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## POTENTIOMETRIC DETECTOR WITH A GLASS ELECTRODE FOR THE ION-EXCHANGE CHROMATOGRAPHY OF CARBOXYLIC ACIDS

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### SUMMARY

A method for the detection of carboxylic acids in the effluent from ion-exchange columns, based on the deviation of the pH of a buffer solution on the addition of Brønsted bases, is described. A high-sensitivity flow-through glass electrode pH meter was designed for this purpose. From 1 to 10  $\mu$ equiv. of carboxylic acids or their salts in the effluent can be detected.

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### INTRODUCTION

Ion-exchange chromatography is a powerful method for the separation or analysis of carboxylic acids, but difficulties with detection have prevented its wider application.

A colorimetric method with an indicator has been described previously<sup>1</sup>, but the reproducibility was unsatisfactory because of non-linearity of the colour development, instability of the indicator and contamination of the photometer cell by oxidized pigment.

A simple method for the detection of carboxylic acids or their salts in the effluent from the ion-exchange columns by direct measurement of pH with a glass electrode is presented in this paper. The principle is based on the deviation of the pH of a buffer solution on the addition of strong Brønsted bases. The effluent containing carboxylate ions is mixed with a standard buffer solution, and the pH is measured with a high-sensitivity pH meter. The deviation of the pH of the mixture from the original value of the standard buffer is proportional to the content of carboxylate in the effluent.

### PRINCIPLES AND THEORETICAL

The pH of buffer solution containing a weak acid HA is represented by

$$\text{pH} = \text{p}K_a + \log \frac{q_{A^-}}{q_{HA}} \quad (1)$$

where  $\text{p}K_a$  is the exponent of the dissociation constant of the acid and  $q_{HA}$  and

$q_{A^-}$  are the amounts of HA and  $A^-$ , respectively, in the solution. When a base  $B^-$  is added to the solution, which has a sufficiently high  $pK_a$  value compared with HA, the following reaction would occur:



The pH of the mixture then becomes

$$pH = pK_a + \log \frac{q_{A^-} + q_{B^-}}{q_{HA} - q_{B^-}} \quad (2)$$

If we plot  $pH - pK_a (= \Delta pH)$  against  $q_{B^-}/q_{A^-}$ , the curve shown in Fig. 1 is obtained.

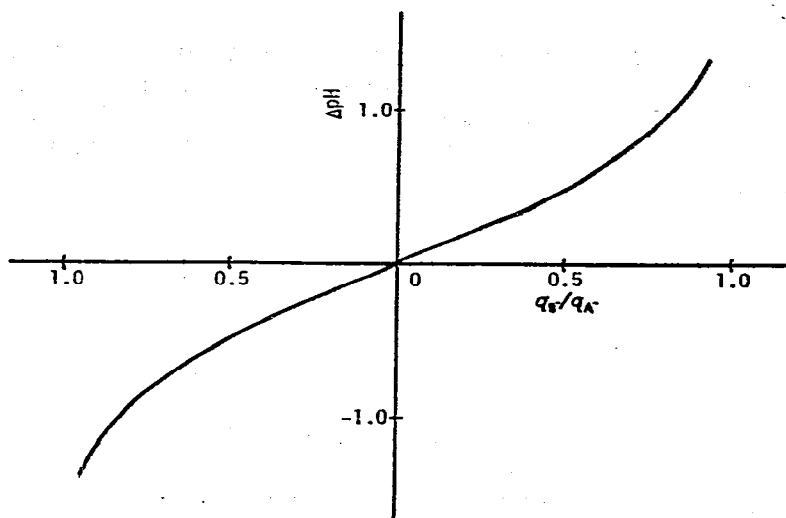


Fig. 1. Deviation of the pH of buffer solution on addition of strong base.

If we assume that  $q_{A^-} = q_{HA} = 1/2 q_0$ , and differentiate eqn. 2 with respect to  $q_{B^-}$  in the neighbourhood of  $q_{B^-} = 0$ , then we obtain

$$dpH = 1.737 \cdot \frac{dq_{B^-}}{q_0} \quad (3)$$

If we use concentration instead of amount, and replaced  $pH$  by  $\Delta pH$  and  $dq_{B^-}$  by  $b$ , the following equation is obtained:

$$\Delta pH = 1.737 \cdot \frac{b}{c} \quad (4)$$

where  $c = q_0/V$ ,  $b = q_{B^-}/V$  and  $V$  is the final volume of the mixture. Eqn. 4 holds in the range  $pH = pK_a \pm 0.2$  with an error of  $\pm 0.1\%$ .

A schematic diagram of the chromatographic system is shown in Fig. 2.

