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Research Article

Fluorinated ethylenepropylene copolymer as a potential capillary material in CE

In this work, a new generation UV-transparent polymer, fluorinated ethylenepropylene copolymer (FEP) exhibiting a low degree of crystallinity, extruded in dimensions similar to the most commonly used CE capillaries of ~80 µm id and about 360 µm od was investigated for its use as a CE capillary. FEP is transparent down to the low-UV region, and as fluorinated polymers in general are good electrical insulators and exhibit reasonable heat conductivity, it has considerable potential as a material for electrodriven analysis in capillary or microchip formats. The FEP capillary has been characterised with regard to some important aspects for its use as a CE capillary, including its profile of EOF *versus* pH, as well as procedures for manipulating EOF by coating the inner capillary wall with various semi-permanent and dynamic layers. The FEP capillaries were tested and compared with fused-silica capillary for the separation of inorganic and small organic ions using conditions involving direct and indirect detection in the low-UV region. Finally, advantages of the use of the FEP capillary for simultaneous detection of a mixture containing nine inorganic cations and anions using indirect photometric detection with a movable light-emitting diode (LED) detector and a novel electrolyte are demonstrated.

1 Introduction

Fundamental to the success of CE and other miniaturised electro-driven analytical techniques, especially using micro-fluidic chips, is the use of materials for capillaries and chips which have suitable physico–chemical properties. The capillary material should be an excellent electrical insulator to withstand high electrical field strength, possess a high thermal conductivity to allow effective heat dissipation, have suitable mechanical properties (flexible but not too soft), and be optically transparent in a wide spectral range and extending to the low-UV region. The material should also be chemically inert so that it will not react with electrolyte components or analytes, it should have a well-defined surface allowing reproducible EOF, and should have well-characterised surface chemistry to aid practical control of the EOF [1]. Since the advent of polymer-coated fused-silica (FS)

technology for capillary GC [2, 3], this material has been used almost exclusively as the material of choice for the separation capillary in CE.

In principle there can be other suitable capillary materials, especially synthetic polymers, and the potential of polymeric capillaries has stimulated the interest of this [1, 4, 5] and other groups [6–16]. Polymer capillaries have the advantages that they can be produced by extrusion at relatively small cost and no additional protective coating is required as is the case for FS. UV-transparent polymer capillaries having a low degree of crystallinity to avoid light scattering also allow optical detection to be performed at any point on the capillary without making a 'detection window'. Optimally, the inner capillary surface should be hydrophilic and uncharged so that analytes do not interact with the capillary wall. This can be achieved in polymer capillaries by chemical modification of the inner capillary wall.

The study of polymer capillaries for CE will also offer valuable insights into the use of polymer materials for CE chips, although there will be some requirements which are specific for only one of these formats.

Fluorinated polymers have considerable advantages over commonly used polymeric materials such as PDMS and poly(methyl methacrylate) (PMMA) in that they do not swell in the presence of organic solvents and they are optically transparent to lower wavelengths. However, their use in microfluidic devices and CE capillaries has been limited to date [17]. Fluoropolymers also exhibit high chemical inert-

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Abbreviations: BMMPA, 2,2-Bis(4-morpholinylmethyl)propanoic acid; **DDAB,** didoceyldimethylammonium bromide; **DS,** dextran sulphate; **FEP,** ethylenepropylene copolymer; **FS,** fused-silica; **HPMC,** hydroxypropylmethylcellulose; **PDDAC,** poly(diallyldimethylammonium chloride); **PTFE,** poly(tetrafluoroethene)

ness, low critical surface tension, and low refractive index making them interesting candidates for electrophoresis in capillary and chip formats [18]. Poly(tetrafluoroethene) (PTFE, or Teflon®) has been the most widely used of these polymers in capillaries but its mechanical softness and a fair degree of crystallinity resulting in light scattering manifested as apparent absorptivity in the low-UV spectral region can be problematic [1, 7, 19].

