



Published in final edited form as:

Anal Chem. 2009 June 15; 81(12): 5102–5106. doi:10.1021/ac900570s.

Ion Exchange Resin Bead Decoupled High-Pressure Electroosmotic Pump

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Abstract

We describe an electroosmotic pump (EOP) that utilizes a cation exchange resin bead as the electric field decoupler. The resin bead serves as a electrical grounding joint without fluid leakage, thus eliminating electrolytic gas interference from the flow channels. The arrangement is easy to practice from readily available components, displays a very low electrical resistance, and is capable of bearing high backpressure (at least 3200 psi). We use a silica xerogel column as the EOP element to pump water and demonstrate a complete capillary ion chromatograph (CIC), which uses a similar bead based microelectrodialytic generator (μ -EDG) to generate a KOH eluent from the pumped water. We observed good operational stability of the complete arrangement over long periods.

An electroosmotic pump (EOP) has no moving parts, can generate substantial pressures, and can pump without pulsations. As a result, there is considerable current interest. There are recent reviews,¹ in particular on application in chip-scale systems.^{2,3} Because the flow from an EOP is driven by an applied electric field, precise flow control, both in direction and magnitude, can be achieved by choosing the direction and the magnitude of the applied electric field. A practical EOP will be a real boon to capillary and chip-scale liquid and ion chromatography.

Commonly, EOPs can be classified as having open tubular or packed pumping element configurations. Open tubular pumping elements can be simply silica capillaries;^{4,5} more current versions of the same concept uses conduits etched in microchips.^{6–9} Porous glass,¹⁰ 11 silica,¹² or silicon¹³ can serve the same purpose. Packed columns^{14–18} or packed channels on a chip^{19,20} generally provide greater pressure capabilities, but fabrication of the frits, necessary to retain the packing, can be nontrivial. For this reason, monolithic porous structures of silica^{21–23} or polymers²⁴ have become increasingly popular.

Two other unique approaches are notable. Imagine a T-channel on a glass chip where the field is applied between one of the horizontal arms of the tee and the bottom of the vertical arm. Further imagine that the vertical arm is deliberately coated (e.g., with a gel coating) such that the electroosmotic flow (EOF) is drastically reduced compared to that in the horizontal arm.

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As a result, only a small amount of the flow generated by the horizontal arm goes down the vertical arm (in principle, the vertical arm can even be coated to generate EOF in the opposite direction) and the balance flow thus proceeds down the other horizontal arm, free of electric field and free of electrolytic gases.²⁵ Culbertson et al.²⁶ later showed that such EOF-induced hydraulic pumping can be used for differential ion transport. The work by Razunguzwa and Timperman²⁷ is in fact very similar to the Ramsey and Ramsey approach except in this case the two horizontal arms of the tee are packed, respectively, with cation and anion exchange resins and voltage of appropriate polarity is applied across the entire horizontal arm, such that EOF is generated in both horizontal arms toward the confluence point, this then flows down the field-free vertical arm.

It is important to note that in both of the above examples flow occurs in the field-free region and in a gas free manner. It has long been demonstrated how electrical grounding can be achieved through an ion exchange membrane⁵ while flow continues past the grounding joint. Ion exchange membranes have been used to isolate the electrodes in several studies since^{7,8,12,21,22} dialysis-type cellulose acetate membranes,¹⁰ porous glass disks,⁶ and gels^{28,29} have also been used for electrode isolation so as to keep gas bubbles away from the pumped flow. Rather than electrode isolation, gas bubbles have been removed from the pumped flow stream also with a PTFE membrane.¹¹ These approaches work fine in low-pressure applications. However, under high pressure, membranes burst and substantial flow can go across a porous disk grounding joint; the grounding provided by the latter can also be imperfect.⁸ Whether gels can adhere to conduit walls with sufficient tenacity to withstand high-pressure extrusion is presently not known.

