Available online at www.sciencedirect.com

SciVerse ScienceDirect

Geochimica et Cosmochimica Acta 77 (2012) 369–382

Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

A new method of calculating electrical conductivity with applications to natural waters

R. Blaine McCleskey [a,*], D. Kirk Nordstrom [a], Joseph N. Ryan [b], James W. Ball [a]

[a] *US Geological Survey, 3215 Marine St., Suite E. 127, Boulder, CO 80303, USA*

[b] *University of Colorado, 428 UCB, 1111 Engineering Drive, ECOT 441, Boulder, CO 80309-0428, USA*

Received 9 May 2011; accepted in revised form 13 October 2011; available online 21 October 2011

Abstract

A new method is presented for calculating the electrical conductivity of natural waters that is accurate over a large range of effective ionic strength (0.0004–0.7 mol kg^{-1}), temperature (0–95 °C), pH (1–10), and conductivity (30–70,000 $\mu S\ cm^{-1}$). The method incorporates a reliable set of equations to calculate the ionic molal conductivities of cations and anions (H^+, Li^+, Na^+, K^+, Cs^+, NH_4^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, F^-, Cl^-, Br^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}, NO_3^-, and OH^-), environmentally important trace metals (Al^{3+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, and Zn^{2+}), and ion pairs (HSO_4^-, $NaSO_4^-$, $NaCO_3^-$, and KSO_4^-). These equations are based on new electrical conductivity measurements for electrolytes found in a wide range of natural waters. In addition, the method is coupled to a geochemical speciation model that is used to calculate the speciated concentrations required for accurate conductivity calculations. The method was thoroughly tested by calculating the conductivities of 1593 natural water samples and the mean difference between the calculated and measured conductivities was −0.7 ± 5%. Many of the samples tested were selected to determine the limits of the method and include acid mine waters, geothermal waters, seawater, dilute mountain waters, and river water impacted by municipal waste water. Transport numbers were calculated and H^+, Na^+, Ca^{2+}, Mg^{2+}, NH_4^+, K^+, Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}, F^-, Al^{3+}, Fe^{2+}, NO_3^-, and HSO_4^- substantially contributed (>10%) to the conductivity of at least one of the samples. Conductivity imbalance in conjunction with charge imbalance can be used to identify whether a cation or an anion measurement is likely in error, thereby providing an additional quality assurance/quality control constraint on water analyses.
Published by Elsevier Ltd.

---

1. INTRODUCTION

Electrical conductivity is a water-quality property often measured when water samples are collected for chemical analyses. Modern instrumentation allows rapid, straightforward, and reliable measurements to be made in the field and laboratory. Electrical conductivity is often used to monitor the water quality of streams (NWIS, 2011) and effluent from industrial sites (Binkley et al., 2000) and wastewater treatment facilities (Prieto et al., 2001). Electrical conductivity measurements have been used to determine the salinity (Lewis, 1980), ionic strength (Lind, 1970), major solute concentrations (Pollak, 1954; McNeil and Cox, 2000), and total dissolved solids concentrations (Gustafson and Behrman, 1939; Lystrom et al., 1978) of natural waters.

In addition, several methods have been reported for calculating the conductivity of a natural water sample from its chemical composition (McNeal et al., 1970; Tanji and Biggar, 1972; Rossum, 1975; Marion and Babcock, 1976; Laxen, 1977; Miller et al., 1988; Talbot et al., 1990; Pawlowicz, 2008; Appelo, 2010; Visconti et al., 2010). There are also theoretical methods intended primarily for industrial applications (Anderko and Lencka, 1997; Wang et al., 2004). These theoretical methods have been successfully extended to concentrated aqueous solutions and may be well-suited for determining the conductivity of brines. However, empirical equations are typically used to

---

* Corresponding author. Tel.: +1 303 541 3079; fax: +1 303 541 3084.

E-mail address: rbmccles@usgs.gov (R.B. McCleskey).

0016-7037/$ - see front matter Published by Elsevier Ltd.
doi:10.1016/j.gca.2011.10.031

determine the conductivity in multi-component systems having low-to-medium concentrations typically studied in environmental research (Visconti et al., 2010).

The existing conductivity methods for natural waters have been limited by the lack of conductivity data in the literature for relevant electrolytes (Pawlowicz, 2008). For several important electrolytes, the literature conductivity data do not span the concentration and temperature range of natural waters. Consequently, existing methods are limited by the number of ions included and are only applicable to a limited range of pH, temperature, and ionic strength. Furthermore, many of the existing methods are subject to large uncertainties because either ion-pairing is not accounted for (McNeal et al., 1970; Tanji and Biggar, 1972; Laxen, 1977) or it is accounted for by using reduction factors based on conductivity (Miller et al., 1988) or by treating the system as a particular sum of salts, each of which has a unique dependence on the ionic strength (Pawlowicz, 2008). The method of Talbot et al. (1990) takes advantage of a geochemical speciation code, but the method is limited by the number of ions included and their estimation of ionic conductivities. Furthermore, several methods are only valid for solutions at 25 °C (Rossum, 1949; McNeal et al., 1970; Tanji and Biggar, 1972; Rossum, 1975; Marion and Babcock, 1976; Laxen, 1977; Miller et al., 1988).

Here we present a new method for calculating the electrical conductivities for a wide range of natural waters including dilute mountain waters, acid mine waters, geothermal waters, seawater, and river water affected by municipal wastewater. Our method incorporates new electrical conductivity measurements for electrolytes found in natural waters having total ionic strengths of up to 1 mol kg^{-1} and temperatures of 5–95 °C (McCleskey, 2011). The method uses speciated water analyses calculated with geochemical models, rather than total solute concentrations. Also, transport numbers for individual ions in natural waters and a quality control method that uses measured and calculated conductivities and charge imbalances to identify erroneous chemical analyses are presented.

2. CONDUCTIVITY CONVENTIONS

The electrical conductivity (κ) of a solution can be determined using a commercially available conductivity meter and probe using the following equation:

$$k = K_{cell} G \tag{1}$$

where K_{cell} is the conductivity cell constant and G is the conductance. The K_{cell} is the ratio of the distance between conductivity cell plates (d) to the area of the plates (A). The electrical conductivity of a solution depends on the ions that are present, their concentrations, and the solution temperature. The SI unit for electrical conductivity is siemens per centimeter (S cm^{-1}) (Mills et al., 1993).

Depending on which electrolytes are present, the electrical conductivity increases 1–3% per °C (Robinson and Stokes, 1965). For natural waters, electrical conductivity measurements typically are used to estimate the dissolved ion concentration (e.g., salinity, ionic strength, and total dissolved solids); therefore, electrical conductivity is typically reported at 25 °C (κ_{25}) because it removes the large effect of temperature (Radtke et al., 2005). The κ_{25} is calculated using the following equation:

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

where κ is the electrical conductivity at the solution temperature (T) in °C and α is the temperature compensation factor. Even though the electrical conductivity (κ) of a solution can be determined with great accuracy, the κ_{25} is subject to much greater uncertainty because it depends on a temperature compensation factor (α), which is not the same for all natural waters and instruments. Most conductivity meters designed for field use have a programmed temperature compensation algorithm and automatically report κ_{25}. Linear (0.019–0.020) and non-linear temperature compensation factors are commonly used by conductivity meters. By measuring the κ_{25} of a standard KCl solution at various temperatures, the temperature compensation factor (α) used by conductivity meters can be determined using Eq. (2) and the known κ for standard KCl solutions. Pratt et al. (2001) determined the κ for aqueous KCl standard solutions with molalities of 0.001, 0.1, and 1.0 mol kg^{-1} in the temperature range of 0–50 °C. Meaningful comparisons of calculated and measured κ_{25} require that the same α be used.

Many of the techniques used to interpret electrical conductivity measurements were introduced by Kohlrausch (1902). He developed the concept of equivalent conductivity, the law of the independent migration of ions, and the square-root law which has been widely used to determine the equivalent conductivity at infinite dilution. For binary-electrolyte solutions, the equivalent conductivity is the electrical conductivity of a solution normalized to the electrolyte concentration (eq L^{-1}) (Harned and Owen, 1958; Robinson and Stokes, 1965). In this study, molal conductivity (Λ) will be utilized rather than equivalent conductivity for three reasons: (1) molality is independent of temperature, (2) many geochemical programs (e.g., WATEQ4F and PHREEQCI) use molality to calculate the chemical speciation, and (3) the International Union of Pure and Applied Chemistry (IUPAC) recommends the use of equivalent conductivity be discontinued (Parsons, 1974). The molal conductivity (Λ) of electrolytes can be determined using the following equation:

$$\Lambda = \frac{\kappa}{m} \tag{3}$$

where m is molality (mol kg^{-1}).

The law of the independent migration of ions states that the equivalent conductivity of a strong electrolyte solution is equal to the sum of the contributions of its negative and positive ionic components (Robinson and Stokes, 1965). The molal conductivity of a strong electrolyte can be determined from its ionic components using the following equation:

$$\Lambda = n_+\lambda_+ + n_-\lambda_- \tag{4}$$

where λ is the ionic molal conductivity and n is a dimensionless number corresponding to the number of moles of the cation (+) and anion (−). Eq. (4) is only applicable for fully dissociated electrolytes. If the molal conductivity of the strong electrolyte solution (Λ) and one of the ionic molal conductivities (e.g., λ_+) are known, the other ionic molal conductivity can be determined by difference (e.g., λ_-).

