

Flow-through Units for Solid-state, Liquid and PVC Matrix Membrane Ion-selective Electrodes to Minimise Streaming Potentials

Theodore K. Christopoulos

Laboratory of Analytical Chemistry, University of Athens, 104 Solonos Street, Athens 106 80, Greece

and Eleftherios P. Diamandis*

Cyberfluor Inc., 179 John Street, Suite 400, Toronto, Ontario, Canada M5T 1X4

When making measurements with ion-selective electrodes in continuous flow systems, potential oscillations are observed which are due to changes in the flow-rate and consequently to changes in streaming potentials. Three different flow-through units suitable for potentiometric measurements with solid-state, liquid and PVC matrix membrane electrodes have been constructed. In all the units, streaming potential oscillations were reduced to ≤ 0.2 mV by minimising the distance between the sensing membrane and the external reference electrolyte - sample solution contact zone. Air-segmented streams were used to evaluate the units at flow-rates of 1.74, 3.64 and 6.70 ml min⁻¹. Sampling rates as high as 60, 120 and 240 h⁻¹, respectively, were achieved.

Keywords: Streaming potential; ion-selective electrodes; continuous flow analysis

Ion-selective electrodes (ISEs) have been employed for continuous flow measurements in industrial process control, biomedical analysis and environmental and pollution research.¹⁻³ For most of these applications, regular dip-type ISEs have been used, either in a flow cell or equipped with a special flow-through cap allowing the sample solution to flow across the sensing membrane surface.³ Newer configurations include the construction of solid-state and liquid-membrane flow-through ISEs in which the measuring stream passes through the sensing electrode membrane.³⁻⁵ In addition, tubular designs have allowed the sensing membrane to become part of the tube which contains the measuring stream.⁶⁻⁸

It is well known that in continuous flow systems in which ISEs are used as sensors, oscillations in the measuring potential caused by the peristaltic pump are always observed. When a liquid is forced through a narrow capillary by a pressure gradient, a potential difference, E_s , is set-up (the streaming potential), which is given by the following equation (it is assumed that the flow is laminar):

$$E_s = \frac{2dD\zeta l}{\pi^2 r^4 \lambda} \quad \dots \quad (1)$$

where d is the flow-rate, D the dielectric constant, ζ the electrokinetic potential, l the length of the tube connecting the ISE with the reference electrode, r the radius of the tube and λ the conductivity.⁹

If all the parameters in equation (1) are kept constant, the streaming potential, E_s , is constant and it is simply added to the e.m.f. of the cell. However, the flow-rate, d , usually oscillates to a certain extent and this leads to oscillation of the value of E_s , which appears in the measuring signal as periodic noise. The problem increases as the flow-rate becomes higher.

The most practical solution for suppressing the streaming potential oscillations is to add a large amount of inert electrolyte, so that a larger value of λ is obtained. However, this solution is not always possible, e.g., when the salt interferes with the electrode response. Other possibilities include the optimisation of the values of d , r and l and the incorporation of pulse suppressors on the manifold in order to decrease the oscillations of the flow-rate.

In this work we have designed flow-through electrode units in which the distance l between the ISE and the reference electrode has been minimised. The salt bridge electrolyte - sample solution contact zone is a porous ceramic cylinder of

1 mm diameter and 6 mm long. The ISE sensing membrane is positioned opposite the ceramic plug so that the distance l is almost zero. Three different flow-through configurations for solid-state, liquid and PVC matrix membrane electrodes are proposed; their performance was evaluated for iodide (solid), perchlorate (liquid) and propantheline (PVC matrix) sensitive membranes. We used air-segmented streams and studied the effect of flow-rate at three levels, viz., 1.74, 3.64 and 6.70 ml min⁻¹. Sampling rates as high as 60, 120 and 240 samples h⁻¹, respectively, were achieved. The observed oscillations of the base-line potential were always very low (≤ 0.2 mV).

Experimental

Chemicals

All chemicals used were of analytical-reagent grade. Standard solutions were prepared with de-ionised, distilled water. Propantheline bromide was obtained from Sigma (St. Louis, MO, USA), poly(vinyl chloride) (PVC) of very high relative molecular mass from Aldrich (Milwaukee, WI, USA) and *o*-nitrophenyl octyl ether (*o*-NPOE) and sodium tetraphenylborate from Fluka (Buchs, Switzerland). The liquid ion exchanger and internal reference solution for the perchlorate ISE were obtained from Orion Research (Cambridge, MA, USA).

