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## ION CHROMATOGRAPHY WITH POTENTIOMETRIC DETECTION

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### SUMMARY

A new potentiometric detection system was designed and investigated. A silver wire, coated with a sparingly soluble silver salt, and a reference electrode served as detector, which proved to be more sensitive to halide and thiocyanate ions than the conductometric detector commonly used in ion chromatography. The dependence of the detector's peak potential on the concentration of the injected ions, on the solubility products of the latter with silver ions and on the properties of the electrode coating are discussed.

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### INTRODUCTION

In ion chromatography, the conductometric detector is undoubtedly the most easily operated and consequently the most commonly used kind of detector. Its output depends on the difference between the conductivity of the eluent and that of the eluent containing the dissolved sample; the conductivity of the sample may be several orders of magnitude lower than the conductivity of the eluent alone.

Three principal ways have been suggested in order to overcome, or compensate for, the high background conductivity of the eluent: (a) the introduction of a suppressor column<sup>1</sup>; (b) electronic compensation<sup>2</sup> and (c) the use of low-conductivity eluents<sup>3,4</sup>. Potentiometric detection, with an ion-specific electrode as indicator, has also been suggested<sup>5</sup>, but its applicability is limited to only one ion at a time. A variety of ions can, however, be detected with this means, depending on the type of electrode used and its sensitivity to the interference caused by other ions present.

In this work the possibility was explored of using a novel kind of potentiometric detector, in which a silver wire coated with a sparingly soluble silver compound serves as detecting electrode for halide and thiocyanate ions. The electromotive force of such a detector depends on the logarithm of the concentration of the emerging ions. It will be shown that this system produces very stable baselines and sharp peaks and that it is sensitive even to small quantities of the ions to be determined.

### EXPERIMENTAL

The chromatographic system used consisted of modular units as shown in Fig.

1. Its main parts are: pump, pressure gauge, sample injection valve and conductivity monitor. These were all purchased from the Wescan Co.

The potentiometric detector was designed and constructed by Dr. Ch. Yarnitzky, Department of Chemistry, Technion, Haifa. The flow cell consisted of a combined pH electrode, the Ag/AgCl part of which served as a reference electrode. The indicator was a 0.5-mm silver wire which was coated with the eluent ions. The coating was carried out in a small electrolytic cell, with a silver wire as anode and a platinum wire as the cathode. The wires were immersed in the eluent solution ( $5 \cdot 10^{-3} M$ ), and a voltage of 6 V was applied for 1 h. This voltage was adjusted to the point at which the evolution of gas bubbles was observed. The precise assembly of the electrodes in the chromatographic system is shown in Fig. 2.

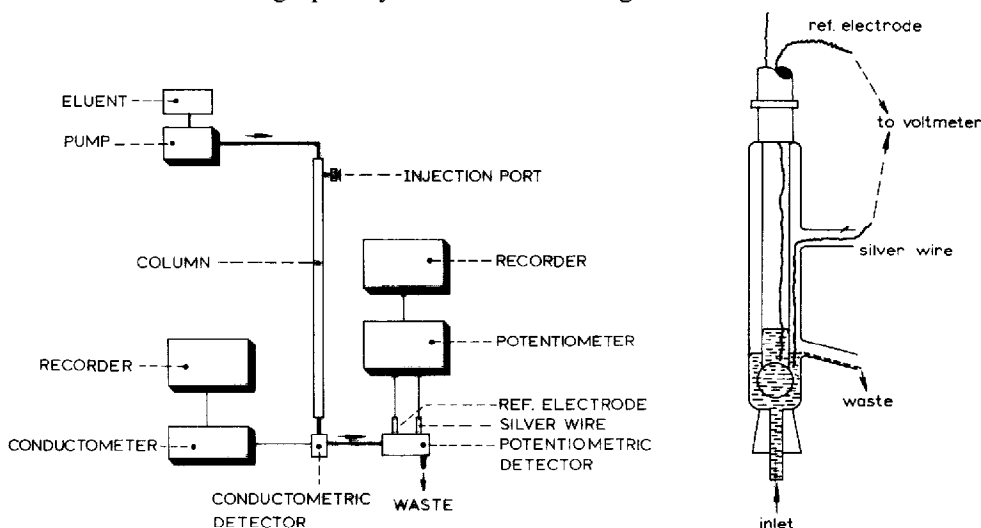


Fig. 1. Schematic diagram of the ion chromatographic system with a conductometric and a potentiometric detector.

Fig. 2. Flow cell for the potentiometric detection of ions in the chromatographic system.

In all experiments the separator column ( $250 \times 4.6$  mm) was filled with Vydac SC 302 anion exchanger (The Separations Group, Hesperia, CA, U.S.A.), bead size  $30\text{--}44 \mu\text{m}$ , capacity  $0.1$  mequiv./g. Other conditions: sample injection volume,  $100 \mu\text{l}$ ; flow-rate,  $2\text{--}2.5$  ml/min; paper speed,  $3$  cm/min.

