# A DERIVATIVE METHOD IN ION EXCHANGE CHROMATOGRAPHY

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As is well known, recording of the elution curve in ion exchange chromatography has been carried out by means of spectrophotometry, (as in the amino acid analyser developed by MOORE AND STEIN), by polarography (*e.g.* as extensively utilized by KEMULA's school), by measurement of radioactivity and by other methods. The application of measurement of the electrical conductance has been studied by several authors[1-4].

If the electrical conductance of the effluent is directly recorded, a signal appears as the sample component comes out of the column outlet. However, since the eluting agent generally also has a considerable conductance, the background deflection of the recorder is prominent and hence the signal–noise ratio is generally low.

In the present study an attempt was made to apply the derivative methodology[5,6] which was developed successfully in gas chromatography, and to record automatically not only the ordinary elution peak but also its derivative curve in ion exchange chromatography at a low noise level.

## EXPERIMENTAL

### Principle

The liquid flow diagram is shown in Fig. 1. The pair of conductance cells $C_1$ and $C_2$ form two arms in a Wheatstone bridge, as shown in Fig. 2, and records the ordinary elution peak. Since there is a dead space of appropriate volume between the two conductance cells $C_3$ and $C_4$, when the pair is connected into the Wheatstone bridge as shown in Fig. 2, one can easily record the absolute value of the difference in the conductances in the cells $C_3$ and $C_4$.

### Apparatus

The ion exchange column and the conductance cells employed in the present study are illustrated in Fig. 3. A glass cylinder is connected to the outlet of the main column by a rubber tube. Six platinum wires in a ladder form are sealed into the cylinder, as shown in Fig. 3. Any electrodes can be used as $C_2$, $C_3$ and $C_4$. Another pair of platinum wire electrodes dipped into the same eluant in a stationary vessel, serve as the cell $C_1$.

The oscillator supplied an alternating voltage of 4 V and 1000 Hz. The recorder was a Yokokawa instrument and was used with a chart speed of 20 cm h$^{-1}$ with suitable sensitivities.
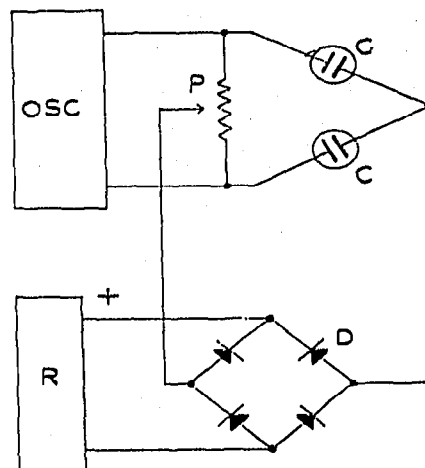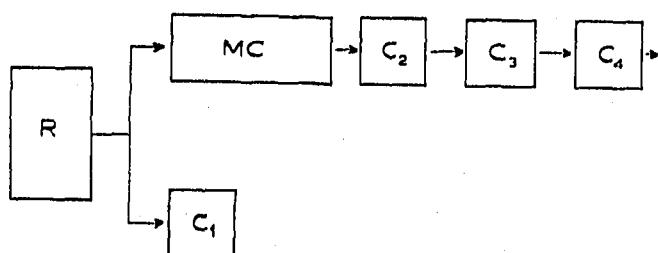
Fig. 1. Flow diagram for derivative liquid chromatography. R = eluant reservoir; MC = main column for separation containing ion exchanger; $C_1$ and $C_2$ = conductance cells for recording the normal peak; $C_3$ and $C_4$ = conductance cells for recording the derivative curve.

Fig. 2. Circuit for recording the conductance difference. OSC = low frequency oscillator; C = a pair of conductivity cells; P = potentiometer, 5 k$\Omega$; D = four-diode full-wave rectifier; R = recorder.

## Reagents

All chemicals were reagent grade. The ion exchanger was Amberlite CG 120, 100 mesh, conditioned as usual.

## RESULTS AND DISCUSSION

The resin was used in the ethylenediammonium form. Cupric ion solution was poured on to the column and eluted with an aqueous solution of 0.1 $M$ ethylene-
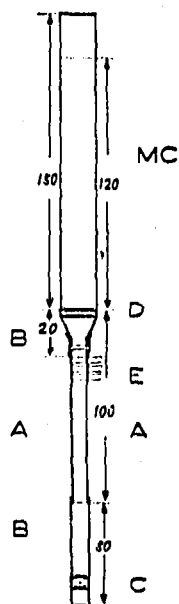
Fig. 3. Ion exchange column and conductance cell assembly. MC = main column, length 12 cm, inner diam. 6 mm; D = diaphragm; A = conductance cell cylinder, inner diam. 3 mm; B = rubber tube for connection; C = tube clip; E = six platinum wire electrodes sealed 10 and 5 mm apart alternatively. Figures show the size in mm.

diamine hydrochloride at a rate of 0.3 ml/min at room temperature. The temperature of the liquid varied in the range $20° \pm 1°$.

