

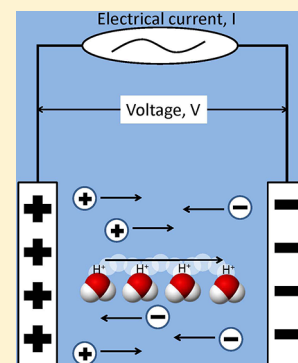
New Method for Electrical Conductivity Temperature Compensation

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Supporting Information

ABSTRACT: Electrical conductivity (κ) measurements of natural waters are typically referenced to 25 °C (κ_{25}) using standard temperature compensation factors (α). For acidic waters (pH < 4), this can result in a large κ_{25} error ($\delta\kappa_{25}$). The more the sample temperature departs from 25 °C, the larger the potential $\delta\kappa_{25}$. For pH < 4, the hydrogen ion transport number becomes substantial and its mode of transport is different from most other ions resulting in a different α . A new method for determining α as a function of pH and temperature is presented. Samples with varying amounts of H₂SO₄ and NaCl were used to develop the new α , which was then applied to 65 natural water samples including acid mine waters, geothermal waters, seawater, and stream waters. For each sample, the κ and pH were measured at several temperatures from 5 to 90 °C and κ_{25} was calculated. The $\delta\kappa_{25}$ ranged from −11 to 9% for the new method as compared to −42 to 25% and −53 to 27% for the constant α (0.019) and ISO-7888 methods, respectively. The new method for determining α is a substantial improvement for acidic waters and performs as well as or better than the standard methods for circumneutral waters.



INTRODUCTION

Modern conductivity meters allow rapid and straightforward measurements to be made in the field and laboratory, and as a result electrical conductivity (κ) is a commonly measured water quality parameter. Measurements of κ have been widely used by researchers to determine salinity,¹ ionic strength,² major solute concentrations,^{3,4} and total dissolved solids concentrations^{5,6} of natural waters. In addition, electrical conductivity is frequently used to monitor the water quality at stream sites⁷ and the effluent from industrial sites⁸ and wastewater treatment facilities.⁹ More recently, conductivity has been used to assess the downstream effects of mountaintop mining and valley fills on macroinvertebrates and fish,^{10,11} and it is now used as a benchmark to protect aquatic life in the Appalachian Region.¹² Conductivity is also used to monitor geothermal solute flux in three major rivers in Yellowstone National Park.¹³

In aqueous solutions, κ is the capacity of water to conduct an electric current and is dependent on the movement of ions through water. Electrical conductivity is a collective measure of dissolved ions¹⁴ and can be calculated as the sum of the products of the ion concentrations and their ionic conductivities:

$$\kappa = \sum \lambda_i C_i \quad (1)$$

where λ_i is the ionic conductivity and C_i is the concentration (often as normality) of the i th ion.^{15–17} The ionic conductivity (S·cm²/equiv), which is a function of temperature and ionic strength, is the electrical conductivity of the i th ion normalized to its concentration.¹⁸

Depending on which electrolytes are present, κ increases by about 1–3% per °C.¹⁹ Therefore, conductivity measurements are referenced to a standard temperature, typically 25 °C (κ_{25}), so that meaningful comparisons of κ can be made.^{20,21} While it

may be more accurate to measure the conductivity at the reference temperature, for many applications, including in situ measurements of natural waters, temperature control is impractical or conductivity is required to be measured in the field at ambient temperature.²⁰ Furthermore, temperature adjustment may cause precipitation of some electrolytes, equilibrium shifts changing the distribution of dissolved species, and changes in the degree of hydration of some electrolytes, all of which may affect κ_{25} . There are several empirical equations that predict the temperature dependence of κ ,²² and the following equation is used by several conductivity meter manufacturers and researchers to determine κ_{25} :

$$\kappa_{25} = \frac{\kappa}{1 + \alpha(t - 25^\circ\text{C})} \quad (2)$$

where κ is the electrical conductivity at the solution temperature, α is the temperature compensation factor, and t is the measured temperature in °C.^{16,21–23} The error arising from eq 2 when applied to natural waters is not typically known.¹⁶ While κ can be determined with great accuracy, κ_{25} is subject to much greater uncertainty because α is not the same for all natural waters.^{23–25} Many conductivity meters designed for field use have a programmed α algorithm and automatically report κ_{25} .²¹ Commercially available field conductivity meters typically use either a constant α (typically 0.019 to 0.020 per °C) or a nonconstant α that often follows the ISO 7888²¹ guidelines. While these commonly used α work well for circumneutral waters, the magnitude of the κ_{25} errors for acidic waters is largely unrecognized by researchers. Figure 1 shows

