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A cation exchange resin bead-based microscale electrolytic suppressor for capillary ion chromatography

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ABSTRACT

A cation exchange resin (CER) bead-based microscale electrolytic suppressor for capillary ion chromatography (CIC) has been fabricated and evaluated. Relative to common ion exchange membrane, the use of CER beads presents a simple way to fabricate a microscale suppressor due to its small surface area and spherical shape. The internal volume of the device is ~600 nL, which matches the requirements by CIC. Continuous online regeneration is readily achieved using pure water or diluted sulfuric acid as the regenerant. The use of a cation exchange functionalized monolithic segment inserted between two CER beads greatly reduces the electrical resistance and improves the suppression efficiency. The device works well only in the electrolytic mode, chemical regeneration alone is ineffective. The suppressed background is ~3 μS/cm for 10 mM KOH eluent generated online by a microscale KOH electrolytic generator operated at the flow rate of 3 μL/min. The preliminary application for capillary ion chromatography has been demonstrated.

1. Introduction

Since introduced in 1975, ion chromatography (IC) has become a routine analytical method for the determination of inorganic ions, especially anions. The suppressor is one of the key components in IC and can reduce the background conductance of the eluent and simultaneously enhance the analyte signal. Various types of suppressors have been developed in the past decades to achieve higher sensitivity, including packed column [1], hollow fiber [2] or monofilament filled fiber [3], micro membrane-based suppressor operated in chemical [4] or electrolytic mode [5,6]. Most of the above devices were designed for conventional IC systems, and less work has been done on capillary IC (CIC), despite the facts that CIC has several advantages over conventional IC such as higher separation efficiency, lower eluent consumption, and easier coupling with MS. Compared to the conventional suppressors, a microscale one is more difficult to fabricate due to much more stringent demands on minimizing extra column broadening. Rokushika et al. used a 200 μm i.d. Nafion tubing suspended in the regenerant (dodecylbenzenesulfonic acid) for the suppression of carbonate/bicarbonate eluents [7]. Subsequent versions of Nafion tubing-based suppressor for CIC were reported by Dasgupta and Bao [8], Sjögren et al. [9] and Boring et al. [10]. Casting Nafion solution to form a microbore tube has been reported by Kuban et al. [11]. They have also demonstrated suppression in a microfluidic device by the use of immiscible liquids [12]; this has never been used in practice. Recently a capillary-scale suppressor that offers desirable characteristics for the analysis of inorganic ions has become commercially available [13]. The device utilizes an ion exchange fiber is embedded within ion exchange resin bed that lowers electrical resistance and improves suppression capacity. While the suppressor demonstrates excellent performance, the fabrication is rather complex. More recently, an arrangement where two packed-column suppressors are alternated has been reported for use in CIC [14]; this is largely similar to the one-valve/three-suppressor commercially offered by Metrohm [15]; additional valving and attendant dispersion present potential disadvantages.

In our recent work, we have presented a two oppositely ion exchange resin (IER) beads-based microscale eluent electrolytic generator (EDG) [16,17]. The spherical shape of the beads makes them ideal candidates for fabricating miniature electrodialytic devices in a simple format. The above dual configuration EDG with slight modification can function as a microscale suppressor. That is, the EDG becomes an anion suppressor when two cation exchange resin (CER) beads are used to replace the combination of one cation bead and one anion bead used in dual configuration EDG; the concept was outlined in [16]. Here the CER bead-based electrolytic microscale suppressor for CIC has been demonstrated. A segment of a cation exchanger monolith (CEM) is inserted between the two CER beads, aiming to lower the electrical resistance and improve suppression efficiency as well. Continuous regeneration is readily achieved online using either pure water or diluted sulfuric acid

