



# The fabrication of micro-porous silica structures for micro-reactor technology

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The formation of porous silica microstructures (frits) in capillaries with an internal diameter of 500  $\mu\text{m}$  has been examined for inducing electroosmotic flow (EOF). Capillaries with this internal diameter are normally considered too large to support efficient EOF, but the discrete pumping devices reported here are able to overcome this limitation. The formation of these structures in the capillaries has been examined, with particular emphasis on identifying parameters within the preparation stage that might give rise to variation in the porosity of the frit. The initial results showed that the induced electroosmotic flow rate increased with frit length (to an optimum of 50 mm) with an applied potential of 700 V. The work offers an opportunity to extend electroosmotic pumping to capillaries of larger internal diameter than was previously thought ideal. It offers a number of potential advantages in the area of fluid propulsion, including the electric control of flow rates, the plug like nature of the flow, and the absence of moving parts. When this technology is applied to micro-reactors, the silica structures offer the dual advantages of providing a pumping mechanism while also retaining the catalyst in the micro-reactor.

## Introduction

Spence and Crouch investigated the internal pressures within capillary flow injection systems<sup>1</sup> and found that while peristaltic and syringe pumps could deliver low volume flow rates, definite improvements were required in pumping technologies. Piezoelectric micro-pumps have been developed with a flow rate range of 1–100  $\mu\text{l min}^{-1}$ , but have some problems with pulsation.<sup>2</sup> An alternative is to employ electroosmotic pumping. This is induced by the application of potential gradients along capillary channels. Liu and DasGupta reported the use of an electroosmotic pump as a fluid propulsion system for flow injection analysis.<sup>3</sup> In their work, high electric fields were applied to capillaries of id 75  $\mu\text{m}$ , giving rise to electroosmotic flow up to the grounding point. Beyond this point, there was induced hydrodynamic flow through the capillary. This approach of induced hydrodynamic flow has a number of applications, such as that described by Ramsey and Ramsey,<sup>4</sup> who have reported electroosmotic pumping for the generation of electrospray from microchip devices. Perhaps a limitation with the use of EOF as a pumping device is the requirement for capillaries of small internal diameter. Since the driving force of the pump requires a double layer formation, there is a clear limitation of the overall internal diameter of the channel. The recent developments in capillary electrochromatography have demonstrated that the surface of the packing material can take part in the induction of EOF, and that a capillary packed with silica particles will enhance EOF rather than reduce it.

A reproducible method for the production of porous ceramic material was reported by Cortes *et al.*<sup>5</sup> Here, a mixture of potassium silicate and formamide was used to form a ceramic bed support for chromatography. The work reported in this paper focuses on the fabrication of porous silica structures (frits) for use in micro-reactor applications. These have been

demonstrated both as discrete pumping devices and as a means to efficiently retain a catalyst within a reactor system. The influence of various production processes has been examined by determining their influence over the volume flow induced during the application of a 700 V potential gradient. Finally, a study is presented which demonstrates the application of the frits for retention of a catalyst in a micro-reactor for the dehydration of hexanol.

## Experimental

Prior to starting the investigation, a number of parameters were identified as perhaps being critical to the reproducible formation of these porous ceramic structures. Most of these variables were associated with the production process, in particular the mixing of the reagents and the overall time from first mixing to placing the capillaries in the oven. Univariate experimental design was performed, where the parameters thought to be potentially most important were examined first.

Microporous silica frits were fabricated from 10% m/m formamide (Avocado Research Chemicals Ltd., Heysham, Lancashire, UK) and potassium silicate (21%  $\text{SiO}_2$ , 9%  $\text{K}_2\text{O}$ , Prolabo, Manchester, UK) solutions at room temperature (20  $^\circ\text{C}$ ). The reagents were manually mixed for 1 min using a glass rod and then drawn into glass 500  $\mu\text{m}$  id micro-capillaries [disposable precalibrated 10  $\mu\text{l}$  pipettes (LIP Equipment and Services Ltd., Shipley, West Yorkshire, UK)] to a predetermined length, at a speed of 0.042  $\text{ml min}^{-1}$  (Ismatec SA, Weston-Super-Mare, UK, MS-Reglo peristaltic pump), using 0.42 cc Accu-rated tubing (Elkay Lab Products Ltd., Basingstoke, Hampshire, UK). In situations where the uptake speed was too great, reagents were deposited as droplets on the capillary wall, which proved impossible to subsequently remove. The solution plug was finally positioned in the centre of the micro-capillaries. The micro-capillaries were then placed in the oven at a designated temperature for 1 h, before being removed and allowed to cool. The capillaries were then trimmed with a glass knife so that 1 cm of empty capillary remained either side of the frit. The prepared capillaries were stored in a desiccator to reduce atmospheric water effects.

