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

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ABSTRACT
Coastal groundwater supplies, when overused, are particularly vulnerable to chloride contamination due to their close proximity to saltwater. Elevated chloride concentration in groundwater 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; Christensen et al. 1999). 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 35 PSU OSIL Atlantic Seawater Standard and 10 dilutions at six different temperatures (66 unique samples). Seawater has an average chloride concentration of 19,000 mg/L (Hem 1992). 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 a seven-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.

APPLICATION OVERVIEW
Coastal groundwater supplies, when overused, are particularly vulnerable to chloride contamination due to their close proximity to saltwater. Elevated chloride concentration in groundwater is the most commonly used indicator of saltwater intrusion in coastal aquifers. Saltwater intrusion decreases freshwater levels in an aquifer and can lead to abandonment of supply wells. Some prominent areas facing saltwater intrusion include the Mediterranean, the Yucatan Peninsula in Mexico, the Middle East, California, and the Atlantic Coast of the United States, especially in densely populated areas.

Inland areas also can experience saltwater intrusion. Many deeper aquifers in the central part of the United States contain saline waters. Saltwater intrusion has occurred along the Mississippi River alluvial plain in Arkansas where groundwater withdrawals for irrigation from an alluvial aquifer have caused upward movement of saline water from the underlying Sparta Aquifer (Morris et al. 1986). Withdrawing water from overlying aquifers increases the potential for saltwater intrusion

from below. In addition, road salts or deicing agents can impact shallow unconsolidated aquifers and surface waters near roads (Kunze et al. 2004).

Chloride was selected as a reliable reference or a chemically conservative constituent to characterize salinity in water samples. Unlike sodium, the ground does not contain or contribute to chloride values. Measuring sodium is not a reliable parameter because the ground retains sodium. Chloride values are preserved even when collecting data some distance away from the source. Chloride is least affected by travel from the source to points further downstream, thus it provides a true representation of contamination levels.

INTRODUCTION

Chloride ISEs use a potentiometric design to measure the total chloride ion concentration in water. Two drawbacks to using ISE chloride sensors are their propensity for measurement drift and their requirements for frequent recalibration to compensate for the drift. The most accurate sensor response is achieved by performing a three-point, bi-thermal calibration, which adds additional complications when performing field calibrations and measurements. Manufacturers recommend performing calibrations on a daily 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 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 and may add costs to long-term monitoring projects.

Alternatively, the use of an electrode-based conductivity cell can be used to infer or estimate 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 for long-term monitoring projects. The following section describes the development of a linear relationship between SC and chloride in OSIL Atlantic Seawater Standard.

METHODS

An OSIL Atlantic Seawater Standard sample (35.0 PSU) was diluted to 10 concentrations: 26.25, 17.5, 9.25, 4.63, 3.5, 2.7, 1.32, 0.64, 0.31, and 0.075 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 66 unique samples (11 concentrations at six temperature set points). These samples were allowed to stabilize for a minimum of one hour at the temperature set points. An Instrulab precision thermometer recorded true temperature values.

Chloride and temperature data was collected using an In-Situ® Inc. TROLL® 9500 water quality instrument with a chloride ISE (see Figure 1). The chloride ISE has a specified operating range of 0.35 to 35,500 mg/L with an accuracy of ±15%. Prior to sample analysis, the chloride ISE was calibrated using a three-point, bi-thermal calibration with NIST-traceable chloride standards (see www.in-situ.com to download the technical note, *Performing a Three-Point, Bi-Thermal Calibration for ISE Sensors*). Five replicate readings were taken at each of the 66 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 instruments (see Figure 2). SC and temperature data were collected. SC values were compared with the corresponding chloride values, and the relationship was evaluated for validity (see Figure 3).