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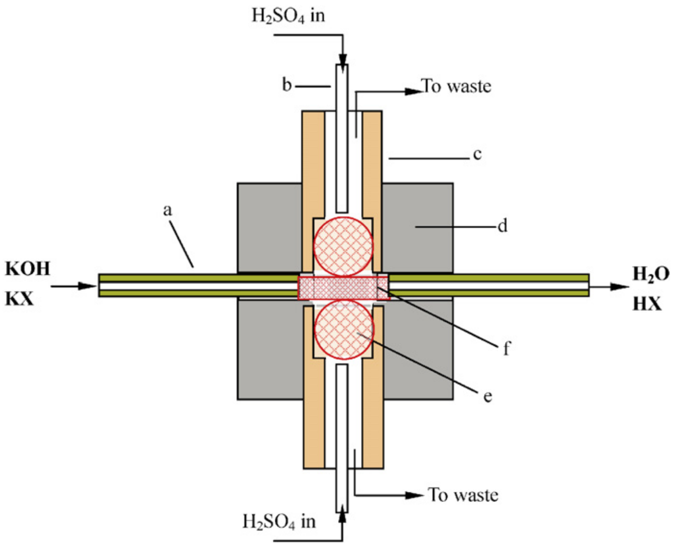

Fig. 1. . Schematic diagram of the bead-based suppressor. a, silica capillary; b, Pt tubing; c, PEEK tubing; d, Plexiglas cartridge; e, cation bead; f, cation monolith. *Note*: the size of the components is not at scale. Detail information see the text.

as regenerant. The suppressed background is ~3 μS/cm for 10 mM KOH eluent. Its utility for CIC has been demonstrated for the separation of anions.

2. Experimental

2.1. Chemicals

Analyte solutions were prepared in the form of either sodium or potassium salts. Typically, these were reagent grade chemicals, used as received. Ultra-pure water (Milli-Q, USA) was used throughout with a specific receptivity of about 18.2 MΩ cm.

2.2. Chromatographic system

The CIC system was similar to that previously described [17]. Briefly, a NanoLC pump (MicroTech Corp., USA) was used for driving pure water to flow through a microscale KOH EDG [18]. Manually prepared KOH eluent was also used in some cases. A 200 nL internal loop injector (P/N CI4W.2, VICI) was used for sample injection. A silica capillary anion exchanger column (0.25 mm i.d. × 210 mm long) used was prepared by coating AS18 latex (Courtesy Dionex Corp., USA) on a monolithic methacrylate-based sulfonate functionality cation exchanger similar to that previously described [19,20]. The column was connected to the suppressor by a segment of silica capillary (0.05 mm i.d. × 0.36 mm o.d. × 50 mm). The suppressor was powered by a constant current source with 0–40 V voltage output (courtesy Prof. Rongzong Hu, Xiamen University, China). A laboratory-built contactless capacitance detector (CCD) was used for analyte detection [21].

2.3. Fabrication of the suppressor

The fabrication procedure of the suppressor was as follows. A cross fitting machined from Plexiglas housed the suppressor and is schematically shown in Fig. 1. Two of the arms of the fitting were for placing PEEK tubing, the others for the silica capillary connecting tubing. For each of two segments of PEEK tubing (0.020 in. i.d. × 1/16 in. o.d.), a cavity (0.8 mm i.d. × 1 mm depth) was made at the bore terminus. Dry CER beads (Rexyn 101 H^+-type, diameter ~0.8 mm) were placed in the respective drilled out cavities in the PEEK tubing and wetted with water whereupon they expanded and lodged tightly in the cavity. These two bead-bearing PEEK tubes were placed opposite each other and fixed in place by epoxy glue, inlet and outlet capillary connecting tubes were fixed in the same way. A platinum needle was put in the PEEK tubing (almost touching the bead), functioning as both the electrode and the liquid inlet tube; the liquid outlet was provided by silica capillary. To reduce the electrical resistance, the eluent channel between two CER beads was packed with fine cation exchange resin or inserted by a segment of CEM. The preparation of sulfonate functionality cation exchange monolith (0.32 mm dia.) was similar to that of the above separation column, except that no capillary wall modification was made so that the monolith could be readily extruded out from the original capillary in which it was made. A 5 mm long segment of CEM was cut and then carefully inserted into the space between two CER beads along the eluent channel (0.4 mm i.d.). It should be mentioned that the final diameter of the CEM depends on the size of the central channel of the suppressor. The smaller diameter leads to lower extra-column effect, which is restricted by the machined skill. As for CEM length, it is enough if it can cover the intersection, e.g., 0.5 mm, while such small length make it difficult to implement. When the length is too long, higher backpressure and extra-column effect caused should be concerned.

