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## Ion chromatography detector based on solid-state ion-selective electrode array

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### Abstract

A variety of neutral carrier type ionophores for monovalent cations were employed to prepare solid-state cation-selective electrodes (SSEs) for use as a detector in single-column ion chromatography (IC). The polyurethane-based pseudoreference electrode made it possible to assemble an array type SSE detector for IC. An SSE-based detector provides not only the overall chromatogram for the separated ion species (monensin methyl ester–nonactin-based membrane), but also the enhanced chromatogram for specified ions of interest (valinomycin as  $K^+$  and nonactin for  $NH_4^+$ ). This feature makes it possible to perform highly quantitative analysis with low detection limits even if the separation efficiency of the ion-exchange is not sufficient. Since SSE-based IC detectors are easily miniaturized and replaceable at low cost, they are an ideal component of a portable IC system. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Solid-state cation-selective electrodes; Ion chromatography

### 1. Introduction

Ion chromatography (IC) based on conductivity detection is one of the most widely used methods for the analysis of trace inorganic and organic ions in environmental, industrial and clinical samples. Spectrometric and various types of electrochemical (amperometric and coulometric) detectors coupled to a single column reactors are often employed to extend the analytical utility of IC. In general, ICs based on these conventional detection schemes are commercially available as bench-top type instruments and are used as a routine analytical system in many modern analytical laboratories [1].

In addition to the common IC detectors already

mentioned, there have been some attempts to develop IC systems with potentiometric ion-selective electrode (ISE) detectors. Since ISEs exhibit a highly selective, rapid and reproducible response to specific classes of ions with low detection limits, their applications have been directed mainly to the enhanced detection of particular ionic species in single-column IC [2–9]. With the aforementioned selectivity of ISE detectors, the suppressor system could be eliminated completely to make it possible to design portable carry-out type IC systems. On the other hand, several researchers attempted to develop ISEs into a general type IC detector, employing membranes with less selective neutral carriers or mixed ionophore systems to provide similar sensitivity to many different ions [10–19]. It was also demonstrated by Hauser and coworkers that coated-wire

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ISEs with limited selectivity were used as detectors in ion chromatography or capillary electrophoresis [20]. And, very recently, arrays of a small number of quite selective ISEs appear to be a viable alternative to non-selective ISE detectors [21].

With the advent of ISE technologies, various types of all-solid state electrodes (SSEs) have been introduced: the exposed end of the metallic conductor printed on a silicon wafer, aluminum plate or other insulating polymer substrates or the silicon nitride surface of the field effect transistor (FET) gate may be modified with the polymeric sensing membranes to fabricate a miniaturized and integrated array of ISEs on a single chip [22]. These SSEs not only exhibit potentiometric performance, i.e., selectivity, detection limits and response times, comparable to that of conventional ISEs with an internal filling solution but are also very suitable for mass fabrication at relatively low cost. Although their long term stability and signal drift remain problematic, such drawbacks of SSEs may be overcome by employing relatively a frequent calibration procedure with a flow-through system and/or by fabricating them as short-term use disposable-type sensor cartridges.

Utilizing the advantages of SSEs, it is possible to design a multipurpose general IC detector based on array-type ISEs, in which several electrodes printed on a small chip are modified with both less and highly selective solvent polymeric membranes. While the ion sensor, fabricated with a less selective membrane that exhibits similar sensitivity to many different ions, provides an overall chromatogram, the highly selective sensors quantitatively resolved chromatograms for specific ions of interest among the chromatographically-separated species. This is particularly advantageous if the separation efficiency of an ion-exchange column employed is not sufficient.

Furthermore, by designing the miniaturized, low cost and easily replaceable detector cartridge with SSE-based ion sensors, construction of a truly portable IC system may be realized. However, the true miniaturization of ion sensor system is often hampered by the lack of a suitable reference electrode. The miniaturized reference electrode systems currently in use in chemical analysis are a Ag/AgCl electrode or the same covered with an electrolyte-doped polymer material or an electrolyte-containing hydrogel under a hydrophobic polymer membrane

with an open end liquid junction [21,23]. These reference electrode systems, however, may be used only for disposable ion sensor cartridges due to their limited lifetimes. Recently, we reported a liquid junction-free solvent processible polymer membrane-based reference electrode for miniaturized ISE systems [24]. It can remove the extra flow route needed for an Ag/AgCl reference electrode in the case of a sample solution containing  $\text{Cl}^-$ .

