Supporting Information for Publication

Local Acidification of Membrane Surface for Potentiometric Sensing of Anions in Environmental Samples

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Calculation of acetic acid loss rate. Figures S-1, S-2 and S-3.

Estimation of acetic acid loss rate from the inner filling solution of the electrode (Protocol A).

The rate of acetic acid loss was estimated based on Fick's first law of diffusion assuming linear concentration gradient in the diffusion layer in aqueous phase:

$$J_{HAc}(t) = -D_{HAc}^{aq} \frac{c_{HAc}^{o,aq} - c_{HAc}^{*,aq}}{\delta^{aq}},$$

where $J_{HAc}(t)$ is the diffusion flux, D_{HAc}^{aq} - diffusion coefficient of acetic acid in the aqueous solution, $c_{HAc}^{o,aq}$ - concentration of acetic acid in the aqueous phase at the electrode membrane surface, $c_{HAc}^{*,aq}$ - concentration of the acetic acid in the bulk of the aqueous phase, δ^{aq} - thickness of diffusion layer in the aqueous phase.

$D_{HAc}^{aq} = 1.2 \cdot 10^{-5} cm^2 \cdot s^{-1}$ [1]

$c_{HAc}^{o,aq}$ was estimated based on the Tris buffer capacity (5 mM Tris, pH 8.3) resulting in $c_{HAc}^{o,aq} = 3.15\ mM$. The estimation is based on the assumption that the resulting proton concentration at the surface is significantly lower than millimolar level and the influence of pH at the electrode surface is negligible compared to the capacity of the buffer. The assumption is in agreement with the data presented by Jadhav at al.[2] and with our data confirming that the pH at the membrane surface is in the working range of nitrite electrode between 4 and 6.5 (see Figure 2).

$c_{HAc}^{*,aq}$ was approximated as 0 considering the large sample volume (100 mL) compared to the volume of inner filling solution (2.2 mL)

δ^{aq} was assumed to be equal to 100 μm (which is thickness of the spacer used to define the thin layer).

REFERENCES

(1) Leaist, D. G.; Lyons, P. A. Diffusion in dilute aqueous acetic acid solutions at 25°C. *J. Solution Chem.* **1984**, *13*, 77-85.

(2) Jadhav, S.; Bakker, E. Acetic acid release from polymeric membrane pH electrodes for generating local pH gradients at ion-selective membranes. *Electrochem. Solid-State Lett.* **1998**, *1*, 194-196.

FIGURES S-1, S-2, S-3

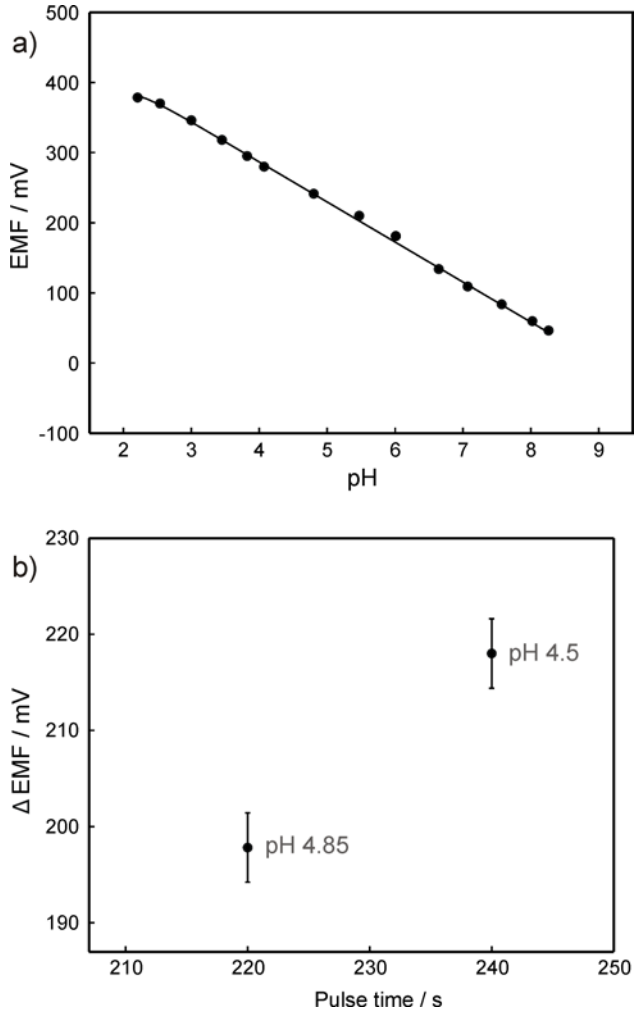

Figure S-1. Protocol C using an all-solid-state hydrogen selective electrode. Experiments in the beaker at pH 8.3 in 5 mM Tris buffer solution with 1 mM NaCl background. (a) Calibration curve in the beaker in 5 mM Tris buffer solution with 1 mM NaCl background (slope -57 mV; stirring conditions when reading the potential). (b) Illustration of the possibility of thin sample layer acidification at pH 8.3 in 5 mM Tris buffer solution with 1 mM NaCl background. Changing the pulse time at constant potential (700 mV, nonstirring conditions when reading the potential). ΔEMF: EMF difference after and before applying the pulse. The indicated pH in the thin sample layer was calculated according to the EMF changes by considering the slope of calibration curve shown above.