Figure 1: TROLL® 9500 water quality instrument

Figure 2: Aqua TROLL® 200 sensor

To evaluate ISE and conductivity sensor drift, hourly readings were taken in a 17 PSU OSIL Atlantic Seawater Standard over a seven-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 instruments and a TROLL 9500 water quality instrument 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 (calibrated with NIST-traceable chloride standards) 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 3 shows the linear relationship between SC (µS/cm) and chloride concentration (mg/L) for samples having chloride concentrations up to 35,000 mg/L. Statistical analysis on the ratio of SC values (y) and chloride concentration (x) showed a strong linearity (r^2 = 0.9845). 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.
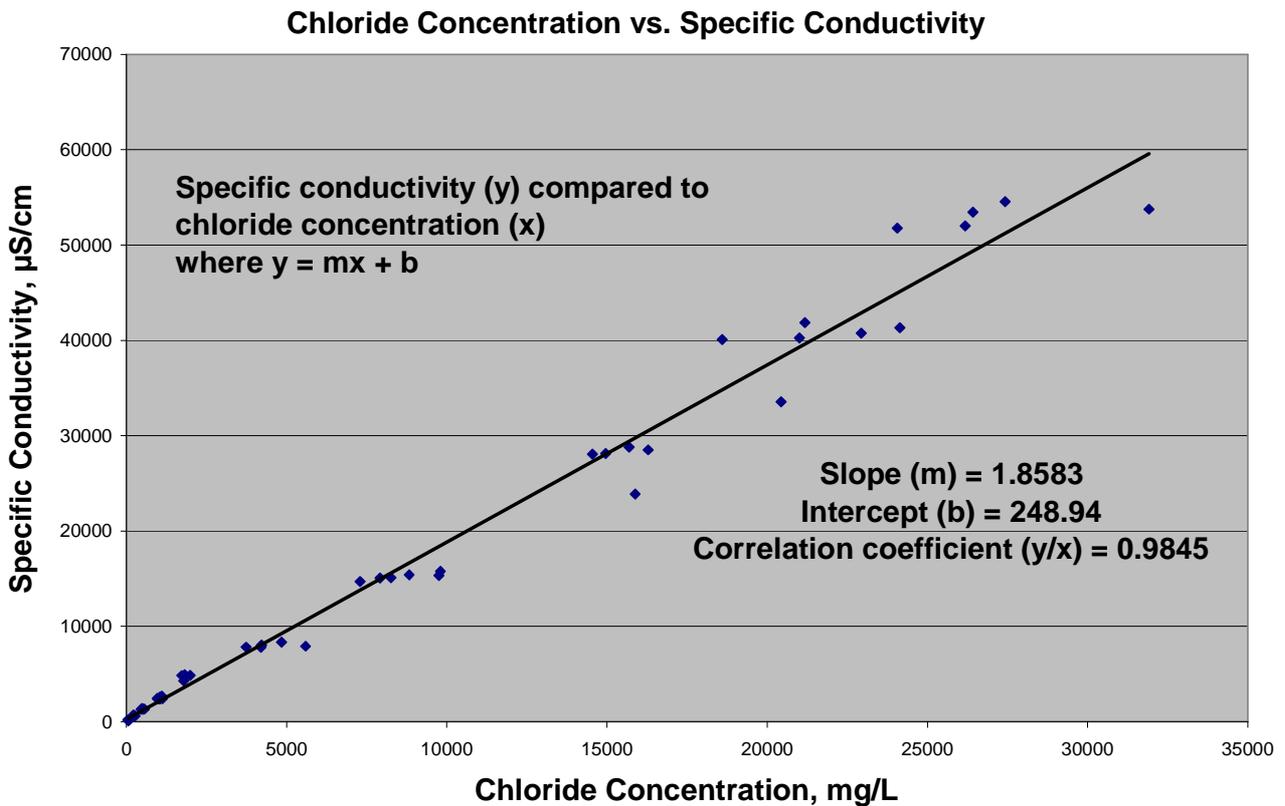
Chloride Concentration vs. Specific Conductivity

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

Slope (m) = 1.8583
Intercept (b) = 248.94
Correlation coefficient (y/x) = 0.9845

Figure 3: Relation of specific conductance to chloride concentration
for chloride concentrations up to 35,000 mg/L.