In some applications, one of the electrode compartments, the nominal pump outlet, is not in the main intended flow stream and is sealed up during operation.²⁰ Obviously, such an arrangement cannot indefinitely work: others have resorted to an arrangement where the accumulated gas is intermittently released.³⁰ Tubular flow through electrodes^{16,17} have been used to deliver the pumped fluid but carries the gas bubbles as well. To summarize, a gas-free EOP that delivers the pumped fluid at a high pressure in a field-free manner has not yet been demonstrated. The ideal field decoupler should lead to gas production outside the flow channel and simultaneously display a minimum in electrical resistance and a maximum in resistance to bulk flow.

A second issue with most actual application of EOPs is that the EOF generated by an EOP is highly dependent on the composition of the pumped fluid. Even though attempts have been made to render flow rates pH-independent,²⁷ the compensation is imperfect. Even when the same fluid is continuously pumped, ongoing electrolysis can change the composition of the fluid in the reservoir.¹² Gradient elution, the mainstay of virtually all forms of liquid/ion chromatography, is generally impossible without simultaneous unintended flow rate changes and/or requiring multiple pumps.

In the context of capillary ion chromatography (CIC) of particular interest to us, microelectrodialytic generators (μ -EDGs) have recently been introduced that generate eluents in a gas-free manner with high Faradaic efficiencies.^{31,32} Ion exchange resin beads were used in this application in the mechanical configuration of miniature “ball-on-seat” valves, permitting ready passage of ions (and ionic current) but not fluid flow. The concept of simply pumping water through an EDG and varying the generator current to affect gradient elution has long been established in IC³³ and constitutes the current state of the art. An EOP that only pumps water (of course, the composition of water does not change as a result of electrolysis) through a μ -EDG would be the ideal minimalistic approach to carry out CIC. Moreover, the same concept of an ion-exchange resin bead simultaneously providing facile ionic conduction

and high resistance to fluid flow can be utilized for electric field decoupling. We demonstrate the realization of this concept in the present communication.

EXPERIMENTAL SECTION

Reagents and Apparatus

Analyte anions used in CIC analysis were prepared in the form of either sodium or potassium salts (reagent grade chemicals, used as received). Ultrapure water (Milli-Q, www.millipore.com) was used throughout. Formamide (www.sial.com) and potassium silicate solution (Kasil No. 2130, www.pqcorp.com) were obtained as indicated.

A high voltage (HV) power supply (LION HV, LIAO Corp., Tianjin, China) was used for powering the EOP. A platinum wire, 0.5 mm in diameter, was used as the HV electrode.

EOP Fabrication

Figure 1 presents the pump configuration. A machined polymethylmethacrylate (PMMA) vial (10 mL capacity) was used as the reservoir for the pump fluid. Pure water was used as the pump fluid throughout. An 1 cm segment of a Teflon tube (0.014 in. (360 μm) i.d. \times $1/16$ in. (1.6 mm) o.d.) was push-fit into a hole drilled into the side of the PMMA vial into which the 365 μm o.d. 250 μm i.d. fused silica column was push-fit. This 30 cm long column served as the EOP element and contained an in situ synthesized silica monolith fabricated to produce a xerogel following the methods of Fields.³⁴ The column was inserted through the Teflon sleeve to protrude on the other side and be in contact with the water in the vial. The water in the vial was also in contact with the platinum wire, used as the +HV electrode. The other end of the column was affixed in one arm of a PEEK (P727, www.upchurch.com), as shown in Figure 1. The pump output proceeded through the PEEK tube affixed to the opposing arm. The vertical arm contained the resin bead electric field decoupler, similar in design to the μ -EDGs. Both terminal bores of a PEEK tube segment (0.75 mm i.d. \times 1.6 mm o.d.) was enlarged with a 1 mm diameter drill bit to a depth of \sim 1 mm. Cation exchange resin (CER) beads (Dow Rexyn 101 H⁺-type) were dried in a desiccator prior to use. A single CER bead with a dry diameter of 0.8–0.9 mm was placed in the drilled out cavity and wetted with water whereupon it immediately expanded and lodged tightly in the cavity. The bead-bearing tubing was fixed in place in the vertical arm of the tee. A stainless steel (SS) tube (0.2 mm i.d. \times 0.4 mm o.d. \times 25 mm long) was put in all the way into the PEEK tube, just short of touching the bead. The SS tube functioned both as the electrode and the water inlet tube; the liquid outlet was provided by a 0.25 mm i.d. silica capillary. Water pressurized by N₂ flow behind the bead at a rate of \sim 0.1 mL/min; this flow rate was not critical. Bringing this tubular electrode close to the bead reduces the voltage drop and associated Joule heating; however, it should not be shoved up into the bead, this can create substantial flow resistance and shut off the flow. A flowing stream, rather than static water, helps flush out any electrolytic gas bubbles formed.