Apparatus

A schematic diagram of the automated analysis flow system which was used to evaluate flow-through electrodes is shown in Fig. 1. A Gilson Minipuls variable-speed peristaltic pump used to pump solutions continuously through the electrode assembly. The sampler was an A40 Sampler II from Hook and Tucker (Surrey, UK). The external reference electrode used was a saturated calomel electrode (Radiometer, Copenhagen, Denmark). All potentiometric measurements were carried out at ambient temperature with a Corning Model 12 Research pH/mV meter and recorded on a Radiometer strip-chart recorder (REC 61) through a high-sensitivity unit (REA 112) interface.

Procedures

Construction of the salt bridge electrolyte - sample solution contact zone

A cylindrical piece of porous ceramic, 6 mm long and 1 mm in diameter, is used as a contact between the measuring solution and the salt bridge of the external reference electrode. The ceramic plug is constructed as follows. A piece of ceramic

* To whom correspondence should be addressed.

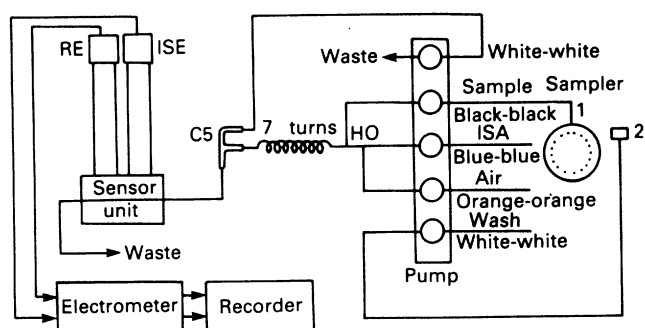


Fig. 1. Schematic diagram of the continuous flow system. The colour code of the pump tubes is that given by Technicon. ISE, Ion-selective electrode; RE, reference electrode; C5, de-bubbler; HO, "cactus"; 1, sampling position; 2, wash position; ISA, ionic strength adjusting solution

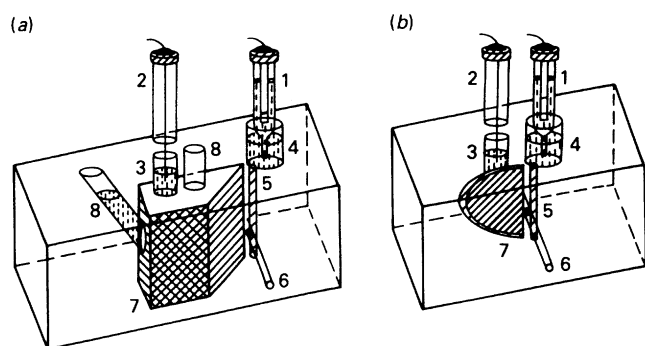


Fig. 2. (a) Flow cell configuration for liquid membrane ISE. 1, External reference electrode; 2, internal reference electrode; 3, internal reference solution; 4, salt bridge; 5, ceramic plug; 6, inlet of measuring stream; 7, G5 glass frit; 8, liquid ion-exchanger reservoir. (b) Flow cell configuration for solid-state ISE. 1-6, As in (a); 7, solid-state membrane. The various parts are not to scale and dimensions are given in the text. The point of contact between the membrane, the ceramic plug and the measuring stream is shown as a black circle. The outlet of the stream is not shown but it is a straight extension of the inlet hole

approximately 3 cm long and 0.5 cm wide is cut from a standard porous ceramic plate by using a pair of pliers. Any sharp edges are smoothed with emery paper. The ceramic piece is then positioned securely on an electric drill (in the hole which usually carries the drill bits) and the drill is turned on. While the ceramic piece rotates, a piece of emery paper is positioned tangentially at one side in such a manner that the ceramic is ground continuously on it. With this procedure, one end of the ceramic piece becomes cylindrical and of progressively smaller diameter. The drill is stopped when the diameter of the cylindrical ceramic piece is approximately 1 mm. From this piece, a tip with a length of 6 mm is cut and used as a junction (see below).

Construction of the flow-through cell for liquid ion exchangers

The final configuration of the cell is shown in Fig. 2(a). A piece of a porous glass frit ($5 \times 5 \times 3$ mm) (obtained from a G5 sintered-glass crucible, pore size about 1–1.6 μm ; Schott, Mainz, FRG) is ground with emery paper so that a trapezoidal shape is achieved [Fig. 2(a)]. The piece is silylated by immersing it in trimethylchlorosilane (Pierce, Rockford, IL, USA) for 10 min. With this procedure the porous glass frit becomes hydrophobic and suitable for supporting the liquid ion exchanger. The silylated frit is washed with water and acetone and dried. The frit is then placed in the liquid ion-exchanger solution for 5 min to wet it. After removing the frit, any excess of the liquid ion exchanger is wiped off with absorbent paper. The ceramic plug is also placed in the salt bridge solution (see below) for 5 min and any excess is removed with absorbent paper. The glass frit and the ceramic

plug are now ready for embedding in the epoxy resin as described below.

