Flow-Through Electrode Unit for Liquid Membrane Electrodes

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The construction of a flow-through electrode unit for the preparation of liquid membrane electrodes is described. The construction is based on the use of a triangular piece of glass frit embedded in a plastic block. The glass frit serves as an inert matrix holding the electroactive liquid phase. A hole drilled through the frit forms the sensing path for the test solution channeling. The unit is equipped with an internal reference solution–Ag/AgCl electrode system and a reservoir for ion exchanger storage. Flow-through liquid membrane electrodes for calcium, nitrate, perchlorate, and picrate ions are prepared by using conventional ion exchangers for the evaluation of the constructed unit. The electrodes are tested for their stability, reproducibility, response time, and working range under various continuous-flow conditions.

Ion-selective electrodes and gas-sensing probes have already been employed for continuous-flow measurements in industrial process control, biomedical analysis, and environmental or pollution research (1–6). Various types of automatic or semiautomatic sytems are now available, using such sensors under the basic configurations of the flow-through cells and the sensor end-cups. In the majority of these applications regular dip-type sensors are used, where the sample solution is flowing across the sensing membrane surface (7). Nevertheless, this design may cause a series of problems, such as, air bubble trapping, easy clogging from particulate matter, instability of the measured potential, and development of streaming potentials due to the improper geometry of the flow-through cell (8). Also, in the case of liquid membrane electrodes the potential response becomes erratic at high flow rates, owing to distortion of the membrane by the high pressure of the stream (1, 7). Most of these drawbacks can be obviated by using a design where the sample solution is channeled through the sensing membrane. Flow-through sensors based on this configuration have been developed recently, but so far these have only been of the solid-state or glass capillary type membrane electrodes (8–10).

The present paper describes the construction of a new flow-through electrode unit for the preparation of liquid membrane electrodes. The design is based on the use of a piece of fine porosity glass frit embedded into a polymeric plastic. The glass frit serves as an inert matrix which holds the electroactive liquid phase. A hole drilled through the glass frit forms the sensing path for the sample stream channeling. The unit has been successfully used for the preparation of several flow-through ion exchange membrane electrodes.

EXPERIMENTAL SECTION

Chemicals. All chemicals used were of reagent grade. Stock solutions of ions and ionic strength/pH adjustors were prepared by using deionized, distilled water.

Liquid ion exchangers and the corresponding internal reference solutions for the nitrate, perchlorate, and calcium ion electrodes (6) were obtained from Orion Research Inc. The liquid ion exchanger for the picrate ion electrode consisted of tetrapentylammonium picrate in 2-nitrotoluene, and it was prepared as described elsewhere (11). A solution of 0.01 M sodium picrate–0.1 M sodium chloride was used as the internal reference solution.

Apparatus. A schematic diagram of the automated analysis flow system employed for the evaluation of the constructed flow-through electrodes is shown in Figure 1. Sampler II and proportioning pump III were from the Technicon Auto-Analyzer II system. The timing functions of sampler II were controlled by a specially designed digital "sample-wash timer" connected to sampler II as described elsewhere (12). The sample–reagent metering system on pump III, consisting of Solvaflex calibrated tubes, was the same for all of the evaluated ion selective electrodes except for the perchlorate electrode.

The constructed flow-trhough electrodes were used in conjunction with an Orion 90-01 single-junction reference electrode. All potentiometric measurements were carried out with a Corning Model 12 Research pH/mV meter and recorded on a Heath-Schlumberger SR-255 B potentiometric recorder.

