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# Important aspects influencing stability of the electrochemical potential of conductive polymer-based electrodes

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**Abstract** In this article, important aspects influencing the signal stability of the potentiometric sensors based on various conductive polymers on platinum support are discussed. The initial step is the choice of a suitable cleaning method (mechanical stripping, burning out) of the platinum support. The second point consists in the selection of an appropriate procedure employed to mature the freshly prepared film on the metallic support (soaking, potential treatment, drying). The third crucial stage involves the application of a proper regeneration procedure (pH value of a buffer, anionic surfactant). The mentioned aspects have been tested using polythiophene, polyaniline, polypyrrole, poly(neutral red), poly(5,15-bis(2-aminophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-porphyrine), poly(5,15,25,35-tetrakis(4-hydroxyphenyl)porphyrine) or poly(2,3-bis-(1H-pyrrol-2-yl)-quinoxalin-5-ol) as sensitive layers. The combination of the prepared electrodes into an electrode array (electronic tongue) and the development of a suitable protocol of the measurement allowed us to distinguish the individual brands of the Czech beers, specifically, Bernard 10°, dark Kozel 10°, Kozel 10°, Bráník 10°, Radegast, and Staropramen. Besides the platinum support, the conductive polymers were also deposited on a nonconductive support (membrane). The latter experiments demonstrated that the introduction of a conductive polymer as the outer layer onto poly(vinyl chloride) membranes led to the significant stabilization of their potentiometric response.

## Introduction

A very important general aspect of the electrochemical sensors is their long-term signal stability. Our attention was directed specifically to the stability of potentiometric sensors based on conductive polymers (CPs). The essential step in the development of potentiometric sensors consists in the preparation of a selective and stable electropolymerized film on a suitable support. Most studies have been devoted to the preparation of the CPs and their application as potentiometric sensors [1]. The chemical composition and the surface and bulk properties of the polymer represent the most important factors determining the sensor characteristics. While the selectivity of CPs may be improved by introducing selective receptors into polymer backbone or combining single electrodes in an array, there is no single recipe on how to improve the stability of CPs [1].

The CPs can be prepared either chemically (with the participation of an oxidant) or electrochemically under potentiostatic [2, 3], galvanostatic [4], or cyclic voltammetry conditions [5, 6]. In the course of the polymerization, the film is held in one specific redox state (for potentiostatic polymerization [3]); its redox state is continuously changed according to the potential applied by the galvanostat to maintain a constant current (galvanostatic polymerization [4]); or the redox state is switched from one to the other form by cyclic voltammetry [5, 6]. For all of these three approaches it is common that the redox state is determined by external factors. After the disconnection of the electrode from the electrical circuit, the film begins to drift toward a state that is in equilibrium with its open-circuit potential. During the redox process, the film changes its volume and absorbs or expels small molecules from its bulk. Most CP films have a porous structure [7–9] and contain counter ions [10], molecules of solvents and

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monomers [11], specific molecules [12], and short chains (oligomers) [13]. These can be exchanged by other ions or molecules from the solution, a monomer, or an oligomer unit can attach to the film, etc. Final rearrangement of the polymer structure takes some time, the length of which depends on the kind of a polymer, polymerization conditions, and other factors like pH, solution redox activity, and temperature. Therefore, it is always very useful to know the relaxation period required for the CP reorganization and the factors affecting this process.

Polyaniline (PANI), poly(pyrrole) (PPy), poly(thiophene) (PT), and their derivatives are the most frequently used polymers in the development of potentiometric sensors based on CPs [14]. In these sensors, the CPs are either selective membranes or ion-to-electron transducers placed between a solid-state electrode support and a typical ion-selective membrane. Stability of CPs has been mostly discussed in the literature for the potentiometric sensors applying CPs in the form of ion–electron transducer. Bobacka et al. [15] have found that a sufficiently high bulk (redox) capacitance of CPs (e.g., poly(3,4-ethylenedioxythiophene, PEDOT) used as the solid contact is a prerequisite for obtaining a stable electrode potential of the all-solid-state ion-selective electrodes (ISEs). In these cases, the redox reaction occurring in CP layer facilitates the transduction of an ionic signal into an electronic one. Moreover, the stability of the PANI solid contact in $K^+$ −ISEs based on plasticized PVC depends on partial conversion of conducting emeraldine salt form to nonconducting emeraldine base form [16]. UV–visible spectroscopic studies show that this conversion takes place during long-term (1–3 months) but not short-term measurements (4 days).

