

**»Programmable« Selective Inexpensive Potentiometric
Detector for Flow Injection Analysis. Potassium
Determination with a Nafion Membrane Modified
Electrode**

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The study of a nafion membrane (ISE membrane) for the inexpensive potentiometric detection of potassium ion in a flow injection system is reported. The nafion membrane doped with potassium ion showed that excellent selectivity could be achieved for various cations, except for Rb^+ , and some interference for Cs^+ . A linear potential response of 10^{-2} – 10^{-6} M for the potassium ion was obtained with a detection limit of about 0.5×10^{-6} M. This approach can be employed for constructing a potentiometric detector for virtually any cation (soluble at basic pH values) by simply changing the electrode pretreatment (or doping solution).

INTRODUCTION

Individually potentiometric ion selective electrodes (ISE) and flow injection analyses (FIA) based techniques have made a great impact in many areas of chemical analyses because of having advantages, such as high precision, high sampling rate for microliter

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sample volumes and application for routine analyses.¹⁻⁸ Also, the use of ion selective membrane electrodes for the determination of a discrete ion in physiological samples has grown tremendously over the years.⁴ Combination of a potentiometric ion selective electrode with flow injection analyses requires only simple low cost instrumentation, and gives rapid analyses and there is usually no need for pretreatment of sample. Although the applicability of the combination of ISE detection with FIA has been demonstrated recently,⁵ it is of interest to develop a simple and inexpensive ISE sensor that can be easily »programmed« to be selective for any desired cation for FIA detection.

Nafion, a perfluorosulfonic acid cation exchange polymer material was developed by E. I. du Pont de Nemours & Co., Inc., in the early 1960s.⁹ Its various applications have been published and numerous patents have been issued especially in the fuel cell area.^{10,11} Nafion membrane electrodes have been developed for numerous electroanalytical applications.¹²⁻¹⁶ In this paper, we present the design and construction of a modified electrode employing a nafion membrane film on a platinum substrate. As an example, its application for selective measurement of the potassium ion in FIA mode is examined. This approach can be used to construct a simple and inexpensive flow ISE detector for virtually any cation by simply changing the electrode pretreatment.

EXPERIMENTAL

Reagents

Unless otherwise stated, the chemicals were ACS reagent grade and were used without further purification. All test solutions were prepared daily by appropriate dilution of a 0.1 M stock solution of potassium ion. The disodium hydrogen phosphate was purchased from Aldrich Chemical Co. and used as received. The water was distilled in house and then further purified using a Sybron/Barnstead NANO Pure II system. The buffer carrier reagent for use in the FIA experiments was varied, so as to maintain different pH values of the mobile phases employed. The mobile phases used were 10^{-2} M sodium acetate plus acetic acid at pH 5.0, 10^{-2} M disodium hydrogen phosphate plus sodium hydroxide at pH 7.0, and 10^{-2} M glycine plus sodium hydroxide at pH of 8.5. To obtain a stable baseline potential, the carrier stream also contained a 10^{-6} M concentration of KCl.

Apparatus and Procedures

A nafion 117 polymeric film was boiled in deionized distilled water for 30 minutes and then treated with 0.6 N KCl at 30°C for 2 hours. The dissolution of the treated nafion membrane was achieved in an isopropanol-water solvent system consisting of a 90% isopropanol and 10% water mixture heated at 100 °C to obtain a 2 mass % solution.

The indicator electrode was a platinum disc electrode (3 mm diameter) in a Teflon block purchased from BAS (MF 1021). An Ag/AgCl reference electrode was inserted into a second Teflon block having the same dimension as the indicator electrode block and sealed with a fast curing epoxy. A Teflon gasket of 0.38 mm thickness was placed between the indicator electrode block and the Teflon block holding the reference electrode. The platinum electrode was initially polished with a 1 μ m diamond polishing kit, then sonicated in a water bath for five minutes after polishing and washed well with a stream of methanol.

A 0.6 μ L syringe was used to place the nafion solution on the platinum electrode. The electrode was then oven dried at 60 °C for 4 hours and then soaked in a 1 M KCl solution 24 hours before use. The selectivity of this electrode can be simply changed by using a different cation salt in this pretreatment.

The flow injection system consisted of an Altex 100A double reciprocating pump followed by an Altex injection valve. Teflon tubing of a 55 cm length and 0.3 mm inner diameter connected the injection valve and the detector cell. A 20 μ L sample loop was used throughout the FIA experiments. The potentiometric measurements were carried out with an Orion Model 601

A Ionanalyzer and the voltage signals from the output of this detector unit were recorded by an Ominiscribe dual pen recorder from Houston Instruments.

RESULTS AND DISCUSSION

Figure 1 shows the potentiometric response of the nafion based ISE electrode for potassium ion. Each standard was injected at least ten times to determine the reproducibility of the signals, which was about ± 2 mV throughout. A linear response from 10^{-2} to 10^{-6} M potassium ion was obtained with a detection limit of

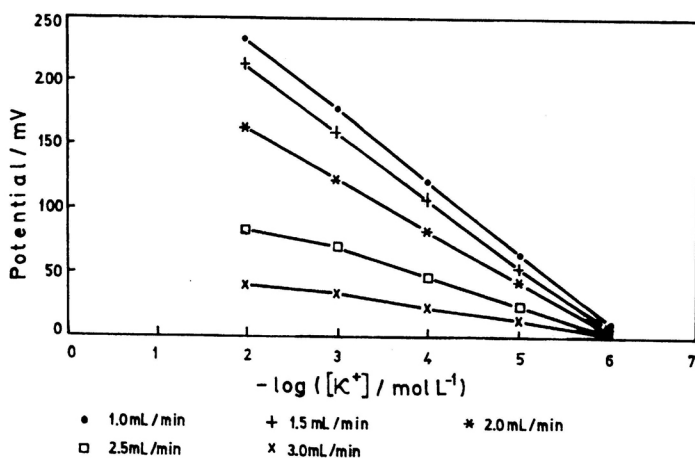


Figure 1. Effect of flow rate on the response behaviour of nafion membrane electrode for potassium ion mobile phase: Glycine, pH = 8.5.