Another important concept used to interpret electrical conductivity data is the transport number (t), which is the relative contribution of a given ion to the overall electrical conductivity. Thus, the transport numbers for all of the ions in a solution sum to unity. For a uni-univalent electrolyte solution, the transport number of an ion is equal to the mobility of the ion divided by the sum of mobilities of the two ions and is equal to the ratio of the ionic molal conductivity of the ion of interest (λ_i) to the molal conductivity (Λ) of the electrolyte solution:

$$t_i = \frac{\lambda_i}{\Lambda} \tag{5}$$

Independent methods can be used to determine the transport numbers of ions in simple solutions (Harned and Owen, 1958; Robinson and Stokes, 1965). By knowing the transport number (t_i) and molal conductivity (Λ) of the electrolyte solution, the ionic molal conductivity (λ_i) can be determined. For mixed electrolyte solutions, the following equation can be used to determine the transport numbers for the individual ions:

$$t_i = \frac{\lambda_i m_i}{\sum_{i=1}^{n} \lambda_i m_i} \tag{6}$$

Transport numbers in mixed electrolyte solutions are useful for identifying the ions that substantially contribute to the electrical conductivity and thus for interpreting the electrical conductivity.

The electrical conductivity (κ) of an aqueous solution can be calculated from its chemical composition using the following equation:

$$\kappa = \sum \lambda_i m_i \tag{7}$$

where λ_i is the ionic molal conductivity and m_i is the speciated molality (mol kg^{-1}) of the i^{th} ion. To determine the electrical conductivity using Eq. (7), the ionic molal conductivity and speciated ion concentration must be known for ions that significantly contribute to the electrical conductivity. The speciated ion concentrations can be calculated using geochemical speciation models.

3. METHODS

One of the objectives of this research was to develop a new method that can be used to reliably calculate the electrical conductivity of natural waters ranging in temperature from 0–95 °C and ionic strengths up to 1 mol kg^{-1}. Because electrical conductivity data in the literature are lacking for many electrolytes, the first step (1) was to measure the electrical conductivities (κ) of 34 electrolytes commonly found in natural waters from 5–90 °C and from 10^{-4}–1.0 mol kg^{-1}. These data, reported by McCleskey (2011), provide a better basis for determining ionic molal conductivities. The next step (2) was to determine the ionic molal conductivities (λ) for the ions found in natural waters at concentrations high enough to affect the electrical conductivity. Then (step 3) equations were developed as functions of temperature and ionic strength that can be used to calculate the ionic molal conductivities (λ). The geochemical speciation computer code WATEQ4F (Ball and Nordstrom, 1991) was modified (step 4) to compute electrical conductivity (κ), electrical conductivity corrected to 25 °C (κ_{25}), and conductivity imbalance ($\delta\kappa_{25}$). As a check of the method, calculated conductivities of the electrolytes reported by McCleskey (2011) were compared to measured values. This methodology was also used to calculate the conductivities of a wide range of natural waters including acid mine waters, geothermal waters, dilute mountain waters, seawater, and river water affected by municipal wastewater.

3.1. Ionic molal conductivities

Accurate electrical conductivity calculations using Eq. (7) depend on reliable calculations of the ionic molal conductivity (λ) at various temperatures and ionic strengths. The equation proposed by Lattey (1927) can be used to reliably predict the equivalent conductivities of electrolytes applicable to natural waters with temperatures ranging from 0–95 °C and ionic strengths up to 1 mol kg^{-1} (McCleskey, 2011). By substituting ionic strength (I) for concentration, Lattey's Equation also can be used to reliably calculate λ at various temperatures and ionic strengths:

$$\lambda = \lambda^{\circ}(T) - \frac{A(T)\mathrm{I}^{1/2}}{1 + B\mathrm{I}^{1/2}} \tag{8}$$

where λ° and A are functions of temperature (°C) and B is an empirical constant. Ionic strength, which is a measure of the concentration of all charged ions in solution, can be calculated using:

$$\mathrm{I} = 1/2 \sum m_i z_i^2 \tag{9}$$

where z_i is the charge of the i^{th} ion. Because electrical conductivity is a collective measure of dissolved ions (Hem, 1982), the incorporation of I into Eq. (8) is appropriate. Eq. (8) is a linear equation when plotted against $(\mathrm{I}^{1/2})(1 + B\mathrm{I}^{1/2})^{-1}$, and for dilute solutions it approaches the behavior of the square root law (Jones and Dole, 1930). The $[A(\mathrm{T})(\mathrm{I}^{1/2})(1 + \mathrm{BI}^{1/2})^{-1}]$ term in Eq. (8) accounts for relaxation and electrophoretic effects. The equations in Table 1 can be used to compute the ionic molal conductivity over a wide range of temperatures and molalities for 28 environmentally relevant ions. The ionic molal conductivities are plotted against $(\mathrm{I}^{1/2})(1 + \mathrm{BI}^{1/2})^{-1}$ in Figs. 1–4. The dashed lines are calculated using the equations in Table 1. The solid symbols are ionic molal conductivities determined from the data presented in McCleskey (2011). In addition, the calculated ionic molal conductivities at 0 °C were calculated for K and Cl and compared to literature values (NRC, 1929) to demonstrate that extrapolation below 5 °C is accurate. The R^2 values ranged from 0.923–1.000 for 174 of the 177 linear regressions suggesting that Eq. (8) can be used to accurately predict the ionic molal conductivity from 0–95 °C and ionic strength of up to

Table 1
Equations used to calculate individual ionic molal conductivities (mS kg cm^{-1} mol^{-1}) for the ions applicable to natural waters. [Eq. (8) parameters; T is temperature (°C)].

Ion	λ^0	A	B
K^+	$0.003046T^2 + 1.261T + 40.70$	$0.00535T^2 + 0.9316T + 22.59$	1.5
Na^+	$0.003763T^2 + 0.8770T + 26.23$	$0.00027T^2 + 1.141T + 32.07$	1.7
H^+	$-0.01414T^2 + 5.355T + 224.2$	$-0.00918T^2 + 1.842T + 39.23$	0.3
Li^+	$0.002628T^2 + 0.7079T + 19.20$	$0.00412T^2 + 0.4632T + 13.71$	0.2
Cs^+	$0.003453T^2 + 1.249T + 43.94$	$0.00646T^2 + 0.7023T + 21.79$	1.3
NH_4^+	$0.003341T^2 + 1.285T + 39.04$	$0.00132T^2 + 0.6070T + 11.19$	0.3
Ca^{2+}	$0.009645T^2 + 1.984T + 62.28$	$0.03174T^2 + 2.334T + 132.3$	2.8
Mg^{2+}	$0.01068T^2 + 1.695T + 57.16$	$0.02453T^2 + 1.915T + 80.50$	2.1
Ba^{2+}	$0.01059T^2 + 2.090T + 68.10$	$0.03127T^2 + 2.248T + 93.91$	1.9
Sr^{2+}	$0.006649T^2 + 2.069T + 61.63$	$0.00702T^2 + 0.9009T + 33.41$	0.1
SO_4^{2-}	$0.01037T^2 + 2.838T + 82.37$	$0.03324T^2 + 5.889T + 193.5$	2.6
Cl^-	$0.003817T^2 + 1.337T + 40.99$	$0.00613T^2 + 0.9469T + 22.01$	1.5
F^-	$0.002764T^2 + 1.087T + 26.66$	$0.00178T^2 + 0.6202T + 19.34$	0.5
Br^-	$0.000709T^2 + 1.477T + 40.91$	$0.00251T^2 + 0.5398T + 12.01$	0.1
CO_3^{2-}	$-0.000326T^2 + 2.998T + 64.03$	$-0.00181T^2 + 5.542T + 120.2$	2.3
HCO_3^-	$0.000614T^2 + 0.9048T + 21.14$	$-0.00503T^2 + 0.8957T + 10.97$	0.1
NO_3^-	$0.001925T^2 + 1.214T + 39.90$	$0.00118T^2 + 0.5045T + 23.31$	0.1
OH^-	$0.003396T^2 + 2.925T + 121.3$	$0.00933T^2 + 0.1086T + 35.90$	0.01
Al^{3+}	$0.02376T^2 + 3.227T + 90.24$	$0.06484T^2 + 5.149T + 76.79$	3.0
Cu^{2+}	$0.00818T^2 + 1.939T + 53.26$	$0.0292T^2 + 6.745T + 151.5$	8.0
Fe^{2+}	$0.009939T^2 + 1.878T + 54.80$	$0.03997T^2 + 3.217T + 164.5$	4.0
Fe^{3+}	$0.02077T^2 + 4.390T + 82.42$	$-0.09676T^2 + 20.76T - 22.18$	4.0
Mn^{2+}	$0.01275T^2 + 2.109T + 46.19$	$0.1071T^2 + 9.023T + 135.4$	7.6
Zn^{2+}	$0.01249T^2 + 1.912T + 48.20$	$0.08284T^2 + 5.188T + 75.73$	7.0
KSO_4^-	$-0.002439T^2 + 4.253T + 129.7$	$-0.01576T^2 + 6.210T + 146.8$	1.3
$NaSO_4^-$	$0.002309T^2 + 5.459T + 219.2$	$0.01454T^2 + 5.193T + 253.6$	0.5
HSO_4^-	$0.000927T^2 + 0.8337T + 29.56$	$0.02887T^2 + 0.8730T + 36.25$	7.0
$NaCO_3^-$	$0.00336T^2 + 3.845T + 89.51$	$0.00061T^2 + 6.387T + 141.7$	2.0

1 mol kg^{-1}. The three other R^2 values were 0.809, 0.879, and 0.884 for the Al^{3+} at 5 °C and Fe^{3+} at 5 and 10 °C linear regressions, respectively. Because it may be useful to incorporate additional ions, a detailed description of the algorithm used to derive the equations in Table 1 is presented in Electronic annex EA-1.

3.2. Conductivity method coupled to geochemical models

Chemical speciation affects the electrical conductivity of electrolyte solutions. Electrical conductivity is so sensitive to the presence of complexes that it has been used to determine numerous dissociation constants (Shedlovsky, 1938; Davies, 1962). Even though the effects of chemical speciation on electrical conductivity are well known, many methods used to calculate the conductivity ignore chemical speciation (McNeal et al., 1970; Tanji and Biggar, 1972; Laxen, 1977). One of the most significant improvements over most methods is the coupling of the electrical conductivity method presented here with the speciated chemistry calculated with geochemical models.