Stock solutions of  $10^{-2} M$  each of  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$  and  $\text{SCN}^-$  were prepared from analytical grade reagents dissolved in high-purity water. As eluent, a stock solution of  $5 \cdot 10^{-3} M$  salicylic acid in high-purity water, adjusted to pH 4.12, was prepared.

## RESULTS AND DISCUSSION

### *Comparison between conductometric and potentiometric detectors*

The main limitation of the conductometric detector is its non-specificity, whereas the silver electrode used in the potentiometric detector is particularly sensitive to those anions which form sparingly soluble salts with silver ions. Because of this non-specificity, the background conductivity is very sensitive to changes in concentra-

tion, pH and temperature, and any change in the working conditions will disturb the stability of the baseline.

Many anions have similar equivalent conductances ( $60\text{--}80\text{ cm}^2/\Omega \cdot \text{equiv.}$ ); and ions that are strongly retained, such as  $\text{I}^-$  or  $\text{SCN}^-$ , produce broad, spread-out chromatographic peaks because of dilution effects, since their elution requires comparatively large amounts of eluent. In order to improve the peaks indicative of strongly held ions the concentration of the eluent must be increased; but this is in contradiction to the requirements for conductometric detection (without suppression), viz. that the concentration of the eluent should be close to that of the injected ions, since otherwise the background conductivity would be too high. With a potentiometric detector, on the other hand, the eluent concentration may be in any range that will result in relatively short retention times and good resolution.

In Fig. 3 two chromatograms of the same ions are shown, recorded under closely similar conditions of pH and eluent concentration. The difference between the two outputs is quite obvious. The first chromatogram (a) has an injection peak, a high chloride peak and a lower bromide peak, while iodide and thiocyanate ions are not seen at all. This is due to dilution effects caused by long retention times. The negative peak after the bromide is that of undissociated salicylic acid. A striking feature of the second chromatogram (b) is that the bromide peak is much higher than that of  $\text{Cl}^-$ . This is due to the lower solubility product of  $\text{AgBr}$  which causes a large shift in the electrode potential. The iodide peak should be even higher, but it is not because of its

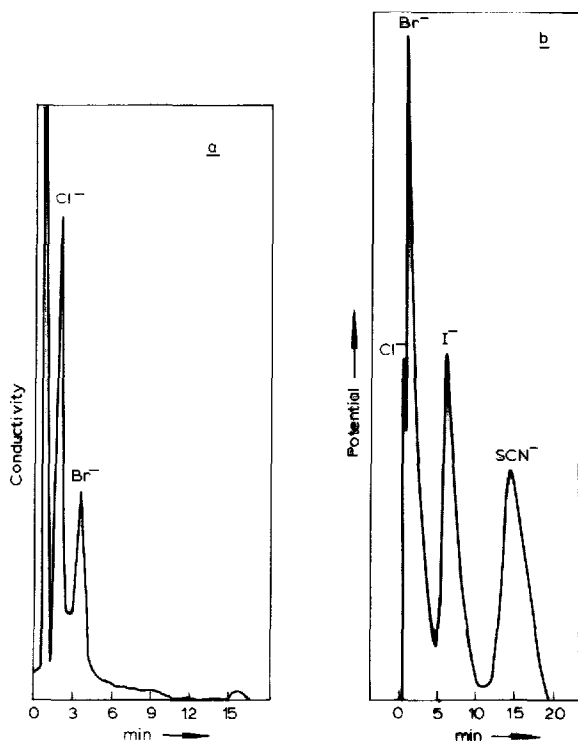


Fig. 3. Comparison of chromatograms: a, conductometric detection; b, potentiometric detection. Eluent:  $10^{-3}\text{ M}$  salicylic acid, pH 4.12. Flow-rate: 2.4 ml/min. Ion concentrations: 50 ppm each.

longer retention time. Nevertheless, the peaks of  $I^-$  and  $SCN^-$  are well defined and can be determined with good accuracy. The resolution between  $Cl^-$  and  $Br^-$ , in chromatogram (b), can be greatly improved by reducing the eluent concentration from  $10^{-3} M$  to  $5 \cdot 10^{-4} M$ , the baseline remaining unaffected.

