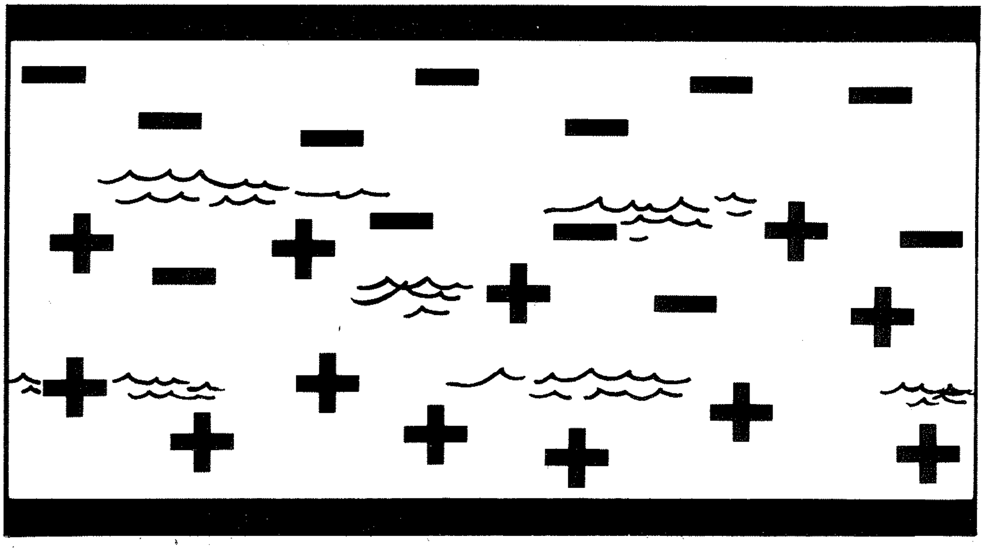
Research



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Checking the Accuracy of Water Analyses Through the Use of Conductivity

John R. Rossum

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The following article provides mathematical means for calculating the conductance from the constituent mineral concentrations in fresh water.

Chemists usually consider a mineral analysis to be satisfactorily accurate if the total anion concentration closely approximates the total cation concentration, recognizing, however, that there may be undetected compensating errors. An independent means of checking analyses minimizes this possibility. An opportunity for such an independent check is provided by a comparison of the measured conductivity with a value calculated from the analyses.

The conductivity of a dilute solution of ionized salt can be calculated if the equivalent conductance of the individual ions at infinite dilution and their valence states are known. The formula was developed by Kohlrausch, empirically, and later theoretically verified by Debye, Huckel, and Onsager. This equation can be written as

$$G = \Lambda_0 C - (K_1 \Lambda_0 + K_2) C^{1.5} \tag{1}$$

where

G is conductivity of the salt solution
C is concentration of the salt solution
Λ_0 is the equivalent conductance of the salt at infinite dilution
K_1 and K_2 are constants that are associated with the relaxation of the ion-cloud effect and the electrophoretic effect relative to ion mobility.

Equation 1 has been found to be applicable to mineral analysis of water. The values of K_1 and K_2 are calculated from temperature, viscosity, and dielectric constant of water and depend upon the equivalent conductance and valence of each ion. The author has used the values of 25C, 0.008949 poise, and 78.55 for the temperature, viscosity, and dielectric constant, respectively.

The first term, $\Lambda_0 C$, is the sum of the products of concentration of each ion (in milliequivalents per litre) and equivalent conductance at infinite dilution of each ion. This is calculated separately for the negative and positive ions.

$$G_{0-} = \Sigma c_- \zeta_- \tag{2}$$

$$G_{0+} = \Sigma c_+ \zeta_+ \tag{3}$$

TABLE 1

Equivalent Ionic Conductance at Infinite Dilution—25C

Anion	ζ_{0-}	Cation	ζ_{0+}
1/2 $CO_3^{=}$	86	1/2 Ca^{++}	59.5
HCO_3^-	44.5	1/2 Mg^{++}	53.1
1/2 $SO_4^{=}$	79.8	Na^+	50.1
Cl^-	76.3	K^+	73.5
NO_3^-	71.4	H^+	349.8
OH^-	197.8		

TABLE 2A

Highly Mineralized Colorado River Water Supplies in Southern California—Anions (Conductivity = 1 186 µmho/cm at 25C; pH = 8.02)

Anion	Concentration	
	mg/l	*meq/l*
$CO_3^{=}$	1.3	0.04
HCO_3^-	156	2.55
$SO_4^{=}$	308	6.41
Cl^-	99	2.79
NO_3^-	1	0.02
Total		11.81

TABLE 2B

Highly Mineralized Colorado River Water Supplies in Youthern California—Cations (Conductivity = 1 186 µmho/cm at 25C; pH = 8.02)

Cation	Concentration	
	mg/l	*meq/l*
Ca^{++}	36	1.80
Mg^{++}	9	0.76
Na^+	206	8.94
K^+	6.2	0.16
Total		11.66

The values for equivalent ionic conductance at 25C in Table 1 are taken from textbooks on physical chemistry, except those for carbonate, which are assigned values that have been estimated by the author.

