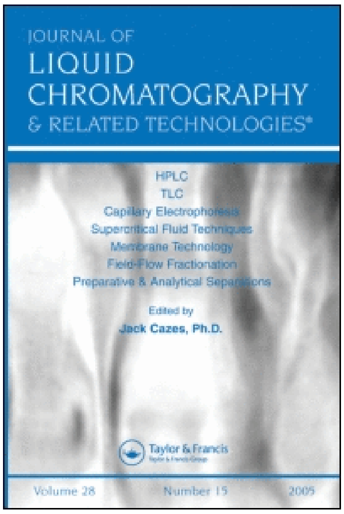

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Ion Chromatography Using an Electrochemical Detector: Response to Non-Electroactive Anions

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ION CHROMATOGRAPHY USING AN ELECTROMECHANICAL DETECTOR : RESPONSE TO NON-ELECTROACTIVE ANIONS

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ABSTRACT

The effect of non electroactive anions on the response of glassy carbon electrode used as an electrochemical detector in an ionic chromatographic system with dual column has been investigated and a method to eliminate this anomalous behaviour has been proposed. The results showed that the response of the electrode observed for non electroactive anions is related to the drop in pH of the eluent during the elution of anions.

INTRODUCTION

Electroactive anions, at low concentrations, may be determined selectively by coupling an electrochemical detector to a conductivity detector in ion chromatography. This makes the technique more versatile. However, the electrochemical detector was found to respond to non electroactive anions such as nitrate and sulphate and to produce current signals which interfere with electroactive anion signals.

This phenomenon was first observed by Tarter(1,2) and was attributed to the variations in the eluent pH during the elution of anions. Based on this observations, Tarter(2) has proposed a method for determining non electroactive anions using an electrochemical detector. Silver electrode was used as the electrochemical detector.

In this paper, a glassy carbon has been used as the working electrode. The effect of pH on the response of glassy electrode has been studied by several authors(3-7).

The results of these studies showed the presence of surface groups having acid-base properties similar to those exhibited by quinones (reversible system) or other carbon-oxygen functionalities (irreversible system)(5). The nature and number of sites were found to depend on the physical structure of the electrode surface. In addition, these functional groups may affect the kinetics of electrochemical reactions, thereby modifying the working range of the electrode. Gunasingham and Fleet(7) have also used glassy carbon as a pH electrode.

The results of Tarter and Gunasingham seem to suggest that the oxidation currents observed for non electroactive anions on a glassy carbon electrode is most probably due to a drop in eluent pH during elution of anions.

In this paper, the behaviour of non electoactive anions at the glassy carbon electrode and a method for eliminating the anomalous signals observed in the chromatograms have been investigated. A chromatography system with a suppressor column as described elsewhere(8,9) was employed for this study. The relationship between the change in eluent pH during anion elution and the electrochemical response has also been established.

APPARATUS

- Analytical column (250x4.6 mm) and precolumn (50x4.6 mm) packed with Zipax-SAX anion exchange resin
- suppressor columns (150x4.6 mm) packed with AG-50W-X12 cation exchange resin
- Knauer pump 64.00 equipped with a pulse dampener
- An eluent flow rate of 3 ml/min was used
- Rheodyne 7125 injection valve with a 200 μl loop
- Wescan 213 conductivity detector
- Metrohm potentiostat VA 641; applied potential: +1.1V with respect to Ag/AgCl/3MKCl reference electrode
- Hewlett-Packard integrator 3390A for processing the signals from the potentiostat.

REAGENTS

All solutions were prepared with demineralized water. 1.4×10^{-3}M succinic acid whose pH was adjusted to 7.0 with KOH was used as the eluent. Anion standards were prepared from Merck reagent grade potassium salt solutions.

The suppressor column was regenerated by the passage of 50 ml of 0.5M of HNO_3 followed by 200 ml water.

RESULTS AND DISCUSSION

The electrochemical detector showed response to anions which are not electroactive, under the experimental conditions used, at concentrations above 10^{-5}M. The retention times of the test anions were identical to those observed with conductivity detector (fig.1).

