Supplementary Materials

The Novel Three-Layer Electrode Based on Poly(Neutral Red) for Potentiometric Determination of Citrates

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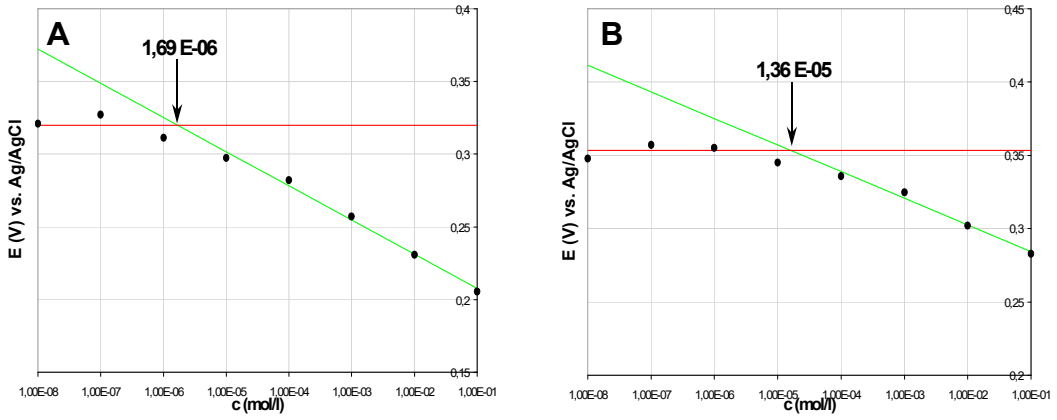
Potentiometry

The abbreviation FIM corresponds to the Fixed interference method that is commonly used in potentiometric practice for determining the potentiometric selectivity coefficients. In this case, it is represented by the measurement of the concentration dependence of the primary ion (I=citrate) at a constant background (BG) of interferent (J, c(J)=10^{-3}M used in the present manuscript). The parameter determined in the presence of interferent (Figure S1) is the detection limit (DL). The values of the experimental coefficients of the potentiometric selectivity are calculated accordingly to the equation:

$$\log K^{pot}_{I,J} = \log a_I(DL) / a_J(BG)^{z_I/z_J}$$



$$k^{pot} = \frac{0,00000169}{(0,001)^{3/2}} = 0,053 \Leftrightarrow \log k^{pot} = -1,27 \qquad k^{pot} = \frac{0,0000136}{(0,001)^{3/2}} = 0,430 \Leftrightarrow \log k^{pot} = -0,37$$

Figure S1. An example of evaluation of detection limit and selectivity coefficient for a simple PNR electrode in citrate solutions on adipates (A); terephthalates (B) background.

The used equation of the standard addition method [30 Koryta 1984] is:

$$c_x = \frac{c_s V_a}{V_0 + V_a} \cdot \frac{1}{10^{\Delta E/S} - \frac{V_0}{V_0 + V_a}}$$

where c_x (mol/l) represents the unknown concentration of the sample, c_s is the concentration of the standard, V_a is the volume of the added standard, V_0 is the sample volume, S is the slope of the calibration dependence, ΔE is the difference between the E_1 and the E_2 potentials measured before and after the standard addition, respectively.

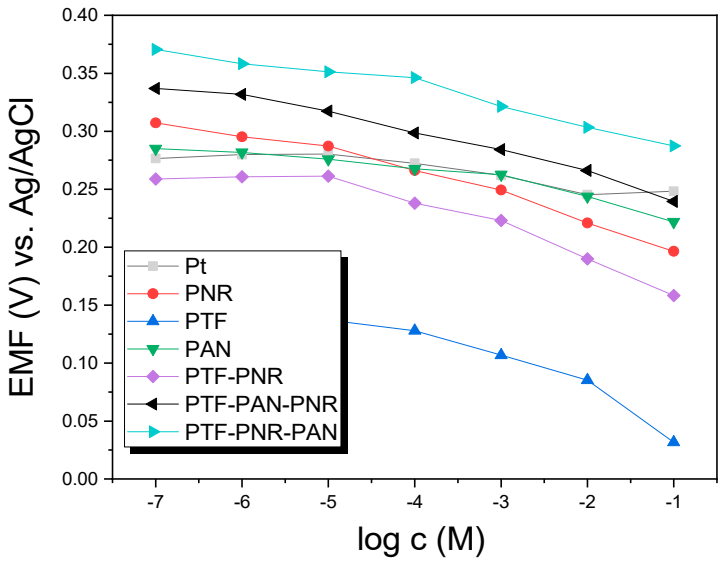


Figure S2. Potential response of mono-, bi-, and three-layer PNR electrodes toward citrates in TRIS with KNO_3.