Flow-Through Electrode Unit Construction. The final configuration of the constructed flow-through electrode unit is shown in Figure 2. Glass frit disks of fine porosity (nominal maximum pore size of approximately 5 μm and thickness of about 2.5–3 mm) were obtained from filtering glass crucibles. An equilateral triangular piece (side length approximately 1 cm) was cut from the disk with a fine hacksaw blade, and the cut sides were smoothed with fine emery paper. All sides of the entire triangular piece were covered with a thin layer of silicon rubber and embedded by using a circular mold in Serifix or Epofix resin, a casting plastic obtained from H. Struers, Scientific Instruments, Copenhagen. The silicon rubber layer serves as a protective film to prevent the absorption of the plastic into the pores of the glass frit. The embedding was made by initially preparing a supporting layer that filled half of the mold and allowing it to harden. Then, the triangular piece of the glass frit was placed on the supporting layer and the mold was filled to the top with a covering layer of plastic. The filled mold was allowed to harden completely for at least 24 h. The resultant cylindrical cast block (3 cm in diameter and 2 cm high) was ground and polished by using various sizes of emery paper. Appropriate diameter holes were made on the cylindrical surface of the block, as shown in Figure 2, by relatively slow speed drilling with regular drill bits. A flow-through channel 1.6 mm in diameter was also drilled on the longitudinal axis of the block crossing the glass frit, in order to form the electrode sensing path. The side filling and deaeration holes were drilled in such a way as to form an angle of about 60°. The upper section of the filling hole was sufficiently enlarged and stuffed with cotton or glass wool, thus serving as a reservoir for the electroactive liquid phase. The internal reference electrode compartment was made of a Plexiglas tube (1 cm o.d.) 5–6 cm long, which was mounted into a hole drilled between the side filling and deaeration holes and sealed with Araldite epoxy resin glue. The junction between the internal reference solution and the liquid electroactive phase,
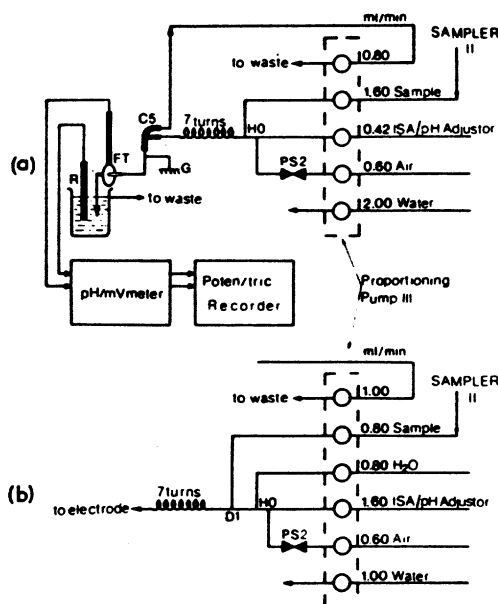
Figure 1. Schematic diagram of the automated continuous-flow analysis system. Manifold arrangements: (a) for nitrate, picrate, and calcium ion electrodes; (b) for perchlorate ion electrode. Key: (R) reference electrode; (FT) flow-through electrode; (G) ground; (C5) debubbler; (HO,D1) "cactus" and "H" connectors; (PS2) pulse suppressor.
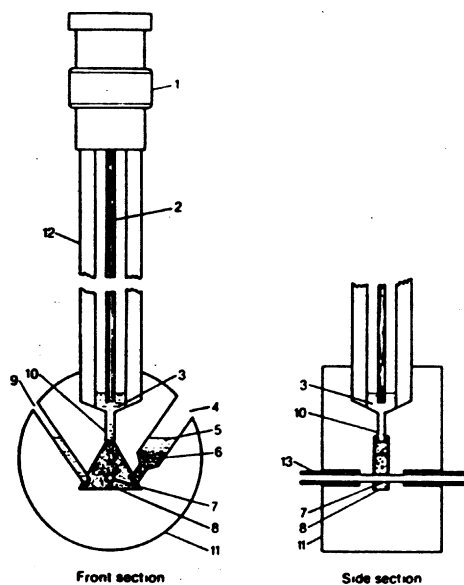

