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A four-electrode microconstant direct current resistance detector for ion chromatography applying ion-exchange membrane and porous electrode

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ABSTRACT

A four-electrode microconstant direct current resistance detector for ion chromatography not sensitive to the effects of electrode polarization, capacitance, and electrolysis by-products is proposed. A constant current of microampere magnitude is applied across the current electrodes of the four-electrode device, and the voltage responses between the detection probes are directly picked up by a high input impedance instrumentation amplifier. The ion-exchange membranes, which separate the detection chamber from the electrolysis chambers, enable the measurement of solution resistance free of the interference of electrolysis by-products. Two resin beds in the detection chamber serve as ion conductors while reduce the dead volume of the detector. Recycled detection effluent supplies water for the electrolysis reactions at the current electrodes to sustain constant current in solution. The porous detection probes provide microchannel for the flowing solution while indicating signals. Owing to the constant current excitation, the electronics setup becomes simple. The cell configuration, operating principle, electronics, and error analysis of this detection mode are discussed along with their use for suppressed anion chromatography. Experimental data show that this four-electrode direct current detection mode is comparable to conventional two-electrode alternating current method.

1. Introduction

Based on the unique effects of ionic solutes on the electrical conductivity of the eluent in ion chromatography (IC), which was introduced in 1975 [1], conductivity detectors have been widely employed in both suppressed and non-suppressed IC methods [2,3]. The IC detector, which continuously monitors the flux of the conductance of the flowing solution, requires a flow-through cell design that occupies a minimal cell volume. To provide accurate and wide-range measurements, the excitation signal, positioning, and alignment of the detection electrodes should be considered carefully.

Through decades of development, a variety of techniques has been applied to conductivity detectors, the most well-known of which is the bipolar pulse technique [4], where square-wave bipolar pulses are applied to a two-electrode conductivity cell. By selective periodic current sampling, the conductance is measured without significant capacitance effects. However, the applied frequency must be chosen carefully, and the electronics applied to such technique are relatively complex. Some detectors apply a sinusoidal wave potential to a two-electrode cell at potentials of up to 20 V, which may cause observable electrode polarization, although no electrolysis occurs [5]. In consideration of this, the four-electrode alternating current (ac) method is the best approach for measuring low resistances [2] since it separates the excitation electrodes from the detection probes, thus can avoid the effects of electrode polarization during detection [6].

Other efforts have been made in applying direct current (dc) for conductivity detection despite electrolysis reactions. For example, the design and utilization of a flow-through two-electrode detector with an applied dc potential has been reported [2]. In this design, two narrow gauge hypodermic needles were inserted inside teflon tubings to serve as detection probes. Although it is inexpensive, requires low cell volumes, and is sensitive to signals, this detector is not suitable for high background conductance IC systems. A Czech study has also reported dc conductometry using wire electrodes in a tubular cell [7]. The potential applied was up to 30 V, resulting in electrolysis reactions at the electrodes. To minimize the interference of the electrolysis by-products, a four-electrode dc conductivity detector with two pairs of electrodes, one pair of two outer excitation electrodes and the other pair of two inner detection probes, positioned in a tubular cell has been reported [8]. The solution is directed into the inlet between the detection probes for measurement and then vented out through the two open ends of the cell along with the electrolysis by-products generated at the outer excitation electrodes. However, two flow paths in the cell

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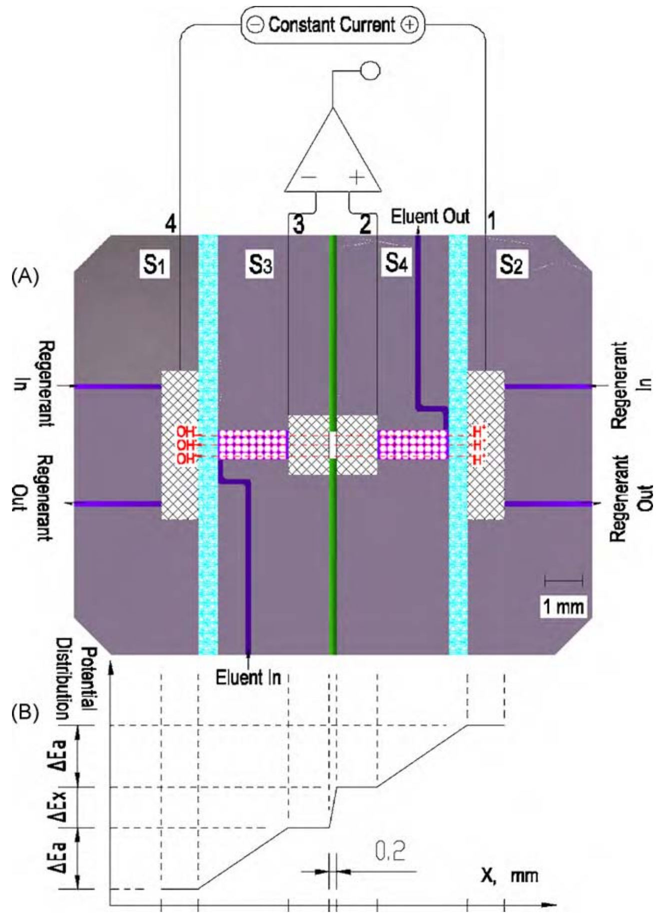

