MEMBRANE-DIALYZER INJECTION LOOP FOR ENHANCING THE SELECTIVITY OF ANION-RESPONSIVE LIQUID-MEMBRANE ELECTRODES IN FLOW SYSTEMS
Part 1. A Sensing System for NO_x and Nitrite

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SUMMARY

A general approach for enhancing the selectivity of anion-responsive liquid-membrane electrodes is described. The method is based on use of the receptor channel of a flow-through dialyzer unit as the injection loop in a flow-injection system. An appropriate membrane in the dialyzer prevents ionic interferents from reaching an inselective electrode in the final flow stream. The concept is demonstrated by developing a highly selective semi-automated method for the determination of dissolved NO_x or nitrite at levels greater than 5 μM. Nitrogen dioxide is trapped across a teflon membrane in the dialyzer and converted to nitrate by a buffered peroxide recipient solution. This solution is injected and carried to a tubular nitrate electrode. The final selectivity and detection capabilities of this gas-sensing arrangement are examined and compared to those of the nitrate electrode alone and more conventional sensing systems based on pH electrodes. A dialyzer unit with wider channels improves the efficiency of gas transfer and thus the detection capabilities of the system.

In recent years, potentiometric ion-selective liquid (or polymer) membrane electrodes have found wide use in various fields. While highly-selective devices based on neutral carriers exist for accurate determinations of cations (e.g., K^+, Na^+, Ca^{2+}, etc. [1]), relatively few liquid membrane systems are known to exhibit selective response to given anions [2—4]. Indeed, most anion-sensitive liquid electrodes reported to date use relatively inselective ion-exchangers as the active membrane components (e.g., Aliquat-336 and other quaternary ammonium species); the resulting electrodes usually show selectivity patterns in accordance with the Hofmeister series [5, 6], i.e., organic anions $> HClO_4^- > SCN^- > I^- > NO_3^- > Br^- > Cl^- > HCO_3^-$. This sequence is based on the relative lipophilicity of the anions and thus their partition coefficients into the organic membranes. As a result, the applications of such electrodes have been rather limited. In this and the following paper, a novel approach is described which should enhance the utility of these electrodes when used as detectors in flow-injection analysis (f.i.a.). In this paper, the development of a new, highly selective NO_x/nitrite sensing system is described. It is based on a relatively inselective nitrate polymer-membrane electrode.

Several liquid-membrane electrodes for nitrate have been suggested [7—12]. The most useful devices are based on poly(vinyl chloride) (PVC) membranes incorporating tridodecylhexadecylammonium nitrate or tris(4,7-diphenyl-1,10-phenanthroline)nickel(II) as the ion-exchanging component. While selectivity over lipophilic anions is generally poor, these electrodes have been used successfully to determine nitrate in samples which do not contain large amounts of such interferents [13, 14] and also to determine nitrogen oxides after their oxidation to nitrate, usually with hydrogen peroxide [15, 16]. Several companies offer a gas-sensing electrode for the determination of the nitrogen oxides (NO_x). This sensor is analogous to the conventional Severinghaus pCO_2 gas sensor in that NO_x diffuses through an outer gas-permeable membrane and alters the pH of a thin electrolyte film in contact with a glass pH electrode [17]. Such a sensor can be used to determine anionic nitrite in solution by acidifying the samples [18—20]. Again, though useful in certain instances, this NO_x sensor displays rather poor selectivity relative to other acidic gases, or anions which can be converted to these gases by acidification of the sample [20] (e.g., sulfite, hydrogencarbonate, acetate, etc.). During progress on this work, a promising new liquid-membrane nitrite-selective electrode was reported which appears to offer rather high selectivity over many interfering anions [4].

It has been demonstrated [21] that an extremely selective sensing arrangement for ammonia gas can be developed by using a dialyzer unit in conjunction with a flow-through polymer-membrane ammonium-ion-selective electrode. In that work, the electrode used was not very selective for ammonium ions but the addition of the upstream gas-permeable membrane rendered the resulting system completely selective for ammonia over potassium and other common interferents. In the present paper, this basic concept is extended by developing a system which uses a relatively inselective anion-responsive electrode as the detector. Because of the selectivity deficiencies of the present NO_x and nitrate sensors described above, a novel system for NO_x determinations based on existing nitrate electrodes was thought to be a suitable model for illustrating the potential of this general approach to developing more practical potentiometric systems.