## Capillary priming

Prior to EOF testing, the micro-capillaries were primed using a  $2 \times 10^{-2}$  mol  $\text{dm}^{-3}$  solution of disodium tetraborate buffer (Fisher Scientific, Loughborough, Leicestershire, UK) and an HPLC pump (SA103, Speck Analytical, Clackmannanshire, UK). Priming was for at least 2 min at a flow rate of 0.2  $\text{ml min}^{-1}$  and it ensured that any excess reagents were removed. At this flow rate, the back pressure was in the order of 700 psi. Poor priming resulted in further reagent reaction and subsequent frit blocking. The extent of frit blocking by poor priming could easily be monitored by examining the back pressure required to force liquid through the capillary. Partial blocking was never observed: if the frit was rehydrated and left without proper priming, the back pressure would exceed 3000 psi and physically break the capillary from the pump connection. (It is

also possible to prime the capillaries by standing them in buffer solution until they are filled, and then use EOF to flush the excess reagent out. This approach was not used generally in this study since it took significantly longer to complete the wash cycle.)

### EOF investigations

Once the capillary had been primed, EOF was then initiated using the apparatus shown in Fig. 1 for a 30 min period with an applied potential of 700 V (high voltage supply, Farnell, Leeds, Yorkshire, UK). This was used as the method of testing for each frit, and was the only comparison tool employed. Flow rate was calculated by measurement of the volume of buffer moved (from the positive reservoir) per minute. The following experimental parameters were investigated for the formation of porous frits.

**Influence of preparation time.** The time between preparation and heating of capillaries was investigated to see if it had any effect on the final structure and hence on the EOF through the frit. Standing times from 5 to 60 min were investigated. Each condition was prepared in duplicate and heated at 150 °C for 1 h. All frits were 2 cm in length.

The following investigations were prepared in duplicate and heated to 100 °C for 1 h. All frits were 2 cm in length unless stated to the contrary.

**Frit washing.** Six frits were prepared, each of length 2 cm. These were subdivided into two groups of three, the first washed with  $2 \times 10^{-2}$  mol dm<sup>-3</sup> disodium tetraborate, and the other with the series of chemicals 1 M ammonium nitrate (Reidel de Haën, Hannover, Germany), 1 M HCl, deionised water and acetonitrile (Fisher Scientific)–water (50 + 50).<sup>5</sup>

**Reagent mixing time.** The 10% m/m solution of formamide in potassium silicate was mixed for varying lengths of time between 10 and 60 s.

**Effect of centrifuging.** The solution was centrifuged (BM402, Denley, Billingshurst, Sussex, UK) at 6000 rpm for 12 min; 5 replicate frits were subsequently prepared.

**Frit length characteristics.** A series of frits of differing lengths were prepared, between 1 and 7 cm. Each length was prepared in duplicate.

Once the individual frits had been primed, the EOF through them was measured. This was used as the mechanism to test the pumping capacity of the frit. The aim of each experiment was to identify the conditions that gave rise to the maximum and most reproducible EOF.

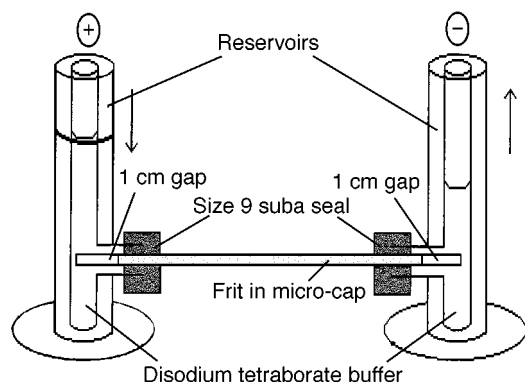


Fig. 1 Diagram of the apparatus designed for the study of EOF.

## Results and discussion

Once the reagents have been mixed, there is a significant delay while the reagents are positioned in the correct place in the capillary before they are transferred to the oven. Since more than one frit is prepared from the reagents, the standing time will vary for each one. This variation in time was examined, and found to have only marginal influence on the magnitude of the EOF produced by the capillaries. It appears that the EOF was greater in capillaries that had been left standing more than 15 min., but that 15 min to 1 h had little effect. **Note.** In this study, it was found that some of the structures formed as several small frits rather than as one continuous length at 150 °C. Since this problem was not apparent at 100 °C, that temperature was used for all future studies.

