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Five-electrode direct current suppressor–detector combiner for ion chromatography: an integration of eluent suppression and resistance detection†

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An integration of eluent suppressor and resistance detector is proposed based upon the application of a common anode (or cathode), a common ion-exchange membrane, and two independent constant current sources.

Since its introduction in 1975 by Small *et al.*,[1] the suppressed conductivity detection has found immediate application in the chromatography of inorganic ions and become the most common detection mode in ion chromatography (IC), termed "suppressed ion chromatography" (SIC). In principle, SIC is based on the addition of a suppressor prior to the conductivity detector (CD) to simultaneously reduce the background conductivity of the eluent and to increase the conductivity detection signals attributable to the sample ions of interest. Although important developments have been made in IC detectors,[2–5] especially in suppressor technology,[6–9] the suppressor and detector are separate units in an SIC system, and accordingly the number of components in this system is increased over those non-suppressed IC systems.[10–13] This, in turn, increases the complexity of an SIC system and also introduces extra-column volume which may decrease the chromatographic resolution and sensitivity.[13] It would be advantageous to incorporate the suppressor and the detector into one unit. However, this involves a challenging combination of engineering issues. Firstly, alternating current (ac) excitation signal[2] is preferred for conductivity detection, meanwhile a direct constant current supply is the first choice for eluent suppression.[6,7,9,14,15] Secondly, a suppressor includes the ion-exchange media, such as ion-exchange membranes or resins or both, making the suppressor a complex device; and a CD is relatively simple in configuration. Thirdly, redox reactions, which should be totally prevented during detection, are of necessity in an electrolytic suppressor. One US patent has disclosed two devices in which the suppressor and detector are integrated.[16] Nevertheless, the first of which allows the electrolysis gases flowing through the sensor electrodes, interfering with the conductivity detection; in its other

device, it is difficult to obtain a stable detection signal although ion-exchange membranes are used to avoid the gas bubbles from entering the detection compartment. In our work, we propose a practical method for incorporating an electrolytic suppressor and a resistance detector into one unit, called "five-electrode direct current (dc) suppressor–detector combiner" (SDC), based upon the three-chamber cell design of a four-electrode micro-constant dc resistance detector,[17] which we have reported recently, and the configuration of an ion reflux-based, continuously regenerated packed-column suppressor.[7,18]

As shown in Fig. 1 (taking the anion analysis as an example), an anion SDC is supported by four quadrate rigid polymer shells, S1, S2, S3 and S4, which are assembled tightly by stainless steel screws (not shown). A thin Teflon film (0.2 mm in thickness) is placed between shells S3 and S4. This composition device consists of a suppression and a detection chamber, three electrolysis electrodes (one common
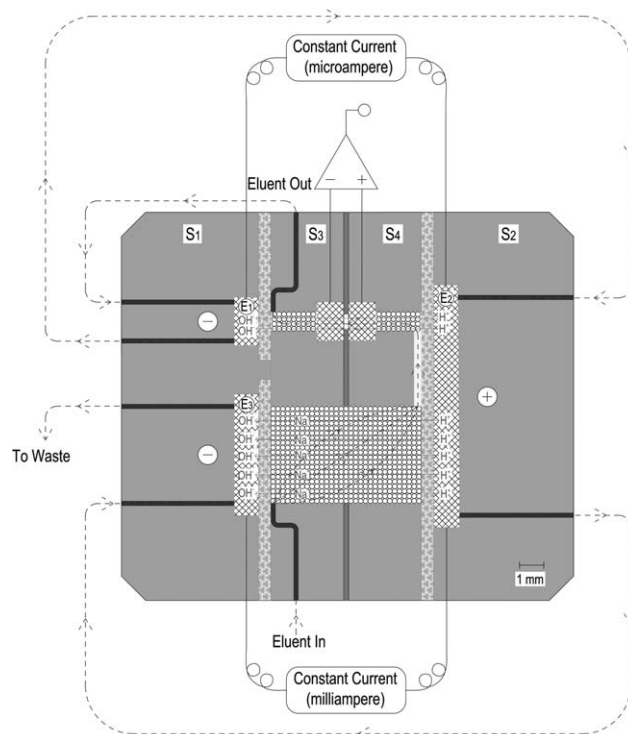

Fig. 1 Design details of an anion SDC.

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anode and the other two independent cathodes) and two sensor electrodes (with a round hole, 0.8 mm i.d. × 0.2 mm, through the Teflon film between them), and three cation-exchange membranes defining the suppression and detection chambers (which are in fluid communication *via* an inner connecting channel). One column of cation-exchange resins (6 mm i.d. × 6.2 mm) is filled in the suppression compartment, and another two columns of the same resins are positioned in the detection compartment. All five electrodes are porous. Two constant current sources are in electrical communication with the cathodes and the common anode, respectively. The sensor electrodes in the detection compartment are connected to a high input impedance ($\cong 10^{12}$ Ω) sampling circuit. Six fluid flow-through channels are set in the device for the flowing mobile phase.

