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Journal of Chromatography A, 753 (1996) 171–176

JOURNAL OF
CHROMATOGRAPHY A

Design of double cell quartz crystal detector for ion chromatography and its applications to determination of organic acids in traditional Chinese herb medicine

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Received 24 January 1996; revised 10 June 1996; accepted 10 June 1996

Abstract

A double cell quartz crystal (DCQC) detector in combination with a single-column IC chromatographic flow system has been developed. First, an electrical equivalent circuit model was built, which was used to determine the optimum detector parameters including the cell constants and the background conductance of the adjusting cell. This method has a low temperature coefficient and a high conductance sensitivity independent of the background from 7.2 to 2500 μS . The detection limit is 0.05 ppm and the linear dynamic range is up to 72 ppm. This detector was applied to determination of citric acid, malic acid and ascorbic acid in Chinese herb medicines including *fructus mume* and *ephedra sinica stapf*.

Keywords: Detection, LC; Quartz crystal detection; Organic acids

1. Introduction

Ion chromatography (IC) has rapidly become a standard technique in water analysis [1], and it has also been demonstrated to be a very suitable technique for the solution of environmental problems [2,3] and in food analysis [4]. Although the conductivity cell is among the most commonly used detectors in IC, the linear dynamic range and the detection limit of this method are subject to background interference of the mobile phase, especially in single-column IC.

The quartz crystal (QC) device has played an important role in probing interfacial processes at

surfaces and thin films [5]. The oscillation frequency of the crystal in contact with a liquid is changed by deposition/removal of surface species, and variations of liquid properties such as density, viscosity, conductivity and permittivity [6,7]. The high sensitivity, low cost and conceptual simplicity of this method portend its development in a variety of commercial and research applications. The series piezoelectric quartz crystal (SPQC) detector and electrode-separated piezoelectric crystal (ESPC) detector, proposed specially for liquid conductivity and permittivity sensing, have been applied in high-performance liquid chromatography (HPLC) [8,9]. The configuration of the two electrodes on opposite sides of the crystal is altered to involve the contacting liquid in the electrical field applied across the crystal. This leads to the vibrating frequency of the QC detector shifting with the liquid conductivity and permittivity.

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In previous papers the use of SPQC as an alternative detector in IC was reported. Inorganic cations in human cerebrospinal fluid, lactic acid and pyruvic acid in serum were determined with this method [10,11]. In this paper we propose a novel use of the QC detector in conjunction with IC flow system by separating the activated electrodes with two flow cells. One cell of the double cell quartz crystal (DCQC) detector is used to adjust the frequency responses of the crystal to the other detection cell. Another aim of this paper was to build an equivalent circuit model for this detector, evaluate the characteristics of the detector independently of the application and to determine the optimum detector parameters. This detector was also used to determine citric acid, malic acid and ascorbic acid in Chinese herb medicines including *fructus mume* and *ephedra sinica stapf*.

2. Experimental

2.1. Materials

The standards were of spectrum grade. All other chemicals were of analytical reagent grade and were used as received without further purification. Distilled deionized water was used for preparation of mobile phase and standard solutions. The mobile phase and sample solutions were filtered through a 0.45- μm filter membrane (Millipore, USA).

For the determination of the optimum experimental conditions, a series of standard solutions of KCl were prepared to obtain different background conductance. Herb medicine samples were taken from the National Anti-Epidemic and Health Station of Hunan without treatment.

2.2. DCQC detector

Fig. 1 shows the schematic diagram of the DCQC detector. The quartz crystal was mounted on the top of a Teflon column with one side facing liquid. The silver electrode on this side was removed, therefore the two opposite electrodes inducing an alternating electrical field across the crystal were separated by two flow-through conductivity cells, Cell 1 and Cell 2. Cell 2 was connected to the IC system with a 0.5