An orthogonal plastic mould (dimensions $4.5 \times 4 \times 2$ cm) is used, in combination with a casting plastic (Epofix resin; H. Struers Scientific Instruments, Copenhagen, Denmark). The embedding was achieved by initially preparing a supporting layer that filled half of the mould and allowing it to harden. Then, the piece of glass frit and the ceramic plug were placed on the supporting layer very close to but not in contact with each other [Fig. 2(a)] and the mould was filled to the top with a covering layer of plastic. The filled mould was allowed to harden completely for at least 24 h. The resulting orthogonal cast block was ground and polished with various sizes of emery paper. Holes of appropriate diameter were made on the upper surface of the block as shown in Fig. 2(a), with slow-speed drilling using regular drill bits. A flow-through channel 1.5 mm in diameter was also drilled at right-angles to the line of the glass frit and the ceramic plug, so that it contacted both of these components, leaving the ion-sensitive membrane opposite the ceramic junction.

Cell organisation

The flow-through unit was filled with the liquid ion exchanger by adding it through the filling holes. The internal reference solution and the salt bridge ($100 \text{ g l}^{-1} \text{ NaNO}_3$) were then added through the appropriate holes. An Ag - AgCl wire was used as an internal reference electrode and a saturated calomel electrode as the external reference electrode. The electrochemical cell was mounted in the continuous flow system by using two stainless-steel nipples.

Construction of the flow-through unit for solid membranes

The configuration of the unit is shown in Fig. 2(b). An AgI - Ag₂S coprecipitate pellet-sensing membrane, prepared according to reference 10, was employed. The pellet, after construction, is ground with emery paper to obtain a semicircular shape as shown in Fig. 2(b). For the construction of the electrochemical cell, the same procedure described for the liquid ion-exchanger unit is followed, with the exception that the glass frit is replaced with the AgI - Ag₂S pellet and there are no liquid ion-exchanger filling holes. The internal reference electrode was silver wire dipped in 10^{-2} M AgNO_3 solution.

Preparation of a PVC membrane sensitive to propantheline

The preparation and analytical characteristics of a propantheline liquid membrane ISE were described previously.¹¹ The ion exchanger was the tetraphenylborate salt of propantheline dissolved in *o*-nitrotoluene. The liquid ion exchanger for the PVC membrane was prepared in the same manner except that *o*-NPOE was used instead of *o*-nitrotoluene, because of its better plasticising properties. The liquid ion exchanger was then entrapped in PVC by a procedure described previously.¹²

Construction of the flow-through cell for PVC membranes

The final configuration of the constructed cell is shown in Fig. 3. The unit consists of two orthogonal Plexiglas pieces A and B, with dimensions of $3 \times 1.7 \times 1.4$ cm. The pieces were assembled as follows.

Piece A. The sample stream enters the cell from hole 1 (inlet) and leaves it from hole 2 (outlet). Both holes have a diameter of 1.5 mm and coincide at point P, which is in the middle of the upper surface of piece A. In the centre of the lower surface of piece A another hole is drilled (hole 3), 8 mm in diameter and 9 mm deep. The hole is further drilled with a 1.2 mm bit until it reaches hole 2 at a point which is approximately 0.5 mm from point P (Fig. 3). In this narrow hole, the ceramic junction plug is inserted in such a way that the one end is positioned approximately in the middle of hole 2 and the other end lies in hole 3. The junction plug is secured in