In this contribution, we will look for such aforementioned possibilities, discussing various aspects of SSE-array type IC detector systems fabricated with a liquid junction-free reference electrode based on a polyurethane membrane.

## 2. Experimental

### 2.1. Reagents

Poly(vinyl chloride) (PVC), 2-nitrophenyl octyl ether (*o*-NPOE), bis(2-ethyl hexyl) adipate (DOA), tridodecylmethylammonium chloride (TDMACl), potassium tetrakis (*p*-chlorophenyl) borate (KTpCIPB), valinomycin and nonactin (now commonly used for preparing potassium- and ammonium-selective membrane electrodes, respectively) were obtained from Fluka (Ronkonkoma, NY). Monensin methyl ester (MME), is known as a sodium ionophore but exhibits a relatively similar sensitivity toward most alkali metal ions [18], was purchased from Calbiochem-Novabiochem (La Jolla, CA). PU60, polyurethane composed of 60 wt% hard segments (4,4'-diphenylmethane diisocyanate), was synthesized as previously described [25]. Analytical reagent grade chemicals and deionized water were used to prepare all solutions.

### 2.2. Solid-state ion-selective electrodes

SSE chips were fabricated by screen printing the Ag paste (product of Gwente Electronics Inc., UK) on an aluminum plate according to the pattern shown in Fig. 1, firing them at 800°C, overcoating the metal electrodes with a layer of dielectric film (product of DuPont) and finally thermally treating them again at 800°C. The dielectric layer was printed on the Ag electrodes through the screen pattern that blocks the

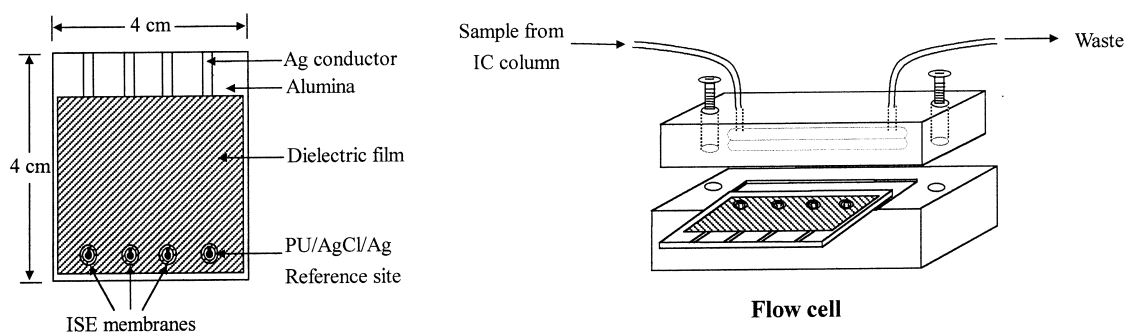


Fig. 1. Schematic of solid-state ion-selective electrode detector assembly for the ion chromatography system.

circular sensing area and electric connectors. The size of each chip is 4 cm×4 cm and the diameter of exposed sensing area is 1 mm [22]. To maintain a stable interfacial potential between the ion-selective membranes and electrodes, the silver electrodes were treated with 0.3 M FeCl<sub>3</sub> solution to form an AgCl layer. The exposed AgCl/Ag sensing sites were then coated with PVC-based ion-selective membrane cocktails dissolved in THF solvent; the compositions of each membrane are given in Table 1. The reference site was coated with the PU60-based membrane cocktail (solvent: 1:10 mixture of DMF and THF) containing equimolar amounts ( $1.75 \times 10^{-3}$  mol/kg) of both cationic and anionic lipophilic additives (TDMACl and KTpCIPB, respectively), incorporated as described in our previous publication [24]. The SSE chips modified with polymeric membranes were dried in a dessiccator at room temperature for 24 h.

