



# Microfluidic membrane suppressor module design and evaluation for capillary ion chromatography<sup>☆</sup>



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## ABSTRACT

A microfluidic ion-suppression module for use in ion-exchange chromatography has been developed and evaluated. The device consists of an ion-exchange membrane clamped between two polymer chips featuring a  $200 \times 100 \mu\text{m}$  (width  $\times$  depth) eluent channel ( $l = 60 \text{ mm}$ ), and a  $300 \times 150 \mu\text{m}$  regenerant channel (60 mm), respectively. The suppression efficacy using a Nafion membrane was compared with that of a styrene-sulfonate grafted fluorinated ethylene propylene (FEP) membrane. The latter was found to outperform Nafion in terms of lowest attainable background signal (suppression efficacy) and dynamic suppression range. Increasing the suppressor temperature or the sulfuric acid regenerant concentration led to an extension of the operational suppression range, this however at the cost of an increased background signal due to enhanced diffusion, inducing sulfate bleed. Under optimized operating conditions, the microfluidic suppressor provided a dynamic capacity of  $0.35 \mu\text{Eq./min}$ , being compatible with gradient separations applying up to 70 mM KOH in combination with  $400 \mu\text{m}$  i.d. capillary columns operated at the optimal flow velocity. The applicability of the miniaturized suppressor is demonstrated for both isocratic and gradient separations of mixtures of inorganic anions. Band-broadening characteristics of the suppressor were optimized with respect to a commercial capillary hollow-fiber suppressor, yielding comparable overall system efficiency, e.g., 8500 plates for nitrate recorded on a 150 mm long capillary column. A second chip device was also constructed, featuring suppression at both sides of the eluent flow path. This double-sided suppressor allowed to increase sample throughput and operate at eluent flow rates of  $10 \mu\text{L/min}$ , while maintaining efficient suppression characteristics.

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## 1. Introduction

War is often a booster for technological advances. Execution of the Manhattan Project (1943–1945) pushed researchers to develop ion chromatography (IC) techniques for the separation, purification, and production of uranium salts [1]. The declassification of the research revealed that a fundamental understanding of the technique was established, *i.e.*, that the ion-exchange retention is mainly governed by charge and ion diameter [2]. Another milestone in the development of IC has been the introduction of the concept of suppressed-conductivity detection by H. Small and coworkers at Dow in 1975 [3]. Using this approach, highly conductive mobile phases are converted into water or weakly dissociated acids or

bases, presenting low background conductivity. This allowed for the commercialization of the technique, now widely adopted for the analysis of inorganic ions and ionizable compounds such as amines, carbohydrates, *etc.* [4–6]. These early suppressors were packed-bed columns which were regenerated offline, a concept still used in some systems [7]. To circumvent the need for offline regeneration, continuous regeneration was made possible by the introduction of (chemically-regenerated) membrane suppressors, either in the form of a hollow fiber or with planar membranes [8,9]. Such devices also addressed band broadening introduced by eddy dispersion in the packed-bed suppressors. Advances in suppressor technology, hyphenation of IC to detectors using suppressor technology, and system hardware in general have been reviewed by Haddad *et al.* [10–12].

As previously demonstrated in high-performance liquid chromatography (HPLC), the reduction of particle size of the packing material in the separation column has allowed to achieve higher efficiencies (when maintaining the same column length) or to

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decrease the analysis time when using smaller particles in combination with shorter columns [13]. Current state-of-the-art IC separations involve the use of capillary-scale column formats that are packed with 4  $\mu\text{m}$  stationary-phase particles, yielding peak volumes in the range of 1–4  $\mu\text{L}$  [14]. In order to maintain high separation efficiencies provided by these columns, the dimensions of peripheral post-column IC modules, such as suppressor and detector, need to be downscaled and preferably integrated, since the total peak variance is the sum of the column contribution and extra-column dispersion. Achievements with respect to this were, for example, recently reported by the research group of Dasgupta who developed open-tubular column technology for IC with an integrated monolithic capillary suppressor [15]. Another suppressor constructed for capillary IC featuring ion-exchange beads presenting a volume of only 600 nL was also reported, but provides a rather limited dynamic ion-suppression capacity [16]. Despite the benefits that chip technology could offer, the potential of microfluidics in IC has seldom been reported [17,18]. These all use non-suppressed detection approaches, which can intrinsically never provide the same detection sensitivity as suppressed conductivity detection. Recently, we introduced a first prototype of a microfluidic chip suppressor [19]. This demonstrated the feasibility of downscaling the concept of membrane suppressors, offering great potential for future integration in a modular IC-platform encompassing separation, suppression, and detection. The design of suppressor and detection modules becomes critical when microfluidic chip-technology concepts are applied.

The present study concerns the design, characterization, and application of robust and versatile microfluidic membrane-suppressor chips for capillary scale ion-exchange separations. Compared to commercially-available electrolytic capillary hollow-fiber suppressors, a capillary-scale chemically-regenerated planar membrane suppressor chip has the potential to improve characteristics such as low burst pressure, reproducibility issues due to variability of capillary i.d. and o.d., reliability of fluidic connections, compatibility with organic modifiers [20], and possibly also lifetime. The latter is related to membrane degradation due to heat development and formation of radicals during the electrolytic conversion of water into hydronium and oxygen, which is prevented in case of chemical suppression [10,20]. Moreover, this concept potentially allows reaching lower detection limits, since lower noise levels may be achieved under these conditions [21].