Fluorinated ethylenepropylene (FEP, also known as tetrafluoroethene hexafluoropropene copolymer) has a higher optical clarity than PTFE, due to a lower crystallinity making it better suited for optical detection [18]. Until recently, narrow bore FEP capillary has not been available commercially so there have been only a limited number of publications dealing with electrophoresis using FEP capillaries. Zhu and Chen [20] used FEP capillaries to electrophorese red blood cells. Schutzner and Kenndler [21] measured the variation of electroosmotic mobility (μ_{EOF}) and zeta-potential (ξ) for FEP capillary as a function of pH. Using 10 mM CAPS, a reversed EOF was observed at low pH and normal EOF for pH>2.5, increasing to a maximum of 48×10^{-9} m^{2}s^{-1}V^{-1} at pH 11. They suggested that the EOF was the result of negatively charged carboxylate groups which formed on the surface of the capillary during manufacture. Unlike the situation in FS capillary, μ_{EOF} and ξ for the FEP capillary reached a plateau after pH 7. This was attributed to the inability of the polymer to adsorb further amounts of OH$^-$ as the pH increased. Rohlícek *et al.* [22] examined the p*I* for PTFE and FEP capillaries and found that these occurred at pH values of 3.25 and 3.0, respectively. They postulated that the EOF in fluoropolymer capillaries was the result of adsorption of ions from the electrolyte rather than the presence of negatively charged functional groups. Sahlin and Webber [18] investigated the feasibility of using FEP as a CE capillary by choosing a mixture of positively charged 200 μM methyl viologen (CH$_3$-N$^+$C$_5$H$_4$-C$_5$H$_4$N$^+$-CH$_3$) and 2 mM phenol (C$_6$H$_5$OH) as a neutral EOF marker with UV detection. This initial investigation found that the adsorption of methyl viologen was problematic in untreated FS but that FEP capillary produced a symmetrical peak shape. Not surprisingly they found that heat dissipation in FS was far superior to that in FEP.

In CE, inner wall coatings are used frequently to modify the EOF and to reduce analyte–wall interactions [23]. Permanent coatings have been applied to FS by direct covalent bonding of the coating agent to the capillary or by cross-linking of adsorbed polymers, however these processes involved tend to be laborious [24, 25]. On the other hand, dynamic and semipermanent coatings are very popular for their flexibility and ease of use [26, 27]. Investigating surface properties and their modification will therefore inevitably be very important in characterising any new material for CE capillaries and/or chips.

EOF reversal was first observed for capillaries made from FS and PTFE by Reijenga *et al.* [28] who added 0.1 mM CTAB to the electrolyte. Tsuda *et al.* [29] used CTAB to reverse the EOF to detect anions with low electrophoretic mobilities.

Ding and Frit [30] found that CTAB was also effective at preventing protein–wall interactions. Huang *et al.* [31] used tetradecyltrimethylammonium bromide (TTAB) to reverse the EOF and a reversed electrode polarity to successfully separate a range of carboxylate ions, including those with a high mobility. Lucy and Underhill [32] characterised a number of cationic surfactants including CTAB, TTAB and octadecyltrimethylammonium bromide (OTAB) as EOF modifiers in FS capillaries. They found that the EOF was constant for surfactant concentrations greater than about 10% of the pure water CMCs. Melanson *et al.* [33] found that double-chained surfactants, such as didoceyldimethylammonium bromide (DDAB), formed more stable dynamic coatings than single-chained surfactants so that reversed EOF was maintained after flushing the capillary with DDAB without the need to include the surfactant in the BGE.

As EOF is strongly pH-dependent in FS and polymer capillaries [26], it is desirable in the interests of reproducibility to identify coatings that produce pH-independent EOF [24]. Strongly adsorbed semipermanent coatings can fill this requirement. Reversed EOF using the cationic polymer, poly-(diallyldimethylammonium chloride) (PDDAC) was introduced by Liu *et al.* [34]. This can be coated on a capillary by simply flushing with a 0.1% solution to achieve a stable and reproducible reversed EOF [35]. Alternative cationic coatings include poly(ethyleneimine) [36], Polybrene [37], poly-(arganine) [38] aromatic polyaniline [39] and double-stranded polyanililine [40] but not all of these produce a stable EOF with pH. In a similar fashion, semipermanent anionic coatings can be applied to a pre-existing cationic coating. Decher [41] demonstrated the technique in 1997, and Katayama *et al.* [42] used the same approach to produce pH-independent EOF on FS capillaries. Yang *et al.* [24] added a layer of dextran sulphate (DS) to an initial coating of α-chymotrypsinogen in a FS capillary to produce a stable, positive pH-independent EOF. Macka *et al.* [1] used a combination of PDDAC and DS in PTFE capillaries to produce the same result.

The aim of this study was to assess the applicability of FEP as a material for electrodriven separations. Mechanical and physical properties and aspects of the practical use of FEP capillaries are examined and compared with FS. EOF is studied for a number of wall chemistries, including unmodified FEP and a range of semipermanent and dynamic coatings. The use of the FEP capillary to perform simultaneous detection of cations and anions using indirect photometric detection based on a mixture of a cationic and anionic dye and an isoelectric buffer 2,2-Bis(4-morpholinylmethyl)-propanoic acid (BMMPA) is also demonstrated.

