Solid Contact Potentiometric Sensors for Trace Level Measurements

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Abstract

A simple procedure for the development of a range of polymeric ion-selective electrodes (ISEs) with low detection limits is presented here. The electrodes were prepared by using a plasticizer-free methylmethacrylate–decylmethacrylate copolymer as membrane matrix and poly(3-octylthiophene) as intermediate layer deposited by solvent casting on gold sputtered copper electrodes as a solid inner contact. Five different electrodes were development for Ag^+, Pb^{2+}, Ca^{2+}, K^+ and I^-, with detection limits mostly in the nanomolar range. In this work the lowest detection limits reported thus far with solid contact ISEs for the detection of silver (2.0×10^{-9} M), potassium (10^{-7} M) and iodide (10^{-8} M) are presented. The developed electrodes exhibited a good response time and excellent reproducibility.

In the past few years, the detection limits of ion-selective electrodes have been drastically improved by minimizing passive zero current ion fluxes from the membrane into the sample solution.[1,2] This has yielded a range of potentiometric sensors that are capable of direct measurements in the nanomolar concentration range.[3–7] Most of these sensors utilize an aqueous inner solution, which must be carefully optimized for each type and composition of membrane and even each anticipated sample.[1,2,8,9] While experimental protocols to evaluate the state of optimization of the inner solution are now available,[10] the requirement of a specialized solution for each single application is a major problem that may deter non-specialists from taking advantage of this exciting technology.

Clearly, there is an important need for a universal recipe that makes the fabrication and optimization of potentiometric sensors with low detection limit a more straightforward task. Recently, a series of papers that make use of solid contacts at the inner membrane side have appeared.[11,12] The historical problem of poor potential stability between the ion conducting membrane and electron conducting substrate[13,14] has been largely solved, for example by utilizing conducting polymers[15] such poly(pyrrole),[16–18] poly(thiophene),[19] poly(3,4-ethylenedioxythiophene),[20] poly(iodole),[21] and poly(aniline)[22–23] as intermediate layers. Recently, it has been demonstrated that another important contribution of instabilities in potential (drifts) was due to the formation of a water layer between polymeric membrane and the solid contact, introduced by Fibbioli and Pretsch.[24] The same authors advocated the use of self-assembled monolayers of a lipophilic redox-active compound to alleviate this problem,[25] and later the use of lipophilic conducting polymers such as poly(3-octylthiophene).[26]

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First efforts to develop solid contact ISEs with low detection limits were reported by Michalska, who showed that a super-Nernstian response slope may be observed by incorporating the complexing agent EDTA in a modified conducting polymer film at the backside of the membrane.[27] More recently, the same group presented an impressive nanomolar detection limit for calcium by using a poly(pyrrole) solid contact doped with the calcium ligand Tiron.[28]

Very recently, the Pretsch group achieved a nanomolar detection limit for a lead-selective electrode by using poly(pyrrole) electropolymerized with hexacyanoferrate as the interface between the polymeric membrane and the metal conductor.[29] A more robust system lacking the potentially leaching hexacyanoferrate was recently presented with ion-selective membranes based on a plasticizer-free methylmethacrylate–decylmethacrylate copolymer, and using a drop cast conducting polymer poly(3-octylthiophene) as solid contact. This work resulted in low detection limits for lead and calcium26 and is here adapted for the construction of solid-contact ion-selective electrodes to detect a wide range of cations and anions down to the nanomolar concentration range.