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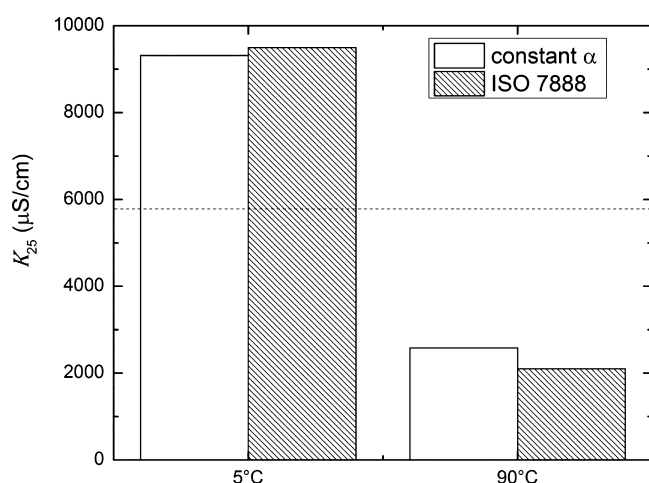


Figure 1. Calculated κ_{25} using a constant (0.019) and ISO 7888²¹ α for a 0.00944 m H_2SO_4 solution reported by McCleskey.²⁶ The dashed line is the κ of the solution measured at 25 °C.

the κ_{25} calculated using a constant (0.019) and ISO 7888²¹ α for a 0.00944 m H_2SO_4 solution reported by McCleskey.²⁶ The κ_{25} errors ($\delta\kappa_{25}$) using either α are greater than $\pm 55\%$ at 5 and 90 °C. As an example of the error that can be introduced using the ISO 7888²¹ method for natural waters, the field-measured κ_{25} was 8300 $\mu\text{S}/\text{cm}$ at 74 °C and the laboratory-measured κ_{25} was 14 700 $\mu\text{S}/\text{cm}$ at 25 °C for an acid-sulfate hot spring sample from Yellowstone (pH 1.45). Furthermore, the α utilized is frequently not reported by researchers.

The electrical conductivity of an electrolyte solution increases with temperature from 0 to 100 °C because decreasing viscosity at higher temperatures causes an increase in ion mobility and reduces the frictional drag according to Stoke's law.²⁷ Viscosity decreases because at higher temperature the greater average kinetic energy of the molecules more easily overcomes the attractive forces between molecules.²⁸ For many ions, the fractional increase in electrical conductivity with increasing temperature is equal to the fractional decrease in the viscosity of water.²⁹ This phenomenon, which is obeyed by many ions, follows Walden's rule¹⁹

$$\eta\lambda_0 \approx \text{constant} \quad (3)$$

where η is dynamic viscosity ($\text{N}\cdot\text{s}/\text{m}^2$) and λ_0 is the limiting ionic conductivity. However, the mode of transport of the H^+ is different from that of most other ions.²⁷ The H^+ ions migrate by what has been termed a "jump" or "transfer" of a proton from one water molecule to the next as H_3O^+ ,¹⁹ whereas the other ions move through the solution as individual entities surrounded by waters of hydration. Therefore, not only is the temperature compensation factor lower, but the ionic conductivity of H^+ is about 5 times larger than that of most other ions.¹⁹ The OH^- has a similar mode of transport as the H^+ ; however, its effects on α are not considered here because (1) λ_{OH^-} is about half that of λ_{H^+} and thus OH^- has less of an effect on κ and (2) there are relatively few natural waters with pH > 12. However, researchers studying basic waters should carefully check electrical conductivity measurements by measuring κ at 25 °C.

The existing temperature compensation factors for natural waters do not account for the unique mobility of H^+ . Consequently, the κ_{25} reported for natural waters with a pH < 4 often have large errors. Furthermore, the uncertainty increases as the temperature departs from 25 °C. Low-pH

waters generated from acid rock and geothermal sources are particularly susceptible to having erroneous κ_{25} reported. The low-pH waters from acid rock and geothermal sources are primarily derived from the oxidation of pyrite and sulfur, respectively, which generates sulfuric acid.

The κ_{25} is a frequently measured water-quality parameter, but the $\delta\kappa_{25}$ for acidic waters can be excessively large using existing α . Because many waters of environmental concern are acidic (i.e., acid mine and geothermal waters), a method that can be used to accurately predict κ_{25} at pH values as low as 0.5 and temperatures of 0–100 °C is essential. In this paper a new electrical conductivity temperature compensation factor is proposed that is applicable for acidic waters and also works well for most natural waters up to pH 11. The new temperature compensation factor can be utilized by multimeters that measure pH, temperature, and κ or it can be calculated after these measurements are made and used to calculate κ_{25} .