Capillary Ion Chromatography System

The capillary IC system was similar to that previously described^{31,32} except that the EOP substituted for the high-pressure mechanical pump. Pure water pumped by the EOP flowed through a μ -EDG,³¹ an internal loop injector (200 nL, P/N CI4W.2, www.vici.com), an anion exchange column prepared by coating AS18 anion exchange latex on a monolithic methacrylate-based sulfonate functionality cation exchanger (0.25 mm i.d., 250 mm long).³⁵ The column was connected to a miniature Nafion fiber-based suppressor³⁶ (80 μm i.d. \times 200 μm o.d., 30 mm long), chemically regenerated with 10 mM H₂SO₄. A capacitance to voltage digital converter was used for detection; it behaves virtually as a contactless conductance detector (CCD).³⁷ Figure 2 schematically shows the EOP- μ -EDG system.

RESULTS AND DISCUSSION

Electrical Conductivity and Pressure Tolerance of Resin Bead Decoupler

The resin bead decoupler simultaneously plays three roles: It (a) transfers electrolytic gas evolution to outside the pump conduit; (b) readily conducts ionically, thus facilitating efficient grounding of the circuit and allowing all downstream components, injector, separator, suppressor and detector, to operate in a field-free zone; and (c) prevents bulk flow leakage into the electrode chamber and hence makes effective use of the EOF generated by the EOP, within the normal limitations of separation column induced backflow.¹

The voltage drop across the resin bead is an indication of the electrical resistance posed by the bead. Measurement of voltage between the stainless steel (SS) tubular ground electrode and the pump outlet point (stainless steel tube substituted instead of PEEK pump outlet) indicated essentially no significant voltage drop across the bead. In an alternative arrangement, the current was measured with and without the bead via the voltage drop across a serial 10 k Ω dropping resistor. Again, there was no statistically significant difference in the current values with and without the bead, indicating that for all practical purposes, the bead provides an effective low-resistance grounding pathway.

Previous experiments with μ -EDGs have shown that the devices withstand at least 2000 psi backpressure.³² It would have been possible here to use a four-way cross, both cation and anion exchange beads (both externally grounded and fed with a common water source). Since a single cation exchange resin bead provided a grounding pathway of sufficiently low resistivity, a dual bead grounding configuration was not investigated. In principle, either a cation exchanger or an anion exchanger bead can be used. There are however advantages to using a cation exchanger. Not only is a cation exchanger more conductive than an anion exchanger (exchange capacities are higher for the former and H⁺ has a much greater mobility than OH⁻), an anion exchange bead tends to be the mechanically weaker one. Whenever we tested EDG devices at pressures significantly higher than 2000 psi, it was invariably the anion exchanger side where leakage first occurred. A device that is based on a single cation exchange bead has recently been shown to have a pressure capability in excess of 3200 psi.³⁸

Applied Voltage and Flow Rate

Without any load on the pump outlet (no column connected), the flow rate was linearly related with the applied voltage in the range of 0–10 kV and could be adequately described by the equation:

$$\text{flow rate } (\mu\text{L}/\text{min}) = 0.196 \pm 0.002 \text{ (kV applied across EOP)} + 0.028 \pm 0.015 \quad (1)$$

At an applied voltage of 7 kV, the flow rate was measured 6 times at 10 min intervals and was found to have a reproducibility of 0.87% as measured gravimetrically.