Fig. 1. Design details (A) and potential distributions (B) of the four-electrode dc device.

may result in unstable flow ratio and poor reproducibility.

In addition to the galvanic detection mode which applies an ac or dc potential in the above examples, another dc method using a constant current for the measurement of the conductance of electrolyte solutions was reported in 1976 [9]. Two pairs of electrodes, an outer set of current excitation electrodes and an inner set of potential probes, were fixed in-line. A constant current of microampere magnitude was applied across the current electrodes, and the potential drop in electrolyte solution between the detection probes was determined with a high-impedance device. Such method minimizes polarization of the detection probes, and therefore, more accurate measurements are obtained. However, this method is not suitable for monitoring the conductivity of a flowing system.

This paper reports the design and utilization of a flow-through four-electrode (all-porous) IC detector that applies a constant current of microampere magnitude. Through a combination of the application of a constant current and the ion-exchange membranes, detection probe polarizations are minimized, and interference from electrolysis gases is eliminated. In addition, the direct potential detection simplifies the sampling circuit.

2. Experimental

2.1. Detection cell

This experimental cell (Fig. 1A), taking the anion detector as an example in which the cation-exchange membranes (Shanghai Shanghua Water Treatment Material Co., Ltd., China) and resins (200–400 mesh, Nankai University, China) are used, consists of four quadrate polyvinyl chloride shells (S_1, S_2, S_3, and S_4) in a symmetrical structure divided by a Teflon film (between Shell S_3 and S_4, 0.2 mm thick, with a 0.8 i.d. hole right in the center) and two cation-exchange membranes (between Shells S_1 and S_3, S_2 and S_4, respectively). Three chambers, the anode chamber with an anode, the cathode chamber with a cathode, and the detection chamber with two detection probes, are separated from each other by two ion-exchange membranes. Four round porous titanium electrodes (all are 50 μm in porosity and 1.0 mm in thickness, Yonglian Rare Metal Co, Ltd., China) are platinized and fitted in specified positions of the four shells: two of them with 6.0 mm i.d. (one fixed in Shell S_1 as the cathode and the other in Shell S_2 as the anode) are used as current electrodes to which a microconstant current is applied, while the other two with 1.6 mm i.d. (embedded in Shell S_3 and S_4, respectively; 0.2 mm apart) as the potential probes in the detection chamber. In addition, two columns (0.8 mm i.d., 2.0 mm in length; in-line with the potential probes) of cation-exchange resins are filled in the detection chamber, serving as the ion conductors. To provide the flow-through channels, all three chambers contain both inlet and outlet, respectively. By replacing the cation-exchange membranes and resins with anion ones, the cation four-electrode dc device was fabricated. Its other structures are the same as the anion detector.

2.2. Operating principle

As shown in Fig. 1A, the suppressed electrolyte solution firstly proceeds to the detection chamber for voltage measurement, and then the detection effluent is recycled to the electrolysis chambers for the water-splitting reactions like suppressors [10,11]. Right after voltage measurement, the detection effluent is directed toward the anode and the cathode chamber in sequence. The waste liquid, along with electrolysis gases, vented out from the cathode chamber is recycled to the electrolysis chambers of suppressor for the same purpose.

A constant current of microampere magnitude is applied across the cell's current electrodes, and the voltage responses over the solution between the potential probes are directly output to a high input impedance sampling circuit. Because of the constant current applied, two electrolysis reactions take place at the surfaces of the current electrodes:

At the anode:

$$H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e \qquad (1)$$

At the cathode:

$$H_2O + 2e \rightarrow 2OH^- + H_2 \qquad (2)$$

Under the influence of the electric field, the hydronium ions generated at the anode migrate across the cation-exchange membrane next to the anode and into the detection chamber, while the equivalent amount of H^+ in the detection chamber are driven across the other membrane and into the cathode chamber to neutralize hydroxide ions generated at the cathode, thus forming a H^+ channel to sustain the constant current in the detection cell.