Experimental

Reagents

The ionophores *o*-xylylenebis(N,N-diisobutyldithiocarbamate) (Copper (II) ionophore (I)), 4-*tert*-butylcalix[4]arene tetrakis(thioacetic acid dimethylamide) (Lead ionophore IV), N,N-Dicyclohexyl-N′,N′-dioctadecyl-3-oxapentanamide (Calcium ionophore IV), Valinomycin (Potassium ionophore I), the lipophilic salt tetradodecylammonium tetrakis(4-chlorophenyl) borate (ETH 500), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB), were purchased in selectophore or puriss grade from Fluka (Buchs, Switzerland). The ionophore [9] mercuracarborand-3 (MC3) was prepared as described previously,30 the solvent methylene chloride obtained from Fisher (New Jersey, USA). Poly(3-octylthiophene) (POT) was kindly donated by Erno Pretsch (ETH Hönggerberg, Switzerland), originally obtained from Applications Chemistry & Technologies (AC&T) (Saint-Egreve, France). Aqueous solutions were prepared by dissolving the appropriate salts in Nanopure purified water. Syntheses of the methylmethacrylate-decylmethacrylate (MMA-DMA) copolymer matrix was prepared as described previously31 and the following chemicals were used: The monomers methyl methacrylate, 99.5 % (MMA) and *n*-decyl methacrylate 99% (DMA) were obtained from Polysciences, Inc. (Warrington, PA), the initiator 2,2'-azobis(isobutyronitrile) 98% (AIBN) from Aldrich (Milwaukee, USA), ethyl acetate and 1,4-dioxane were reagent grade and obtained from Fisher (New Jersey, USA). The used monomers were purified by washing with a caustic solution containing 5% (w/v) NaOH and 20% (w/v) NaCl in a 1:5 (monomer: caustic solution) ratio. After purification the monomers were washed with an excess of water, treated with anhydrous Na_2SO_4 and filtered before use, while AIBN was recrystallized from warm methanol prior to use.

Membranes

Different membranes were prepared by dissolving 200 mg of components in 2.0 mL of methylene chloride: copper (II) ionophore (I), lead ionophore IV, calcium ionophore IV, potassium ionophore I and MC3 (15 mmol kg^{-1} for cation-selective membranes and 1 mmol kg^{-1} for the iodide-selective membrane) and lipophilic ionexchanger (5 mmol kg^{-1} NaTFPB for cation-selective membranes and 0.75 mmol kg^{-1} TDMACl for the iodide membrane). ETH 500 (10 mmol kg^{-1}) was used to increase the conductivity of each membrane and the polymeric matrix was MMA-DMA. The membrane cocktail was degassed by sonication for 10 min and poured on the surface of the gold coated electrode by drop-casting.

Electrodes

Tips of copper rod of 1 cm height and 5 mm diameter were soldered to the conductor wire and used as inner electrodes for all solid-contact ISEs. The copper tips were carefully cleaned by first polishing with sand paper, treating with dilute H_2SO_4, washing with acetone, and then dried in air. The electrodes were then sputtered using an EMS 550X sputter coater device (Emltech Ltd. Ashford, Kent, England) with gold using a current of 25 mA during 4 min at 0.1 mbar (according to specifications of the sputter coater, these conditions yield approximately 60 nm thick gold films). The electrodes were then washed with methylene chloride and POT was applied on the sputtered gold (SG) by drop-casting 10 μL of a 25 mM (respective monomer) chloroform solution, repeated three times. The film was left to dry for at least 5 minutes. The electrode was then introduced into a fitting PVC tube at a depth of 1 mm, allowing the casting of approximately 100 μL of membrane cocktail on the top of the POT layer and left to dry for 1 h at room temperature, resulting in a membrane thickness of 216 ± 37 μm as measured with a micrometercaliper.

The following conditioning protocols were used for each electrode. Silver ISEs: Protocol 1: 1 d in 10 μM $AgNO_3$ followed by 2 d in 1nM $AgNO_3$. Protocol 2: 1 d in 100 μM $AgNO_3$ followed by 2 d in 1 nM $AgNO_3$. Protocol 3: 1 d in 1 mM $AgNO_3$ followed by 2 d in 1 nM $AgNO_3$. Calcium and Potassium ISEs: 1d in 1 mM of the chloride salt of the primary ion followed by 2 d in 1 nM of the same salt. Lead ISEs: 2 d in 10 μM $Pb(NO_3)_2$ at pH 4 (adjusted with HNO_3) followed by 1 d in 1 nM $Pb(NO_3)_2$ at pH 4. Iodide ISE: 1 d in 100 μM NaI at pH 3 (adjusted with H_3PO_4) followed by 1 d in 10 nM NaI at pH 3. The washing step required for the electrode to return to the starting potential after performing calibration was about 30 min, with a standard deviation in the potential of ± 5 mV.

