

- d. Wash bottle, 500 mL.
e. Magnetic stirrer (optional).

3. Reagents

- a. *Ozone-demand-free water*: See Section 2350D.3a.
b. *Sulfuric acid*, H₂SO₄, 2*N*: Cautiously add 56 mL conc H₂SO₄ to 800 mL ozone-demand-free water in a 1-L volumetric flask. Mix thoroughly, cool, add up to mark with ozone-demand-free water.
c. *Potassium iodide*, KI: Dissolve 20 g KI in about 800 mL of ozone-demand-free water in a 1-L volumetric flask. Make up to mark with ozone-demand-free water.
d. *Standard sodium thiosulfate titrant*, Na₂S₂O₃, 0.1*N*: See Section 4500-Cl.B.2c.
e. *Standard sodium thiosulfate titrant*, Na₂S₂O₃, 0.005*N*: Dilute the proper volume (approximately 50 mL) of standardized 0.1*N* Na₂S₂O₃ to 1 L.
f. *Starch indicator solution*: See Section 4500-Cl.B.2e.

4. Procedure

Determine the output of the ozone generator by passing the ozone gas through two serial KI traps (Traps A and B) for about 10 min. For best results, keep gas flow below approximately 1 L/min. Each trap is a gas washing bottle containing a known volume (at least 200 mL) of 2% KI. Quantitatively transfer contents of each trap into a beaker, add 10 mL of 2*N* H₂SO₄, and titrate with standardized 0.005*N* Na₂S₂O₃ until the yellow iodine color almost disappears. Add 1 to 2 mL starch indicator solution and continue titrating to the disappearance of blue color.

Put a known volume (at least 200 mL) of sample in a separate gas washing bottle (label gas washing bottles to avoid contaminating the reaction vessel with iodide). Direct ozone gas through this reaction vessel. For ozone demand studies, direct gas stream leaving reaction vessel through a KI trap (Trap C) prepared as above. Ozonate sample for a given contact time. For ozone demand studies, turn ozonator off at end of contact time and pour contents of Trap C into a beaker. Add 10 mL 2*N* H₂SO₄ and titrate with 0.005*N* Na₂S₂O₃ as described above. For ozone requirement studies, remove a portion from the reaction vessel at the end of contact time and measure residual ozone concentration by the indigo method.

5. Calculation

- a. *Ozone dose*:

$$\text{Ozone dose, mg/min} = \frac{(A + B) \times N \times 24}{T}$$

where:

- A = mL titrant for Trap A,
B = mL titrant for Trap B,
N = normality of Na₂S₂O₃, and
T = ozonation time, min.

- b. *Ozone demand*:

$$\text{Ozone demand, mg/min} = \text{ozone dose, mg/min} - \frac{C \times N \times 24}{T}$$

where:

- C = mL titrant for Trap C.

Report sample ozone demand and blank ozone demand, ozone dose, ozonation time, sample temperature, sample pH, sample volume, and analytical method. Because the ozone transfer rate is highly dependent on experimental conditions, also report vessel volume, vessel type, gas flow rate, and sample volume.

c. *Ozone requirement*: The ozone requirement in the semi-batch test is the ozone dose, mg/min, required to obtain the target ozone residual after the desired ozonation time. See Section 2350E.5a to calculate dose. When reporting ozone requirement, also include target oxidant residual as well as other experimental characteristics listed in ¶ b above.

6. Precision and Bias

See Section 2350B.6.

7. Bibliography

See Section 4500-O₃.B.7 and 8.

2510 CONDUCTIVITY*

2510 A. Introduction

Conductivity, *k*, is a measure of the ability of an aqueous solution to carry an electric current. This ability depends on the presence of ions; on their total concentration, mobility, and

valence; and on the temperature of measurement. Solutions of most inorganic compounds are relatively good conductors. Conversely, molecules of organic compounds that do not dissociate in aqueous solution conduct a current very poorly, if at all.

* Approved by Standard Methods Committee, 1997.
Joint Task Group: 20th Edition—Robert M. Bagdigian (chair), Stephen W. Johnson, William F. Koch, Russell W. Lane, Misha Plam.

