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Application of a low impedance contactless conductometric detector for the determination of inorganic cations in capillary monolithic column chromatography

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ABSTRACT

Poly(glycidyl methacrylate) cation exchange monolithic column was prepared in fused-silica capillaries of 320 μm i.d. by thermally initiated radical polymerization and utilized in capillary ion chromatography. With 15 mM methanesulfonic acid as the mobile phase, the separations of a mixture of inorganic cations (Li^+, Na^+, $NH_4{}^+$, K^+) was tested by using a capacitively coupled contactless conductivity detector (C^4D) and a low impedance C^4D (LIC^4D). The LIC^4D is the series combination of a C^4D and a quartz crystal resonator. At the resonant frequency of the series combination, the capacitor impedance from capillary wall was offset by the inductance impedance from the quartz crystal resonator. A minimum impedance was obtained in the impedance–frequency curve of the combination. The responses of the C^4D and LIC^4D were analyzed based on an equivalent circuit model. It was shown that the sensitivity of the C^4D to the change in analyte concentration is rather poor due to the high ratio of the impedance from the capillary wall capacitor to the solution impedance. The LIC^4D has the similar sensitivity as a contact conductivity detector but a much smaller cell volume. The on-column detection model was realized by LiC^4D without preparation of optical detection window in monolithic column.

1. Introduction

In the field of ion chromatography (IC), there are many important environmental and industrial applications that require the separation and detection of a small number of ions [1–3]. The conventional columns employed in IC for the analyte separation are particle-packed, which have disadvantages, such as high flow resistance, high back-pressure and particle splitting at elevated flow rates. The introduction of monolithic chromatographic stationary phases in the 1990s marked a major advance in column technology [4,5]. The monolithic columns need no frits because the monolith is permanently fixed in the separation capillary by covalent bonding to the capillary inner surface. The monolithic columns offer the advantages including easy control of permeability and surface charge and the greater phase ratios than open tubular columns. Monolithic columns are prepared from organic and silica monomers. The polymer-based monolithic columns are prepared by *in situ* polymerization of a monomer mixture with a porogenic solvent in fused silica capillaries with inner diameters 0.1–0.4 mm. Advances in monolithic column technology and their applications have been reviewed in some recent articles [6–9].

At present, the development of sensitive detection techniques is one of the important research fields on monolithic column chromatography. On-column optical detection models, such as UV absorption detection, are the most commonly used owing to their broad applicability and relatively low cost. But the preparation of detection window on capillary monolithic column is technically difficult due to the frailness of optical window [10]. Other detection systems, such as fluorescence [11,12], mass spectrometry [13–15], chemiluminescence [16–20], amperometry [21], and evaporative light scattering [22], are applied for monolithic column detection.

Conductivity detection is a simple and universal detection technique in IC for inorganic and organic ions, which are often not readily detected by other techniques. The metal electrodes can be in direct contact with liquid (galvanic detection), or separated from liquid with an insulating film (contactless detection) in conductivity detectors. Capacitively coupled contactless conductivity detection (C^4D) has been gaining popularity in recent years [23,24] as it allows the determination of any charged species. Applications of C^4D in monolithic column detection in general have been very limited to date. Previously, applications of C^4D in high-performance liquid chromatography [25] and capillary electrochromatography

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[26] with monolithic column were reported. To our knowledge, the application of C^4D to IC employing a monolithic stationary phase has not yet been reported. In this work, poly(glycidyl methacrylate) cation exchange monolithic column was prepared in capillary of 320 μm i.d for IC. With 15 mM methanesulfonic acid (MSA) used as the mobile phase, the mixture of inorganic monovalent cations (Li^+, Na^+, $NH_4{}^+$, K^+) was well separated. Because such chromatographic conditions were not compatible with the conductivity detection in the C^4D, the sensitivity of the C^4D was rather poor. To enhance the sensitivity of the C^4D, three approaches, including increasing operation frequency, increasing electrode gap distance and decreasing wall capacitor impedance, were investigated. Recently, our group proposed the concept of a low impedance C^4D (LIC^4D) [27], which is the series combination of a piezoelectric quartz crystal (PQC) resonator and the C^4D. The responses of the C^4D and LIC^4D were compared analyzed based on their equivalent circuit models. At the resonant frequency of the series combination, the impedance from the capacitance of C^4D was completely offset by the impedance from the equivalent inductance of the PQC. Thus, a minimum impedance was obtained in the impedance–frequency curve of the series combination. The minimum impedance is close to the solution resistance in detection cell. Hence, the LIC^4D has the similar sensitivity as the contact conductivity detector but a much smaller cell volume. The on-column conductivity detection model in capillary monolithic column was realized easily by an LiC^4D. The determination of inorganic cations (Na^+, $NH_4{}^+$, K^+) in water samples demonstrates clearly the benefits of the use of an LIC^4D in IC with capillary monolithic column.

2. Experiment

2.1. Materials

Fused silica capillary with 320 μm I.D. and 560 μm O.D. was purchased from Yongnian Optical Fiber Factory (Hebei, China). All the reagents were of analytical grade or better. Glycidyl methacrylate (GMA), γ-methacryloxypropyltrimethoxysilane (γ-MAPS) and ethylene dimethacrylate (EDMA) were obtained from Sigma (St. Louis, MO). Before use, GMA was distilled under a vacuum and EDMA was extracted with 5% aqueous sodium hydroxide solution and dried over anhydrous magnesium sulfate. Azobisisobutyronitrile (AIBN) was obtained from Shanghai Fourth Reagent Plant (Shanghai, China) and was recrystallized in methanol prior to use.

