (MO, USA); acetonitrile, methanol, and acetone were purchased from Merck (Darmstadt, Germany). Chromatography paper and porous polypropylene hollow fibers (I.D., 0.6 mm; wall thickness, 0.2 mm; averaged pore size; 200 nm) were obtained from Advantec (Japan) and Membrana (Model, PPQ3/1; Wuppertal, Germany), respectively.

Apparatus

The mass spectrometer (Finnigan LCQ Classic LC/MS/MS) used in this study was the same instrument that was used in our previous study [15]. The mass signal was recorded under the full scan mode (*m/z*, 100 ~ 400). An Xcalibur data system was used for data collection, and the data were converted into an ASCII text file. The capillary temperature and spray voltage were set at 200°C and 3.0 kV, respectively. The tube lens offset and capillary voltage were set at -36 V and 36 V, respectively. A scanning electron microscope (SEM; JSM-6510, JEOL Ltd.) was also used for surface observations.

Procedures for microextraction

In Figure 1, the left photo shows the microextraction setup used in this study; the right photo shows a SEM (scanning electron microscope) image of one of the ends of the porous-polypropylene hollow fiber. As mentioned above, the averaged pore size was about 200 nm. A 15 mL aliquot of an aqueous stock solution, which was placed in

***Corresponding author:** Cheng-Huang Lin, Department of Chemistry, National Taiwan Normal University, 88 Sec. 4, Tingchow Road, Taipei, Taiwan, Tel: +886277346170; Fax: +886229324249; E-mail: chenglin@ntnu.edu.tw

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a 20 mL sample vial, contained 0.1 μg/ml of *p*-chloroamphetamine. In order to improve the effect of the liquid-liquid extraction, 3.5 g NaCl was added to the stock solution, and pH value was adjusted to 11.0 by using a NaOH solution (0.1 M). In the beginning, one end of a section of a PP hollow fiber (length, 7 cm; weight, 0.01 g) was connected the needle of a HPLC syringe (left in the photo) and the other end to a medical syringe (right in the photo), respectively, that had been ultrasonically cleaned in acetone for 5 minutes, and air-dried. The PP hollow fiber that was attached to the needles was then immersed in *n*-dodecane as a solvent. After several seconds, the inner *n*-dodecane was removed by blowing air through the interior of the fiber that was attached to the medical syringe, and 20 μL of methanol was injected into the lumen of the fiber. The solvent used for the extraction can be changed if necessary, depending on the type of analyte. Meanwhile, some *n*-dodecane was retained by the porous fiber-wall. The fiber-wall, with the absorbed *n*-dodecane, plays a very important role as a boundary between the stock solution and the organic solvent used for the extraction. Following this, the PP hollow fiber was placed in the stock solution (mentioned above), which was stirred at 700 rpm for 30 minutes. Finally, the PP hollow fiber was removed and air-dried under ambient conditions.

Experimental conditions

Figure 2 shows a photo of the beveled porous PP hollow fiber spray-mass spectrometry setup used in this study. After completion of the microextraction processes, a portion (2 cm in length) of the PP fiber was used in the following experiments. One of the ends of the hollow fiber was cut into a beveled shape at a 25° angle. The shaped fiber was connected to an ESI needle, in which a high voltage and auxiliary solvent can be applied simultaneously. In this case, the applied voltage was +3 kV and the optimized distance from the tip to the MS inlet was ~ 5 mm. In order to continuously rinse the bevel-shaped PP hollow fiber and the elute the extract, methanol (at a rate of 6 μL/min) was used as an auxiliary liquid. The inset photo shows an expanded portion of the MS inlet and the bevel shaped PP hollow fiber. For comparison, a piece of chromatography paper was cut into a triangular shape (tip degree, 15°), 10 mm in length and 3 mm wide. The sample solution was dropped on the triangular spray-paper, and then directly placed on a paper-holder, in which a high voltage power supply and auxiliary solvent also can be simultaneously applied.

Results and Discussion

Frame A and B in Figure 3 show typical mass spectra of the test sample (*p*-chloroamphetamine; concentration level, 0.1 μg/ml) obtained from the regular triangle chromatography paper-spray and the beveled end hollow fiber-spray mass spectrometry, respectively. As can be seen, a very minor peak is produced with the regular method, i.e., a triangle-shaped chromatography paper is used, although the concentration level is extremely low. The ion intensity is only 5.86×10^4 counts. It is also clear that an extraction procedure is definitely necessary if the limit of detection is to be improved. In contrast to this, when a microextraction was performed using the new method, the ion intensity was dramatically improved to 1.08×10^6. In the other words, a 20-fold improvement was achieved. Furthermore, when the optimized experimental conditions were used, the extract (*p*-chloroamphetamine) can be eluted and ionized during ~ 1 min. This indicate that the sample molecules in the porous-polypropylene hollow fiber are transported and evaporated nearly instantly, and, as a result, many more sample molecules can be detected within a very short period of time. Instead of the stock solution described above, a real urine sample was also analyzed. A 15 mL aliquot of a urine sample obtained from a human volunteer; the research on humans complied with the code of ethics of the World Medical Association. After dilution to 1/10, the diluted urine sample was placed in a glass tube and then spiked with a mixture of *p*-chloroamphetamine, ketamine and 3,4-MDMA (concentration of each, 1 μg/ml, respectively), without any other treatments. Following this, the PP hollow fiber was used for microextraction (extraction time, 30 min). Figure 4 shows a typical mass spectrum obtained from the urine sample. As can be seen, the spiked drugs of abuse can be clearly detected. Some unknown peaks are also observed due to the fact that urine is composed of a complex mixture of compounds. The other compounds in the urine sample interfered with the detection when a triangle-shaped chromatography paper was used (data not shown). However, when the microextraction method was used, not only were the effects of such other compounds depressed, but the target molecules were also concentrated. Thus, we can conclude that the combination of microextraction and a beveled end hollow fiber provide a new approach to the analysis of samples that are present at very low concentrations.