■ EXPERIMENTAL SECTION

Field and Laboratory Measurements. The κ of laboratory solutions and natural waters was determined by using commercially available conductivity meters and probes, and the following equation:

$$\kappa = K_{\text{cell}}G \quad (4)$$

where K_{cell} is the conductivity cell constant (in cm^{-1}) and G is the conductance (in S). The K_{cell} is the ratio of the distance between two plates (d) and their area (A). Laboratory κ measurements were made with a benchtop conductivity meter (YSI, Inc., model 3200) equipped with a dip-style conductivity cell having a cell constant of 1.0 cm^{-1} (YSI, Inc., model 3253). Field κ measurements were made using a hand-held conductivity meter (WTW 3300i) with a probe having a cell constant of 0.475 cm^{-1} and a temperature sensor. The K_{cell} for each conductivity cell was determined using eq 4 and KCl solutions of known conductivity.³⁰ For laboratory temperature measurements, a digital thermometer (VWR International, LLC) with a resolution of 0.001 °C and an uncertainty of ± 0.01 °C between 0 and 100 °C was used for all temperature measurements. The thermometer conforms to the International Temperature Standard (ITS-90) and was calibrated by the manufacturer to standards provided by NIST. A refrigerating/heating water bath circulator (Thermo Scientific NESLAB, model RTE-7) was used to control the temperature of all solutions measured in the laboratory. The temperature stability of the water bath, reported by the manufacturer, was ± 0.01 °C. The electrolyte solution was allowed to thermally equilibrate with the water bath before its conductance was measured.

Measurement solutions were placed in 50-mL high-density polyethylene (HDPE) vessels containing the conductivity and temperature probe. The measurement vessels and the conductivity probes were cleaned by soaking in HCl (0.6 M) for at least 24 h and rinsing three times with deionized water (18 M Ω ·cm). The lid containing the probes was tightly sealed to minimize evaporation.

Forty solutions were prepared in the laboratory containing various concentrations and mixtures of H_2SO_4 (0, 0.0001, 0.0005, 0.001, 0.005, 0.01, 0.05, 0.1, and 0.2 M) and NaCl (0, 0.001, 0.01, 0.1, and 0.5 M). These solutions were used to develop temperature compensation factors by measuring κ from 5 to 90 °C. The H_2SO_4 concentration was determined by Gran titration using standardized NaOH,³¹ and the NaCl was gravimetrically prepared (Sartorius R160P analytical and

GP5202 5 kg top-loading balances). The water used in all preparations was passed through a deionizing system (18 M Ω ·cm). The deionized water used in all preparations was allowed to equilibrate with atmospheric CO₂ for several days before use.

In addition to the laboratory solutions, the new temperature compensation method was applied to 65 natural water samples (Table 1). Twenty-one of the samples were acid rock/mine

Table 1. Ranges of pH and Electrical Conductivity (κ) and the Maximum Solute Concentration in the 65 Natural Waters Studied

field-measured properties	
pH	0.88 – 8.71
κ_{25} (μ S/cm)	69 – 76200
maximum solute concentration (mg/L)	
Ca	480
Mg	1200
Na	10000
K	410
HCO ₃	340
SO ₄	55000
Cl	18000
SiO ₂	670
NH ₄	27
Al	780
Cu	200
Fe(T)	17000
Fe(II)	17000
Mn	45

waters (AMW). These samples were collected from Questa, NM, Summitville, CO, Iron Mountain, CA, and Handcart Gulch, CO. For the AMW samples, the pH ranged from 0.88 to 3.8, the κ_{25} ranged from 460 to 76 200 μ S/cm, and the Fe concentration ranged from 0.05 to 17 000 mg/L. Because a visible Fe precipitate formed in several of the samples above about 50 °C, laboratory measurements were limited to 5, 10, 25, 35, and 45 °C. Furthermore, 47.1 °C was the highest underground temperature found at Iron Mountain, which has the lowest known pH (−3.6) of any water in the environment.³² Twenty-four samples were collected from acidic geothermal sources in Yellowstone National Park. The pH of this group ranged from 1.3 to 4.8 and the κ_{25} ranged from 1100 to 23 000 μ S/cm. The remaining twenty samples were circumneutral pH. They were collected from rivers and springs in Yellowstone, WY, several rivers in CO, and seawater from San Diego, CA. The pH of this group ranged from 6.8 to 8.7 and the κ_{25} ranged from 69 to 50 800 μ S/cm.