Initial potentiometric evaluation of various membranes was conducted by employing a static arrangement. Electrodes were connected through a high-impedance amplifier to an IBM AT-type computer equipped with a home-made high-impedance input 16-channel analog-to-digital converter. Selectivity coefficients were determined by using the separate

solution-matched potential method at an interfering cation concentration of 0.1 M [26]. The potentiometric responses and stability of the polyurethane-based solid-state reference electrode to varying cation (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup> and H<sup>+</sup>) concentrations were examined with a static experimental setup (background electrolyte; 0.05 M Tris-HCl, pH 7.4 for alkali metal cations and 11.4 mM boric acid/10 mM sodiumdihydrogenphosphate for H<sup>+</sup>). The detection limits of the membrane electrodes were obtained from the calibration curves as described elsewhere [27]. The SSE sensor chip was then placed in a specially designed flow-through cell (see Fig. 1), which is directly connected to the outlet of IC column. The flow cell consists of two blocks that can be clamped with two screws: the upper one has an inlet and an outlet at both ends and a flow channel (2 mm×36 mm); and the bottom block has a fixing site for the chip.

### 2.3. Ion chromatography

Chromatographic measurements were carried out using a HPLC pump (Model CCPD; Tosoh, Japan), a sample injector (Model 7125; Rheodyne, Cotati, CA) equipped with a 70- $\mu$ l sample loop, a cation-sepa-

Table 1

Compositions (w/w%) of ISE membranes<sup>a</sup>

	Matrix	Ionophore	Plasticizer	Lipophilic additives
M1	PVC, 33	Valinomycin, 1	DOA, 66	None
M2	PVC, 33	Nonactin, 1	DOA, 66	None
M3	PVC, 32.6	MME, 1 Nonactin, 0.6	<i>o</i> -NPOE, 65.3	KTpCIPB, 0.5

<sup>a</sup> The membrane components were dissolved in 5 ml tetrahydrofuran.

ration column (Schodex IC Y-521; Showa denko, Tokyo, Japan) and an SSE array detector assembly. The eluent used was 8.0 mM nitric acid and its flow-rate was maintained at 0.5 ml/min. Potential differences between the ISEs and the reference electrodes were measured as described in the previous section.

### 3. Results and discussion

In order to apply the SSE to the IC detector, we should solve the reference electrode problem. In an IC system, the second reference channel could/should be eliminated and it can be achieved in various ways. In this contribution, we proposed a new approach of fabricating potentiometric reference electrodes employing polymeric membranes. Researchers who have been engaged in developing solvent polymeric membrane-type ISEs would have had a frustrated experience with a hardly responsive membrane towards most ionic species. However, if such a membrane is systematically developed and characterized, it may serve as a reference electrode that does not required a salt bridge.

Development of the aforementioned reference electrode was already published separately [24,28]. The liquid junction-free reference electrode proposed in the present work could be placed adjacent to the ISEs within the sample channel, making it possible to eliminate the use of an additional reference channel. The reference site was coated with fabricated reference membrane electrode. The dynamic response characteristics of the reference electrode to various cations are exhibited in Fig. 2; this reference membrane electrode hardly responds to the every ionic species, we examined, under  $10^{-1}$  M concentration.

Preliminary potentiometric evaluation of membranes doped with various types of neutral carriers against the developed reference electrode was conducted by employing a static arrangement. Table 2 summarizes the results. For comparison purposes, the potentiometric selectivity coefficients are presented with respect to potassium (i.e., as the primary ion) for all of membranes. Those values should not be confused with the concept of chromatographic selectivity: the more positive the value of the selectivity

