Supporting information

Ion-selective membrane plasticizer leakage in all-solid-state electrodes – an unobvious way to improve potential readings stability in time

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The effect of leakage of the plasticizer from the ion-selective membrane into the ion-to-electron transducer of all-solid-state potentiometric sensors is considered for the first time. The plasticizer can be transferred to the transducer phase, either during ion-selective membrane application or later, in both cases its presence can affect performance of the sensors. Clearly this effect is most pronounced if the transducer is dispersable in the plasticizer. Towards this end it is shown that application as the transducer of plasticizer dispersable poly(3-hexylthiophene) compared to typically used (non-dispersable) poly(3-octylthiophene) results in sensors offering higher reproducibility of recorded potentials equal to ±1.4 mV and ± 2.5 mV, respectively (within day test, n = 6). Although poly(3-hexylthiophene) was also found in the membrane in solvent dispersed, neutral emission active form, analytical parameters of poly(3-hexylthiophene) based sensors including selectivity were improved or comparable with those of classical poly(3-octylthiophene) transducer sensors.

Key words: all-solid-state ion-selective electrodes, potentiometry, polythiophenes, plasticizers, ion-to-electron transducer, potential reproducibility

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The details of polythiophene polymers specified by producer are as follows: poly(3-octylthiophene-2,5-diyl) (POT) regioregular (molecular weight 50-70kD), poly(3-hexylthiophene-2,5-diyl) (PHT) regiorandom (molecular weight 30-90kD).

Table S1. Logarithms of selectivity coefficients determined for tested sensors, using separate solution method within the concentration range from 10^{-1} to 10^{-4} M, using theoretical slope. PHT and POT transducer type used.

Transducer material	Log K_{ij}^{pot}, j:			
	Mg^{2+}	Ca^{2+}	Na^{+}	H^{+}
PHT	-3.8±0.5	-3.6±0.4	-3.2±0.1	-4.2±0.5
POT	-3.7±0.2	-3.6±0.1	-3.1±0.2	-4.0±0.6

Table S2. Results of PT quantification for ASS-ISEs from UV-Vis absorbance and fluorescence measurements. In all cases 0.02 mg of the polymer was applied on GC substrate. The CV of polymer contents determination is estimate to be ± 5 %. The results obtained for dispersed membranes were compared with calibration lines constructed using standard solutions of PT purposely added to membrane cocktail solution, details of procedures are given in [19]. The CV of determination (both for emission and absorption mode, for membrane, bulk, surface and support separately) was estimated taking into account mean value of replicates of nominally the same sensors prepared (n = 3).

Transducer:	PHT		POT	
	absorbance	emission	absorbance	emission
	% (w/w) of applied polymer			
Membrane (bulk)	45	45	20	30
Membrane (surface)	30	30	70	50
Substrate electrode	25	15	10	-