#### *The silver electrode coating*

The response of the indicator electrode in the potentiometric system depends very much on the silver salt with which the silver wire is coated. In Fig. 4 two chromatograms of chloride ions, obtained with two different coatings, are shown, using the same eluent concentration and pH conditions ( $5 \cdot 10^{-3} M$  salicylic acid at pH 4.12). In the first chromatogram (a) a silver wire coated with silver chloride is used as indicator electrode. Chloride injections of 10 and 100 ppm are shown. The peaks are broad, the baseline is not well defined and a tailing effect is evident. The salicylate ions in the eluent compete with the chloride ions on the electrode, as a result of which the concentration of silver ions changes continuously, making it very difficult to achieve steady state conditions. This is the reason why the difference between the EMFs at the peak elution volumes of 10 and 100 ppm, respectively, is only 42 mV, which is quite far from a Nernstian slope. The second chromatogram (b), on the other hand, recorded with the aid of a salicylate ion-coated indicator electrode, shows much sharper peaks and the baseline is well defined. The reason is that the anions are common to the eluent and the electrode coating, leading to the very rapid establishment of steady state conditions. With this coating the potential difference between 10 ppm and 100 ppm  $Cl^-$  is only 32 mV, due to the strong competition between chloride

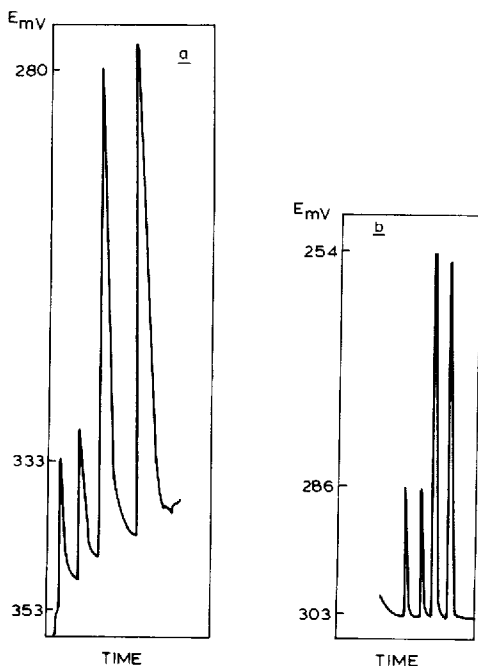
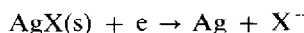


Fig. 4. Comparison of potentiometric detection chromatograms using different electrode coatings: a, chloride coating; b, salicylate coating. Ion injected: chloride ion, 10 ppm and 100 ppm. Eluent:  $5 \cdot 10^{-3} M$  salicylic acid, pH 4.12.

and salicylate ions. Nevertheless, the correlation between EMF and  $\log C$  is linear, although the slope is not Nernstian. Experimentally this system, featuring a silver electrode coated with salicylate ions and using salicylic acid (in various concentrations) as eluent has proved to be very useful in the determination of halide and thiocyanate ions.

#### *Relation between electrode potential and concentration*

A silver electrode coated with a sparingly soluble silver salt,  $\text{AgX}$ , is a second-degree electrode, the potential of which may be expressed as follows:



$$E = E_{\text{AgX}}^0 - \frac{RT}{F} \ln a_{\text{X}^-}$$

$$E_{\text{AgX}}^0 = E_{\text{Ag}/\text{Ag}^+}^0 + \frac{RT}{F} \ln K_{\text{sp}(\text{AgX})}$$

In a dynamic system where  $\text{X}^-$  (salicylate ions in the present case) constantly flows through the electrode, a steady state is established, which in turn will maintain a certain concentration of  $\text{Ag}^+$  on the surface of the electrode. The concentration of  $\text{Ag}^+$  can be calculated from the experimental data shown in Fig. 4b, the baseline potential being 303 mV, the potential of the reference electrode 224 mV and the standard potential of silver 799 mV:

$$E = E_{\text{Ag}/\text{Ag}^+}^0 - E_{\text{ref.}}^0 + \frac{RT}{F} \ln[\text{Ag}^+]$$

$$\log[\text{Ag}^+] = \frac{E - E_{\text{Ag}/\text{Ag}^+}^0 + E_{\text{ref.}}^0}{0.059} = -4.61$$

When the eluent consists of  $5 \cdot 10^{-3} M$  salicylic acid, at pH 4.12, and the indicator electrode is a silver wire coated with silver salicylate, the concentration of free silver ions is  $10^{-4.6} M$ . This concentration is lower than that calculated from the solubility product ( $K_{\text{sp}} \approx 10^{-7}$ ) because of the common-ion effect. If, now, another anion,  $\text{Y}^-$ , which forms a sparingly soluble salt with silver ions, is injected into the chromatographic system, the concentration of free silver ions will change and will depend on the solubility product of  $\text{AgY}$  compared with silver salicylate, and on mass transfer effects. The EMF of the system will change accordingly.