Use of ethylenediammonium chloride as an eluant for zinc(II) and lanthanum (III) has been reported by FRITZ AND KARRAKER[7]. In the present study 0.2 $\mu$mole of copper(II) ion was investigated. The result is shown in Fig. 4. The maximum of the ordinary curve A corresponds to the cut-in in the full-wave rectified derivative curve B and the two inflection points in curve A appear now as maxima in curve B.
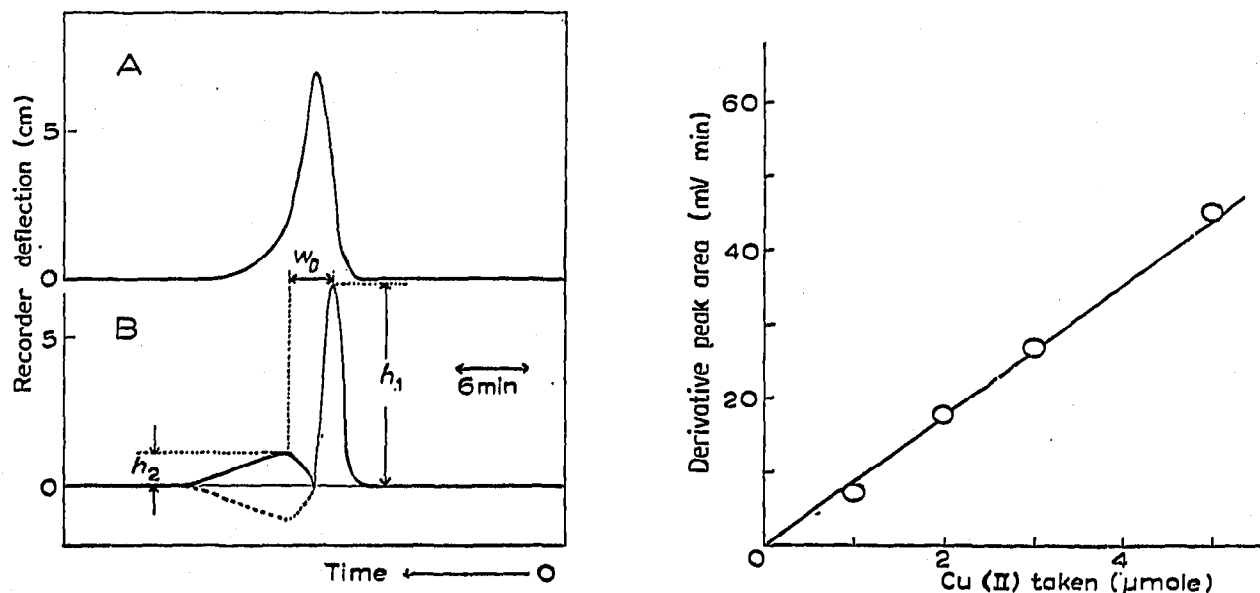


Fig. 4. Comparison of the ordinary elution peak (curve A) and its full-wave rectified derivative curve (curve B). The theoretical derivative curve is given by the dashed line. Curves A and B were recorded with the aid of the pair of conductance cells $C_1-C_2$ and $C_3-C_4$, respectively.

Fig. 5. Calibration curve for Cu(II) ion eluted by 0.1 $M$ ethylenediamine hydrochloride. The sum of the derivative heights $h_1$ and $h_2$ multiplied by the derivative width $w_D$ is plotted against the absolute amount of Cu(II) taken.
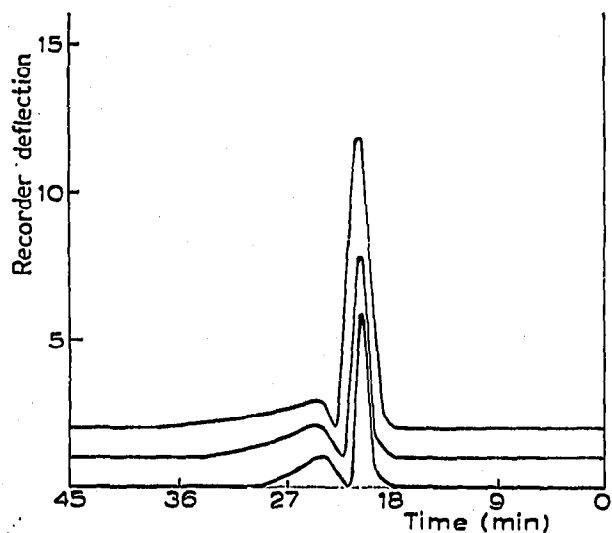


Fig. 6. Variation of the derivative chromatograms with the amount of Cu(II) taken. From upper to lower curves the Cu(II) amounts eluted are 5, 2 and 1 $\mu$mole and the recorder sensitivity is 500, 100 and 50 mV per 25 cm full-scale.

The horizontal distance $w_D$ between the maxima in the derivative curve in Fig. 4 may now be defined as the derivative peak width, and the two vertical heights $h_1$ and $h_2$ at the maxima in the derivative curve correspond to the slopes at the inflection points in the ordinary elution curve.

In Fig. 5 the calibration curve obtained by the derivative method is shown. The derivative chromatograms recorded for the construction of the calibration curve are shown in Fig. 6.

SUMMARY

A new method for the automatic recording of the elution curve in ion exchange chromatography is proposed. It is shown that measurement of the difference in the electrical conductances at the inlet and outlet of the column provides the recording of the ordinary elution curve. The same measurement of the difference across a dead space at the column outlet makes it possible to record the full-wave rectified derivative curve of the elution curve. The derivative method gave a calibration curve of good linearity in an experiment using cupric ion eluted with ethylenediamine hydrochloride.

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