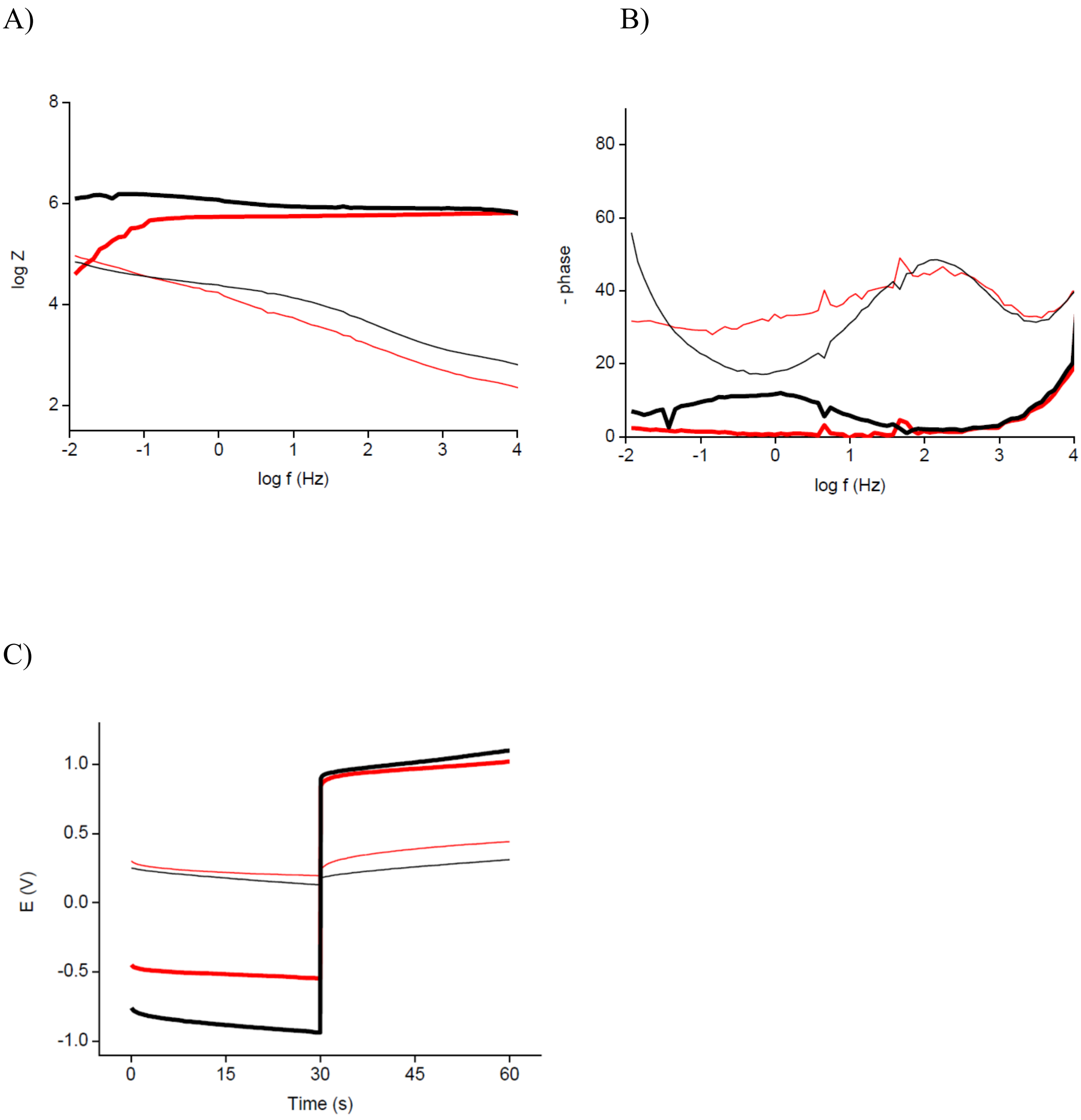


Figure S1. A) and B) The impedance spectra, Bode plots and C) chronopotentiometric dependence recorded while passing current 1·10^{-6} A of polythiophenes – NaTFPB films (**thick lines**) in the presence of DOS and (thin lines) in the absence of plasticizer: (red line) PHT, (black line) POT.