Figure 1 outlines the flow instrument and chemistry underlying the proposed NO_x/nitrite sensing system. A variation introduced here which was not present in the earlier work [21] is the use of the upper channel of the gas dialyzer unit as an injection loop in a flow-injection mode. This variation offers improvements in detection limits compared to operating the recipient stream on a continuous basis; if lower detection limits are required, a larger volume of sample can be passed through the lower channel of the dialyzer and the analyte gas can be continuously trapped in a small static volume of recipient solution (within the upper channel of the dialyzer unit) prior to injection to the electrode. It will be shown that this NO_x-sensing arrangement can be used to detect nitrite with significantly greater selectivity than existing NO_x sensors. Further, the dialysis/flow-injection method of operation
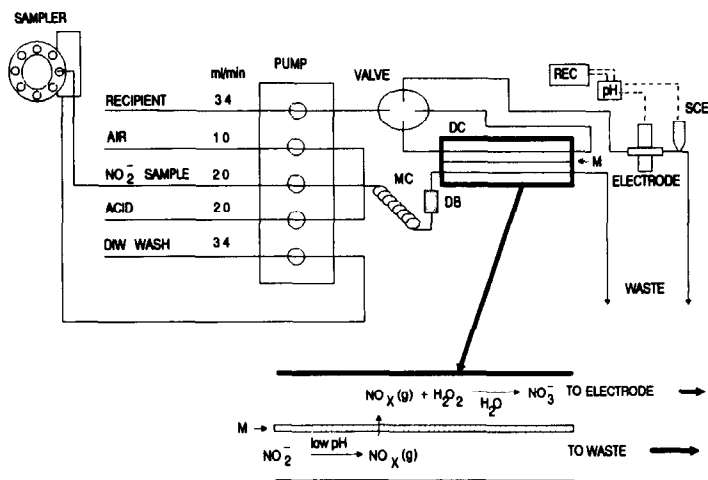
Fig. 1. Schematic diagram of the semi-automated dialyzer/flow-injection instrument for detection of NO_x/nitrite: (DC) dialysis chamber; (MC) mixing coil; (M) microporous membrane; (pH) pH/mV meter; (REC) strip-chart recorder; (SCE) saturated calomel electrode; (DB) tubular debubbler.

does indeed yield superior sensitivity over analogous systems in which the recipient stream flows continuously through the dialyzer.

EXPERIMENTAL

Apparatus

Figure 1 is a schematic diagram of the semi-automated flow system. A Rainin (Woburn, MA) peristaltic pump was used to deliver the sample (2.0 ml min^{-1}), acid (2.0 ml min^{-1}), air (1.0 ml min^{-1}), and recipient (3.4 ml min^{-1}) streams through the system. A Rheodyne model 5020 4-way rotary injection valve was used to control the recipient/carrier stream flow. A Technicon Sampler II served as the autosampler, and was operated with a throughput rate of 30 samples per hour, at a 1:1 sample:wash ratio (for 1-min sample times). Potentiometric measurements were made with a Fisher Accumet pH Meter (Model 620) and recorded on a Fisher Recordall Series 5000 strip-chart recorder. All potentials were measured vs. a saturated calomel reference electrode (SCE) placed downstream from the working electrode.