Figure 2. Front and side view of the flow-through electrode unit: (1) BNC connector (UG-88/U); (2) Ag/AgCl wire reference electrode; (3) internal reference solution; (4) ion-exchanger filling hole and reservoir (4 mm i.d.); (5) ion-exchanger liquid; (6) stuffed cotton or glass wool; (7) sensing path (1.5 mm i.d.); (8) glass frit; (9) deaeration hole (1.5 mm i.d.); (10) ion exchanger–reference solution junction hole (1.3 mm i.d.); (11) plastic cast block; (12) reference electrode compartment (plexiglas tube, 10 mm o.d.); (13) stainless steel nipples (2.5 mm o.d.)

absorbed on the glass frit, was established through a narrow hole connecting the reference electrode compartment to the glass frit triangle apex. A Ag/AgCl wire electrode of appropriate length carried by a BNC male connector was used as the internal reference electrode.

Preparation of the Electrode. The flow-through unit was filled with the liquid ion exchanger by adding 4–5 drops of it into the filling hole reservoir and waiting for the ion exchanger to be dispersed uniformly through the whole glass frit and to fill up the deaeration hole and the reservoir to the height of the triangle apex. Then 3–4 drops of the internal reference solution was added to the bottom of the reference electrode compartment by using a long needle syringe. The prepared electrode was mounted in the continuous flow system by using two stainless steel nipples.

Prior to the electrode mounting, care was taken to remove any excess of ion exchanger from the sensing path by using a pipe cleaner.

The unit can be reused for the preparation of another electrode by removing the old ion exchanger. This can be accomplished by filling the reservoir with ethanol and applying a stream of compressed nitrogen. The washing procedure should be repeated several times, so that all the ion exchanger is washed out. Then the nitrogen stream is allowed to pass through for some time until the glass frit dries completely.

RESULTS AND DISCUSSION

In addition to the glass frit, several other materials were tested for the electrode unit construction, e.g., Millipore Mitex (Teflon) filters or cellulosic absorbent pads. The electrode units obtained exhibited unsatisfactory mechanical and operational properties. For example, the operative life of electrodes prepared from Teflon filters was very short (2–3 days) due to the fast deterioration of the surface of the sensing path.

Fine porosity glass frit was found to be the most satisfactory material as inert matrix for this design. It offers several advantages, such as easy mechanical treatment, strong capillary action, large ion-exchanger capacity, minimum maintenance, the possibility of reuse, etc.

Several precautions should be taken during the preparation of each new flow-through liquid membrane electrode. The amount of the internal reference solution should be kept at the lowest possible level. If a large amount of reference solution is added, the hydrostatic pressure overcomes the capillary action which holds the electroactive liquid in the glass frit and the reference solution tends to move into the frit. This results in an erratic response of the electrode and a short lifetime. Also, the density and the viscosity of the electroactive liquid play an important role in the equilibrium between the two phases. Liquid ion exchangers with a density lower than that of water (e.g., perchlorate ion exchanger) tend to move upward, reinforcing the capillary action against the hydrostatic pressure of the reference solution. On the contrary, liquid ion exchangers with a density higher than that of water (e.g., picrate liquid ion exchanger) tend to move downward, causing continuous leakage through the sensing path when the ion exchanger level in the reservoir is too high. These problems can be eliminated by keeping the ion exchanger in the reservoir and the reference solution in the reference electrode compartment at a low level, thus minimizing the hydrostatic pressure effect. The normal loss of ion exchanger during the electrode operation within the continuous flow system is compensated by replenishment from the reservoir. One drop of ion exchanger daily is sufficient to compensate the loss, even after a full day of continuous use.

The electrode performance can also be affected by extremely drastic substances in the measured solutions, e.g., substances reacting with the ion exchanger or high sodium ion concentrations in alkaline solutions. In the last case, the electrode behaves as a sodium ion selective electrode of the glass type.

The prepared flow-through electrodes for perchlorate, nitrate, and picrate anions and calcium cations exhibited characteristics similar to those of the corresponding conventional dip types. They developed Nernstian response in the 10^{-1} to 10^{-4} M concentration range. Measurements were carried out with the continuous-flow system shown in Figure 1 without the use of sampler II. Solutions of the measured ions were aspirated into the system via the sampling tube from each stock solution bottle. The calculated Nernstian response values and the experimental conditions for each of the tested electrodes are summarized in Table I.