By analogy, a cation SDC has the same configuration as depicted in Fig. 1, where all the membranes and resins are anion-exchangeable, and all the electrolysis electrodes are opposite charged.

In operation, the highly conducting eluent (in this case Na_2CO_3/$NaHCO_3$) along with the analyte ions separated by the analytical column is introduced into the left end of the suppression chamber, where the incoming sodium counter-ions are displaced with the electrically generated hydronium ions, leaving the eluent in its weakly conducting acid form and converting the analyte ions into their relatively more conductive H^+ form. The eluent suppression is performed based on the principle of "ion reflux", offering technical benefits of reasonably high dynamic suppression capacity, high back-pressure tolerance, and low baseline noise.[7] Exited from the right end of the suppression chamber, the suppressed eluent and analyte ions proceed to the detection chamber through the inner connecting channel. In the detection chamber, one H^+ channel, supported by a microampere constant current supply, is created, and the voltage drops between two sensor electrodes are collected by the high input impedance sampling circuit, producing a stable background baseline response of the flowing suppressed eluent. When the analyte ions accompanied with the suppressed eluent flow through the sensor electrodes, chromatographic peaks appear in the negative direction in accordance with the decrease of solution resistance attributable to the analyte ions, as shown in Fig. 2.

After detection, the cell effluent is directed back to the detection cathode (E_1), the common anode (E_2), and the suppression cathode (E_3) in sequence to supply water for electrolysis reactions. At E_1, the hydroxide ions from the water-splitting reaction are neutralized by hydronium ions of the H^+ channel under the influence of an electric field. A vast majority of the hydronium ions generated at the common anode migrate across the ion-exchange membrane and into the suppression compartment to displace the counter-cations, while the others are used for sustaining the H^+ channel in the detection chamber. The displaced counter-cations are driven through another ion-exchange membrane into E_3 to combine with the electrically generated hydroxide ions to form base. All the electrolysis gas by-products, H_2 from E_1 and E_3 and O_2 from E_2, and the base produced at E_3, are swept out of the device as waste by the recycled flowing detection effluent.

The SDC would be a more integrated device if the suppression and detection chambers were incorporated into one compartment in which only one constant current source could be applied. However, this is impractical. In SDC, the suppressed eluent arriving at the detection chamber will be pure water, which features a very high resistivity of 18.2 MΩ cm, when the eluent is methanesulfonic acid for cation analysis or sodium hydroxide for anion analysis. After suppression, the analyte ions are converted into their base (in the
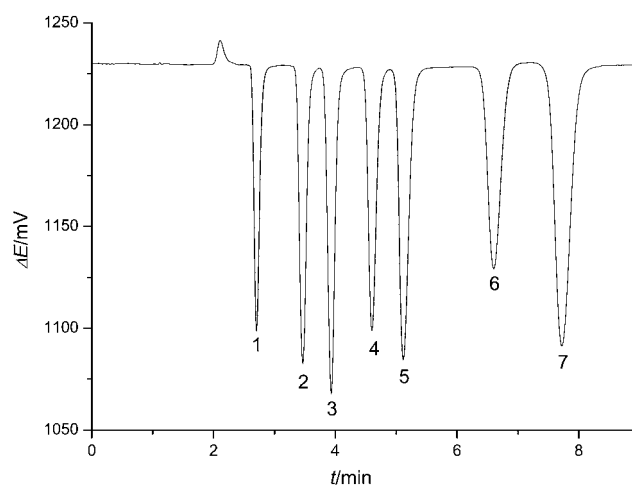

Fig. 2 Chromatogram of seven anion standards derived from an anion SDC. Column: AS14; eluent: 3.5 mM Na_2CO_3/1.0 mM $NaHCO_3$; suppression current: 40 mA; detection current: 2.0 µA; flow rate: 1.2 mL min⁻¹; injection volume: 25 µL; chromatographic peaks: (1) F^-, 5.0 mg L⁻¹; (2) Cl^-, 10.0 mg L⁻¹; (3) NO_2^-, 15.0 mg L⁻¹; (4) Br^-, 25.0 mg L⁻¹; (5) NO_3^-, 25.0 mg L⁻¹; (6) PO_4^{3-}, 40.0 mg L⁻¹; (7) SO_4^{2-}, 30.0 mg L⁻¹.