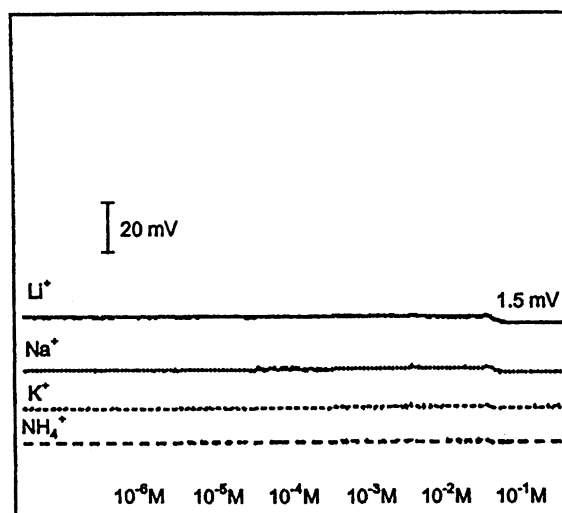


Fig. 2. Potentiometric responses of the polyurethane-based solid-state reference electrode to varying cation concentrations: background electrolytes, 0.05 M Tris-HCl, pH 7.2.

coefficient, the greater the electrode's response for the interfering ion [25]. When the selectivity coefficient is zero, the membrane electrode exhibits equal selectivity toward the primary ion and interfering ions. As listed in Table 2, the potentiometric characteristics of SSE membranes are in good agreement with the conventional macroelectrodes that contain an inner reference solution. The detection limits of different ions other than the listed ion in parentheses for each electrode can be estimated roughly by comparing its selectivity coefficients. Finally, the pH response is negligible for all membranes (M1, M2 and M3). Thus, it is not necessary to employ a buffer system to maintain pH.

To evaluate the potentiometric responses of the SSE-based IC detector, we obtained the chromatogram of a  $10^{-4}$  M mixture of four monovalent

Table 2  
Electrochemical properties of membranes

	Slope (mV/dec)	Selectivity coefficient <sup>a</sup>			Detection limit (log[M])
		Li <sup>+</sup>	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	
M1	58.1	-2.8	-2.7	-1.7	-5.9 (for K <sup>+</sup> )
M2	57.3	-2.2	-1.8	0.8	-6.1 (for NH <sub>4</sub> <sup>+</sup> )
M3	56.2	-0.2	0.6	-0.6	-5.4 (for Na <sup>+</sup> )

<sup>a</sup> Selectivity coefficient:  $\log(K_{K^+}^{pot})$ ; Buffer condition: 0.05 M Tris-HCl pH 7.2.

cations (i.e.,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$  and  $\text{K}^+$ ), which was injected to the IC system. The MME-based membrane was fabricated as a less selective membrane that exhibits similar sensitivity to many different ions provides an overall chromatogram. However, the response time of only the MME-based SSE (Fig. 3) is not suitable for obtaining quality chromatogram of cations at the ionic concentrations below  $10^{-4}$  M. These slow responses, which are confirmed by the static arrangement set up, could be corrected by addition of a small aliquot of nonactin to the MME-based membrane. Incorporating more than 0.5 mg of nonactin into the MME-based SSE enhanced the response time to obtain a better chromatogram without affecting the selectivity coefficient to the cations applied. At the flow-rate we employed, as seen in Fig. 3, the chromatogram was significantly improved by using the nonactin-added MME-based membrane and the MME membranes containing over 1.2–1.5 mg of nonactin in 200 mg of membrane mixture exhibited sufficient response times without significantly affecting selectivity towards the cations.

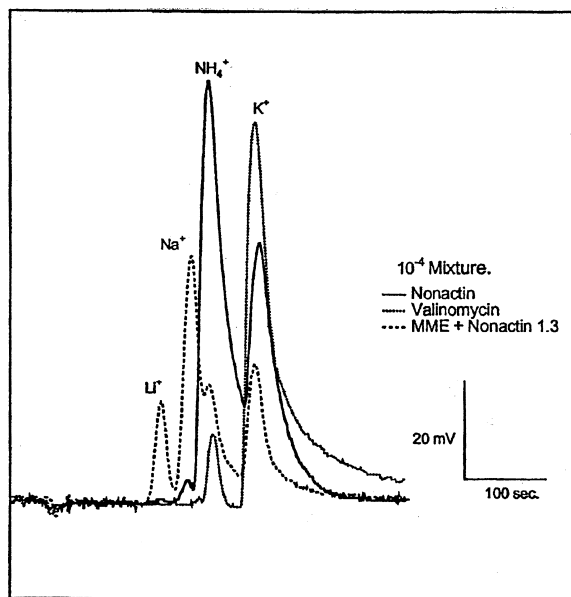


Fig. 3. Potentiometric responses of the methylinonensin ester and varying amount of nonactin-doped membranes to the chromatographically-separated cations ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{NH}_4^+$ ), which are contained in a  $10^{-4}$  M mixture, in a flow-through cell. (See Experimental section of the text for the details of chromatographic conditions.)