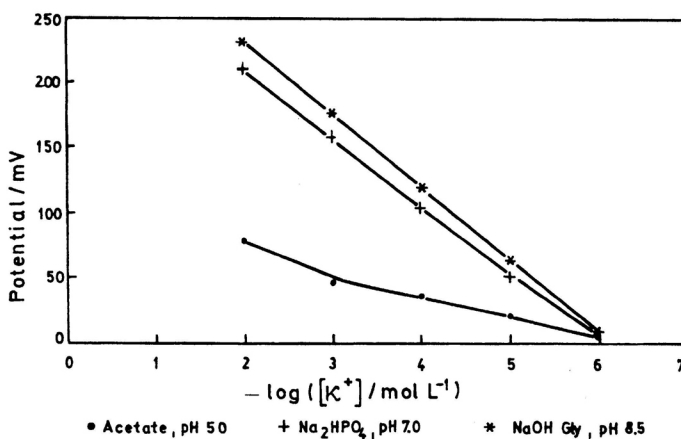


Figure 2. Effect change in the mobile phase pH on the potential response of potassium ion doped nafion membrane electrode. Flow rate: 1.0 ml/min.

about 0.5×10^{-6} M. The magnitude of the signal depended on the flow rate. At a flow rate of 1.0 mL/min or lower, the response was »Nernstian« at 55 mV decade and $r^2 = 0.998$. At higher flow rates, the response was less than »Nernstian«. Virtually identical results were obtained for the potentiometric FIA determination of K^+ , Na^+ and Cs^+ when the nafion electrode was soaked in 1 M chloride solutions of these cations prior to use. Increasing the flow rate should result in a diffusion layer decrease, thereby increasing the rate of mass transport to the electrode surface. However, at high flow rates, the sample slug was evidently flushed out before the maximum sample concentration reached the electrode surface and the net signal decreased.

The effect of the mobile phase pH and nature on the response characteristics of the nafion based electrode for potassium ion is shown in Figure 2. In acidic media, the response is not »Nernstian«. In neutral or slightly basic media, the response is »Nernstian« and linear over a greater concentration range. In acidic media, the nafion membrane probably has a lower doping level with potassium ion as the competition to the proton as the dopant increases.

Table I gives the selectivity coefficients determined by the mixed solution technique¹⁷ for various cations when the nafion membrane was doped with potassium ion and used in the flow injection mode. A good selectivity ratio for various ions was achieved except for Rb^+ and Cs^+ . The electrode response time was fast compared to the time of the analyte slug passing across the electrode surface.

TABLE I

Selectivity coefficients of the nafion-based K^+ selective electrode. The potassium concentration was 10^{-5} M throughout. The pH = 7.0.

Cations	Selectivity coefficients
Na^+	3×10^{-3}
Rb^+	2.4
Cs^+	4×10^{-1}
Ca^{2+}	2×10^{-3}
Mg^{2+}	1×10^{-3}
Li^+	1×10^{-3}

With respect to the electrode life-time, the potential response of the electrode did not change appreciably during the first two days of continuous use at a flow rate of 1.0 ml/min. On the third day and on the fourth day the potential response decreased somewhat, but the slope of the curve remained »Nernstian«. However, after the fourth day, the slope of the response decreased markedly. On the seventh day the response virtually disappeared. The loss of response was a result of the electrode nafion membrane visibly cracking and flaking.

CONCLUSION

By simply changing the cation of the nafion film pretreatment solution (doping), a simple and inexpensive flow ISE detector for virtually any positively charged species that is soluble at basic pH values and is exchanged in the nafion membrane can be readily constructed. As this loss of response with time is a structural failure of the nafion only, other methods of film preparation could circumvent this problem. Exemplary analytical FIA and selectivity results were obtained.

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SAŽETAK

»Programirani« jeftini selektivni potenciometrijski detektor za protočnu injekcijsku analizu. Određivanje kalija modificiranom nafionskom membranom

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Prikazano je istraživanje nafionske membrane za pripremu jeftine ion-selektivne elektrode (ISE) pogodno za potenciometrijsko određivanje kalijevih iona u protočnom injekcijskom sustavu. Nafionska membrana dopirana kalijevim ionima pokazala je izvanrednu selektivnost u nazočnosti različitih kationa, osim Rb^+ i djelomično Cs^+ . Utvrđen je linearan odziv potencijala elektrode u području koncentracija kalija od 10^{-2} do 10^{-6} M. Izneseno načelo pripreme može se primijeniti pri konstrukciji potenciometrijskog detektora za gotovo bilo koji kation; jednostavnom izmjenom postupka predobradbe elektrode ili dopirajuće otopine.