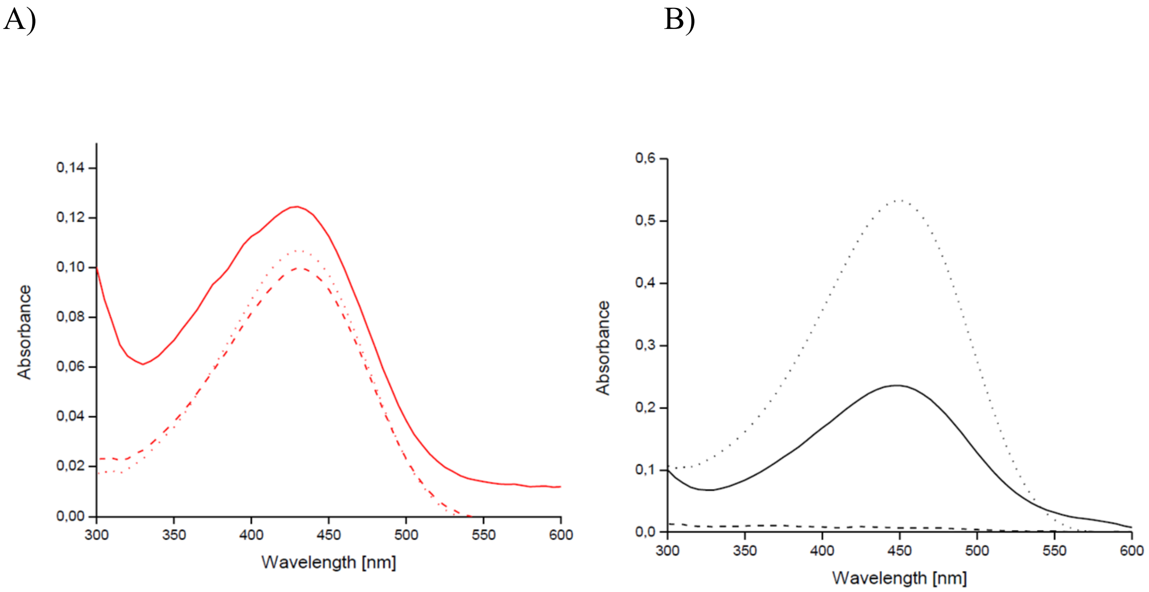


Figure S2. Absorption spectra recorded for the chloroform or mixture of THF/chloroform dispersion of potassium-selective membrane of solid contact sensors (line), dispersion of polythiophene washed off the GC substrate electrode (dashed line) and dispersion washed off from bottom layer of ion-selective membrane (dots) for A) (red) PHT and B) (black) POT.

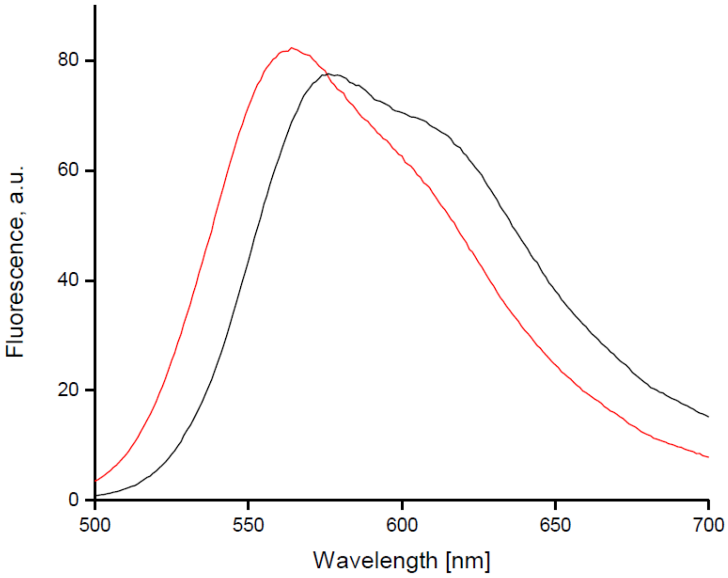
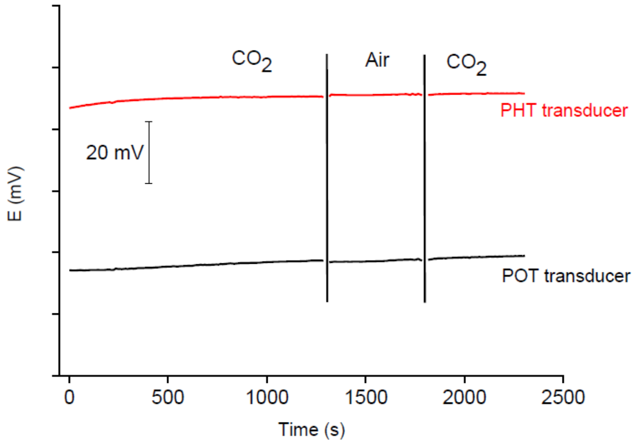


Figure S3. Emission spectra recorded for the chloroform or mixture of THF/chloroform dispersion of potassium-selective membrane ((PVC, plasticizer, ionophore and ion-exchanger) of solid contact sensors based on (red line) PHT and (black line) POT.