2.3. Apparatus and reagents

A Dionex ICS-1500 ion chromatograph (Sunnyvale, CA, USA) with an injection volume of 25 μL and a flow rate of 1.2 mL min^{-1} was used in all IC experiments. The four-electrode dc detector was serially connected after a Dionex DS6 Heated Conductivity Cell with a narrow bore tube. The voltage output of the dc device was picked up by a homemade sampling circuit. A separation column, AS14 (4 mm i.d., Dionex Corp., USA), and a suppressor, ASRS (Dionex Corp., USA), were utilized. The eluent for anion sep-

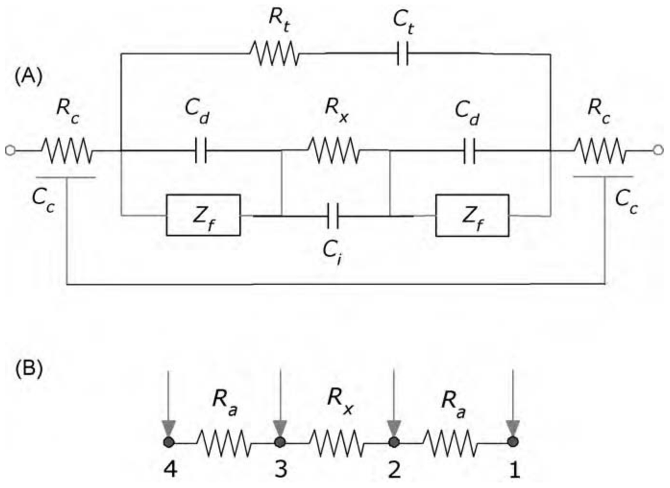

Fig. 2. Equivalent circuits of the conventional two-electrode ac conductivity cell (A) and the four-electrode dc device (B). C_c: contact and lead capacitance; C_d: double-layer capacitance; C_i: inter-electrode capacitance; Z_F: Faradaic impedance; R_c: contact and lead resistance; R_x: solution resistance to be measured; R_a: the resistance between the current electrode and potential probe.

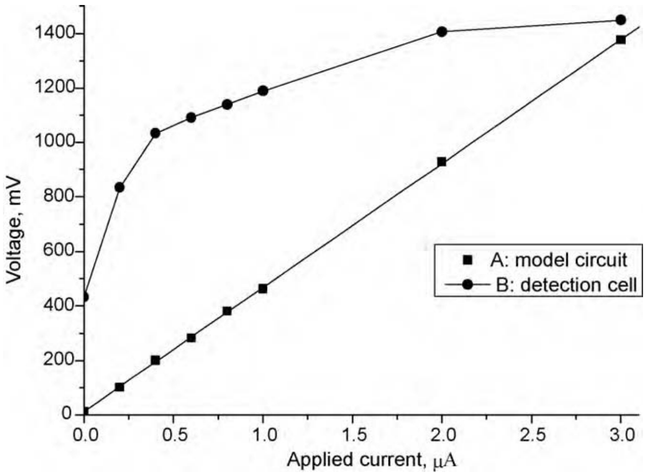

Fig. 3. Voltage–current curve of R_x in both the model resistors and the detection cell.

aration was a mixture of 3.5 mM Na_2CO_3 and 1.0 mM $NaHCO_3$. Calibration standards of 7 anions (F^-: 5.0 mg L^{-1}; Cl^-: 10.0 mg L^{-1}; $NO_2{}^-$: 15.0 mg L^{-1}; Br^-: 25.0 mg L^{-1}; $NO_3{}^-$: 25.0 mg L^{-1}; $PO_4{}^{3-}$: 40.0 mg L^{-1}; $SO_4{}^{2-}$: 30.0 mg L^{-1}) were prepared from their corresponding potassium or sodium salts, and diluted 4-, 10-, 40-, and 100-fold, respectively, for plotting the calibration curve. All chemicals were of analytical reagent grade and the water used was distilled and deionized to a specific resistivity of 18.2 MΩ cm.

3. Results and discussion

3.1. Four-electrode dc resistance detection mode

3.1.1. Avoidance of effects of electrode polarization and double-layer capacitance

ac methods are most widely used in commercial IC conductivity detectors in order to avoid the effects of electrode polarization and double-layer capacitance on measurement. However, they are difficult to be completely overcome as the equivalent circuits of these ac devices consist of a complex network of capacitances and resistances (Fig. 2A) [4]. In addition, the error analysis is often complicated, and the frequency applied must be chosen carefully to obtain a reliable measurement.

