Verifying the Use of Specific Conductance as a Surrogate for Chloride in Seawater Matrices

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ABSTRACT

Coastal ground water supplies, when overused, are particularly vulnerable to chloride contamination due to their close proximity to saltwater. Seawater has an average chloride concentration of 19,000 mg/L (Hem 1992). Elevated chloride concentration in ground water is the most commonly used indicator of saltwater intrusion in coastal aquifers. Rather well-defined relationships of specific conductance (SC) to chloride exist (Hem 1992). To validate the relationship between SC and chloride, SC measurements by electrochemical conductivity cells and chloride concentration measurements by ion-selective electrode (ISE) were determined for five concentrations of Standard Atlantic Seawater OSIL at six different temperatures (30 unique samples). A strong linear relationship was established thus demonstrating the validity of using SC as a surrogate for chloride estimation. This study also compared inherent measurement drift of a chloride ISE and a conductivity sensor under controlled laboratory conditions over an 11-day period. Minimal drift of the conductivity sensor coupled with a large drift of the chloride ISE demonstrates a significant advantage of the conductivity sensor for long-term field deployments.

INTRODUCTION

Chloride ISEs use a potentiometric design to measure the total chloride ion concentration in water. One downfall to using an ISE is the propensity for measurement drift and requirement for frequent recalibration to compensate for the drift. The most accurate sensor response is achieved by performing a bi-thermal, three-point calibration. This adds obvious complication when performing field calibrations and measurements. Manufacturers recommend performing calibrations on a weekly basis at a minimum, implying long-term instability of the ISE. In addition to chloride ISEs, titrimetric methods can be used. Titrimetric reagents for determining chloride in seawater are hazardous (e.g., mercuric nitrate, silver nitrate) and require appropriate disposal. Interferences may require neutralization or elimination. *Standard Methods* (Eaton, A.D., et al., 2005, pp. 4-3, 4-70) notes that ion chromatography is the preferred method for determining chloride because it eliminates the use of hazardous reagents, distinguishes among halides, and provides a single instrumental technique for rapid, sequential measurement. However, unlike conductivity sensors, ion chromatography is not suitable for field applications or real-time monitoring. Alternatively, the use of an electrode-based conductivity cell can be used to compute the chloride concentration of a solution—provided the conductivity-chloride relationship is known or developed for the matrix of interest. This method uses a much more stable measurement technology that minimizes calibration and maintenance issues. To estimate chloride concentrations, conductivity sensors can be used to spot-check various sites or installed to collect data continually. The following section describes the development of a linear relationship between SC and chloride in standard seawater.

METHODS

A Standard Atlantic Seawater OSIL sample (35.0 PSU) was diluted to five concentrations: 35, 26.25, 17.50, 9.25, and 4.63 PSU. These samples were divided into six subsamples of each concentration. A sample at each concentration level was brought to a temperature of 0, 10, 20, 30, 40, and 50° C, respectively, using a VWR Programmable Thermal Bath, for a total of 30 unique samples (five concentrations at six temperature set points). These samples were allowed

to stabilize for a minimum of one hour at the temperature set point. An Instrulab precision thermometer recorded true temperature values.