Examples of typical recordings from nitrate and perchlorate electrodes obtained under continuous-flow conditions are
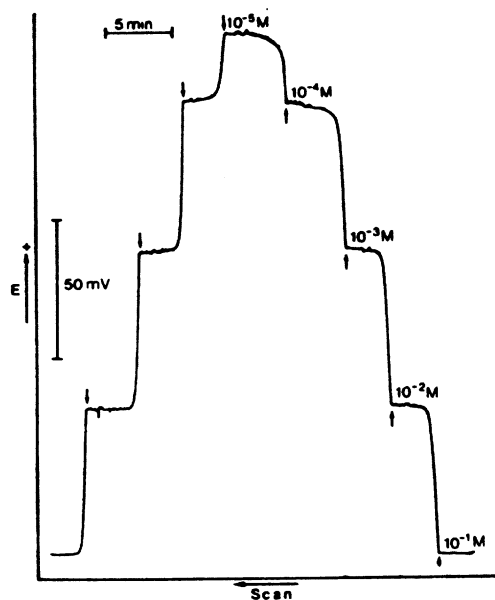
Figure 3. Nitrate ion electrode response to tenfold step changes in NO_3^- concentration under continuous-flow conditions. The arrows indicate the point at which the new solution first reaches the electrode.
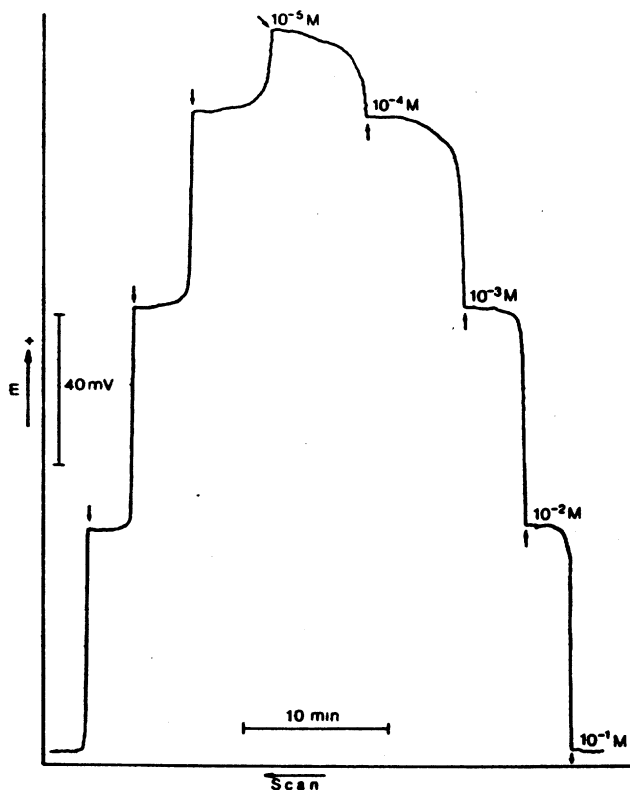

Figure 4. Perchlorate ion electrode response to tenfold step changes in ClO_4^- concentration under continuous-flow conditions. The arrows indicate the point at which the new solution first reaches the electrode.

presented in Figures 3 and 4. The flow rates were about 2.6 mL/min for the nitrate, picrate, and calcium electrodes and 3.8 mL/min for the perchlorate electrode. The practical response time, $t_{95\%}$, of the prepared electrode was about 15 s for a tenfold increase in concentration and slightly longer in the opposite direction, especially at low concentrations.

