

The Pitzer pH Scale: Implications for pH Determinations in Estuarine Waters

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We have evaluated a method of pH determination using the Pitzer pH scale for estuarine waters by means of cells without liquid junctions. Two cells are suggested for pH measurements: one cell is composed of a glass electrode for hydrogen and a glass electrode for sodium ions, and another cell is composed of a glass electrode for hydrogen and a chloride selective electrode for chloride ions. The Pitzer method [1] was used as the theoretical basis for the assignment of pH values for three reference buffer solutions (NaH_2PO_4 - Na_2HPO_2 - NaCl - H_2O , TRISHCl-TRIS- NaCl - H_2O , and TRISHCl-TRIS-seawater) [2], which are recommended for the calibration of cells without liquid junctions. The results showed that these three buffer systems are in agreement with each other to better than 0.01 pH units for the 5 to 35 °C temperature range. The standard deviation of pH measurements in seawater and estuarine waters with salinities higher than 2 is 0.003 pH units, when cell a composed of hydrogen and sodium glass electrodes was used. Comparison of the pH measurements obtained for the Razdolnaya River-Amursky Bay (Japan/East Sea) estuary by the two above noted cells, showed that the average systematic differences between the two data sets is 0.0034 pH units with a standard deviation of 0.006 pH units for the whole salinity range (0.15 to 34). Potential errors caused by interference effects of the hydrogen ions on the sodium electrode and effects of the composition of river waters on estuarine waters when the salinity is less than 2 are discussed. The presented results of the pH measurements for the Razdolnaya River-Amursky Bay estuary obtained at low river water and just after a typhoon, suggest that a phytoplankton bloom in the seaward part of the estuary occurred after the typhoon, and was caused by an enhanced supply of nutrients in the upper layer when there was a sharp increase of river discharge.

[1] K.S.Pitzer, In: *Activity Coefficients in Electrolyte Solutions*. K. S. Pitzer Ed.; 2nd Edition; CRC Press: Boca Raton, Ann Arbor, Boston, London, 1991, pp. 75-153.

[2] P.Ya. Tishchenko, *Russ. Chem.Bull.* **49**, 680 (2000).