TABLE 2510:I. EQUIVALENT CONDUCTIVITY, Λ , AND CONDUCTIVITY, k , OF POTASSIUM CHLORIDE AT 25.0°C.*²⁻⁴

KCl Concentration <i>M or equivalent/L</i>	Equivalent Conductivity, Λ <i>mho-cm²/equivalent</i>	Conductivity, k_s <i>μmho/cm</i>
0	149.9	
0.0001	148.9	14.9
0.0005	147.7	73.9
0.001	146.9	146.9
0.005	143.6	717.5
0.01	141.2	1 412
0.02	138.2	2 765
0.05	133.3	6 667
0.1	128.9	12 890
0.2	124.0	24 800
0.5	117.3	58 670
1	111.9	111 900

* Based on the absolute ohm, the 1968 temperature standard, and the dm³ volume standard.² Values are accurate to $\pm 0.1\%$ or 0.1 μ mho/cm, whichever is greater.

1. Definitions and Units of Expression

Conductance, G , is defined as the reciprocal of resistance, R :

$$G = \frac{1}{R}$$

where the unit of R is ohm and G is ohm⁻¹ (sometimes written mho). Conductance of a solution is measured between two spatially fixed and chemically inert electrodes. To avoid polarization at the electrode surfaces the conductance measurement is made with an alternating current signal.¹ The conductance of a solution, G , is directly proportional to the electrode surface area, A , cm², and inversely proportional to the distance between the electrodes, L , cm. The constant of proportionality, k , such that:

$$G = k \left(\frac{A}{L} \right)$$

is called "conductivity" (preferred to "specific conductance"). It is a characteristic property of the solution between the electrodes. The units of k are 1/ohm-cm or mho per centimeter. Conductivity is customarily reported in micromhos per centimeter (μ mho/cm).

In the International System of Units (SI) the reciprocal of the ohm is the siemens (S) and conductivity is reported as milli-siemens per meter (mS/m); 1 mS/m = 10 μ mhos/cm and 1 μ S/cm = 1 μ mho/cm. To report results in SI units of mS/m divide μ mhos/cm by 10.

To compare conductivities, values of k are reported relative to electrodes with $A = 1$ cm² and $L = 1$ cm. Absolute conductances, G_s , of standard potassium chloride solutions between electrodes of precise geometry have been measured; the corresponding standard conductivities, k_s , are shown in Table 2510:I.

The equivalent conductivity, Λ , of a solution is the conductivity per unit of concentration. As the concentration is decreased toward zero, Λ approaches a constant, designated as Λ° . With k

in units of micromhos per centimeter it is necessary to convert concentration to units of equivalents per cubic centimeter; therefore:

$$\Lambda = 0.001k/\text{concentration}$$

where the units of Λ , k , and concentration are mho-cm²/equivalent, μ mho/cm, and equivalent/L, respectively. Equivalent conductivity, Λ , values for several concentrations of KCl are listed in Table 2510:I. In practice, solutions of KCl more dilute than 0.001M will not maintain stable conductivities because of absorption of atmospheric CO₂. Protect these dilute solutions from the atmosphere.

2. Measurement

a. Instrumental measurements: In the laboratory, conductance, G_s , (or resistance) of a standard KCl solution is measured and from the corresponding conductivity, k_s , (Table 2510:I) a cell constant, C , cm⁻¹, is calculated:

$$C = \frac{k_s}{G_s}$$

Most conductivity meters do not display the actual solution conductance, G , or resistance, R ; rather, they generally have a dial that permits the user to adjust the internal cell constant to match the conductivity, k_s , of a standard. Once the cell constant has been determined, or set, the conductivity of an unknown solution,

$$k_u = CG_u$$

will be displayed by the meter.

Distilled water produced in a laboratory generally has a conductivity in the range 0.5 to 3 μ mhos/cm. The conductivity increases shortly after exposure to both air and the water container.

The conductivity of potable waters in the United States ranges generally from 50 to 1500 μ mhos/cm. The conductivity of domestic wastewaters may be near that of the local water supply, although some industrial wastes have conductivities above 10 000 μ mhos/cm. Conductivity instruments are used in pipelines, channels, flowing streams, and lakes and can be incorporated in multiple-parameter monitoring stations using recorders.

Most problems in obtaining good data with conductivity monitoring equipment are related to electrode fouling and to inadequate sample circulation. Conductivities greater than 10 000 to

TABLE 2510:II. SAMPLE ANALYSIS ILLUSTRATING CALCULATION OF CONDUCTIVITY, k_{calc} , FOR NATURAL WATERS.⁷

Ions	mg/L	mM	$ z \lambda_{\pm}^\circ$ mM	z^2 mM
Ca	55	1.38	164.2	5.52
Mg	12	0.49	52.0	1.96
Na	28	1.22	61.1	1.22
K	3.2	0.08	5.9	0.08
HCO ₃	170	2.79	124.2	2.79
SO ₄	77	0.80	128.0	3.20
Cl	20	0.56	42.8	0.56
			578.2	15.33

50 000 $\mu\text{mho/cm}$ or less than about 10 $\mu\text{mho/cm}$ may be difficult to measure with usual measurement electronics and cell capacitance. Consult the instrument manufacturer's manual or published references.^{1,5,6}

Laboratory conductivity measurements are used to:

- Establish degree of mineralization to assess the effect of the total concentration of ions on chemical equilibria, physiological effect on plants or animals, corrosion rates, etc.