The mobile phase was prepared by dissolving methanesulfonic acid (MSA) in Millipore water. Stock solutions of the target cations (Li^+, Na^+, $NH_4{}^+$, K^+) were prepared by dissolving the corresponding chloride salts in Millipore water. All solutions were degassed by ultrasonication and filtered through 0.2 μm nylon syringe filters prior to use. Real water samples were collected from Daming Lake and Xiaoqing River in Jinan City and filtered through 0.2 μm nylon syringe filters prior to analysis.

2.2. Preparation of monolithic capillary columns

A monolithic column was prepared by *in situ* polymerization in fused silica capillary by a method similar to the one described previously [28–32]. Prior to the polymerization, the capillary was pretreated with the following procedure. First, the void capillary tubing was flushed in turn by 0.1 M NaOH and 0.1 M HCl for 2 h, respectively. Then the capillary was washed with water until the outflow reached pH 7. After subsequent flushing with methanol for about 30 min, the capillary was dried by passage of nitrogen gas. γ-MAPS solution by its dilution with methanol at a volume ratio of 1:1 was injected into the capillary with a syringe. Then, the capillary was sealed with rubber at both ends and submerged in a water bath at 40 °C for overnight. Finally, the capillary was washed with acetone to remove the residual reagents and dried by a nitrogen stream. Thus, the inner wall of the capillary was modified by a layer of γ-MAPS.

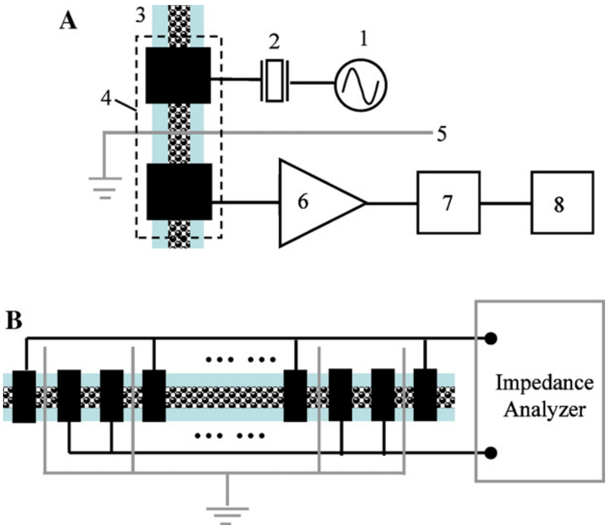

Fig. 1. Block diagram of the electronic circuitry of the detector system (A) and parallel combination of C^4D for impedance measurement (B) (not to scale). (1): function generator; (2): piezoelectric quartz crystal; (3): capillary monolithic column; (4): C^4D; (5): shielded ground copper plate; (6): current-to-voltage converter; (7): rectification, filter and offset circuitry; (8): chromatographic working station.

A polymerization reaction of mixtures consisting of the following monomers: 30% (v/v) GMA, 10% (v/v) EDMA, mixed porogenic solvent of 36% (v/v) 1-propanol, 18% (v/v) 1,4-butanediol and 6% (v/v) water and using AIBN (0.4 wt%) as an initiator was sonicated for 20 min to obtain a homogeneous solution and then purged with nitrogen for 10 min. The solution was filled into the silanized capillary. Sequentially, the capillary was sealed at both ends with silicon rubber and submerged into a water bath at 60 °C for 20 h. The resultant monolithic capillary column was washed with ethanol using a pump to remove porogens and unreacted monomers. After subsequent flushing with water for about 24 h, the monolithic column was flushed with 1 M Na_2SO_3 solution at a flow rate of 0.5 μL/min at 75 °C for 18 h for the ring-opening reaction. Then the capillary was rinsed with water and 10 mM HNO_3 successively to flush out the residual reagents. Finally, the prepared monolithic column was cut off at both ends to a total length of 28 cm and connected to the injection valve. After equilibrating with the mobile phase, the column was ready for use.

2.3. Apparatus and setup

The block diagram of the electronic circuitry and the arrangement of the detector electrodes are illustrated in Fig. 1. The contactless electrodes were fabricated from pinhead with inner diameter of 0.6 mm and length of 4 mm. Two contactless electrodes were separated by a gap distance (d) of 0.5 or 5 mm. A ground copper plate was mounted between the contactless electrodes to minimize the stray capacitance between them. The electrodes and shield plate were tin-soldered to the detector electronics and fixed to the end of the monolithic column using 704 glue. The C^4D detector was on the column at the distance of 25 cm from the injection valve. A home-made function generator was designed to provide an actuator voltage of 1–10 Vp–p with frequency breadth less than 1 Hz. The actuator voltage was applied to the series combination of a PQC (AT-cut, 1000 kHz, Beijing Chenjin Quartz Crystal Manufactory) and the C^4D on the monolithic column. The circuitry on the pick-up side comprises a current-to-voltage converter, followed by rectification, low-pass filtering, and an offset stage for baseline suppression. The output signal was scanned with the operation frequency by a user program in PC computer. The frequency corresponding to the maximum output was used in LIC^{4}D for chromatographic detection.

