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Short Communication

Potentiometric detection in ion chromatography using multi-ionophore membrane electrodes

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ABSTRACT

The incorporation of ionophores selective for ammonium, potassium, sodium and calcium ions in an appropriate proportion into a plasticized poly(vinyl chloride) membrane provides a potentiometric membrane sensor with similar sensitivity to ammonium, alkali and alkaline earth metal ions. Such a sensor was employed in single-column ion chromatography using the wall-jet flow-cell arrangement, and was shown to exhibit similar detectability to that observed for conductivity detection.

INTRODUCTION

Conductivity is certainly the most commonly used detection method in modern high-performance ion chromatography [1,2]. A possible alternative in some applications is the use of inexpensive potentiometric devices. These can be applied by using two types of electrode [3]. The first type of electrodes are half-cells in which an element (usually a metallic one) is in equilibrium with its ions in solution. In the second type a metallic element and its insoluble salt are in equilibrium with the counter ion of the salt present in the solution. In addition, membrane electrodes employing various types of membranes are very often used. For example it has been shown that sensitive potentiometric pH detection in suppressed ion chromatography can in some cases give better detection limits than conductivity detection [4]. Replacement ion chromatography with in-line Donnan dialysis also allows the potentiometric detection of various ions with a similar sensitivity using selective membrane electrodes with particularly low detection limits for a given ion [5,6].

The direct application of common potentiometric membrane electrodes with plasticized

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polymer membranes containing selective complexing ionophores does not allow the detection of different ions with similar sensitivity [7,8]. One way of achieving similar detectability of different ions is to use a less selective ionophore in a plasticized membrane or to select a suitable plasticizer [3].

This work presents another approach to designing a potentiometric sensor for ion chromatography. A detector with similar sensitivity to several ions can be achieved by incorporating several selective ionophores in suitable proportions in a polymer membrane. The results of the optimization of such a membrane composition and the study of its selectivity in flow-injection measurements have been presented elsewhere [9]. Membrane electrodes containing three different ionophores in different ratios in a polymer membrane were also applied recently in arrays of ion-selective electrodes for the simultaneous determination of sodium, potassium and calcium in a flow-injection system [10].

EXPERIMENTAL

Flow-injection measurements were performed using a system consisting of a Rabbit peristaltic pump from Rainin (Woburn, MA, USA), a Rheodyne Model 5020 injection valve (Cotati, CA, USA), an Accumet Model 925 digital pH meter from Fisher Scientific (Romulus, MI, USA) and a Fisher Recordall Series 5000 strip-chart recorder.

Chromatographic measurements were carried out using a Model 200 pump from Scientific Systems (State College, PA, USA), a Rheodyne Model 7125 injection valve with 250-μl sample loop and an ION-210 cation-exchange column from Interaction Chemicals (Mountain View, CA, USA). Potentiometric detection was with the same instrumentation as described above for the flow-injection measurements.

The composition of the multi-ionophore membrane was as follows: 66 mg of poly(vinyl chloride) (PVC) from Fluka (Milwaukee, WI, USA) or a mixture of 52.8 mg of polyurethane (PU) Tecoflex SG-80A (Thermedies, Woburn, WA, USA) and 13.2 mg of a copolymer of vinyl chloride–vinyl acetate–vinyl alcohol (80:5:15,

%, w/w) from Scientific Polymer Products (New York, NY, USA) as the matrix, 132 mg of dioctyl adipate (DOA) as the plasticizer, 0.1 mg of valinomycin (selective ionophore for potassium), 0.16 mg of nonactin (selective ionophore for ammonium ions), 8 mg of calcium ionophore II (N,N,N′,N′-tetracyclohexyl-3-oxapentanediamide), 0.3 mg of sodium ionophore III (N,N,N′,N′-tetracyclohexyl-1,2-phenylenedioxydiacetamide) and 0.12 mg of potassium tetrakis (4-chlorophenyl) borate (KTpClPB) as active components. All ionophores, DOA and KTpClPB were purchased from Fluka. Details of selectivities can be found in ref. 13. All the membrane components (200 mg) were dissolved in tetrahydrofuran and cast into a 22 mm I.D. glass ring placed on a glass plate for evaporation. A piece of 5 mm diameter membrane disc was then cut out of the master membrane and mounted in the Philips ISE-561 electrode body from Glasblaserei Moller (Zurich, Switzerland). A mixture containing 0.02 M of each KCl, NH$_4$Cl, NaCl and CaCl$_2$ was used as internal solution.