EMF Measurements

Potentials were monitored with a PCI MIO16XE data acquisition board (National Instruments, Austin, TX) utilizing a four-channel high Z interface (WPI, Sarasota, FL) at room temperature (22 °C) in stirred solutions, in the galvanic cell Ag/AgCl/ 3M KCl/1M LiOAc/sample solution/ ISE-membrane/POT/Gold with a double-junction reference electrode (type 6.0729.100, Methrom AG, Herisau, Switzerland). The experiments were performed in a 100 mL polyethylene beaker pretreated overnight in 0.1 M HNO_3. All EMF values were corrected for liquid-junction potentials according to the Henderson equation. Activity coefficients were calculated by the Debye-Hückel approximation.

Cyclic Voltammetry was carried out with an EC Epsilon potentiostat from Bioanalytical Systems, Inc. (West Lafayette, Indiana, USA) with a scan rate of 100 mV/s. A saturated calomel electrode (SCE) as a reference, a platinum wire as a counter and a solid-contact electrode covered with POT as working electrode were used in a three-electrode system. Oxygen in the system was removed by bubbling nitrogen through the solution.

Results and Discussion

The goal of this work was to produce a series of ion-selective electrodes with low detection limits by using a single fabrication and conditioning protocol. Recent work by the Pretsch group introduced monolithic column electrodes with liquid inner contacts with the same goal, and it was shown that the composition of the inner solution did not influence the electrode detection limit.[32] Here, solid-contact electrodes were explored for the same purpose. The plasticizer-free methylmethacrylate–decylmethacrylate (MMA-DMA) copolymer matrix was chosen as membrane material. It has been shown to be promising for the fabrication of plasticizer-free ion-selective membranes by traditional solvent casting, and has yielded potentiometric sensors for a range of different ions with selectivities comparable to their

traditional counterparts based on plasticized poly(vinyl chloride).[31] Moreover, the reported small diffusion coefficients in this material may make it relatively robust to chemical changes at the inner membrane side.[33] Recently, MMA-DMA was utilized as an appropriate membrane material for developing solid-contact ISEs with low detection limits.[26] A possible drawback of this material in view of general use is that it is currently polymerized in house. This material was solvent cast onto undoped poly(3-octylthiophene) films, which have recently been found as a suitable intermediate layer between the membrane and the electron conductor.[26] Instead of the solid gold substrates reported thus far, we used commercially available copper rods sputtered with gold as a less expensive substrate. This should form a viable platform for a screen printing or photolithographic approach to the sensor development.

To our best knowledge, no solid contact electrodes with low detection limits for the detection of silver ions had been reported so far. It was therefore decided to explore such silver-selective sensors as model systems, and to extend the same basic procedure to other ions without significant modification. For silver-selective electrode the ionophore *o*-xylylenebis(N,N-diisobutydithiocarbamate) (copper(II)ionophore(I)) was chosen since it possesses very high selectivity toward silver ions, as recently demonstrated in the fabrication of optical sensors with extremely low detection limits.[34] The electrodes were first conditioned in 1 mM $NaNO_3$ to characterize the response performance of the membrane void of primary ions. Upon initial exposure to samples of increasing silver concentration a super-Nernstian step around log a = −7 was observed (see Fig. 1, curve A, 61.0 ± 2.0 mV slope between log a = −6 and −4), which is at lower concentrations than with plasticized membranes[35] and in line with the smaller reported diffusion coefficients in this material.[33] This super-Nernstian step is indicative of the mass transport limited counterdiffusion flux of silver ions into the membrane, as reported.[37] Subsequently, the membrane was conditioning for 1 day in 1 mM $AgNO_3$, to fully replace the original sodium ions in the membrane by silver and to mimic traditional conditioning procedures. The corresponding silver calibration curve is shown in Curve B (58.5 ± 1.5 mV slope between log a = −6 and −4) in Figure 1 as a separate trace. Although the super-Nernstian response step has disappeared, indicating appropriate saturation of the membrane with silver, the observed detection limit of log a = −7 is not yet ideal. This behavior is normally observed with conventional liquid inner contact electrodes and is attributed to the continuous release of ions from the membrane phase to the sample.[1,38] Here, the high concentration of silver nitrate in the conditioning solution may lead to significant electrolyte coextraction into the membrane, perhaps leading to back-extraction upon exposure to dilute samples. After this experiment, the electrodes were conditioned for 1 d in 1 nM $AgNO_3$. A calibration of such membrane yielded curve C (57.3 ± 1.5 mV slope between log a = −7 and −4) in Figure 1, indicating a decreased detection limit owing to a smaller outward silver flux. Conditioning for one more day produced electrodes with a nanomolar detection limit ($2.0 \cdot 10^{-9}$ M) and a Nernstian slope (59.0 ± 1.0 mV) between log a = −8 and −4, shown as curve D in Figure 1. Continuous conditioning in even more dilute silver solutions did not further improve the detection limit.