Chromatographic experiments were carried out by using a home-made IC system consisting of a pump (K-120, KNAUER, Germany), an injection valve (model 7520, Rheodyne) with a 500 nL injection loop and an LIC^{4}D or C^{4}D detector. All the components of the system were linked with a capillary monolithic column. The column was mounted in a column oven with temperature controlled within 0.1 °C.

2.4. *Impedance measurement of the C^{4}D and LIC^{4}D*

To analyze and compare the responses of the LIC^{4}D and C^{4}D, their impedances were measured in an impedance analyzer (Model 4294A, Agilent) through a 16047E test fixture for axial lead components. A user program written in Visual Basic 6.0 was used to control the impedance analyzer and to acquire and process data. For the consideration to increase the signal-to-noise ratio in the impedance measurements of the C^{4}D, the parallel combination of 15 pairs of C^{4}Ds (Fig. 1B) was fabricated. The impedance of a single C^{4}D was 15 times of the total impedance of the parallel C^{4}D array. In the series combination of a PQC and a C^{4}D, the total impedance magnitude was scanned 401 frequencies in the resonant region of the PQC. The minimum impedance ($|Z|_{\min}$) in the impedance–frequency curve was recorded (see Fig. 6). The frequency corresponding to $|Z|_{\min}$ was the resonant frequency of the series combination (f_0). The series combination of a PQC and a C^{4}D at the resonant frequency is the LIC^{4}D.

3. Results and discussion

3.1. *Equivalent circuit analysis of C^{4}D detector*

Physically, an LIC^{4}D detector is the series combination of a PQC and a C^{4}D detector at its resonant frequency. Hence, the response of the C^{4}D detector was discussed ahead. According to the principle of the C^{4}D, when an alternating actuator voltage of V is applied to the detector, the signal current (I) to detect is given by

$$I = \frac{V}{|Z|} = \frac{V}{\sqrt{R^2 + X^2}} \qquad (1)$$

where R, X and $|Z|$ are the resistance (real part), reactance (imaginary part) and magnitude of the impedance of the C^{4}D, respectively.

As a conductometric detector in IC, the current change due to the variation in analytes concentration in the column is considered as the signal. From the viewpoint of peak separation, the detector with a smaller volume cell is desired. As cell volume of the C^{4}D detector is related mainly to the gap between the contactless electrodes, a separation distance of d = 0.5 mm was employed. Based on the consideration for chromatographic separation, 15 mM MSA was used as the mobile phase in the prepared monolithic column for the analysis of inorganic monovalent cations in this work. As shown in Fig. 2, however, the sensitivity of the C^{4}D is rather poor. Only a systemic peak of water was seen in the chromatogram.

To explore the reason of low sensitivity of C^{4}D detector under the condition of monolithic column, the response of the C^{4}D was analyzed by a simplified equivalent circuit model [33,34]. As can be seen in Fig. 3, there were two current ways when an alternating actuator voltage was applied to the C^{4}D detector. One way was passed through the wall capacitance (C_W) then the parallel combination of the solution resistance (R_S) and solution capacitance (C_S). Another one was passed through the leakage capacitance (C_L). It should be noted that only the current passing through R_S is the useful signal current for ion concentration detection in IC. The bypass current through C_L is harmful for IC detection.

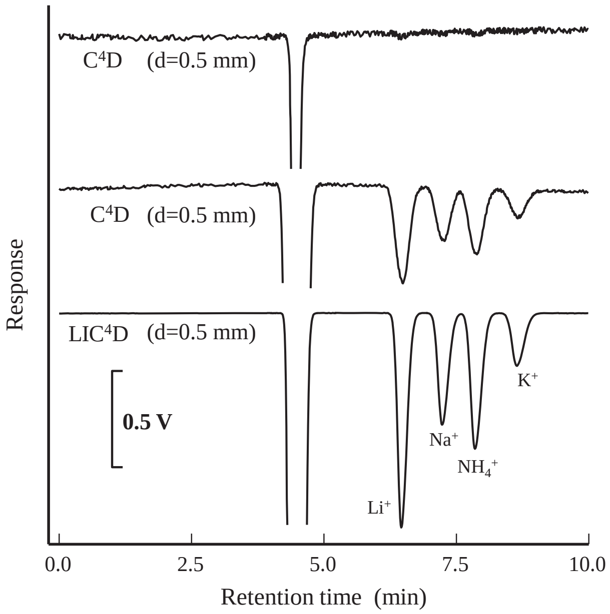

Fig. 2. Chromatograms in prepared monolithic column with contactless conductivity detectors under frequency of ca. 1 MHz. Mobile phase: 15 mM MSA, injection volume: 500 nL, flow rate: 5 (l/min. Sample: 2 mg/L Li$^+$, 5 mg/L Na$^+$, 5 mg/L NH$_4$$^+$, 5 mg/L K$^+$.