The regenerant driven by peristaltic pump was continuously flowing through the donor chamber at the flow rate of ~0.5 mL/min. The regenerant was either recycled or sent to waste.

While the removal of potassium may be tested by other means, e.g., atomic spectroscopy, in operation, the practical parameter is the background conductance. The background conductance of 20 μM KOH solution is readily computed to be ~5.5 μS/cm. If suppressing 10 mM KOH, 99.8% removal will indicate a background conductance of ~5.5 μS/cm. We arbitrarily set this as the successful performance criterion. Note that the presence of any impurities in the KOH will increase the suppressed conductance.

3. Results and discussion

3.1. Choice of regeneration solution

The choice of suitable regenerant for a suppressor is a key step. Obviously, the use of pure water as the regenerant eliminates the manual preparation and possible leakage of regenerant across the CER beads into the eluent. Firstly we tried to use pure water as the regenerant for our initial design of the suppressor, in which no CEM was inserted. The results indicated that the suppressor did work but the suppressed background was too high to be effectively used for CIC. This resulted from two reasons, firstly, high constant current needed could not be applied (commonly only 5–10 μA could be applied) due to high electrical resistance of the device, and secondly, the constant current source used had limited voltage output (0–40 V). To address this, two approaches were explored (1) used sulfuric acid as regenerant in place of pure water and (2) packed fine CER particles into the eluent channel. 100 mM sulfuric acid was firstly tested to be regenerant. Under this condition, good suppression could be obtained and the suppressed background was ~5 μS/cm. A typical suppression curve is shown in Fig. 2. In addition, we have tried to reduce the electrical resistance of the suppressor by packing fine CER particles into the eluent channel, which has been adopted in some design of membrane sheet-based suppressors. This attempt was not successful as it was difficult to retard the fine CER particles in place or the connecting tubing was always observed to be blocked by the particles, although we tried to use PTFE filter to retard the particles. Finally a segment of CEM in place of CER particles was used. For such design, the use of pure water as regenerant was found to be feasible and ~5 μS/cm of the suppressed level for 4 mM KOH eluent at the flow rate of 3 μL/min

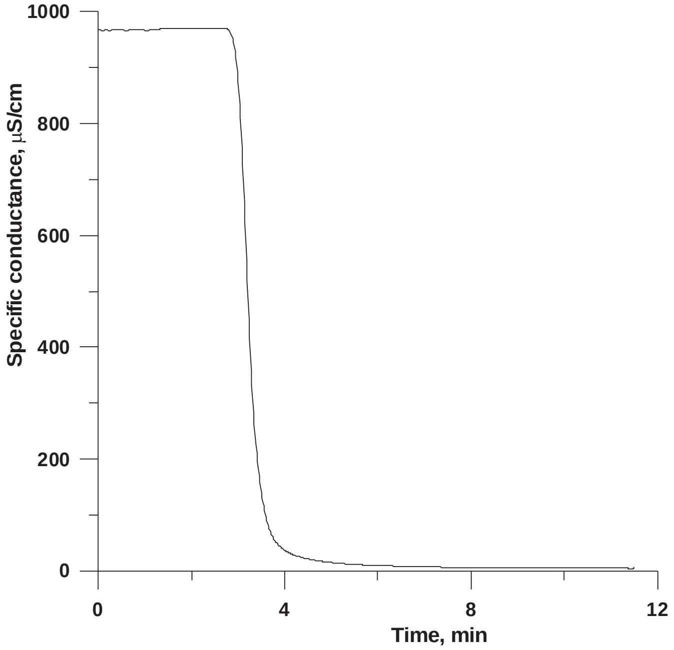

Fig. 2. . Suppression curve for the bead-based electrolytic suppressor. Conditions: no CEM was inserted between two beads and the eluent channel was open; constant current, 60 μA; KOH eluent, 4.5 mM; Flow rate, 3 μL/min; regenerant, 100 mM sulfuric acid.

