# **Measurement of Electrolytic Conductance**

STACY L. GELHAUS. WILLIAM R. LACOURSE

Department of Chemistry and Biochemistry, University of Maryland, Baltimore County, Baltimore, MD, USA

## I. INTRODUCTION

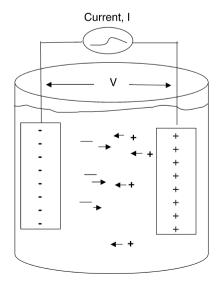
The foundations of conductivity were established throughout the 19th century by four scientist in particular, Alessandro Volta, Georg Ohm, Michael Faraday, and Friedrich Kolrausch. In 1800, Volta invented the first electric battery. The invention of a battery that supplied a continuous electric current paved the way for Georg Ohm who began measuring electric current through metals and in 1837, established Ohm's law. Around the same time Ohm established this law, Faraday was working on the law of electrolysis and determined that aside from electric current being carried by metals, ions in solution could carry a current as well. However, it was not until 1869, that Kolrausch began measuring the conductivity of electrolytes, giving electrolytic conductivity a physical and mathematical basis. All solutions possess some degree of conductivity. The conductance of a solution is an important characteristic for a variety of fields and applications to industry, from measuring the purity of water to monitoring the conditions of processes in the dairy and brewing industries. All along, instrumentation has developed to meet the needs of the new and changing applications. Bench top conductivity meters have been replaced by handheld field devices: nonintrusive electrodeless sensors have been developed, and conductivity cells have been reduced so much in size that they are now able to fit inside microchips or even slide along the outside of capillary tubing.

The two main type of non-faradaic electrochemical analysis can be categorized as potentiometric, discussed in a previous chapter, and conductometric. This chapter will focus on conductometric measurement techniques, specifically those which provide information about the total ionic content of an aqueous solution—the electrolytic conductance. The motion of ions in a solution can be altered by the application of a potential difference between two electrodes immersed in the solution. When a voltage is applied across two platinum electrodes (usually platinized) placed in an electrolytic solution, an electric current will be transferred to an extent that is in accordance with the amount and mobility of free positive and negative ions present in the solution. This characteristic of the solution is nonspecific, a bulk property, and this can be perceived as a drawback in some detection scenarios because measuring conductivity will give the overall solution conductance, not the conductance of each individual analyte. However, there are many situations where the bulk property of conductivity can be useful. One obvious case is in characterizing the purity of potable waters and monitoring the effectiveness of water demineralizers. Conductance can be used effectively to measure the concentration of acids and bases, as it gives a monotonic, though not always linear, conductance-concentration plot over wide concentration ranges. As electrolytes vary with respect to their ability to conduct current, conductance measurements provide a valuable method of analyzing binary mixtures of electrolytes. By measuring conductance, ionic mobilities, diffusion coefficients, and transport numbers can also be determined. Conductometric titrimetry is a useful method for following the course of reactions involving electrolytes. Along with titrimetry, electrode cells and sensors have also been developed both in lab and commercially for the measurement of conductance. Conductance detectors with flowthrough cells are commonly used for the detection of inorganic ions and organic acids following separation by high performance liquid chromatography (HPLC). There are many different types of instrumentation available for conductivity measurement. It is through the principles and theory of conductivity that the reader will obtain an adequate understanding of the available instrumentation and applications of conductivity.

# A. Principles of Conductivity

By applying a rapidly oscillating field ( $>1 \, \text{kHz}$ ) in an electrochemical cell, the mobility of ions in solution, or conductivity can be measured (see Fig. 1). No oxidation or reduction takes place in conductivity detection, but charging and discharging of cell electrodes do occur (LaCourse, 1997). The fundamental measurement used to study conductivity is resistance, R, of the solution. Under the precautions required the earlier experimental description should follow Ohm's law in which

$$R = \frac{\rho l}{A} \tag{1}$$



**Figure 1** The movement of ions in solution under an applied potential. Anions move to the cathode and cations move to the anode.

where resistance, R, equals the resistivity ( $\rho$ ) multiplied by the length (l) between electrodes divided by the area (A) of that geometry between electrodes. The resistivity, also called specific resistance, has the units of ohms/centimeters. For solutions, the area is usually taken as the area of each parallel electrode and the length becomes the distance between them. The conductance of a solution, G, is the inverse of the resistance, R, of the solution; therefore, G = 1/R. As resistance is expressed in ohms ( $\Omega$ ), conductance is expressed in  $\Omega^{-1}$ . The reciprocal ohm used to be called mho, but it is now officially called Siemens, S, and  $1 S = 1\Omega^{-1}$ .

