Journal of Chromatography, 589 (1992) 201–207
Elsevier Science Publishers B.V., Amsterdam

CHROM. 23 723

Mixed potential response at metallic electrodes in potentiometric detection for ion chromatography

Peter W. Alexander

Department of Analytical Chemistry, University of New South Wales, P.O. Box 1, Kensington, NSW 2033 (Australia)

Bronisław K. Głód

Institute of Physical Chemistry of the Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw (Poland)

Paul R. Haddad*

Department of Analytical Chemistry, University of New South Wales, P.O. Box 1, Kensington, NSW 2033 (Australia)

(First received July 6th, 1991; revised manuscript received August 15th, 1991)

ABSTRACT

The response characteristics of metallic copper and silver–silver chloride electrodes in a single potentiometric detector were evaluated in an ion chromatographic system. A cell design was used in which the position of the electrodes can be moved easily. Response to inorganic anions was found to be possible with either the copper or the silver–silver chloride electrode acting as the indicator electrode in the same cell where a change in function is achieved by simple movement of the electrodes in the cell. Either negative or positive peaks may be observed in direct or indirect detection modes depending on the choice of mobile phase composition and on the electrode positions in the detector. Optimum separations and the best potentiometric response were achieved with 1 m*M* sodium perchlorate as the eluent. The response to chloride and bromide is shown to be more sensitive at the silver electrode and to nitrate, nitrite, iodide, thiosulphate and thiocyanate at the copper electrode. The best detection limit was found to be 10 pmol for bromide at the silver–silver chloride electrode.

INTRODUCTION

The development of potentiometric detectors for ion chromatography (IC) has been reported previously with various types of indicator electrodes [1–6], but the sensitivity and working ranges were limited. The studies reported here were made with an improved cell design and resulted in better sensitivity for some anions and a wider detector dynamic range. This study was also concerned with the control of the selectivity of the electrodes used in a cell design in which the position of each electrode can be altered easily.

In conventional potentiometric cells, the indicator (or sensor) electrode and the reference electrode are separated by a salt bridge. Cell designs used for chromatographic detection have been reported using a variety of sensor electrodes and usually with a reference electrode of either saturated calomel or silver–silver chloride (Ag/AgCl). The latter has also been used as an indicator electrode for IC detection by several research groups [3], and the electrode potential has been measured with respect to another Ag/AgCl ectrode separated from the mobile phase by a salt bridge, such as an agar-agar. The metallic copper indicator electrode has also been used in several configurations, such as tubular and wire designs, for flow-injection analysis and liquid chromatography [1,2,7–9]. In these earlier studies, the electrode potential was measured relative to a reference

0021-9673/92/$05.00

electrode separated by a salt bridge from the flowing stream.

The electrodes used in this study were metallic copper and Ag/AgCl electrodes but without any salt bridge between them. It is shown that the response of the cell depends on the positioning of the electrodes in the flow path. Detector selectivity can therefore be controlled for response to various anions. For comparison, the response of a UV detector placed in series with the potentiometric detector was also examined.

EXPERIMENTAL

Instrumentation

The electrodes used were metallic wires made from copper and silver metal (both 0.5 mm in diameter). The latter was coated with silver chloride according to the electrolytic method described elsewhere [10]. The wire electrodes were placed in a Perspex cell of dimensions 4 × 3 × 1 cm, as shown in Fig. 1, with a 1-mm flow-through channel. It was possible to change the position of the silver electrode from point A to B. The cell is similar to a design reported previously [2], with Omnifit connectors (supplied by Activon, Sydney, Australia) and rubber septa. The copper electrode was connected to the positive input of an Activon pH/mV-meter and the silver electrode to the negative input connection. The potential difference between the electrodes was then measured.

The potentiometric cell was mounted at the outlet of an ion-exchange chromatographic column (Waters IC-PAK A, 50 mm × 4.6 mm I.D., 30 μequiv./ml). This low-capacity ion-exchange column gave us the possibility of using a low buffer concentration. A Waters (Milford, MA, USA) liquid chromatographic system was used with a pump (Type 510), injection valve (Type U6K) and UV detector (Type 484) connected in series with the potentiometric cell. The UV detector was set at 210 nm (direct detection) or 280 nm (indirect detection) and the UV data were recorded on an ABB SE 120 two-pen strip-chart recorder (Goerz Metrawatt, Vienna, Austria) together with the potentiometric response from the mV-meter.