Based on the equivalent circuit model in Fig. 3, the impedance of the C^{4}D was expressed as

$$Z = \frac{R_S}{\alpha^2 + R_S^2\omega^2(C_L + \alpha C_S)^2} - j\left[\frac{1}{\omega(C_L + C_W)} + \frac{R_S^2\omega[C_L C_W/(C_L + C_W) + C_S]}{\alpha^2 + R_S^2\omega^2(C_W + \alpha C_S)^2}\right] \qquad (2)$$

where $C_W = C_{W1}C_{W2}/(C_{W1} + C_{W2})$, is the total series wall capacitor, $j = \sqrt{-1}$, $\alpha = 1 + C_L/C_W$, $\omega = 2\pi f$, f is the measuring frequency.

The relationships of the resistance (R) and reactance (X) of the C^{4}D and the measuring frequency are illustrated in Fig. 4. With increasing measuring frequency, the absolute value of the reactance reduced because the capacitive impedance of a capacitor is

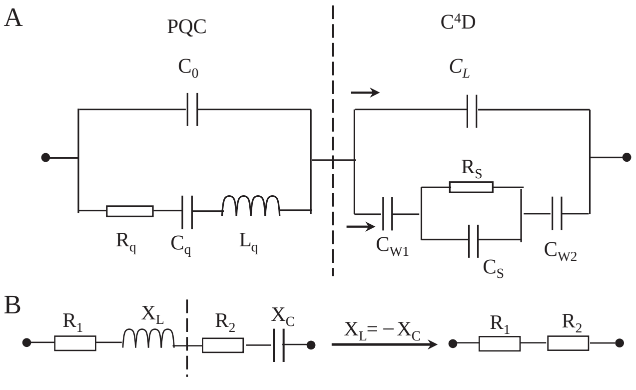

Fig. 3. Equivalent circuit model for LIC^{4}D system (A) and simplified representation (B). C_0, R_q, L_q and C_q are the static capacitance, motional resistance, motional inductance and motional capacitance of the PQC, respectively. C_L and C_W are the leakage capacitance and wall capacitance, R_S and C_S are the solution resistance and solution capacitance, respectively. R_1 and X_L are the total series resistance and inductance of the PQCs, R_2 and X_C are the total series resistance and capacitance of the C^{4}D, respectively.

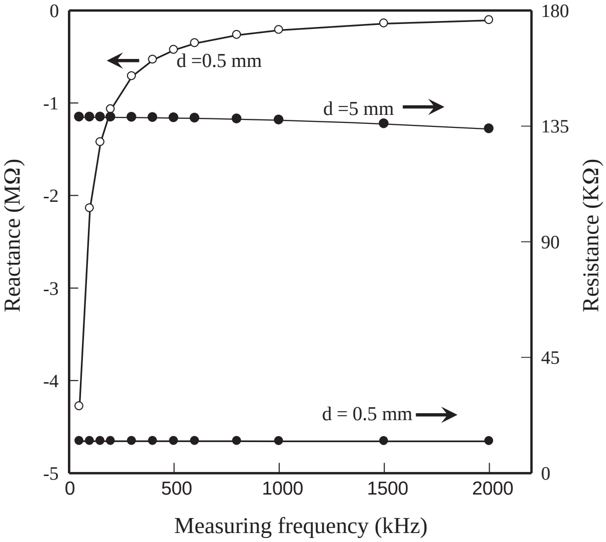

Fig. 4. Influence of the measurement frequency on the reactance and resistance of the C^4D. The capillary monolithic column was filled by 15 mM MSA. The reactance of the C^4D with d = 5 mm is close to that of the C^4D with d = 0.5 mm.

in an inverse proportion to the measuring frequency. But the resistance of C^4D decreased only slightly with increasing frequency.

Usually, the operating frequency used in C^4D is in the range of 50–200 kHz [23,24]. As shown in Fig. 4, the absolute value of the reactance of the C^4D is much larger than the value of resistance, especially for the C^4D with d = 0.5 mm in low frequency region. This result reveals the reason of the poor sensitivity of the C^4D under the experimental conditions used in this work. To illustrate this conclusion, the complicated expression of the impedance of the C^4D in Eq. (2) was simplified under two assumptions. Firstly, the influence of the leakage capacitance (C_L) can be much reduced and the leakage current can be neglected under well shield conditions. Under this assumption, there is $\alpha \approx 1$ and Eq. (2) is simplified as:

$$Z \approx \frac{R_S}{1+R_S^2\omega^2{C_S}^2} - j\left[\frac{1}{\omega C_W} + \frac{R_S^2\omega C_S}{1+R_S^2\omega^2(C_W+C_S)^2}\right] \qquad (3)$$

Secondly, the influence of the solution capacitor on the solution impedance is neglected in highly conductive solutions. Under the conditions used in this work, the resistance of the monolithic column filled 15 mM MSA was estimated to be 35.2 kΩ/mm according to the voltage-to-current ratio in an electrophoresis experiment. The value of C_S can be estimated by:

$$C_S = \frac{\beta\pi r^2\varepsilon_0\varepsilon_r}{d} \qquad (4)$$

where r = 160 μm is the inner radii of the capillary, $\varepsilon_0 = 8.854 \times 10^{-12}$ F/m, ε_r = 78 is the relative permittivity of water at 25 °C, β = 0.73 is the porosity of the prepared monolithic column. With d = 0.5 mm, we have R_S = 17.6 kΩ, $C_S = 8 \times 10^{-14}$ F and $R_S\omega C_S = 0.0009$ (f = 100 kHz). Thus, the C^4D was equivalent to the series combination of solution resistance and wall capacitor. The impedance of the C^4D and the signal current can be further simplified as

