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Background Current Elimination in Thin Layer Ion-Selective Membrane Coulometry

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Abstract

A promising method for the elimination of undesired capacitive currents in view of realizing a potentially calibration free coulometric ion detection system is presented. The coulometric cell is composed of a porous polypropylene tube doped with a liquid calcium-selective membrane and a silver/silver chloride wire as an inner electrode, forming a thin layer sample between wire and tubing. The total charge passed through the system during potential controlled electrolysis of the thin layer sample is indeed found to be proportional to the amount of calcium present, but non-Faradaic processes do contribute to the obtained signal. We introduce here a multi-pulse procedure that allows one to perform a second excitation pulse at the same excitation potential after exhaustive ion transfer voltammetry of calcium has taken place. The intercept of the calibration curve after background subtraction is found as $20.6 \pm 0.6 \mu\text{C}$, significantly lower than the value of $54.1 \pm 0.8 \mu\text{C}$ for the uncorrected curve. Changes in sample temperature (from 23 °C to 38 °C) did equally not affect the background corrected coulometric readings, supporting that the procedure renders the readout principle more robust.

Keywords

ion-selective electrode; calcium ionophore; ion transfer voltammetry; calibration free sensing; thin layer coulometry; polypropylene hollow fiber membrane

1. Introduction

Electrochemical sensors have traditionally been applied in the fields of clinical and laboratory analysis, where undesired signal instabilities can be compensated by frequent recalibration. However, there are important applications in the fields of environmental analysis (remote monitoring) and *in vivo* diagnostics where more robust, calibration free sensing methodologies are desired to achieve miniature, self contained sensing devices that can be left unattended without complicated fluidics.

Building on the earlier work by Sanchez-Pedreno [1], Osakai [2] and Kihara [3], we recently introduced a new methodology to use ionophore-based ion-selective membranes in a thin layer coulometric detection mode [4]. Specifically, the membrane was formulated to contain cation-exchanger sites, in analogy to well established potentiometric sensors [5]. This is in

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contrast to traditional ion voltammetric sensing approaches [6-10], where ion-exchanger properties are normally avoided in order to render the sample-membrane interface polarizable. The presence of a cation-exchanger results in a permselective membrane, which means that only one charge type may effectively be transported across the membrane [11]. This is beneficial in view of realizing robust sensors based on relatively thin membranes, and also allows one to observe the open circuit potential across the membrane in analogy to potentiometric sensing devices.

The protocol recently introduced involves 1) the measurement of the open circuit potential, 2) the application of an excitation potential relative to this open circuit potential, during which the ion of interest is exhaustively transferred into and across the tubular membrane, and 3) the subsequent regeneration of the membrane by reapplying the open circuit potential across the cell [4]. This approach was confirmed to give coulomb numbers that linearly depend on the calcium concentration in the sample. Nonetheless, the intercept of the calibration curve was not found to be zero, suggesting undesired non-Faradaic processes. Since parameters such as solution conductivity, temperature and the magnitude of the applied potential can influence the capacitance of the membrane (and the double layers on both sides) one cannot strictly consider this residual charge as a constant. This makes the previously described protocol not yet calibration free. Ideally, these contributions need to be eliminated *in situ* to achieve a desired robust calibration free sensing methodology. This paper explores an expanded multipulse procedure to achieve this important goal.

2. Experimental

2.1 Reagents, materials and equipment

Dodecyl 2-nitrophenyl ether (DDNPE), tetradodecylammonium tetrakis(4-chlorophenyl)borate ETH 500, potassium tetrakis[3,4-bis(trifluoromethyl)phenyl]-borate (KTFPB), calcium ionophore IV (ETH 5234), high molecular weight poly(vinyl chloride) (PVC), tetrahydrofuran (THF), calcium chloride dihydrate and potassium chloride were purchased in the highest quality available from Fluka. Aqueous solutions were prepared by dissolving the appropriate salts in MilliQ-purified distilled water. The polypropylene hollow fiber Accurel PP Q3/2 was supplied by Membrana GmbH (Wuppertal, Germany) and Sterling Silver Round wires of 250 and 500 μm dia. by AEMETAL (Sydney, Australia).