Lewenstam′s group has presented results on the stability of the potentiometric signal of electrodes based on the PPy and PEDOT doped with adenosine triphosphate (ATP) and heparin [17, 18]. There has been a correlation between the film topology and the potentiometric response of PEDOT doped with ATP, which was sensitive to $Ca^{2+}$ and $Mg^{2+}$ [17]. In general, smoother films have shown a more stable potentiometric response than the rougher ones. The response remained unchanged even after one year of soaking indicating the exceptionally high stability of this type of electrodes [18]. The influence of various chemical processes on properties, structure, composition, and possible degradation of PPy (often used as potentiometric sensors) has been discussed in detail in an excellent article of Maksymiuk [19]. Such chemical processes can be based on participation of typical components of surrounding media (i.e., oxygen, acids, bases, redox reactants, water, and organic vapors) or on the incorporation of nonreactive ions and surfactants from solutions. The benefits and disadvantages of such processes for analytic characteristic of PPy-based electrochemical sensors have been evaluated.

Various analytic applications of CPs have been developed since the 1980s, and they have been discussed in several reviews over the past few years [20–22]. These include the application of CPs in biomedical engineering [21], in chemical sensors, and arrays [14, 20, 22], and they reflect the wide interest in this subject within the scientific community.

The aim of this study is to summarize the experience acquired in an effort to suppress the signal drift of potentiometric sensors based on CPs prepared in our laboratory. The results refer to the stand-alone coated-wire electrodes, their arrays, and the conventional PVC electrodes coated with a conductive polymer. We believe that the approaches discussed in this study can contribute to the widespread application of the potentiometric sensors in the analysis of real samples.

## Materials and methods

### Reagents

3-Amino-7-dimethylamino-2-methylphenazine (neutral red, NR), sodium dodecylsulfate (SDS), all inorganic salts, and acids were obtained from Lachema, Penta, and Lach-Ner (Czech Republic). 2-(N-Morpholino)ethanesulfonic acid hydrate (MES), tris(hydroxymethyl)aminomethane (TRIS), acetonitrile, tetrabutylammonium perchlorate (TBAP), aniline.$H_2SO_4$, pyrrole, and thiophene were obtained from Sigma–Aldrich (Germany). 5,15-bis(2-aminophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-porphyrine (TTP), 5,15,25,35-tetrakis(4-hydroxyphenyl)porphyrine (THP), and (2,3-bis-(1H-pyrrol-2-yl)-quinoxalin-5-ol (BPQ) were prepared according to the general procedure described elsewhere [23, 24]. Poly(vinyl chloride) high molecular weight (PVC), 2-nitrophenyl octyl ether (NPOE), tridodecylmethylammonium chloride (TDDMACl), tetrahydrofuran (THF) (stored over a molecular sieve), persulfate ammonium, and aniline hydrochloride were purchased from Fluka (Switzerland).

Working solutions for potentiometric measurements were prepared using redistilled water. The Czech beers (Bernard 10°, dark Kozel 10°, Kozel 10°, Bráník 10°, Radegast, Staropramen) originated from local stores, all samples being taken from the same manufacturing batch.

### Preparation and stability evaluation of conductive polymers on various supports

#### *Metallic support*

Platinum electrodes, used as metallic support, were designed either as wires (0.4 mm diameter, 8 mm length) or a set of rings (1 mm diameter). The electrodes were polished with alumina (0.3 μm) or burned out in an oxidative or reductive part of the flame. The stability of the potential was verified by measuring the potential in 0.05 M MES solution with pH 5.5. The potentiometric signal of the bare platinum surface was examined by measuring the pH and chloride dependences for the individual platinum electrodes (number of electrodes $n = 4$).

Polymer-coated platinum electrodes were prepared by polymerization of the corresponding monomers onto the platinum electrode using cyclic voltametry. BPQ was specifically reduced before electropolymerization to the corresponding 5-aminoquinoxaline derivative [25]. Before polymerization, the working electrodes were polished with alumina powder slurry and then rinsed with distilled water. The polymerization conditions used are summarized in Table 1. The prepared electrodes were stored in distilled water. The signal stability was tested both independently with single electrodes and simultaneously within a group of electrodes combined into an electrode array.

Postpolymerization treatment of the polymer film based on poly(neutral red) (PNR) was carried out one day after deposition. According to the postpolymerization treatment, these electrodes were divided into three groups. The first group of electrodes was held at constant potential of 150 mV vs. Ag/AgCl reference electrode for 2 h in the stirred background electrolyte (0.02 M TRIS + 0.1 M $KNO_3$ + 0.001 M sodium citrate). The second group of electrodes was dried for 2 h at 60°C. The third group of electrodes was left without any treatment with the goal to compare the effect of the individual postpolymerization treatment procedures. Then, the stability of their potentiometric signal was measured in background electrolyte.