Figure 4 shows the linear relationship between SC (µS/cm) and chloride concentration (mg/L) for the samples of chloride concentrations up to 2,000 mg/L. Statistical analysis on the ratio of SC values and chloride concentration showed a strong linearity (r^2 = 0.9887).

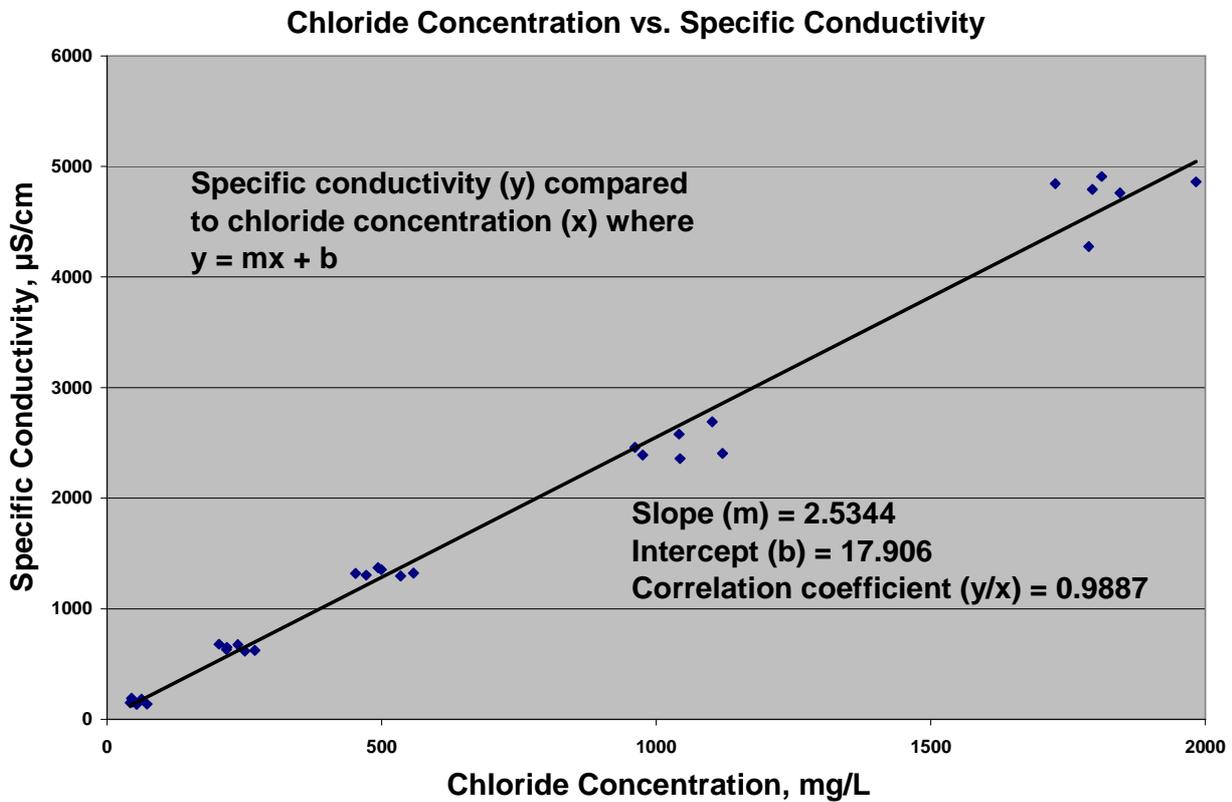## Chloride Concentration vs. Specific Conductivity

Figure 4: Relation of specific conductance to chloride concentration
for chloride concentrations up to 2,000 mg/L

To determine sensor drift, the absolute variation for the conductivity and chloride sensors was calculated and compared with true reference meter results over a seven-day period (see Figure 5). Chloride ISEs were calibrated using a three-point, bi-thermal calibration with NIST-traceable chloride standards (see www.in-situ.com to download the technical note, *Performing a Three-Point, Bi-Thermal Calibration for ISE Sensors*).