Reagents and solutions

All reagents were of analytical-reagent grade and were dissolved in water purified on a Milli-Q water purification system (Millipore, Bedford, MA, USA). Mobile phases were degassed using an ultrasonic bath and filtered through a 0.45-μm membrane filter prior to use. A range of mobile phases was used, with the best results being obtained with 1 m*M* sodium perchlorate or 0.4 m*M* potassium hydrogenphthalate adjusted to pH 7.0 with sodium hydroxide. Stock solutions of solute anions were prepared as 10 m*M* solutions in Milli-Q water and diluted to the required concentrations when necessary.

Procedures

The anion sample solutions were injected into the chromatographic system with 10- and 100-μl syringes (Hamilton, Reno, NV, USA) through the injection port. Volumes injected were varied from 0.2 to 100 μl and the signal output of each detector was monitored continuously on the chart recorder. The potentiometric cell was used in two configurations, as shown in Fig. 1, where the Ag/AgCl electrode was placed in either position A or B before recording chromatographic data. The chromatograms could then be compared to determine the effect of the change in the position of the electrodes.

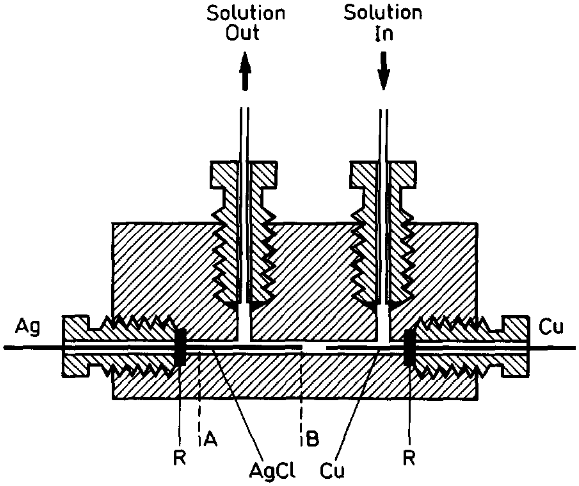


Fig. 1. Schematic diagram of the flow cell used for potentiometric detection, constructed of Perspex and showing the two electrodes used. A and B refer to the two positions used for the Ag/AgCl electrode when recording chromatograms and R represents the rubber septa.

RESULTS AND DISCUSSION

Response mechanisms

The main aim of this work was to determine the optimum conditions for the most sensitive potentiometric response while still maintaining the optimum chromatographic separation of the common inorganic anions tested. Chromatographic peaks could be observed as either positive or negative changes in the measured potential of the electrochemical cell shown in Fig. 1. The direction of the change in potential depended on the mobile phase composition and on the configuration of the two electrodes, which could be positioned in two ways: (A) where the Ag electrode was effectively out of the liquid stream and (B) where it was in the stream, close to the copper electrode.

These factors were found to control the detector response characteristics according to the following mechanisms: (1) direct detection of halide ions at the Ag/AgCl electrode due to an increase in halide concentration at the electrode surface, resulting in decreased silver ion concentration; this causes a decrease in the silver electrode potential and therefore a *positive peak* (as the detector signal is given by the potential of the copper electrode minus that of the Ag/AgCl electrode); (2) direct detection of copper complexing anions at the copper electrode, as a result of the decreasing Cu^{2+} and Cu^{+} concentration due to anion complexation, giving a decrease in the potential of the copper electrode and hence a *negative peak*; and (3) indirect detection (*i.e*, vacancy detection) at the copper electrode caused by an increase in Cu^{2+} concentration where the injected anion was less strongly complexing than the buffer, producing a *positive peak*.

The above mechanisms can be described according to the following equations for the measured detector voltages:

$$E_B = E^{Cu}{}_B - E^{Ag}{}_B$$

$$E_S = E^{Cu}{}_S - E^{Ag}{}_S$$

where E_B is the baseline buffer potential and E_S is the potential due to the buffer plus eluted sample at the peak maximum. The peak height, E_p, is therefore given by:

$$E_p = E_S - E_B = (E^{Cu}{}_S - E^{Cu}{}_B) - (E^{Ag}{}_S - E^{Ag}{}_B)$$

In previous studies reported with the copper electrode [2], the term in the second set of parentheses was zero because a salt bridge was used to separate the silver electrode as a reference electrode from the mobile phase. In this study, the silver electrode is no longer a true reference electrode.