We then similarly measured the flow rates over the same applied voltage range with the column in place. The flow rate could be adequately described by the equation:

$$\text{flow rate } (\mu\text{L}/\text{min}) = 0.112 \pm 0.005 \text{ (kV applied across EOP)} + 0.021 \pm 0.042 \quad (2)$$

It will be observed that in the second case, the flow rate is only 57% of the first case. Consider that when confronted by a nonzero resistance to flow, the flow generated by the EOP has a

choice to flow not only as intended through the analytical column and other downstream components but also to flow in the reverse direction back through the EOP. Obviously the relative distribution of the flow will depend on the resistance to fluid flow offered by the separation column and the EOP itself, respectively. We measured the resistance to flow both for the EOP and the analytical column in the 0–2 $\mu\text{L}/\text{min}$ flow range. The pressure drop for the EOP was 434 ± 12 psi min/ μL while that for the column was 152 ± 2 psi min/ μL . The EOP thus has a 2.9 times greater resistance to fluid flow than does the separation column. Relative to the flow generated when there is no resistance to flow at the outlet of the EOP, we would expect that 74% ($2.9/(2.9 + 1) = 0.74$) will still flow through the separation column while 26% of the original flow will now be flowing back through the EOP itself. Inasmuch as only 57% of the zero backpressure flow is observed, the pump thus exhibits only 77% of the maximum theoretical efficiency. We do not at this time understand why full theoretical efficiency is not attained.

Attainable pressure and flow rates for an EOP are functions of the applied voltage, the separation column flow resistance, and the EOP flow resistance. With 14 kV applied to the EOP, the separation column we used had a flow of ~ 1.6 $\mu\text{L}/\text{min}$ and generated a backpressure of 240 psi. With the EOP dead-ended against a pressure transducer, at this applied voltage, the measured static pressure was ~ 1300 psi. The single cation exchange bead, in an essentially identical configuration but used as a single bead eluent generator has recently been demonstrated to withstand >3200 psi. We continue to work on the EOP element, both in terms of the geometric dimensions and the nature of the packing, and expect to report in the near future on more detailed characterization of pressure-flow characteristics as a function of EOP geometry and applied voltage.

Performance

The intended use of the present EOP is to pump through a μ -EDG. Regardless of the flow stability of the EOP, the stability of the EDG itself is also important and the two together determine the generated eluent concentration. The effluent conductivity was monitored at an EOP applied voltage of 7 kV and an EDG current of 10 μA over a period of ~ 2 h. The specific conductance remained constant at 3.93 ± 0.026 mS/cm (corresponding to a generated KOH concentration of 5.75 ± 0.029 mM). This corresponds to a relative standard deviation of 0.51%, a very respectable figure considering no temperature stabilization was attempted. The data are shown in Figure 3.

Chromatography

By combining of a resin bead decoupled EOP with a μ -EDG that generates KOH, a homemade monolithic separation column (admittedly more efficient commercial columns are available), and a capillary fiber suppressor (possibly too large, not optimized for this application), we can nevertheless construct a complete EOP driven CIC system. The separation of five common anions is shown in Figure 4. The relative standard deviation (RSD) of the retention times for the analytes ranged from 0.9–1.8% ($n = 4$).

ACKNOWLEDGMENT

This research was supported by National Natural Science Foundation of China (Grant No. 20805047). It was partially supported by National Key Technology R&D Program in the 11th Five Year Plan of China (Grant No. 20707026). P.K.D. acknowledges the support of NSF Grants CHE-0731792 and CHE-0821969. S.L. acknowledges the support of the National Institute of Health (Grant 1R21EB008512-01A1). We thank PQ Corporation for the gift of the potassium silicate solution and Dionex Corporation for the gift of the AS-18 latex.