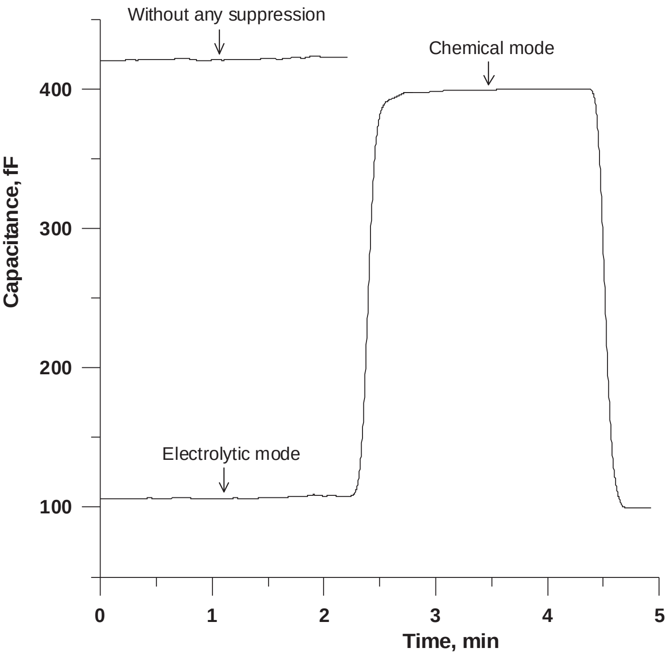

Fig. 3. . Comparison of the suppressor operated in chemical and electrolytic mode. The conditions same to Fig. 2 except using CCD replacing conductivity detector.

was achieved. For KOH eluent with higher concentration, higher current was needed to ensure the effective suppression, but it was found that higher constant could not be effectively applied, indicating the still-high resistance of the device when the regenerant is pure water. This problem was finally solved using diluted sulfuric acid (20–50 mM).

When sulfuric acid is used for regenerant, a direct concern is the possible penetration of the forbidden ions (in this case, it is SO_4^{2-}) across the CER beads. It is known that a consequence of using the regenerant with high concentration (e.g., >25 mM) for membrane sheet-based suppressor is great penetration, thus leading to higher background and then poorer detection limit. Here the possible penetration of sulfuric acid was checked. Briefly, sulfuric acid was flowing through the regenerant chamber and water flowed in the eluent channel at the flow rate of 4 μL/min. The conductivity of the effluent was monitored by a conductance detector. For 100 mM sulfuric acid, the penetration could be negligible and no observable change of background conductance was found. As for diluted sulfuric acid (commonly 20–50 mM is used), the penetration could be absolutely negligible. The results were consistent with our previous report, in which no measurable penetration was found for KOH eluent with concentration less than 200 mM [16]. Less penetration probably results from the significant thickness and the small size of CER beads.

3.2. Comparison of the suppressor operated in chemical and electrolytic mode

The bead-based electrolytic suppressor is first of all a chemical suppressor when sulfuric acid is used as regenerant; it is therefore possible to be operated in the chemical mode. The performance of the device operated in chemical and electrolytic mode was checked, respectively. The test conditions were as follows. KOH and H_2SO_4 were used to be eluent and regenerant, respectively, and the suppression effect under two modes were indicated by monitoring the effluent conductance from the suppressor with a CCD and a conductivity detector connected in serial. In contrast to the common membrane sheet-based suppressor which works well operated in the chemical mode, the bead-based suppressor behaved bad in the absence of the electrical field (chemical mode), as shown in Fig. 3. The suppressed background (~150 μS/cm) when operated in chemical mode was so high that it could not be suitable for effective suppression. This could probably be explained that the transport of permitted ions (H^+) to the eluent channel only by diffusion is insufficient far enough to suppress the eluent ions (OH^-). The significant thickness of the bead (relative to the thin membrane sheet) should be responsible for this. In contrast, when operated in electrolytic mode, the device showed good suppression effect (~3 μS/cm of background level) and a distinct background difference of the effluent from the suppressor operated in between chemical and electrolytic mode was observed. Obviously, the use of the electrical field improves the transport of the desired ions and plays a major role in the suppression process.