The individual electrode potentials in the above equation are given by the Nernst equation as described previously [2] and are dependent on the free metal ion concentrations at the electrode surfaces. These potentials will depend on the extent of complex formation at the surfaces due to the presence of complexing or precipitating agents in both the buffer and sample solutions, as discussed in numerous previous publications and reviewed by Haddad and Jackson [1]. The slope of the calibration graph for each anion is therefore dependent on the relative

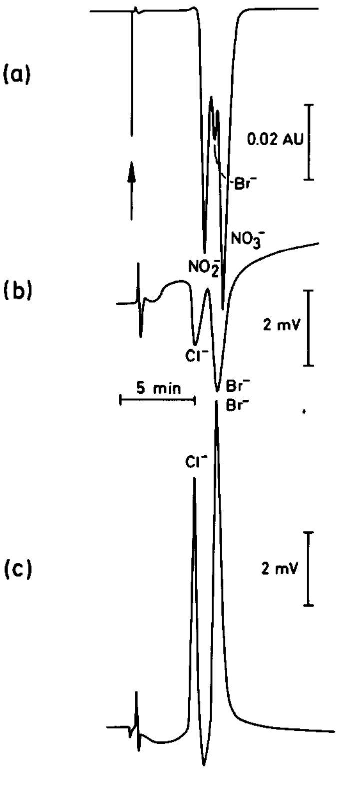


Fig. 2. Chromatograms recorded using 1.0 m*M* perchlorate as eluent with the following detectors: (a) the UV detector at 210 nm; (b) the copper electrode as the sensor with the Ag/AgCl electrode in position A in Fig. 1; and (c) using the silver electrode as the sensor in position B in Fig. 1. Flow-rate of the eluent, 1 ml/min; injection volume, 20 μl.

stability constants or solubility products for the formation of the complexes or precipitates at the silver and copper electrodes. The slope is also dependent on the buffer concentration used. The above mechanism is confirmed by the chromatographic results shown in Figs. 2–4, as discussed below.

Chromatograms observed with potentiometric detection

In chromatography, the best conditions from the standpoint of chromatographic separation are often different from those required for optimum detector sensitivity. Optimum conditions for the potentiometric IC method should be characterized by complete separation of components and detection limits comparable to, or better than, those given by a UV detector, with retention times no longer than about 20 min.

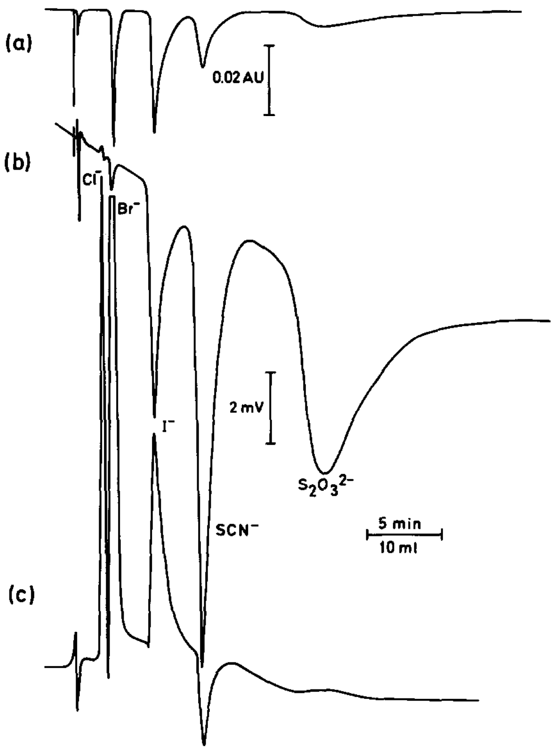
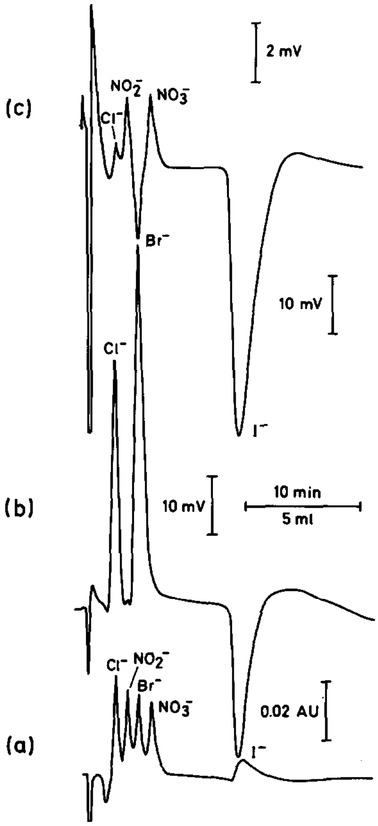