Chloride and temperature data was collected using an In-Situ® Inc. TROLL® 9500 water quality sonde with chloride ISE. Prior to sample analysis, the chloride ISE was calibrated using a three-point, bi-thermal calibration with NIST-traceable chloride standards. Five replicate readings were taken at each of the 30 chloride/temperature test points. The five readings were averaged to determine a final response value for each testing point. The testing procedure was repeated using two factory calibrated In-Situ Aqua TROLL® 200 sensors. SC and temperature data were collected. SC values were compared with the corresponding chloride values, and the relationship was evaluated for validity (see Figure 1).
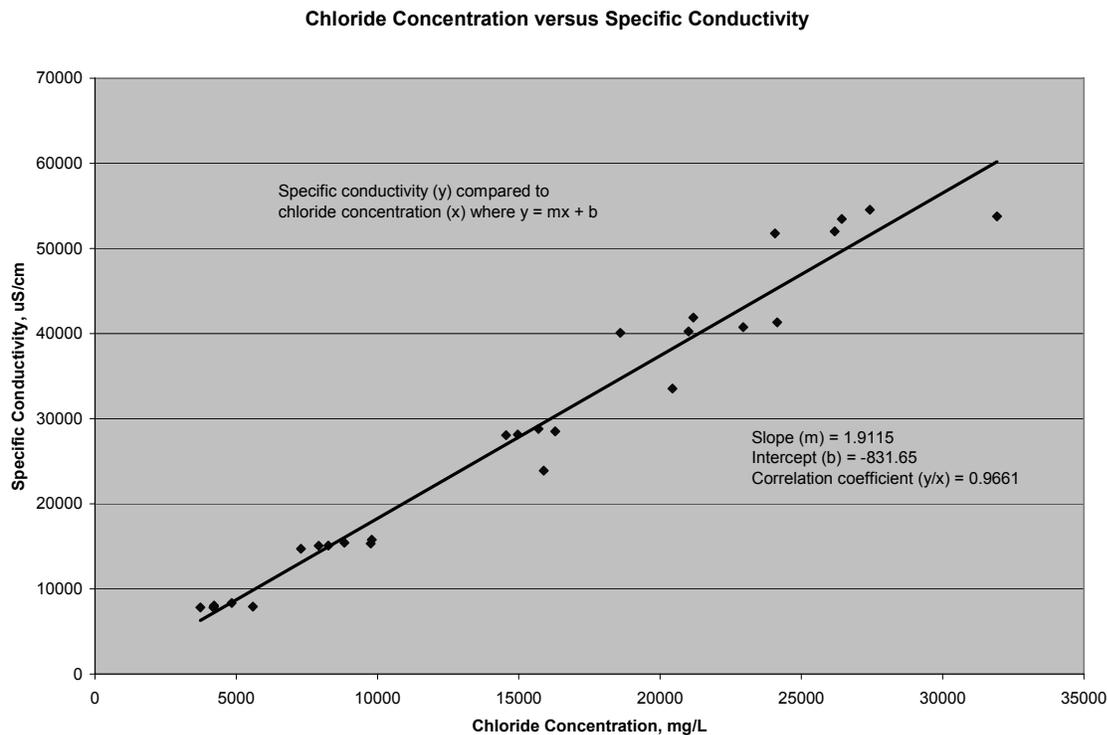
Chloride Concentration versus Specific Conductivity

Specific conductivity (y) compared to chloride concentration (x) where y = mx + b

Slope (m) = 1.9115
Intercept (b) = -831.65
Correlation coefficient (y/x) = 0.9661

Figure 1. Relation of specific conductance to chloride concentration

To evaluate ISE and conductivity sensor drift, hourly readings were taken in a 17 PSU Standard Atlantic Seawater Standard over an 11-day period under controlled laboratory conditions. The sample was closed to the environment to prevent evaporation or any potential change to the solution. Two Aqua TROLL 200 sensors and a TROLL 9500 with chloride ISE were set to log data at hourly intervals. A third party, NIST-calibrated conductivity sensor was used to record daily values of the test solution. A freshly calibrated chloride ISE was used to measure final chloride concentration of the solution. Drift values were calculated based on the final test instrument reading minus the initial test instrument reading, and compared to the actual readings generated by the reference sensors to ensure that there was no solution drift.

RESULTS

Figure 1 shows the linear relationship between SC (µS/cm) and chloride concentration (mg/L). Statistical analysis on the ratio of SC values (y) and chloride concentration (x) showed a strong linearity ($R^2 = 0.9661$). Two outliers were removed from the data set due to a large offset in

these readings; the suspected cause for the erroneous data was a loss of electrical ground contact from the chloride sensor.