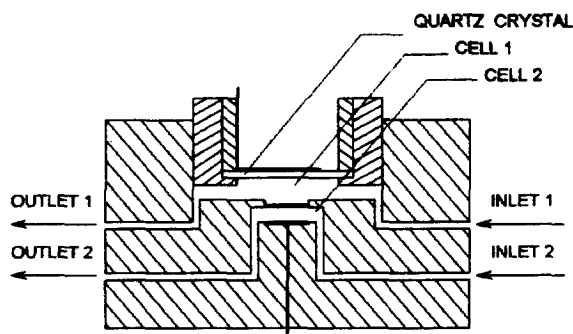


Fig. 1. Schematic diagram of the DCQC detector.

mm diameter inlet and outlet and the platinum electrodes in Cell 2 were pre-treated with 6 M HNO_3 first, then by water and acetone. The cell constant of Cell 1 can be adjusted by changing the position of the PTFE column with the crystal device. However, during an experiment the cell constant as well as the adjustment solution in Cell 1 were kept unchanged to provide stable experimental conditions. The DCQC detector was connected to a laboratory-made TTL-IC oscillating circuit, and frequency signals were transferred to a Baseline 810 chromatographic workstation (Waters, Japan) through a frequency/voltage converter made in this laboratory [12]. The impedance spectrum of the detector was also analysed by an HP 4192A LF impedance analyser (5 Hz–13 MHz).

2.3. Chromatographic system

Chromatographic separation was performed by using a Shimadzu IC-6A ion chromatography system, including a LC-6A liquid delivery pump, a SLC-6B system controller, an SIL-6B auto injector, and a CTO-6A column oven. The column used was a Shim-pack IC-A1 (10 cm \times 4.6 mm I.D. stainless column), packed with an anion-exchange resin on polymethacrylate support, incorporating a quaternary ammonium base as a functional group. A Shim-pack IC-GA1 guard column (10 \times 4.6 mm I.D.) was equipped. Mobile phase was 2.0 mmol/l potassium hydrogenphthalate (KHP) at a flow-rate of 1.0 ml/min, which was degassed prior to use. The temperature of column and detector was set at 40 °C. A

CDD-6A conductivity detector was also used to compare performance of the DCQC detector.

2.4. Procedure

The eluent was pumped into the chromatographic system. The sample solution was introduced by the auto injector after the baseline was stabilised (f_0 and v_0), and the frequency (f_1) and voltage signals (v_1) were recorded vs. time. The concentrations of the tested ions were calculated from the obtained frequency shift Δf ($\Delta f = f_1 - f_0$) vs. time chromatogram by comparison with the standard.

3. Results and discussion

3.1. Theoretical considerations for the design of DCQC cell

The electrical circuit representation of the DCQC detection cell is illustrated in Fig. 2. The circuit of the series combination of a capacitor (C_m), an inductance (L_m) and a resistor (R_m) in parallel with a capacitor (C_0) is equivalent electrically to the quartz crystal. The solution capacitance (C_1 , C_2) and the solution resistance (R_1 , R_2), which are the reciprocal of the solution conductance (G_1 , G_2), depend on the solution conductivity (κ_1 , κ_2), the solution permittivity (ϵ_1 , ϵ_2), the cell constants (k_1 , k_2) and the parasitic capacitance (C'_1 , C'_2). The motional impedance (Z_m), the static impedance (Z_0) of the quartz crystal and the solution impedance (Z_s) are:

$$Z_m = R_m + j\omega L_m(j\omega C_m)^{-1} \quad (1)$$

$$Z_0 = (j\omega C_0)^{-1} \quad (2)$$

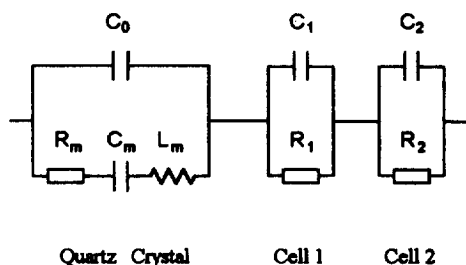


Fig. 2. Electrical equivalent circuit of the DCQC detector.