The group of ring electrodes ($n = 16$) was combined into an electrode array and then used to test the signal stability of the CPs during the measurement of real samples (various beer samples).

### *PVC support*

PVC/NPOE (2:1 mass ratio) membranes with 3 wt. % TDDMACl were cast using a conventional method for the ion-selective electrode membrane preparation [26]. The experimental membranes were immersed in a freshly prepared solution consisting of aniline hydrochloride (0.08 M) and persulfate ammonium (0.08 M) in 1.5 M HCl at 0°C [27]. After polymerization, the polymer coated membranes ($m = 0.1$ g, diameter 1.28 cm, thickness 0.11 mm) were removed, rinsed with 1.5 M HCl aqueous solution, treated in an ultrasonic bath for 10 min in 1.5 M HCl aqueous solution, and dried at ambient temperature.

## Apparatus and measurement conditions

### *Single electrodes based on conductive polymers*

Cyclic voltammetry was carried out using the PAR263 potentiostat/galvanostat (Princeton Applied Research, USA) controlled with GPIB commands using LabView. An analog PA2 polarographic analyzer (Laboratory Devices Prague, Czech Republic) was used for constant potential treatment. An Ag/AgCl (3 M KCl) and platinum plate electrode (area ca 0.25 cm$^2$) were used as a reference and auxiliary electrode, respectively. The pH was monitored using a type SEUJ 212 glass electrode (Monokrystaly Turnov, Czech Republic) with a PHI 04 MG pH-Meter (Labio, Czech Republic). The potential dependence of the platinum electrodes ($n = 4$) on pH was tested in Britton-Robinson buffer over a pH range from 2 to 12.

All potentiometric measurements were carried out at 25°C with the cells of the following type:

**Table 1** Conditions of polymer preparation on metallic support

| Composition of polymerization bath | | | | Polymerization parameters | | Application |
|---|---|---|---|---|---|---|
| Monomer | Monomer concentration (M) | Solvent | Supporting electrolyte | Potential limits (V) vs Ag/AgCl | Time (min) | |
| Aniline $H_2SO_4$ | 0.05 | 1 M $H_2SO_4$ | 1 M $H_2SO_4$, 60 μM PVP | 0.00–1.20 | 15 | s, a |
| Thiophene | 0.4 | Acetonitrile | 50 mM TBAP | −0.20–1.90 | 4 | a |
| Pyrrole | 0.2 | Acetonitrile | 50 mM TBAP | −0.30–1.25 | 5 | s, a |
| Neutral red [21] | 0.005 | Acetonitrile | 50 mM TBAP | −0.20–1.80 | 20 | s, a |
| Neutral red [21] | 0.005 | 3 M $H_2SO_4$ | 3 M $H_2SO_4$ | −0.05–1.25 | 20 | s |
| THP | 0.0025 | Acetonitrile | 50 mM TBAP | −0.20–1.30 | 15 | a |
| TTP | 0.005 | 3 M $H_2SO_4$ | 3 M $H_2SO_4$ | −0.05–1.50 | 30 | a |
| BPQ [19] | 0.005 | Glacial acetic acid | 1 M $H_2SO_4$ | −0.30–1.25 | 30 | a |

Electrodes used as a part of an electrode array (*a*) or as a single electrode (*s*)

Ag|AgCl|3MKCl|sample solution|membrane|inner filling solution|AgCl|Ag

and

Ag|AgCl|3M KCl|sample solution|conductive polymer|Pt

The electrochemical potentials were measured using a custom-made five- and seven-channel ISE tester for membrane and coated wire electrodes (Academy of Sciences in cooperation with the Institute of Chemical Technology, Czech Republic) [28].

### *Electrode array based on conductive polymers*

The electrode array was composed of 16 ring platinum electrodes (diameter of 1 mm). Two electrodes for each type of polymer, PANI, PPy, PT, PNR, poly(BPQ), poly(THP) and poly(TTP), were prepared (Table 1), and two electrodes were left without a polymer (bare platinum electrodes). All polymerizations were carried out by cyclic voltammetry with a scan rate of 100 mV $s^{-1}$.

