Sensors and Actuators B 191 (2014) 264–269

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

# Photonic crystal fibres as efficient separation component in capillary electrophoresis

Matías Calcerrada [a,*], Philippe Roy [b], Carmen García-Ruiz [a], Miguel González-Herráez [c]

[a] Department of Analytical Chemistry, Physical-Chemistry and Chemical Engineering, University of Alcalá, Multipurpose Building of Chemistry, Madrid 28871, Spain
[b] XLIM – Fibre Photonics Department, Faculty of Sciences and Techniques, 123, Avenue Albert Thomas, Limoges 87060, France
[c] Department of Electronics, University of Alcalá, Polytechnic School DO-231, Madrid 28871, Spain

ARTICLE INFO

*Article history:*
Received 12 April 2013
Received in revised form
14 September 2013
Accepted 20 September 2013
Available online 5 October 2013

*Keywords:*
Capillary electrophoresis
Photonic crystal fibres
Laser induced fluorescence
Chemical sensing
Micro-structure
Bundle of capillaries

ABSTRACT

Telecommunication developments are leading to original and new fibre designs which indeed are being used in a huge variety of fields. In this manuscript we show that Photonic Crystal Fibres (PCFs) can be used as efficient chemical separation devices in commercial capillary electrophoresis (CE) equipment. A comparison of conventional capillaries, PCFs and new devices inspired on PCFs named Smart Micro-Structured Capillaries (SMSCs) is made. Results showed the usefulness and efficiency of these physical supports in CE through the detection of fluorescein. In addition, some considerations to take into account for SMSCs manufacturing are discussed. Further work should allow coupling the separation advantages achieved by these elements with the wide variety of detection techniques available in fibre-optics.


## 1. Introduction

Developed in the middle 90s and initially considered as a daunting challenge, photonic crystal fibres (PCFs) have evolved from being components used solely in communications to become important elements in a huge variety of fields. Depending on the designs, waveguiding or manufacturing materials, one can use PCFs in diverse applications [1]. Taking advantage of the success of nanoscience and nanotechnology, some authors have used PCFs as new components in analytical techniques and chemical sensing [2]. Analytical chips and biochips are some devices where PCFs are being widely used [3–10]. For instance, PCFs have been integrated in chips in order to improve detection of biological samples [3,4]. Suspended-core PCFs (SC-PCFs), have been used in DNA detection since a higher fraction of evanescent field is produced and long-range guided interactions between the light and the matter under study take place [9]. Mass spectrometry is another analytical technique which has also taken advantage of the use of micro-structured fibres, for instance in multichannel electrospray emitters that use these structures to allow an efficient desolvation [10]. Photonic fibres and multicapillaries have also been used in surface-enhanced Raman scattering sensors [11,12], as well as hollow-core PCFs in Raman spectroscopy to enhance Raman signal [13]. Other reported applications include pH, humidity and salinity sensors [8,14,15]. Among the remaining analytical techniques, capillary electrophoresis (CE) is an efficient and economical one capable of separating tens of components simultaneously providing better resolutions than other separation techniques, by using small amounts of samples and reagents, which makes it environmentally friendly. In addition, the variety of options when using this technique (different voltages, sample and cartridge temperatures, and a wide range of detectors, capillaries, electrophoretic modes, injection modes, etc.) makes it highly versatile. [16]. Being the use of PCFs more common in microchip CE [5,6], only one work was focused on their use in conventional CE [17]. However, the use of PCFs in commercial equipment has not been reported in the literature. In this paper a preliminary study on the use of PCFs in commercial CE equipment is made. This manuscript is structured as follows: first, we will provide a description of the technique and some theoretical advantages of using PCFs over conventional capillaries. Then we will show various experiments using fluorescein as target compound. The use of PCFs and new designs named Smart Micro-Structured Capillaries (SMSCs) in

* Corresponding author at: Department of Analytical Chemistry, Physical-Chemistry and Chemical Engineering, Multipurpose Building of Chemistry, University of Alcalá, Ctra., Madrid-Barcelona km. 33.600, 28871 Alcalá de Henares, Madrid, Spain. Tel.: +34 91 885 4971/00617271829; fax: +34 91 885 4971.
*E-mail address:* matias.calcerrada@uah.es (M. Calcerrada).

0925-4005/$ – see front matter. 
http://dx.doi.org/10.1016/j.snb.2013.09.087

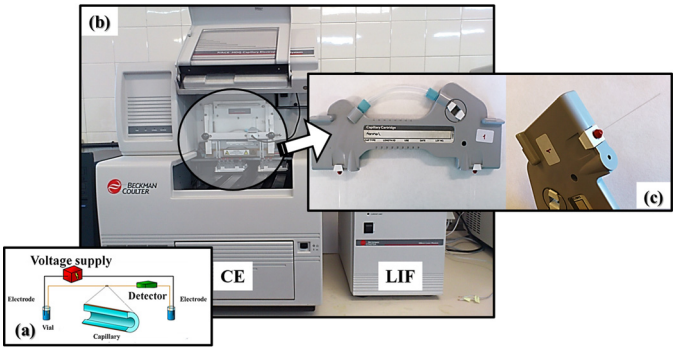


**Fig. 1.** (a) Basic scheme of the CE technique; (b) commercial equipment and detector used (Beckman Coulter P/ACE MDQ and LIF system); and (c) capillary cartridge used in the equipment and detail of a fibre inside it.

commercial CE equipment is proved in this study, as well as preliminary comparisons between these new structures and conventional capillaries currently used in CE.