The electrode equipped with a wall-jet cup [11] was placed in a beaker, in which a constant level of effluent from the measuring system was maintained and its potential was measured *versus* a double junction reference electrode Model 13-620-47 from Fisher Scientific.

RESULTS AND DISCUSSION

Flow-injection potentiometric response of the multi-ionophore detector

Flow-injection measurement with a non-selective detector and without an on-line analyte separation step cannot be utilized for practical analytical purposes; however, it can be a very useful tool for estimating the usefulness of such a detector for chromatographic detection. In the flow-injection system employed in this study, 50 μl of sample solution were injected into a water carrier stream, which was then merged with a stream of 50 mM Tris–HCl buffer solution, pH 7.2, and through the 50-cm mixing coil to the flow-through detector.

In this work we used both electrodes with PVC-based membranes optimized previously [9] and electrodes with PU-based membranes con-

taining the same proportion of ionophores, which are more suitable for producing solid-state sensors [12].

Electrodes with both types of membranes exhibit very similar properties. As one can observe from the flow-injection peaks recorded (Fig. 1), the dynamic response towards monovalent cations is satisfactory, and only in the case of calcium was a much slower return of the electrode potential value to the baseline level found. With PVC-based membrane electrodes, for all monovalent cations except lithium flow-injection peaks are followed by a potential dip below the baseline level, which was not observed with PU-based membranes. As demonstrated by the flow-injection response for various concentrations of ammonium ions (Fig. 2), with a lower concentration of analyte in the injected sample this disturbance disappears and should not affect the chromatographic detection.

The largest signal magnitude was obtained for ions for which selective ionophore was incorporated into a polymer membrane (Table I), although at the proportion of ionophores used the
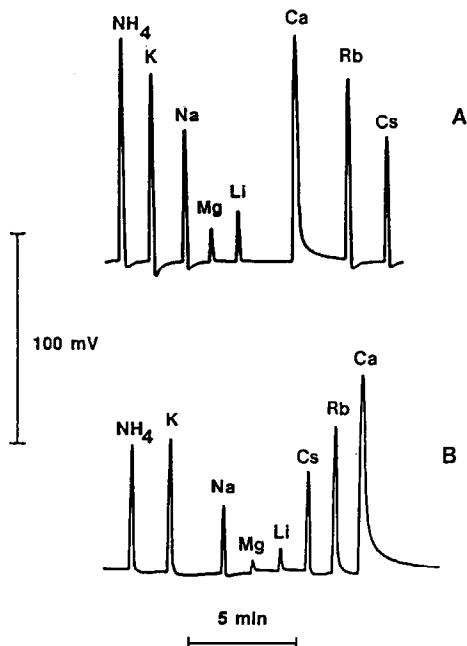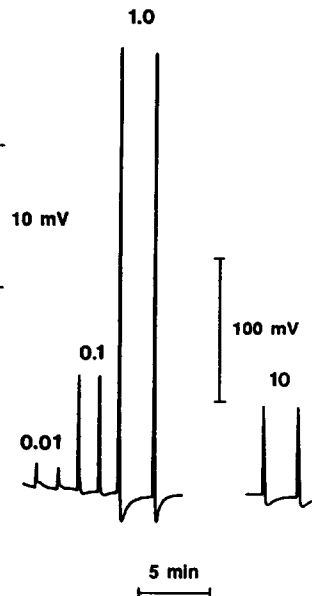

Fig. 2. Flow-injection response obtained for the injection of 50 μl of ammonium chloride solution of the concentration shown in mM with a PVC-based multi-ionophore membrane electrode.

peak height for 1 mM sodium is three times smaller than for the same concentration of calcium. High sensitivity to rubidium and caesium ions can be attributed to the presence of valinomycin in the membrane phase. The sensitivity of valinomycin-based membrane to these cations is known to be relatively high [13]. For the concentration range from 1 to 10 mM analyte in the injected sample, the Nernstian electrode slope was found for calcium only. As in real chromatographic measurements observed potential changes usually do not exceed 15 mV, it is more likely that a linear relationship between the signal magnitude and analyte concentration in injected samples should be expected.