The effect of anion concentration on the response of electrochemical detector are shown in figures 2 and 3, where peaks

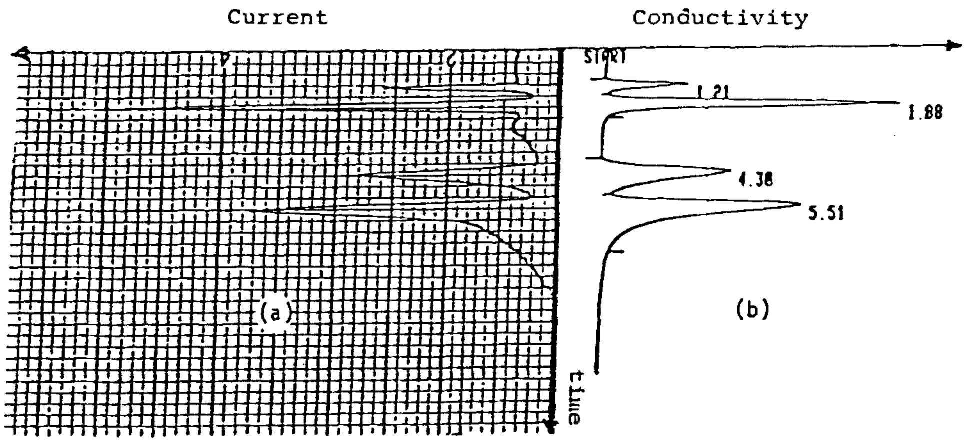

FIGURE 1: Response of (a)electrochemical and (b)conductivity detectors to 5×10^{-4}M chloride, nitrate and sulfate ions; retention time: Cl^- 1.88 min; NO_3^- 4.30 min; SO_4^{2-} 5.51 min.

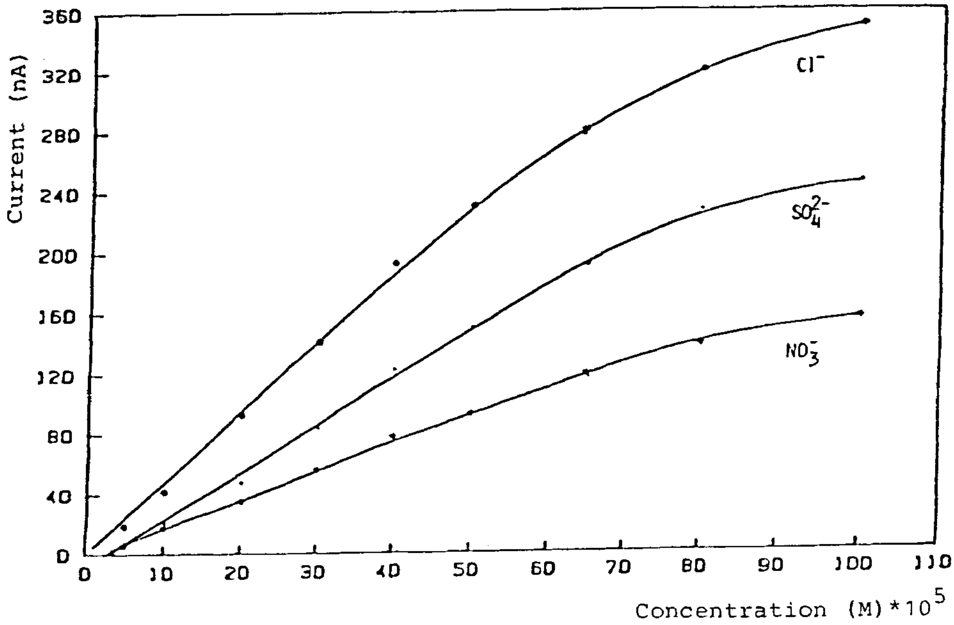

FIGURE 2: Relationship between peak currents (peak height) and the concentration of test anions like chloride, nitrate and sulfate.