The electrodes were tested in continuous-flow measurements of discrete samples, where each sample was separated from the next by a wash solution. These measurements were performed with the flow system shown in Figure 1, using the reagents shown in Table I. Typical recordings obtained with the nitrate, perchlorate, and calcium electrodes are presented

Table I. Characteristics of the Constructed Flow-Through Electrodes Based on Liquid Ion Exchangers

| determinand	electroactive material (manufacturer)	internal filling solution (manufacturer)	ISA/pH adjustor	range of Nernstian response, M (actual range, M)	response slope, mV/decade (correl coeff)
Ca^{2+}	calcium di(n-decyl)phosphate in dioctylphenylphosphate (Orion, Catalog No. 92202)	1 M $CaCl_2$	0.4 M KCl	10^{-1}–3×10^{-4} (6.1×10^{-2}–1.8×10^{-4})	27.8 (0.9999)
NO_3^-	Ni(o-phen)$_2$$^{2+}$ in p-nitrocymene (Orion, Catalog No. 920702)	10^{-1} M NaCl + 10^{-2} M NaNO$_3$ + sat. AgCl (Orion, Catalog No. 920703)	0.1 M phosphate buffer pH 6.5	10^{-1}–10^{-4} (6.1×10^{-2}–6.1×10^{-5})	55.1 (0.9999)
ClO_4^-	Fe(o-phen)$_3$$^{2+}$ in p-nitrocymene (Orion, Catalog No. 928102)	?? (Orion, Catalog No. 928103)	0.1 M phosphate buffer pH 6.5	10^{-1}–10^{-4} (2.1×10^{-2}–2.1×10^{-4})	56.5 (0.9998)
picrate ion	tetrapentylammonium picrate in 2-nitrotoluene (ref 11)	10^{-2} M sodium picrate + 10^{-1} M NaCl (ref 11)	1 M Na_2SO_4	10^{-1}–10^{-4} (6.1×10^{-2}–6.1×10^{-5})	58.6 (0.9993)
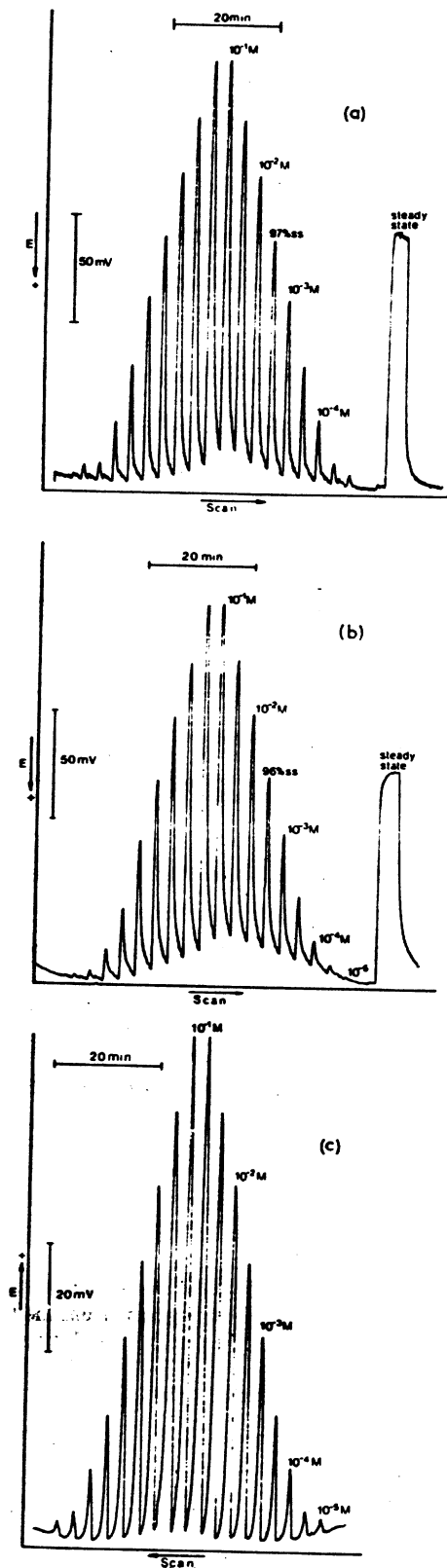
Figure 5. Typical recordings of continuous-flow measurements of discrete samples with (a) nitrate, (b) perchlorate, and (c) calcium ion electrodes. Sampling rate was 20 samples/h. Sample-to-wash ratio was 1:5.