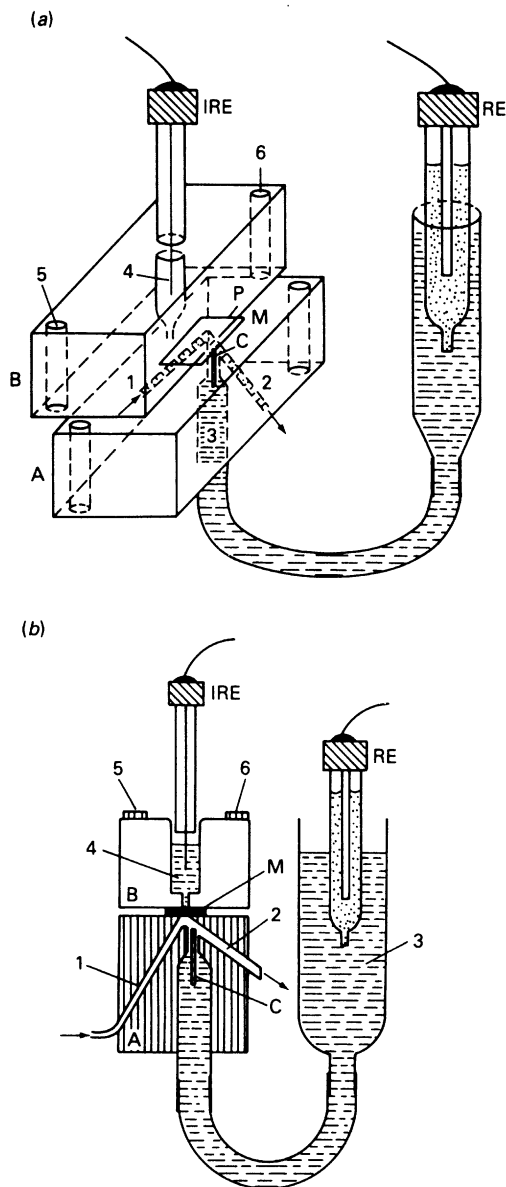


Fig. 3. Flow cell configuration for PVC matrix membrane ISE. Numbers correspond to the following holes: 1 and 2, inlet and outlet of the measuring stream; 3, salt bridge electrolyte; 4, internal reference solution; 5 and 6, screws; M, PVC matrix membrane; P, point of sample contact with the membrane; C, ceramic plug; RE, external reference electrode; IRE, internal reference electrode. The various parts are not to scale and dimensions are given in the text

place with Araldite epoxy adhesive, which is added from point P and from the bottom of hole 3. The adhesive fills the space between the plug and the Plexiglas and is left for 2 h to harden. The excess of the adhesive is removed by using a 1.5-mm bit in holes 1 and 2 and a 2-mm bit in hole 3. It is essential that both ends of the ceramic plug are free from excess of adhesive, otherwise electrolytic contact may not be established.

A 4 cm long glass tube with approximate internal and external diameters of 5 and 7.5 mm, respectively, is inserted in hole 3 and stuck with Araldite adhesive as shown in Figure 3(b). This glass tube is connected with a wider "reservoir" tube via PVC tubing (approximately 10 cm long).

Piece B. In the centre of the upper surface of this piece, hole 4 is drilled 7 mm in diameter and 8 mm deep. The hole is further drilled with a 2-mm diameter bit until it reaches the lower surface of the piece.

The two pieces can be stacked together by means of two screws which are positioned in holes at the two corners of the pieces (holes 5 and 6).

Cell organisation

A 5 × 5 mm piece of PVC membrane is cut and placed at point P of Plexiglas piece A, so as to cover the small hole at this point, which is created by the coincidence of the inlet and outlet holes. Piece B is placed over piece A and the screws are fastened. Hole 3, the PVC tube and the reservoir tube are filled with 3 M KCl solution (salt bridge). The level of fluid in the reservoir tube must be at least 5 cm higher than the level of the ceramic junction so that a positive hydrostatic pressure difference exists. Hole 4 of piece B is filled with internal reference solution (10^{-2} M propantheline bromide - 0.1 M NaCl solution, saturated with AgCl by adding one drop of a 10^{-2} M AgNO_3 solution). An Ag - AgCl wire is dipped in the internal reference solution as shown in Fig. 3. A saturated calomel electrode dipped in the salt bridge serves as an external reference electrode.

During measurements, the sample stream contacts the sensing ISE membrane at point P. The liquid junction is positioned slightly further from this point so as to be downstream.

Results and Discussion

The silylated G5 glass frit holds the liquid ion exchanger strongly and therefore it does not leak under the pressure of either the internal reference solution or the sample stream. This frit performs better than the unsilylated G4 frit used previously for the same purpose.⁵ The construction of the frit in this configuration is such that the back part is wider and serves as a liquid ion-exchanger reservoir. At the point of contact of the membrane with the measuring stream, the frit is very thin (1 mm wide) because in this way the membrane is washed out faster and the response of the electrode is fast.¹³

The electrochemical cell configuration which is proposed for the PVC membrane electrodes has the advantage that the membrane can be replaced very easily in a few minutes. The units for the liquid and solid-state membranes are not re-usable for different ions.