To improve the efficiency of gas transfer, a modified gas dialyzer unit was machined from plexiglas (termed the wide-channel unit here). Each channel of this unit had a greater surface-to-volume ratio than the commercially available dialyzers used previously [21] (26.4 cm^{-1} rather than 16.3 cm^{-1}). Figure 2 illustrates the design and dimensions of this modified unit. To reduce movement of the membrane and uneven solution flow caused by variable pressure within the dialyzer, each channel contains two support ribs to
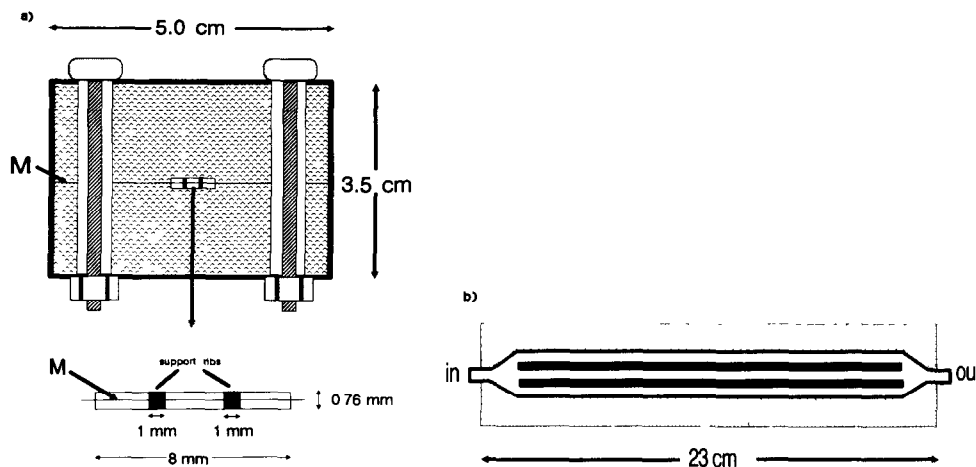
Fig. 2. (a) Normal and expanded end-on view of the wide-channel dialyzer; (M) microporous membrane. (b) Expanded top view of each channel of the dialyzer.

hold the gas-permeable membrane securely in place. For all experiments reported here, the dialyzer was fitted with a microporous polytetrafluoroethylene membrane (0.2 μm pore size; W. L. Gore Associates, Elkton, MD).

Reagents

All chemicals used were of analytical-reagent grade. Standard solutions and buffers were prepared with distilled or reverse osmosis-deionized water. The nitrate exchanger was obtained from Corning. *o*-Nitrophenyl octyl ether (Fluka), and PVC powder (Scientific Polymer Products, Ontario, NY) were used. The final nitrite-sensing system utilized a 0.005 M phosphate buffer, pH 2.8, containing 0.1 wt.% hydrogen peroxide and 1 μM nitrate, as the recipient/carrier stream.

Preparation and characterization of the tubular flow-through nitrate electrode

The tubular nitrate-sensitive electrode was fabricated from 0.89-mm i.d. PVC tubing in a manner similar to that described for the preparation of potassium electrodes [22]. In this case, however, the casting solution contained 30% PVC, 65% *o*-nitrophenyl octyl ether, and 5% of the Corning nitrate exchanger (all by weight). The membrane components were dissolved in enough tetrahydrofuran to form a viscous solution. A solution containing 0.05 M sodium nitrate and 0.05 M sodium chloride saturated with silver chloride, was used as the internal reference solution. The electrode was tested for nitrate response with continuously flowing nitrate standards prepared in the recipient/carrier buffer passing directly through the electrode. The resulting steady-state response was evaluated by measuring the change in potential from the baseline value (potential when only recipient stream buffer flows

through the electrode). The change in potential (ΔE) was then plotted vs. the logarithm of the nitrate concentration. This method showed that the detection limit for nitrate in the recipient/carrier buffer was 1 μM.

Evaluation of final membrane dialyzer/flow-injection arrangement

In these studies, standard solutions of nitrite or other anions were placed in the autosampler. Within the system, the samples are acidified with 0.5 M phosphoric acid and segmented by air bubbles. The sample plug then enters a mixing coil where NO_x is generated (from nitrite). Before entering the mixing coil, the sample stream is debubbled using a tubular debubbler [23]. At the moment the sample plug begins to enter the dialyzer, the rotary injection valve controlling the flow of the recipient/carrier stream is turned so that this stream bypasses the dialyzer unit. Five seconds after the end of the sample plug exits the dialyzer (65 s after sample enters the dialyzer for a 1-min sampling time), the rotary valve is positioned so that the recipient stream plug, contained in the upper channel of the dialyzer, is injected through the electrochemical cell and on to waste. The sample stream goes immediately to waste after exiting the dialyzer. Calibration and selectivity data were obtained by measuring the resulting peak height (in mV) for each sample.

