Development of a Combined Multi-Sensor/Signal Processing Architecture for Improved In-Situ Quantification of the Charge Balance of Natural Waters

by
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Abstract

This thesis details the design, implementation, and testing of a new electrochemical instrument for the in situ measurement of both major and environmentally relevant minor ions in fresh waters, namely Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, Cl^-, NO_3^-, and SO_4^{2-}. The instrument is built on a hybrid multi-probe / signal processing architecture and is implemented using commercial sensor hardware (primarily ion-selective electrodes (ISEs)) paired with a novel neural network processor designed to take advantage of *a priori* chemical knowledge about the system. Adaptation of this architecture to in-situ conditions and quantification of relatively minor ions required overcoming a number of challenges, including: (1) lack of a standardized method for unsupervised recording of ISE equilibrium potential, (2) non-availability of commercial electrodes for some ion species, and (3) detection of ion concentrations that fall below the ISE linear response region and/or are confounded by the presence of relatively large quantities of interfering ions. As such, a methodology is proposed and validated for standardization of ISE potential readings, resulting in consistent measurements completed in <6.5 min., improving replicability, and facilitating simultaneous measurement of up to 12 ion channels. The sensor suite is then designed such that each ISE provides information about more than one analyte, and finally, the artificial neural network (ANN) architecture is optimized for use on environmental chemical data by including software constraints implementing known chemical relationships, i.e., the concept of charge balance and the total ion-conductivity relationship. Two experiments are conducted using environmentally-relevant data sets (one semi-synthetic, one created in the lab) to characterize the effectiveness of the proposed ANN architecture. Final results demonstrate over an order of magnitude decrease in relative error (as measured against use of ISEs as stand-alone sensors) without concentration-dependent error bias, including estimates for analytes for which no specific ISE exists (SO_4^{2-}, Mg^{2+}, HCO_3^-). Simultaneous un-biased quantification of all eight ions is achieved with ˜20% error on most channels including NO_3^- (concentrations $\leq$100 μM) and ˜50% error for NH_4^+ ($\leq$100 μM), however it is also demonstrated that errors of ˜10% are achievable for N-species ions even at low concentration if slightly higher uncertainties on other channels can be tolerated.

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