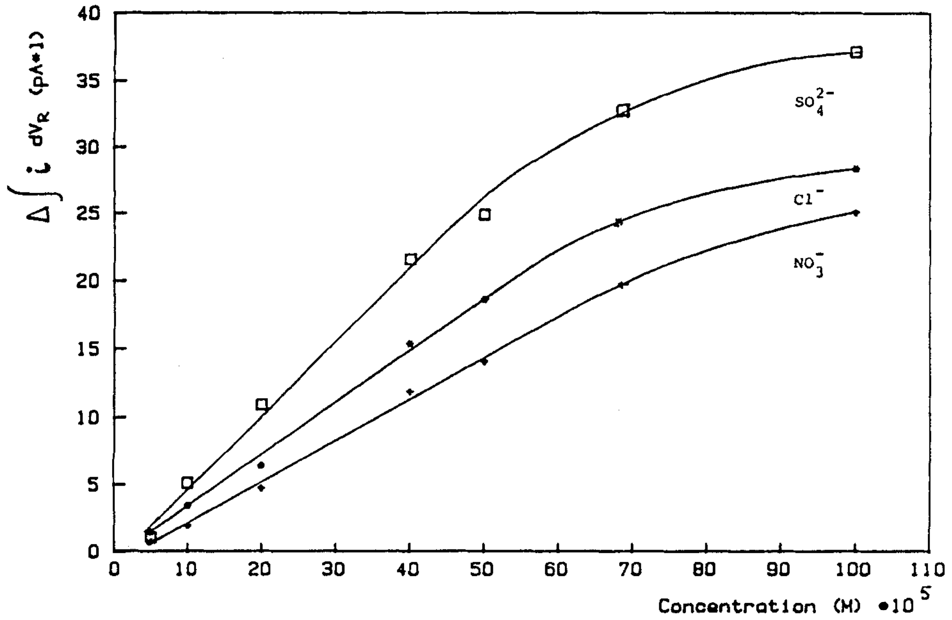

FIGURE 3: Integration of current vs retention volume (V_R) (peak area) plotted vs concentration of anions as chloride, nitrate and sulfate.

currents (peak height) and quantity of electricity (peak area) versus anion concentration are plotted respectively. It can be seen that the plots are linear over a small range of concentration i.e. slightly less than a decade concentration.

Elimination of the non electroactive anions effect at the electrochemical detector

The presence of high concentrations of anions that are not electroactive, causes serious interferences in the determination of electroactive anions such as nitrite. Hence these interferences must be eliminated prior to the determination of nitrite. One way of suppressing this is to add a buffer solution to the sample under investigation, at the outlet of the conductivity cell i.e. before the sample enters the electrochemical cell. Acetic acid/acetate buffer (pH 3.6) was chosen for this purpose. The pH indicated corresponds to the pH measured at the conductivity cell outlet. A flow rate of 1 ml/min was used. Acetic acid/acetate buffer was selected because it is electroinactive, under the experimental conditions used, and has a high buffer capacity. In order to determine the optimal buffer concentration, its concentration was varied over the range $2x10^{-1}$ to 1M. The results indicated that interferences due to electroactive anions at concentrations lower than 10^{-3}M may be eliminated by using $5x10^{-1}\mu$ buffer solution. Typical chromatograms obtained before and after the addition of buffer are shown in fig. 4.

In order to ascertain that acetic acid/acetate buffer does not interfere in the determination of electroactive anion such as nitrite, NO_2^- calibration curves were constructed in the presence and absence of the buffer acetate. It is apparent from fig. 5 that acetate buffer does not interfere in nitrite determination over the studied concentration range. It must be pointed out that the introduction of buffer produces a dilution of the test anion concentration of the sample and under our experimental conditions the dilution factor was 1.33.

Relationship between changes in pH and the electrochemical detector response

The effect of pH variations on the response of electrochemical detector was studied. This was done by computing the difference in the eluent pH between the base line and chromatographic peak of the test anion.