Chromatographic detection with multi-ionophore membrane electrode

For most of cations examined, a larger signal magnitude was obtained with PVC-based membranes, and thus an electrode with such a membrane was employed for all subsequent ion chromatography experiments.

According to the manufacturer, the cation-exchange column ION-210 is most suitable for

Fig. 1. Flow-injection response obtained for the injection of 50 μl of a 10 mM solution of metal ions with PVC-based (A) and PU-based (B) multi-ionophore membrane electrodes.

TABLE I

FLOW-INJECTION RESPONSE OF MULTI-IONOPHORE MEMBRANE ELECTRODES IN THE SYSTEM SHOWN IN FIG. 1 FOR VARIOUS MATRIX POLYMERS

Sample injection volume 50 μl. Total flow-rate in detector 5.1 ml/min

Cation	PVC-based membrane		PU-based membrane	
	Peak height (mV)[a]	Slope (mV/pM)[b]	Peak height (mV)[a]	Slope (mV/pM)[b]
Li^+	5	19	2	8
Na^+	24	39	7	25
K^+	46	43	25	37
Rb^+	51	34	32	38
Cs^+	28	32	16	30
NH_4^+	58	47	26	32
Mg^{2+}	12	4	4	2
Ca^{2+}	78	30	64	30

[a] For 1 mM concentration of injected solution.
[b] Between 1 and 10 mM concentration of injected solution.

the chromatography of transition metal ions; however, it can also be used to obtain satisfactory results for the chromatography of alkali metals and ammonium ions [4,5]. Of the eluents examined, 10 mM nitric acid, 2 mM picolinic acid, 10 mM citric acid (recommended by Aldrich as eluents for mono- and divalent cations using their universal cation column) and Tris buffer, satisfactory results were obtained with 50 mM Tris–HCl buffer, pH 7.2, as eluent, as used previously for flow-injection measurements (Fig. 3). However, this eluent was not suitable for resolution of rubidium and caesium ions.

The importance of incorporating four different ionophores into the membrane phase is demonstrated by the chromatograms shown in Fig. 4, obtained using conventional ion-selective electrodes for ammonium, potassium and sodium ions with a single, selective ionophore in a PVC-based membrane. However, single-ionophore detectors may serve as very effective selective detectors for some real applications, e.g. the determination of ammonia in high-sodium matrices.

From the calibration plots obtained from chromatograms recorded for potentiometric detection with PVC-based multi-ionophore membrane

electrodes (Fig. 5) the detection limit for the determined cations was estimated. The amplitude of the baseline noise equal, for the instrumentation used, to 40 μV was compared with the signal magnitude obtained from the injection of 10 μM solutions of the examined metal ions. For a signal-to-noise ratio of 3 and 250 μl sample volume the detection limit was
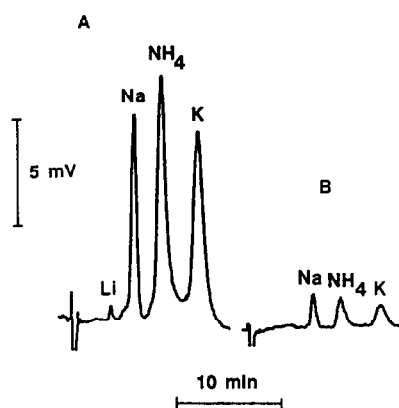

Fig. 3. Ion chromatograms obtained for the injection of 250 μl of a mixture containing 0.25 mM (A) and 25 μM (B) lithium, sodium, ammonium and potassium chlorides at a flow-rate of 2.5 ml/min using 50 mM Tris–HCl buffer, pH 7.2, as eluent with a PVC-based multi-ionophore membrane electrode for detection.
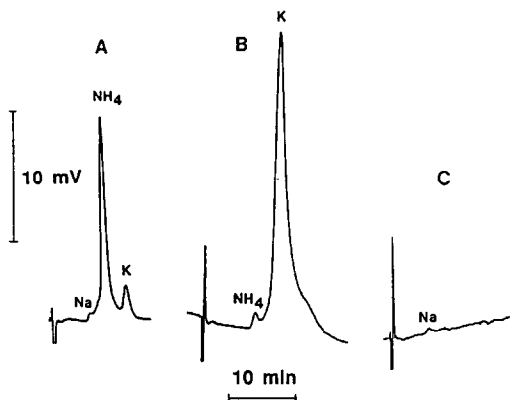
Fig. 4. Ion chromatograms obtained for the injection of 250 μl of a mixture containing 0.25 mM lithium, sodium, ammonium and potassium chlorides using as detectors ammonium (A), potassium (B) and sodium (C) ion-selective electrodes at a flow-rate of 2.5 ml/min using the same eluent as in Fig. 3.