2   Materials and methods

2.1   Instrumentation

An Agilent Technologies ^{3D}CE (Waldbronn, Germany) was used with capillaries of 48.5 cm total length and length to

detector 40.0 cm, or 40.0 cm total length and length to detector 31.5 cm (see figure captions). Injections were performed hydrodynamically at a pressure of 20 mbar used with 2 s injection time unless specified otherwise. Absorption spectra of FEP and FS capillaries were both measured relative to air as a reference.

2.2 Chemicals

All chemicals used were of analytical reagent grade. The surfactants used for dynamic coating of the capillary, SDS and DDAB were purchased from Aldrich (Sydney, Australia). Semipermanent coatings were made using PDDAC and DS were purchased from Aldrich. The PDDAC coating was applied by flushing with 1% PDDAC for 2 min, waiting for 5 min and flushing with electrolyte for 2 min. The final semipermanent coating was applied to the PDDAC coating by flushing the capillary with a 3% solution of DS dissolved in water for 15 min and then leaving it for 30 min before flushing with the electrolyte [42]. All of these procedures were carried out at 25°C.

Chromic acid, Tris and hydroxypropylmethylcellulose (HPMC) were purchased from Aldrich. Chrysoidine (4-phenylazo-*m*-phenylenediamine and Orange G (1-phenylazo-2-naphthol-6,8-disulphonic acid disodium salt) of standard Fluka quality were obtained from Fluka (Buchs, Switzerland). They were purified using the approaches previously reported [43–45]. BMMPA was synthesised in house by Dr. T. Rodemann [46]. Water was treated with a Millipore (Bedford, MA, USA) Milli-Q water purification system.

The FS capillaries were purchased from Polymicro Technologies (Phoenix, AZ, USA). The FEP capillary with an unknown internal diameter (~80 µm) and an external diameter of (~370 µm) was obtained from Dr. P. Schuman (OPRI, Gainesville, USA).

2.3 Procedures

All solutions and electrolytes were degassed using vacuum sonication and filtered through a 0.45 µm syringe filter (Activon Thornleigh, Australia) before use. Absorbance values in Table 1 were measured for FEP and FS with both capillaries being filled with water. Baseline noise was measured with capillaries filled with a 10 mM phosphate buffer pH 7.0 and +30 kV separation voltage. Conductance (G) was measured as a function of the power *per* unit length (P/L) for each capillary by analysing the current and voltage data collected by the CE instrument.

Table 1. Noise levels at several wavelengths in UV region

Capillary	Baseline noise (mAU)		
	200 nm	214 nm	248 nm
FEP	0.80	0.22	0.05
FS	0.10	0.08	0.05

3 Results and discussion

3.1 Mechanical properties and practical aspects of usage of FEP capillaries

As a result of observations by several users and over prolonged periods of time and using two CE instruments (Waters CIA and Agilent 3D CE) it can be concluded that the mechanical properties of the capillary are less than optimal. The material is fully flexible, but due to its relative softness, it is especially prone to kinking and being squeezed in parts of the instrument. These properties caused some instrument-specific problems, such as in installation of the capillary in the CE instrument, and this step must be performed with considerable care to avoid mechanical damage to the capillary. With the Agilent CE, a pair of fine, long tweezers was required to guide the ends of the capillary into the conical holes leading to the tubular electrodes. Considerable care was also necessary when inserting the capillary into the optical interface. Although the mechanical properties of FEP capillary are superior to those of PTFE capillary, properties more similar to those of FS capillaries would be desirable for routine use.

3.2 Heat dissipation and measurement of internal diameter

A method previously described by this group was used to find accurately the internal diameter of the FEP capillary [1, 47]. This relies on the fact that a plot of G *versus* power *per* unit length (P/L) is linear (see Fig. 1) enabling values of G free from Joule heating to be extrapolated. Equation (1) was used to find the internal diameter of the FEP capillary.

$$\frac{id_{FEP}}{id_{FS}} = \sqrt{\frac{G_{0(FEP)}}{G_{0(FS)}}} \tag{1}$$

where G_0 is the conductance extrapolated to zero voltage or power. This gave the average value for $id_{FEP} = 80.3$ µm.