Furthermore, the quality of the chromatograms (Fig. 4) with the M1-, M2- and M3-coated SSEs detailed in Table 1 was very comparable to those with the corresponding membranes in a flow arrangement (wall jet flow cell [18]).

The SSE-array type detector provides not only the overall chromatogram for separated ion species (nonactin-added MME-based membrane), but also the enhanced chromatogram for specified ions of interests (valinomycin for  $\text{K}^+$  and nonactin for  $\text{NH}_4^+$ ). For instance, with membrane M3, the  $\text{NH}_4^+$  peak is overlapping with the  $\text{Na}^+$  peak, but the nonactin-based membrane M2 (Fig. 4) cleanly resolves the  $\text{NH}_4^+$  peak from the tail of  $\text{Na}^+$  peak with excellent detectability. Detection limits for  $\text{Li}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$  are greatly improved with the use of a valinomycin-based membrane electrode (M1). This feature makes it possible to perform highly quantitative analysis with low detection limits even if the separation efficiency of an ion-exchange column is not sufficient. And all of aforementioned chromatograms are obtained simultaneously.

To examine the linearity of the  $\log[M^+]$  vs. potentiometric signal under the influence of poorly separated interfering ion, in this case, mixtures of  $\text{NH}_4^+$  from  $10^{-4}$  to  $10^{-6}$  M with 100 times diluted artificial sea water were injected and the emf responses of nonactin-based membrane, M2 were recorded. Fig. 5 shows that the chromatogram with excellent response to the primary ion (in this case, ammonium ion) and acceptable linearity in a very low concentration range was obtained in a very high concentration of interfering ions like environmental samples. The cation ( $\text{Na}^+$  and  $\text{K}^+$ ) content in commercial drinking water were analyzed with this system and the results are in very good agreement with inductively coupled plasma atomic emission spectroscopic data within an acceptable deviation.

#### 4. Conclusion

- (1) A variety of neutral carrier type ionophores for monovalent cations were employed to prepare solid-state cation-selective electrodes (SSEs) for use as a detector in single-column ion chromatography (IC).
- (2) The polyurethane-based pseudoreference elec-