The conductance of a sample is highly dependent on the cross-sectional area and the length between electrodes. The conductance will decrease as *l* increases and increases with cross-sectional area (Atkins, 1998).

$$G = \frac{\kappa A}{I} \tag{2}$$

In the equation above,  $\kappa$ , is the conductivity. The units of  $\kappa$  are S/m. This equation is also the inverse of the resistivity where  $\kappa = 1/\rho = (1/R)(d/A) = G(d/A) = G\theta$ . In this instance,  $\theta$ , is equal to d/A in cm<sup>-1</sup>. As  $\theta$  is a function of the geometry of the electrode and is a cell constant; it is useful in the characterization of cells. When electrode geometry diverges from plane and parallel, the cell constant can be best determined by measuring solutions of known specific conductance ( $\kappa = G\theta$ ). Reference solutions for this purpose have been characterized in cells of known geometry. A number of such solutions are listed in Table 1.

As conductance is determined by the totality of ions present in a solution, largely acting independently of each other, it can be expressed as a summation. The  $\kappa$  can be thought of as the conductance of one cubic centimeter of solution. Suppose 1 cm<sup>3</sup> contains 1 gram-equivalent

**Table 1** Reference Solutions for Calibration of Cell Constants

Approx. molarity	Method of preparation	Temp (°C)	G (μS/cm)
1.0	74.2460 g KCl per L of	0	65,176
	solution at 20°C	18	97,838
		25	111,342
0.1	7.4365 g KCl per L of	0	7,138
	solution at 20°C	18	11,167
		25	12,856
0.01	0.7440 g KCl per L of	0	773.6
	solution at 20°C	18	1,220.5
		25	1,408.8
0.001	Dilute 100 mL of 0.01 M to 1 L at 20°C	25	146.93

Source: ASTM (1992).

of electrolyte. The equivalent conductivity  $\Lambda$  can be written in the following terms:

$$\Lambda = \frac{1000}{c} \kappa \tag{3}$$

The molar concentration is c and the SI units of equivalent conductivity is Siemens meter-squared per mol (S m²/mol). The summation covers all ions of both signs. For some purposes it is desirable to define a molar conductivity, for which the usual symbol is  $\lambda_{\rm m}$ . Typical values for this are  $10~{\rm mS}~{\rm m}^2/{\rm mol}$  where  $1~{\rm mS}=10^{-3}~{\rm S}$ . The  $\lambda_{\rm m}$  is given by the relation

$$\lambda_{\rm m} = \lambda^+ + \lambda^- = \frac{\kappa}{c} \tag{4}$$

The molar conductivity,  $\lambda_{\rm m}$ , is a property of ions (either positive or negative) that gives quantitative information about their relative contributions to the conductance of the solution (Atkins, 1998; Dahmen, 1986). Arrhenius postulated in 1887, that an appreciable amount of electrolyte will dissociate into free ions in solution. This value is to some extent dependent on the total ionic concentration. increasing with increasing dilution. The molar conductivity of an electrolyte would be independent of concentration if  $\kappa$  were proportional to the concentration of the electrolyte (Dahmen, 1986). Unfortunately, the molar conductivity is found to vary with concentration experimentally. A possible reason for this is that the number of ions in the solution might not be proportional to the concentration of the electrolyte. The concentration of ions in a weak acid solution depends on the concentration of the acid in a complicated way and doubling the concentration of acid does not double the number of ions. Secondly, because ions act strongly with one another, the conductivity of the solution is not exactly proportional to the number of ions present. This concentration dependence indicates that there are two possible classes—strong electrolytes and weak electrolytes. The classification of electrolytes into either category depends not only on the solute, but also the solvent (Atkins, 1998).

# B. Strong Electrolytes

Strong electrolytes are substances that completely ionize in solution and include ionic solids (NaCl) and strong acids (HCl). As they completely ionize, the concentration of ions in solution is proportional to the concentration of electrolyte added (Atkins, 1998). In an extensive series of experimentation during the 19th century, Friedrich Kohlrausch showed that at low concentrations the molar conductivities of strong electrolytes vary linearly with the square root of the concentration:

$$\lambda_{\rm m} = \lambda_m^0 - Kc^{1/2} \tag{5}$$

This variation is called Kohlrausch's law (Atkins, 1998). The constant  $\lambda_m^0$  is the limiting molar conductivity, or in other words, the molar conductivity in the limit of zero concentration (when ions are effectively far apart and do not interact with one another). The constant K is found to depend more on the stoichiometry of the electrolyte (MA or  $M_2A$ ) rather than on its specific identity (Atkins, 1998). He was also able to show that  $\lambda_m^0$  can be expressed as the sum of contributions from its individual ions. If the limiting molar conductivity of cations is denoted  $\lambda_+$  and the anions  $\lambda_-$ , then his law of the independent migration of ions states that

$$\lambda_{\rm m}^0 = \nu_+ \lambda_+ + \nu_- \lambda_- \tag{6}$$

where  $\nu_+$  and  $\nu_-$  are the numbers of cations and anions per formula unit of electrolyte.