$$Z \approx R_S - \frac{j}{\omega C_W} \qquad (5)$$

$$I \approx \frac{V\omega C_W}{\sqrt{1+R_S^2\omega^2C_W^2}} \qquad (6)$$

The value of C_W was measured to be 0.64 pF with the electrode length of 4 mm. In the C^4D with d = 0.5 mm and f = 100 kHz, we have $(\omega C_W)^{-1}$ = 2.6 MΩ and $R_S\omega C_W = 0.0069$. According to Eq. (6), there is $I \approx V\omega C_W$ because $R_S^2\omega^2C_W^2 \ll 1$. Consequently, the signal current is insensitive to the change in R_S. For example, if a 100% increase in R_S occurs due to the decreases in solution conductivity, only a decrease of 0.007% in signal current was expected according to Eq. (6). Obviously, the sensitivity of the C^4D under such conditions is rather poor. According to Eq. (6), the sensitivity of the C^4D may be improved by increasing the value of $R_S\omega C_W$.

3.2. *Approaches to improve the sensitivity of C^4D detector*

To improve the sensitivity of the C^4D for monolithic column detection, three approaches were tested. The first approach is to operate the C^4D at higher frequency. When operating frequency was increased from 100 to 1000 kHz, the impedance of the wall capacitor was reduced 10 times, the value of $R_S\omega C_W$ was increased from 0.0069 to 0.069. Consequently, the relative change in signal current was increased from 0.007 to 0.7% with a 100% increase in R_S. That is to say, the sensitivity of the C^4D was improved about 10^2 times. But this strategy is limited by two factors. One is that the bypass current through C_L was also increased with the increasing operation frequency. Another is the operating characteristics of amplifiers declines at higher frequency. Hence, the operation frequency of 1 MHz was used in this work.

The second approach is to increase the value of R_S by using a larger gap distance between the electrodes. In the C^4D with d = 5 mm and f = 1000 kHz, we have R_S = 176 kΩ and $R_S\omega C_W = 0.69$. The relative change in the signal current is ±2.6% with the change of ±10% in R_S. As can be seen in Fig. 2, the peaks of Li^+, Na^+, NH_4^+ and K^+ are detected in the C^4D with d = 5 mm. But the strategy to improve the sensitivity of the C^4D by using larger electrode gap is limited by the fact that the cell volume of the detector increases with increasing gap. It is well known that a larger cell volume results in a broader peak, which is disadvantage for the peak separation in chromatogram. It should be noted that the value of R_S is also increased with decreasing inner diameter of the capillary and the conductivity of the mobile phase. When the running buffer of low conductivity and capillary with smaller inner diameter was used, the sensitivity of C^4D was satisfactory in the electrochromatography with monolithic column [26].

In the third approach, the impedance of the wall capacitor was reduced by a resonant method. As can be seen in Fig. 4, the resistance and reactance of the impedance in C^4D with d = 0.5 mm at f = 1000 kHz are 12.4 and −218 kΩ, respectively. Consequently, we have $|Z| = \sqrt{R^2+X^2} = 218.4\,\text{k}\Omega$. Obviously, the impedance magnitude of the C^4D depends mainly on its imaginary part because the absolute value of the reactive is much lager than the resistance. In order to reduce the impedance from the wall capacitor, an inductance element (L) can be added in series combination with the C^4D as the impedances of an inductance and a capacitance are in an opposite sign. When the impedance of the inductance is equal to the negative capacitance impedance of the C^4D, i.e., $\omega L = -(\omega C_W)^{-1}$, the imaginary part of the total impedance of combination of C^4D and inductance will be zero. Thus, the impedance from wall capacitor in the C^4D can be reduced significantly. As a result, the resistance will be the main contributor for the magnitude of the impedance of the C^4D and the sensitivity of the C^4D can be much improved.

Under the experimental condition used, the value of C_W was about 0.62 pF, an inductance of 4.1 and 0.041 H was needed to offset this capacitor impedance at frequency of 100 and 1000 kHz, respectively. To fabricate such a large loop inductance seemed to be technically difficult because the serious energy loss of an inductance at high frequency. Hence, an equivalent inductance element from quartz crystal resonator was used for this purpose and the principle was illustrated below.

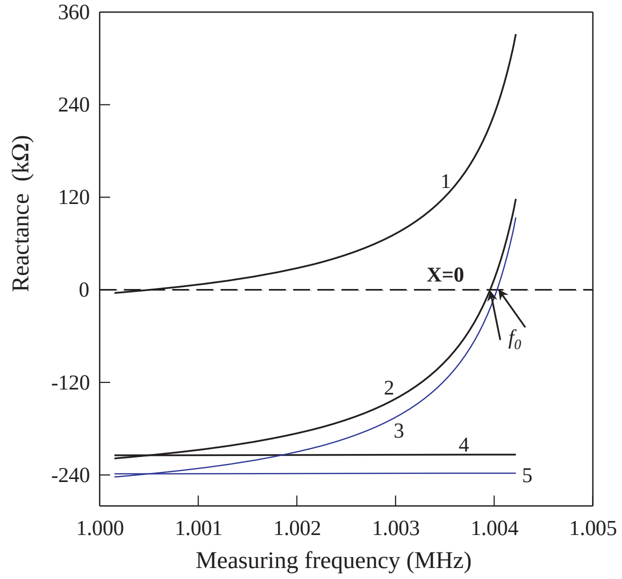

Fig. 5. Influence of the measurement frequency on the reactance of the C^{4}D, PQC and their combination. (1): PQC; (2): PQC + C^{4}D with d = 0.5 mm; (3): PQC + C^{4}D with d = 5 mm; (4): C^{4}D with d = 0.5 mm; (5): C^{4}D with d = 5 mm. The capillary monolithic column was filled by 15 mM MSA.