Fig. 3. Chromatograms recorded using 1.0 *M* perchlorate as eluent with the following detectors: (a) the UV detector at 210 nm; (b) the copper electrode as the sensor with the Ag/AgCl electrode in position A in Fig. 1; and (c) the silver electrode as the sensor in position B in Fig. 1. Flow-rate of 0.5 ml/min.



Fig, 4. Chromatograms recorded using 0.4 m*M* phthalate as eluent with (a) the UV detector at 280 nm, (b) the silver electrode as the sensor in position B in Fig. 1 and (c) the copper electrode as the sensor with the Ag/AgCl electrode in position A in Fig. 1. Flow-rate, 0.5 ml/min.

The response of the Ag/AgCl electrode was found to be critical with respect to its position in the flow path of the eluent stream and the position of the copper electrode. The silver electrode could be moved between positions A and B in Fig. 1 without dismantling the cell. When the electrodes were situated close together (position B in Fig. 1), the response of the potentiometric detector was controlled by the response at both electrodes, but mainly by the potential changes occurring at the Ag/AgCl electrode. However, when the electrodes were in position A, the potential was controlled almost solely by changes occurring at the copper electrode. These conclusions can be deduced from the chromatographic data shown in Figs. 2–4. Movement of the Ag/AgCl electrode into intermediate positions between A and B had little effect on the peaks observed until the electrode had been moved completely out of the main stream into position A. The working end of the electrode was not moved through the septum and it was therefore possible to move the electrode many times without affecting the AgCl surface layer. For this reason, reproducibility of the repsonse was not affected.

For optimum peak separation [1], it is known that a high buffer concentration, a high buffer pH and a high anion-exchange selectivity coefficient for the buffer anion cause a decrease in retention time. However, from the point of view of optimizing the potentiometric detection response at metallic electrodes, the above conditions are not ideal. Low buffer concentrations and buffer components known to have small complexation constants with the metal ions from each electrode are required for the best detection limit in the direct detection mode. It is also known [1,2] that a sensitive direct response at a copper metal electrode requires strong complexation of copper ions by solute anions.

To achieve these optimum conditions, different mobile phases were examined, including phosphate, phthalate, carbonate, sulphate, perchlorate, naphthalenemonosulphonate, naphthalenedisulphonate and camphorsulphonic acid. Various pH values and flow-rates were also used. In all instances, it was found that the optimum conditions for the chromatographic separation were not the same as those for sensitive detection of inorganic anions. It was then necessary to compromise in order to select conditions suitable for the separation and detection of various anion mixtures. An example of such a compromise is presented in Fig. 2, which shows the chromatogram obtained for chloride, nitrite, bromide and nitrate using 1 m*M* perchlorate as the mobile phase with the electrodes in different positions, (a) is the UV (210 nm) response, (b) is the copper and (c) is the silver electrode potentiometric detector response. It was found that the potentiometric detector was more sensitive than the UV detector for chloride and bromide when the silver electrode detector was used as the sensor electrode (position B in Fig. 1), and positive peaks were observed for chloride and bromide. Negative peaks and significant peak tailing evident in Fig. 2b on the copper electrode were due to the copper acting as the sensor electrode. Under these conditions nitrate and nitrite could not be detected on the silver or the copper electrode. This may be of some advantage when serious peak overlap occurs, as with the UV detector.

Fig. 3 shows another example of a separation with the same mobile phase (1 m*M* perchlorate) but with a different mixture of anions (chloride, bromide, iodide, thiocyanate and thiosulphate). Again, chloride and bromide were the most sensitive at the Ag–AgCl electrode, showing positive peaks. However, thiocyanate and thiosulphate were most sensitive at the copper electrode and gave negative peaks. At times, a mixed potential response arising from both electrodes was observed. For example, thiocyanate gave a small negative peak (Fig. 3c) which was the sum of a large, negative peak on the copper electrode and a smaller, positive peak on the silver electrode. On the other hand, iodide gave a negative peak on the Cu electrode and a positive peak on the silver. The iodide peak observed in Fig. 3c was therefore of mixed potential origin due to the difference between the silver and copper electrode potentials.