In a dual column ion chromatographic system, the eluent is found in the acid form after the passage through the suppressor column. The proton concentration at the outlet of the suppressor column may be evaluated from the eq.(1)

$$|H^+|_E = I_{HE} \times C_E \qquad (1)$$

where I_{HE} is the degree of dissociation of the acid form of the eluent HE and C_E is its total concentration; I_{HE} may be computed in the following way:

$$K_E = \frac{|H^+| x |HE|}{|H_2E|} \tag{1a}$$

$$I_{HE} = \frac{|HE|}{C_E} \tag{1b}$$

$$C_E = |H_2E| + |HE| \tag{1c}$$

Combining eqs. (1a),(1b), and (1c) and rearranging yields:

$$I_{HE} = \frac{\{-K_E + (K_E{}^2 + 4K_E x C_E)^{1/2}\}}{2xC_E} \tag{1d}$$

$pK_E = pK_{a1}$: the first acid dissociation constant of the eluent. Proton concentration at the maximum of chromatographic peak was calculated from equation (2) after modification of equation (11) given in reference 10:

$$|H^+|_E{}^A = I_{HE}{}^A x(C_E - C_E') + nxC'_A \tag{2}$$

where $I_{HE}{}^A$ is the degree of dissociation of the eluent in the presence of anion, the latter being associated with H^+. $I_{HE}{}^A$ is given by equation (2a) after modification of equation (19) given in reference 10:

$$I_{HE}{}^A = \frac{-nxC'_A - K_E + \sqrt{(nxC'_A + K_E)^2 + 4xK_E x(C_E - C'_E)}}{2x(C_E - C'_E)} \tag{2a}$$

where C'_A is the true concentration of the test anion and corresponds to the concentration when the detector signal is at its maximum (i.e. maximum of the peak). C'_A is given by:

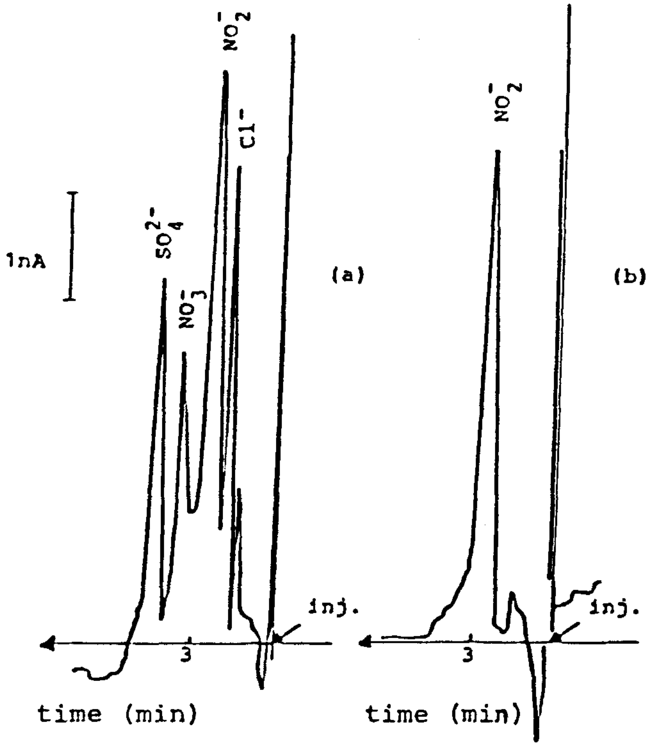

FIGURE 4: Chromatograms of nitrite (1.4×10^{-7}M) in the presence of 10^{-4}M of chloride, nitrate and sulfate; (a)without the buffer and (b)with a buffer: 5×10^{-1}M CH_3COOH/CH_3COONa pH=3.6.

$$C'_A = \frac{C_A}{\{V_R/V_0 x 2/N\}} \qquad (2b)$$

where C_A is the initial concentration of the test anion, V_R is given by V_R=t_RxD; t_R and D being the retention time (min) and flow rate of the eluent (ml/min) respectiviely. $N=5.54x(t_R/\delta)^2$; δ is the peak half width (min) and V_0 is the volume injected (ml).

C'_E is the total concentration of eluent fixed on the resin of the analytical column at the time of elution of the test anion.

The proportion of the eluent as E^{2-} and E^{-} in the analytical column depends on the pH of the eluent solution. During the elution of test anions, the sites left vacant by leaving anions are occupied by either HE^{-} or E^{2-}. The former occupies one site whereas the latter two sites. C'_E may be therefore expressed as:

$$C'_E = C'_{HE^-} + C'_{E^{2-}} \qquad (3)$$

where C'_{HE^-} and $C'_{E^{2-}}$ are the concentrations of HE^- and E^{2-} fixed on the resine.