3.3. Principle and response of LIC^{4}D detector

The principle of the LIC^{4}D is illustrated in Fig. 1 and its equivalent circuit model is presented in Fig. 3. Accordingly, the impedance of the series combination of PQC + C^{4}D is expressed as

$$Z = R_1 + R_2 + j(X_L + X_C) = \frac{R_q}{M^2+N^2} + \frac{R_S}{\alpha^2 + R_S^2\omega^2(C_L+\alpha C_S)^2} - j\left[\frac{\omega L_q - (\omega C_q)^{-1} - (\omega C_0)^{-1}}{M^2+N^2} + \frac{1}{\omega C_0} + \frac{1}{\omega(C_L+C_W)} + \frac{R_S\omega[C_L C_W/(C_L+C_W)+C_S]}{\alpha^2+R_S^2\omega^2(C_W+\alpha C_S)^2}\right] \quad (7)$$

where $M = 1 + C_0/C_q - \omega^2 L_q C_0$, $N = R_q\omega C_0$, C_q, L_q, R_q and C_0 are the motional capacitance, motional inductance, motional resistance and static capacitance of the PQC, respectively.

It should be pointed out that impedance of the PQC is sensitive to the change in measuring frequency. As shown in Fig. 5, the reactance of the PQC was increased with increasing measuring frequency while reactance of the C^{4}D was near constant in such a narrow frequency region. Hence, the total reactance of the PQC + C^{4}D combination was shifted from negative value to positive value with increasing measuring frequency. At the resonant frequency of the PQC + C^{4}D combination (f_0), the total reactance ($X_L + X_C$) is equal to zero, where the $|Z|$ value of the PQC + C^{4}D combination has a minimum (see Fig. 6). Hence, the PQC + C^{4}D combination operating at its resonant frequency is known as LIC^{4}D. According to Eq. (7), we have under the condition of $X_L + X_C = 0$.

$$|Z|_{\min} = R_1 + R_2 = \frac{R_q}{M^2+N^2} + \frac{R_S}{\alpha^2 + R_S^2\omega^2(C_L+\alpha C_S)^2} \quad (8)$$

The values of M and N in Eq. (7) were calculated by using the resonant frequency of f_0, which can be estimated from the resonant condition of $X_L + X_C = 0$. Hence, the following equation is obtained in the LIC^{4}D.

$$PM^2 - M + PN^2 = 0 \quad (9)$$

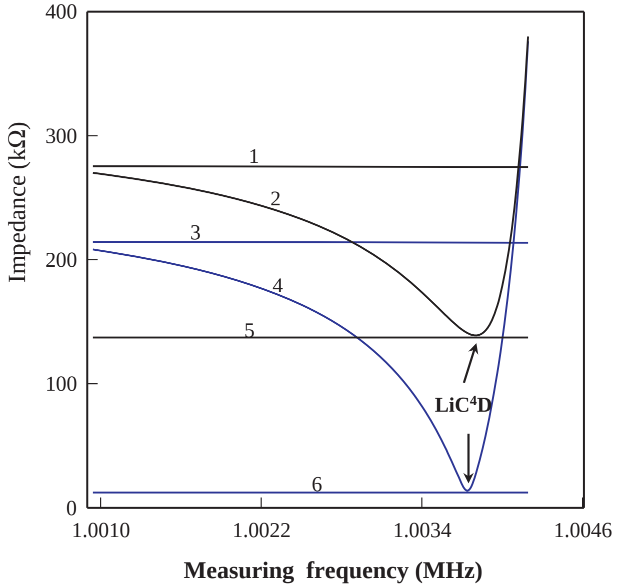

Fig. 6. Influence of the measurement frequency on the resistance of the C^{4}D and the impedance magnitude of the C^{4}D and C^{4}D + PQC. (1): $|Z|$ of C^{4}D with d = 5 mm; (2): $|Z|$ of PQC + C^{4}D with d = 5 mm; (3): $|Z|$ of C^{4}D with d = 0.5 mm; (4): $|Z|$ of PQC + C^{4}D with d = 0.5 mm; (5): resistance of C^{4}D with d = 5 mm; (6): resistance of C^{4}D with d = 0.5 mm. The capillary monolithic column was filled by 15 mM MSA.

$$P = 1 + \frac{C_0}{C_L + C_W} + \frac{R_S^2\omega^2 C_0[C_L C_W/(C_L+C_W)+C_S]}{\alpha^2 + R_S^2\omega^2(C_W+\alpha C_S)^2} \quad (10)$$

Because the value of M is much more sensitive to the measuring frequency than P and N, only M was considered as the variable in Eq. (9). From this equation, two roots for M are obtained. The root in Eq. (11) is corresponded to the point of $|Z|_{\min}$.