Dc method can eliminate capacitance effects because of their infinite equivalent resistances ($R_c = 1/2\pi fC$, $f \to 0$) in dc circuits. A two-electrode detector with dc potential excitation has been reported [2], but it is impossible to completely avoid the effect of electrode polarization on detection. In this paper, it is overcome by a four-electrode cell design with a constant current excitation, in which the detection probes are separated from the excitation electrodes, leaving the electrode polarization only occurs at the current electrodes. Moreover, the polarization of the detection probes is minimized while indicating potential signals due to the high input impedance of the sampling circuit, which results in an extremely small current flowing through the detection probes.

Because of dc excitation, a simple equivalent circuit of this device (Fig. 2B) is obtained: three resistances connected in series, free of any capacitance components, resulting in a simple error analysis (which will be discussed later). R_x represents the solution resistance to be measured between the potential probes, and R_a the resistance between the current electrode and potential probe, consisting of the contact and lead resistance, the Faradaic impedance and the resistance of ion-exchange membranes and resins. A complete equivalent circuit in this detection mode and a simplification process of the circuit are shown in Supporting Information.

In order to confirm the dc methods' independence of the influence of capacitance components, a model circuit, three 900 KΩ resistors connected in series, was tested firstly. The voltage–current relationship of R_x (Fig. 3A) shows a good linearity ($r^2 = 0.999$) with a slope of 455.3 KΩ, nearly half of the model resistor, proving the precision of the applied constant current (IA was operated at a gain of 0.5). And then each model resistor was paralleled to a capacitor of microfarad magnitude. No significant differences were observed, indicating that the dc detection mode is independent of the capacitance components.

For the resistance detector connected to an IC system, the background voltage response is a function of the applied current (Fig. 3B), comprising three zones: the linear zone at current 0.4–2.0 μA, the saturation zone at current above 2.0 μA, and the non-linear zone at current below 0.4 μA. The saturation of signal is due to the limited voltage supply of the constant current source, usually not excess 10 V. The non-linear response at very low current maybe results from the weakly founded electric field in the detection chamber. At current below 0.4 μA, the H^+ channel supported by the weak electric field may be disturbed by the flowing through fluid. At current above 0.4 μA, the electric field would become strong enough to eliminate the influence of the disturbance from the flowing liquid. Interestingly, about 400 mV baseline response has been observed at zero applied current, which may derive from the surface asymmetry of the porous detection electrodes. According to Fig. 3B, a working current sufficient enough, such as 1.0–2.0 μA, is preferable.

3.1.2. The constant current excitation and direct potential sampling

A conventional ac/dc conductivity detector uses the voltage excitation and current sampling, often requiring a sampling resistor, current-to-voltage converter, and a signal amplification circuitry. In the four-electrode experimental cell, to which a constant current is applied, the voltage responses in the electrolyte solution between the potential probes are directly output to a high input impedance instrumentation amplifier (IA), and therefore a sampling resistor is unnecessary. The electronic setup for this detection mode is simple (Fig. 4): the constant current applied is controlled via a combination of a 16-digit digital-to-analog converter (DAC) and an operational amplifier. The voltage responses over R_x directly picked up by IA are transformed into digital signals

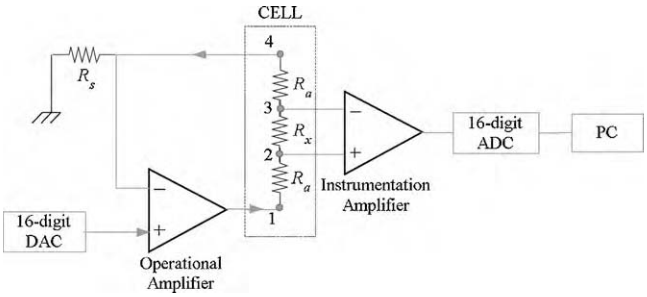

Fig. 4. Block diagram of the electronic setup for the four-electrode dc device.

by a 16-digit analog-to-digital converter (ADC) before being sent to computer (PC).