In many continuous flow applications in which flow-through ISEs are used as sensors, the external reference electrode is usually placed in the beaker of the waste solution, generally at a distance 5–10 cm away from the flow-through ISE.³ We have studied the base-line noise of the electrochemical cell for occasions (a) when the external reference electrode is very close to the ISE (proposed configurations) and (b) when the external reference electrode is 10 cm away from the ISE and it is in the waste beaker which contains 0.1 M Na_2SO_4 . For this study, the measuring stream was a 10^{-4} M solution of the ion in water or in 0.05 M Na_2SO_4 . Recordings were obtained at flow-rates of 1.74 and 3.64 ml min^{-1} . The results are presented in Figs. 4 and 5 for the iodide and propantheline electrodes, respectively.

It can be seen that for the iodide ISE, when the sample is dissolved in water and the external reference electrode is 10 cm away from the ISE, the base-line noise is 40–50 mV because of the low conductivity of the sample. For the same experiment, when the solvent is 0.05 M Na_2SO_4 , the noise is in the range 1–2 mV with both ISEs. When the external reference electrode is adjacent to the ISE (proposed configurations) the base-line noise is of the order of 0.2 mV with either water or Na_2SO_4 solution as solvent. The base-line noise was similar at both flow-rates tested.

The proposed flow-through electrodes for iodide and perchlorate anions and for the propantheline cation exhibited characteristics similar to those of the corresponding conventional dip-type electrodes. Measurements were carried out with the continuous flow system shown in Fig. 1 without the use of the sampler. Solutions of the measured ions were aspirated continuously into the system, via the sampling tube, from each stock solution bottle. The bottles were inter-

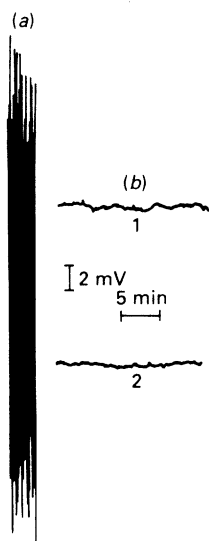


Fig. 4. Recordings of the base-line noise for the iodide electrode with the external reference electrode positioned (a) 10 cm from the ISE in the waste beaker (the noise is similar at flow-rates of 1.74 and 3.64 ml min⁻¹) and (b) very close to the ISE [proposed configuration shown in Fig. 2(b)]. Flow-rate: (1) 1.74 and (2) 3.64 ml min⁻¹. In all experiments water was pumped through the ISA channel. Sample solution, 10⁻⁴ M NaI in water

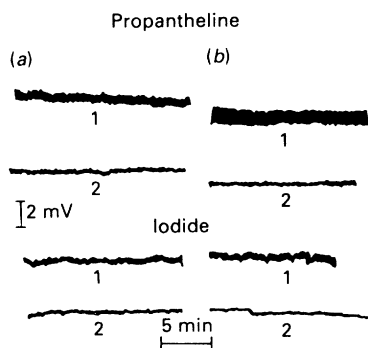


Fig. 5. Recordings of the base-line noise for the propantheline and the iodide ISE. In all experiments the ISA solution was 0.05 M Na₂SO₄. Flow-rates: (A) 1.74 and (B) 3.64 ml min⁻¹. The external reference electrode was either (1) 10 cm away from the ISE, in the waste beaker, or (2) very close to the sensing membrane [proposed configuration as shown in Figs. 3 and 2(b)]. Sample solution, 10⁻⁴ M of the ion of interest in 0.05 M Na₂SO₄

changed manually every few minutes. With this method the steady-state response of the electrodes is recorded.

Typical steady-state recordings for the iodide, perchlorate and propantheline electrodes are shown in Fig. 6. The flow-rate was 3.64 ml min⁻¹. Calibration graphs based on these recordings, and the calculated electrode slopes and linear response ranges, are shown in Fig. 7.

The prepared electrodes were also tested in continuous flow measurements on discrete samples where each sample was separated from the next by a wash solution. These measurements were performed at three flow-rates, viz., 1.74, 3.64 and 6.78 ml min⁻¹, and at sampling rates of 60, 120 and 240 determinations per hour, respectively. The wash solutions used contained either constant dilute (Fig. 8) or concentrated (Fig. 9) background levels of the measured ions. With this method, the response of the electrodes from dilute to concentrated solutions and *vice versa* can be evaluated under continuous flow conditions. The sample to wash ratio was 1:1 or 3:1 when dilute and concentrated background wash solutions were used, respectively.