Measurements of pH, both in the field and laboratory, were made with an Orion 3 Star pH meter with an Orion Ross combination electrode and temperature probe. The temperature probe, pH electrode, and calibration buffers were equilibrated to sample temperature prior to calibration and measurement. The system was calibrated using at least two bracketing standard buffers (chosen from among 1.68, 4.01, 7.00, or 10.00) corrected to their values at the sample temperature. After calibration, the pH electrode was placed in the sample water and monitored until no change in temperature (± 0.1 °C) or pH (± 0.01 standard unit) was detected for at least 30 s. For laboratory solutions with pH < 1.7, the pH was calculated by charge balance using the geochemical computer program PHREEQCI.^{33,34}

Temperature Compensation Factor. Since κ is the sum of the products of the ion concentrations and ionic conductivities (eq 1), the solutions' α should be equal to a weighted average of each ion's α . Except for H⁺, most ions have similar α because their mobility is dependent on the solution's viscosity. Because the H⁺ ion migrates via a proton jump from one water molecule to the next as H₃O⁺ and its α is not as dependent on the viscosity,¹⁹ the following α was developed in this study to be used in combination with eq 2 to calculate κ_{25} :

$$\alpha = T_H \alpha_H + T_* \alpha_* \quad (5)$$

where T_H is the H⁺ transport number, α_H is the H⁺ temperature compensation factor, T_* is the sum of all transport numbers excluding H⁺ (i.e., $T_* = 1 - T_H$), and α_* is a temperature compensation factor representative of all ions except H⁺. The transport number (T) is the relative contribution of a given ion to the overall electrical conductivity and is defined as the

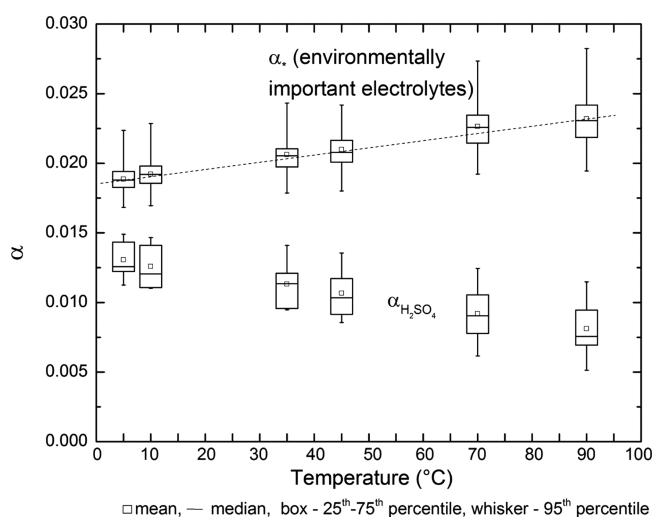


Figure 2. Temperature compensation factors for environmentally important electrolytes (α_*) and H_2SO_4 ($\alpha_{\text{H}_2\text{SO}_4}$). The dashed line corresponds to eq 10.

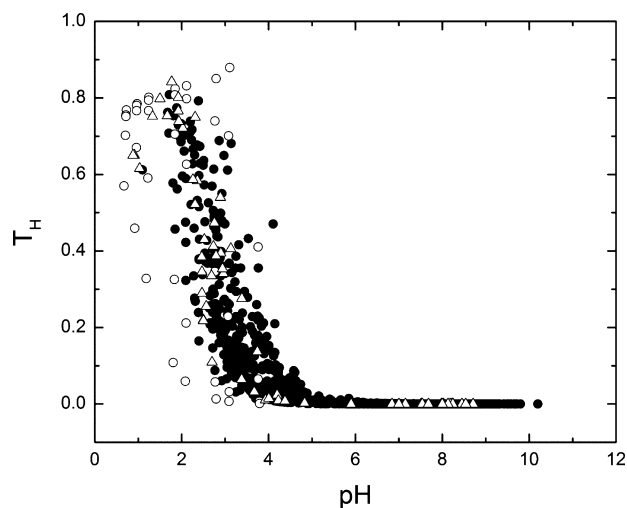


Figure 3. H⁺ transport numbers (T_H) for 1593 natural water samples reported by McCleskey et al.¹⁵ (solid circles), 40 laboratory solutions containing various concentrations and mixtures of H_2SO_4 and NaCl (open circles), and 65 natural water samples studied in this investigation (open triangles).