The conductance contributed by the hydroxyl ion is not significant if the pH is < 9; that contributed by the hydrogen ion is not significant if the pH is > 5.

Values for ionic charge of the negative and positive ions are calculated as the sum of the products of the concentration of each ion (in milliequivalents per litre) and the square of its charge (valence) divided by the sum of the products of concentration and the first power of the valence [Eq(4,5)]. The only justification for this method of calculating the effective ionic charge, rather than using the weighted mean value, is that the former procedure works, whereas the latter gives values that are far too low.

$$Z_- = \Sigma c_- z_-^2 / \Sigma c_- z_- \tag{4}$$
$$Z_+ = \Sigma c_+ z_+^2 / \Sigma c_+ z_+ \tag{5}$$

Average values are computed for ionic conductance of the negative and positive ions. The total ionic conductance is their sum.

$$\lambda_- = G_{0-} / \Sigma c_- \tag{6}$$
$$\lambda_+ = G_0 + / \Sigma c_+ \tag{7}$$
$$\Lambda_0 = \lambda_+ + \lambda \tag{8}$$

The calculated conductivity in micromhos per centimeter at 25C is found from Eq (9).

$$G = G_{0+} + G_{0-} - \left[\frac{\Lambda_0 Z_+ Z_-}{115.2(Z_+ + Z_-)} \left(\frac{2Q}{1+\sqrt{Q}} \right) + 0.668 \right] \left[(Z_+ + Z_-)C \right]^{1.5} \tag{9}$$

where

$$Q = \frac{Z_+ Z_- \Lambda_0}{(Z_+ + Z_-)(Z_+ \lambda_- + Z_- \lambda_+)}$$

The use of this equation is illustrated by the analysis in Table 2 (A, B).

Since the pH is between 5 and 9, neither the hydroxyl or hydrogen ions will contribute significantly to the conductivity.

$$G_{0-} = \Sigma c_- \zeta_- = 0.04 \times 86 + 2.55 \times 44.5 + 6.41 \times 79.8 + 2.79 \times 76.3 + 0.02 \times 71.4 = 842.74$$

Similarly

$G_{0+} = 607.11$

$\Sigma c_- z_-^2 = (0.04 + 6.41) \times 2^2 + (2.55 + 2.79 + 0.02) \times 1^2 = 31.16$

$\Sigma c_- z_- = (0.04 + 6.41) \times 2 + (2.55 + 2.79 + 0.02) \times 1 = 18.26$

$Z_- = 31.16/18.26 = 1.707$

Similarly

$Z_+ = 1.360$

$\lambda_- = G_{0-}/\Sigma c_- = 842.738/11.81 = 71.36$

Similarly

$\lambda_+ = 52.07$

$\Lambda_0 = \lambda_- + \lambda_+ = 71.36 + 52.07 = 123.43$

$Q = 0.502$

$C = (11.81 + 11.66)/2 = 11.735$

$G = 842.74 + 607.11 - (0.476 + 0.668)\ (35.99)^{1.5} = 1449.8 - 247.0$
$= 1202.8$ (1.42 per cent high)

In order to verify Eq (9), the conductance of the water was calculated using 100 consecutive chemical analyses from the California Wtr. Svce. Co.'s laboratory. The water tested represented a wide range of chemical types with conductivities ranging from < 100 µmho/cm to more than 1 400 µmho/cm. The average percentage error between the calculated conductivity and the measured conductivity was 1.81 per cent with a relative standard deviation of 1.86 per cent. The corresponding error in ion balance was 0.79 per cent with a relative standard deviation of 1.56 per cent.

The difference between calculated and measured conductivity is not sufficiently sensitive to detect gross errors in minor constituents, nor will it be likely to detect the situation that may occur if one ion is reportedly too high and another ion of the same charge is equivalently too low. This can occur when both hardness and calcium are determined by EDTA titration and magnesium is found by calculating the difference. A significant error in hardness will be detected, but because there is only a slight difference between the equivalent conductance of the magnesium and calcium ions, the calculated conductivity will be very close to the measured value if calcium is erroneously reported as magnesium or vice versa.

It is presently routine practice to compute the calculated conductivity on all mineral analyses from the California Water Service Co.'s laboratory on a time-share computer terminal. This not only provides assurance that the accuracy of determination of the principal constituents is within self-imposed tolerance limits but is very helpful in locating an error when one occurs. For example, if the ion balance indicated that the sum of the negative ions exceeds that of the positive ions and the calculated conductivity is too low, it is likely that the error is a low value in one of the positive ions, whereas if the calculated conductivity is too high, the error is probably the result of a high value in one of the negative ions.