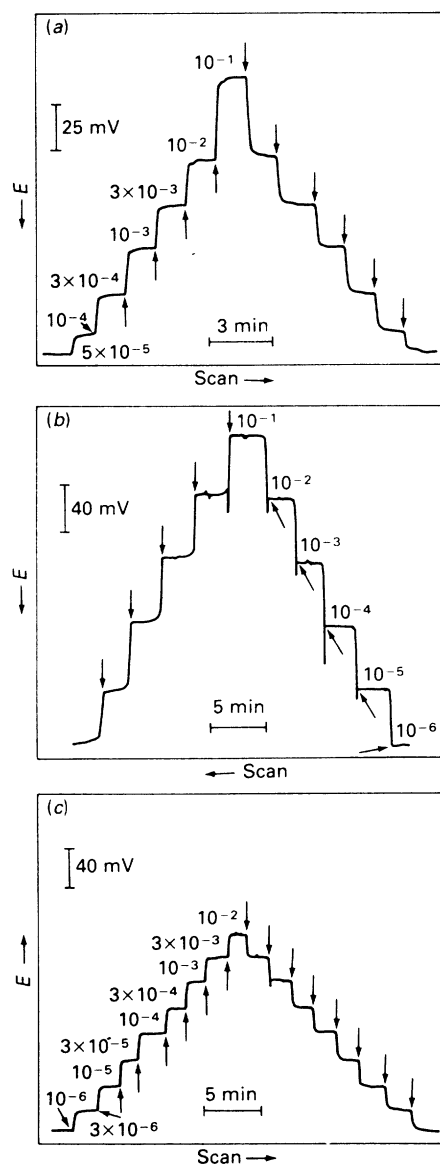


Fig. 6. (a) Perchlorate, (b) iodide and (c) propantheline ISE responses to changes in concentration, under continuous flow conditions. The arrows indicate the point at which the new solution first reaches the electrode. All concentrations are final, after the dilution in the manifold

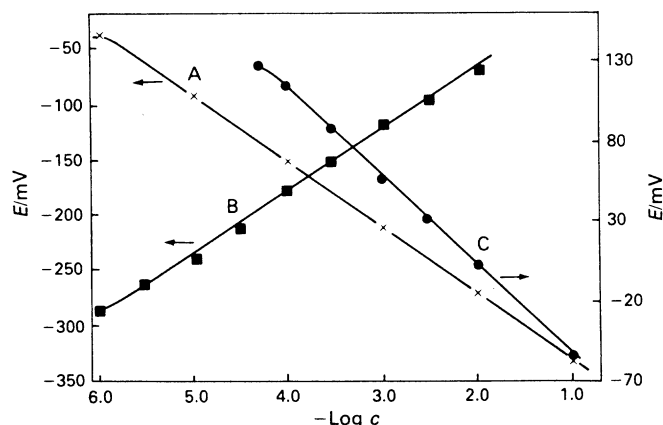


Fig. 7. Calibration graphs of the constructed electrodes under continuous flow conditions (from Fig. 6). The electrode slopes (in mV) are: (A) 60.2 (iodide); (B) 57.1 (propantheline); and (C) 55.7 (perchlorate). Potential axes correspond to propantheline and iodide (left) and perchlorate (right)