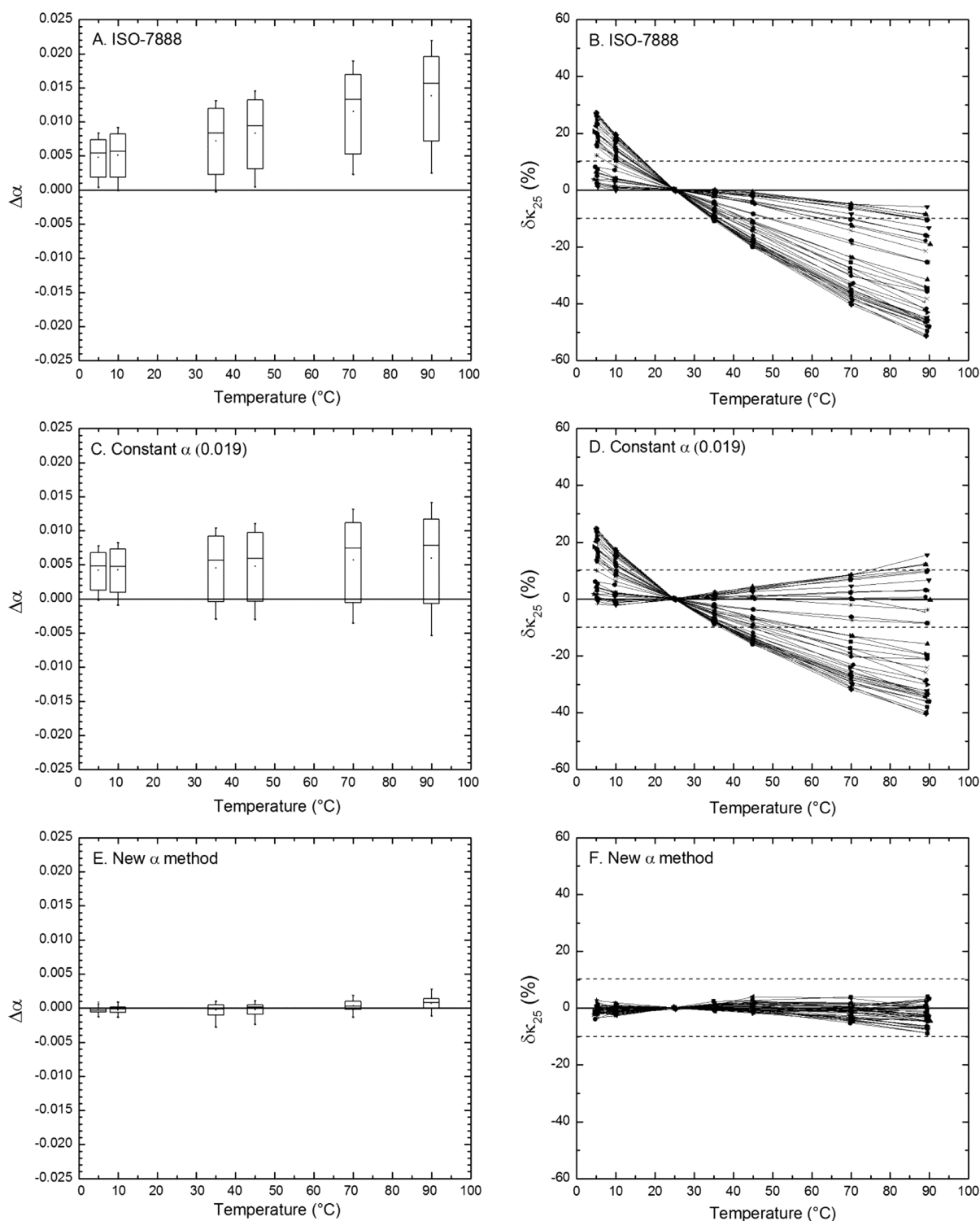


Figure 4. Values of $\Delta\alpha$ and the resulting $\delta\kappa_{25}$ for the 40 laboratory solutions determined using (A and B) the ISO-7888²¹ method, (C and D) a constant α (0.019), and (E and F) the new α method. The dashed lines (B, D, and F) are at $\pm 10\%$ for reference.

fraction of the current carried by a given ionic species.¹⁹ Therefore, the transport numbers of all ions in solution sum to unity. The transport number of individual ions (T_i) can be determined in natural waters using:

$$T_i = \frac{\lambda_i C_i}{\sum_{i=1}^n \lambda_i C_i} = \frac{\kappa_i}{\kappa} \quad (6)$$

where κ_i is the conductivity of the i th ion.

To determine α (eq 5), first measure the solution's κ , temperature (t), and pH. Then determine κ_H :

$$\kappa_H = 10^{(1.51 \times 10^{-4} t - 1.01) \text{pH} + (-3.10 \times 10^{-5} t^2 + 6.65 \times 10^{-3} t + 5.44)} \quad (7)$$

where t is temperature in °C. Once κ_H is determined, calculate T_H (as T_i) using eq 6 and the measured κ . The H^+ temperature compensation factor (α_H) can be determined using the following equations.

For $\text{pH} > 2.1$:

$$\alpha_{\text{H}} = (5.70 \times 10^{-5} \text{pH} - 2.63 \times 10^{-4})t + (8.73 \times 10^{-4} \text{pH} + 1.14 \times 10^{-2}) \quad (8)$$

For $\text{pH} < 2.1$:

$$\alpha_{\text{H}} = (-5.53 \times 10^{-5} \text{pH} - 3.27 \times 10^{-5})t + (3.40 \times 10^{-3} \text{pH}^2 - 7.04 \times 10^{-3} \text{pH} + 1.36 \times 10^{-2}) \quad (9)$$

Finally, determine α_* :

$$\alpha_* = (5.37 \times 10^{-5}t) + (1.85 \times 10^{-2}) \quad (10)$$

and then determine κ_{25} from eq 2.