Figure 1 also demonstrates that the heat dissipation for FEP was somewhat poorer than FS. The larger rate of increase in G with P/L for the FEP capillary is associated with a greater rise in the mean temperature of the BGE for the polymer capillary. Using the relationship in Eq. (2), and the gradients and intercepts from Fig. 1 it may be shown that the increases in the mean temperature of the electrolyte (ΔT_{Mean}) in the FS and FEP capillaries were 3.45 and 6.77°C at $P/L = 1.00$ W/m, respectively. Clearly, the magnitudes of these increases will depend also on the cooling efficiency of the instrument used.

$$\Delta T_{Mean} = \frac{(G_T/G_0) - 1}{0.0205°C^{-1}} \tag{2}$$

In Eq. (2), G_T refers to the conductance at the unknown temperature, G_0 is the conductance extrapolated to $P/L = 0$
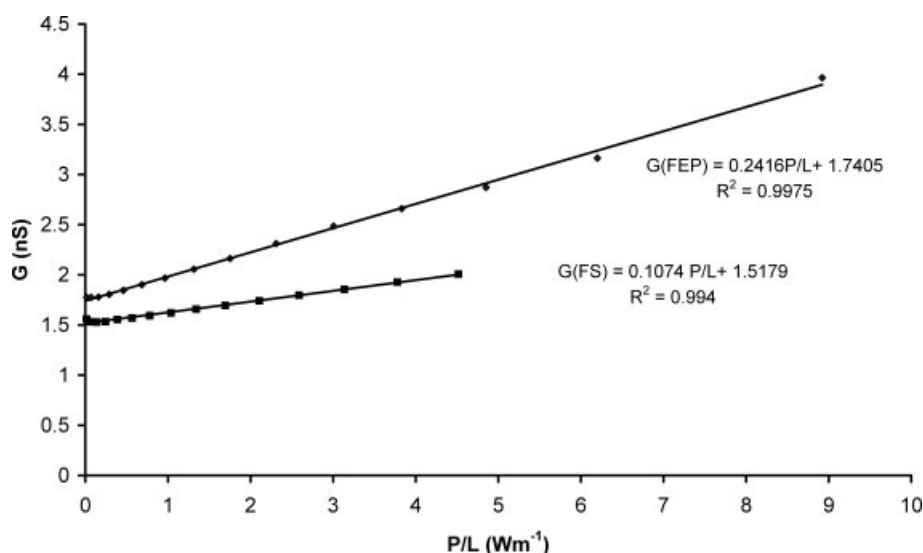
Figure 1. Conductance (*G*) *versus* power *per* unit length (*P/L*) for FEP and FS capillaries. Conditions: FS capillary id = 74.0 μm and FEP capillary of unknown id; BGE, 10 mM phosphate buffer pH 7.21.

(the intercept of the *G vs. P/L* graph) and 0.0205°C^{-1} is the temperature coefficient of electrical conductance for this electrolyte [48].

It has previously been demonstrated by this group [47] that the rise in temperature of the electrolyte inside the FEP capillary is almost double that for the FS capillary over a range of different power values. This is primarily the result of poor heat dissipation across the polymer capillary wall. The effective thermal conductivity for the FEP was just 0.099 Wm^{-1}K^{-1} compared to 0.863 Wm^{-1}K^{-1} for the poly-(imide)-coated FS material. The lower effective thermal conductivity of FEP limits the maximum power *per* unit length that can be used if bubble formation and boiling of the electrolyte are to be avoided. Satisfactory results could be obtained if the separation current did not exceed 140 μA.

3.3 Optical properties

Absorption of light by polymers is the result of two phenomena: 'true' absorbance caused by absorption of light by molecules of the compound, and 'pseudo-absorbance' caused by light scattering. The pseudo-absorbance contribution is often significant with polymers that have some degree of crystallinity. The light scattering contribution increases with decreasing wavelength and causes an apparent absorption spectrum of crystalline polymers increasing into the low-UV region [49]. This behaviour can be observed in absorption spectrum of the FEP capillary when measured in a diode-array spectrophotometer of the Agilent CE (see Fig. 2). It can be expected that the transparency of the capillary at a given wavelength would correlate with the baseline noise and this is shown in the data presented in Table 1. Above 400 nm a contribution to baseline noise from pseudo-absorbance caused by light scattering is observed, similar although on of a smaller scale compared to the PTFE capillaries investigated previously by this group [1].