A)



B)

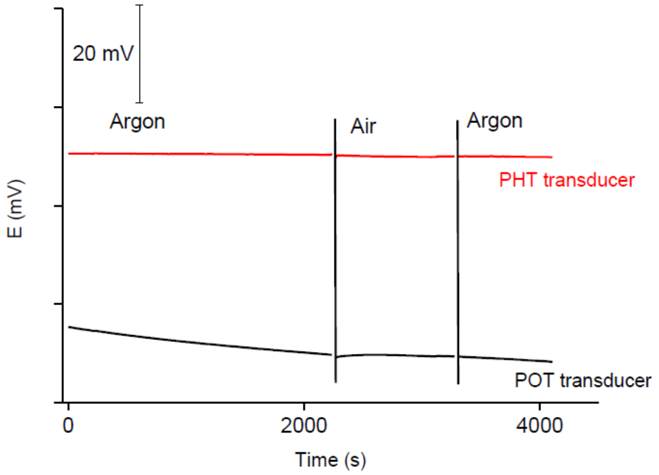


Figure S4. Effect of various factors: A) the effect of CO_2 bubbling, B) the influence of aeration/ deaeration (argon) on potentials recorded for tested sensors with (red line) PHT, (black line) POT on potential stability, tests were performed in 10^{-3} M KCl solution. Dependencies were shifted on Y axis to enable comparison.

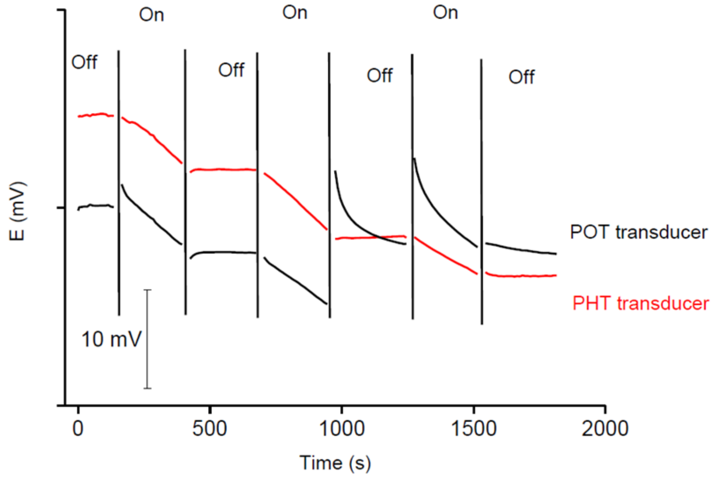


Figure S5. The effect of light pulses (light source power 250 W) on potentials recorded for tested sensors with (red line) PHT or (black line) POT transducer, dependencies recorded were shifted on Y axis to yield similar initial potential values to enable comparison. “Off” denotes that room light was applied. The experiment was performed on different nominally the same sensors (n =5, both for PHT and POT), exemplary results are shown.

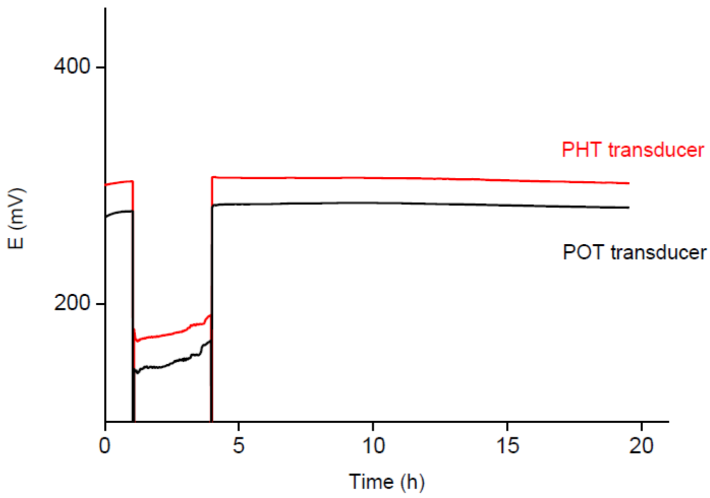


Figure S6. Water layer test experiment performed for tested sensors with (red line) PHT or (black line) POT, the tests were performed in 10^{-3} M KCl, 10^{-3} M NaCl, and again in 10^{-3} M KCl solutions.