RESULTS AND DISCUSSION

Characterization of the nitrate electrode

Table 1 includes the selectivity coefficients of the Corning PVC membrane electrode for nitrate reported by Davies et al. [24]. This membrane does not exhibit high selectivity over many other anions, especially those which are more lipophilic than nitrate. A similar selectivity pattern was observed for the tubular flow-through nitrate electrode used here. Operating in the flowing system, the electrode exhibited near-Nernstian response (slopes of 55–60 mV/pNO_3) down to 10 μM nitrate when the 0.005 M phosphate buffer at pH 2.8 was used as the background electrolyte. The membrane components utilized in the Orion nitrate electrode [8] offer similar selectivity and response to nitrate when incorporated into the tubular flow-through design and could be used, if desired, in place of the Corning membrane exchanger.

Characterization of the membrane dialyzer/flow injection system for NO_x/nitrite

Effect of dialyzer geometry. When acidified nitrite samples are allowed to flow through the lower channel of the dialyzer, the NO_x generated diffuses through the microporous teflon membrane into the recipient solution contained within the upper channel. This solution traps the NO_x by oxidation to nitrate, thereby maintaining a gradient of NO_x across the membrane. Subsequent injection of the recipient buffer results in the potentiometric response by the nitrate-sensitive electrode to the final concentration of nitrate trapped

TABLE 1

Comparison of apparent selectivity coefficients (K_{ij}^{pot})

| Anion | Apparent selectivity coefficients[a] | | |
| | This work | | Previous work [24] |
	pH electrode	Nitrate electrode	
NO_2^-	1	1	0.066
HCO_3^-	5×10^{-3}	5×10^{-5}	—
F^-	5×10^{-2}	2×10^{-4}	8.7×10^{-4}
Cl^-	5×10^{-2}	5×10^{-5}	5.0×10^{-3}
Br^-	5×10^{-5}	5×10^{-5}	—
I^-	—	—	17
$CH_3CO_2^-$	3×10^{-2}	5×10^{-5}	—
$HOC(CH_2CO_2H)_2CO_2^-$	5×10^{-5}	5×10^{-5}	—
NO_3^-	5×10^{-5}	5×10^{-5}	1.0
SO_3^{2-}	0.17	6×10^{-2}	—
SO_4^{2-}	—	—	1×10^{-5}
ClO_3^-	—	—	1.66
ClO_4^-	—	—	800

[a]Separate solutions method using interferent concentration of 0.1 M.

in the upper channel of the dialyzer. To improve the detection capabilities of the system, the modified wide-channel dialyzer unit was fabricated which had a greater surface-to-volume ratio than the commercially available dialyzers (see Experimental). Figure 3 illustrates how the response of the system depends on the dialyzer geometry. Under exactly the same flow conditions and sampling times, the use of the modified dialyzer results in greater mass
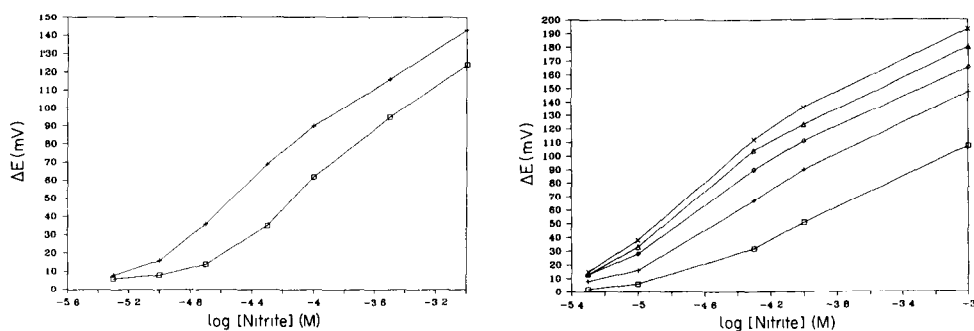

Fig. 3. Comparison of potentiometric response of the dialyzer/flow-injection system for NO_x/nitrite with the conventional (□) and modified (+) dialyzers. Sampling time, 1 min.