$$Z_s = (G_1 + j\omega C_1)^{-1} + (G_2 + j\omega C_2)^{-1} \quad (3)$$

where ω is the angular frequency of the quartz crystal ($\omega = 2\pi f$). R_m is negligible compared with the reactance part of the crystal. Then the real part (R_e) and the imaginary part (X_e) of the total impedance (Z_e) of the DCQC can be expressed as:

$$R_e = \frac{G_1}{G_1^2 + \omega^2 C_1^2} + \frac{G_2}{G_2^2 + \omega^2 C_2^2} \quad (4)$$

$$X_e = \frac{\omega L_m - (\omega C_m)^{-1}}{1 + C_0 C_m^{-1} - \omega^2 L_m C_0} + \frac{-\omega C_1}{G_1^2 + \omega^2 C_1^2} + \frac{-\omega C_2}{G_2^2 + \omega^2 C_2^2} \quad (5)$$

When the DCQC detection cell is connected into a feedback loop, there are two criteria that must be satisfied for an oscillation to occur in the network: the magnitude of loop gain is unity and the phase shift around the loop is zero. If the amplifier used in the oscillator has a phase lag of $-\theta$ then the phase angle of DCQC must be θ . Let $-A = \tan \theta = X_e/R_e$. The oscillation equation can be derived on the basis of the circuit network theory [13,14]:

$$\frac{\omega L_m - (\omega C_m)^{-1}}{1 + C_0 C_m^{-1} - \omega^2 L_m C_0} + \frac{G_1 A - \omega C_1}{G_1^2 + \omega^2 C_1^2} + \frac{G_2 A - \omega C_2}{G_2^2 + \omega^2 C_2^2} = 0 \quad (6)$$

The above equation, which is a quadratic function of frequency, yields the necessary frequency of the quartz crystal to satisfy the phase shift requirement of the detector. So the frequency shift of the DCQC detector can be predicted theoretically by solving Eq. (6) with the numerical solution method. The oscillation equations provide a theoretical basis for our design of the DCQC detector.

3.2. Effect of solution conductance of Cell 1

When conductivity and permittivity in the chromatographic flow in Cell 2 are varied, the vibrating frequency of the crystal will shift until a new oscillation equilibrium is achieved. The magnitude of the frequency shift depends on the conductivity, permittivity, phase angle and other electrical parameters of the detector which are constants in the

experiment. The permittivity variation is negligible because only aqueous dilute solution is used in IC. Therefore the frequency response is proportional to the conductance change in Cell 2. For single-column IC analysis of anions, the conductance of the mobile phase increases when the tested ions elute out, resulting in a decrease in the frequency of the DCQC. The phase angle of the crystal can be shifted by conductance of Cell 1, G_1 . In this work G_1 is changed to investigate the effect of phase shift on the frequency characteristics of the DCQC and determine the optimum value of G_1 . Theoretical sensitivity of DCQC to conductance variation in Cell 2, S ($\Delta f/\Delta G$), at different background conductance G_1 and G_2 is illustrated in Fig. 3. Electrical parameters used in calculations are: $L_m=10.5$ mH, $C_m=0.03$ pF, $C_0=5$ pF, $A=-0.6$, $C'_1=0.4$ pF, $C'_2=0.4$ pF, and $k_1=k_2=1$ cm. It can be seen that the conductance/sensitivity of DCQC is independent of background when G_1 is ca. $500 \mu\text{S}$, which make it more advantageous than the conventional conductimetric method.

3.3. Effect of cell constant of Cell 2

As both the solution conductance and capacitance are dependent on cell constant. It is worth examining the effect of the cell constant of Cell 2, k_2 on the DCQC. The theoretical sensitivity of DCQC at different G_2 with k_2 from 0.01 cm to 5 cm is

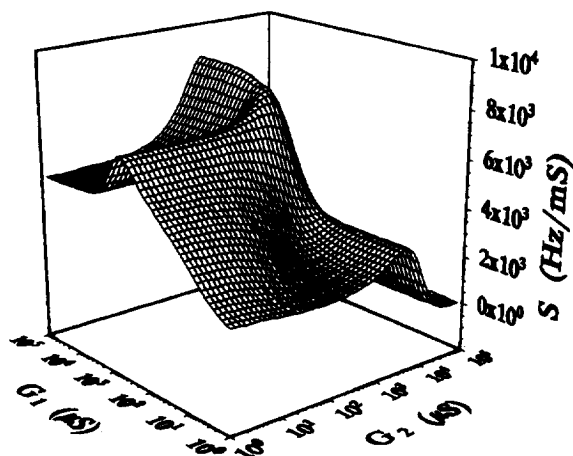


Fig. 3. Sensitivity characteristics of the DCQC at different background conductance of Cell 1 and Cell 2.