There are numerous geochemical speciation models that reliably calculate the distribution of chemical species in solutions. We chose to couple the electrical conductivity method to the U.S. Geological Survey geochemical speciation codes WATEQ4F (Ball and Nordstrom, 1991) and PHREEQCI (Parkhurst and Appelo, 1999; Charlton and Parkhurst, 2002), which share the same thermodynamic database and use the ion association model. The SELECTED_OUTPUT feature of PHREEQCI, which was coded to include the molalities of all ions in Table 1, was used to generate the molalities and the speciated ionic strength required to calculate the ionic molal conductivities for the equations in Table 1. The WATEQ4F code was modified to calculate the conductivity using the new method. The programming for the text output (*.out) and the spreadsheet output (*.eqp) were modified to include the κ_{25} as well as the conductivity imbalance ($\delta\kappa_{25}$) using the following equation:

$$\delta\kappa_{25} = \frac{\kappa_{25\,calculated} - \kappa_{25\,measured}}{\kappa_{25\,measured}} \qquad (10)$$

The $\delta\kappa_{25}$ is a comparison of calculated and measured conductivity and can be used to identify erroneous chemical analyses. The reliability of geochemical model simulations was discussed in detail by Nordstrom (2004) and largely depends on the thermodynamic database utilized. In a comparison of 14 different geochemical codes, WATEQ was found to perform favorably for seawater and river water analyses (Nordstrom et al., 1979). Furthermore, Nordstrom et al. (1990) compiled and evaluated thermodynamic data utilized by WATEQ4F for the range 0–100 °C and up to 1 molal ionic strength for major univalent and divalent ions, a limited set of minor and trace elements, iron and manganese redox species, and major carbonate minerals.

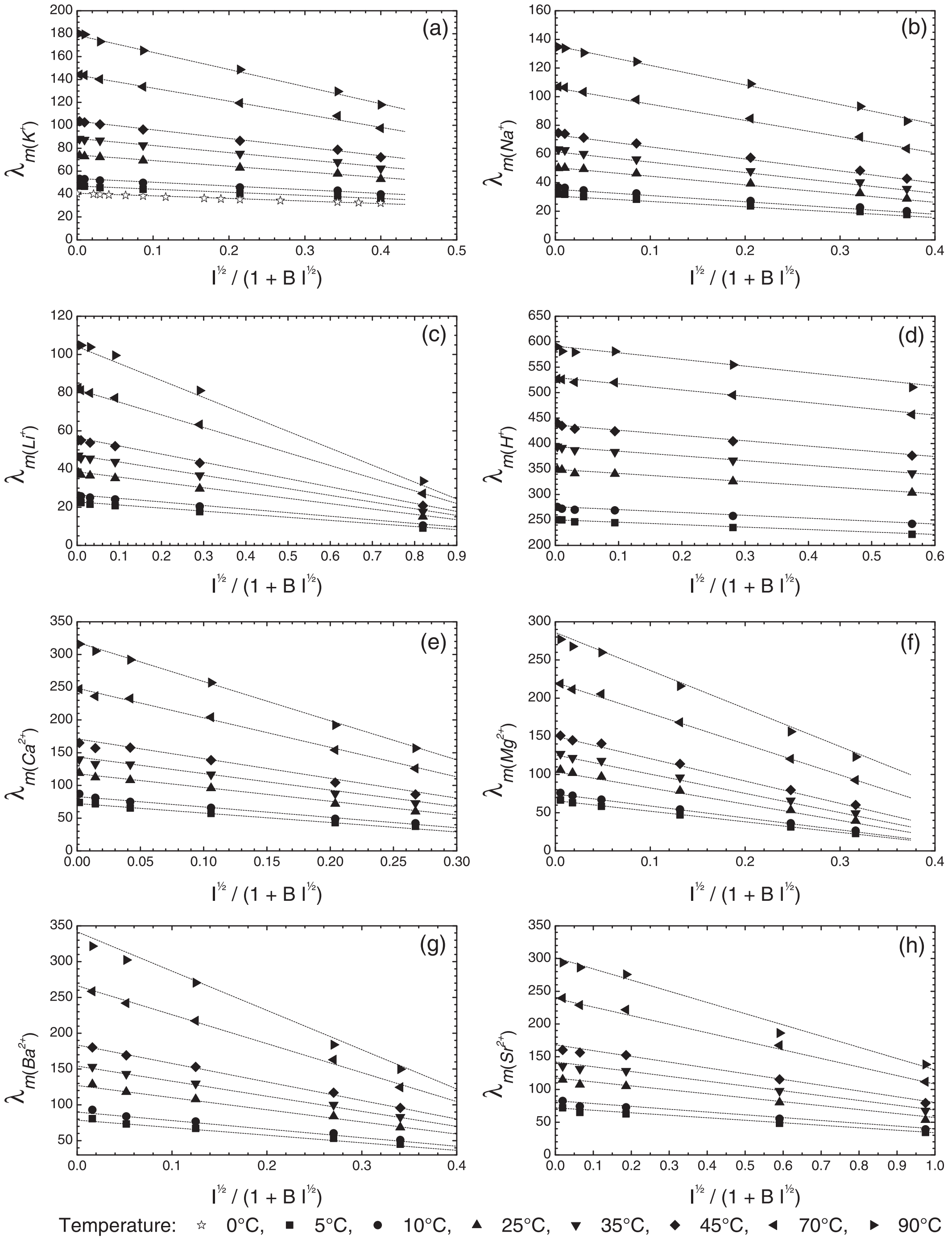

Fig. 1. Graphs of ionic molal conductivities (mS kg cm^{-1} mol^{-1}) as a function of $(I^{1/2})(1 + BI^{1/2})^{-1}$ for K^+ (a), Na^+ (b), Li^+ (c), H^+ (d), Ca^{2+} (e), Mg^{2+} (f), Ba^{2+} (g), and Sr^{2+} (h). The dashed lines are calculated using equations in Table 1.

4. RESULTS AND DISCUSSION

4.1. Calculated conductivity of laboratory solutions

The κ_{25} of each electrolyte reported in McCleskey (2011) was calculated using WATEQ4F to confirm that the method reliably predicts the conductivity of electrolyte solutions containing ions relevant to natural waters. This consistency check also verifies the accuracy of the WATEQ4F code modifications. The same linear temperature compensation factor (0.019) was used for the measured and calculated conductivities. With that source of uncertainty removed, differences between the measured and calculated conductivities are mainly attributable to the calculation of ionic molal conductivities.

The $\delta\kappa_{25}$ was calculated for the electrolytes in McCleskey (2011) (Fig. 5). For 1250 comparisons, the mean and median $\delta\kappa_{25}$ were both 0.1% and the first standard

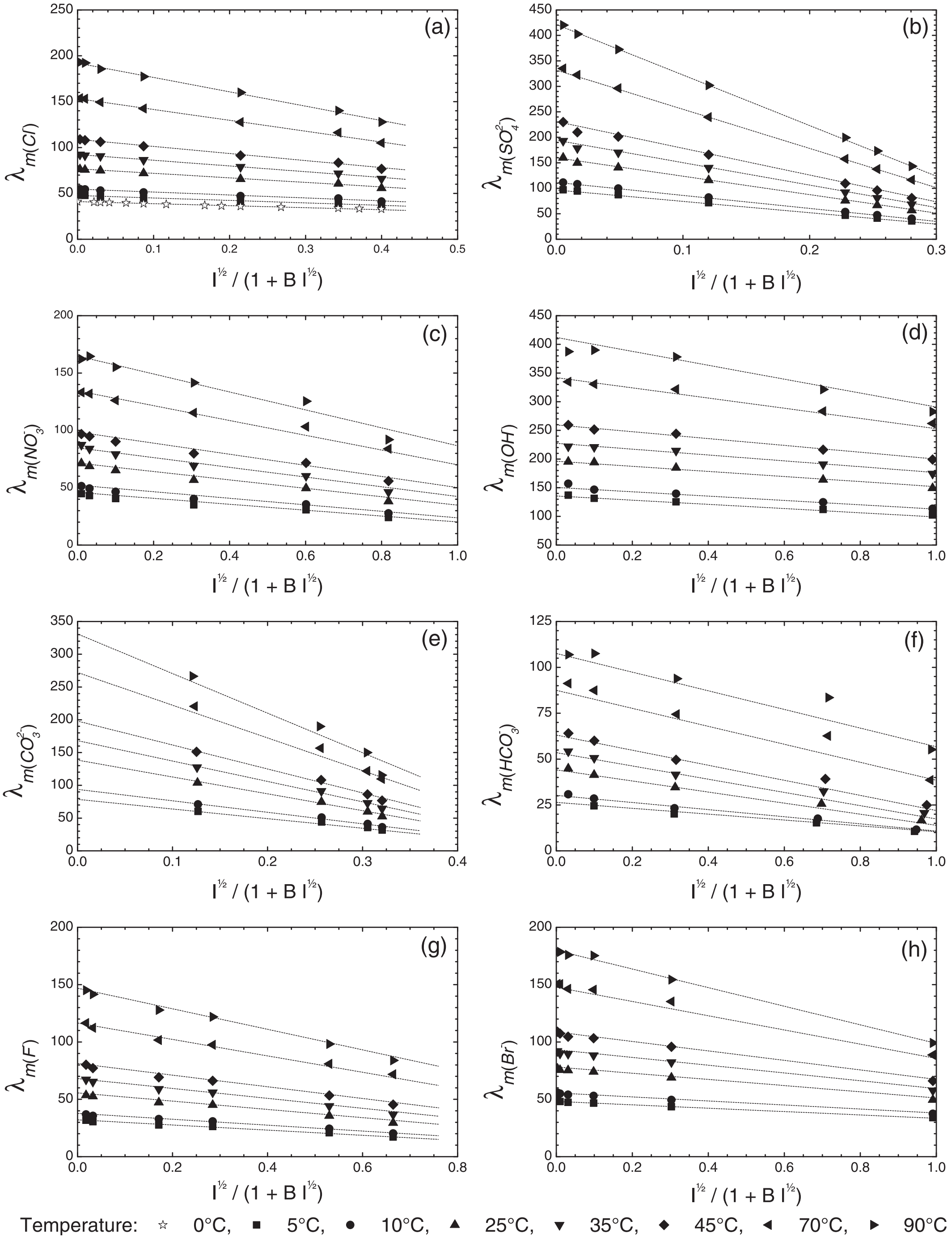

Fig. 2. Graphs of ionic molal conductivities (mS kg cm^{-1} mol^{-1}) as a function of$(I^{1/2})(1 + BI^{1/2})^{-1}$ for Cl^- (a), SO_4^{2-} (b), NO_3^- (c), OH^- (d), CO_3^{2-} (e), HCO_3^- (f), F^- (g), and Br^- (h). The dashed lines are calculated using equations in Table 1.