cation analysis case) or acid form (in the anion analysis case), resulting in an enhanced reduction in solution resistivity and thus producing negative chromatographic peaks. Therefore, similar to that described in those suppressed conductivity detection methods, the suppressed resistance detection mode performs better signal-to-noise ratio than those non-suppressed IC approaches. We should notice that the constant current supply must be kept at microampere level for the resistance detection due to the very high resistivity of the suppressed eluent, and the two sensor electrodes should be very close to each other (*e.g.*, 0.2 mm apart). Both experimental data and theoretical calculation show that 1.0 µA can generate a background response up to several volts in a resistance detector. In an electrolytic suppressor, it is well-known that the applied suppression current is usually tens or even hundreds of milliamperes in accordance with different eluent concentrations and flow rates in order to supply efficient dynamic suppression capacity.[6,7,14,19] If the detection chamber is incorporated into the suppression compartment, the constant current supply for eluent suppression is far too large for the signal measurement. One compromising solution is filling ion-exchange resins between two sensor electrodes, as disclosed in the US patent,[16] to reduce the background voltage response, but the analyte signal would be significantly reduced at the same time due to the filled ion-conductive resins, resulting in poor sensitivity. Thus, the suppression and detection chambers should be separate and accordingly two independent constant currents, one is at milliampere level and the other is of microampere magnitude, are required.

To integrate the four-electrode resistance detector and the ion reflux-based pack-column suppressor into one unit, we designed the SDC with a common anode and a common ion-exchange membrane as shown in Fig. 1. At the common anode, hydronium ions are generated, migrate across the common cation-exchange membrane under the influence of the electric field, and divide into two ion streams, the big one of which toward the suppression chamber is for eluent suppression, and the small one toward the detection chamber serves to signal measurement. The three ion-exchange membranes in the integrated device define the suppression and detection chambers,
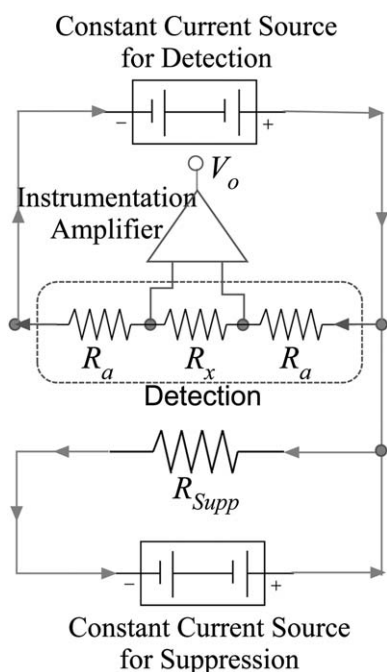
Fig. 3 Equivalent circuit of an anion SDC.

separating them from the electrolysis electrodes, thus preventing the electrolysis gas by-products from entering the suppression and detection chambers and ensuring a low noise level (see Fig. S1† in the ESI). In addition to their original functionality, the porous electrolysis electrodes provide micro-channels for the flowing solution and gas by-products. No external fluid flow paths are required in the electrolysis chambers. The detection effluent recycled to the porous electrolysis electrodes is the water source for electrolysis reactions, and thus the plumbing scheme in such an SIC system is simplified. The extra-column volume in this SIC system is minimized because the suppression and detection units are integrated into a single device, in which the inner channel connecting the suppression and detection chambers is very short and narrow. Fig. 3 shows the equivalent circuit of an anion SDC. Although two constant currents are applied to the common porous anode, theoretical analysis and experimental data demonstrate that the two current sources are independent, offering significant technical benefits in adjusting the suppression or detection current or both currents without interfering with each other.

In contrast to the conventional galvanic CDs,[2,4] we have developed a linear equation relating the reciprocal of voltage response of peak height ($1/\Delta E$) and the reciprocal of concentration of analyte ($1/C$) for the four-electrode dc resistance detection mode:[17]

$$-\frac{1}{\Delta E} = K\frac{1}{C} + b \qquad (1)$$

where K and b are constant. The equation also provides the quantitative basis for SDC. Experimental data show that the integrated device offers the benefits of efficient eluent suppression (Fig. S2† in the ESI), and very sensitive and accurate detection of analyte ions (Fig. S3† in the ESI). Average detection limits of common anions derived from an anion SDC are about a little lower in comparison with the conventional suppressed conductivity detection method in which an ASRS suppressor and traditional CD are used (Table S1 and Fig. S2 in the ESI†).

In summary, based on the application of the common anode, the common ion-exchange membrane, and the two independent constant current sources, we successfully fabricated the SDC, which provides both efficient eluent suppressions and sensitive resistance detections. The configuration of an SIC system using the integrated device is as simple as that of non-suppressed IC systems. In addition, this device may be applied in portable ion chromatograph and the integrated principle may find its further application in miniaturized IC systems, such as capillary and microchip-based IC systems.

Acknowledgements

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