Taking Advantage of Current Polarization at Phase Boundary between Aqueous Solution and Solvent Polymeric Membrane of Ion-Selective Electrode

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It is now well established, both fundamentally and experimentally, that the dynamic range of ionophore-based ion-selective electrodes (ISEs) is determined by the electrolyte co-extraction: from the internal solution for the lower detection limit (LDL), and from the sample for the upper detection limit (UDL). Although significant efforts were made in different research groups to extend the ISEs' detection limits, the commercially available sensors have 10^{-7} M LDL, the lowest, and 0.1 M UDL, the highest. This, at least partly, is due to low versatility of the most of the approaches aimed at the improvement of the ISEs dynamic range. Unlike other ways, galvanostatic polarization appears the most versatile and easy to implement [1].

Earlier we showed the advantage of applying optimized cathodic current pulses to ISE membrane in order to sense submicromolar concentrations [2, 3]. The idea was to compensate trans-membrane ion fluxes resulting from co-extraction at the inner membrane side and leading to contamination of the sample in the membrane vicinity. It appears attractive to use the same approach to improve the UDL of ISEs, now with anodic current pulses, since the reason for sensitivity loss at higher concentrations is proved to be co-extraction as well, in this case at the sample side of the membrane.

Here we demonstrate that the method of tuned galvanostatic polarization (TGP) of ISEs can be generalized for extending their detection limits drastically towards extremely high as well as very low concentrations, without loss in selectivity. This makes simple and inexpensive ISE an all-purpose analytical tool suitable for reliable measurements within the range from 10^{-10} to 1 M (see figure), and higher. It will be proved that in the whole concentration range the algorithmization of the calibration in TGP mode can be performed on the basis of fundamental regularities found in our work. Furthermore, analysis of the samples outside the conventional dynamic range is proved to be feasible with polarized ISEs.

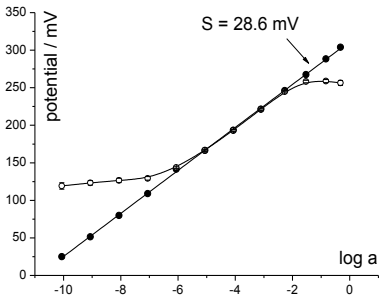

Fig. 1. Broadening ISE measuring range with tuned GP; empty symbols – zero-current calibration, solid symbols – response of polarized ISE

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