3.3. Performance evaluation

The residence volume of the suppressor was estimated to be ~600 nL by the equation of $F(t_1 - t_2)$, where F denotes the flow rate and t_1 and t_2 are the retention times of KCl plug for the device (including the connecting capillary) and the connecting capillary only.

For the initial design of the bead-based suppressor with open eluent channel, one drawback was its high noise level of suppressed background (~800 nS/cm). To reduce the noise level, we have tried to use a restrictor placed at the exit of the detector and tried the constant voltage mode to replace the constant current mode as well. But the problem was still on. This probably resulted from the poor hydrodynamic flow of the suppressor with the eluent channel open. Another drawback of the initial design was its high operational electrical resistance, which made the use of pure water as regenerant very difficult or impossible. The strategy of using a segment of CEM inserted in the eluent channel was found to be able to overcome the above problems to a great extent. The performance of the suppressor with CEM inserted was evaluated by suppressing KOH eluent prepared manually or online electrolytic generated.

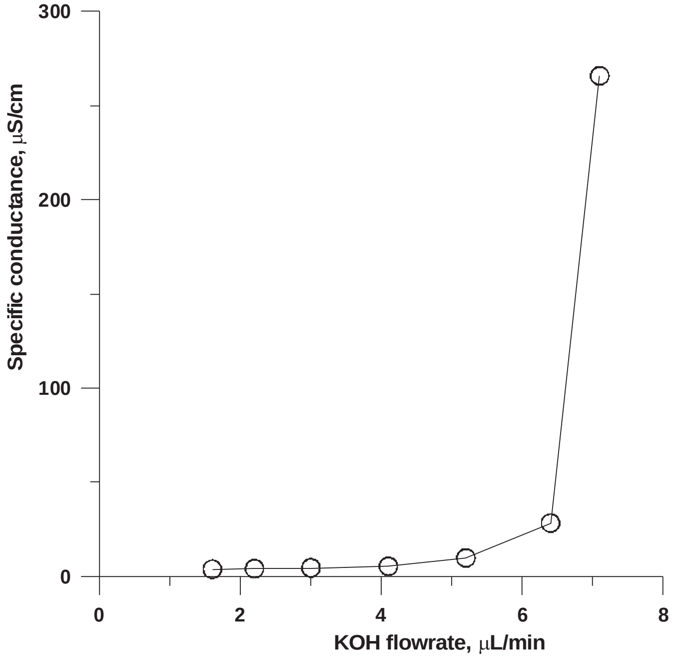

Fig. 4. . Dynamic capacity suppression curve of the bead-based suppressor. Conditions: KOH eluent, 10 mM; current, 100 µA.