3.4 EOF characteristics of unmodified and modified FEP and the potential of FEP as a separation capillary in CE

3.4.1 Unmodified FEP

The EOF *versus* pH profile of a FEP capillary is plotted in Fig. 3 and shows that FEP exhibited a pH-dependence somewhat similar to that of FS, although FEP theoretically possesses no ionisable groups. The significant cathodic EOF observed at pH >4.5 was also reported for PTFE and can be similarly explained by the presence of surface carboxylic groups formed by oxidation under the influence of UV light and/or ozone [50]. The significant anodic (reversed) EOF at pH <4.0, reaching approximately -30×10^{-9} m^{2}s^{-1}V^{-1} at pH 2.5, suggests that the presence of basic impurities or additives in the FEP that would acquire positive charge at pH <4.

The main differences in the surface chemistry of FEP compared to FS are the hydrophobicity of FEP and the absence of the silanol groups on FEP. It follows that solute–wall interactions between inorganic cations and the wall for FEP capillaries are less likely than for FS capillaries, so that FEP has the potential to separate higher valent cations without the need for complexing electrolytes.

3.4.2 FEP modified for anodic (reversed) EOF

In previous work by this group [1] using a PTFE capillary, attempts to apply dynamic coatings with CTAB resulted in an unstable and gradually decreasing anodic EOF, rendering this approach unusable. Therefore in this work, stable EOF reversal was established by the application of a dynamic coating of DDAB, or a semipermanent coating of PDDAC. In both cases reversed EOF was maintained without the need for an additive in the BGE. The variation of the reversed EOF
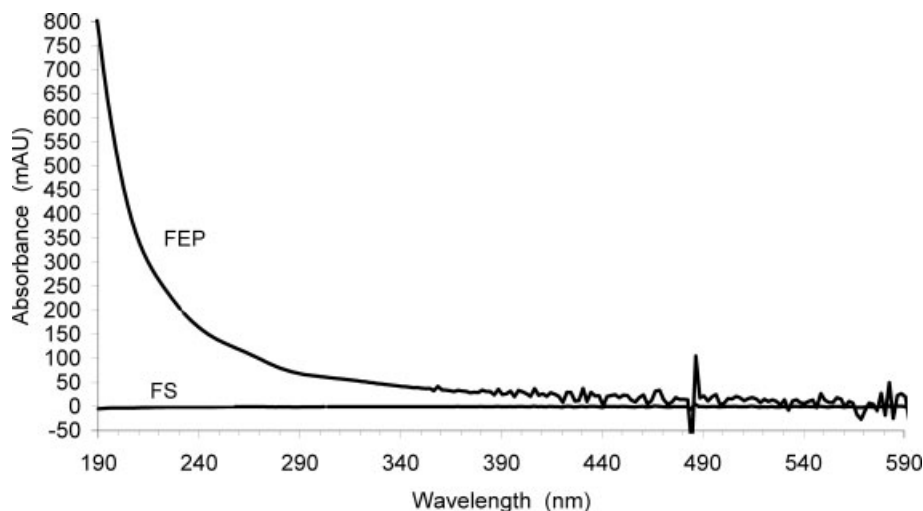
Figure 2. Spectra of a FEP capillary relative to FS. Conditions: both capillaries filled with water, measured in a diode array spectrophotometric detector of Agilent 3D CE.
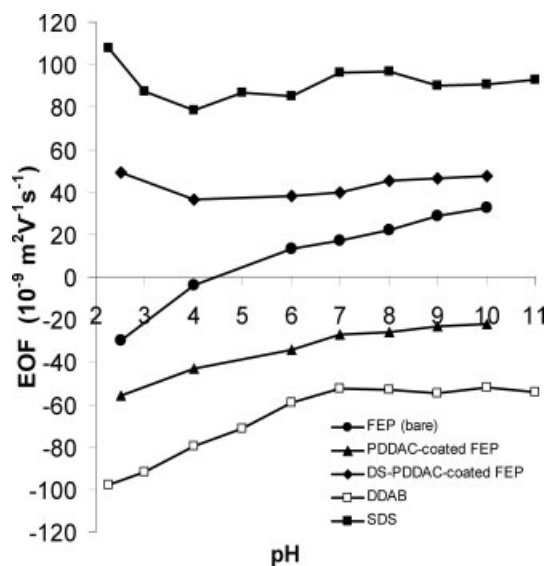