When a constant current of microampere magnitude is applied to the experimental cell, significant background voltage responses up to several volts can be obtained due to the great increase of the resistivity of the eluent after suppression. At the same time, Analytes accompanied with the eluent lead to a decrease of the total solution resistance, results in negative peaks in this detection mode, as shown in Fig. 5. Therefore, the microconstant current excitation detector features a sensitive measurement where signal amplification is unnecessary. For example, an electrolyte solution with a conductance of 1.0 μS can generate a voltage signal as high as 1.0 V with the application of a constant current of 1.0 μA. Nevertheless, in traditional galvanic detectors, the same solution can only yield a small signal of 5.0 mV under a condition of 0.5 V excitation signal and 5.0 KΩ sampling resistor, thus resulting in a requirement of signal amplification (if a sampling resistor of high value were used here to obtain a higher detection signal, the noise would be simultaneously amplified).

3.1.3. *Resistance detection for IC*

In contrast to most of the conventional galvanic conductivity detectors in which voltage excitation sources are applied, this paper presents a four-electrode dc device featuring a constant current excitation and direct potential sampling circuit. According to Ohm's Law, the resistance of the measured solution is directly proportional to the voltage response under a microconstant current applied. And therefore, the dc device is named four-electrode microconstant direct current resistance detector.

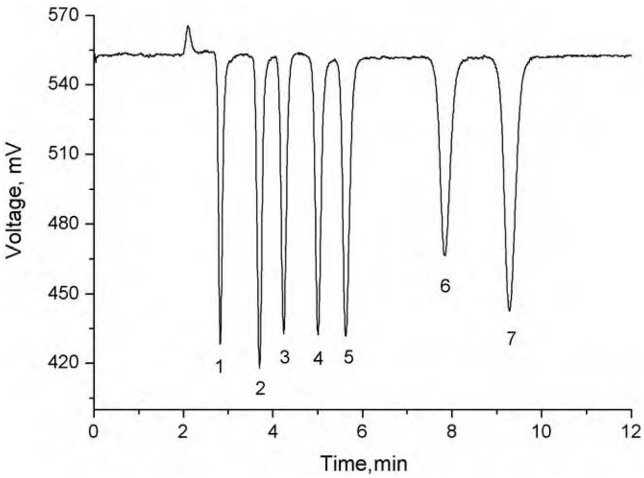

Fig. 5. Chromatogram of seven anion standards derived from the four-electrode dc device. Column: AS14; suppressor: ASRS; eluent: 3.5 mM Na_2CO_3/1.0 mM $NaHCO_3$; suppressing current: 50 mA; flow rate: 1.2 mL $min^{-1;}$ injection volume: 25 μL; chromatographic peaks: 1. F^-, 5.0 mg L^{-1}; 2. Cl^-, 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}.

Theoretical calculation demonstrates a linear relationship between the reciprocal of the analyte's peak height ($1/\Delta E$) in V^{-1} and that of the analyte's concentration ($1/C_S$) in L mol^{-1} given by:

$$-\frac{1}{\Delta E} = m\frac{1}{C_S} + n \tag{3}$$

where

$$m = \frac{10^3(\lambda_{E^+} + \lambda_{E^-})^2 C^2 \alpha^2}{KI[(\lambda_{E^+} + \lambda_{S^-}) - (\lambda_{E^+} + \lambda_{E^-})\alpha_E]\alpha_S} \tag{4}$$

$$n = \frac{10^3[\lambda_{E^+}(1-\alpha_E) + (\lambda_{S^-} - \lambda_{E^-}\alpha_E)](\lambda_{E^+} + \lambda_{E^-})C_E\alpha_E}{KI[(\lambda_{E^+} + \lambda_{S^-}) - (\lambda_{E^+} + \lambda_{E^-})\alpha_E]} \tag{5}$$

When $\alpha_E = \alpha_S = 1$, Eq. (3) is simplified as follows:

$$-\frac{1}{\Delta E} = m'\frac{1}{C_S} + n' \tag{6}$$

where

$$m' = \frac{10^3(\lambda_{E^+} + \lambda_{E^-})^2 C_E{}^2}{KI(\lambda_{S^-} - \lambda_{E^-})} \tag{7}$$

$$n' = \frac{10^3(\lambda_{E^+} + \lambda_{E^-})C_E}{KI} \tag{8}$$

λ_{E^+}, λ_{E^-}, and λ_{S^-} are the limiting equivalent conductances of the eluent cations, anions, and the sample anions in S cm^2 mol^{-1}, respectively. C_E is the concentrations of the eluent in mol L^{-1}. α_E and α_S are the dissociation degrees of the eluent and samples, respectively. K is the cell constant in cm^{-1}, and I the applied current in μA. The minus sign in Eq. (3) means the negative sample peaks will be obtained during elution when $\lambda_{S^-} > \lambda_{E^-}$, which occurs in most IC analyses. The detailed derivations are described in Supporting Information.