The electrochemical potential of the electrodes intended for the measurement of different beer samples was determined by an Electronic Tongue instrument [29] and evaluated by principal component analysis (PCA; Camo Unscrambler 7.8 and MathWorks Matlab 6.0). The beer samples were percolated with nitrogen for 10 min before the analysis. The testing sequence consisted of alternating sequences of two washes with the same washing solution (0.1 M acetic buffer at pH 5.5 or 0.001 M SDS in 0.1 M acetic buffer at pH 5.5) followed by two measurements of the same beer sample, and this was repeated five times overall. Electrochemical potential was measured at a fixed time 4 min and 40 s from the beginning of the measurement of each sample. The dead time of the cell was 1 min and 30 s.

### *Leaching studies*

Quantitative leaching studies were carried out using membranes based on TDDMACl and coated with the PANI film. The membranes uncoated with the PANI film were used for the comparison purposes. The membranes were exposed to 10 mL of 0.01 M NaCl (soaking solution), and they were vigorously shaken in this solution for several hours. A 20 µl aliquot of soaking solution with the leached TDDMACl was withdrawn and then added to 1 mL of methanol. The obtained methanolic solutions were analyzed by a mass spectrometer (Q-Tof Micro$^{TM}$, Waters, USA). Absolute magnitudes of leached TDDMACl in water phase (ng $mL^{-1}$) were determined using a calibration curve obtained for a series of TDDMACl standard solutions of different concentrations in methanol.

## Results and discussion

### Effect of platinum support on stability of potentiometric signal

The stability of the potentiometric signal of the electrodes based on CPs depends on the treatment of the support material as well as the surface properties of the deposited polymer. First, bare platinum electrodes were employed to evaluate the effect of the pretreatment process and the effect of the platinum oxide layer on the stability of the potentiometric signal. Second, the stability of the potentiometric signal of the CP-coated platinum electrodes was evaluated. Two kinds of polymers, the frequently used PPy and PNR, recently introduced by us [30], were used in these experiments.

Platinum used as the electrode material supports the electron transfer across the platinum/solution phase boundary and accelerates polymerization because of the catalytic effect of the platinum oxide layer. The thickness and structure of this oxide layer depends on the surface treatment conditions [31, 32]. The first factor affecting the stability of the signal is the cleanliness of the surface of the

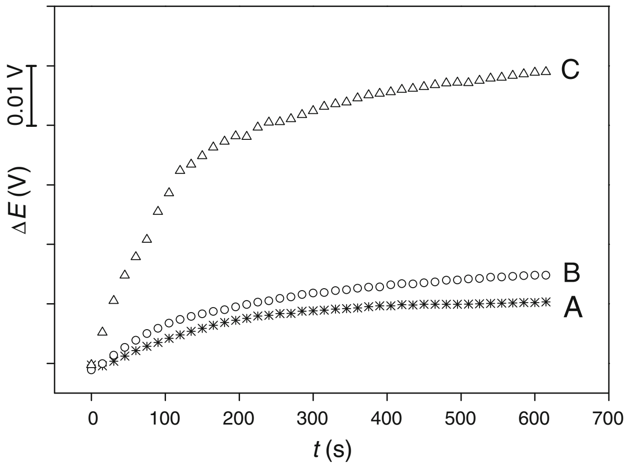

**Fig. 1** Stability of the potential of bare platinum electrode measured in 0.05 M MES solution at pH 5.5 after polishing with alumina (*A*), burning out in oxidative (*B*) and reductive (*C*) part of the flame. For more facile comparison, the curves are adjusted to the same initial point

electrode support. The recycling and stripping off the old polymeric film constitute the key procedure. Mechanical abrasion by alumina and burning the polymers from the metal surfaces in a flame belong to the well-established techniques. Cleaning by abrasion using alumina is the most convenient method because the resulting electrodes produce the lowest signal drift (Fig. 1—curve A). The surface layer of the platinum oxides [32] is removed by polishing and then the signal drifts until a new layer is established. The stability of the signal is significantly different for burning in the oxidative (Fig. 1—curve B) or reductive (Fig. 1—curve C) part of the flame. The platinum should not be exposed to the reductive flame because this leads to the formation of non-stoichiometric platinum carbides [33] and, as a consequence, to a high drift of the electrode potential.