### 1.1. Potential advantages of using PCFs in CE

CE is an analytical technique based on the separation of ions of diverse interest through a polyimide-coated glass capillary (usually 20–100 cm length and 50–75 μm of inner diameter (i.d.)) and the use of a high voltage supply. Fig. 1 shows a basic scheme with the main components of this equipment. Between the two ends of the capillary (submerged in an ionic solution) a high voltage (5–30 kV) is applied. The resulting electric field generated is capable of producing various forces. On one hand, different mass/charge ratios of compounds cause electrophoretic mobility, which produces the movement of ionic species to both electrodes, depending on the charge. On the other hand, an electroosmotic flow can be induced if the capillary is properly conditioned, producing a constant flow from one electrode to another. As a result, these forces cause different speeds for each compound, achieving the separation among them. While separating, the species also travel along the capillary and may be detected through a wide variety of detectors such as ultraviolet absorption (UV) or laser-induced fluorescence (LIF). The detection is usually done by transversal illumination on the capillary, making a window on the polyimide coating. Results are presented in an electropherogram and substances appear as peaks of different shapes.

Towards efficient separation, high voltages and narrow capillaries should allow to achieve, respectively, higher speed and less band broadening. However, these extreme conditions may give rise to peak overlapping if the time is not enough to achieve entire separations or low sensitivity if the sample introduced is minimal due to the capillary narrowness. In addition, the Joule effect in the capillary (heat generation due to the current) is also an important limitation when attempting higher resolutions and analysis speeds. The current causes a temperature gradient which results in increase longitudinal diffusion, resulting in band broadening [16].

Some premises make the PCFs interesting devices to solve these handicaps:

- A bundle of capillary tubes. A conventional capillary with small i.d. could reduce the Joule effect, but minimal analyte volumes would have to be injected to obtain narrow peaks, and a considerable loss in sensitivity should be expected. When using an array of small homogeneous channels, advantages of small i.d. remain, but sample volumes similar to those injected in wider conventional capillaries (50 μm i.d.) can be injected, achieving a good sensitivity as well as better resolutions and efficiencies. However, certain homogeneity among channels inside the micro-structure is needed, as different i.d. could lead to different electrophoretic behaviours for each channel, and subsequently an extra band-broadening similar to the A term in Van Deemter equation, which does not exist in CE when using conventional capillaries.
- Large surface to volume ($S/V$) ratio. $S/V$ ratio relates the total inner surface ($2\pi rh$) according to a specific capillary volume ($\pi r^2 h$). Joule effect is reduced when the same heat is spread over a larger capillary area. As such, PCFs offer higher $S/V$ ratios compared to standard capillaries, as more surface is available for heat dissipation.

Taking these premises, a series of experiments using these structures in commercial equipment was carried out to: (i) test PCF in commercial equipment; (ii) compare between microstructures and conventional capillaries.

## 2. Materials and methods

### 2.1. Equipment and reagents

A P/ACETM MDQ-Beckman CE System, from Beckman Coulter Inc. (Fullerton, CA, USA) equipped with a LIF detector (4-mW argon-ion laser with excitation at 488 nm and emission filter of 520 nm) was used for CE detection (Fig. 1b shows a picture of the equipment). A conventional PCF and a custom SMSC (manufactured by using the stack-and-draw technique taking as raw materials silica tubes from General Electric (Fairfield, CT, USA) and a transparent polymer model No. 3471-2-136 from DeSolite (Elgin, IL, USA), and both a conventional capillary and a transparent-coated capillary from Polymicro Technologies (Phoenix, AZ, USA) were compared as CE separation components. For both the PCF and the SMSC an equivalent conventional capillary was theoretically calculated, in such a way as this structure had the same total cross area than those of the PCF and the SMSC. Table 1 summarizes geometrical parameters of all the devices employed and Fig. 2 depicts some images of these structures. Fluorescein disodium salt (Beckman Coulter Inc) was the target analyte studied, as this compound emits fluorescence at 520 nm and absorbs at 490 nm. An aqueous borate buffer (sodium borate/boric acid 0.3/0.4% (m/m)) was used for the electrophoretic separation (Sigma–Aldrich). NaOH 1 M (Sigma–Aldrich) was used for the capillary conditioning. Ultrapure $H_2O$ purified through a

**Table 1**
Geometrical parameters of PCFs and SMSCs used.

| | No. of channels | Channel i.d. (μm) (RSD)[a] | Total cross area (μm²) | $S/V$ | Equivalent capillary | |
|---|---|---|---|---|---|---|
| | | | | | i.d. (μm) | $S/V$ |
| (a) SC-PCF | 84 | 4.3 ± 0.2 (5.1) | 1220 | 0.930 | 39 | 0.101 |
| (b) SMSC | 85 | 5.6 ± 0.3 (5.6) | 2094 | 0.714 | 52 | 0.077 |
| (c) Capillary | 1 | 50 ± 3 | 1964 | 0.08 | – | – |
| (d) T-capillary | 1 | 50 ± 3 | 1964 | 0.08 | – | – |

[a] For the microstructures, all measurements from one section ($n = 85$ in the case of the SMSC and $n = 84$ in the case of the PCF) were collected and both the average and standard deviation were calculated.