From the stoechiometry of the reaction:

$$nxC'_A = 2xC'_{E^{2-}} + C'_{HE^-} \qquad (4)$$

Assuming that the affinity of E^{2-} for the resin is twice as that of HE^- and that the amount of this anions fixed on the resin is proportional to their initial concentrations, then:

$$\frac{C'_{E^{2-}}}{C'_{HE^-}} = \frac{C_{E^{2-}}}{C_{HE^-}} x2 = \frac{I'_{E^{2-}}}{I'_{HE^-}} x2 \qquad (5)$$

where I' is the calculated degree of dissociation of the eluent at a given pH.

Combining equations 4 and 5 and rearranging one obtains:

$$C'_{HE^-} = \frac{nxC'_A}{\{(I'_{E^{2-}}/I'_{HE^-})x4\}+1\}} \qquad (6)$$

$$C'_{E^{2-}} = \frac{nxC'_A}{\{(I'_{HE^-}/I'_{E^{2-}})x2\}+2\}} \qquad (7)$$

Hence the variation in H^+ concentration is given by $|H^+|_E^A - |H^+|_E$. The drop in pH at the chromatographic peak (maximum) as a function of the concentration of various anions were calculated from the experimental data used for figure 2. Plots of ΔpH versus the concentration of various anions (Cl^-, SO_4^{2-} and NO_3^-) are shown in fig.6.

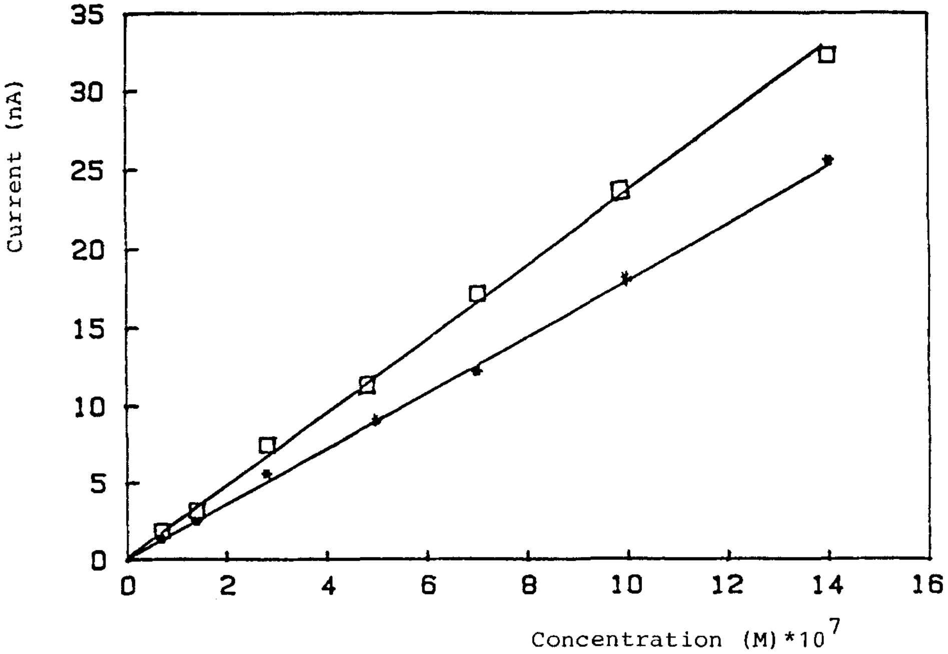

FIGURE 5: Calibration curve for nitrite (*) in the presence of buffer and (□) absence of buffer.

The drop in pH was also measured experimentally for five different concentrations of chloride anions. A comparison of the theoretically calculated ΔpH values with those of the experimentally measured ones (Table 1) shows that there is a good agreement indicating the validity of the derived mathematical expression for ΔpH (eq. 1 and 2)

As expected, the amount of protons released by sulphate was found to be almost twice that monovalent anions (NO_3^- and Cl^-; fig. 3). The wider differences between the values observed in the case of chloride compared to nitrate ions may be attributed to an systematic error in the integration of the peaks. The peak of chloride is narrow whereas that of nitrate and sulphate are relatively wider.