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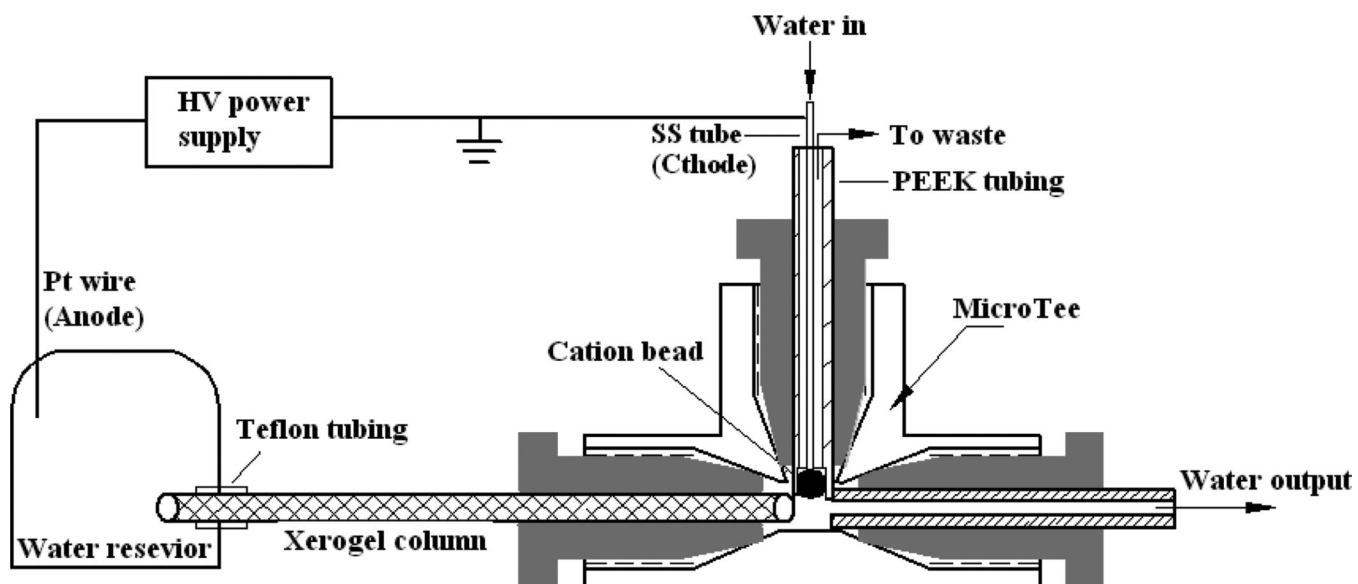


Figure 1.
Bead decoupler-based EOP configuration.

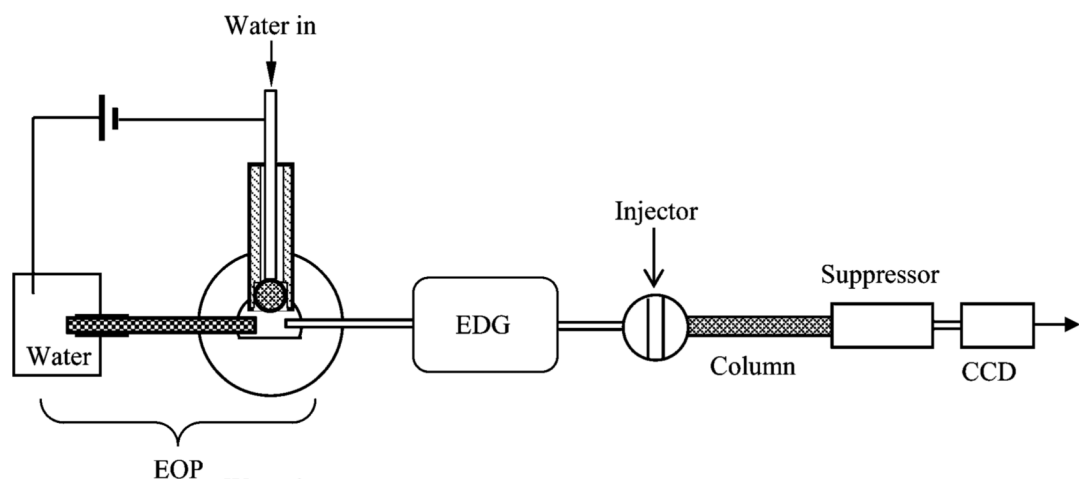


Figure 2.
Schematic of the experimental setup.