Eluent (1) is supplied by a pump (2) through a sample injector (3) to the main column (4), which is maintained at a constant temperature with a circulating thermostat bath (5). Samples are injected into the stream of eluent with the sample injector. Effluent from the main column containing carboxylate ions flows through an after-treatment column, "pH control column" (6), which is packed with a weak acid-type cation-exchange resin. The resin works as a solid-phase buffering agent, and the effluent is neutralized and maintained at pH 8.5–9.5, in which range most carboxylic acids exist as carboxylate ions. Then the effluent is led into the electrode system (9) and mixed with equal volume of standard buffer solution (7). As the carboxylate ions act as a strong base, the pH of the mixture deviates from the original value of the standard buffer. The pH of the mixture is measured with a high-sensitivity pH meter (11) and recorded on a recorder (12). A pH meter (10) is used to monitor the pH of the effluent from the pH control column.

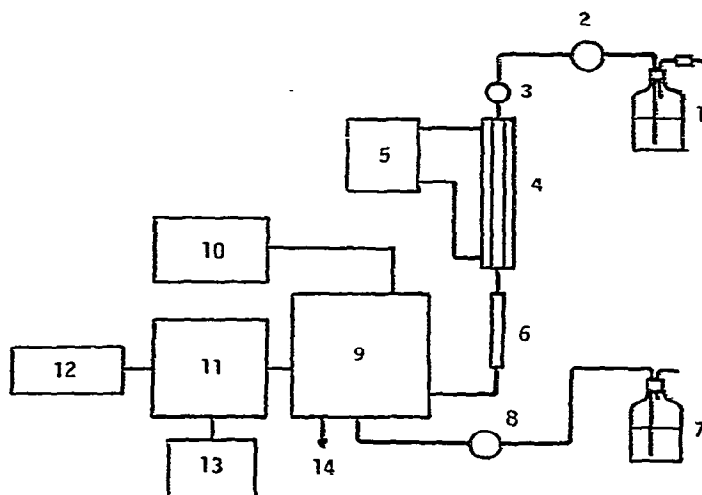


Fig. 2. Schematic diagram of the chromatographic system. 1 = Eluent; 2 = pump; 3 = sample injector; 4 = main column; 5 = circulating thermostat bath; 6 = pH control column; 7 = standard buffer solution; 8 = pump; 9 = electrode system; 10 = monitoring pH meter; 11 = high-sensitivity pH meter; 12 = recorder; 13 = digital voltmeter; 14 = waste.

## EXPERIMENTAL

### Columns

A strongly basic anion-exchange resin (Hitachi custom resin 2630,  $\text{Cl}^-$ , 16–20  $\mu\text{m}$ ) was packed into a glass column (180  $\times$  5 mm I.D.) and used as the main chromatographic column. The column was jacketed and circulated with water from the thermostat bath to maintain a temperature of 30°C.

The pH control column (100  $\times$  5 mm I.D., glass) was packed to half its height with a weakly acidic cation-exchange resin (Amberlite XE-64,  $\text{K}^+$ , 44  $\mu\text{m}$ ) and the  $\text{H}^+$  form of the same resin was packed on top of it.

### Solutions

Potassium chloride solution (0.2 and 0.3 M) containing 0.01 M potassium

hydroxide was used as the eluent. A mixed solution of 0.01 *M* phthalic acid and 0.01 *M* potassium hydrogen phthalate was used as the standard buffer solution in potentiometric detection. These two solutions were degassed under reduced pressure and stored in an incubator at 50°C.

Buffer solutions for calibration of the pH meters were supplied by Horiba (Kyoto, Japan).

### Detector

Two flow-through glass electrodes (Hitachi-Horiba Model 6901-25T) were used in the detection system as shown in Fig. 3 (5, 12). As a reference electrode, silver chloride electrodes (Hitachi-Horiba Model 2401-15T) (7, 14) were connected to the respective glass electrodes. The effluent from the column system was passed into the detection system from the right-hand side of Fig. 3. The solution first contacted with the effluent monitor electrode (5) which connected with the pH meter (Hitachi-Horiba Model F-7DE). Then the solution was mixed with the standard buffer solution, and driven into the second glass electrode (12) through a dropping insulator (11), which also worked as a mixer of the solutions. The glass electrode was connected to the high-sensitivity pH meter. The waste solution from the detector electrode was drained off through another dropping insulator (16). The whole assembly of the electrode system was placed in a thermostat chamber maintained at 25°C.