$$M = \frac{1+\sqrt{1-4P^2N^2}}{2P} \quad (11)$$

Submitting the M vale in Eq. (8), we obtain

$$|Z|_{\min} = \frac{2P^2 R_q}{1+\sqrt{1-4P^2N^2}} + \frac{R_S}{\alpha^2 + R_S^2\omega^2(C_L+\alpha C_S)^2} \quad (12)$$

Under the conditions of $C_L \approx 0$ and $R_S\omega C_S \ll 1$, the expression for $|Z|_{\min}$ can be simplified as

$$|Z|_{\min} \approx \left(1 + \frac{C_0}{C_W}\right)^2 R_q + R_S \quad (13)$$

With C_0 = 2.9 pF and R_q = 54 Ω for the PQC used in this work, the value of $(1 + C_0/C_W)^2 R_q$ is equal to1.7 kΩ, which is only 10% and 1% of the value R_S in the C^{4}D with d = 0.5 and 5 mm, respectively. Hence, the value of $|Z|_{\min}$ is determined mainly by the value of R_S, which is supported by the result in Fig. 6. It can be seen that the values of $|Z|_{\min}$ are only slightly larger than the resistance of the C^{4}D. Because of the influence of C_S and C_L, the value of $|Z|_{\min}$ is less than that of R_S.

According to the M value in Eq. (11), the resonant frequency corresponding to the point of $|Z|_{\min}$ is given by

$$f_0 = \frac{1}{2\pi\sqrt{L_q C_q}}\left[1 + \frac{C_q}{2C_0}\left(1 - \frac{1+\sqrt{1-4P^2N^2}}{2P}\right)\right] \quad (14)$$

It can be seen that the resonant frequency in the LIC^{4}D is higher than the resonant frequency of the PQC itself and is related to the experimental conditions. Hence, the operating frequency of the LIC^{4}D should be optimized under different experimental conditions. As can be seen in Fig. 6, the operating frequency region of

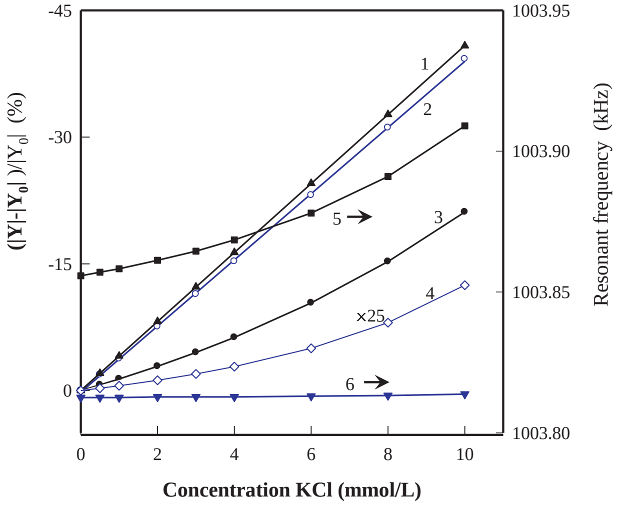

Fig. 7. Influence of the concentration of on the admittance magnitude of the C^{4}D and LIC^{4}D and the resonant frequency of the LiC^{4}D. (1): LIC^{4}D with $d = 5$ mm; (2): LIC^{4}D with $d = 0.5$ mm; (3): C^{4}D with $d = 5$ mm; (4): C^{4}D with $d = 0.5$ mm; (5): resonant frequency for LIC^{4}D with $d = 5$ mm; (6): resonant frequency for LIC^{4}D with $d = 0.5$ mm. The solutions were prepared by mixed 15 mM KCl and 15 mM MSA and the total concentration of KCl and MSA is 15 mM.

the LIC^{4}D is very narrow. The width of the valley is about 5 and 30 Hz in the LIC^{4}D with $d = 0.5$ and 5 mm respectively. It should be emphasized that the frequency breadth of actuator voltage used for LIC^{4}D should be less than that of the valley. A digital actuator voltage with half-peak breadth of 1 Hz was suggested to use.

3.4. Comparison of the response of LIC^{4}D and C^{4}D detectors

When the PQC is shorted by a wire, the LIC^{4}D is returned to the classic C^{4}D. The responses of LIC^{4}D and C^{4}D to the change in concentration of analyte in the monolithic column are shown in Fig. 7. The magnitude of admittance, $|Y| = |Z|^{-1}$, which is in proportional to the signal current, is used as the indictor. In this experimental, the total concentration of KCl and MSA was equal to 15 mM. As the concentration of KCl increases, the concentration of MSA reduces, the total solution conductivity decreases because the conductivity of KCl is less than that of MSA. Hence, it was observed that the $|Y|$ values of C^{4}D and LIC^{4}D decreased with increasing KCl concentration. The LIC^{4}D has higher sensitivity to the change in solution conductivity than that of C^{4}D, especially in the case of $d = 0.5$ mm. When KCl concentration increases from 0 to 10 mM, the $|Y|$ values of LIC^{4}D decrease linearly. The decrease percentages of 39.2 and 40.8% was measured in the LIC^{4}D with $d = 0.5$ and 5 mm, respectively, which are slightly less than the decrease percentages of 42.7% in solution conductance. The decrease percentage is 0.5 and 21% in the C^{4}D with $d = 0.5$ and 5 mm, respectively. The experimental results in Fig. 7 support the analysis in the responses of LIC^{4}D and C^{4}D.