3.2. *Functions of ion-exchange membranes and resins*

3.2.1. *Avoidance of interference of electrolysis by-products*

Aside from the effect of electrode polarization on detection which has been avoided by the four-electrode cell design, the interference of the electrolysis by-products on detection is another main problem in dc methods. Although many efforts have been made, the dc methods reported do not provide excellent solutions to this problem [2,8]. The ion-exchange membranes are widely used in suppressors due to their selective ion conductive and gas impermeable property [10]. By reference to their functions, the ion-exchange membranes are used in the resistance detector, separating the detection chamber from the electrolysis chambers, thus keeping the gas by-products away from the detection chamber. In this way, the interference of the gas by-products is thoroughly prevented in the detection.

3.2.2. *Current transfer by ions and reduction of dead volume*

Serving as ion conductor media [12], the resin beds, as well as the ion-exchange membranes, are used to sustain the constant current passing through the detection cell. Although they are ion conductive, the ion-exchange membranes and resins behave the nature of resistances. Experimental data show that the resistance between the detection probe and current electrode is up to 10^6 Ω. However, theoretical calculation indicates that without these ion conductors, the voltage supply for the detection cell will be about 5-fold higher at the same constant current applied.

In order to obtain a relatively low dead volume, the detection chamber should be in minimal scale. Owing to the requirement of the inlet and outlet for the flowing solution, the thinnest thicknesses of Shell S_3 and S_4 are 3 mm in our cell design. In addition to their original functionalities, the resins are filled in the detection chamber to reduce the dead volume otherwise the resistance detector would occupy too large cell volume to be a sensitive IC detector.

3.3. Porous detection probes

Several types of sensor electrodes have been used for IC detectors, including planar [4], needle [2], and wire electrodes [7]. Porous electrodes, ever used as the current electrodes in IC [12,13], were employed as the detection probes in the resistance detector for three reasons:

(i) To monitor the potential drop in electrolyte solution between them.
(ii) To provide microchannels for the flowing solution.
(iii) To keep the resins away from the measured solution.

The resistance detector was serially connected after a Dionex DS6 Heated Conductivity Cell for calculating the cell constant of the homemade device. An apparent value of 8.0 cm^{-1} was obtained. The porous detection probes can be equivalent to two planar probes (0.2 mm apart, with a surface in 0.56 mm i.d.). The appropriate potential distribution in the resistance cell is plotted in Fig. 1B. All the four porous electrodes are equivalent to equipotential bodies. An assumption that the ion-exchange membranes and resins own equal resistivity has been made. In consideration of the low dead volume of the detection cell, the porous potential probes should be as thin as possible.

3.4. Theoretical error analysis

3.4.1. Errors arising from electronics

Errors in conventional ac conductivity measurement mainly derive from the capacitance components, resulting in a relatively complicated error analysis. In the resistance detector, which is independent of capacitance components, the error analysis becomes simple. Two main sources are included: the potential sampling and current excitation. In Fig. 4, the current flowing through R_x is shunted by IA, which will decrease the current passing through R_x, resulting in a negative deviation in the measurement of the potential drop over R_x. However, due to the high input impedance ($\cong 10^{12}\ \Omega$) of IA, the current shunting from R_x is so small that it has a negligible influence on the potential sampling. Under a condition of an R_x of $10^6\ \Omega$ and an applied current of 1.0 μA, the error of voltage measurement would be -10^{-4}%, small enough to be omitted. As for the error arising from the constant current applied, the current source can provide a constant current at nanoampere level through the combination of a 15 V power supply, 16-digit DAC, and a high accurate R_s (sampling resistor) of 499 kΩ. Therefore, the constant current applied is precise enough for the requirement of a value of microampere magnitude. In fact, the stability of the current applied is more important than the precision of the current. A reliable stability was observed when the constant current was applied to a model resistor.

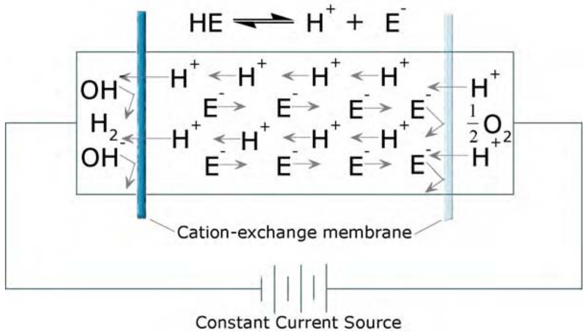

Fig. 6. Ion conduction in an electrolyte solution separated by two cation-exchange membranes under constant current supply.