# C. Weak Electrolytes

Weak electrolytes do not fully ionize in solution and they include Brønsted acids and bases, such as CH<sub>3</sub>OOH and NH<sub>3</sub>. The marked concentration dependence of their molar conductivities arises from the displacement of the equilibrium toward products at low molar concentrations.

$$HA(aq) + H_2O(l)H_3O^+(aq) + A^-(aq)K_a$$

$$=\frac{a(\mathrm{H}_3\mathrm{O}^+)a(\mathrm{A}^-)}{a(\mathrm{HA})}$$

A weak electrolyte has a molar conductivity, which is normal at concentrations close to zero, but then falls drastically to low values as the concentration increases (Atkins, 1998). When Kolrausch plotted weak electrolyte conductivity vs. the square root of concentration graph was tangential. The conductivity depends on the number of ions in the solution, and therefore, on the degree of ionization,  $\alpha$ , of the electrolyte. Equivalent conductivity reaches a limiting value for infinite dilution (see Table 2).

$$\lambda_0 = \lambda_0^+ + \lambda_0^- \tag{7}$$

The degree of dissociation from conductivity,  $\alpha$ , the activity.

$$\alpha = \frac{\lambda}{\lambda_0} \tag{8}$$

so that

$$\lambda = \alpha \lambda_0 = \alpha (\lambda_0^+ + \lambda_0^-)$$

This was also derived by Arrhenius and is similar to Ostwald's dissociation of a weak acid (Dahmen, 1986).

$$K = \frac{[H+][A-]}{[HA]} = \frac{\alpha^2 c}{1-\alpha}$$
 or  $K = \frac{\alpha^2}{(1-\alpha)V}$ 

For 1 equivalent of HA in c = 1/V.

Cations <sup>a</sup>	$\Lambda_0$	Temp. coeff.b	Anions (a)	$\Lambda_0$	Temp. coeff.b
$H^+$	349.8	0.0139	OH <sup>-</sup>	109.6	0.018
$Co(NH_3)_6^{3+}$	102.3	_	$Fe(CN)_6^{4-}$	110.5	0.02
$K^+$	73.5	0.0193	$Fe(CN)_6^{3-}$	101.0	_
$NH_4^+$	73.5	0.019	$Co(CN)_6^{3-}$	98.9	
$Pb_2^+$	69.46	0.02	$SO_4^{2-}$	80.0	0.022
La <sub>3</sub> <sup>+</sup>	69.6	0.023	$\mathrm{Br}^-$	78.14	0.0198
Fe <sub>3</sub> <sup>+</sup>	68.0	_	$I^-$	76.8	0.197
$\mathrm{Ba}_2^+$	63.64	0.023	Cl <sup>-</sup>	76.4	0.0202
$Ag^+$	61.9	0.021	$C_2O_4^{2-}$	74.2	0.02
Ca <sub>2</sub> <sup>+</sup>	59.5	0.0230	$NO_3^-$	71.42	0.020
$Cu_2^+$	53.6	0.02	$CO_3^{2-}$	69.3	0.02
$Fe_2^+$	54.0	_	$ClO_4^-$	67.3	0.020
$Mg_2^+$	53.06	0.022	$HCO_3^-$	44.5	_
$Zn_2^+$	52.8	0.02	$\mathrm{CH_3CO}_2^-$	40.9	0.022
Na <sup>+</sup>	50.11	0.0220	$HC_2O_4^-$	40.2	_
Li <sup>+</sup>	33.69	0.0235	$C_6H_5CO_2^-$	32.4	0.023
$(n\text{-Bu})_4\text{N}^+$	19.5	0.02	Picrate <sup>-</sup>	30.4	0.025

**Table 2** Equivalent Ionic Conductivity of Selected Ions at Infinite Dilution in  $S^*cm^{2*}mol$  at  $25^{\circ}C$ 

The degree of ionization is defined so that, for the acid HA at molar concentration, c, at equilibrium

$$[H_3O^+] = \alpha c \quad [A^-] = \alpha c \quad [HA] = (1 - \alpha)c$$

If we ignore activity coefficients, the acidity constant,  $K_a$ , is approximately

$$K_{\rm a} = \frac{\alpha^2 c}{1 - \alpha} \tag{9}$$

from which follows that

$$\alpha = K_{\rm a} \left[ \frac{(1+4c)^{1/2}}{K_{\rm a}} - 1 \right] \tag{10}$$