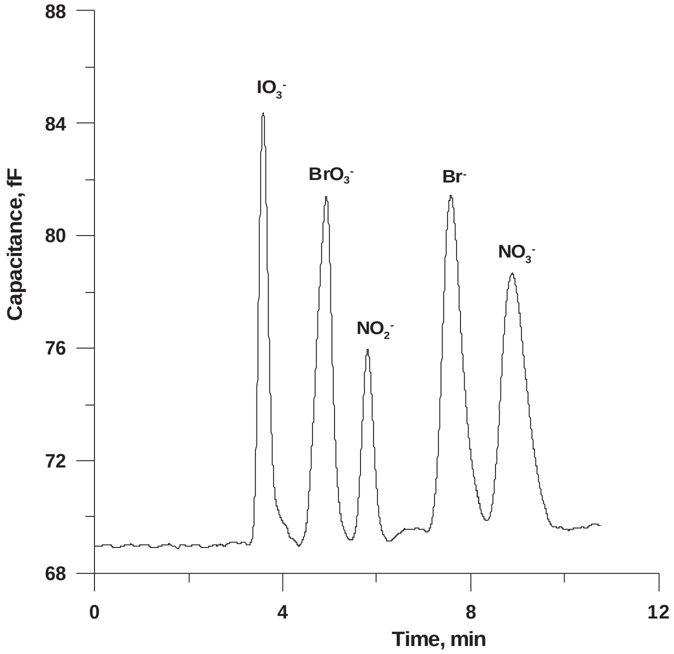

Fig. 5. . Chromatogram achieved by the bead-based suppressor. Conditions: eluent, KOH EDG, $I = 10$ µA; suppressor, $I = 60$ µA, regenerant, 25 mM H_2SO_4; sample, 0.25 mM IO_3^-, BrO_3^-, NO_2^-, Br^-, NO_3^-; flow rate, 3 µL/min.

For the manually prepared 10 mM KOH eluent at the flow rate of 3 µL/min, the original background conductivity of ~2203 µS/cm could be reduced to be ~4 µS/cm, which was comparable with that of Nafion fiber-based chemical suppressor [16]. While for the KOH eluent with similar concentration generated online by a KOH EDG, the suppressed background was ~3 µS/cm. When KOH eluent concentration was up to 15 mM, the suppressed background (~37 µS/cm) was too high to be effectively used for CIC, indicating limited suppression capacity of the device. In addition, the noise level of the suppressor was greatly improved (~100 nS/cm) compared with the one without CEM inserted. Another point should be mentioned that the backpressure produced by CEM inserted could be almost negligible. This is probably due to small length and high porosity of CEM. Actually, in our previous experience of making GMA-based cation monolithic column, the column prepared always showed very high permeability, e.g., the measured backpressure of a column (20 cm × 0.25 mm i.d.) was only ~152 psi.

The dynamic suppression capacity of the device was checked by plotting the suppressed conductance and the flow rate of KOH eluent at given concentration, as shown in Fig. 4. Less than 10 µS/cm of the background for KOH eluent with given concentration was achieved when the eluent flow rate was less than 5.2 µL/min, indicating good suppression effect. Further increasing the eluent flowrate, the suppressed background dramatically increased and reached at an unacceptable level. The dynamic suppression capacity of the device is about 52 neq/min, and the suitable flow rate for the tested KOH concentration should be less than 5 µL/min. The use of KOH eluent with lower concentration would increase the dynamic suppression capacity. The calculated current efficiency for 10 mM KOH eluent at 5.2 µL/min was about 83%. Optimization of CEM would probably further increase the current efficiency.

To demonstrate the utility of the suppressor, it was coupled with a home-built CIC system. A typical chromatogram was given in Fig. 5, which showed the separation of five inorganic anions using KOH eluent generated by a microscale KOH EDG. In this case, the suppressed background level was indicated by a CCD in place of conventional conductivity detector, aiming to reduce the extra column band broadening. The suppressed background capacitance was ~69 fF, in comparison, the capacitance of pure water on the CCD was ~65 fF, while the suppressed background by Nafion fiber-based chemical suppressor was ~110–120 fF in our previous report [16]. It should be noted that the performance of the separation monolithic anion column used was not satisfactory. We just demonstrated the application of the suppressor for CIC and no attempts were made to optimize the column. Using commercial available capillary columns with higher separation efficiency, it believed that good chromatograms could be achieved. The relative standard deviation (RSD) values of retention times and peak heights for the tested anions in four successive measurements were smaller than 1.5% and 0.8–2.2%, respectively.

In summary, a CER bead-based microscale electrolytic suppressor for CIC has been fabricated. Replacing CER beads with anion exchange resin beads, the suppressor described above would behave a microscale anion suppressor. The advantages of the device include low dead volume, ease to fabricate and high ability to bear backpressure. The last point would make the suppressor find a potential application in two-dimension IC system. The use of CEM inserted inside was found to greatly improve the performance of the device. By preparing the CEM in the manner of in situ polymerization inside of the suppressor or further optimizing the reaction recipe of the CEM, it is probably to further reduce the electrical resistance of the suppressor and simplify the fabrication procedure as well. In addition, we hope to further increase the suppression capacity of the suppressor by this strategy.

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