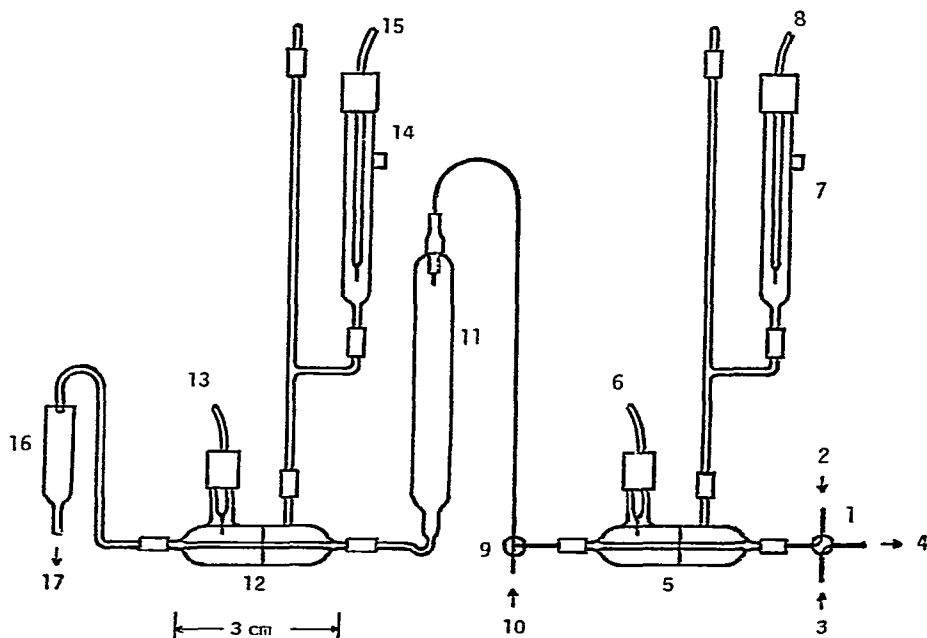


Fig. 3. Electrode system. 1 = Four-port valve; 2 = effluent from the column system; 3 = calibration buffers; 4 = waste; 5 = monitor electrode; 6 = output wiring of the monitor electrode; 7 = reference electrode for the monitor electrode; 8 = output wiring of the reference electrode; 9 = mixing joint; 10 = standard buffer solution; 11 = dropping insulator; 12 = detector electrode; 13 = output wiring of the detector electrode; 14 = reference electrode for the detector electrode; 15 = output wiring of the reference electrode; 16 = dropping insulator to waste; 17 = waste.

The high-sensitivity pH meter was specially designed for the potentiometric determination of pH deviation. The electrical circuit is shown in Fig. 4. The output of the glass electrode is converted into alternating current with a vibrating-reed condenser (VLC), and amplified with an amplifier with a junction-type field-effect transistor on its first stage. The amplified signal is rectified with a synchronous rectifier and output to a pen recorder (Hitachi Model QPD 33) and a digital voltmeter (Yokogawa Type 2805) through an integrating amplifier. Part of output signal was fed back to another terminal of the VLC. The integrating amplifier smoothed the signal and stabilized the feedback loop.

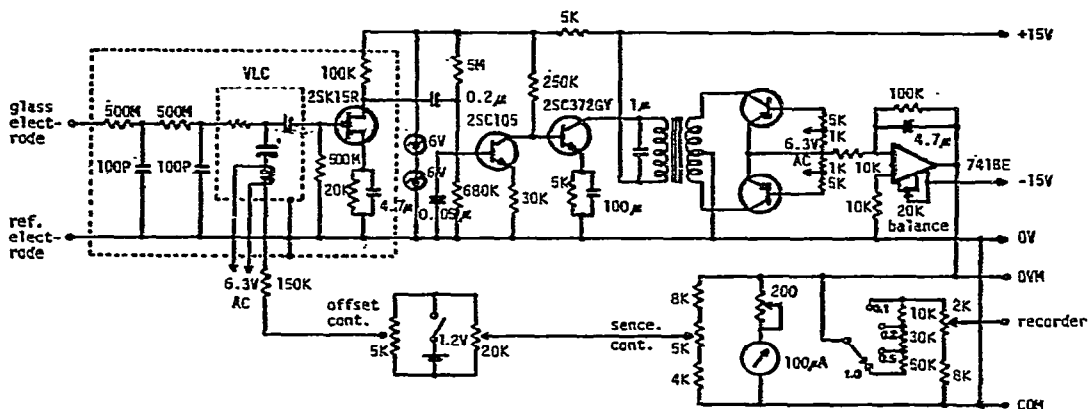


Fig. 4. Circuit diagram of the high-sensitivity pH meter. K = k $\Omega$ ; M = M $\Omega$ ;  $\mu$  =  $\mu$ F; P = pF.

### Pumps and valves

A plunger pump (Kyowa Seimitsu, Model KHU-W52) was used for pumping the eluent. A reciprocal pump (produced by Hitachi for an amino acid analyser) and a peristaltic pump (Tokyo Rikakikai, Type MP-2) were used to supply the standard buffer and the calibrating buffers, respectively.