Other conditioning protocols were also tested, see Experimental. Protocol 1, which used an initial conditioning step with 10 μM, rather than 1 mM $AgNO_3$ yielded super-Nernstian response slopes of nearly 140 mV between 10^{-8} and 10^{-6} M Ag^+, indicating incomplete saturation of the membrane with silver. Protocol 2 utilized 100 μM $AgNO_3$ for 1 day, but the super-Nernstian response slope was still visible (ca. 100 mV in the same concentration range). The relatively long required conditioning times may be understood on the basis of the reported diffusion coefficients (nearly 10^{-11} $cm^2 s^{-1}$[33]) in this matrix, which is 2 to 3 orders of magnitude smaller than with traditional plasticized poly(vinyl chloride) membranes.[36]

The nanomolar detection limit observed in Figure 1 does not yet reflect the thermodynamic detection limit of the sensor, which would be expected to be many orders of magnitude lower. [39] Simple stir experiments were performed to evaluate whether a silver ion flux in direction

of the sample is relevant in the absence of added silver ion to the sample. As reported, a reduction in the aqueous diffusion layer by sample stirring should lead to a drop in the membrane potential because of a lowering of the expelled silver concentration at the membrane surface.[10] In our experiment no considerable stir effect was observed: the potential decreased by 3.0 ± 1.0 mV (n = 4) upon stirring the silver-free sample (data not shown). Since no super-Nernstian response slope was observed for this electrode, which would have indicated a flux in direction of the membrane,[37] it indicates that ion leaching is not substantial and the detection limit is likely dictated by silver ion impurities in the sample. The response times were also studied, and a $t_{95\%} = 10$ min was found for a concentration change from 10^{-9} M to 10^{-8} M silver nitrate. Previous work on solid contact lead-selective electrodes also showed improved response times[26] compared to their liquid contact counterparts.[4]

The minimizing influence of POT on the long term potential drift was demonstrated as well. Without POT as an intermediate layer, a drift of 9.2 mV/h was observed in 1 nM silver nitrate samples, which was reduced to 2.7 mV/h with ISEs containing POT. When the electrodes containing POT were exposed to a high concentration of Ag^+ (10^{-3} M) for many hours, no potential drift was observed (inset of Figure 2). In addition, cyclic voltamograms were recorded for solid-contact electrodes covered only with POT in solutions with different concentrations of Ag^+ (from 10^{-5} to 10^{-3} M). No change in the voltammetric behavior was observed in the range from 0 to 1 V.

Separate calibration curves for a number of ions on membranes conditioned in 1 mM sodium nitrate were performed to further evaluate this issue (Figure 2). As established,[40] such a protocol allows one to obtain near-Nernstian response slopes, and hence unbiased selectivity coefficients, for highly discriminated ions because they may more easily ion-exchange into the membrane. The most preferred ion silver was measured at the end of the experiment, and the potential was continuously recorded in the highest silver concentration for more than 10 hours. If silver reaches the inner membrane side and influence the potential in any way, on the basis of a reconditioning of a water layer or the redox properties of silver (I), a slow potential drift is expected. As shown in Figure 2, the potential was stable, indicating that no such water layer is present and the redox properties of POT, rather than silver, are responsible for the inner boundary potential. These results are further supported by recent work of Vazquez, Bobacka and Ivaska, who have observed good silver selectivity for undoped POT used as ion-selective membranes, without any evidence for oxidation of POT by silver ions even after 20 h of continuous exposure.[41]

The slopes and calculated logarithmic selectivity coefficients, $\log K_{Ag,J}^{pot}$, for each measured interfering ion J are presented in Table 1. Note that the discriminated ions still showed sub-Nernstian slopes. While the respective selectivity coefficients are likely still biased to some extent, the calculated selectivity coefficients suggest a somewhat greater silver selectivity compared to literature values based on the same ionophore.[42] This is perhaps due to the use of a different membrane material rather than plasticized poly(vinyl chloride).