Figure 6. Calibration curves of the constructed anion flow-through electrodes. Sampling rate was 20 samples/h and sample-to-wash ratio was 1:5. Noted values correspond to the actual ion concentration measured by the electrode.

Figure 7. Calibration curve of the constructed calcium flow-through electrode. Sampling rate was 20 samples/h and sample-to-wash ratio was 1:5. Noted values correspond to the actual ion concentration measured by the electrode.

In Figure 5. The sampling rate was 20 samples/h and distilled, deionized water was used as wash solution at a 1:5 sample to wash ratio. The choice of such a long wash time was necessary in order to avoid development of hysteresis by the electrode (electrode memory), especially at low concentrations. The hysteresis effect which is common to liquid membrane electrodes decreases the detection limit and affects
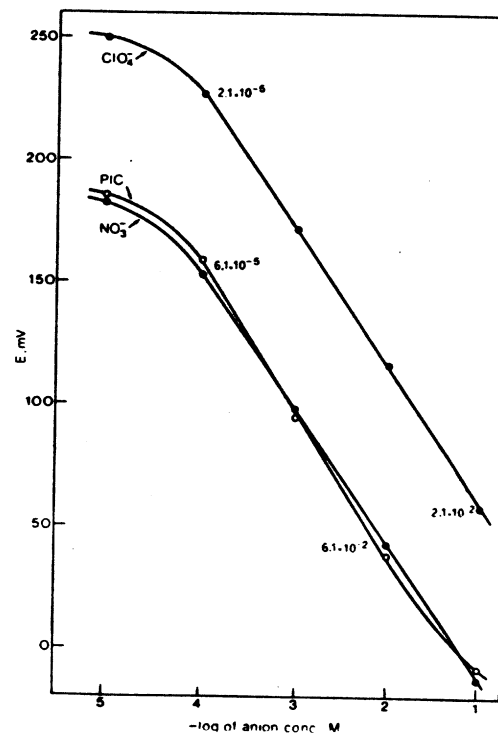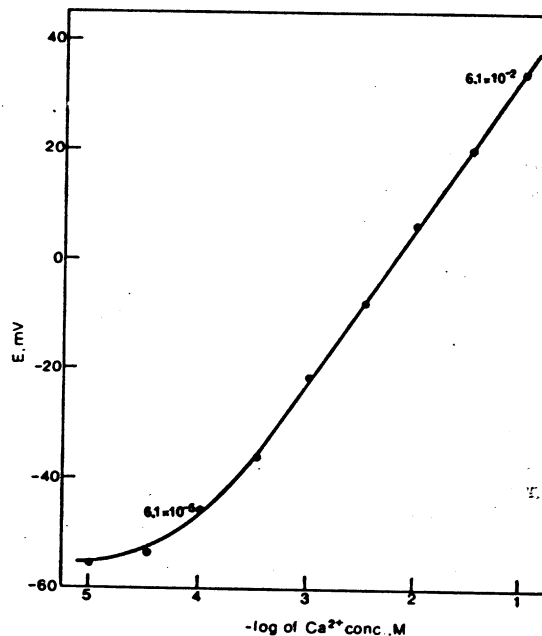
the stability and the reproducibility (6, 13). Under the above conditions all the tested electrodes developed Nernstian response for 3 decades of initial ion concentration, ranging from 10^{-1} to 10^{-4} M, as demonstrated by the calibration curves shown in Figures 6 and 7. In fact, the lower limit of the linear range is smaller by a factor of 0.6 for the nitrate, picrate, and calcium electrodes and 0.2 for the perchlorate electrode, because of the sample dilution.