The electrolyte is fully ionized at infinite dilution, and its molar conductivity is then  $\lambda_m^0$  (Dahmen, 1986). As only a fraction of  $\alpha$  is actually present as ions in the actual solution, the measured molar conductivity  $\lambda_m$  is given by Robinson and Stokes (1959) to Table 3:

$$\lambda_{\rm m} = \alpha \lambda_{\rm m}^0 \tag{11}$$

#### D. Ion Mobility and Transport

To interpret conductivity measurements, it is useful to know why ions move at different rates, why they have different molar conductivities, and why the molar conductivities of strong electrolytes decrease with the square root of the molar concentration. The motion of ions in solution is largely random; however, the presence of an electric field does bias this movement causing the ions to undergo net migration through solution (Brett and Brett, 1993). The current, I, that passes between two parallel electrodes is related to the flux or charge, j, and to the potential difference between them,  $\Delta \emptyset$ , by

$$I = jA = \kappa \frac{\Delta \emptyset A}{I} = \kappa EA \tag{12}$$

**Table 3** Mobilities of Some Ions in Water at Infinite Dilution

Cations	$10^{-4}~\mu/cm^2~s~V$	Anions	$10^{-4}  \mu/cm^2  s  V$
$\overline{\mathrm{H^+}}$	36.2	OH <sup>-</sup>	20.6
Li <sup>+</sup>	4.0	$\mathbf{F}^-$	5.7
Na <sup>+</sup>	5.2	$Cl^-$	7.9
$K^+$	7.6	$\mathrm{Br}^-$	8.1
$Rb^+$	8.1	$I^-$	8.0
Cs <sup>+</sup>	8.0	$NO_3^-$	7.4
$NH_4^+$	7.6	$ClO_4^-$	7.0
$Mg_2^+$	11.0	$SO_4^{2-}$	8.3
$Ca_2^+$	6.2	$CO_3^{2-}$	7.5
$Cu_2^+$	5.6		
$Zn_2^+$	5.5		
-			

Source: Brett and Brett (1993).

<sup>&</sup>lt;sup>a</sup>For ions of charge z, the figures given are on an equivalent basis, so that they apply to the fraction (1/z) of a mole.

<sup>&</sup>lt;sup>b</sup>The temperature coefficient, when known, is given as  $(1/\lambda_0)(d\lambda_0/dT)$  with units of K<sup>-1</sup>. *Source*: Frankenthal (1963).

The ions in the solution between them experience a uniform electric field of magnitude

$$E = \frac{\Delta \emptyset}{I} \tag{13}$$

For each ion

$$\kappa_i = z_i c_i u_i F \tag{14}$$

In such a field, an ion of charge ze experiences a force of magnitude

$$F = zeE = ze\frac{\Delta\emptyset}{l} \tag{15}$$

A cation responds to the application of the field by accelerating toward the negative electrode and an anion responds by accelerating toward the positive electrode. As the ion moves through, the solvent experiences a frictional retarding force,  $F_{\rm fric}$ , proportional to its speed (Brett and Brett, 1993). The two forces act in opposite directions, and the ions reach a terminal speed, the drift speed (s), when accelerating force is balanced by the viscous drag. The net force is zero when

$$s = \frac{zeE}{f} \tag{16}$$

Because the drift speed governs the rate at which charge is transported, we might expect the conductivity to decrease with increasing solution viscosity and ion size.

Molar conductivity

$$\lambda_{\text{mi}} = \frac{\kappa_i}{c_i} = z_i u_i F \tag{17}$$

and the equivalent conductivity

$$\Lambda_{\rm m} = \sum \lambda_i = \sum \frac{\kappa_i}{c_i} \tag{18}$$

Unfortunately this measurement is not species selective and individual ionic conductance can only be calculated if conductance or mobility of one ion is known.

