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Office of Water Quality Water-Quality Information Note 2006.01

Subject: Field Methods— Specific conductance standards

Introduction

Conductivity standards supplied by the National Field Supply Service (NFSS) between July 2004 and November 2005 were sodium chloride (NaCl)-based rather than potassium chloride (KCl)-based like those supplied in past years. For conductivity meters that use automatic temperature compensation based on KCl standards, calibration with NaCl standards at temperatures less than 13 degrees Celsius (˚C) may result in a bias of 3 percent or more. The NFSS began to ship KCl standards on November 14, 2005. These standards are identified with brightly-colored starburst stickers. Field staff should determine whether any conductivity standards currently in use are NaCl solutions. These standards are labeled as such by the manufacturer, but an additional visual identifier might be prudent until current Water Science Center (WSC) inventories are replaced. Records affected by the use of NaCl standards may have their rating adjusted or be corrected at the option of individual projects or offices using information provided below.

Background

Standard reference materials for measurement of conductivity are defined by ASTM and Standard Methods as solutions of potassium chloride (KCl). The electrical conductivity of these standards and all ionic solutions varies with temperature, generally by about 2 percent per degree Celsius (˚C) in environmental waters. Most conductivity meters used in the field provide for automatic adjustment to the 25˚C reference temperature and assume calibration with KCl standards.

When the Ocala Lab was supplying conductivity standards to the field, they were made in-house using KCl. During the transition of the Field Supply Service from Ocala to the NWQL, NaCl conductivity standards were purchased from Ricca Chemical Company and supplied to the field beginning in July 2004. Labels on the original containers state that the standard was prepared with ACS Reagent Grade Sodium Chloride.

After the situation was noticed this past summer, the NFSS worked with their contracting group to return to KCl standards with their next order. The first of the 500 ųS/cm, KCl standards began shipping on November 14, 2005 and the 750ųS/cm, 250 ųS/cm, and 1,000 ųS/cm standards will begin shipping soon and others will follow as the stock arrives. Neon starburst labels with “KCl” emblazoned are being placed on the boxes and individual containers to alert customers of new KCl standards.

The temperature coefficients for KCl and NaCl solutions differ slightly, which may result in biased specific conductance measurements. For temperature-compensated meters calibrated with NaCl solutions at temperatures less than 13˚C under common procedures, the bias may be 3 percent or more. Published methodologies such as Standard Methods (APHA, 1998; Ricca Chemical Company, 2003) typically use the following relations between specific conductance at 25˚C and conductivity (uncorrected for temperature) for KCl and NaCl standards:

KCl standard $$k, \text{ųS/cm} = \frac{k_m}{1 + 0.0191(t\text{-}25)}$$

NaCl standard $$k, \text{ųS/cm} = \frac{k_m}{1 + 0.0212(t\text{-}25)}$$

where: k = specific conductance at 25˚C
k_m = conductivity measured at t˚C
t = temperature (˚C)

These are the temperature compensation equations used by many meter manufacturers. In reality, the temperature coefficient is itself temperature dependent, so a quadratic equation would provide a closer fit for temperatures far from the reference temperature (Arnerich, written communication, 2005).

The attached Excel spreadsheet shows the effects of using NaCl standards for calibrating meters that use KCl-based equations to estimate specific conductance at 25˚C. The conductivities of both solutions for a range of temperatures are computed from the value of a standard (uS/cm at 25˚C) entered in the gray box in row 5. For example, a KCl standard of 500 ųS/cm at 25˚C has a conductivity of 357 ųS/cm at 10˚C, and a NaCl standard of 500 ųS/cm at 25˚C has a conductivity of 341 ųS/cm at 10˚C. If you calibrate a meter to a single point using this NaCl standard at 10˚C and the meter's temperature compensation algorithm assumes you used KCl, you have introduced a bias of +16 ųS/cm.

The general procedure for calibrating conductivity meters (National Field Manual (NFM), Chapter 6.3) requires calibration to a single conductivity standard near the conductivity of the environmental sample, followed by a check measurement of a different conductivity standard. If both conductivity standards contained NaCl, the check measurement would be in good agreement, but the environmental measurements would still be biased. Even if one standard were NaCl and the other KCl, the check measurement might be within the required 3 percent if the calibration temperature were between 13˚C and 40˚C.

Recommended Action

Field staff should promptly determine whether any conductivity standards currently in use are NaCl solutions. Such standards should be clearly labeled and may be used in laboratory or other situations where bias will be minimal.

If NaCl standards are continued in use when calibrating a meter with temperature compensation based on KCl standards, the nominal standard value should be adjusted based on the temperature during calibration, as indicated in the final column of the spreadsheet. For example, at 10 °C a NaCl standard of 500 ųS/cm is equivalent to a KCl standard of 478 ųS/cm. Therefore, the nominal 500 ųS/cm NaCl standard could be used at 10 ˚C by setting the meter to 478 ųS/cm. Alternatively, if a WSC decides that potential bias of 3 percent or less, for example, is acceptable in their operations, the NaCl standards could be used without adjustment for single-point calibrations between 13 and 40˚C. Field notes should clearly indicate the standards and procedures used.

Correction of records, including shifting of continuous monitor data, is at the discretion of individual projects and/or offices. Correcting for biased measurements requires knowledge of the conductivity standard that was used, the calibration temperature, and the algorithm for temperature compensation built into the meter. If the field notes do not identify the standard that was used, it will be difficult to make corrections with confidence, particularly because both KCl and NaCl standards were probably available simultaneously in many offices. Field staff should consult the appropriate product manual to verify the algorithm used for temperature compensation in a particular meter. Applying a percentage change is most appropriate for continuous monitor records. A fixed correction may be used for discrete measurements.

Alternatively or additionally, continuous monitor records may be rated appropriately to reflect the impact of the use of NaCl standards on the accuracy of the record. As noted above, the correction depends on the temperature at which the meter was calibrated, not the temperature of the environmental water when measured. It is incorrect, for example, to apply the correction factors shown in the spreadsheet using the individual temperatures recorded by a continuous temperature-conductivity monitor.

Please contact the Regional Water-Quality Specialists to discuss situations not addressed by this memorandum.

References

American Public Health Association (APHA) and others, 1998, Conductivity, part 2510 *in* Standard Methods for the examination of water and wastewater, 20th edition.

Arnerich, Tony, In-Situ Inc., December 1, 2005, written communication.

Ricca Chemical Company, 2003, Conductivity (Specific Conductance): Technical reference document 18, revision 2, http://www.riccachemical.com/techsupp/docs/trd18.pdf

Wu, Y. C., and Koch, W. F., 1991, Absolute determination of electrolytic conductivity for primary standard KCl solutions from 0 to 50°C: Journal of Solution Chemistry, Vol. 20, No. 4, Pages 391 – 401.

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