

Redox potential – field measurements - measured vs. expected values

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Oxidation and reduction (redox) potential is an important and theoretically very well defined parameter and can be calculated accurately. Its value is determinative for management of many electrochemical processes, chemical redox technologies as well as biotechnologies. To measure the redox value that would correspond with the accuracy level of theoretical calculations in field or operational conditions is however nearly impossible. Redox is in practice measured using combined argentochloride electrode with subsequent value conversion to standard hydrogen electrode (EH). Argentochloride electrode does not allow for precise calibration. Prior to the measurement the accuracy of measurement of particular electrode can only be verified in comparative/control solution with value corresponding with oxic conditions (25°C: +220 mV argentochloride electrode, i.e.+427 mV after conversion to EH). A commercial product of stabile comparative solution for anoxic conditions is not available and therefore not used in every day practice – accuracy of negative redox is not verified. In this presentation results of two tests will be presented: a) monitoring during dynamic groundwater sampling from eight monitoring wells at a site contaminated by chlorinated ethenes (i.e. post-oxic to anoxic conditions) and b) laboratory test of groundwater contaminated by arsenic from two sites during reaction with highly oxidized compounds of iron (ferrates) – i.e. strongly oxic conditions. In both tests a simultaneous measurement by four argentochloride electrodes was implemented – all four electrodes were prior to the test maintained expertly. The redox values of testing electrodes in a comparative solution varied by max. 6 mV. The redox values measured by four electrodes in both anoxic and oxic variant varied by tens to a hundred mV, while with growing time of test the variance of measured redox values increased in both oxic and anoxic variant. Therefore the interpretation of measured redox data must be approached keeping in mind that their accuracy does not correspond with theoretical calculations and their values must be assessed in combination with other parameters – e.g. in case of interpretations of measured redox during remediation of contaminated sites it is appropriate to assess these values together with determined concentrations of significant terminal electron acceptors (TEA) whose laboratory determination is more accurate (NO_3^- , NO_2^- , Fe^{2+} , Mn^{2+} , SO_4^{2-} , $\text{H}_2\text{S}+\text{S}^{2-}$, CH_4 ...).

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