As mentioned above, experiments were also performed with other mobile phases. With phthalate buffer as the mobile phase, as shown in Fig. 4, the separation and detection of chloride, nitrite, bromide, nitrate and iodide was found to be possible. The detection of iodide was most sensitive with the copper electrode (Fig. 4c). The silver electrode detector (Fig. 4b) appeared to be sensitive only to the halides. On the copper electrode it was possible to detect all analysed components but with lower sensitivity than for the halides. Chloride, nitrate and nitrite gave positive peaks on the copper electrode due to the indirect response. Bromide and iodide gave negative peaks due to the direct electrode response. These results confirmed the mechanisms discussed above whereby the mode of detection depends on the ratio of buffer and sample concentrations and their compexation constants with copper ions. UV detection at 280 nm (Fig. 4a) was found to give indirect detection under the conditions used in this study.

Different selectivities and baseline drifts were observed for the three types of detectors. For example, chloride gave a large peak only on the silver electrode detector and thiosulphate only on the copper electrode, and hence there is an opportunity to control the selectivity. With respect to baseline stability, from Fig. 3 it may be observed that the copper electrode detector is characterized by a higher drift than the silver electrode. Further, some anions, especially iodide, caused a long response time and a drifting baseline potential after the injection of a high concentration (10 m*M*).

Calibration

Figs. 5 and 6 show calibration graphs for the two different electrode configurations determined from the chromatograms in 1 m*M* perchlorate. The plots are shown in a semilogarithmic format in order to display the wide concentration range studied. These plots indicate the curvature expected [1–3] for potentiometric detectors and show the working concentration ranges for each anion on the silver and copper electrodes. In Fig. 5, when the electrodes were situated close together, as discussed previously, the calibration response was different from that shown in Fig. 6, when the Ag/AgCl electrode was out of the main solution stream.

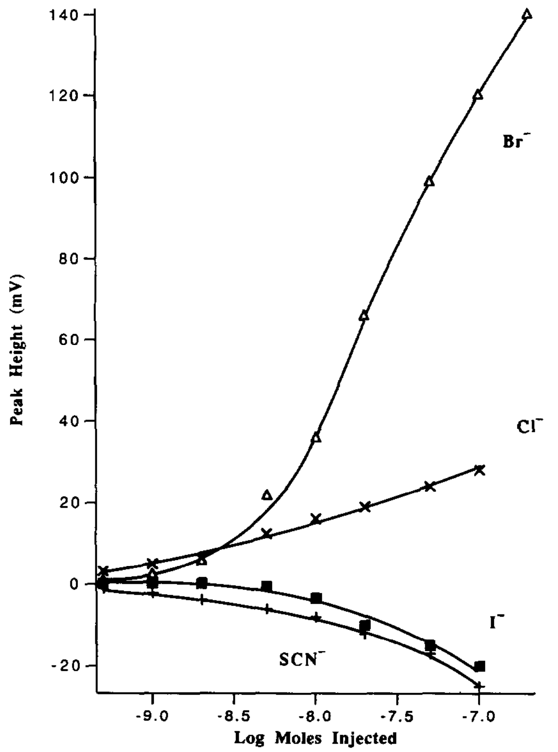


Fig. 5. Calibration graphs for each anion determined with the Ag/AgCl electrode as the sensor in position B in Fig. 1.