Fig. 4. Effect of sampling time on the response of the dialyzer/flow-injection system for NO_x/nitrite: (□) 1 min (continuous flow); (+) 1 min (f.i.a.); (◊) 2 min (f.i.a.); (▲) 3 min (f.i.a.); (×) 4 min (f.i.a.).

transfer of NO_x between the two streams. This occurs because decreasing the depth of the two streams limits the aqueous diffusion-layer factor in the flux equation governing mass transfer [25]. Based on the results shown in Fig. 3, it appears that the efficiency of gas transfer is improved to a greater extent at lower pNO_x than at higher values. Thus, the wide-channel dialyzer offers the advantage of better detection capabilities without a concomitant decrease in sample throughput. Neither reproducibility nor wash-out times were adversely affected by replacing the commercial dialyzer with the wide-channel design.

Choice of recipient/trapping solution

Two methods of trapping NO_x in the recipient stream are possible: an oxidative trap in which nitrite is converted to nitrate, or a high-pH buffer trap which forces the equilibrium of the $2NO_2^- + H_2O = NO_3^- + NO_2^- + 2H^+$ reaction to the right. The high-pH trap was tested first by using 0.05 M Tris-phosphate, pH 8.5, as the recipient solution. This method gave very poor response to the nitrite standards, probably because of the inherent potentiometric response of the electrode to the high concentration of phosphate, and the differences in response of the electrode to nitrate and nitrite. The latter effect contributes because in this buffer-trap mode half of the total nitrogen oxide species is converted to nitrite, for which the membrane electrode has a selectivity coefficient of only 0.066 [24].

For the oxidizing trap, three different oxidants ($KMnO_4$, $K_2Cr_2O_7$, and H_2O_2) were examined, all in a phosphate buffer at low pH. Both permanganate and dichromate proved to be major interferents. Hydrogen peroxide did not interfere, and was the most effective in oxidizing and trapping the NO_x. Consequently, a phosphate buffer containing hydrogen peroxide was chosen as the carrier/trapping solution. Optimization of this buffer involved studying the effect of buffer strength, pH and peroxide concentration. In general, it was found that lower pH and more dilute buffer concentrations resulted in better detection limits toward nitrite. However, requirements for the nitrate electrode to operate in solutions above pH 2.5 [24] and electrode noise problems associated with low ionic strength impose a practical lower limit on these two parameters. In addition, it was found that 0.1 wt.% hydrogen peroxide in the recipient buffer was sufficient for the conversion of nitrite to nitrate in the concentration range of interest (i.e., 5—100 μM). Surprisingly, significant increases in the peroxide concentration decreased the response of the system, particularly at low nitrite levels. Based on these observations, a 0.005 M phosphate buffer, pH 2.8, containing 0.1% hydrogen peroxide and 1 μM potassium nitrate was used. The addition of nitrate speeded the return to baseline and improved the magnitude of the response at lower nitrite levels; various workers have shown for the determination of many other analytes in flow-injection systems that addition of a low concentration of analyte to the carrier stream improves the responses at low levels.

Dependence of response on sampling time

Figure 4 shows a plot of the response vs. sampling time of the nitrite-sensing system. The longer the sampling time, the greater the potentiometric response for a given nitrite concentration. The increased sensitivity obtained with the injection-loop approach is readily observed when contrasted to the response obtained when the system is operated in a continuous-flow mode (i.e., recipient/carrier stream continuously pumped through the upper channel of dialyzer). The injection loop effectively concentrates the NO_x from the large volume of the sample plug into the much smaller recipient volume. This preconcentration step explains the increased detection capabilities of the membrane dialyzer/flow-injection arrangement. Figure 5 shows a typical strip-chart recording of the response obtained when standards of nitrite are introduced into the system using a 1 min sampling time. Peak potentials (measurement off baseline) for replicate standard samples ($n = 4$) were generally reproducible to within 2.5 mV whereas absolute peak potentials (measurement off chart zero) were more reproducible (<1 mV), particularly at nitrite levels >50 μM. This difference in precision is due to a small but constant negative drift in the baseline potential of the tubular nitrate electrode when operated on a continuous basis in the presence of nitrate.
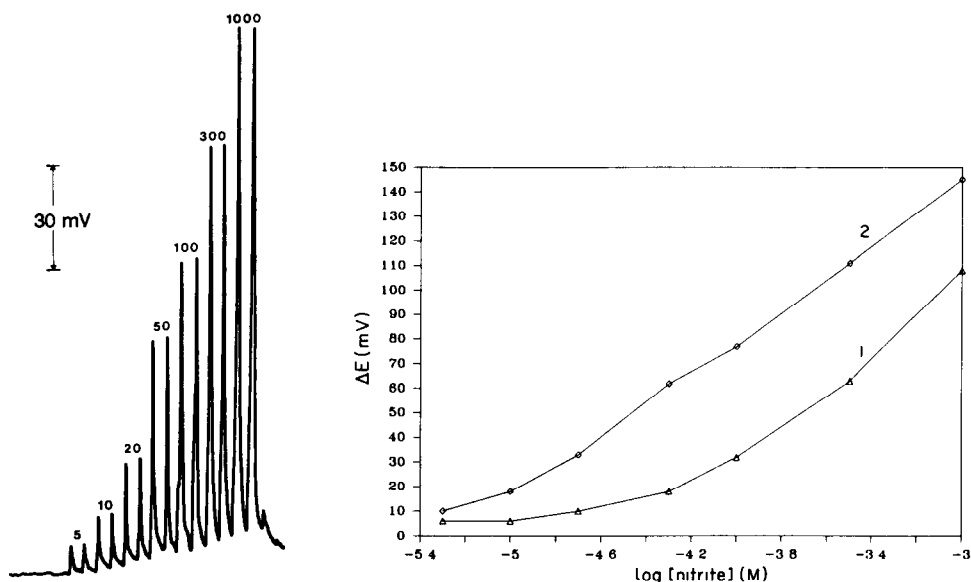