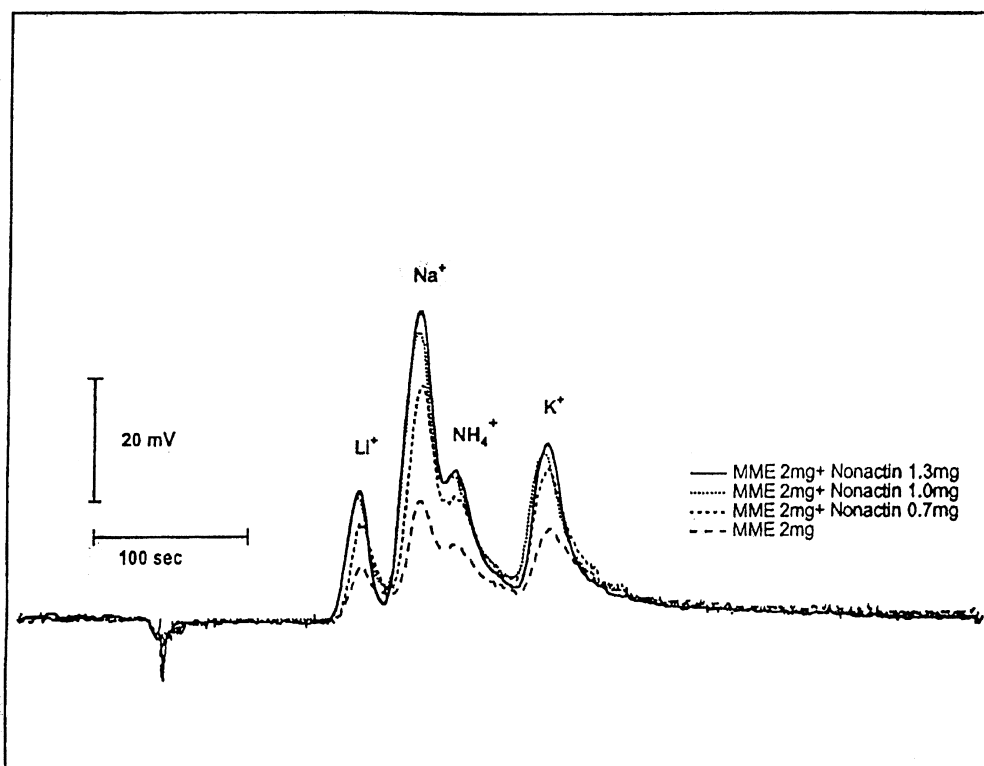


Fig. 4. Chromatograms of the ion-chromatography system with a solid-state ion selective electrode detector. It can be seen that the electrode with the methylmonensin ester–nonactin-doped membrane provides a relatively uniform response to all cations examined, while those with valinomycin- and nonactin-doped membranes amplified the chromatogram for potassium and ammonium, respectively. Experimental conditions as in Fig. 3.

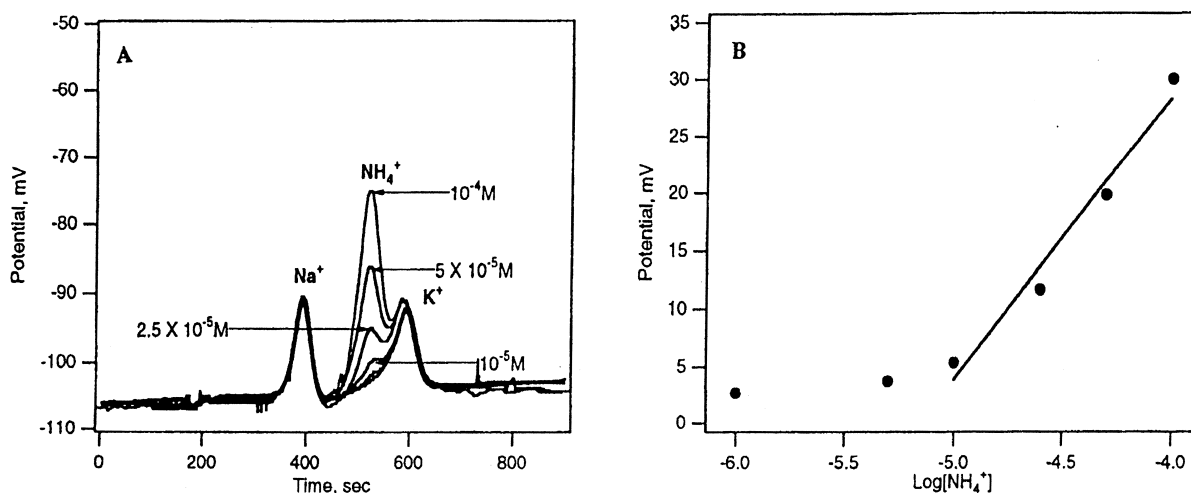


Fig. 5. Calibration plots obtained from the electrode with nonactin-doped membranes: A is the chromatogram and B the calibration plots for a series of solutions containing different concentrations of ammonium in dilute artificial sea water. Experimental conditions as in Fig. 3.

trode made it possible to assemble an array type SSE detector for IC.

(3) SSE-based detector provides not only the overall chromatogram for separated ion species (monensin methyl ester–nonactin-based membrane), but also an enhanced chromatogram for specified ions of interests (valinomycin for  $K^+$  and nonactin for  $NH_4^+$ ). This feature makes it possible to perform highly quantitative analyses with low detection limits even if the separation efficiency of an ion-exchange is not sufficient.

(4) Now, our laboratory is processing the development of an IC system for simultaneous measurement of anions and cations.

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