A second key factor, which affects the potentiometric response of CP-coated-wire ISEs, is the compactness of the coverage of the platinum support by the polymeric film. In the case of compact polymeric coating, the response of the electrode should be determined by the polymeric film itself, and the influence of the platinum support should be marginal [34]. The platinum itself is sensitive to pH [31, 32], the presence of redox compounds [35], and many various ions, especially halogenides [36]. Therefore, the platinum support often significantly affects the potentiometric response obtained with electrodes based on CPs in cases where the coating is insufficiently compact. On the other hand, the compact PPy coating remarkably improves the reproducibility of the potentiometric signal toward pH (Fig. 2a) and chlorides (Fig. 2b). In the case of the bare Pt electrodes, a significant variability of the individual potentiometric calibration points demonstrates the incomplete coverage of the platinum with an oxide layer (with an ill-defined composition [31, 32]). The potential variability was about 80 mV for pH (Fig. 2a) and 40 mV for the chloride response (Fig. 2b). The variance of the potential responses of bare platinum electrodes toward pH was nearly four times higher than that for PPy electrodes. PPy electrodes show a half of the variance of bare platinum electrodes for chlorides. The presumption that a suitable coverage is vital for the correct and stabile electrode function was independently verified using electrodes based on PNR. The polymerization of PNR runs better in organic media leading to the formation of highly compact films [30]. On the other hand, the polymerization of the same compound from aqueous solution resulted in an incompact hole-containing film. Electrodes made in organic media provide a lower variability for all calibration points (20 mV) in comparison to the electrodes made in aqueous media (about 40 mV) (Fig. 2c). Thus, the complete coverage of the support metal improves significantly the reproducibility of the obtained potentiometric signal. From the mentioned experiments, it is evident that the negative effects of the support material may be avoided or at least significantly restricted forming the more compact and adherent polymeric film on the surface of the support.

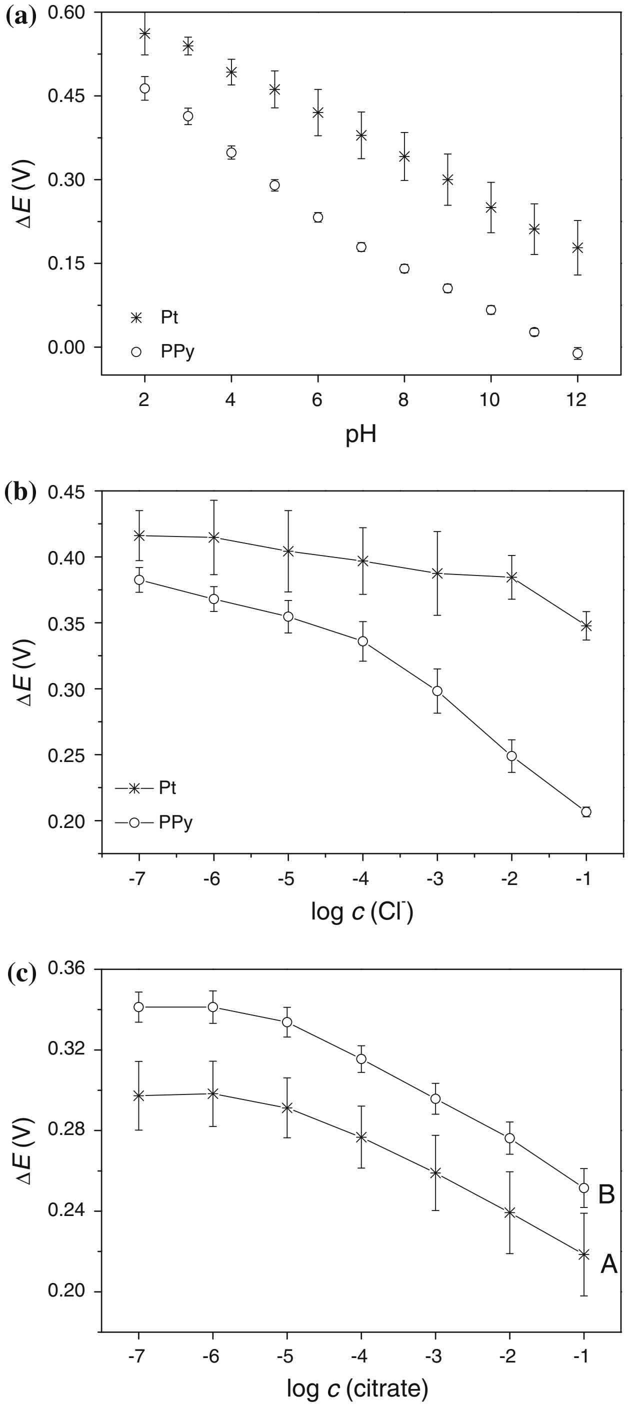

**Fig. 2** Dependence of potentiometric responses of bare (Pt) and polypyrrole (PPy)-coated platinum electrodes on pH (**a**) and chloride concentration (**b**). Dependence of potentiometric responses of poly(neutral red) electrode with inhomogeneous (*curve A*) and homogeneous polymer film (*curve B*) on citrate concentration (**c**); standard deviation expressed as error bars, $n = 4$