It is important to note, that for $\text{pH} > 5$, $\alpha_* \approx \alpha$ because $T_{\text{H}} \approx 0$. A spreadsheet with example calculations of κ_{H} , T_{H} , T_* , α_{H} , α_* , α , and κ_{25} are provided in the Supporting Information (SI).

RESULTS AND DISCUSSION

Method Development and Temperature Compensation of Laboratory Solutions. The forty laboratory solutions containing various concentrations and mixtures of H_2SO_4 and NaCl along with the λ_{H} presented by McCleskey et al.¹⁵ were used to develop eqs 7–9. Using conductivity data reported by McCleskey,²⁶ α_* (Figure 2) was determined at 5, 10, 25, 35, 45, 70, and 90 °C for many important electrolytes found in natural waters (KCl , NaCl , NH_4Cl , CaCl_2 , MgCl_2 , Na_2SO_4 , K_2SO_4 , KHCO_3 , K_2CO_3 , NaHCO_3 , KF , KNO_3). The median α_* at each temperature was used to determine eq 10. Besides viscosity, the degree of hydration and equilibrium constants are affected by temperature, which accounts for some of the variation in α_* . The α is also shown for H_2SO_4 solutions (0.0001–0.5 M),²⁶ which are lower than α_* for all temperatures (Figure 2).

The T_{H} for 1593 natural water samples including acid mine waters, geothermal waters, seawater, dilute mountain waters, and river water affected by municipal wastewater reported by McCleskey et al.¹⁵ are shown in Figure 3. For samples with $\text{pH} < 4$, the T_{H} becomes substantial (> 0.1) for many natural water samples. The largest T_{H} for this sample set was 0.81 for a sample with a pH 1.8. The T_{H} values for the 40 laboratory solutions and the 65 natural waters used in this study are also shown in Figure 3. The H^+ has a large effect on κ for acidic waters and its unique temperature compensation needs to be accounted for. However, for waters with $\text{pH} > 5$ the $T_{\text{H}} \approx 0$ and α can be determined using only eq 10.

Figure 4 shows plots of $\Delta\alpha$ ($\Delta\alpha = \alpha - \alpha_{\text{m}}$) determined using the ISO-7888²¹ method, a constant α (0.019), and the new α method (eq 5) for the 40 laboratory solutions studied. The measured temperature compensation factor (α_{m}) was determined at each temperature (5, 10, 25, 35, 45, 70, and 90 °C) using the following equation by rearranging eq 2:

$$\alpha_{\text{m}} = \frac{\kappa - \kappa_{25\text{m}}}{\kappa_{25\text{m}}(t - 25^\circ\text{C})} \quad (11)$$

where $\kappa_{25\text{m}}$ is the electrical conductivity of the solution measured at 25 °C.

The new method better predicts the α than either of the commonly used approaches. Thus, the κ_{25} determined using the new method is a substantial improvement over the κ_{25} found with commonly used α . The error ($\delta\kappa_{25}$) between the

calculated (κ_{25}) and measured ($\kappa_{25\text{m}}$) electrical conductivity was determined using the following equation:

$$\delta\kappa_{25}(\%) = \frac{\kappa_{25} - \kappa_{25\text{m}}}{\kappa_{25\text{m}}} \times 100 \quad (12)$$

The difference between κ_{25} and $\kappa_{25\text{m}}$ may not always be zero because temperature adjustment to 25 °C may cause precipitation of some electrolytes, equilibrium shifts which may change the distribution of dissolved species, and changes in the degree of hydration of some electrolytes. However, $\delta\kappa_{25}$ provides a reasonable estimate of the error resulting from temperature compensation. The $\delta\kappa_{25}$ for the 40 laboratory solutions using the new method ranged from −8.8 to 4% (Figure 4), which is a much narrower range compared to the constant α and ISO-7888²¹ approaches. The $\delta\kappa_{25}$ for the ISO-7888²¹ method ranged from −52 to 27% and $\delta\kappa_{25}$ for the constant α (0.019) ranged from −41 to 25%. For the two commonly used α approaches, the largest errors were for the samples with the largest T_{H} . Furthermore, the $\delta\kappa_{25}$ is greater than $\pm 10\%$ for $t < 15$ °C and $t > 35$ °C.

To correct κ_{25} measurements that were made with a conductivity meter that incorporates the commonly used α , the κ must be determined using eq 2. The α utilized is likely in the instrument manual or can be determined using eq 11 and standard conductivity solutions.³⁰ To determine α using eq 11, $\kappa_{25\text{m}}$ is the electrical conductivity of the standard solution at 25 °C. For nonconstant α , κ must be determined at several temperatures and the $\alpha - t$ correlation determined.

