Non-Equilibrium Mode of Measurements with Ion-Selective Optodes

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The reduction of analysis time plays a key role in a variety of sensor application: time-resolved imaging, medical diagnostics, point-of-care platforms [1]. Reducing the time in the cycle "sampling — analysis — result" allows to quickly diagnose and prescribe the correct treatment. Bulk sensors, in particular – bulk optodes, are promising candidates for the wide use in analytical routine: they are easy to fabricate and use, deliver reproducible results, and typically demonstrate stable analytical signal.

The establishing of the equilibrium analytical signal means equality of the (electro)chemical potentials of the analyzed species in the sample phase and in the sensor phase. Typically, diffusion process is responsible for the equilibration. Hydrophobic bulk optodes are not an exception, and being viscous polymeric films of finite thickness, they of course have significant response time [2]. Herein, we report on the concept of reducing the analysis time by implementation of the non-equilibrium measurement mode. The concept is theoretically grounded based on the classical Fick's diffusion formalism [3], and verified with conventional colorimetric Na+/pH-selective optode as well as with the pH-optode proposed in [4] for measuring individual ion activity. The influence of the measurement time both on the analytical characteristics (span, range, median and sensitivity) of the response and on the metrological parameters (error, reproducibility, precision) of the analysis was traced. At least the 2-fold reduction of analysis time was achieved without any loss in the response characteristics and analytical accuracy as compared with the conventional equilibrium read-out mode (see Fig. 1). The developed measuring non-equilibrium protocol can be introduced into analytical routine without any change in measuring instrumentation, sampling and pretreatment steps and in data processing.

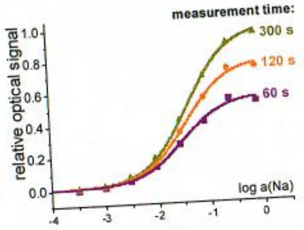

Fig. 1. The response of the Na^+-optode at different measurement times. Equilibrium response: 300 s.

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Ionic Liquid Plasticized Optodes

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Bulk optical sensors are widely used in various fields of research and typically are based on the same compounds as ion-selective electrodes (ISEs). However, not all of the components successfully utilized for the ISE membranes are to the same extent explored for application in optodes. Ionic liquids (ILs) are used to enhance sensitivity of the ISEs, as a plasticizer for the ISE membranes and/or as an additive to stabilize the electrode boundary potential when developing solid-state electrodes [1]. A growing number of works is devoted to the application of the ILs in bulk optodes, both as an active microcomponent, and as a matrix material, the latter mainly referring to the gas sensors [2]. However, no systematic study of the ILs effect in the optode performance is available.

In this contribution we show how the gradual replacement of the traditional plasticizer with the IL changes the characteristics of the optode response. The properties of the optodes with indicators ETH2439 and ETH5350, and ionophores NaX and NaVI, respectively, were studied upon variation of the IL amount in the plasticizing mixture (Fig. 1). Three effects of different nature were observed. First, the IL addition drastically shifts the optode working range, which can be used for the tuning of the sensor response. Second, the Na-response of the sensors turns out to be suppressed at the IL content higher than 50% (Fig. 1, right) thus making the pH response dependent on the single ionic activity. The latter is in full accordance with [1] were similar IL was utilized for stabilizing electrode boundary potential, and with [3] were the moderately lipophilic electrolyte added to the membrane allowed to develop an optode for individual ionic activities. Third, the response time of the IL-containing optodes decreases noticeably with the increase of the IL content. The grounded explanation to the observed effects will be given in our contribution and supported with the comprehensive experimental data.

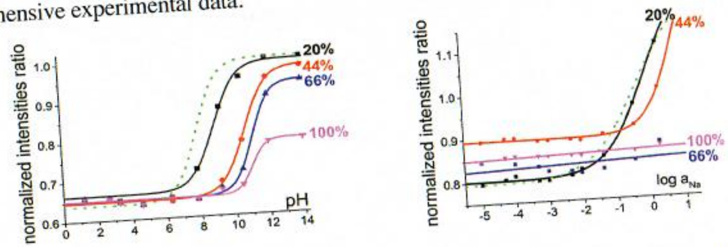

Fig. 1. The response of the optodes with different IL (1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl) amide) content (denoted in the plot in w.% of the plasticizing mixture with bis(ethylhexyl)sebacate). Dotted lines: no IL in plasticizing mixture.

References

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