Figure 3. EOF *versus* pH profile for bare, PDDAC-coated and PDDAC-DS-coated FEP. Conditions: capillary, FEP 75 μm × 48.5 cm (total); electrolyte, 10 mM sodium phosphate; pH 6.5. Coating procedures: flushing with 1% PDDAC for 30 min, waiting for 30 min and flushing with the electrolyte for 2 min for PDDAC coating, or flushing with 1.5% DS for 30 min, waiting for 30 min and flushing with the electrolyte for 2 min for PDDAC-DS coating. Dynamic coating for reversed EOF of 0.1 mM DDAB applied by preflush for 90 s at 95 kPa. Dynamic coating for enhanced normal EOF of 5 mM SDS applied by preflush for 150 s at 95 kPa.

with pH for both coatings is shown in Fig. 3. Very high reversed EOF at low pH was observed using DDAB. A value of -98×10^{-9} m^{2}s^{-1}V^{-1} was observed at pH 2.25, but this value is likely to be inflated somewhat by Joule heating [47, 51, 52]. Moderate reversed EOF was produced by the PDDAC, with the EOF decreasing smoothly over the pH range 2.5-10.

3.4.3 FEP modified for enhanced cathodic EOF

Creation of pH-independent EOF can be useful for acidic electrolytes where the EOF is normally small. A semipermanent coating of DS was applied over the top of the PDDAC by flushing a PDDAC-coated capillary with a solution of DS. The slightly elevated EOF at pH 2.5 (see Fig. 3) may be related to increased Joule heating as a result of the higher ionic strength electrolyte rather than as a result of a pH effect. SDS was applied as a dynamic coating by flushing the capillary with the coating solution prior to filling it with the BGE. The cathodic EOF averaged approximately 90×10^{-9} m^{2}s^{-1}V^{-1} over the pH range of 2.25–11 (see Fig. 3). The elevated value of μ_{EOF} at low pH was undoubtedly influenced by Joule heating [47, 52, 53].

3.5 Separations using FEP capillaries

While it is most unlikely that polymer chips would be used for indirect photometric detection of inorganic ions due to sensitivity limitations, this technique provides a simple system for evaluating the functionality of FEP for CE separations.

3.5.1 PDDAC-coated FEP capillary

PDDAC-coated FEP and FS capillaries were applied to the separation of a range of anions using indirect photometric detection at 380 nm using a buffered chromate electrolyte (see Fig. 4). Similar separation performance was recorded for both coated capillaries, although peak tailing was evident for analytes with lower electrophoretic mobilities in the FEP capillary. Peak efficiencies observed with both capillaries are shown in Table 2 from which it can be seen that the performance of the FEP capillary was significantly better than FS for SO_4^{2-} and CO_3^{2-}. The data for Table 2 were obtained under identical separation conditions.

Table 2. Efficiency values

Capillary	Efficiency ($\times 10^5$ TP)								
	Cl^-	SO_4^{2-}	NO_3^-	ClO_4^-	ClO_3^-	SCN^-	BrO_3^-	PO_4^{3-}	CO_3^{2-}
FP	2.385	5.542	1.070	1.888	1.949	1.293	0.647	0.345	1.519
FS	2.059	3.456	1.163	3.330	2.714	1.098	0.430	0.660	0.731

Conditions as in Fig. 4, FS capillary coated with PDDAC, 75 μm × 48.5 cm total.
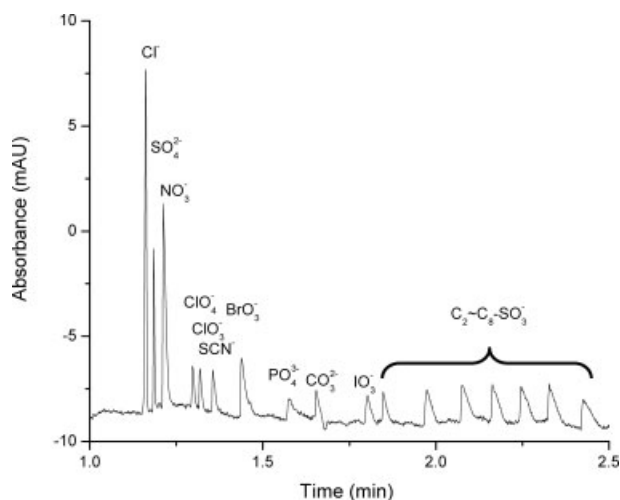
Figure 4. Separation of anions on PDDAC-coated FEP capillary. Capillary, 80.3 μm × 48.5 cm (total), −25 kV; electrolyte, 2.5 mM chromate/10 mM Tris, pH 8.0; analytes, 0.05 mM; injection, 20 mbar × 2 s; detection, 370, 10 nm (ref 585, 30 nm).