- Assess degree of mineralization of distilled and deionized water.

- Evaluate variations in dissolved mineral concentration of raw water or wastewater. Minor seasonal variations found in reservoir waters contrast sharply with the daily fluctuations in some polluted river waters. Wastewater containing significant trade wastes also may show a considerable daily variation.

- Estimate sample size to be used for common chemical determinations and to check results of a chemical analysis.

- Determine amount of ionic reagent needed in certain precipitation and neutralization reactions, the end point being denoted by a change in slope of the curve resulting from plotting conductivity against buret readings.

- Estimate total dissolved solids (mg/L) in a sample by multiplying conductivity (in micromhos per centimeter) by an empirical factor. This factor may vary from 0.55 to 0.9, depending on the soluble components of the water and on the temperature of measurement. Relatively high factors may be required for saline or boiler waters, whereas lower factors may apply where considerable hydroxide or free acid is present. Even though sample evaporation results in the change of bicarbonate to carbonate the empirical factor is derived for a comparatively constant water supply by dividing dissolved solids by conductivity.

- Approximate the milliequivalents per liter of either cations or anions in some waters by multiplying conductivity in units of micromhos per centimeter by 0.01.

b. Calculation of conductivity: For naturally occurring waters that contain mostly Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , SO_4^{2-} , and Cl^- and with TDS less than about 2500 mg/L, the following procedure can be used to calculate conductivity from measured ionic concentrations.⁷ The abbreviated water analysis in Table 2510:II illustrates the calculation procedure.

At infinite dilution the contribution to conductivity by different kinds of ions is additive. In general, the relative contribution of each cation and anion is calculated by multiplying equivalent conductances, λ_+° and λ_-° , mho-cm²/equivalent, by concentration in equivalents per liter and correcting units. Table 2510:III contains a short list of equivalent conductances for ions commonly found in natural waters.⁸ Trace concentrations of ions generally make negligible contribution to the overall conductivity. A temperature coefficient of 0.02/deg is applicable to all ions, except H^+ (0.0139/deg) and OH^- (0.018/deg).

At finite concentrations, as opposed to infinite dilution, conductivity per equivalent decreases with increasing concentration (see Table 2510:I). For solutions composed of one anion type and one cation type, e.g., KCl as in Table 2510:I, the decrease in conductivity per equivalent with concentration can be calculated, $\pm 0.1\%$, using an ionic-strength-based theory of Onsager.⁹ When mixed salts are present, as is nearly always the case with natural and wastewaters, the theory is quite complicated.¹⁰ The following semiempirical procedure can be used to calculate conductivity for naturally occurring waters:

TABLE 2510:III. EQUIVALENT CONDUCTANCES, λ_+° AND λ_-° , (MHO-CM²/EQUIVALENT) FOR IONS IN WATER AT 25.0 C.⁸

Cation	λ_+°	Anion	λ_-°
H^+	350	OH^-	198.6
$1/2\text{Ca}^{2+}$	59.5	HCO_3^-	44.5
$1/2\text{Mg}^{2+}$	53.1	$1/2\text{CO}_3^{2-}$	72
Na^+	50.1	$1/2\text{SO}_4^{2-}$	80.0
K^+	73.5	Cl^-	76.4
NH_4^+	73.5	Ac^-	40.9
$1/2\text{Fe}^{2+}$	54	F^-	54.4
$1/3\text{Fe}^{3+}$	68	NO_3^-	71.4
		H_2PO_4^-	33
		$1/2\text{HPO}_4^{2-}$	57

First, calculate infinite dilution conductivity (Table 2510:II, Column 4):

$$k^\circ = \sum |z_i| (\lambda_{+i}^\circ)(mM_i) + \sum |z_i| (\lambda_{-i}^\circ)(mM_i)$$

where:

$|z_i|$ = absolute value of the charge of the i -th ion,
 mM_i = millimolar concentration of the i -th ion, and
 $\lambda_{+i}^\circ, \lambda_{-i}^\circ$ = equivalent conductance of the i -th ion.