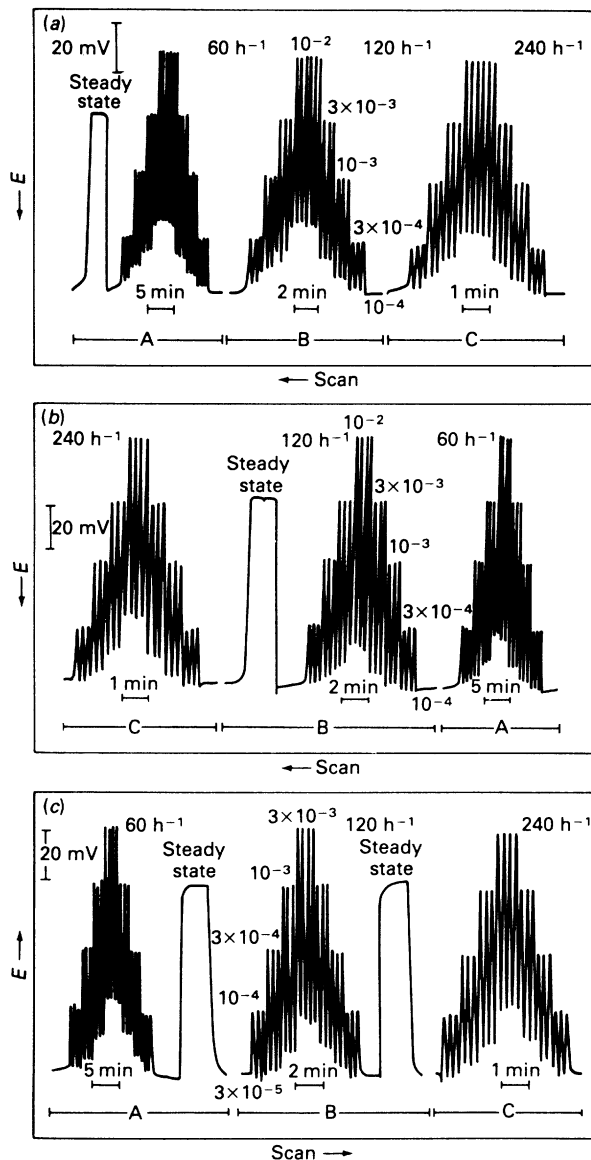


Fig. 8. Typical recordings of continuous flow measurements of discrete samples with (a) perchlorate, (b) iodide and (c) propantheline ISEs at flow-rates (A) 1.74; (B) 3.64 and (C) 6.70 ml min⁻¹. The concentrations of the standards and the sampling rates are shown. Sample to wash ratio, 1:1

On increasing the flow-rate, the response time of the electrodes decreases, as has been shown previously.¹³⁻¹⁵ This is due to the fact that the width of the aqueous static diffusion layer which is in contact with the ISE sensitive membrane decreases as the flow-rate increases. The diffusion of the measuring ion through this layer is the rate-limiting step in the response time of these electrodes.

With the iodide solid-state ISE as sensor, sampling rates of up to 360 h⁻¹ have been obtained at high flow-rates (9.2 ml min⁻¹) in continuous flow air-segmented streams.¹⁵ Data obtained here with the proposed electrode units for response time studies are given in Table 1. The response in all instances is expressed as the percentage of the peak height observed with respect to the peak height of the steady-state response.

The precision of the measurements can be appreciated by examining the peaks in Figs. 8 and 9. The average coefficient of variation in all instances was better than 1%.

Conclusion

We have proposed new flow-through units for solid-state, liquid and PVC membrane ISEs. The units are complete