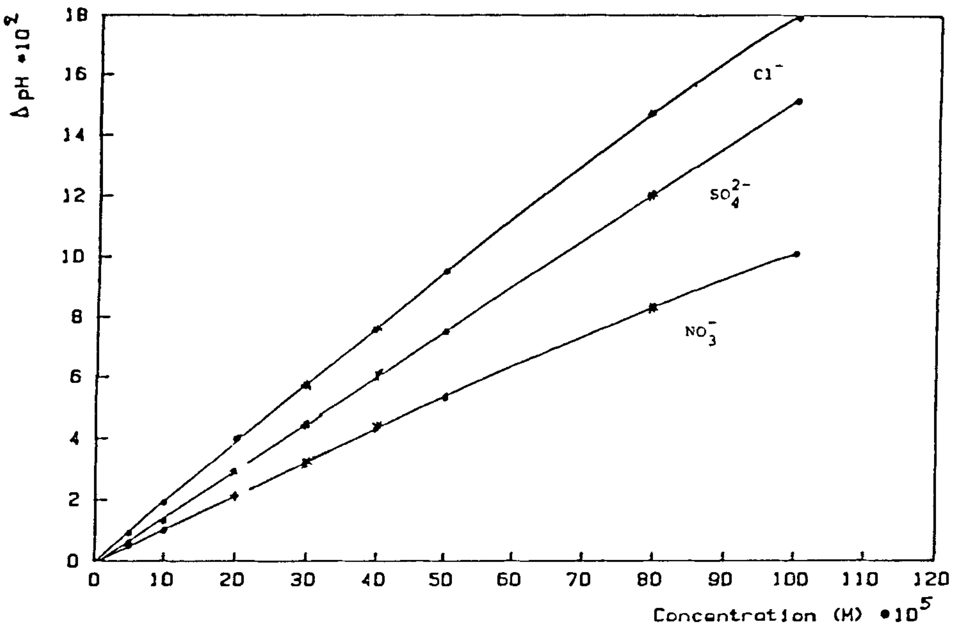

FIGURE 6: Drop in pH at the peak (pH) vs concentration of anions chloride, nitrate and sulfate; pH calculated using eqs (1) and (2); pK_E=4.19 succinic acid.

Concentration (M)	ΔpH measured	ΔpH calculated
2.00×10^{-4}	0.03	0.04
3.00×10^{-4}	0.05	0.06
5.00×10^{-4}	0.08	0.09
7.00×10^{-4}	0.11	0.11
1.00×10^{-3}	0.15	0.14

The position of the anions NO_3^-, Cl^- and SO_4^{2-} are identical in the plots of current (fig. 2) and pH (fig. 6) versus anion concentration. The intensity of the signal is dependent on the effective concentration of the anion at the maximum of the peak, hence their values are influenced by the peak widths. For instance $5x10^{-5}M$ solutions of chloride, nitrate and sulphate exhibit the following half peak widths: Cl^-:0.27 min; NO_3^-:0.5 and SO_4^{2-}:0.75 min.

It should be noted that the current signals observed for non electroactive anions may be either capacitive (due to double layer) or Faradaic (redox reactions of quinones present at the electrode surface). These two types of currents may be distinguished by the A.C. method, but as the measured currents were so small (<μA) it was not possible to make a.c. measurement.

CONCLUSION

The behaviour of non electroactive anions at the glassy carbon electrode was analogous to that found at the silver electrode using a HPLC system with a suppressor column. A comparison of the variation in pH during elution of anions with that of the peak current of the anion reveals that the anomalous behaviour of electroactive anions is influenced by ΔpH. These interferences may be eliminated by adding a buffer to the eluent solution before entering the electrochemical cell.

The use of the anomalous behaviour of anions for the determination of the non electroactive anions using an electrochemical detector does not seem to offer any particular advantage over the conventional conductivity detector. The sensitivity of the electrochemical detector is roughly the same as that of conductivity detector. Moreover the domain of linearity of current vs concentration is smaller than that of conductivity detector.

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