3.5.2 PDDAC/DS-coated FEP capillary

The performance of the doubly coated FEP capillary was compared with a similarly treated FS capillary for the separation of several organic cations (see Fig. 5). The time taken for the separation on the FEP capillary was longer despite the higher field strength employed. The significant tailing for the benzyltributylammonium ion suggested a strong hydrophobic interaction between the analyte and the wall.

3.5.3 Simultaneous separation of cations and anions on unmodified FEP using dual indirect photometric detection

The FEP capillary was applied to the simultaneous separation of anions and cations using a BGE which enabled both the anions and cations to be detected by indirect photometry. The BGE used contained 5 mM BMMPA as an isoelectric buffer, 3 mM orange G and 3 mM chrysoidine as indirect detection probes for anions and cations, respectively, and 0.04% HPMC for EOF suppression. BMMPA has one car-
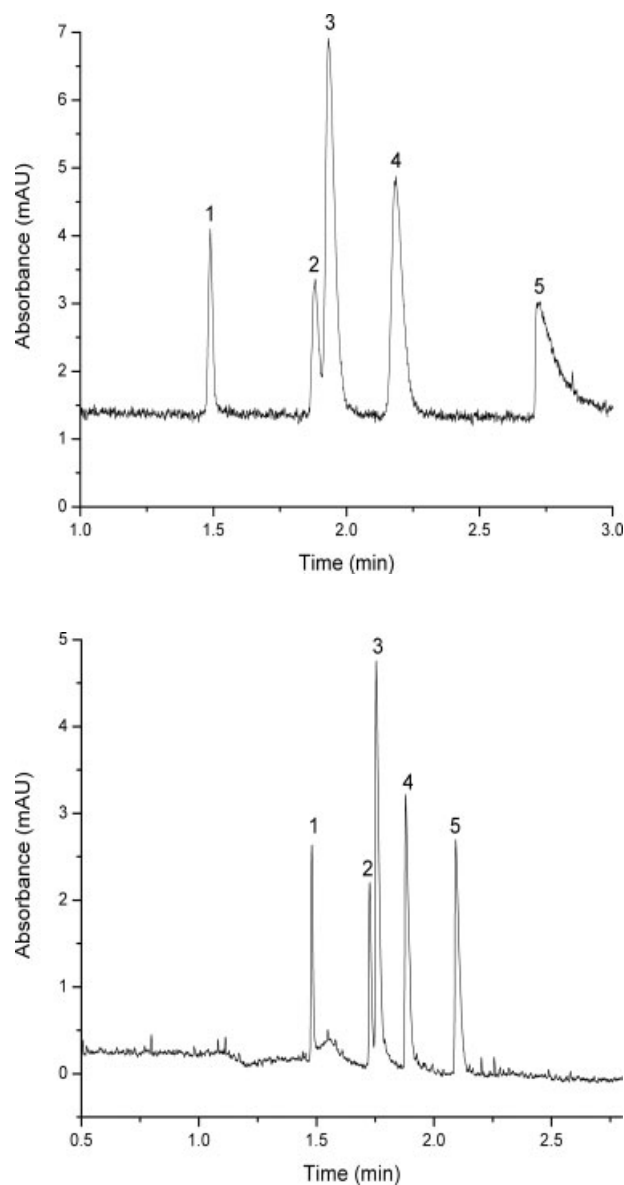

Figure 5. Electropherograms of organic cations with direct UV detection at 214 nm in (a) an FEP capillary and (b) an FS capillary. Conditions: capillary, PDDAC/DS-coated (a) FEP 80.3 μm × 48.5 cm or (b) FS 75 μm × 40.0 cm; electrolyte, 5 mM phosphate at pH 3.0; voltage: (a) +20 kV or (b) +15 kV. Analytes: 1 = imidazole, 2 = $C_6H_5CH_2NH_2$, 3 = $C_6H_5CH_2N(CH_3)_3^+$, 4 = $C_6H_5CH_2N(C_2H_5)_3^+$, 5 = $C_6H_5CH_2N[(CH_2)_3CH_3]_3^+$.

boxylic acid group and two buffering amino groups with a p*I* at pH 6.5 [46]. Purification of the dyes was essential to remove ions with the same charge as the dye as these lead to system peaks through competitive displacement processes. A high concentration of methanol (80% v/v) in the BGE was necessary to maintain the solubility of the dyes and to minimise their adsorption onto the capillary wall. A light-emitting diode (LED) with an emission maximum at 475 nm was used for detection, with this wavelength being chosen so that it was intermediate between the absorption maxima of the two dyes and closer to the wavelength of the less absorbing dye. Orange G has an absorption maximum at 478 nm (ε = 19 511 Lmol^{-1}·cm^{-1}) [44] and chrysoidine has an absorption maximum at 453 nm (ε = 23 427 Lmol^{-1}·cm^{-1}) [43].