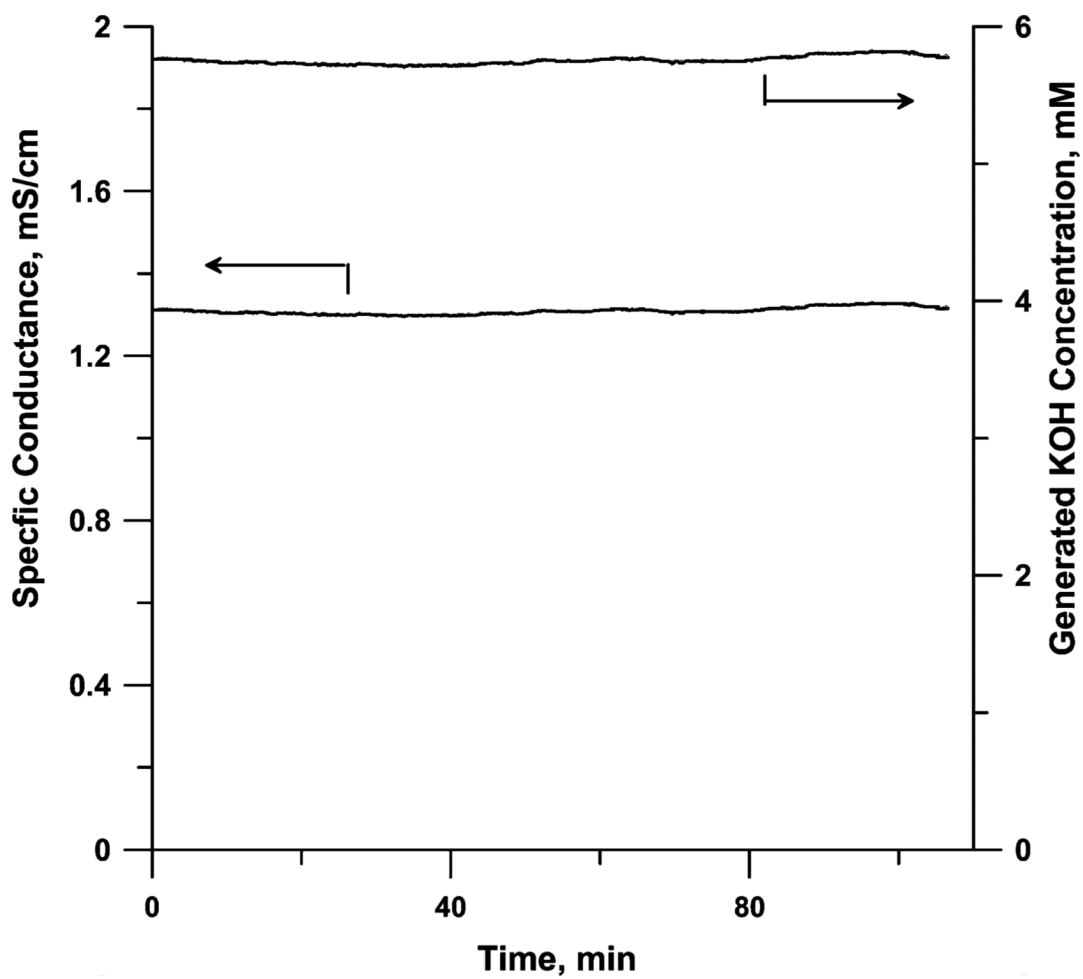


Figure 3. Specific conductance and the generated KOH concentration by the EOP- μ -EDG combination over a 2h period. Approximately 32 000 discrete measurements are plotted. EOP applied voltage 7 kV, μ -EDG operated at 10 μ A. Measured EOP output flow rate (no column connected): 1.2 μ L/min.