The quantitative interpretation of elution peaks with a potentiometric detector is different from that of a linear concentration-dependent detector, such as the conductivity detector. With the latter the half-peak height is related to half-peak concentrations, whereas with the potentiometric detector a change of 18 mV, which is equal to  $(RT/F) \ln 0.5$ , indicates the same change in concentration, provided that a Nernstian slope has been established. The absolute EMF at peak elution volume is well correlated to the actual concentrations, although a Nernstian slope is not always maintained.

#### *Calibration graphs*

The correlation of the chromatographic peak EMFs vs.  $\log C$  is shown in Fig. 5

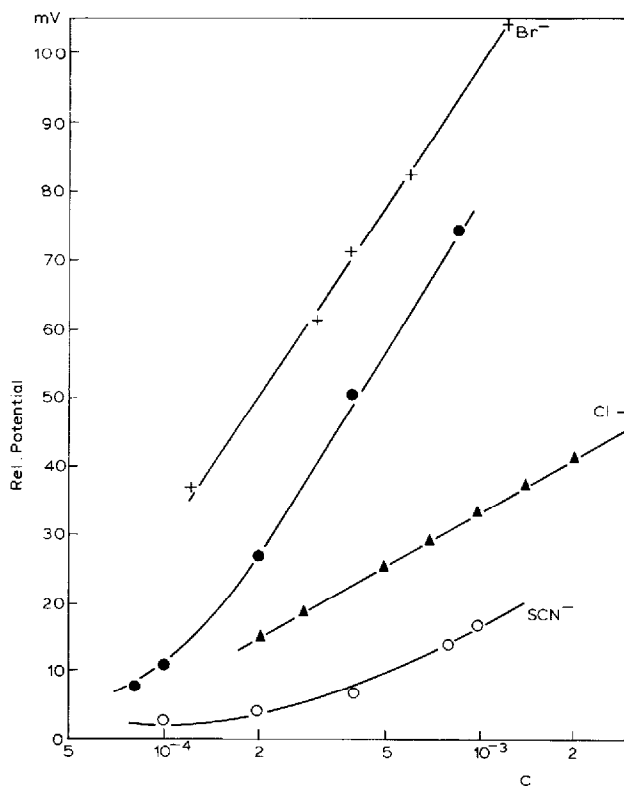


Fig. 5. Calibration graphs for  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$  and  $\text{SCN}^-$  obtained with the potentiometric detector. Eluent:  $10^{-3}$  M salicylic acid, pH 4.12. Flow-rate: 2.4 ml/min.

for  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$  and  $\text{SCN}^-$ . For the halide ions, straight lines are obtained which permit quantitations. For  $\text{Br}^-$  and  $\text{I}^-$ , the slope of the lines is very close to Nernstian in the concentration range  $10^{-3}$ – $10^{-4}$  M. At lower concentrations, the plots for  $\text{I}^-$  tend to deviate from linearity because of long retention times. For bromide ions, whose retention times are shorter, the plots are linear down to  $10^{-5}$  M, and thus very dilute solutions of bromide, below 1 ppm, can be accurately determined.

The slope of the chloride line is only 31 mV per decade, because chloride ions reaching the coated electrode do not replace salicylate ions as do  $\text{Br}^-$  and  $\text{I}^-$ , but are adsorbed on the electrode surface. The resulting potential is the difference between the Nernstian and the zeta potential (which is approximately 30 mV per decade<sup>6</sup>). In spite of the lower slope, the chloride peak potential is very sensitive to concentration changes, and accurate determinations, even of low concentrations (below 1 ppm), can be achieved. The calibration graph for thiocyanate ions deviates somewhat from linearity because of long retention times, which cause dilution effects. The slope of the graph is lower than that for chloride ions, due to the effect of zeta potential already described.

An interesting feature of this system is that the combined influence of solubility product, adsorption and rate effects determines the peak potentials. If only  $K_{\text{sp}}$  were involved a difference of 223 mV would be expected between the peak EMF of  $\text{I}^-$  and

that of  $\text{Br}^-$ , when both are measured at the same concentration ( $E_{\text{AgI}}^0 = -0.152 \text{ V}$ ;  $E_{\text{AgBr}}^0 = 0.071 \text{ V}$ ). The actual difference, however, as seen in Fig. 5, is only 21 mV.

#### CONCLUSION

The potentiometric detector developed in the course of this work represents what appears to be a considerable advance in ion chromatography. It may be assumed that it will find its place alongside the conductometric detector rather than replace it. The potentiometric detector has a number of advantages: (1) more concentrated solutions than those customary with the conductometric detector may be used for elution; (2) no suppressor column is needed; (3) it is free from interference by ions with which the coated silver wire does not react; (4) the peak voltage of the ions that do react with the coated silver wire is a very sensitive parameter.

This detector opens up new possibilities for developing other potentiometric detectors having different indicator electrodes, *e.g.*, lead coated with lead salicylate, which would be sensitive to low concentrations of sulphates.

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