From the early work, it was apparent that without adequate washing, excess reagent remained, and would block the frit after it was rehydrated. This fact was confirmed when a frit was examined by IR spectroscopy. Evidence of remaining formamide was found on a non-washed frit. It was found that washing with disodium tetraborate successfully removed all excess reagents, and was not detrimental to the EOF. The process which gives rise to the frit formation involves the reaction of 10% m/m formamide and potassium silicate (21% SiO<sub>2</sub>, 9% K<sub>2</sub>O), followed by dehydration in an oven at 100 °C. This will leave some residues or unreacted reagents. Where these are not flushed completely from the structure, it is possible for the reaction to re-start, thus depositing further silica in the porous structure. This is sufficient to block the frit completely. For an unexplained reason, the sequential wash with ammonium nitrate, HCl, deionised water, acetonitrile, and finally deionised water again, resulted in a total loss of EOF. However, this wash removed excess reagent and the subsequent frit was physically porous.

To examine the structure of the frit, a section from a capillary was examined by electron microscopy. The structure is highly porous, consisting of a rigid silica backbone with openings of between 2 and 10 μm. The physical geometry is random, without any apparent regular lattice structure. The structure could best be described as similar in appearance to a natural sponge, and can be seen in Fig. 2.

In order to achieve maximum reproducibility between batches of mixed reagent, the influence of reagent mixing time was investigated. Employing a stirring action with a glass rod, a series of times were used. The optimum was identified as 30 s; the results can be seen in Fig. 3. The results show that 30 s mixing time is the optimum. When the reagents are mixed for less than this time they are not homogeneously mixed, and beyond this time excess air is introduced into the reagents, thus lowering the porosity of the frit. Once the reagents were mixed, the effect of centrifuging them was examined. It had been found<sup>2</sup> that centrifuging the mixed reagents increased the porosity, but in this study the effect was not observed.

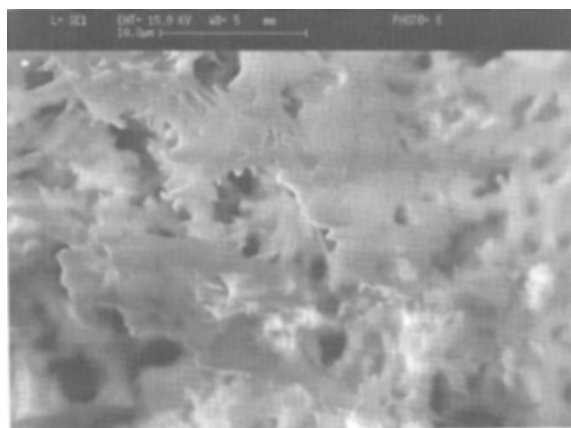
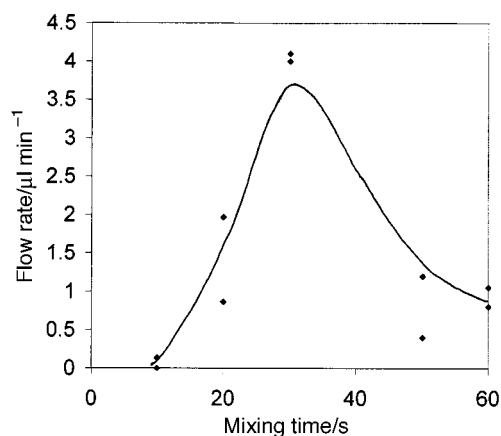


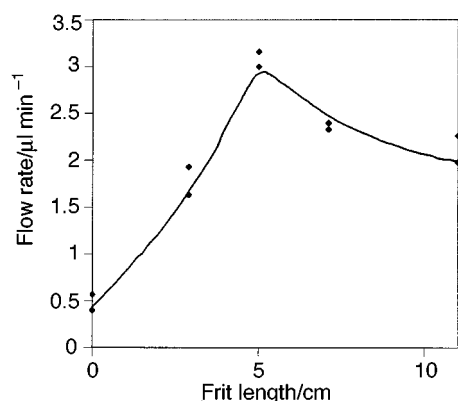
Fig. 2 Scanning electron microscopy picture of the porous silica structure.

The influence of frit length on the volume flow rate delivered for a fixed applied voltage was the final parameter examined, and 700 V was applied across each capillary. The length of the capillary in all experiments was 110 mm, with the start of the frit at the end of the capillary next to the positive reservoir. The results can be seen in Fig. 4, and clearly shows that the magnitude of the volume flow rate increases with increasing frit length, to a maximum of 5 cm. Beyond this, a decrease was observed in the volume flow rate. It must be remembered that these flow rates were obtained without the application of any physical pressure. In order to mechanically pump liquid through the capillaries several hundred psi were required for the longer frits. The results show that efficient pumping can be induced with very low back pressures through frit structures of 50 mm length. The importance of this work is that it is now possible to electro-osmotically induce flow in capillaries normally considered too large to sustain flow, and to locate the fabricated pumping devices at precise locations.