deviation was 2.5%. Based on this evaluation, 99% of the calculated conductivities were within 7.5% of the measured value for data ranging in temperature from 5–90 °C, conductivity from 10–200,000 μS cm^{-1}, and ionic strength from 10^{-4}–1 mol kg^{-1}. Detailed plots for selected electrolytes (NaCl, $NaHCO_3$, $CaCl_2$, $CaSO_4$, H_2SO_4, and $Fe_2(SO_4)_3$) of $\delta\kappa_{25}$ against κ_{25} are shown in Fig. 6. The good agreement between the calculated and measured conductivities demonstrates that the equations listed in Table 1 are reliable and that the programming of WATEQ4F is correct. The conductivity of H_2SO_4 can be calculated accurately at pH values as low as 0.4. Sulfuric acid is generated in natural waters by pyrite oxidation (Nordstrom, 2000) and sulfur oxidation (Nordstrom et al., 2009). Both oxidation scenarios can generate waters with pH values below 2 where SO_4 hydrolysis

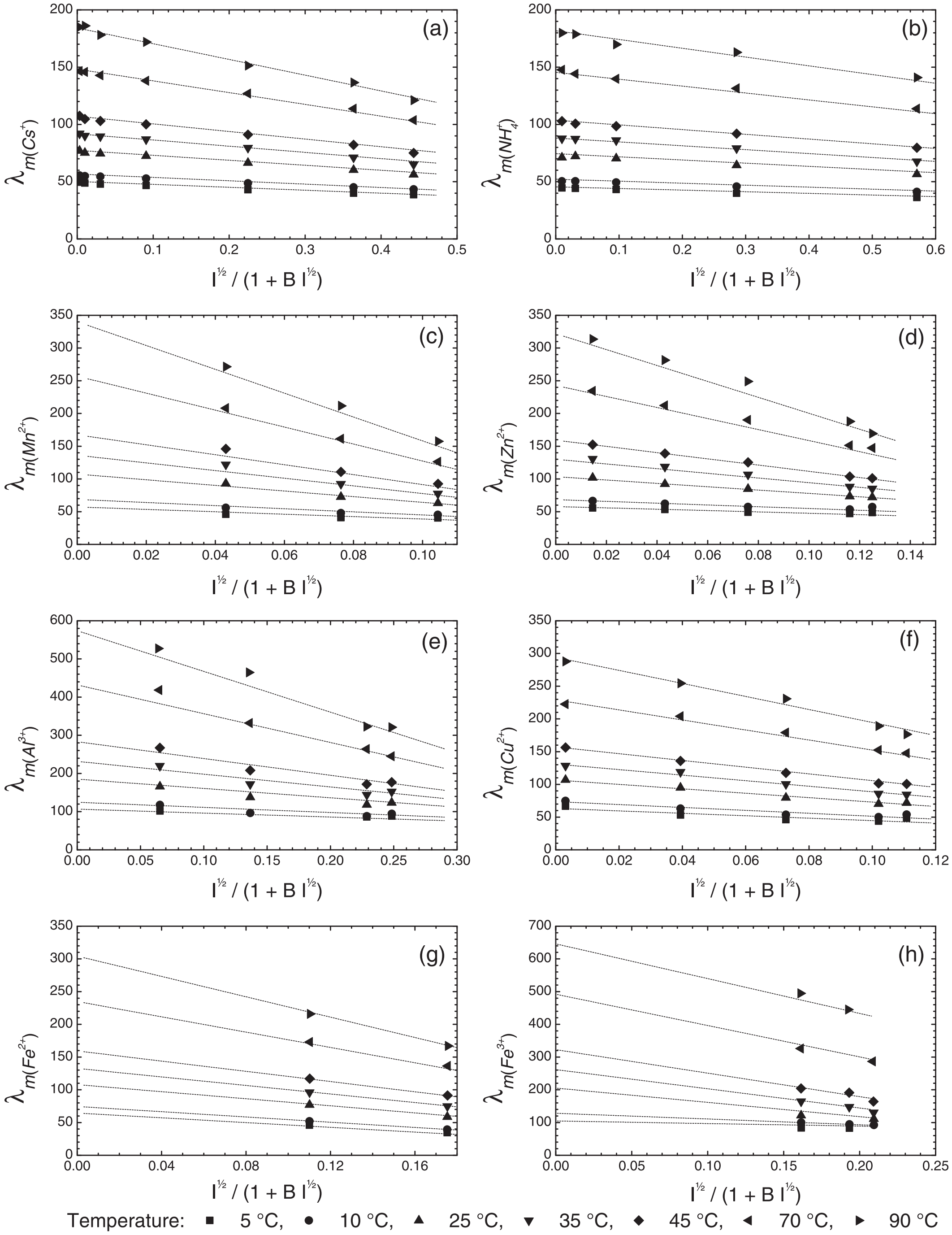

Fig. 3. Graphs of ionic molal conductivities (mS kg cm^{-1} mol^{-1}) as a function of $(I^{1/2})(1 + BI^{1/2})^{-1}$ for Cs^+ (a), NH_4^+ (b), Mn^{2+} (c), Zn^{2+} (d), Al^{3+} (e), Cu^{2+} (f), Fe^{2+} (g), and Fe^{3+} (h). The dashed lines are calculated using equations in Table 1.

($pK_{a2} = 1.98$; Nordstrom and Munoz, 1994) becomes significant. The low $\delta\kappa_{25}$ for H_2SO_4 suggests that the ionic molal conductivities for HSO_4^-, H^+, and SO_4^{2-} are reliably calculated. The $\delta\kappa_{25}$ for HCl solutions is also low ($\delta\kappa_{25} < \pm 2\%$), but HCl is rarely generated by natural processes. The largest values of $\delta\kappa_{25}$ occurred for the 70 and 90 °C measurements for $Fe_2(SO_4)_3$ (Fig. 6f), where the fraction of fully dissociated ions was small. Errors in the Fe-SO_4 speciation at these higher temperatures could account for the larger observed $\delta\kappa_{25}$ values. Another possible explanation is that the predicted Fe^{3+} molal conductivity may be in error at temperatures above 45 °C because of the limited amount of ionic molal conductivity data available for Fe^{3+} at higher temperatures.

4.2. Calculated conductivity of natural waters

Values for κ_{25} of acid mine waters, geothermal waters, seawater, dilute mountain waters, and river water impacted by municipal wastewater were calculated. A water-quality

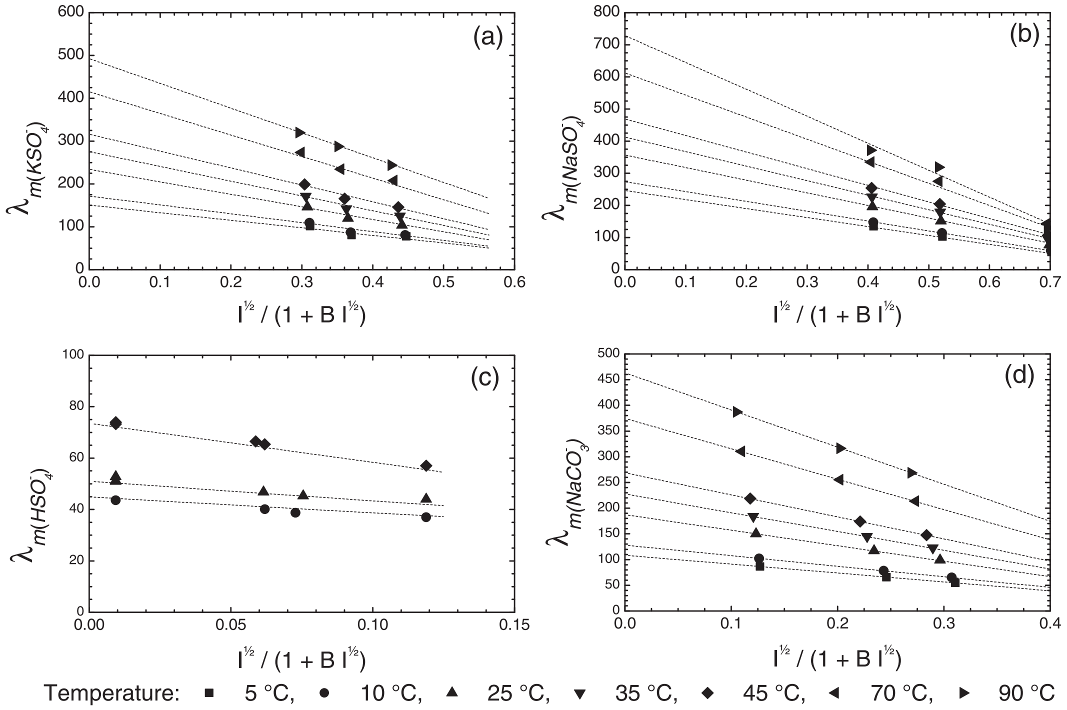

Fig. 4. Graphs of ionic molal conductivities (mS kg cm^{-1} mol^{-1}) as a function of $(I^{1/2})(1 + BI^{1/2})^{-1}$ for KSO_4^- (a), $NaSO_4^-$ (b), HSO_4^- (c), and $NaCO_3^-$ (d). The dashed lines are calculated using equations in Table 1.