Temperature Compensation of Natural Waters. The goal of this study was to develop an electrical conductivity temperature compensation technique that would accurately predict κ_{25} of a wide range of natural waters, including low-pH waters. To confirm that the new α method accurately predicts κ_{25} , 65 natural water samples including acid mine waters (21 samples), geothermal waters (24 samples), and circumneutral pH waters (20 samples) were tested. The range of electrical conductivity, pH, and the maximum solute concentration for the major ions for the natural waters tested are shown in Table 1. The samples have a wide range of pH (0.88–8.71) and solute concentrations. Figure 5 is a ternary plot showing

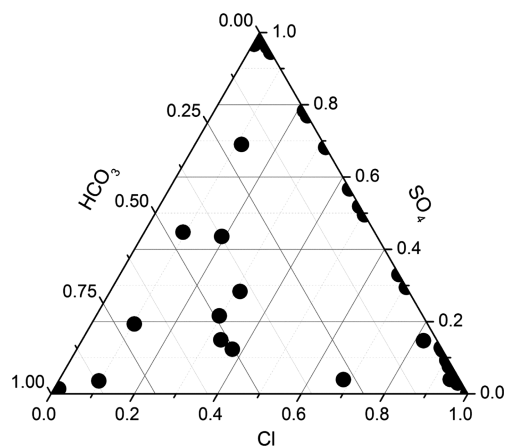


Figure 5. Ternary plot showing the equivalent fraction of HCO_3^- , Cl , and SO_4 for the 65 natural waters tested.

equivalent fractions of Cl , HCO_3^- , and SO_4 for the waters tested. The major ion composition encompasses several water types, thus providing a good test of the new α .