### Stabilization of potentiometric signal of single electrodes

In order to stabilize the potentiometric signal and to reduce the signal drift, the electrodes based on CPs traditionally undergo the postpolymerization treatment before their subsequent application [4]. According to the applied postpolymerization treatment, the experimental electrodes based on PNR were assigned into three groups. The first group of freshly prepared electrodes was left in distilled water, and its potential was recorded for about 50 days in 0.001 M citrate solution with TRIS and $KNO_3$ at pH 8.5 [37]. The soaking of the coated-wire electrodes in a suitable background electrolyte is one of the frequent procedures of the electrode treatment. For example, electrodes based on the PPy [2] and poly(1-aminoanthracene) [38] films were conditioned in phosphate buffer, and PT electrodes [39] were macerated in 0.1 M KCl. For PNR based electrodes, the initial change in potential was in the range of tens of milivolts (Fig. 3a—curve A). The drift of the signal significantly decreased after eight days, but the potential was not perfectly constant, and the remaining drift must be taken into account. This remaining minor drift could be eliminated by a frequent calibration preferably immediately before the measurement.

The second group of PNR electrodes was treated by maturation at constant potential at background electrolyte (see “Materials and Method” section) (Fig. 3a—curve B). In contrary to the treatment based on sole soaking of the electrodes, the initial change in the potential of the matured film was in the range of few milivolts and, in addition to that, it remained nearly constant throughout the long-term period. The conditioning time was a half of that required for the treatment in the absence of the applied potential.

The third group of the tested electrodes was measured immediately after their drying. A lower drift of the potential was achieved at the beginning of the measurement (during 1–3 days; Fig. 3a—curve C). However, the film gradually absorbed water and swelled. Swelling changed the properties of the polymeric layer, and this was reflected in the potential change and, also in the decrease of the adhesion of the film to the metal surface.

It is important to note that the postpolymerization treatment applied for the PNR electrodes had a similar effect on their potentiometric behavior as it was observed for the classical PANI electrodes (Fig. 3b). The best signal stability was obtained for the electrodes treated with a constant potential, using the same protocol as for PNR. Their potential was stable for about six weeks since their preparation. This demonstrates that the treatment of the polymeric films at a constant potential can be successfully applied also for other polymeric films to stabilize the potentiometric signal of the prepared electrodes.

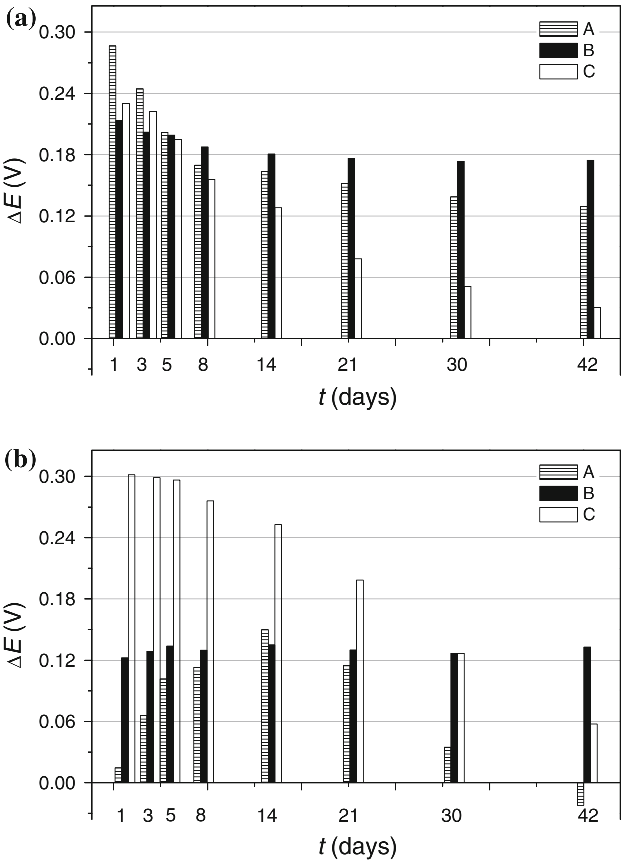

**Fig. 3** Influence of postpolymerization treatment of electrodes based on poly(neutral red) (PNR) (**a**) and polyaniline (PANI) (**b**) on their long-term stability in 0.001 M sodium citrate dissolved in 0.02 M TRIS with 0.1 M $KNO_3$ at pH 8.5: (*A*) no treatment, (*B*) at constant potential vs Ag/AgCl, (*C*) dried at 60°C for 2 h ($n = 3$)

### Stabilization of potentiometric signal of electrode array

The development of an electrode array—electronic tongue—[29] is of special interest in many prosperous and practically oriented fields of industry including, for instance, the brewing industry as the well-designed electrode array can provide quick and reliable data on the quality and authenticity of beer samples. As it can be seen in Fig. 4, the assembled electrode array is capable to distinguish the individual brands of the Czech beers.