Unless otherwise specified, all measurements were performed at room temperature (23 $^{\circ}\text{C}$) vs. a double-junction Ag/AgCl/sat. KCl/1 M LiOAc reference electrode (Mettler-Toledo AG, Schwerzenbach, Switzerland) placed in the outer aqueous solution. The ion-selective hollow-fiber cell served as the working electrode and a high surface area Pt electrode (MT Electrodes, Perth, Australia) as the counter electrode in coulometric measurements. 10^{-3} M CaCl_2 in a 10^{-2} M KCl background electrolyte served as an outside electrolyte. The coulometric measurements were performed with an Autolab PGSTAT128N (Metrohm Autolab, Utrecht, The Netherlands) controlled by personal computer using Nova 1.5. Experiments were performed by feeding the cell with appropriate solutions using an ISMATEC peristaltic pump (Glattbrugg, Switzerland) with a flow rate of $25 \mu\text{L min}^{-1}$. The peristaltic pump was always off during the following measurements.

For the thermostated experiments, the cell was equilibrated with a thermostated water bath. Samples of different calcium concentration were then passed through the cell. After incorporation into the cell, each sample was kept under stagnant conditions for two minutes before the measurement was started to ensure its temperature was adjusted to the temperature of the outside solution.

2.2 Preparation of the coulometric system

The coulometric cell was prepared according to the procedure described before [4], with the following variation. The membrane cocktail was composed of 266.7 mg of DDNPE, 30 mg (10 wt-%) of ETH 500, 2.4 mg (10 mmol·kg⁻¹) of Caionophore IV and 0.9 mg of KTFPB (30 mol-% relative to the ionophore), which was dissolved in 1.5 ml THF. The solvent was subsequently allowed to evaporate overnight. 100 µL of THF-free cocktail was cast on a 120 mm long, fully assembled, THF-washed and dried tubular cell. Excess of the liquid membrane was wiped with a paper tissue. The resulting inner active surface area of the membrane was about 226 mm², as estimated from the nominal dimensions. Before use, the inner side of the cell was washed for a day by continuously flowing 1 mM CaCl₂ solution at the flow rate mentioned above.

3. Results and discussion

After applying a 60-s analyte extracting potential pulse (OCP + 150 mV) one may assume for the system described here that the residual amount of analyte left in the thin sample layer is negligibly small. Yet, the solution contains mainly the background electrolyte at the same temperature, pressure and conductivity conditions as the initial sample solution. At this point in time, therefore, the repeated application of exactly the same pulse may give information about the background current. The ion-selective membrane, however, underwent polarization during the initial perturbation pulse that requires relaxation before applying a renewed excitation pulse [12]. The previously suggested procedure is therefore expanded by two additional modules after the first excitation pulse, as illustrated in Figure 1: a 2-min zero current pulse required for membrane relaxation (pulse 4) and a subsequent 60-s chronoamperometric pulse at the same potential as during the first excitation pulse (shown as pulse 5). Note that according to the Nernst equation, the open circuit potential after the first excitation pulse must be different from that for the original, unperturbed sample, because of the diminished concentration of analyte ions [5], and this difference may be a source of inaccuracy in the proposed protocol.

The background subtraction procedure was explored by comparing the coulomb numbers obtained from the first and second chronoamperometric ion transfer pulses at OCP + 150 mV (pulse 3 and 5 in Figure 1), and plotted against the calcium concentration in the sample. As shown in Figure 2 the calibration curve for the first excitation pulse is linear with an intercept of $54.1 \pm 0.8 \mu\text{C}$ (SD, N=10). After background subtraction from the second pulse, with an intercept of $33.5 \pm 0.5 \mu\text{C}$, the slope of the calibration curve remained very similar ($29.3 \pm 0.2 \text{ C/M}$), but with a reduced intercept of $20.6 \pm 0.6 \mu\text{C}$.

Figure 3 shows variations of the background concentration, either 10, 15 or 20 mM KCl with an equal calcium concentration of 50 µM. Interestingly the charges generated during the first excitation pulses were found to be the same within 0.6 mC (SD, N=3). This is supportive of the methodology used here, in which excitation pulses are imposed relative to the observed open circuit potential. Variations in the background chloride concentration will result in potential changes at the silver/silver chloride element in contact with the thin layer sample, which need to be accounted for. The charges calculated for the second excitation pulse were found to introduce a slope of 134 mC per molar concentration of background electrolyte to the linear regression fit. This can be best explained with lower open circuit potentials for increasing potassium concentrations. For the second excitation pulse, the potential step and hence the capacitive charging current will increase for increasing potassium levels.