Extra-column band-broadening contributions of different microchip-suppressor designs are discussed and optimized, while identifying important design parameters. The ion-suppression efficacy and operational range have been investigated for two types of cation-exchange membranes, while studying the effects of temperature and regenerant concentration. Overall system efficiency is reported in isocratic mode, and the gradient separation of a complex sample mixture is demonstrated. Finally, a double-sided membrane chip suppressor design is presented to increase the suppression capacity, enabling high-throughput analysis at higher flow rates.

## 2. Experimental

### 2.1. Materials and chemicals

Potassium chloride (KCl, 99.99% trace analysis) and sulfuric acid ( $\text{H}_2\text{SO}_4$ , 97%) were purchased from Sigma Aldrich (Diegem, Belgium). A 7-anion standard (containing 20 mg/L fluoride, 100 mg/L bromide, 100 mg/L chloride, 100 mg/L nitrate, 100 mg/L nitrite, 150 mg/L phosphate, and 150 mg/L sulfate) and a complex sample containing 28 anions were obtained from Thermo Fisher Scientific (Sunnyvale, USA). Cyclic olefin copolymer (COC,

TOPAS grade 6017) was purchased from Kunststoffzentrale Leipzig (Leipzig, Germany), Nafion sheets (grade N117, thickness (dry) 180  $\mu\text{m}$ ) were purchased from Ionpower (Munich, Germany) and a styrene-sulfonate radiation grafted fluoroethylene propylene (FEP) cation-exchange membrane (thickness (dry) 150  $\mu\text{m}$ ) was provided by Thermo Fisher Scientific. Poly(ether ether ketone) (PEEK) foil (Aptiv 1000 series, thickness 100  $\mu\text{m}$  and 150  $\mu\text{m}$ ) was kindly donated by Victrex (Lancashire, UK). Deionized water (18.2  $\text{M}\Omega \times \text{cm}$ ) was used for all dilutions.

### 2.2. Hardware fabrication

Microfluidic COC chips were created in-house via micromilling, allowing rapid prototyping of different designs. The channel layouts were created in AutoCAD (Autodesk, San Rafael, USA), jobs were programmed using PrimCAM (Primus Data, Einsiedeln, Switzerland), and executed by a Datron M7 compact milling machine (Datron, Mühlthal-Traisa, Germany). Membranes were hydrated, cut to size, and sandwiched between the eluent and regenerant substrate plates (dimensions 70  $\times$  15  $\times$  1.5 mm). To connect the microfluidic devices to peripheral equipment, the stack is placed in a custom-made PEEK holder with integrated 1/32" Nanoport connections compatible with 1/32" o.d. capillary PEEK tubing (both obtained from Upchurch Scientific, Oak Harbor, USA), which were bolted together with aluminum backing plates while applying controlled torque. Total holder dimensions are 85  $\times$  25  $\times$  15 mm.

### 2.3. Chip-performance characterization

Characterization of the in-house developed hardware was performed using an ICS-5000 capillary ion-chromatography system (Thermo Fisher Scientific). The dual-pump module consists of an isocratic capillary pump and a quaternary gradient analytical pump, both equipped with online degassers. The eluent-generator module, fitted with a capillary cartridge, was used to generate potassium hydroxide (KOH) eluent online for isocratic and gradient anion-exchange separations and a continuously regenerated capillary trap column was installed. The system features a capillary scale eluent degasser, a 4-port injection valve with internal 400 nL loop, a column-oven compartment, a capillary electrolytic hollow-fiber suppressor (CES300), and two capillary conductivity detectors (set at 35  $^\circ\text{C}$ ). The capillary pump was used to deliver flow to the column and the analytical pump was used to establish regenerant flow for the microfluidic membrane suppressor (applying a 3:1 split ratio). A well-plate autosampler was coupled to the system. Capillary format columns (400  $\mu\text{m}$  i.d.) IonPac AS18 (150 mm) and IonPac AS11-HC (250 mm) were used. Both are packed with 4  $\mu\text{m}$  macroporous (1500–2000 Å) ethylenevinylbenzene-divinylbenzene particles, coated with 70 nm nanobeads functionalized with alkanol quaternary ammonium ion functionalities. The carbonate-removal module [12] was bypassed to limit extra-column band broadening and to assess true suppressor performance, as this would also lower the background signal.

To record band-broadening characteristics of different suppressor designs, a set-up with two conductivity detectors installed after the separation column and electrolytic hollow-fiber suppressor was used. In these experiments, different chip modules were placed in between the two capillary conductivity detectors. As such, this set-up provides realistic peak volumes and peak widths at the detector. The peak variance induced by extra-column band broadening introduced by passage through the microfluidic suppressor chip is the total peak variance measured in the second detector subtracted with the peak variance recorded in the first detector, and the variance contribution measured for the connection tubing. The dispersion characteristics of the hollow-fiber suppressor design were

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