Fig. 5. Typical strip-chart recording obtained with the NO_x/nitrite sensing system with a 1-min (f.i.a.) sampling time and standard nitrite solutions. Numbers on the peaks refer to concentration (μM).

Fig. 6. Comparison of potentiometric response to nitrite obtained with the dialyzer/flow-injection system (1-min sampling time) and different electrodes: (1) pH electrode; (2) nitrate-sensitive electrode.

Comparison of the nitrate and pH electrodes as detectors in the dialyzer/flow-injection system

To compare the proposed system with the conventional NO_x sensing approach, which utilizes a pH electrode behind a gas-permeable membrane [17], the nitrate-sensitive electrode was replaced by a tubular polymer pH electrode [26], and the recipient/trapping solution was changed to 0.01 M sodium nitrite, which is the recommended fill solution for the static NO_x sensors [17]. The response to nitrite standards and other potential interfering anions was then determined. As shown in Fig. 6, when the same sampling times and flow parameters are used, the detection limits for nitrite are about one order of magnitude lower when the nitrate-sensitive electrode is used as the detector. The detection limits found for the flow-through pH-sensing mode are similar to those obtained with the conventional static gas-sensing designs [20].

Table 1 compares the apparent selectivity coefficients of the two detection systems with those reported earlier for the nitrate electrode alone [24]. The superior selectivity of the gas sensing system based on the nitrate-sensitive electrode is due to the ability of the nitrate-responsive membrane to discriminate against anionic forms of the various acidic gases. All the volatile acids tested, or their respective anions, gave response with the system based on the pH electrode while only sulfite yielded any significant response when the nitrate electrode was used. The actual selectivity over sulfite is even better than indicated in Table 1 because the selectivity coefficients listed were determined for fixed interferent concentrations of 0.1 M; at sulfite levels <1 mM, there was essentially no potentiometric response when 0.1% hydrogen peroxide was used because of the oxidation of SO_2 to sulfate in the recipient stream. The nitrate-sensitive electrode has high selectivity over sulfate but only marginal selectivity over hydrogensulfite (the major form of sulfite in the recipient solution based on $pK_a = 7.2$). Thus, SO_2 levels approaching the concentration of oxidant in the recipient stream will be completely oxidized to undetectable sulfate, whereas above this oxidant concentration, excess diffusing SO_2 will form more detectable hydrogensulfite.

Conclusions

Under optimized conditions, the semi-automated dialyzer/flow-injection system provides a throughput of 30 samples per hour with good selectivity for nitrite over many common anions. The system exhibits good precision and detection limits and should prove useful for the direct determination of nitrite as NO_x in a variety of samples. It appears that the use of this dialyzer/flow-injection concept could be applied advantageously to detect other species for which a membrane can separate the analyte in some detectable form from possible interferents. Such a system is reported for salicylate in the following paper [27].

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