The recognition pattern obtained with the electrode array was shifted slightly after three days (data not shown). This finding demonstrates the need for the regular recalibration of the array. Taking into account the chemical composition of beer, it is clear that it represents a very complex sample for the analysis. It consists of many various low- and high-molecular weight compounds (e.g., minerals, proteins, sugars) [40, 41]. These compounds gradually contaminate/block the CP surface of the electrodes. Therefore, a suitable washing procedure constitutes a substantial part of the measuring cycle of the beer

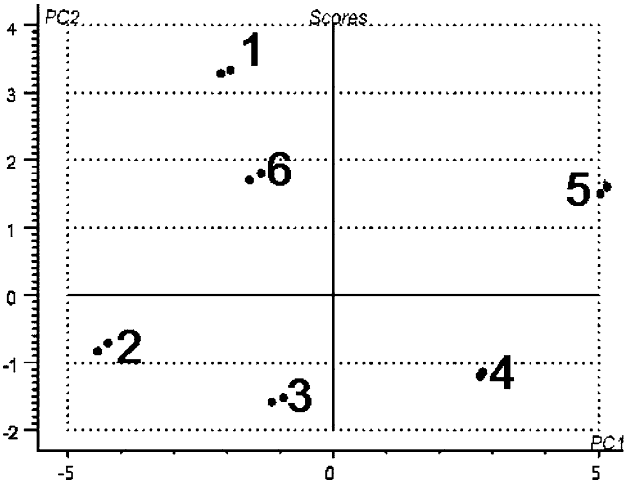

**Fig. 4** PCA score plot showing the ability of the electrode array to distinguish the Czech beers of different brands. The recognition pattern was measured with the following beer samples: *1* Bernard 10°, *2* dark Kozel 10°, *3* Kozel 10°, *4* Bráník 10°, *5* Radegast, *6* Staropramen ($n = 5$). These measurements were carried out in thermostated cell at 25°C. The tested electrodes were washed with distilled water between measurements

samples. To eliminate the undesirable effect of the dissolved gases, especially carbon dioxide and oxygen, the beer samples are bubbled with nitrogen before each individual measurement. In addition to the possible poisoning of the electrodes by the components of the complex matrix of the sample, a variability of pH values of the measured samples might adversely influence the response of the electrodes and thus, negatively affect reliability of the measurement. Thus, we proposed two potential washing/regenerating solutions, (i) a plain acetate buffer, pH 5.5, and (ii) the same buffer with the addition of an anionic surfactant, SDS.

In the first step the sole acetate buffer with pH 5.5 as washing solution was tested. In this case, the stabilization of the potential of the electrode array was relatively fast (~20 min) in the plain buffer solution. However, in real beer samples the stabilization took about 2 h. Thus, our results showed that a simple pH control of the washing solution is insufficiently effective.

In the second step with SDS added into the acetate buffer, the stabilization time decreased very significantly to about 20 min even in the real beer samples. It is important that the addition of the anionic surfactant to the acetate buffer did not change the recognition pattern obtained by the electrode array for beer samples. We assume that the presence of SDS in the washing solution effectively suppresses the sorption of polysaccharides and other potential contaminants onto the electrodes' surface. Thus, the simultaneous presence of the acetate buffer (pH 5.5) and the anionic surfactant in the washing solution stabilized the electrode array calibration and extended its applicability from three days to two weeks.

## Stability of potentiometric signal of PANI-coated membrane ion-selective electrodes

The use of CPs as the active/contact layer of coated-wire ion selective electrodes is not the only application in potentiometric sensors [1]. CPs, such as PANI, can be deposited also on the surface of a PVC membrane by chemical polymerization. In this case, the PANI layer influences the ion exchange processes occurring at the membrane–solution phase boundary [27, 42, 43]. The polycationic layer of the PANI partially plays the role of a lipophilic additive in the membrane based on a neutral carrier (calix [4]pyrrole). Such phenomenon might result from the synergistic effects of both the polycationic character of the PANI layer on the