The intercept for a batch of 3 different electrodes showed a standard deviation of 2.5 mV, indicating excellent reproducibility for a solid contact system. No considerable loss of electrode slope (55 ± 3 mV) was observed even after continuous use for more than two months. The detection limit increased by just half an order of magnitude after one month, indicating good long term stability.

These satisfactory results obtained for Ag^+ motivated us to test similar systems containing other ionophores in order to develop a unifying, simple recipe for the preparation of robust solid-contact electrodes with low detection limits. Such membranes were prepared for calcium, potassium, lead and iodide, bringing the number of explored systems to five, including one for

anions. All observed calibration curves are presented in Figure 3. For calcium, a 4 nM detection limit and Nernstian response slope was observed. Note that no potentially leachable complexing agents were used here, compared to the recent work reported by Michalska.[28] That work yielded a detection limit in the nanomolar range as well, using poly(pyrrole) doped with the complexing agent Tiron as intermediate layer.[28]

Potassium electrodes based on the ionophore valinomycin and fabricated according to the same recipe showed a 1×10^{-7} M detection limit and Nernstian response slopes as well (Figure 3). Previous solid contact potassium electrodes with electropolymerized poly(pyrrole) had been doped with the water soluble[43] hexacyanoferrate as additive in the intermediate layer (which can potentially leach by ion-exchange), exhibiting a 2×10^{-7} M detection limit.[44] The lowest detection limit reported thus far is about 5.0×10^{-9} M, for a potassium ISE using a liquid inner contact system.[9]

The lead ion-selective electrode response shown in Figure 3 exhibits a nanomolar detection limit, which is essentially identical to previous reported work with a poly(3-octylthiophene) intermediate layer on solid gold electrodes.[26] This good correspondence demonstrates the robustness of the approach. The iodide selective electrode response shown in Figure 3 is, to our knowledge, the first solid contact electrode for anions that exhibits a low detection limit. Here, the 10 nM detection limit is somewhat inferior compared to that of an optimized liquid inner contact system, reaching a 2 nM detection limit.[7] It is a welcome, albeit surprising finding that the same intermediate redox polymer layer, essentially without any modification, may be used for the detection of anions. Response times for this electrode were found as $t_{95\%} = 25$ min for a sample iodide concentration change from 10^{-8} M to 10^{-7} M.

Conclusions

A simple fabrication procedure was used to develop ion selective electrodes for the detection of five different ions at low concentrations. This was accomplished with solid contact electrodes utilizing an undoped conducting polymer as intermediate electron and ion conductive layer. The selection of this redox layer and actual polymeric sensing matrix were found to be important. Related work by Vazquez, Bobacka and Ivaska[41] suggests that undoped POT must have some ion-exchange properties sufficient for a robust ion-selectivity of the conducting polymer. Additionally, POT is difficult to oxidize and more lipophilic than most other conducting polymers routinely used. An appropriate conditioning protocol was necessary to yield the desired low detection limits. Prolonged exposure of a silver-selective membrane conditioned with sodium to silver ions yielded an immediate large potential increase that remained stable. This is a strong indication that the inner redox layer is not influenced by the redox properties of the silver ions, and provides evidence for the lack of an intermediate water layer between the membrane and the inner solid contact element. The low detection limit achieved with the same general procedure for the fabrication of iodide-selective electrodes is rather suprising, because it was achieved with the same undoped POT layer. It is anticipated that such a simplified preparation procedure will make it possible for other researchers to more easily develop and apply potentiometric sensors for measurements at trace levels.