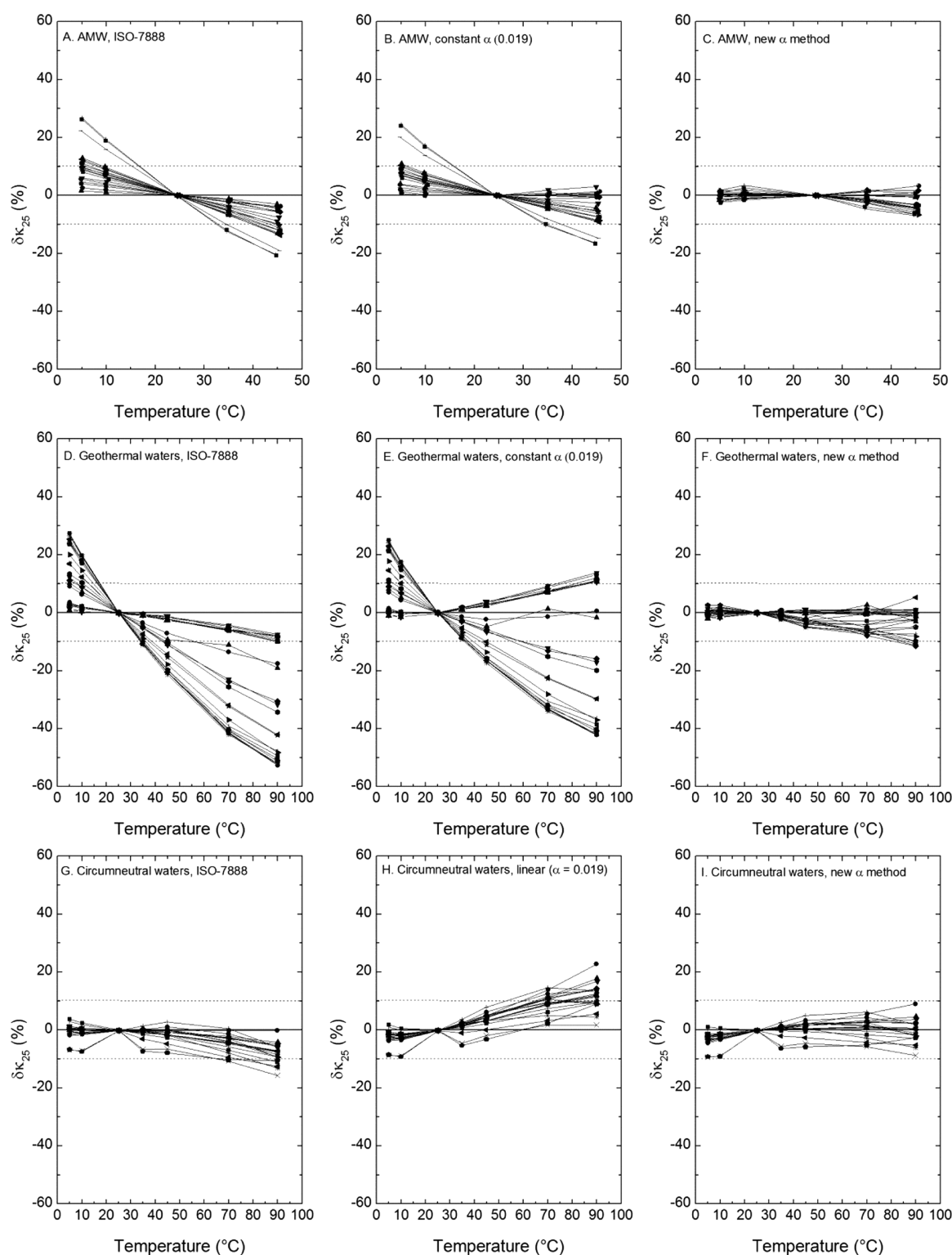


Figure 6. Values of $\delta\kappa_{25}$ determined for the 65 natural waters tested using the ISO-7888²¹ method, the constant α (0.019), and the new α method are shown for (A–C) 21 acid mine waters (AMW), (D–F) 24 geothermal waters, and (G–I) 20 circumneutral pH waters.

The accuracy of calculated κ_{25} for the natural waters determined using the new α method was compared to the ISO-7888²¹ and constant α (0.019) methods. For the 21 acid mine waters tested (Figure 6A–C), the $\delta\kappa_{25}$ for the new method ranged from -8.4 to 3.5% (Figure 6C), which is a substantial improvement compared to the ISO-7888²¹ and constant α (0.019) methods. The $\delta\kappa_{25}$ for the ISO-7888²¹

method ranged from -21 to 27% (Figure 6A) and $\delta\kappa_{25}$ for the constant α ranged from -17 to 25% (Figure 6B). Note that the temperature of AMW could be close to $0\text{ }^{\circ}\text{C}$ during the winter, increasing the $\delta\kappa_{25}$ for the ISO-7888²¹ and constant α methods. For the 24 geothermal waters tested (Figure 6D–F), the $\delta\kappa_{25}$ for the new method ranged from -11 to 5.2% (Figure 6F), a substantial improvement over the common ISO-7888²¹ and

constant α methods. The $\delta\kappa_{25}$ for the ISO-7888²¹ method ranged from -53 to 27% (Figure 6D) and $\delta\kappa_{25}$ for the constant α ranged from -42 to 25% (Figure 6E). For the circumneutral pH waters (Figure 6G–I), the new method performed as well as or better than the other two methods. The $\delta\kappa_{25}$ for the new method ranged from -9.5 to 9% (Figure 6I) whereas for the ISO-7888²¹ method it ranged from -16 to 4% (Figure 6G) and $\delta\kappa_{25}$ for the constant α ranged from -9 to 23% (Figure 6H). Figure 7 contains box plots of the $\delta\kappa_{25}$ for the 65 natural waters

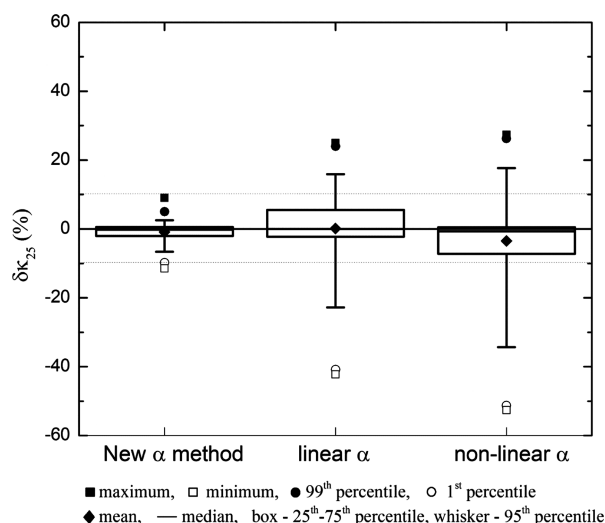


Figure 7. Box plots showing the electrical conductivity error ($\delta\kappa_{25}$) for the 65 natural water samples studied using the new α method, the constant α (0.019), and ISO-7888²¹ methods.

tested using the α methods compared here. For the 413 measurements, the $\delta\kappa_{25}$ (mean $\pm 1s$) for the new method was $-0.8 \pm 2.7\%$ whereas the ISO-7888²¹ was $-3.5 \pm 13.3\%$ and $\delta\kappa_{25}$ for the constant α was $0.1 \pm 11.2\%$.

Accurately predicting the κ_{25} for all natural waters is challenging because α is not the same for all waters, since temperature adjustment to 25°C may cause precipitation of some electrolytes, equilibrium shifts changing the distribution of dissolved species, and changes in the degree of hydration of some electrolytes. Consequently, a generalized approach for calculating κ_{25} may not work perfectly for all natural waters. Nonetheless, the new method accounts for the unique mobility of the H^+ , which has a large effect on α , and as a result is a more reliable method for determining κ_{25} for natural waters than the commonly used α methods.

■ ASSOCIATED CONTENT

Supporting Information

An Excel spreadsheet with example calculations. This information is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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