On the other hand, a larger $|Y|$ value corresponds to a higher signal current level, which is helpful for to improve the signal-to-noise ratio of the detection electronics. Under the experimental conditions used, the value of $|Y|$ in the LIC^{4}D with $d = 0.5$ mm was 74.8 μS, which is much larger than that in LIC^{4}D with $d = 5$ mm (7.06 μS), C^{4}D with $d = 0.5$ mm (4.67 μS) and $d = 5$ mm (3.61 μS). The changes in the resonant frequency of the LIC^{4}D are also shown in Fig. 7. When the concentration of KCl was increased from 0 to 10 mM, the resonant frequency was increased by 1.4 and 53 Hz in the LIC^{4}D with $d = 0.5$ and 5 mm, respectively. As shown in Fig. 6, the width of the valley in the impedance–frequency curve is about 5 and 30 Hz in the LIC^{4}D with $d = 0.5$ and 5 mm respectively. The change in the resonant frequency in the LIC^{4}D with $d = 0.5$ mm was within the width of the valley. Hence, a constant operating frequency can be used in LIC^{4}D for the monolithic column ionic chromatography as the change in ion concentration is small in a separation processes, except the water systemic peak.

3.5. Determination of inorganic monovalent cations in water samples

After optimization of the chromatographic conditions, the separation of Li$^+$, Na$^+$, NH$_4^+$ and K$^+$ were performed on the prepared monolithic column. As shown in Fig. 2, the LIC^{4}D had higher signal-to-noise ratio than the C^{4}Ds at same analytes concentration. As listed in Table 1, the detection limit and linear range of the LIC^{4}D are better than those of C^{4}D. On the other hand, as shown in Fig. 2, the peak separation in the LIC^{4}D with $d = 0.5$ mm is better than that in the C^{4}D with $d = 5$ mm as the cell volume in the former (ca. 30 nL) is much smaller than that in the latter (ca. 300 nL). The separation and determination of Na$^+$, NH$_4^+$ and K$^+$ in real water samples were performed by using the prepared monolithic column and LIC^{4}D. As shown in Table 2, the recoveries of the method were in the range of 98.3–101.5%. This result demonstrated the applicability of the LIC^{4}D detector in capillary ion chromatography. If a commercial contact conductivity detector, an additional link capillary is needed to connect the monolithic column and the detector. The connection between the separation and link capillaries is a difficult

Table 1
Performance parameters for determination of cations by IC with the monolithic column and C^{4}D and LIC^{4}D detectors.

Analyte	C^{4}D ($d = 5$ mm)		LIC^{4}D ($d = 0.5$ mm)	
	Linearity range (mg/L)	Detection limit (mg/L)	Linearity range (mg/L)	Detection limit (mg/L)
Li$^+$	1–50	0.27	0.1–100	0.031
NH$_4^+$	1.5–100	0.56	0.2–200	0.075
Na$^+$	2–100	0.72	0.3–200	0.10
K$^+$	3–200	1.1	0.5–400	0.16

Table 2
Determination of ammonium, potassium and sodium ions in water samples by IC with the monolithic column and LIC^{4}D detector.

Water sample	Cation	Concentration[a] (mg/L)	Amount added (mg/L)	Recovery[a] (%)
Xiaoqing River	K$^+$	5.74 ± 0.29	5.00	98.2 ± 3.4
	Na$^+$	16.8 ± 0.71	5.00	97.5 ± 6.7
	NH$_4^+$	7.43 ± 0.25	5.00	101.2 ± 4.8
Daming Lake	K$^+$	3.29 ± 0.15	5.00	99.3 ± 4.2
	Na$^+$	11.2 ± 0.44	5.00	100.7 ± 5.3
	NH$_4^+$	4.51 ± 0.29	5.00	98.8 ± 3.9

[a] The values are mean ± standard deviation in five determinations.

task, as the capillary ends must be cut off perpendicularly to make a tight connection. Moreover, the section of link capillary between the monolithic column outlet and the detector represents a significant dead volume, which definitely contributes to the analyte zone dispersion [10]. On the other hand, the cell volume of a commercial contact conductivity detector in IC is larger than 1 μL, which will result in larger peak widening in the chromatogram.

4. Conclusions

This work clearly demonstrates the benefits of the use of a low impedance capacitively coupled contactless conductivity detector (LIC^{4}D) in ion chromatography with capillary monolithic column. As the impedance of wall capacitor in the capillary column was efficiently eliminated, the contactless electrodes with smaller dimensions could be employed in the LIC^{4}D. The impedance of the LiC^{4}D is close to the solution impedance. The sensitivity of LiC^{4}D is similar to that of a contact conductivity detector. But the LIC^{4}D offers the advantage in simplicity in detection cell design, much smaller volume and on-column detection without extra peak broadening. Under the chromatographic conditions used, the mixture of inorganic cations (Li^+, Na^+, NH_4^+, K^+) was well separated in the prepared monolithic column. The detection limits of LiC^{4}D to Li^+, Na^+, NH_4^+ and K^+ were 0.031, 0.075, 0.10 and 0.16 mg/L, respectively.

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