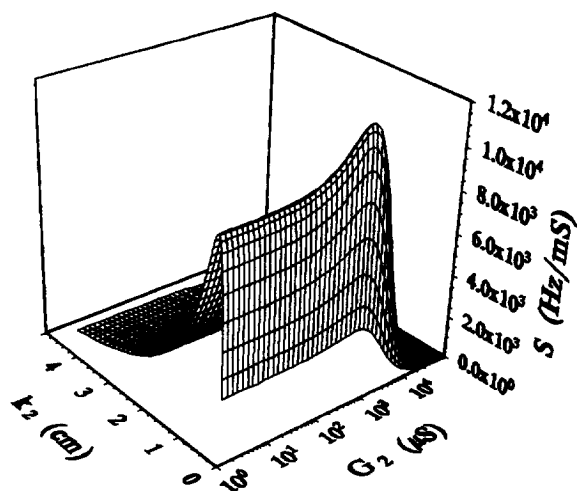


Fig. 4. Optimum cell constant of Cell 2 for the DCQC detector.

demonstrated in Fig. 4. It can be seen that in a certain cell constant region the DCQC detector has a rather higher conductance sensitivity which, however, becomes very dependent on the background. It thus reduces the work region of the detector. An optimum cell constant k_2 can be found as the best compromise between the sensitivity and the work region. Experimental results are shown in Fig. 5 with

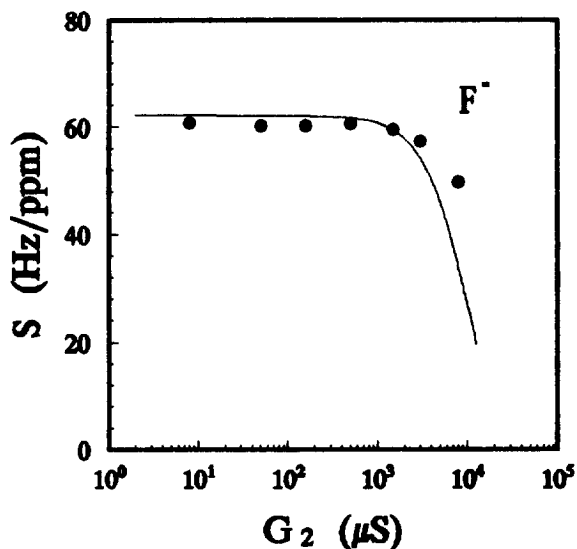


Fig. 5. Conductance/sensitivity of the DCQC in mobile phase of different background conductance. The solid line is calculated theoretically from Eq. (6).

cell constants $k_2 = 0.87$ cm and $G_1 = 500$ μ S, where solid line is calculated from Eq. (6). Comparison indicates that the values predicted theoretically agree well with the experimental results. The DCQC has a satisfactory frequency response to conductance change at background from 7.2 to 2500 μ S, which covers the normal eluent conductance region of single-column IC, and is also much wider than the SPQC and ESPC. So these conditions were selected in the later experiment.

3.4. Performance of the DCQC detector

Detector temperature greatly influences the baseline, noise, and hence detection limit of the conventional conductivity method. A conductivity/temperature coefficient as much as 2%/°C was reported. The DCQC detector, however, depends slightly on the temperature in the range of 25–45 °C. In 2 mmol/l KHP mobile phase the noise frequency was found to within 1 Hz by reducing the temperature variation to ± 0.5 °C. In our experiment, to keep the thermal equilibrium the detector temperature was maintained at 40 °C, the same as that of the column.

The noise level and baseline drift of the DCQC detector are very small, in contrast to the ESPC detector, because the crystal is not in direct contact with the mobile phase in Cell 2, thus it is independent of the change in viscosity and density of the chromatographic flow. In our experiment, the baseline drift was found to be 5 Hz/h and noise was less than 1 Hz in all response regions.