If mM is used to express concentration, the product, $(\lambda_{+i}^\circ)(mM_i)$ or $(\lambda_{-i}^\circ)(mM_i)$, corrects the units from liters to cm³. In this case k° is 578.2 $\mu\text{mho/cm}$ (Table 2510:II, Column 4).

Next, calculate ionic strength, IS in molar units:

$$IS = \sum z_i^2 (mM_i) / 2000$$

The ionic strength is $15.33/2000 = 0.00767 M$ (Table 2510:II, Column 5).

Calculate the monovalent ion activity coefficient, γ , using the Davies equation for $IS \leq 0.5 M$ and for temperatures from 20 to 30°C.^{9,11}

$$\gamma = 10^{-0.5[IS^{1/2}/(1 + IS^{1/2}) - 0.3IS]}$$

In the present example $IS = 0.00767 M$ and $\gamma = 0.91$.

Finally, obtain the calculated value of conductivity, k_{calc} , from:

$$k_{\text{calc}} = k^\circ \gamma^2$$

In the example being considered, $k_{\text{calc}} = 578.2 \times 0.91^2 = 478.8 \mu\text{mho/cm}$ versus the reported value as measured by the USGS of 477 $\mu\text{mho/cm}$.

For 39 analyses of naturally occurring waters,^{7,12} conductivities calculated in this manner agreed with the measured values to within 2%.

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2510 B. Laboratory Method

1. General Discussion

See Section 2510A.

2. Apparatus

a. Self-contained conductivity instruments: Use an instrument capable of measuring conductivity with an error not exceeding 1% or 1 $\mu\text{mho/cm}$, whichever is greater.

b. Thermometer, capable of being read to the nearest 0.1°C and covering the range 23 to 27°C. Many conductivity meters are equipped to read an automatic temperature sensor.

c. Conductivity cell:

1) Platinum-electrode type—Conductivity cells containing platinum electrodes are available in either pipet or immersion form. Cell choice depends on expected range of conductivity. Experimentally check instrument by comparing instrumental results with true conductivities of the KCl solutions listed in Table 2510:I. Clean new cells, not already coated and ready for use, with chromic-sulfuric acid cleaning mixture [see Section 2580B.3b2)] and platinize the electrodes before use. Subsequently, clean and replatinize them whenever the readings become erratic, when a sharp end point cannot be obtained, or when inspection shows that any platinum black has flaked off. To platinize, prepare a solution of 1 g chloroplatinic acid, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, and 12 mg lead acetate in 100 mL distilled water. A more concentrated solution reduces the time required to platinize electrodes and may be used when time is a factor, e.g., when the cell constant is 1.0/cm or more. Immerse electrodes in this solution and connect both to the negative terminal of a 1.5-V dry cell battery. Connect positive side of battery to a piece of platinum wire and dip wire into the solution. Use a current such that only a small quantity of gas is evolved. Continue electrolysis until both cell electrodes are coated with platinum black. Save platinizing solution for subsequent use. Rinse electrodes thoroughly and when not in use keep immersed in distilled water.

2) Nonplatinum-electrode type—Use conductivity cells containing electrodes constructed from durable common metals (stainless steel among others) for continuous monitoring and field studies. Calibrate such cells by comparing sample conductivity with results obtained with a laboratory instrument. Use properly designed and mated cell and instrument to minimize errors in cell constant. Very

long meter leads can affect performance of a conductivity meter. Under such circumstances, consult the manufacturer's manual for appropriate correction factors if necessary.

3. Reagents

a. Conductivity water: Any of several methods can be used to prepare reagent-grade water. The methods discussed in Section 1080 are recommended. The conductivity should be small compared to the value being measured.

b. Standard potassium chloride solution, KCl, 0.0100M: Dissolve 745.6 mg anhydrous KCl in conductivity water and dilute to 1000 mL in a class A volumetric flask at 25°C and store in a CO_2 -free atmosphere. This is the standard reference solution, which at 25°C has a conductivity of 1412 $\mu\text{mhos/cm}$. It is satisfactory for most samples when the cell has a constant between 1 and 2 cm^{-1} . For other cell constants, use stronger or weaker KCl solutions listed in Table 2510:I. Care must be taken when using KCl solutions less than 0.001M, which can be unstable because of the influence of carbon dioxide on pure water. For low conductivity standards, Standard Reference Material 3190, with a certified conductivity of 25.0 $\mu\text{S/cm} \pm 0.3 \mu\text{S/cm}$, may be obtained from NIST. Store in a glass-stoppered borosilicate glass bottle.