A further test was performed for samples at different temperatures, from laboratory ambient temperature of 23 °C to a thermostated 38°C. As seen in Figure 4 the temperature change

gave a significant increase to the charge passed during both extraction pulses, presumably owing to an increase in the capacitance of the cell. Note also that the initial currents are much higher at the elevated temperature, owing to the increased ion mobility in the membrane phase. However, after background subtraction the obtained calibration curve was found to quantitatively overlap with the one obtained at 23°C with an intercept of 20.6 ± 0.6 mC and a slope of 29.4 ± 0.2 C/M.

4. Conclusions

Using a second excitation pulse after exhaustive thin layer ion transfer electrolysis across a permselective membrane shows significant promise in view of reducing undesired non-Faradaic components of the signal. This is evidenced by a significantly reduced intercept of the calibration curve and the demonstrated insensitivity to temperature steps. It is noted that the compensation is not yet perfectly effective, and this is here explained by the inability to hold the sample before and after exhaustive electrolysis at the same open circuit potential without inducing undesired Faradaic ion transport processes across the membrane during the background compensation pulse [13]. While this residual error is likely not problematic for measurements at higher concentrations, a refined method will need to be developed to allow for the reliable measurement at trace levels.

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6. References

1. Sanchez-Pedreno C, Ortuno JA, J. Hernandez, Anal. Chim. Acta 2002;459:11.
2. Sawada S, Taguma M, Kimoto T, Hotta H, Osakai T. Anal. Chem 2002;74:1177. [PubMed: 11924981]
3. Yoshizumi A, Uehara A, Kasuno M, Kitatsuhi Y, Yoshida Z, Kihara S. J. Electroanal. Chem 2005;581:275.
4. Grygolicz-Pawlak E, Bakker E. Anal. Chem 2010;82:4537–4542. [PubMed: 20429515]
5. Bakker E, Bühlmann P, Pretsch E. Chem. Rev 1997;97:3083. [PubMed: 11851486]
6. Amemiya S, Yang X, Wazenegger TL. J. Am. Chem. Soc 2003;125:11832. [PubMed: 14505401]
7. Lee HJ, Beriet C, Girault HH. J. Electroanal. Chem 1998;453:211.
8. Samec Z, Trojanek A, Langmaier J, Samcova E. Electrochem. Commun 2003;5:867.
9. Samec Z, Samcova E, Girault HH. Talanta 2004;63:21. [PubMed: 18969401]
10. Shirai O, Kihara S, Suzuki M, Ogura K, Matsui M. Anal. Sci 1991;7:607.
11. Morf, W. The Principles of Ion-Selective Electrodes and of Membrane Transport. Elsevier; New York: 1981.
12. Zook JM, Lindner E. Anal. Chem 2009;81:5155. [PubMed: 19459602]
13. Jadhav S, Bakker E. Anal. Chem 1999;71:3657. [PubMed: 10489520]

Figure 1.

Schematic representation of potential and time changes during the proposed potentiostatic/galvanostatic pulses sequence, consisting of: 1) an open circuit (OCP) measurement, 2) OCP applied as baseline to confirm zero current conditions, 3) the first excitation pulse at $OCP + \Delta E$, 4) membrane relaxation at zero current, 5) second excitation pulse at $OCP + \Delta E$, and 6) and system regeneration upon applied OCP.

Figure 2. Observed chronoamperograms for the thin layer coulometric system during two excitation pulses (150 mV vs open circuit potential) for samples of the different calcium concentrations indicated on the graph and a constant 10 mM KCl background. The inset presents the calculated charge as a function of sample concentration obtained for a) the first excitation pulse and b) the second excitation pulse and c) after subtraction of the two.

Figure 3.

Chronoamperograms as for Figure 2, but for samples of a constant $5.0 \cdot 10^{-5}$ M calcium concentration and a 10, 15 or 20 mM KCl background solution. The inset presents the calculated charge as a function of background concentration for a) the first and b) the second excitation pulse and c) after subtraction of the two.

Figure 4.

Chronoamperograms as for Figure 2, but for $2.5 \cdot 10^{-5} \text{ M}$ calcium concentration and 10 mM KCl background solution at two indicated temperatures. The inset shows the calculated charge as a function of background concentration obtained at 23°C indicated as circles and at 38°C indicated as triangles for a) the first and b) the second excitation pulse and c) after subtraction of the two.