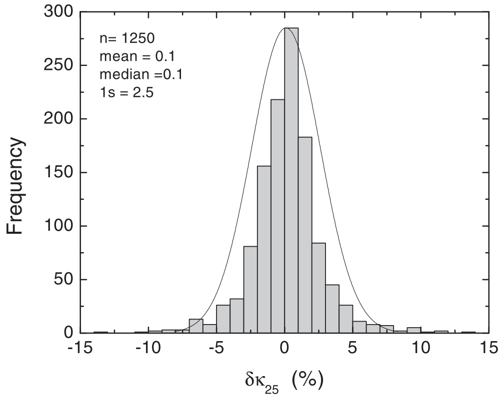

Fig. 5. A frequency plot of the conductivity imbalance $\delta\kappa_{25}$ (for all electrolytes measured in McCleskey (2011).

database with nearly 1800 water samples was created and speciated charge imbalances were calculated using WATEQ4F. The majority of the water quality data were produced by the USGS laboratory in Boulder, Colo., and can be found in a series of reports on Yellowstone National Park (Ball et al., 2001; Ball et al., 2002; McCleskey et al., 2005; Ball et al., 2006), the Questa baseline and pre-mining ground water quality investigation (McCleskey et al., 2003; Naus et al., 2005; Nordstrom et al., 2005; Verplanck et al., 2006), the Boulder Creek Watershed (Verplanck et al., 2003), and the Leviathan Mine drainage basin (Ball and Nordstrom, 1985). Additional water-quality data generated by the USGS for samples from Summitville Mine, Iron Mountain, Upper Animas River, San Diego Bay, and forty-one USGS Major ion (M) standard reference water samples (SRWS) are also included in the database. Each M SRWS is a natural surface water sample where the major ion concentrations and conductivities have been determined by multiple laboratories and the most probable values (MPV) reported. Additional information about the USGS SRWS program, including how the MPV values are determined, can be obtained at URL http://bqs.usgs.gov/srs. All the water analyses used in this study are reported in Electronic annex EA-2 and include pH, temperature, κ_{25}, alkalinity, and concentrations of Ca, Mg, Na, K, Cl, SO_4, Fe(total), Fe(II), SiO_2, NH_4, Al, F, NO_3, Li, Sr, Ba, Br, Mn, Cu, and Zn. The quality of the chemical analyses was checked by calculating the charge imbalance (CI) for each sample. WATEQ4F uses the following equation to calculate CI:

$$CI = \frac{(\sum \text{cations} - \sum \text{anions})}{(\sum \text{cations} + \sum \text{anions}) \div 2} \tag{11}$$

where $\sum$cations and $\sum$anions are in meq L^{-1}. The charge imbalance calculated by WATEQ4F (Eq. (11)) is twice the value often calculated because the denominator is the average of the cation and anion sum rather than just the sum (APHA, 1985). Nordstrom and Munoz (1994) have suggested that analyses having a CI of less than ±10 % are appropriate for speciation calculations. Samples with poor CI (>10 %) were purged from the database and conductivity values were calculated for the remaining 1593 samples (EA-2) and compared to the measured values (Fig. 7). The ranges of conductivity, temperature, pH, and major-ion and trace-metal concentrations for all the samples in

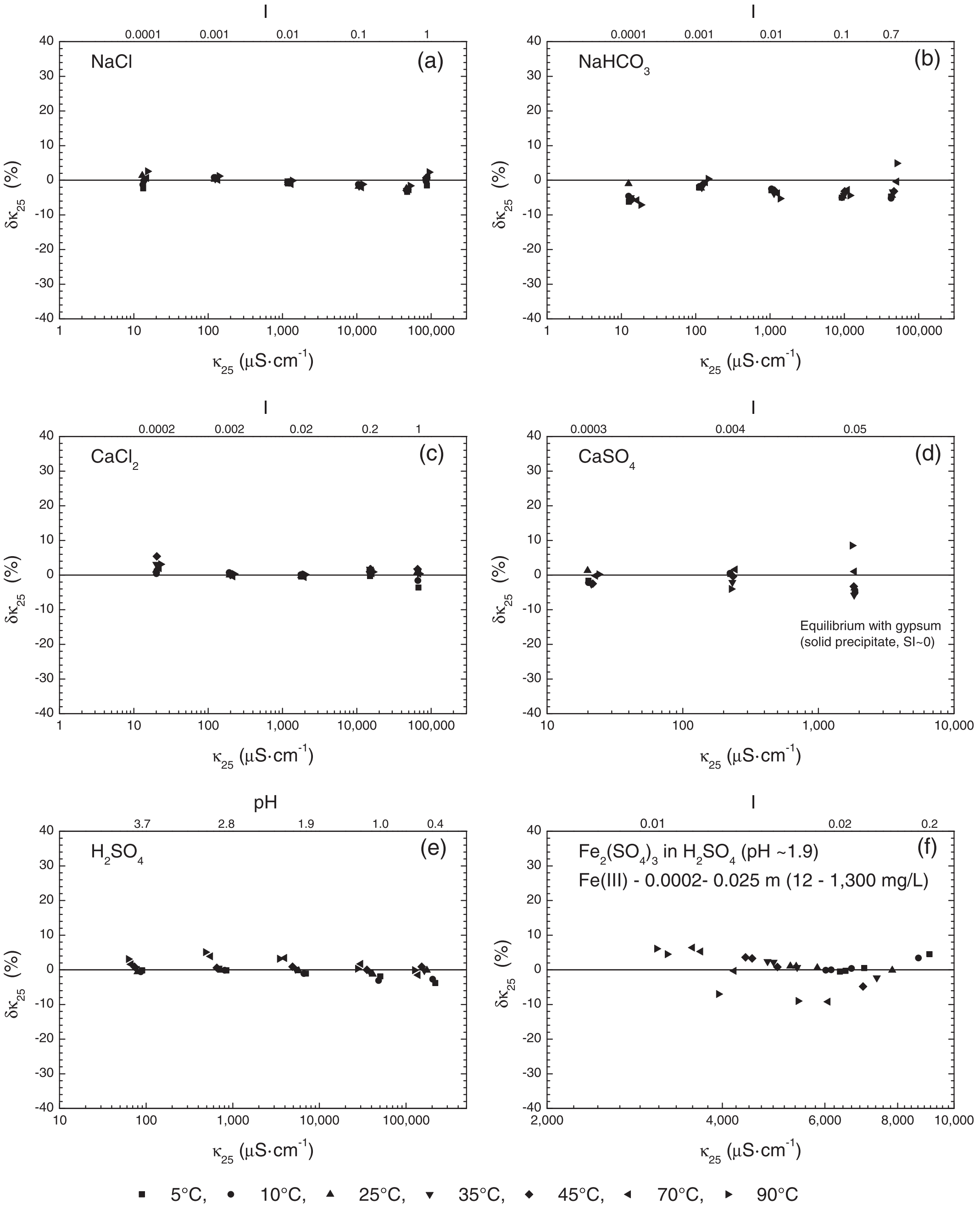

Fig. 6. Conductivity imbalance ($\delta\kappa_{25}$) (as a function of conductivity (κ_{25}) and either ionic strength (I) or pH for NaCl (a), $NaHCO_3$ (b), $CaCl_2$ (c), $CaSO_4$ (d), H_2SO_4 (e), and $Fe_2(SO_4)_3$ (f).

the database are shown in Table 2. The dissolved organic carbon concentrations in the 1593 samples ranged from below detection to 33 mg/L. Naturally occurring DOC is not expected to substantially contribute to the conductivity because of its low mobility, but as far as we know these effects have not been studied. A frequency plot of $\delta\kappa_{25}$ for all the samples in the database is shown in Fig. 8. The mean is −0.7% with a standard deviation of 5.2%. Approximately 95% of the calculated κ_{25} were within 10% of the field measurement. Fig. 9 shows plots of $\delta\kappa_{25}$ against ionic strength, temperature, pH, and conductivity. The method presented here reliably calculates the electrical conductivities of natural water samples having a large range of speciated ionic strength (0.0004–0.7), temperature (0–95 °C), pH (1–10), and conductivity (30–70,000 μS cm^{-1}).

The method is very effective at calculating the κ_{25} for SRWS. The MPVs reported for the SRWS (EA-2) are expected to be very accurate and as a result SRWS are ideal test samples for determining the accuracy of the conductivity method. The SRWS had a wide range of pH (2.74–10.2), ionic strength (0.0012–0.026), and κ_{25} (102–2079 μS cm^{-1}; Fig. 9). The calculated κ_{25} for the 41 U.S. Geological

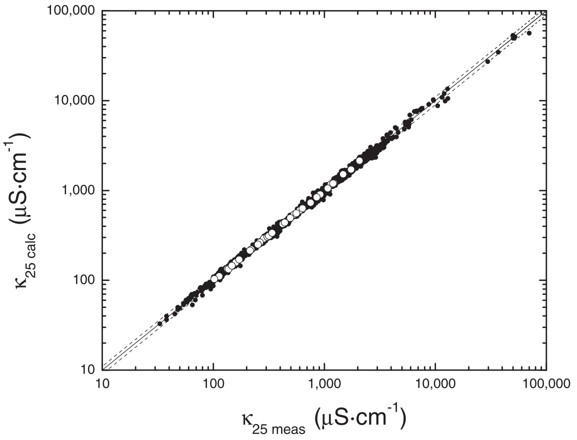

Fig. 7. Calculated conductivity (κ_{25calc}) plotted against measured conductivity (κ_{25meas}) for 1593 natural water samples. The solid line is a 1:1 correlation and the dashed lines are ±10%. The open symbols are U.S. Geological Survey SRWS and the closed symbols are the remaining natural water samples included in EA-2.