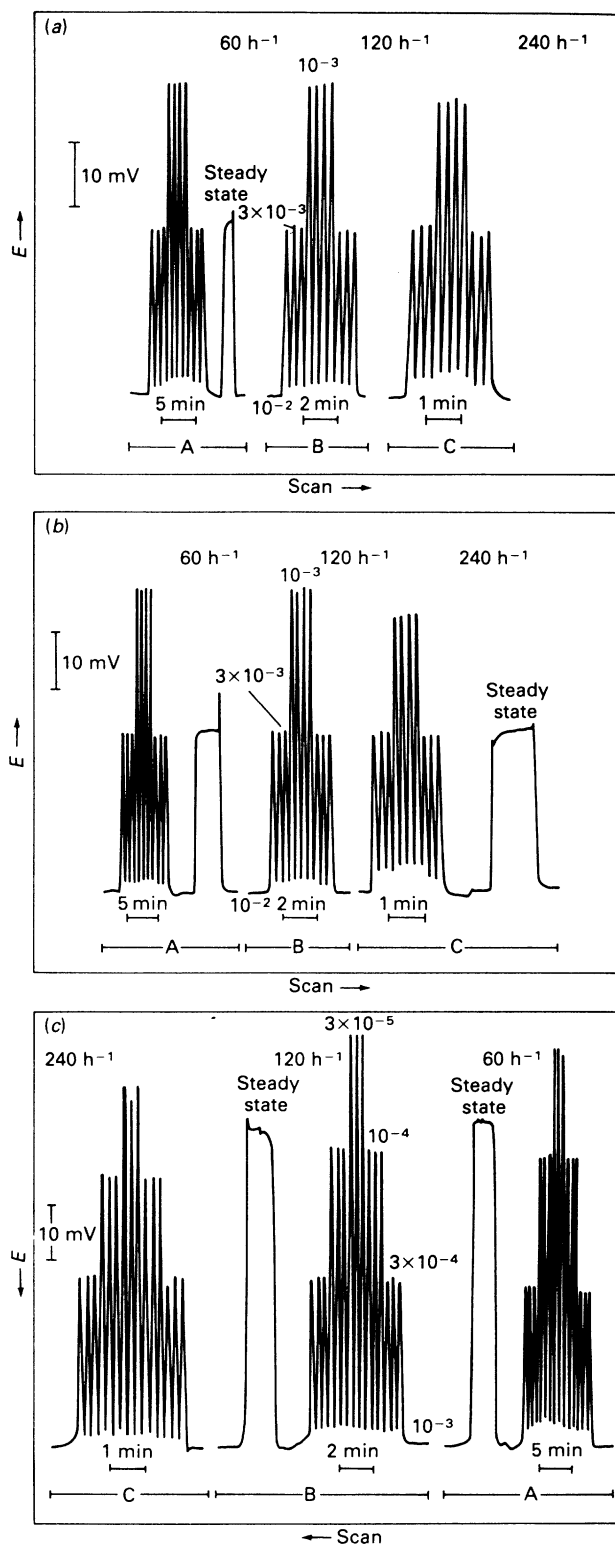


Fig. 9. Typical recordings of continuous flow measurements with (a) perchlorate, (b) iodide and (c) propantheline ISEs using concentrated wash solutions. Flow-rates as in Fig. 8. Sample to wash ratio, 3:1

electrochemical cells with the external reference electrode positioned very close to the sensing membrane of the ISE. With this arrangement we have minimised the streaming potential effects and achieved a base-line noise of ≤ 0.2 mV. Excellent response times have been achieved working under low to high concentration changes, and *vice versa*, under continuous flow conditions. Sampling rates of up to 240 h⁻¹ have been achieved with these units with a precision of

Table 1. Response times of the proposed electrodes at various flow-rates and sampling rates

Flow-rate/ ml min ⁻¹	Sampling rate/h ⁻¹	Percentage of steady state					
		Perchlorate		Propantheline		Iodide	
		I*	II†	I*	II†	I*	II†
1.74	60	100	97	99	99	100	99
3.64	120	99	96	99	99	100	99
6.70	240	98	96	97	98	98	98

* The concentration changes for all electrodes were from 10⁻⁴ to 3 × 10⁻³ M.

† The concentration changes were from 10⁻² to 3 × 10⁻³ M (perchlorate and iodide) and from 10⁻³ to 3 × 10⁻⁴ M (propantheline).

generally better than 1%. We believe that these units will be useful in continuous flow measurements where ISEs are applied as sensors. We are currently investigating the possibility of applying the same cell configurations in flow-injection analysis.¹⁶

References

1. Arnold, M. A., and Solsky, R. L., *Anal. Chem.*, 1986, **58**, 84R.
2. Arnold, M. A., and Meyerhoff, M. E., *Anal. Chem.*, 1984, **56**, 20R.
3. Hadjiioannou, T. P., Papastathopoulos, D. S., and Diamandis, E. P., in Rubin, M., *Editor*, "Computerization and Automation in Health Facilities," CRC Press, Boca Raton, FL, 1984, pp. 169-196.
4. Thomson, H., and Rechnitz, G. A., *Chem. Instrum.*, 1972, **4**, 239.
5. Papastathopoulos, D. S., Diamandis, E. P., and Hadjiioannou, T. P., *Anal. Chem.*, 1980, **52**, 2100.
6. Meyerhoff, M. E., and Kovach, P. M., *J. Chem. Educ.*, 1983, **60**, 766.
7. Alegret, S., Alonso, J., Bartroli, J., Paulis, J. M., Lima, J. L. F. C., and Machado, A. A. S. C., *Anal. Chim. Acta*, 1984, **164**, 147.
8. Van Staden, J. F., *Anal. Chim. Acta*, 1986, **179**, 407.
9. Van den Winkel, P., Mertens, J., and Massart, D. L., *Anal. Chem.*, 1974, **46**, 1765.
10. Papastathopoulos, D. S., and Karayannis, M. I., *J. Chem. Educ.*, 1980, **57**, 904.
11. Mitsana-Papazoglou, A., Christopoulos, T. K., Diamandis, E. P., and Hadjiioannou, T. P., *Analyst*, 1985, **110**, 1091.
12. Craggs, A., Moody, G. J., and Thomas, J. D. R., *J. Chem. Educ.*, 1974, **51**, 541.
13. Lindner, E., Toth, K., and Pungor, E., *Anal. Chem.*, 1976, **48**, 1071.
14. Mertens, J., Van den Winkel, P., and Massart, D. L., *Anal. Chem.*, 1976, **48**, 272.
15. Alexander, P. W., and Seegopoul, P., *Anal. Chem.*, 1980, **52**, 2403.
16. Růžička, J., and Hansen, E. H., "Flow Injection Analysis," Wiley, New York, 1981.

Paper A6/476

Received December 17th, 1986

Accepted March 23rd, 1987