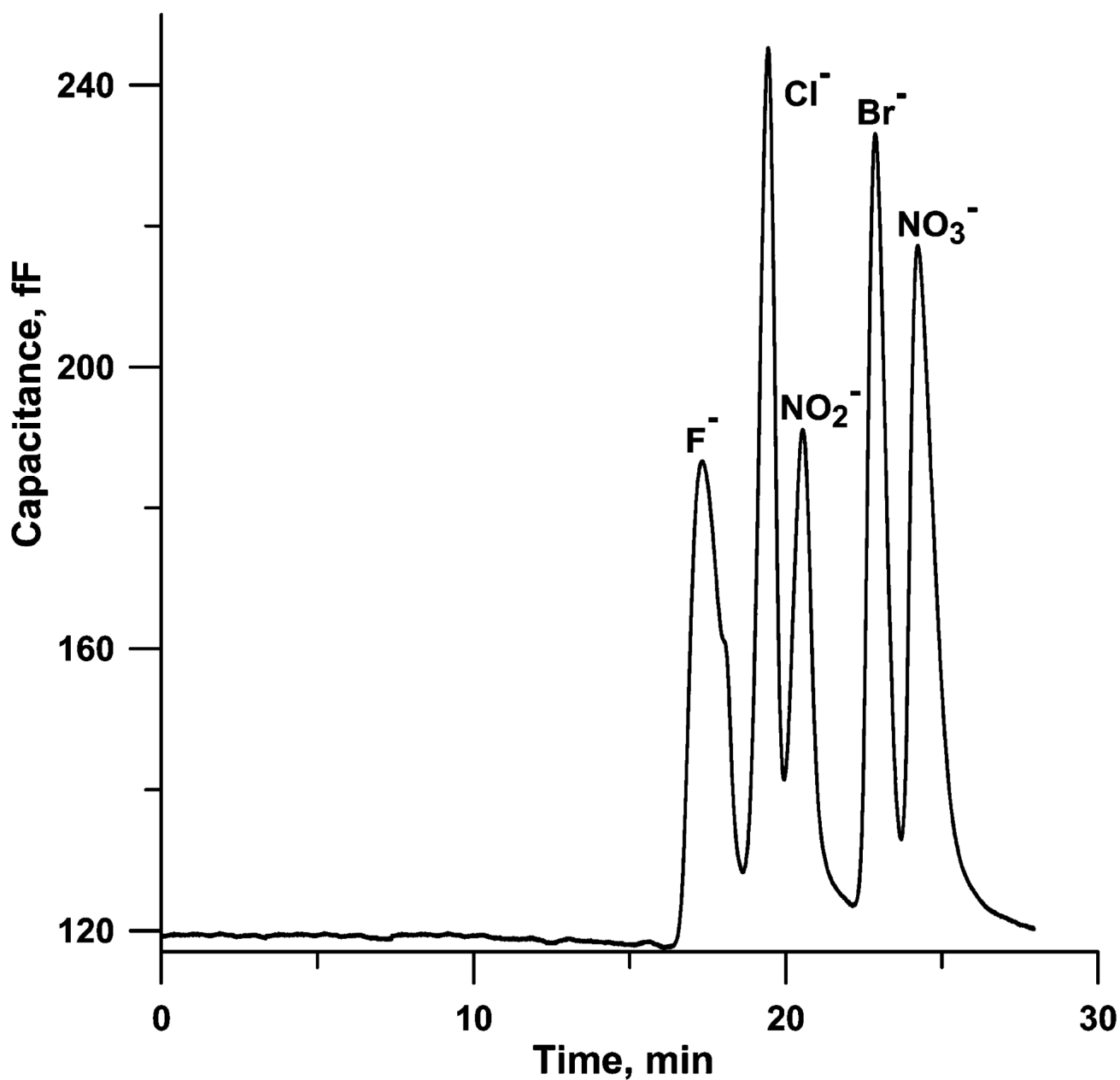


Figure 4.

Typical chromatogram obtained by the resin bead decoupled EOP- μ -EDG-CIC system.

Conditions: EOP, 7 kV; μ -EDG, 10 μ A; sample, 100 pmol of each ion in 200 nL; column, 0.25 mm i.d. \times 250 mm long, sulfonate functionalized acrylate monolith with anion exchanger latex coating; flow rate, \sim 0.8 μ L/min; hollow fiber suppressor chemically regenerated with 10 mM H₂SO₄; Detector Analog Devices AD 7746 capacitance to voltage converter; system void time, \sim 15.5 min.