estimated to be 0.7, 0.5 and 1.0 μM for sodium, ammonium and potassium, respectively, which corresponds to 4, 2 and 7 ng. This detectability can be further improved by increasing the Tris concentration in the eluent solution, however it is accompanied by the loss of the baseline resolution for concentrations higher than 10 μM in injected solution.

The detectability obtained without any pre-concentration step should be considered as satisfactory. It is for all examined ions almost of an
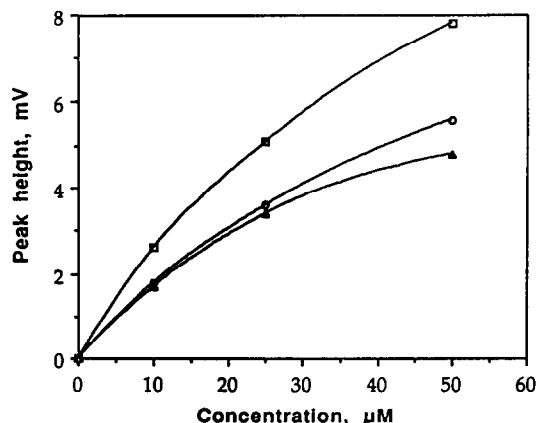
order of magnitude better than obtained previously for pH detection in suppressed ion chromatography [4]. The sensitivity of detection of the alkali metal ions studied is similar to the sensitivity of single-column chromatography with conductivity detection [14,15].

Further study on the use of this detection for other columns and simultaneous separations of mono- and divalent ions are in progress, as well as study on development of solid-state sensor with multi-ionophore membranes.

Fig. 5. Calibrations plots obtained for ion chromatography of sodium (O), ammonium (□) and potassium (◇) with a PVC-based multi-ionophore membrane electrode as detector.

REFERENCES

1 J.G. Tarter (Editor), Ion Chromatography, Marcel Dekker, New York, 1987.
2 P.R. Haddad and P.E. Jackson, Ion Chromatography —Principles and Applications, Elsevier, Amsterdam, 1990.
3 M. Trojanowicz, A. Ivaska (Editor), Contemporary Electroanalytical Chemistry, Plenum Press, New York, 1990, pp. 255–266.
4 M. Trajanowicz and M.E. Meyerhoff, Anal. Chem., 61 (1989) 787.
5 M. Trojanowicz and M.E. Meyerhoff, Anal. Chim. Acta, 222 (1989) 95.
6 M. Trojanowicz, E. Pobozy and M.E. Meyerhoff, Anal. Chim. Acta, 222 (1989) 109.
7 K. Suzuki, H. Aruga and T. Shirai, Anal. Chem., 55 (1983) 2011.
8 K. Watanabe, K. Tohda, H. Sugimoto, F. Eitoku, H. Inoue, K. Suzuki and S. Nakamura, J. Chromatogr., 566 (1991) 109.
9 Y.S. Park, M.J. Cha, S.H. Han, D.S. Shin, H.D. Kim and G.S. Cha, J. Korean Chem. Soc., 37 (1993) 259.
10 R.J. Forster and D. Diamond, Anal. Chem., 64 (1992) 1721.
11 M. Trojanowicz and W. Frenzel, Fresenius' Z. Anal. Chem., 328 (1987) 653.

12 G.S. Cha, D. Liu, M.E. Meyerhoff, H.C. Cantor, A.R. Midgley, H.D. Goldberg and R.B. Brown, *Anal. Chem.*, 63 (1991) 1666.

13 W.E. Morf and W. Simon, in H. Freiser (Editor), *Ion-Selective Electrodes in Analytical Chemistry*, Vol. 1, Plenum Press, New York, 1978.

14 H. Shintami, K. Tsuji and T. Oba, *Bunseki Kagaku*, 24 (1985) 109.

15 P.E. Jackson, T. Bowser and P.G. Alden, *LC · GC*, 10 (1992) 787.