The injection technique used involved the initial application of negative pressure at the anodic end of the capillary for a specified time, followed by application of positive pressure at the cathodic end for half the time used at the cathodic end. This resulted in equal volumes of sample remaining in each end of the capillary after the injection. The position of the detector was initially adjusted to approximately the middle of the capillary to maximise the distance over which ions moved so as to maximise separation. A small adjustment of the detector position was then required to avoid the overlap of peaks from anions and cations (see Fig. 6) [54]. The benefits of a movable point of detection when optimising the apparent selectivity in simultaneous separations of anions and cations have been previously amply demonstrated with a contactless conductivity detector [55]. The LOD obtained for each of the ions are shown in Table 3. The values for the cations are superior to those obtained using traditional cationic probes, such as imidazole, but the values for anions were higher than those obtained using an optimised BGE containing orange G alone [54] and lower baseline noise was obtained.

4 Concluding remarks

FEP is useful as a material for CE capillaries and also has potential for electrodriven microfluidic devices. For the particular FEP capillary examined in this study, the mechanical properties made it more difficult to work with than FS in that it lacked robustness and was easily kinked. Although light scattering increased baseline noise appreciably for λ <200 nm, detection at higher wavelengths was completely satisfactory. Optical transparency over the entire length of the capillary facilitated the use of a movable optical detector, which was not possible for conventional FS capillaries. This allowed the use of a novel BGE based on a mixture of a cationic and an anionic dye to facilitate dual indirect photometric detection of cations and anions in a single run. The EOF of the FEP material could be adjusted using semipermanent coatings to achieve moderate normal or moderate reversed EOF, and dynamic coatings could also be used to increase the magnitude of μ_{EOF}. The strongly hydrophobic nature of the FEP material allowed cationic or anionic sur-
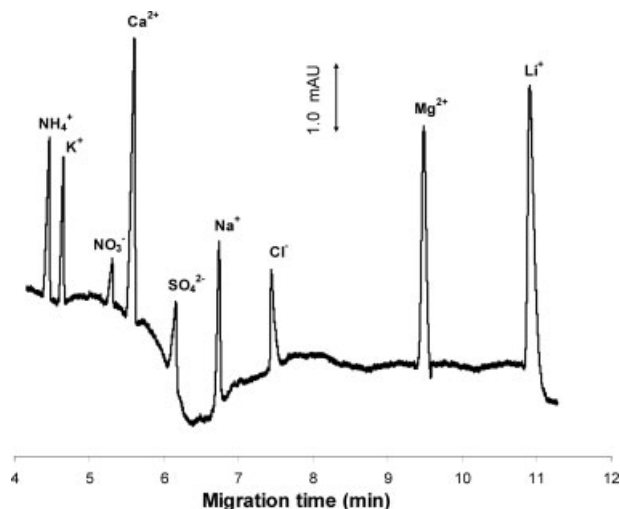

Figure 6. Simultaneous indirect visible detection of anions and cations by dual opposite end injection. Conditions: FEP capillary 80.3 μm × 82 cm (total); length to detector 38 cm from positive electrode; electrolyte, 3 mM orange G, 3 mM chrysoidine, 5 mM BMPA, 0.04% HPMC, 80% CH$_3$OH, pH* ∼ 6.5, voltage +30 kV, detection using 475 nm ('blue LED'), injection, 8 s × 40 mbar + 4 s × 40 mbar. Absorbance scale reversed.

Table 3. Sample concentrations and LOD for anions and cations from dual indirect photometric detection

Ion	NH$_4^+$	K$^+$	NO$_3^-$	Ca^{2+}	SO$_4^2$	Na$^+$	Cl$^-$	Mg^{2+}	Li$^+$
c (μM)	20	10	30	10	20	20	30	10	10
LOD (μM)	0.59	0.33	1.6	0.17	0.94	0.68	1.06	0.24	0.21

Conditions as in Fig. 6.

factants to be coated onto the capillary wall by means of a short preflush, without the necessity for subsequent inclusion of the surfactants in the BGE. For certain analytes where hydrophilic wall interactions are problematic, an FEP capillary may provide higher separation efficiencies than those attainable using an FS capillary.

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