The conductivity sensor drift was 25 µS/cm or 0.08% 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 seven-day test. The chloride sensor drift was 1,036 mg/L or 8.4% of reading. The secondary chloride ISE reading confirmed the significant drift of the chloride sensor.
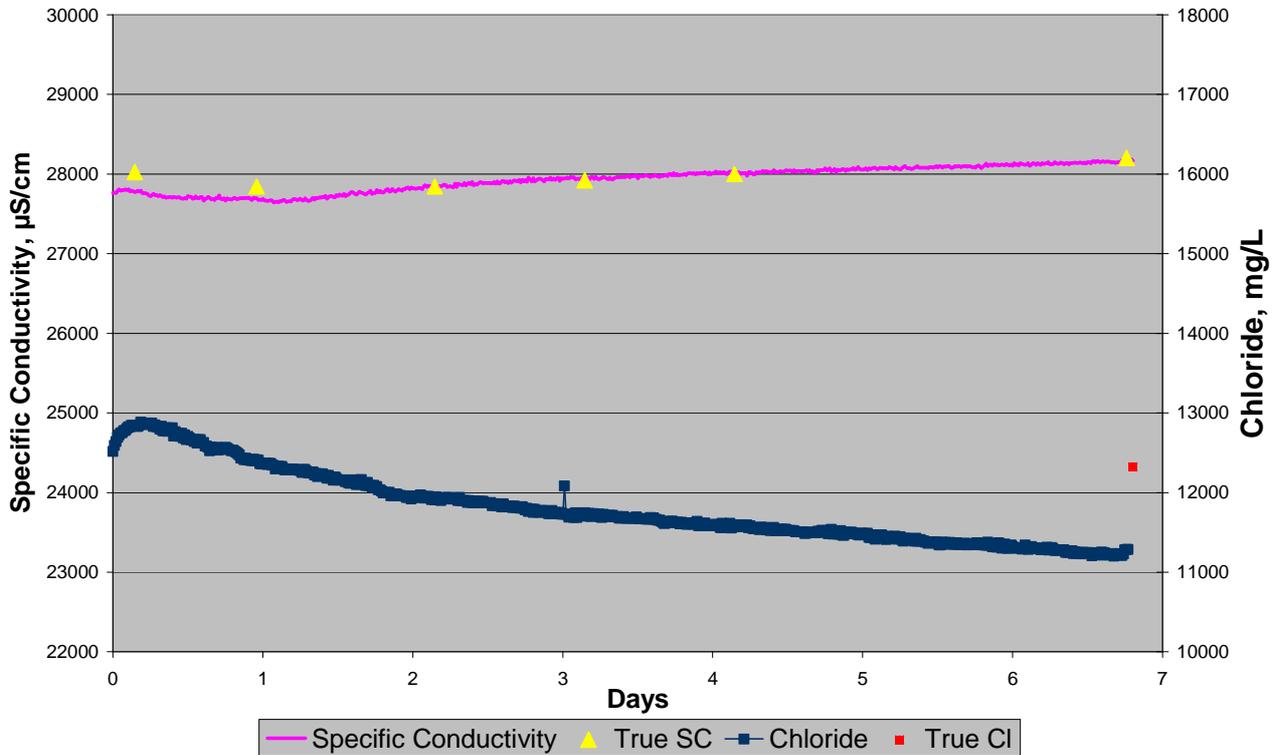
Sensor Drift Over One-Week Period

Figure 5: Comparison of chloride sensor drift and conductivity sensor drift.

The stability of the conductivity sensor and the strong linear correlation of SC and chloride indicate a clear advantage for using a conductivity sensor in estimating chloride over currently available methods. This is especially true for field deployment applications or long-term monitoring projects, in which sensor stability 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 long-term field deployments. The chloride ISE accuracy is ±15% of reading or 5 mg/L, whichever is greater. Conductivity sensor accuracy is ±0.5% of the reading.

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. Ion chromatography is useful when establishing initial correlation data for a specific sample matrix and when verifying chloride values, but laboratory testing of numerous samples can lead to high analytical costs.

To generate real-time field data that avoids using costly methods or methods sensitive to drift, fouling, and other instabilities, SC and chloride relationships can be developed. This 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.

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