Table 2
Ranges of conductivity (κ_{25}), pH, temperature, and major-ion and trace-metal concentrations for all samples in the database.

Field-measured properties	
κ_{25} (μS cm^{-1})	33–70,000
pH	1.1–10.2
T (°C)	0–96
Concentration (mmol kg^{-1})	
Ca	0.001–18
Mg	0.00001–52
Na	0.006–470
K	<0.00003–11
HCO_3	<0.02–14
SO_4	0.0006–570
Cl	0.001–500
F	<0.003–2.9
Br	<0.0006–0.79
NO_3	<0.0008–4.5
SiO_2	0.0008–13
NH_4	<0.003–49
Al	<0.00003–35
Cu	<0.00002–3.5
Fe(II)	<0.00004–160
Fe(III)	<0.00004–100
Li	<0.0001–1.6
Mn	<0.00002–9.1
Sr	<0.00001–0.22
Zn	<0.00002–19

Survey SRWS are in good agreement with the reported κ_{25} (Figs. 7 and 9). The mean $\delta\kappa_{25}$ for the U.S. Geological Survey SRWS is −0.5% with a standard deviation of 1.3%.

4.3. Transport number of ions in natural waters

The method presented here allows the transport number of individual ions in natural waters to be calculated. The transport number was calculated for each ion listed in Table 1 using Eq. (6). Transport numbers are useful for identifying the ions that significantly contribute to the electrical conductivity and can be used to predict the concentrations of major ions for water-quality monitoring. The transport number was determined for every ion listed in Table 1 for the 1593 natural water samples included in the database (EA-2). Fig. 10 contains box plots displaying the distribution of transport numbers for the major cations, major anions, trace metals, and ion pairs. The transport numbers for Ba, Cs, and Sr were not plotted because their contribution to the electrical conductivity was negligible (<1%). Using the maximum transport number, the ions can be group into three categories. The first group includes those ions that may contribute significantly ($t_{max} > 10\%$) to the electrical conductivities of natural waters (H^+, Na^+, Ca^{2+}, Mg^{2+}, NH_4^+, K^+, Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}, F^-, Al^{3+}, Fe^{2+}, NO_3^-, and HSO_4^-). The ions in this group are essential for accurate conductivity calculations. The next group includes those ions than contribute a moderate amount ($2\% < t_{max} < 10\%$) to the electrical conductivities of natural waters (Li^+, Fe^{3+}, Cu^{2+}, Mn^{2+}, Zn^{2+}, OH^-, $NaSO_4^-$, and $NaCO_3^-$). The last group includes those ions that contribute very little ($t_{max} < 2\%$) to the electrical conductivities of natural waters (Ba^{2+}, Br^-, Cs^+, Sr^{2+}, and KSO_4^-).

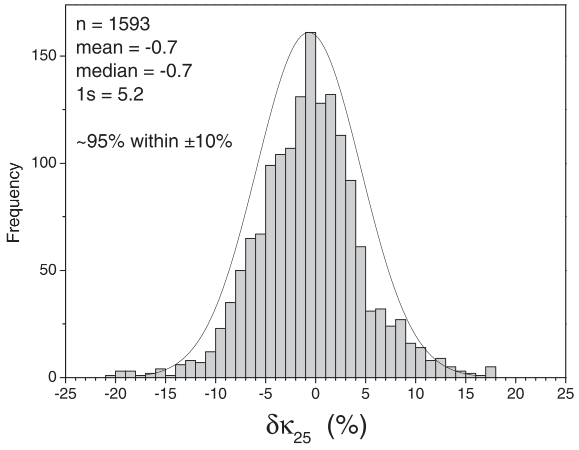

Fig. 8. Frequency plot of conductivity imbalance ($\delta\kappa_{25}$) for all 1593 natural waters samples tested.

4.4. Quality control method for water analyses

The calculated κ_{25} can be used as an analytical quality-control method for a wide range of natural water samples. Rossum (1949) was the first to document the use of electrical conductivity as a quality-control method for checking water analyses. In Rossum's approach, the electrical conductivity is calculated for a sample that is diluted to a range in which ion pairs are unlikely to exist. This approach proved to be a good check for the analytical accuracy of the anions, but does not work very well for samples with high or low pH values, high Na concentrations, or low electrical conductivities. Laxen (1977) calculated electrical conductivity from the chemical composition and compared it to the measured conductivity, with a discrepancy indicating an error in the analyses. Miles and Yost (1982) used the difference between calculated and measured electrical

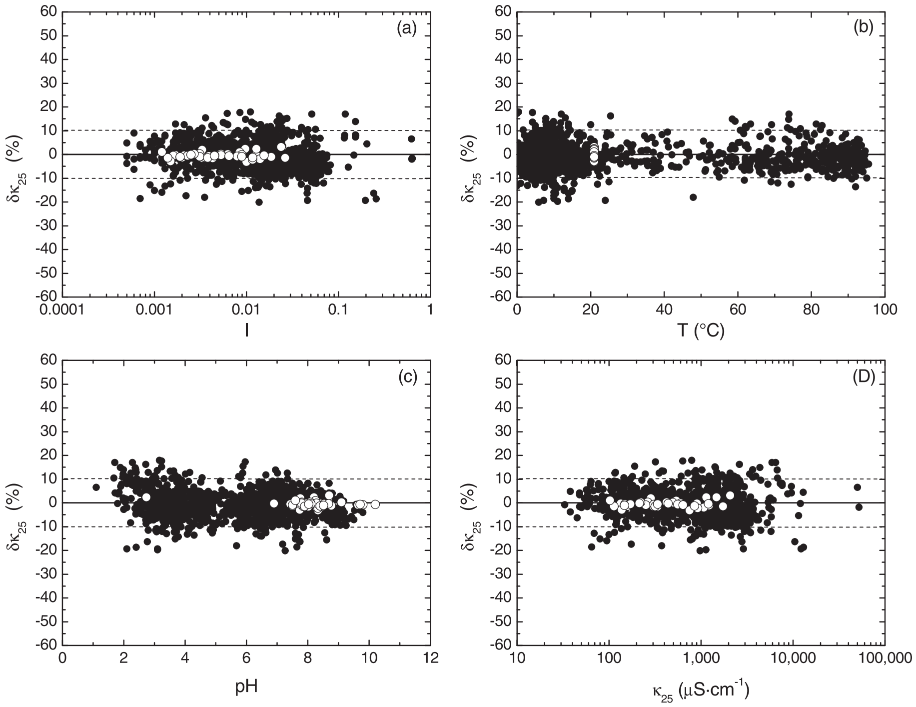

Fig. 9. Plot of the conductivity imbalance ($\delta\kappa_{25}$) for 1593 natural waters against ionic strength (a), temperature (b), pH (c), and conductivity (κ_{25}) (d). The open symbols are U.S. Geological Survey SRWS and the closed symbols are the remaining natural water samples included in EA-2.

conductivity in conjunction with the ion charge balance as an analytical quality-control check, but their technique was limited to samples with conductivities of about 100 μS cm^{-1}.

The use of charge imbalance is regularly used to check the quality of water analyses (APHA, 1985). However, when a large charge imbalance exists there is no indication whether the error is caused by a cation or an anion. A second constraint is helpful to identify the constituent most likely in error. Considering the importance of reliable water-quality analyses and the time and expense of analyzing samples, the ability to identify inaccurate determinations is important.

To demonstrate the utility of identifying the constituent or measurement most likely in error using a $\delta\kappa_{25}$–CI plot, the effects of artificially increasing or decreasing the major cation (meq L^{-1}) were tested for 50 samples originally having a CI and $\delta\kappa_{25} \leqslant \pm 1\%$ (Fig. 11). Increasing the major cation by 20% resulted in an increase in $\delta\kappa_{25}$ and an increase in CI, while decreasing the major cation by 20% resulted in a decrease in $\delta\kappa_{25}$ and a decrease in CI (Fig. 11). Pawlowicz (2008) suggests that CI/2 is a good estimate for $\delta\kappa_{25}$ caused by charge imbalance in natural water analyses. The dashed box in Fig. 11 (CI = ±10% and $\delta\kappa_{25} = \pm 5\%$) is the area where the analyses are acceptable or the errors are too small to identify using this approach. However, the size of the target is somewhat arbitrary and for some sample sets a larger target may be justified (CI = ±10% and $\delta\kappa_{25} = \pm$ 10%). For example we found that approximately 95% of the calculated $\delta\kappa_{25}$ were within 10% of the field measurements for a large variety of natural waters (Fig. 8). It is possible that multiple erroneous analytical values may have a canceling or additive effect for both CI and $\delta\kappa_{25}$. This type of situation may be identified if either the CI or $\delta\kappa_{25}$ is low and the other is high. For example, if both a major cation and anion are overestimated, the CI may be low but the $\delta\kappa_{25}$ may be high. Conversely, if the analytical errors for the major cation and anion are in opposite directions, the $\delta\kappa_{25}$ may be low and the CI high. In addition, the error associated with the field conductivity measurement may be larger for some samples. Nonetheless, a $\delta\kappa_{25}$–CI plot is straightforward to use and in many cases can identify the measurement most likely in error.