A double-four-port valve (Kyowa Seimitsu, Model KMM-4V-2) was used as a loop injector to add samples to the chromatographic column. A four-port valve (Kyowa Seimitsu, Model KMM-4V) was inserted prior to the inlet of the electrode system to supply the calibration buffers to the glass electrodes.

### Methods

The monitoring pH meter was calibrated with buffer solution of pH 7 and 4 by the usual method. The high-sensitivity pH meter was adjusted with buffer of pH 4 and the standard buffer for detection itself so that the reading on the digital voltmeter was 100 mV/pH.

Samples were injected with a loop injector into the stream of eluent. The eluent and the standard buffer solution were supplied at the rate of 60 ml/h.

The resins used for the pH control column were regenerated after several experiments by washing with three volumes of 2 M hydrochloric acid, and converted into the appropriate forms if necessary.

## RESULTS AND DISCUSSION

*Example of chromatogram*

A typical example of the separation of aliphatic acids by the method described is shown in Fig. 5. Sample solution (500  $\mu$ l) containing 5  $\mu$ moles of each acids was injected; 0.2 M solution was used as the starting eluent, and changed to 0.3 M after 24 min.

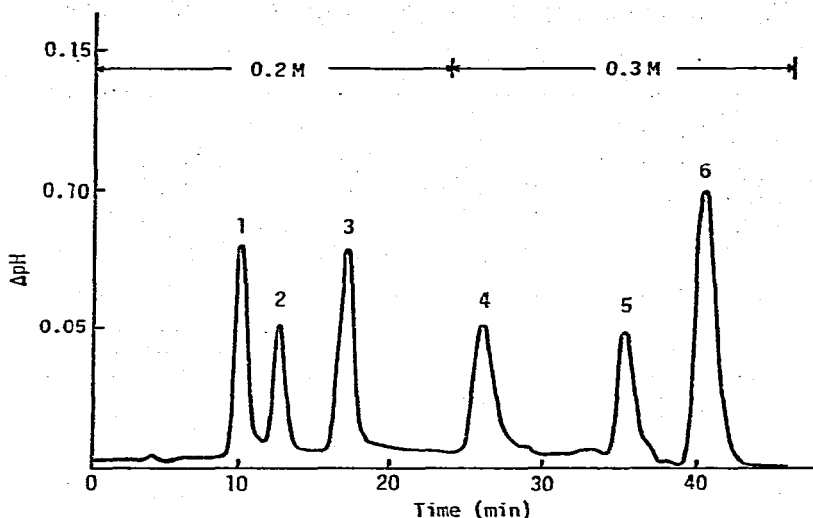


Fig. 5. Chromatography of aliphatic acids. Main column: 180  $\times$  5 mm I.D., Hitachi custom resin 2630 ( $\text{Cl}^-$ ). pH control column: 100  $\times$  5 mm I.D., Amberlite XE-64 ( $\text{H}^+$  50 mm +  $\text{K}^+$  50 mm). Eluent: 0.2 M KCl (0–24 min) and 0.3 M KCl (24–45 min), both containing 0.01 M KOH. Temperature, 30°C, flow-rate, 60 ml/h; pressure, 3.5 MPa. Peaks: 1 = acetic acid; 2 = formic acid; 3 =  $\text{CO}_3^{2-}$ ; 4 = succinic acid; 5 = oxalic acid; 6 = citric acid.

*Effect of variation of flow-rates of solutions*

It can be predicted from eqn. 4 that variation of the flow-rates of the effluent and the standard buffer solution affects the response of the detector and leads to noise or drift on the chromatogram. Constancy of the flow-rate should, therefore, be more strictly maintained in this method than in other methods. However, the short-period pulses from the plunger pump did not have any observable effect on the detection. Rather long-period changes in flow-rate led to a small amount of noise on the chromatogram, but this could be overcome by using an air damper.

*Effect of temperature*

The electromotive force of the glass electrode varies with temperature according to the Nernst equation. When the detector electrode was placed in a thermostat chamber, however, variations in room temperature had no effect on the output.

*Noise from electrical circuits*

Because the thermal noise from high-impedance circuits around the glass electrode is estimated to be of the order of microvolts, it can be neglected. Noise from

the transistor circuits can be depressed to levels below the sensitivity of the detector system by use of a low-noise junction-type field-effect transistor on the first stage of the amplifier.

*Life of the pH control column*

About 250 ml of the effluent could be treated with one batch of the above column. As significant drift was observed in the initial stage of the life of the column, conditioning for 30 min or more is desirable. The exhausted resins were regenerated and recycled as described previously.

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REFERENCE

- 1 S. Egeshira, *Bunseki Kagaku (Jap. Anal.)*, 15 (1966) 1356.