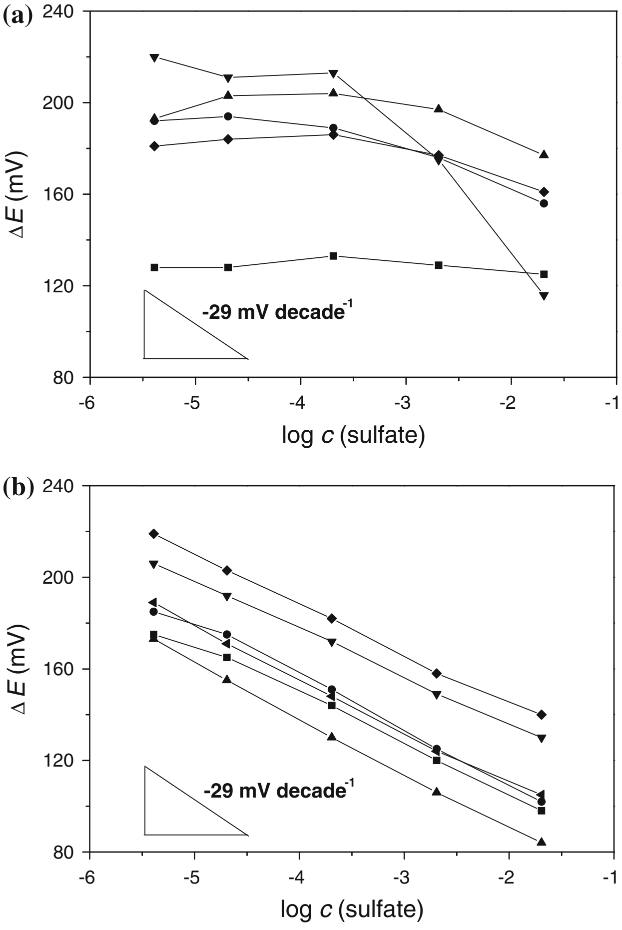

**Fig. 5** Potentiometric responses of TDDMACl-based membrane (PVC/NPOE mass ratio 2:1 and 3 wt. % of TDDMACl) uncoated (**a**) and coated (**b**) with the PANI film toward sodium sulfate in time: *filled square* fresh membrane; after *filled circle* 1 day, *filled triangle* 7 days, *filled left pointing triangle* 10 day, *filled inverted triangle* 18 days, *filled diamond* 35 days. Membranes were conditioned in 0.1 M $Na_2SO_4$ before these measurements were carried out

**Table 2** Absolute amount of TDDMACl leached from NPOE/PVC (1:2 m/m) membrane uncoated and coated with the PANI film ($n = 3$) into water phase

| Contact time (h) | Amount of TDDMACl leached from membrane (ng $mL^{-1}$) | |
|---|---|---|
| | Uncoated membrane | PANI coated membrane |
| 2.5 | 461 ± 23 | 89 ± 5 |
| 8 | 563 ± 43 | 103 ± 6 |
| 32 | 461 ± 27 | 105 ± 15 |
| 96 | 489 ± 35 | 96 ± 6 |
| 168 | 372 ± 6 | 113 ± 16 |

membrane surface and the bulky cation of the lipophilic additive in the membrane phase [42].

The NPOE/PVC (1:2 m/m) membrane based on TDDMACl shows a fast and near-Nernstian potentiometric response toward anions after being coated with the PANI film [27, 43]. The long-term stability of PANI-coated membranes based on TDDMACl toward hydrophilic sulfate anions was proved and successfully verified by the repeated calibration measurements (Fig. 5). As it can be seen from the comparison of Fig. 5a, b, the membranes coated with the PANI layer provided a stable and reproducible potentiometric response toward sulfate for 35 days. In addition, the PANI layer onto the TDDMACl-based membrane is capable to prevent the leaching of the active anion-exchanger from the membrane (Table 2). Thus, a suitable coating procedure represents one of the possible methods to stabilize the potentiometric signal of the ion-selective electrodes. In addition, this approach does not require the covalent attachment of an active component to the membrane matrix.

## Conclusions

We discussed and proposed several procedures enabling to reach a substantial suppression of signal drift in potentiometric sensors with conductive polymers. Our experimental findings indicate that a suitable pretreatment of the support material followed by a formation of the compact polymeric film possess prerequisites necessary to obtain electrodes with the stable electrochemical potential. Moreover, we also demonstrated that postpolymerization treatment of the prepared electrodes can further significantly improve the stability of the prepared electrodes. The discussed factors are of crucial significance, and they must be always considered when CP-based ion-selective electrodes are designed and prepared.

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