5. SUMMARY

A new method has been developed for calculating the electrical conductivities of natural waters having a large range of effective ionic strength (0.0004–0.7 mol kg^{-1}), temperature (0–95 °C), pH (1.0–10), and conductivity (30–70,000 μS cm^{-1}). The method was used to calculate the conductivity of 1593 natural water samples and the mean difference between the calculated and measured conductivity was −0.7 ± 5%. Many of the samples tested were selected to determine the limits of the method and include acid mine waters, geothermal waters, seawater, dilute mountain waters, and river water impacted by municipal waste water.

Compared to other conductivity methods in the literature, three important advancements have been made. First, the electrical conductivities of 34 electrolyte solutions ranging from 10^{-4}–1 mol kg^{-1} in concentration and from 5–90 °C in temperature were used to calculate the ionic

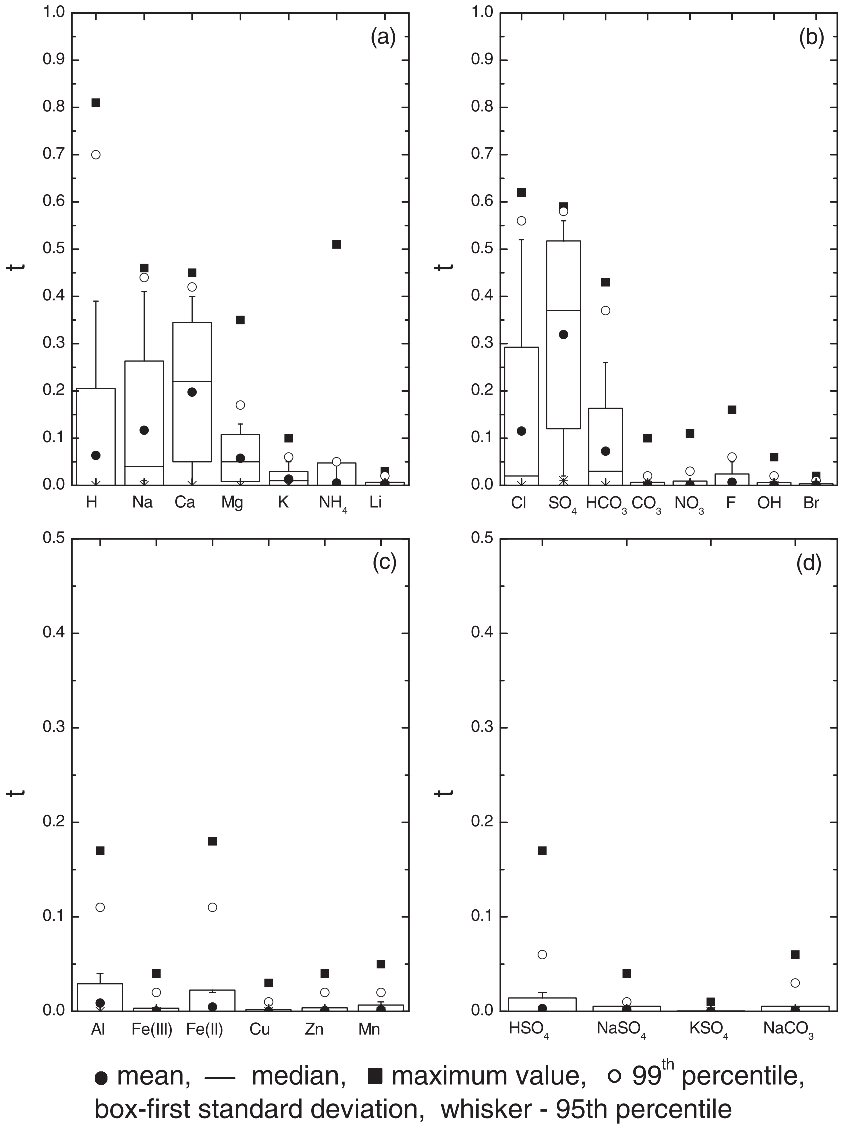

Fig. 10. Box plots displaying the distribution of transport numbers (t) for the major cations (a), major anions (b), trace metals (c), and ion pairs (d).

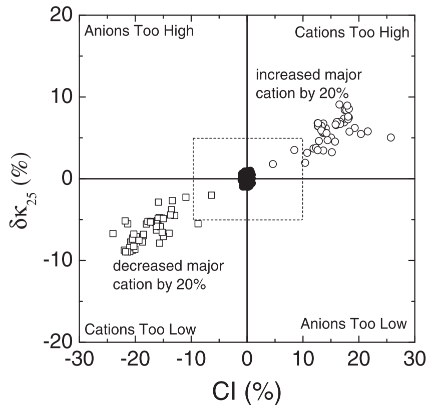

Fig. 11. The effects on conductivity imbalance and charge imbalance of increasing or decreasing the major cation concentration for natural waters.

molal conductivity for the ions pertinent to natural waters. Second, using the new electrical conductivity measurements, a reliable set of equations was developed that can be used to calculate the ionic molal conductivities of cations and anions (H^+, Li^+, Na^+, K^+, Cs^+, NH_4^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, F^-, Cl^-, Br^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}, NO_3^-, and OH^-), environmentally important trace metals (Al^{3+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, and Zn^{2+}), and ion pairs (HSO_4^-, $NaSO_4^-$, $NaCO_3^-$, and KSO_4^-). The ionic molal conductivity equations are functions of both temperature and ionic strength and are the most comprehensive presented to date. Third, the effects of ion pairing have been accounted for by determining the concentrations of ion pairs and complexes using geochemical speciation models. Treating ion pairs in the same manner as other ions allows the method to be reliable at much greater ionic strengths.

For the wide range of natural waters tested in this study, transport numbers were calculated to identify the ions that contribute significantly to the conductivity (H^+, Na^+, Ca^{2+}, Mg^{2+}, NH_4^+, K^+, Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}, F^-, Al^{3+}, Fe^{2+}, NO_3^-, and HSO_4^-). Besides identifying the ions that contribute significantly to the conductivity, transport numbers can also be used to better predict the concentrations of ions in natural waters.

Another important application of the conductivity method is checking the accuracy of water analyses. By coupling charge imbalance and conductivity imbalance, the measurement most likely in error can be identified or narrowed down to a few possibilities. Considering the time, expense, and importance of reliable water quality analyses, the ability to identify inaccurate determinations is extremely useful.

The method presented to calculate the electrical conductivity of natural waters has been incorporated into the USGS geochemical speciation code WATEQ4F. The WATEQ4F program can be obtained at: http://wwwbrr.cr.usgs.gov/projects/GWC_chemtherm/software.htm.

ACKNOWLEDGEMENTS

We would like to thank Kate Campbell and Randall Chiu of the USGS for their assistance on many occasions during this study and manuscript preparation. We also would like to thank Niel Plummer and David Roth for their constructive comments and reviews. This study would not have been possible without the support of the National Research Program of the USGS. The use of trade, product, industry, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2011.10.031.

REFERENCES

Anderko A. and Lencka M. M. (1997) Computation of electrical conductivity of multicomponent aqueous systems in wide concentration and temperature ranges. *Ind. Eng. Chem. Res.* **36**, 1932–1943.

APHA (1985) *Standard Methods for the Examination of Water and Waste Water*. American Public Health Association, Inc.

Appelo C. A. J. (2010) Specific conductance: how to calculate, to use, and the pitfalls. Available from: <http://www.xs4all.nl/~appt/exmpls/sc.html>.

Ball J. W. and Nordstrom D. K. (1985) Major and trace-element analyses of acid mine waters in the Leviathan Mine drainage basin, California/Nevada; October, 1981 to October, 1982. *U.S. Geol. Surv. Water-Resour. Invest. Rep 85-4169*, p. 46.

Ball J. W. and Nordstrom D. K. (1991) User's manual for WATEQ4F, with revised thermodynamic database and test cases for calculating speciation of major, trace, and redox elements in natural waters. *U.S. Geol. Surv. Open-File Rep. 91-183*, p. 189.

Ball J. W., Nordstrom D. K., McCleskey R. B., Schoonen M. A. A. and Xu Y. (2001) Water-chemistry and on-site sulfur-speciation data for selected springs in Yellowstone National Park, Wyoming, 1996–1998. *U.S. Geol. Surv. Open-File Rep. 01-49*, p. 42.

Ball J. W., McCleskey R. B., Nordstrom D. K., Holloway J. M. and Verplanck P. L. (2002) Water-chemistry data for selected springs, geysers, and streams in Yellowstone National Park, Wyoming, 1999–2000. *U.S. Geol. Surv. Open-File Rep. 02-382*, p. 104.

Ball J. W., McCleskey R. B., Nordstrom D. K. and Holloway J. M. (2006) Water-chemistry data for selected springs, geysers, and streams in Yellowstone National Park, Wyoming, 2003–2005. *U.S. Geol. Surv. Open-File Rep. 2006-1339*, p. 137.

Binkley J., Simpson J. A. and McMahon P. (2000) Characterisation of textile aerobic-activated sludge plant by conductivity and pH measurement. *J. Text. Inst.* **91**, 523–529.

Charlton S. R. and Parkhurst D. L. (2002) PHREEQCI – a graphical user interface to the geochemical model PHREEQC. *U.S. Geol. Surv. Fact Sheet FS-031-02*, p. 2.

Davies C. W. (1962) *Ion Association*. Butterworth, Washington, DC.

Gustafson H. and Behrman S. (1939) Determination of total dissolved solids in water by electrical conductivity. *Ind. Eng. Chem. Anal. Ed.* **11**, 355.

Harned H. S. and Owen B. B. (1958) *The Physical Chemistry of Electrolyte Solutions*. Reinhold Publishing Corporation, New York.

Hem J. D. (1982) Conductance: a collective measure of dissolved ions. In *Water Analysis Inorganic Species*, vol.1 (eds. R. A. Minear and L. H. Keith). Academic Press, New York, pp. 137–161.