To determine sensor drift, the absolute variation for the conductivity and chloride sensors was calculated and compared with true reference meter results over an 11-day period (see Figure 2). The conductivity sensor drift was 54µS/cm or 0.2% of reading, which was within the manufacturer's stated accuracy specification of 0.5%. Secondary conductivity meter results indicated no drift of the solution throughout the 11-day test. The chloride sensor drift was 7,374 mg/L or 39% of reading. The secondary chloride ISE reading confirmed the significant drift of the chloride sensor.
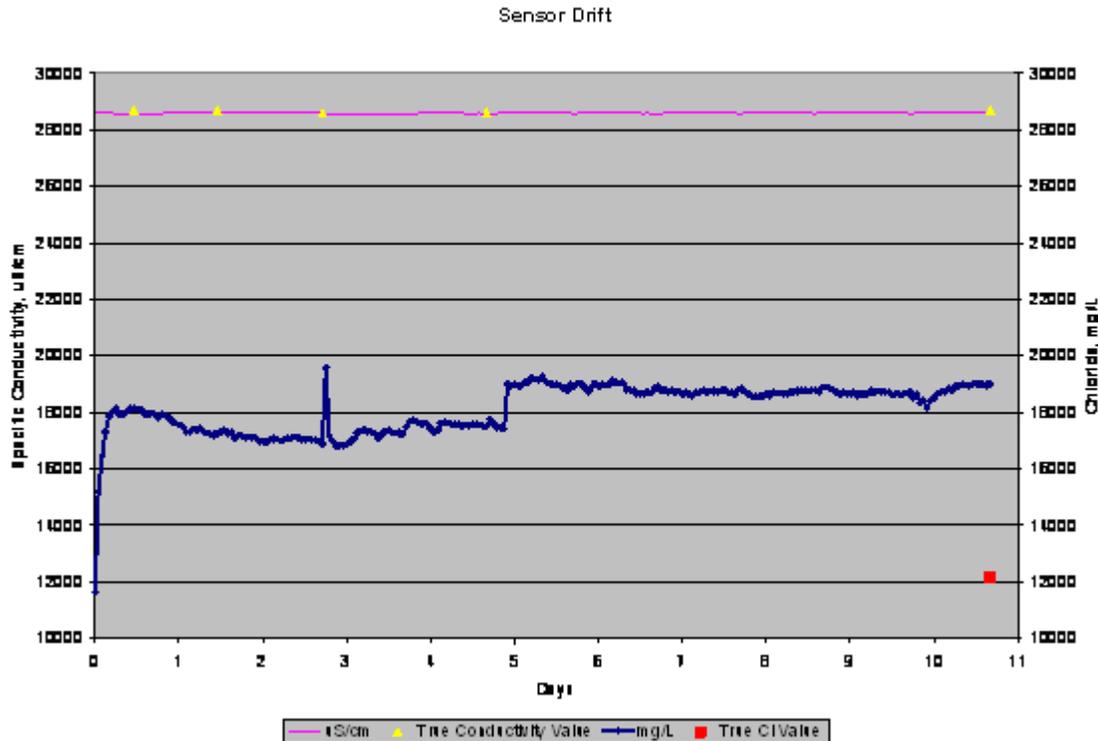

Figure 2: Comparison of chloride sensor drift and conductivity sensor drift

The stability of the conductivity sensor and the strong linear correlation of these two parameters indicate a clear advantage for use in chloride estimation over currently available methods. This is especially true for field deployment applications or long-term monitoring projects, in which sensor reliability is essential for accurate results.

DISCUSSION AND CONCLUSIONS
The conductivity sensor is a proven, stable method for measuring SC. Using this technology to estimate chloride concentrations offers several advantages over currently available chloride analysis methods, such as chloride ISEs, titrations, or ion chromatography. ISEs are accurate when recently calibrated, but are sensitive to drift, fouling, and are not ideal for field monitoring. Titrimetric methods are less precise than conductivity measurements (Farland 1975) and can generate hazardous wastes that require disposal. Ion chromatography is an accurate laboratory method, but cannot produce real-time data needed for rapid decisions in the field. To generate real-time field data that avoids using methods sensitive to drift, fouling, and other instabilities,

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SC (surrogate) and chloride relationships can be developed. The study verifies the strong linear relationship between SC and chloride for seawater and demonstrates that SC is much less susceptible to drift and requires less maintenance than available ISEs. SC can provide more robust data sets for long-term projects such as saltwater intrusion studies of coastal aquifers, salt marsh studies, and coastal wetlands monitoring projects.

REFERENCES

Christensen, V.G., J. Xiaodong, and A.C. Ziegler. 1999. Regression analysis and real-time water-quality monitoring to estimate constituent concentrations, loads, and yields in the Little Arkansas River, South-Central Kansas, 1995-1999. U.S. Geological Survey, Water-Resources Investigations Report 00-4126.

Eaton, A.D., L.S. Clesceri, E.W. Rice, and A.E. Greenberg. 2005. Standard Methods for the Examination of Water and Wastewater. American Public Health Association. Washington, DC.

Farland, R.J. 1975. Salinity intercomparison report, the oceanographic subprogramme for the GARP Atlantic tropical experiment (GATE). Nat. Oceanogr. Instrum. Center, Washington, DC, November 1975.

Hem, J.D. 1992. Study and interpretation of the chemical characteristics of natural water (3rd edition). U.S. Geological Survey, Water-Supply Paper 2254.

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