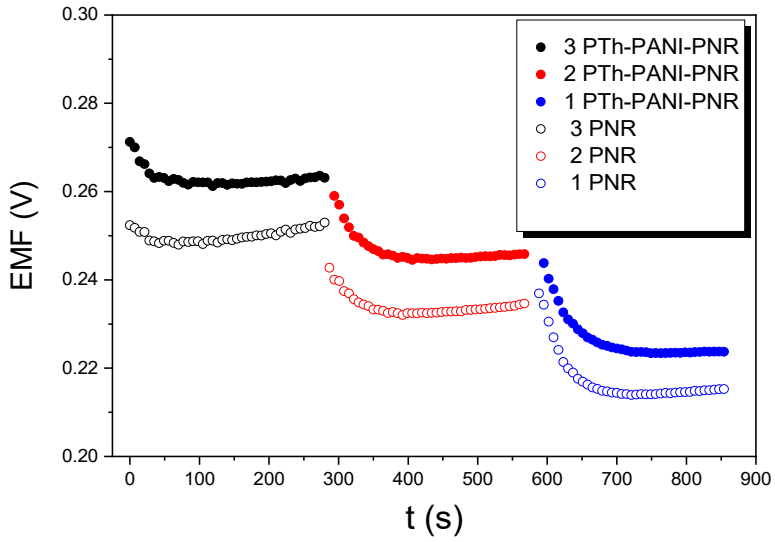


Figure S3. Time response of simple PNR and three-layer electrodes (Pth-PANI-PNR) in 0.001 M (3), 0.01 M (2), and 0.1 M (1) citrate.

Capillary electrophoresis

Experimental

Capillary electrophoresis was used as a reference method for the determination of citrates in real samples. A detailed description was presented in our previous study [17 Broncova 2008].

Electrophoresis experiments were performed in an untreated fused-silica capillary of length 39 cm (30 cm to the detector) and 75 µm ID purchased from Composite Metal Service (The Chase Hallow, Worcester, USA). A CAPEL 105 electrophoresis system (Lumex, Saint Petersburg, Russia) was used with indirect UV detection (254 nm). The base electrolyte was 5 mM K_2CrO_4 with 0.5 mM TDTABr at pH 8.0. All samples and standards were filtered through a disc filter with 0,45 µm pores (Millex HV, Bedford, USA). The capillary was conditioned by sequential washing with 0.1 M HCl (5 min), water (5 min), 0.1 M NaOH (5 min), and water again (5 min) before the start of the acquisition. A five-minute washing with the background electrolyte was done between each measurement. The conditioning was repeated after every beverage sample because of the issue of deposition of the sample on the capillary wall.

The samples were injected into the capillary hydrodynamically (1.5 kPa/30 s) and the analyses were run at reverse polarity, -10 kV, at 20 °C for 8 min. The instrument was first calibrated using standards of citrate in water at concentrations from 0.01 mM to 0.2 mM. The peak citrate concentration was registered at around the 6th minute (Figure S4). The citrate contents were calculated from the peak areas.

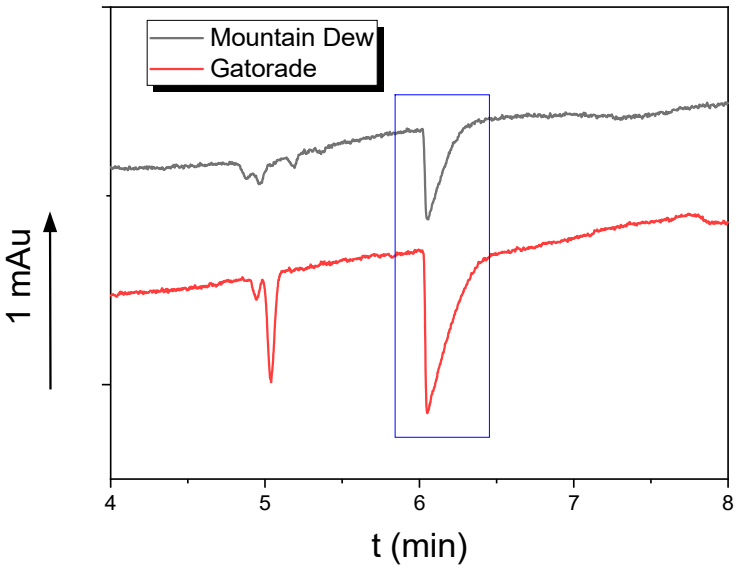


Figure S4. Electrophoregrams of soft drinks for citrate determination. The citrate peak is marked by the blue rectangle.

Reference

17. Broncová, G.; Shishkanova, T.V.; Krondak, M.; Volf, R.; Král, V. Optimalization of Poly(neutral red) Coated-wire Electrode for Determination of Citrate in Soft Drinks. Sensors 2008, 8, 594–606, https://doi.org/10.3390/s8020594

30. Koryta, J.; Štulík, K. Iontově-selektivní elektrody (Ion-selective electrode). Academia: Prague, 1984, ISBN: 21-035-84.