3.4.2. Errors arising from electrolysis reactions

When an excitation signal is applied to electrodes immersed in an electrolyte solution, phenomena occurring at the electrode–electrolyte interface, such as the Faradaic impedance and double-layer capacitance, must be considered while the extracting the solution's resistance (or conductance) [14]. For the given four-electrode cell design of the resistance detector, the effect of the Faradaic process (which only occurs in the electrolysis chambers) are avoided during measurement because of the three-chamber structure defined by ion-exchange membranes; and the influences of the double-layer capacitance are eliminated owing to the dc detection mode.

But one basic phenomenon, the solute's dissociation equilibrium in the measured solution, should be noticed in the dc resistance detection. A model of the dc cell configuration that occupies two cation-exchange membranes is shown in Fig. 6. The hydronium ions, generated at the anode, migrate across one membrane into the bulk solution (the zone between the ion-exchange membranes); simultaneously the same amount of H^+ in the bulk solution migrates across another membrane, and arrives in the cathode zone, where the neutralization reaction occurs. Because of the ion-exchange membranes, the anions, OH^- and E^-, and the gases, H_2 and O_2, are kept in the electrolytic zones. To sustain the current carried by H^+ channel, the concentration of free H^+ (C_{H^+}) in bulk solution should be higher (or equal at least) than that of H^+ generated at the anode zone. Otherwise, the dissociation degree of HE, α_E, must be increased to supply enough free H^+ in the bulk solution. If that happens, the resistance of the bulk solution will be decreased, resulting in a negative deviation in measuring the resistance of the bulk solution.

According to Eqs. (1)–(3), a linear relationship between $1/\Delta E$ and $1/\Delta C$ requires every term in Eqs. (2) and (3) to remain at constant. Except for α_E and α_S, the other terms are constant. In an IC system of anion analysis, samples are often strong anions, which means $\alpha_S = 1$. Table 1 shows that the concentrations of hydronium ions in different suppressed eluents and the effects of samples on them. For a NaOH eluent, C_{H^+} in the bulk solution is lower than that in the anode zone, which will result in a variable α_E when a chromatographic peak of NaCl sample emerges upon the back-

Table 1
C_{H^+} in different zones of the resistance detector dissociated from different suppressed eluents and mixtures of eluent and NaCl sample.

Before suppression	After suppression	C_{H^+} from electrolysis of water in anode zone (mol L^{-1})	C_{H^+} in detection zone	
			From suppressed eluent	From sample
NaOH	H_2O	1.2×10^{-6}	1.0×10^{-7}	–
NaOH, NaCl	H_2O, HCl	1.2×10^{-6}	1.0×10^{-9}	1.0×10^{-5}
$Na_2CO_3/NaHCO_3$	H_2CO_3	1.2×10^{-6}	5.0×10^{-5}	–
$Na_2CO_3/NaHCO_3$, NaCl	H_2CO_3, HCl	1.2×10^{-6}	$\sim 5.0 \times 10^{-5}$	1.0×10^{-5}

Flow rate: 1.0 mL min^{-1}; constant current applied: 2.0 μA; C_{HCl}: 1.0×10^{-5} mol L^{-1}; $C_{H_2CO_3}$: 5.0×10^{-3} mol L^{-1}.

Table 2
Comparisons of performance between the four-electrode dc resistance detection and conventional two-electrode ac conductivity measurement.

			F^-	Cl^-	$NO_2{}^-$	Br^-	$NO_3{}^-$	$PO_4{}^{3-}$	$SO_4{}^{2-}$
ac	Calibration equation: $\Delta G = KC + b$	K	1.951	1.348	0.778	0.529	0.638	0.251	0.546
		b	−0.125	−0.085	−0.120	−0.171	−0.216	−0.156	−0.215
		r^2	0.999	0.999	0.999	0.999	0.998	0.998	0.999
	Reproducibility R.S.D. [%]	Within-day ($n = 11$)	0.22	0.29	0.27	0.20	0.20	0.28	0.12
		Between-day ($n = 6$)	5.23	6.42	5.63	3.52	2.73	1.67	1.78
	Detection limits (mg L^{-1}); S/N = 3		0.013	0.016	0.037	0.040	0.097	0.101	0.048
dc	Calibration equation: $1/\Delta E = K/C + b$	K	0.042	0.040	0.106	0.125	0.111	0.435	0.109
		b	0.006	0	−0.004	0.001	−0.003	−0.030	0.002
		r^2	0.999	0.996	0.999	0.999	0.998	0.992	0.999
	Reproducibility R.S.D. [%]	Within-day ($n = 11$)	1.40	1.12	1.04	1.01	0.90	0.82	0.75
		Between-day ($n = 6$)	5.20	5.19	4.85	2.83	2.27	2.19	1.23
	Detection limits (mg L^{-1}); S/N = 3		0.020	0.017	0.044	0.050	0.086	0.158	0.058
dc	Calibration equation: $\Delta E = KC + b$	K	21.66	15.06	8.863	5.997	6.735	3.152	5.896
		b	0.027	5.225	1.550	3.957	5.598	0.875	6.477
		r^2	0.999	0.994	0.998	0.995	0.992	0.998	0.991