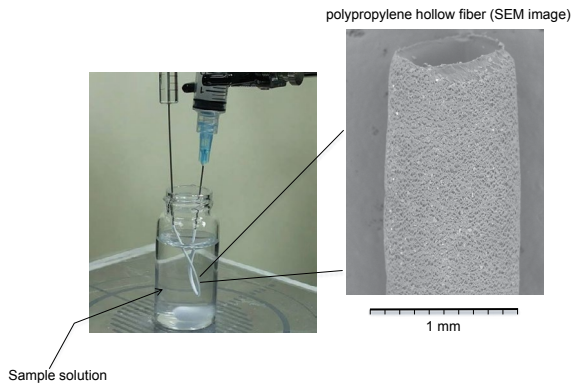

Figure 1: Left photo: Microextraction setup used in this study; Right photo: A SEM image of one of the ends of the porous-polypropylene hollow fiber.

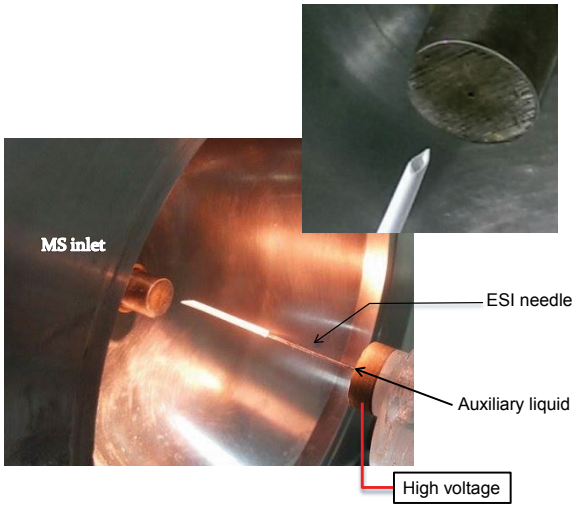

Figure 2: A photo of the beveled porous PP hollow fiber spray-mass spectrometry setup used in this study. The inset photo shows the expanded portion of the MS inlet and the shape of the PP hollow fiber.

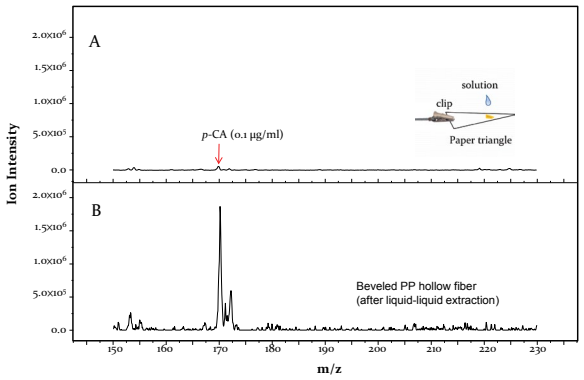

Figure 3: Mass spectra of the test sample (*p*-chloroamphetamine; concentration level, 0.1 μg/mL) obtained for the regular triangle chromatography paper-spray procedure and beveled end hollow fiber-spray mass spectrometry, respectively. Frame A, mass spectrum obtained by the regular method, i.e., use of a triangular shaped chromatography paper; Frame B, a microextraction was performed and the data obtained by the beveled end hollow fiber method.

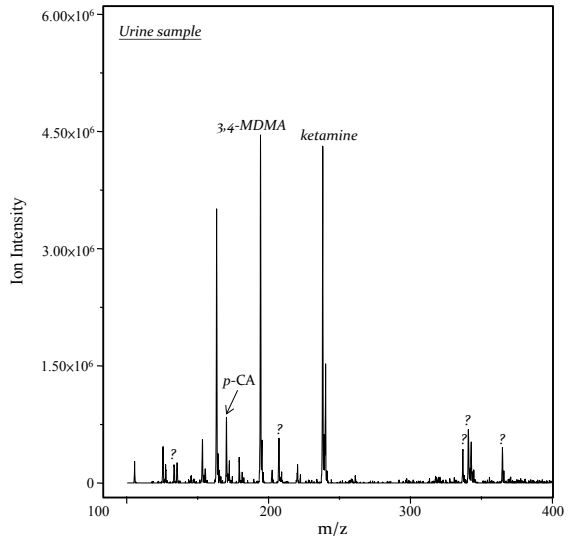

Figure 4: Mass spectra of a urine sample, spiked with a mixture of p-chloroamphetamine, ketamine and 3,4-MDMA (concentration level of each, 1.0 μg/mL, respectively). The spiked urine sample was made alkaline by the addition of 1g of potassium carbonate and was then shaken for 1 min. Following this, the PP hollow fiber was used for microextraction (extraction period, 30 min). A mass spectrum was obtained for the microextraction process followed by the beveled end hollow fiber method.

Conclusion

The development of a novel method for paper-spray mass spectrometry by combining the microextraction method is described, for the first time. When a commercial porous-polypropylene hollow fiber was used for the extraction, the beveled end of the hollow fiber a play the role in ESI similar to that of the typically used triangular shaped chromatography paper. As a result, the limit of detection can be dramatically improved. In addition to a PP hollow fiber, many other types of hollow fibers can be used, as indicated by the results reported in this study. This method is simple and economical, and is suitable for use in the rapid screening of drugs, since it has a high degree of sensitivity, the operating procedure is simple and an ion signal can be observed immediately. We believe this method has the potential for use in practical analyses and can also be regarded as a helpful tool for use, not only in forensic and clinical analysis, but also biomolecules. Further applications are currently being explored.

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