There are advantages and disadvantages with employing EOF as a pumping device. The control of flow rates by application of voltage, that flat flow profiles that minimise dispersion, the absence of back pressure, the absence of moving parts and the controllable low volume flow rates attainable are clear advantages with the approach. In addition, the low cost of such devices would permit ready disposal on malfunction, such as blocking. Disadvantages include the limitations in types of fluids applicable to EOF induced flow, the limited range of flow rates possible, and the susceptibility to blocking. While it is potentially difficult to use these devices as pumps for flow injection analysis, particularly for the construction of flow manifolds, it is evident that by varying the applied voltage across each unit, different reagent delivery rates could be easily



**Fig. 3** Graph to show the influence of mixing time on the volume flow rate. Movement of the liquid was induced by EOF.



**Fig. 4** Graph showing the influence of frit length on the volume flow rate. Movement was induced through the frit by EOF.

obtained. It is perhaps in the area of micro-reactors where this technology will find most application.

## The development of micro-reactors

Most micro-reactors require a catalyst to be trapped inside a channel; this can prove quite difficult for catalysts that are fine powders. We are now able to fabricate frits in precise locations within a capillary channel, thus permitting the fabrication of catalyst beds within a micro system. In order to evaluate this approach, a preliminary study was performed using a capillary reactor packed with  $4.04 \times 10^{-4}$  mol of sulfated zirconia (kindly donated by MELCat, Manchester, UK). The catalyst was located by means of two retaining frits. The first frit was formed in the capillary, against which the catalyst was packed. A second frit was then formed after the catalyst in order to prevent movement and loss. The packed reactor was approximately 3 cm in length, with the catalyst representing the majority of this length. The reactor was heated to 155 °C using NiChrome heating wire, with the temperature monitored using a digital thermometer.

Hexanol (98%, Aldrich, Gillingham, Dorset, UK) was pumped through this reactor using a Gilson pump, at a volume flow rate of  $0.02 \text{ ml min}^{-1}$ . The initial experiments showed that coking (the formation of carbon deposits on the catalyst) was a problem, but this was overcome by de-gassing the hexanol with nitrogen prior to reaction. This approach has been used by other workers on a larger scale process. With this problem eliminated, a new reactor system was tested with experiments lasting in excess of 100 min. Under these conditions, the percentage conversion rate of hexanol to hexene averaged at 2.64%, with an RSD of 8.7%. While this conversion seems low, it should be remembered that the conversion rate is normally only 30–35% for an industrial system with a far longer contact time.

One problem here is that the contact time is too low for greater conversion to be obtained. The simplest way to achieve this will be to reduce the flow rate through the catalyst. The ongoing research in this area is to utilise EOF as the pumping mechanism in order to reduce the volume flow rate. This is a challenging task, and will be an important step once complete. While hexanol alone has been found to display no EOF movement, the addition of a surfactant at a 1 : 1 ratio permits EOF to be employed.

Methanol has also been examined as a solvent for the electroosmotic pumping of hexanol. With methanol alone, flow rates of  $10 \mu\text{l min}^{-1}$  were possible, but for a mixture of hexanol–methanol at a ratio of 1 : 2, flow rates of  $4 \mu\text{l min}^{-1}$  (% RSD below 10%) were achieved in the micro-reactor system with an internal diameter of  $50 \mu\text{m}$  and a frit length of 40 mm.

The importance of this work to micro-reactors has started to become apparent since it permits the incorporation of a pumping device into the reactor, thus creating a discrete entity *i.e.*, reactor and pump. Most micro-reactors require a catalyst to be trapped inside the channel, and this can be difficult, particularly where catalysts are fine powders. This study has provided a simple method to trap the catalyst in place while also providing a pumping mechanism. While currently applicable to glass channels, the temperature of formation is such that it should be applicable to many polymeric materials.

## References

- 1 D. M. Spence and S. R. Crouch, *Anal. Chim. Acta*, 1998, **358**, 95.
- 2 B. H. Schoot, S. Jeanneret and A. Berg, *Anal. Methods Instrum.*, 1993, **1**, 38.
- 3 P. K. DasGupta and S. Lui, *Anal. Chem.*, 1994, **66**, 1792.
- 4 R. S. Ramsey and J. M. Ramsey, *Anal. Chem.*, 1997, **69**, 1174.
- 5 H. J. Cortes, B. E. Pfeiffer and T. S. Stevens, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1987, **10**, 446.

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