4. Procedure

a. Determination of cell constant: Rinse conductivity cell with at least three portions of 0.01M KCl solution. Adjust temperature of a fourth portion to $25.0 \pm 0.1^\circ\text{C}$. If a conductivity meter displays resistance, R , ohms, measure resistance of this portion and note temperature. Compute cell constant, C :

$$C, \text{ cm}^{-1} = (0.001412)(R_{KCl})[1 + 0.0191(t - 25)]$$

where:

$$R_{KCl} = \text{measured resistance, ohms, and}$$

$$t = \text{observed temperature, } ^\circ\text{C.}$$

Conductivity meters often indicate conductivity directly. Commercial probes commonly contain a temperature sensor. With such instruments, rinse probe three times with 0.0100M KCl, as above. Adjust temperature compensation dial to 0.0191

C^{-1} . With probe in standard KCl solution, adjust meter to read 1412 $\mu\text{mho/cm}$. This procedure automatically adjusts cell constant internal to the meter.

b. Conductivity measurement: Thoroughly rinse cell with one or more portions of sample. Adjust temperature of a final portion to about 25°C. Measure sample resistance or conductivity and note temperature to $\pm 0.1^\circ\text{C}$.

5. Calculation

The temperature coefficient of most waters is only approximately the same as that of standard KCl solution; the more the temperature of measurement deviates from 25.0°C, the greater the uncertainty in applying the temperature correction. Report temperature-compensated conductivities as “ $\mu\text{mho/cm}$ @ 25.0°C.”

a. When sample resistance is measured, conductivity at 25°C is:

$$k = \frac{(1\,000\,000)(C)}{R_m[1 + 0.0191(t - 25)]}$$

where:

k = conductivity, $\mu\text{mhos/cm}$,

C = cell constant, cm^{-1} ,

R_m = measured resistance of sample, ohms, and

t = temperature of measurement.

b. When sample conductivity is measured without internal temperature compensation conductivity at 25°C is:

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

where:

k_m = measured conductivity in units of $\mu\text{mho/cm}$ at $t^\circ\text{C}$, and other units are defined as above.

For instruments with automatic temperature compensation and readout directly in $\mu\text{mho/cm}$ or similar units, the readout automatically is corrected to 25.0°C. Report displayed conductivity in designated units.

6. Precision and Bias

The precision of commercial conductivity meters is commonly between 0.1 and 1.0%. Reproducibility of 1 to 2% is expected after an instrument has been calibrated with such data as is shown in Table 2510:I.

2520 SALINITY*

2520 A. Introduction

1. General Discussion

Salinity is an important unitless property of industrial and natural waters. It was originally conceived as a measure of the mass of dissolved salts in a given mass of solution. The experimental determination of the salt content by drying and weighing presents some difficulties due to the loss of some components. The only reliable way to determine the true or absolute salinity of a natural water is to make a complete chemical analysis. However, this method is time-consuming and cannot yield the precision necessary for accurate work. Thus, to determine salinity, one normally uses indirect methods involving the measurement of a physical property such as conductivity, density, sound speed, or refractive index. From an empirical relationship of salinity and the physical property determined for a standard solution it is possible to calculate salinity. The resultant salinity is no more accurate than the empirical relationship. The precision of the measurement of a physical property will determine the precision in salinity. Following are the precisions of various physical measurements and the resultant salinity presently attainable with commercial instruments:

Property	Precision of Measurement	Precision of Salinity
Conductivity	± 0.0002	± 0.0002
Density	$\pm 3 \times 10^{-6} \text{ g/cm}^3$	± 0.004
Sound speed	$\pm 0.02 \text{ m/s}$	± 0.01

Although conductivity has the greatest precision, it responds only to ionic solutes. Density, although less precise, responds to all dissolved solutes.

2. Selection of Method

In the past, the salinity of seawater was determined by hydro-metric and argentometric methods, both of which were included in previous editions of *Standard Methods* (see Sections 210B and C, 16th edition). In recent years the conductivity (2520B) and density (2520C) methods have been used because of their high sensitivity and precision. These two methods are recommended for precise field and laboratory work.

3. Quality Assurance

Calibrate salinometer or densimeter against standards of KCl or standard seawater. Expected precision is better than ± 0.01 salinity units with careful analysis and use of bracketing standards.

* Approved by Standard Methods Committee, 2000.