Acknowledgments

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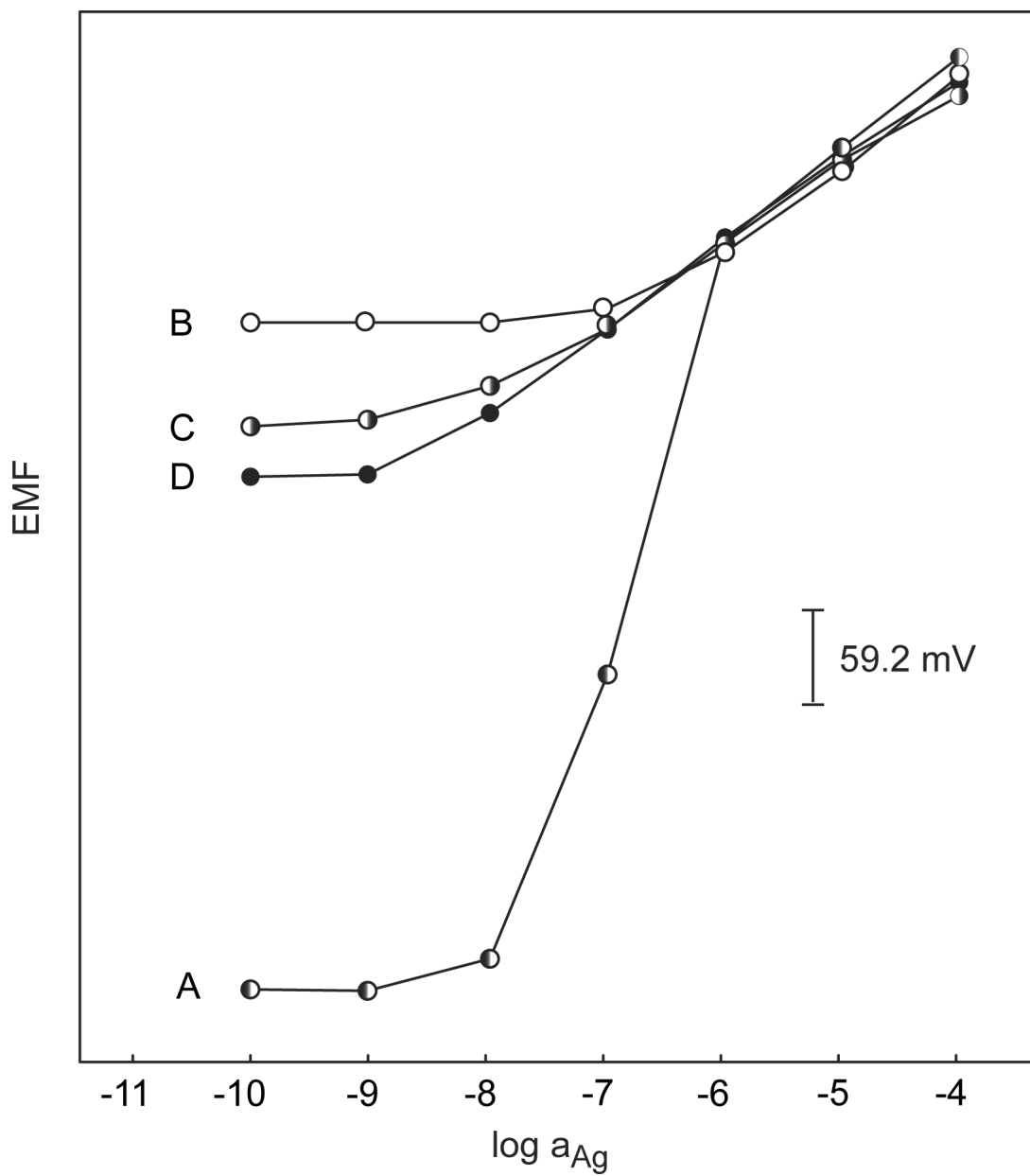
Fig. 1.
Silver ion calibration curves for a silver-selective electrode recorded after each of the consecutive conditioning protocols. A: exposure to 1 mM $NaNO_3$ for 1 d. B: 1 mM $AgNO_3$ for 1 d. C: 1 nM $AgNO_3$ for 1 d. D: 1 nM $AgNO_3$ for one more day.
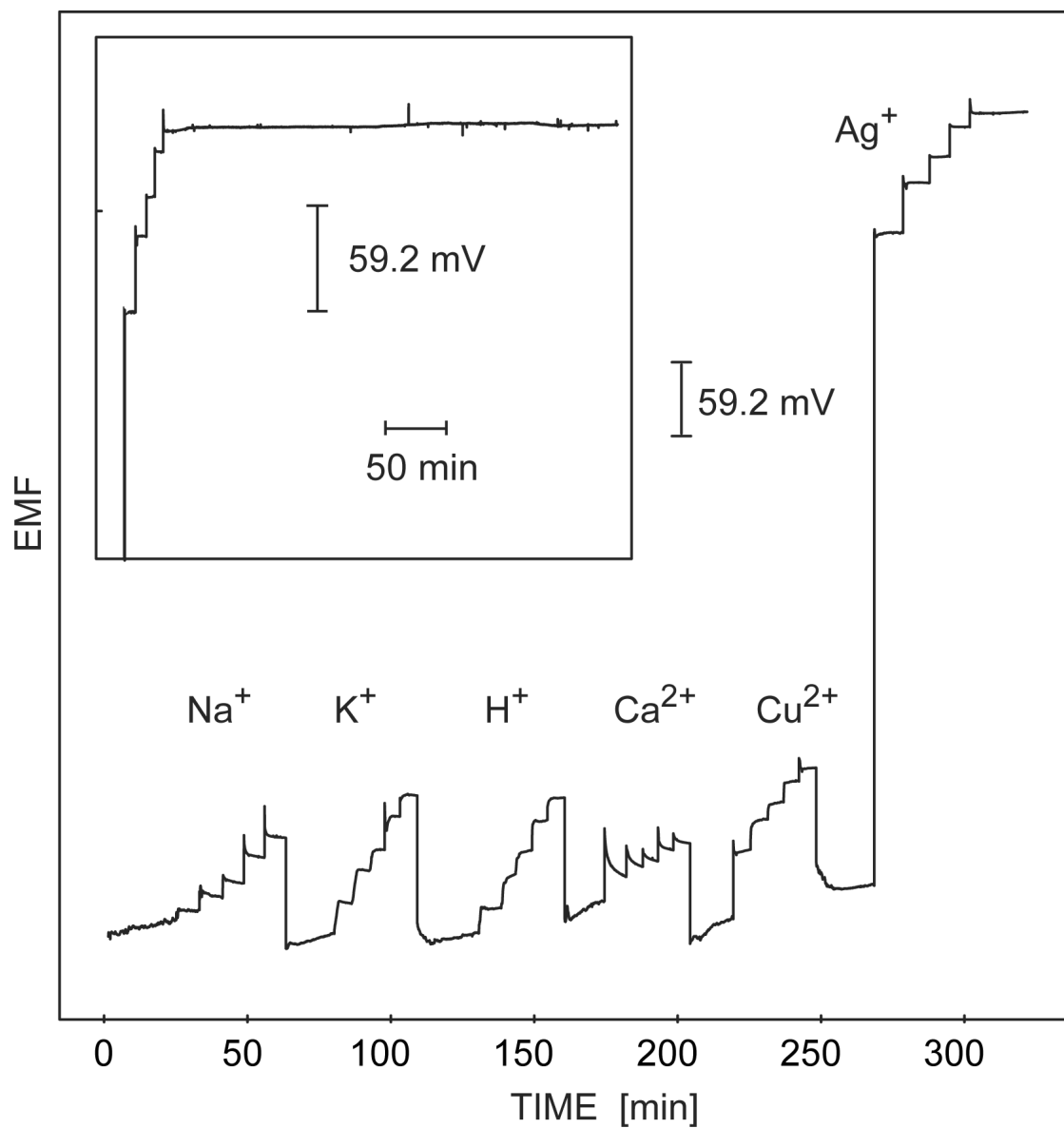
Fig. 2.
Potential time traces for the selectivity characterization of solid contact Ag^+-selective electrodes, by exposing to incremental