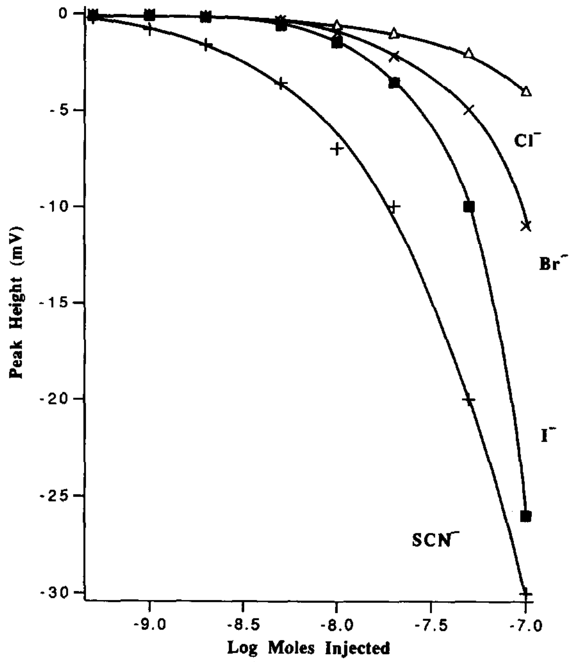


Fig. 6. Calibration graphs for each anion determined with the copper electrode as the sensor with the Ag/AgCl electrode in position A in Fig. 1.

The detection limits for each anion with the two different cell configurations are shown in Table I, together with retention times in the eluent used. Again, it is clear from Figs. 5 and 6 and Table I that chloride and bromide are best detected with the silver electrode and iodide and thiocyanate at the copper electrode. The detection limits compare favour-

TABLE I

RETENTION TIMES AND POTENTIOMETRIC DETECTION LIMITS[a] AT THE SENSOR ELECTRODES FOR 1.0 m*M* PERCHLORATE AS ELUENT

Anion	Retention time (min)	D_L^{Ag} (mol)	D_L^{Cu} (mol)
Cl^-	1.9	$1 \cdot 10^{-11}$	$2 \cdot 10^{-9}$
Br^-	2.7	$1 \cdot 10^{-11}$	$2 \cdot 10^{-9}$
I^-	5.6	$1 \cdot 10^{-9}$	$5 \cdot 10^{-10}$
SCN^-	9.0	$2 \cdot 10^{-10}$	$2 \cdot 10^{-11}$

[a] D_L^{Cu} is the detection limit using copper as the sensor electrode and D_L^{Ag} that using silver as the sensor electrode.

ably with those reported previously for potentiometric detectors [3]. The UV detector was far less sensitive than the potentiometric detectors under the conditions used in this study.

CONCLUSIONS

The results show clearly that there is an advantage in varying the flow-cell design in order to achieve the desired selectivity of electrode response. The function of each electrode can be changed according to its position in the cell used, and the sensor electrode can be chosen by use of the appropriate configuration. It was shown that the UV detector and both potentiometric detectors are characterized by different selectivities.

The value of this work to the practising chromatographer is that the cell configuration can be chosen according to the requirements for a particular application, for example in the analysis of sea water where there is a high concentration of chloride. However, the calibration graphs must be constructed for the particular configuration chosen for the analytical application of interest.

Detection limits are of the order of 10 pmol injected for the anions detected, and are in some instances lower than with UV detection. The silver electrode sensor is characterized by a smaller drift and faster response time than the copper electrode. The potentiometric detector developed in this study therefore offers improvements over other detection methods in terms of sensitivity, selectivity, cost effectiveness, simplified construction and ease of maintenance.

REFERENCES

1 P. R. Haddad and P. E. Jackson, *Ion-Chromatography: Principles and Applications*, Elsevier, Amsterdam, 1990, pp 323–343.
2 P.W. Alexander, M. Trojanowicz and P. R. Haddad, *Anal. Lett.*, 17 (1984) 309.
3 J. E. Lockridge, N. E. Fortier, G. Schmuckler and J. S. Fritz, *Anal. Chim. Acta*, 192 (1987) 41.
4 E. C. V. Butler and R. M. Gershey, *Anal. Chim. Acta*, 164 (1984) 153.
5 M. P. Keuken, J. Slanina, P. A. C. Jongejan and F. P. Bakker, *J. Chromatogr.*, 439 (1988) 13.
6 F. A. Schultz and D. E. Mathis, *Anal. Chem.*, 46 (1974) 2253.
7 P. W. Alexander and C. Maitra, *Anal. Chem.*, 53 (1981) 1590.
8 P. W. Alexander, P. R. Haddad and M. Trojanowicz, *Anal. Chem.*, 56 (1984) 2417.
9 P. R. Haddad, P. W. Alexander and M. Trojanowicz, *J. Chromatogr.*, 324 (1985) 319.
10 R. G. Bates, *Determination of pH, Theory and Practice*, Wiley, New York, 2nd ed., 1973, p. 330.