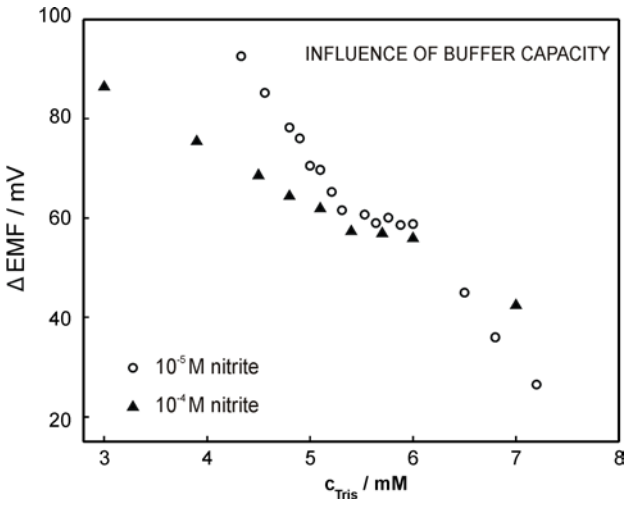

Figure S-2. Influence of the buffer concentration on the response of the all-solid-state nitrite selective electrode when applying protocol C. Experiments performed at pH 8.2 in Tris buffer solution with 1 mM NaCl background (nonstirring conditions when reading the potential). Changing the concentration of Tris buffer in the solution with constant nitrite concentration 10^{-5} M (white circles, applied pulse: 900 mV, 500 s) and 10^{-4} M (black triangles, applied pulse: 900 mV, 380 s). ΔEMF: EMF difference after and before applying the pulse.

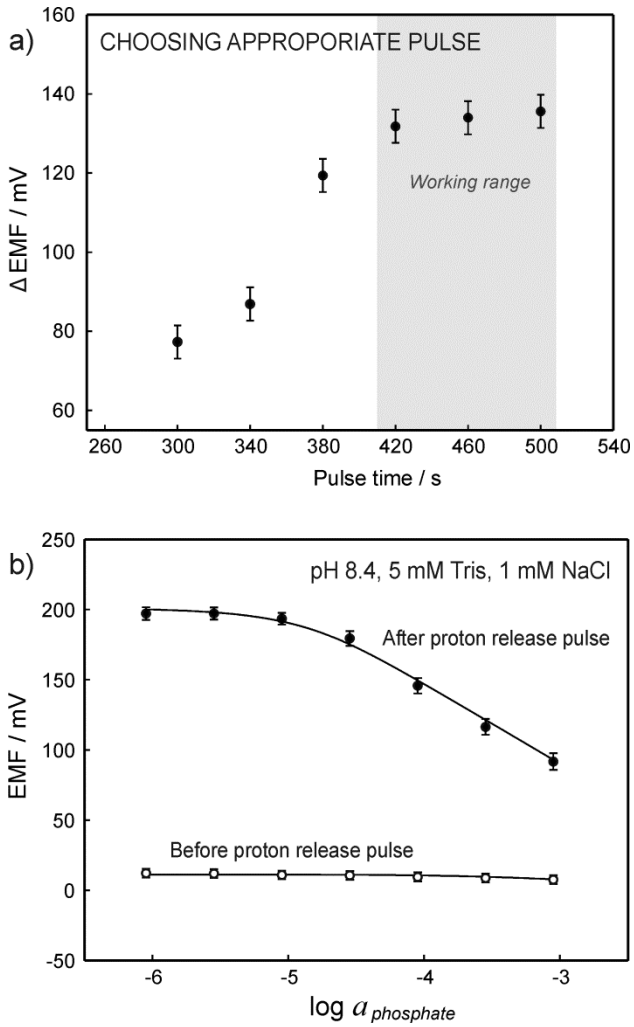

Figure S-3. Protocol C using an all-solid-state dihydrogen phosphate selective electrode. Experiments in the beaker at pH 8.4 in 5 mM Tris buffer solution with 1 mM NaCl background. (a) Choosing the optimum conditions for the experiment at fixed total phosphate concentration (10^{-4} M): changing the pulse time at constant potential (1000 mV, nonstirring conditions when reading the potential). ΔEMF: EMF difference after and before applying the pulse. The plateau in coordinates Δ*EMF-pulse time* indicates the appropriate working range in the given conditions. (b) Black markers: nitrite detection by applying the protocol C (1000 mV, 500 s, nonstirring conditions when reading the potential). White markers: potential readings for the same electrode before applying the pulse (nonstirring conditions when reading the potential).