The sensitivity of DCQC depends on the ion to be determined, because of its different ionic conductivity. The frequency sensitivity for fluoride is 62 Hz/ppm under the optimum experimental condition, and the detection limit, defined as a signal-to-noise ratio of 3, is 0.05 ppm. The linear dynamic range is up to 72 ppm with the correlation coefficient of 0.993 for the F^- ion. The sensitivity and detection

limit for other inorganic anions and cations are listed in Table 1. It can be seen that the DCQC is competitive with the conductimetric method for single-column IC in this respect.

Dead-volume of the detector is an important factor for the chromatographic separation; if the dead volume is too big, the chromatographic peaks will get wider. As for the DCQC detector, dead-volume was determined by the distance between the inlet and the conductivity electrode as well as the diameter of the detection cell. In our work, a detection cell (Cell 2) with a dead-volume of 10 μ l, was employed.

3.5. Determination of organic acids in traditional Chinese herb medicine

Citric acid, malic acid and ascorbic acid are major active components of *fructus mume* and *ephedra sinica* staph. Determination of the three organic acids is important to evaluate the medical effectiveness of these Chinese herb medicines. In this experiment, a glass DCQC detector of the same parameters a Shim-pack SCR-102H column and a 0.5 mmol/l *p*-toluenesulfonic acid mobile phase (flow-rate 1.1 ml/min) were used. A 0.22- μ m filter was also used to remove fine particles. Fig. 6 shows frequency signals of the DCQC detector with separation of single-column IC. The results are in fairly good agreements with those from a conventional CDD-6A conductivity detector (Table 2).

4. Conclusions

A double cell quartz crystal (DCQC) detector for single-column IC has been developed. An electrical equivalent circuit model was built and used to determine the optimum experimental parameters of the detector. The method has a low temperature coefficient and a high conductance sensitivity, in-

Table 1
Sensitivity and detection limit of the DCQC detector for inorganic anions and cations

	Ion					
	F^-	Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+
Sensitivity (Hz/ppm)	62	48	28	37	45	41
Detection limit (ppm)	0.05	0.06	0.11	0.08	0.07	0.07

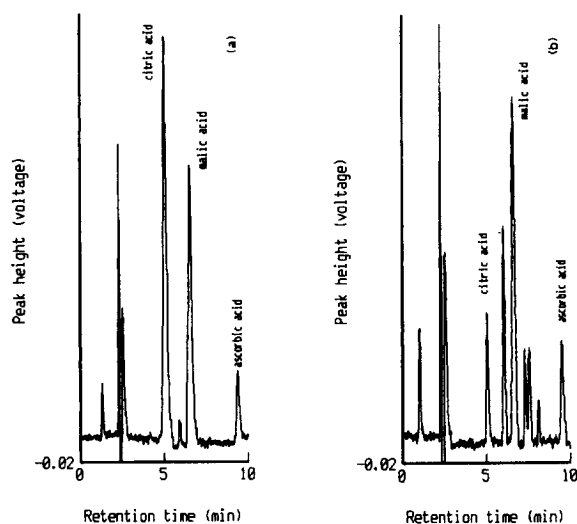


Fig. 6. Chromatograms of (a) *fructus mume* and (b) *ephedra sinica stapf* samples obtained by DCQC detector in combination with single-column IC.

dependently of the background conductance, from 7.2 to 2500 μS . The linear response range is up to 72 ppm with the detection limit being 0.05 ppm. Further improvements in frequency stability of the DCQC detector and reducing the noise level to 0.1 Hz or even less would result in a greater gain in activity and a lower detection limit. This aspect is under study.

Acknowledgments

This work was supported by the Natural Science Foundation and Education Commission Foundation of China.

Table 2
Comparison of the DCQC detector and conventional conductivity cell

Sample	Component detected	Content found (mg/g)	
		DCQC detector	Conductivity cell
<i>Fructus mume</i>	Citric acid	230	233
	Malic acid	67.1	64.3
	Ascorbic acid	2.43	2.6
<i>Ephedra sinica stapf</i>	Citric acid	2.13	2.02
	Malic acid	13.9	13.5
	Ascorbic acid	8.92	9.1

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