It can be seen from Figure 5 that the behavior of the prepared flow-through electrodes is remarkable in terms of base line stability and reproducibility of the peak heights. It should
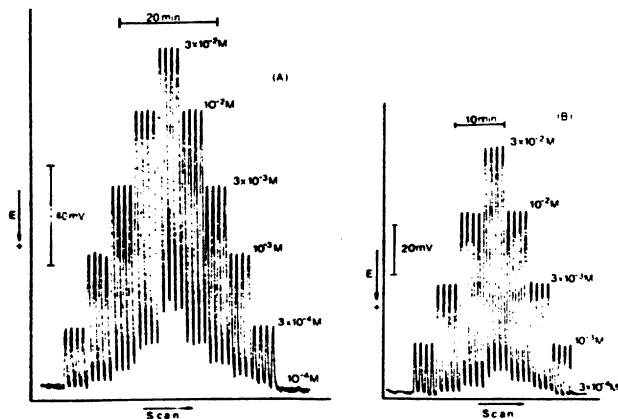
Figure 8. Typical recordings of continuous-flow measurements with nitrate (A) and perchlorate (B) ion electrodes using diluted wash solution of the measured ion. Sampling rate was 50 samples/h and sample-to-wash ratio was 1:2.
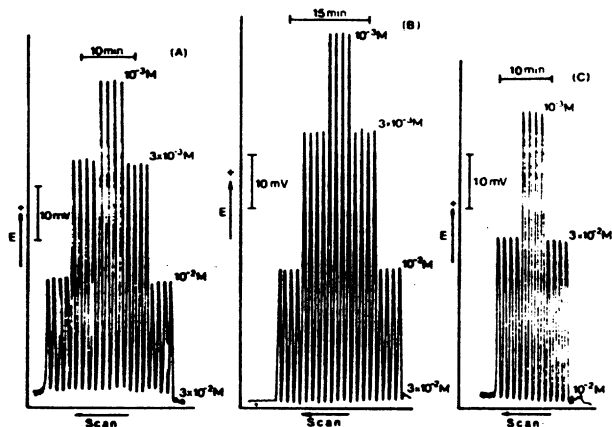

Figure 9. Typical recordings of continuous-flow measurements with (A) picrate, (B) nitrate, and (C) perchlorate ion electrodes using concentrated wash solution of the measured ion. Sampling rate was 50 samples/h, and sample-to-wash ratio was 1:1.

also be noted that the actual analyses carried out at the 20 samples/h rate agree quite well (95–97%) with the steady-state response obtained under continuous sample flow conditions; this indicates that electrode response times are not response-limiting.

The prepared electrodes were also tested under high sampling rate conditions (50 samples/h) using wash solutions containing constant dilute (10^{-4} M) or concentrated (10^{-2} M) background levels of the measured ions. The sample to wash ratio was increased to 1:2 or 1:1 when dilute or concentrated background wash solutions were used, respectively, while the other parameters in the experimental system remained the

same. Typical recordings of such measurements are shown in Figures 8 and 9. It can be seen that the tested electrodes exhibited better base line stability and reproducibility of the peak heights than those obtained when water was used as the wash solution. Thus, the utility of these electrodes can be expanded to the analysis of other species. This can be accomplished by employing an appropriate coupling reaction, where the ions sensed by the electrode are participating as reagent or product (14). For example, it has been found that human serum albumin can be determined automatically in a continuous flow system employing a flow-through picrate ion electrode, by a method based on the direct reaction of albumin with picrate ions (15).

The constructed new flow-through electrode unit for liquid membrane electrodes offers certain advantages over the conventional flow-through cells and sensor end-cups using dip-type electrodes. The unit is simple, durable, inexpensive, and reusable, and once established it requires minimum maintenance. The unit can be used for the preparation of any type of liquid membrane ion electrode based on ion exchangers or neutral carriers. The capabilities of the proposed flow-through unit can be further appreciated from the excellent characteristics of stability and reproducibility of the tested electrodes.

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