concentrations (10^{-5}, $5.0 \cdot 10^{-5}$, 10^{-4}, $5.0 \cdot 10^{-4}$ and 10^{-3} M) of the indicated nitrate salts of potentially interfering ions followed by silver. Inset: long term potential behavior upon prolonged exposure to 10^{-3} M silver nitrate.
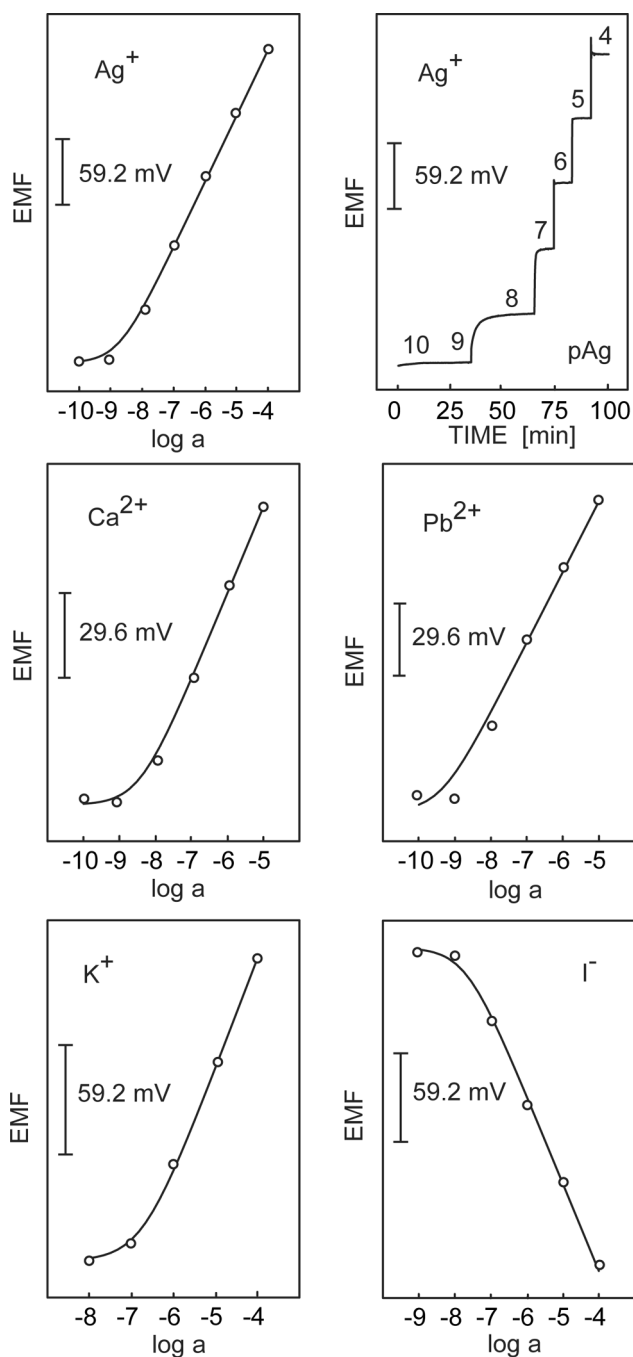
Fig. 3.
Calibration curves for solid contact electrodes developed with the same universal recipe for the detection of silver, calcium, lead, potassium, and iodide. Recorded potential time traces for the silver-selective electrode are shown in the top right plot.

Table 1

Observed electrode slopes and experimental selectivity coefficients obtained for the silver ion-selective solid contact electrodes.

Ion J^{z+}	Slope (mV decade^{-1})[a]	$\log K_{Ag,J}^{pot}$ [a]
Na$^+$	29.1 ± 1.1	−10.7 ± 0.1
K$^+$	37.4 ± 0.8	−10.2 ± 0.1
H$^+$	36.4 ± 0.4	−10.2 ± 0.1
Ca^{2+}	11.0 ± 0.9	−12.3 ± 0.1
Cu^{2+}	33.7 ± 0.9	−11.1 ± 0.2

[a] Average and standard deviations from at least 3 different electrodes obtained from the same parent membrane; slopes calculated between log a = −5 and −3.3.