Jones G. and Dole M. (1930) The electrical conductance of aqueous solutions of barium chloride as a function of the concentration. *J. Am. Chem. Soc.* **52**, 2245–2256.

Kohlrausch F. (1902) The resistance of the ions and the mechanical friction of the solvent. *Proc. R. Soc. London* **71**, 338–350.

Lattey R. T. (1927) On the dilution law for strong electrolytes. *Philos. Mag.* **7**, 831–836.

Laxen D. P. H. (1977) A specific conductance method for quality control in water analysis. *Water Res.* **11**, 91–94.

Lewis E. L. (1980) The practical salinity scale 1978 and its antecedents. *IEEE J. Oceanic Eng.* **5**, 3–8.

Lind C. J. (1970) Specific conductance as a means of estimating ionic strength. *U.S. Geol. Surv. Prof. Pap. 700-D*, D272–D280.

Lystrom D. G., Rinella R. A. and Knox W. D. (1978) Definition of regional relationships between dissolved solids and specific conductance, Susquehanna River and New York. *U.S. Geol. Surv. J. Res.* **6**, 541–545.

Marion G. M. and Babcock K. L. (1976) Predicting specific conductance and salt concentration in dilute aqueous solutions. *Soil Sci.* **122**, 181–187.

McCleskey R. B. (2011) Electrical conductivity of electrolytes found in natural waters from (5 to 90) °C. *J. Chem. Eng. Data* **56**, 317–327.

McCleskey R. B., Nordstrom D. K., Steiger J. I., Kimball B. A. and Verplanck P. L. (2003) Questa baseline and pre-mining ground-water-quality investigation. 2. Low-flow (2001) and snowmelt (2002) synoptic/tracer water chemistry for the Red River, New Mexico. *U.S. Geol. Surv. Open-File Rep. 2003-0148*, p. 166.

McCleskey R. B., Ball J. W., Nordstrom D. K., Holloway J. M. and Taylor H. E. (2005) Water-chemistry data for selected springs, geysers, and streams in Yellowstone National Park, Wyoming, 2001–2002. *U.S. Geol. Surv. Open-File Rep. 2004-1316*, p. 94.

McNeal B. L., Oster J. D. and Hatcher J. J. (1970) Calculation of electrical conductivity from solution composition data as an aid to in-situ estimation of soil salinity. *Soil Sci.* **110**, 405–414.

McNeil V. H. and Cox M. E. (2000) Relationship between conductivity and analysed composition in a large set of natural surface-water samples, Queensland, Australia. *Environ. Geol.* **39**, 1325–1333.

Miles L. J. and Yost K. J. (1982) Quality analysis of USGS precipitation chemistry data for New York. *Atmos. Environ.* **16**, 2889–2898.

Miller R. L., Bradford W. L. and Peters N. E. (1988) Specific conductance: theoretical considerations and application to analytical quality control. *U.S. Geol. Surv. Water-Supply Pap. 2311*, p. 16.

Mills I., Cvitaš T., Homann K., Kallay N. and Kuchitsu K. (1993) *International Union of Pure and Applied Chemistry: Quantities, Units, and Symbols in Physical Chemistry*. Blackwell Science, Oxford.

Naus C. A., McCleskey R. B., Nordstrom D. K., Donohoe L. C. and Hunt A. G. (2005) Questa baseline and pre-mining groundwater quality investigation. 5. Well installation, water-level data, and surface- and ground-water geochemistry in the straight Creek Drainage Basin, Red River valley, New Mexico, 2001–03. *U.S. Geol. Surv. Sci. Invest. Rep. 2005-5088*, p. 232.

Nordstrom D. K. (2000) Advances in the hydrogeochemistry and microbiology of acid mine waters. *Int. Geol. Rev.* **42**, 499–515.

Nordstrom D. K. (2004) Modeling low-temperature geochemical processes. In *Treatise of Geochemistry Surface and Ground Water Weathering and Soils*, vol. 5 (ed. J. I. Drever). Elsevier, Amsterdam, pp. 37–72 (chapter 2).

Nordstrom D. K. and Munoz J. L. (1994) *Geochemical Thermodynamics*, second ed. Blackwell Scientific Publications, Caldwell, New Jersey.

Nordstrom D. K., Plummer L. N., Wigley T. M. L., Wolery T. J., Ball J. W., Jenne E. A., Bassett R. L., Crerar D. A., Florence T. M., Fritz B., Hoffman M., Holdren Jr. G. R., Lafon G. M., Mattigod S. V., McDuff R. E., Morel F., Reddy M. M., Sposito G. and Thrailkill J. 1979. A comparison of computerized chemical models for equilibrium calculations in aqueous systems. In *Chemical Modeling of Aqueous Systems* (ed. E.A. Jenne). Am. Chem. Soc. Symp. Ser. 93, Washington, DC. pp. 857–892.

Nordstrom D. K., Plummer L. N., Langmuir D., Busenberg E., May H. M., Jones B. F. and Parkhurst D. L. (1990) Revised chemical equilibrium data for major water-mineral reaction and their limitations. In *Chemical Modeling of Aqueous Systems II* (eds. D. C. Melchior and R. L. Bassett) Am. Chem. Soc. Symp. Ser. 416, Washington, DC. pp. 398–413.

Nordstrom D. K., McCleskey R. B., Hunt A. G. and Naus C. A. (2005) Questa baseline and pre-mining ground-water quality investigation. 14. Interpretation of ground-water geochemistry in catchments other than the Straight Creek catchment, Red River valley, Taos County, New Mexico, 2002–2003. *U.S. Geol. Surv. Sci. Invest. Rep. 2005-5050*, p. 84.

Nordstrom D. K., McCleskey R. B. and Ball J. W. (2009) Sulfur geochemistry of hydrothermal waters in Yellowstone National Park, Wyoming, USA. IV. Acid-sulfate waters. *Appl. Geochem.* **24**, 191–207.

NRC (1929) *International Critical Tables of Numerical Data Physics, Chemistry and Technology Volume VI*. National Research Council, McGraw-Hill, New York.

NWIS (2011) National Water Information System: USGS Water-Quality Data for the Nation. Available from: <http://waterdata.usgs.gov/nwis/qw>.

Parkhurst D. L. and Appelo C. A. J. (1999) User's guide to PHREEQC (Version 2) – a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. *U.S. Geol. Surv. Water-Resour. Invest. Rep. 99-4259*, p. 312.

Parsons R. (1974) Manual of symbols and terminology for physicochemical quantities and units, Appendix III – electrochemical nomenclature. *Pure Appl. Chem.* **37**, 499–516.

Pawlowicz R. (2008) Calculating the conductivity of natural waters. *Limnol. Oceanogr. Meth.* **6**, 489–501.

Pollak M. J. (1954) The use of electrical conductivity measurements for chlorinity determination. *J. Mar. Res.* **13**, 228–231.

Pratt K. W., Koch W. F., Wu Y. C. and Berezansky P. A. (2001) Molality-based primary standards of electrolytic conductivity. *Pure Appl. Chem.* **73**, 1783–1793.

Prieto F., Barrado E., Vega M. and Deban L. (2001) Measurement of electrical conductivity of wastewater for fast determination of metal ion concentration. *Russ. J. Appl. Chem.* **74**, 1321–1324.

Radtke D. B., Davis J. V. and Wilde F. D. (2005) 6.3 Specific electrical conductance. In *National Field Manual for the Collection of Water-quality Data: U.S. Geol. Surv. Tech. Water-Resour. Invest., book 9*. Available from: <http://pubs.water.usgs.gov/twri9A> (chapters A1–A9).

Robinson R. A. and Stokes R. H. (1965) *Electrolyte Solutions*. Butterworth Publications Limited, London.

Rossum J. R. (1949) Conductance method for checking accuracy of water analyses. *Anal. Chem.* **21**, 631.

Rossum J. R. (1975) Checking the accuracy of water analyses through the use of conductivity. *J. Am. Water Works Assn.* **67**, 204–205.

Shedlovsky T. (1938) Computation of ionization constants and limiting conductance values from conductivity measurements. *J. Franklin Inst.* **225**, 739–743.

Talbot J. D. R., House W. A. and Pethybridge A. D. (1990) Prediction of the temperature dependence of electrical conductance for river waters. *Water Res.* **24**, 1295–1304.

Tanji K. K. and Biggar J. W. (1972) Specific conductance model for natural waters and soil solutions of limited salinity levels. *Water Resour. Res.* **8**, 145–153.

Verplanck P. L., McCleskey R. B. and Roth D. R. (2003) Inorganic water chemistry of the Boulder Creek watershed, Colorado, during high-flow and low-flow conditions, 2000. In *Comprehensive water quality of the Boulder Creek watershed, Colorado, during high-flow and low-flow conditions, 2000* (eds. S. F. Murphy, P. L. Verplanck and L. B. Barber). U.S. Geol. Surv. Sci. Invest. Rep. 03-4045. pp. 71–102.

Verplanck P. L., McCleskey R. B. and Nordstrom D. K. (2006) Questa baseline and pre-mining ground-water quality investigation. 20. Water chemistry of the Red River and selected seeps, tributaries, and precipitation, Taos County, New Mexico, 2000–2004. *U.S. Geol. Surv. Sci. Invest. Rep. 2006-5028*, p. 154.

Visconti F., De Paz J. M. and Rubio J. L. (2010) An empirical equation to calculate soil solution electrical conductivity at 25 °C from major ion concentrations. *Eur. J. Soil Sci.* **61**, 980–993.

Wang P., Anderko A. and Young R. D. (2004) Modeling electrical conductivity in concentrated and mixed-solvent electrolyte solutions. *Ind. Eng. Chem. Res.* **43**, 8083–8092.

Associate editor: Robert H. Byrne