Column: AS14; suppressor: ASRS; eluent: 3.5 mM Na_2CO_3/1.0 mM $NaHCO_3$; suppressing current: 50 mA; flow rate: 1.2 mL min^{-1}; injection volume: 25 μL.

Table 3
Determinations of seven anions in tap water with the application of calibration equations in different detection modes.

Detection mode	Calibration equation	Concentrations of anions in tap water (mg L^{-1})						
		F^-	Cl^-	$NO_2{}^-$	Br^-	$NO_3{}^-$	$PO_4{}^{3-}$	$SO_4{}^{2-}$
ac	$\Delta G = KC + b$	0.12	1.8	–	–	2.0	–	4.0
dc	$1/\Delta E = K/C + b$	0.23	1.8	–	–	2.2	–	4.3
dc	$\Delta E = KC + b$	0.26	2.3	–	–	2.4	–	5.1

ground eluent. Inverse situation happens when $Na_2CO_3/NaHCO_3$ eluent is used. A solution for the resistance detector to be used in an IC system with a NaOH eluent is to reduce the applied current to a low level that the concentration of H^+ from electrolysis reactions in the anode zone is obviously lower than that from the dissociation equilibrium in the bulk solution. To obtain a satisfactory linear equation for the resistance detector, the constant current applied should be chosen carefully according to different chromatographic conditions. Detailed discussions about the current range at different background eluents for both anion and cation analysis will be revealed in subsequent papers.

3.5. *Performance as an IC detector*

A series experiments has been performed to evaluate the resistance detector through comparison with the Dionex DS6 Heated Conductivity Cell. Data were recorded from both detectors using the same samples. Table 2 shows the linearity, reproducibility (within-day and between-day), and detection limits of seven common anions for both detection modes. Except for with-day reproducibility, the resistance detector is comparable to the ac method.

For the resistance detector depicted in Fig. 1A, the calculated void space between the potential probes was about 100 nL (0.8 mm i.d. × 0.2 mm thick). The porosity of the detection electrodes and the interstices among the filled resins must be considered when dealing with the dead volume of the detector, which is believed to be about 1 μL.

Eq. (3) indicates that the linear relationship between the peak response and concentration of analyte in the dc detection mode is not as simple as in the ac mode. Table 2 also shows the linearity data (collected from the dc detection mode) reprocessed according to $\Delta E = KC + b$. Bigger intercepts and more poor correlation coefficients were obtained when compared with the data processed by Eq. (3). We applied both detection modes to determine the concentrations of seven anions in a tap water sample, with data shown in Table 3. The concentrations of four anions (F^-, Cl^-, $NO_3{}^-$, and $SO_4{}^{2-}$) determined by the dc mode, with data processed by Eq. (3), are much closer to the results from the ac detection mode, thus supporting the linear response equation.

For a given cell design and flow rate, the observed noise levels are related to the applied current but do not increase linearly with the increase of current due to the signal process (low-pass filter and data smoothing). The noise was about 0.12 mV when the applied current varied from 0.4 to 1.0 μA, and 0.17 mV when the current was increased to 2.0 μA. As compared to a background response of more than 500 mV, the noise detected was rather small. This DC detection shows a baseline deflection of ~0.5 mV min^{-1} without temperature compensation.

4. Conclusions

This work has demonstrated the feasibility of the four-electrode device as an alternative suppressed IC detector, providing an accurate measurement of solution resistance independent of electrode polarization, double-layer capacitances, and electrolysis by-products because of the three-chamber cell design. The micro-constant current excitation and the direct voltage sampling mode simplify the electronics setup for the IC detector. The success of this detection mode is based on the application of the ion-exchange membranes, resins, and the porous detection probes.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2010.07.003.

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