In electric fields of high intensity (order of 100 kV/cm) the conductivity increases with field strength. This is experimentally true for large bulky ions, but not for small ones. Strong electrolytes move without a solvent sheath as relaxation time for the ionic atmosphere becomes too large; a limiting current is reached as field strength is increased. The molar conductivities for alkali metals increase from Li<sup>+</sup> to Cs<sup>+</sup> even though atomic radii increase. This is due to the fact that smaller ions have stronger electric fields; therefore, they are able to solvate more extensively, giving them a larger hydrodynamic radius. This increase is inversely proportional to the atomic number of alkali metals. Stoke's law states that there is a decrease of size in that order for entire ionic moiety as it is moved by electric driving force because

of the decreasing degree of hydration of alkali metal ions (Dahmen, 1986). However, weak electrolytes in the electric field interact with dipoles of undissociated molecules, increasing the dissociation constant. H<sub>3</sub>O<sup>+</sup> and  $\bar{\ }$ OH have exceptionally high mobilities. This is caused by the proton transfer between neighboring H<sub>2</sub>O molecules and is confirmed by the special properties of acids and bases. The mobility of Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> is nearly equal to that of K<sup>+</sup>. Diffusion potentials are avoided in cells when these combinations of salt bridges are employed (Dahmen, 1986). Relaxation mobility and the diffusion coefficient are related by the chemical potential.

$$\mu_i = \mu_i^{\theta} + RT \ln c_i \tag{19}$$

One can also differentiate with respect to distance

$$\left(\frac{\partial \mu_i}{\partial x}\right)_{P,T} = \frac{RT}{c_i} \left(\frac{\partial c_i}{\partial x}\right)_{P,T} \tag{20}$$

and the diffuse force felt by the particle is

$$F = -\left(\frac{\partial \mu_i}{\partial x}\right)_{P,T} = \frac{RT}{c_i} \left(\frac{\partial c_i}{\partial x}\right)_{P,T} \tag{21}$$

The number of flux ions, i,  $J_i$ , is

$$J_i = \frac{j_i}{z_i e} = c_i \mu_i E \tag{22}$$

Substituting for electric field intensity, E

$$J_i = \frac{\mu_i RT}{z_i F} \left(\frac{\partial \mu_i}{\partial x}\right)_{P,T} \tag{23}$$

A comparison with Fick's law shows that

$$D_i = \frac{\mu_i RT}{z_i F} \tag{24}$$

This is the Einstein relation and shows the direct proportionality between the diffusion coefficient and mobility. The relation between conductivity and diffusion coefficient can be seen in the Nernst–Einstein relation and is easily derived from

$$\lambda_i = \frac{z_i^2 F^2 D^2}{RT} \tag{25}$$

This permits the estimation of diffusion coefficients from the conductivity measurements (Brett and Brett, 1993).

The transport number  $t_{\pm}$  is defined as the fraction of total current carried by the ions of a specified type. For a solution with two kinds of ion, the transport numbers of

the cations  $(t_{+})$  and anions  $(t_{-})$  are

$$t_{\pm} = \frac{I_{\pm}}{I} \tag{26}$$

where  $I_{\pm}$  is the current carried by the cation  $(I_{+})$  or anion  $(I_{-})$  and I is the total current through the solution. It follows that the sum of total current of anions and cations must be equal to 1 (Atkins, 1998). The limiting transport number  $t_{\pm}^{0}$  is defined in the same way, but for the limit of zero concentration of the electrolyte solution. The current that can be ascribed to each type of ion is related to the mobility of the ion by the following equation:

$$t_{\pm}^{0} = \frac{z_{+}v_{+}u_{+}}{z_{+}v_{+}u_{+} + z_{-}v_{-}u_{-}}$$
 (27)

Because the ionic conductivities are related to the mobilities, it follows that

$$t_0^+ = \frac{\lambda_0^+}{\lambda_0}$$
 and  $t_0^- = \frac{\lambda^-}{\lambda_0}$  (28)

The transport number varies with ionic constitution of solution and is another way of expressing conductivities or mobilities. The transport number for each ion at infinite solution was determined by Hittorf (1854–1859). Another method for determining mobilities from  $\Lambda+/\Lambda-$  ratio can be calculated on the basis of absolute velocities of ions under the influence of a potential gradient. The idea was postulated by Lodge in 1886, and the experiments were performed by Masson in 1899 (Dahmen, 1986).

Much information pertaining to ionic equilibria can be obtained from conductometric data, particularly in situations where ions tend to be removed from solution by an equilibrium process. This applies, for example, to the combination of anions with hydrogen cations to form partially dissociated molecular acids, to the formation of complexes between metallic cations and various ligands, and to the formation of sparingly soluble salts. Thus the measurement of conductance can lead to the establishment of acidic and basic dissociation constants, stability constants, and solubility product constants. Further details of theory can be found in any modern text on physical chemistry or in a textbook on electrochemistry.

# II. INSTRUMENTATION

There are two general types of devices for measuring conductance. The first, and most widely used, employs a pair of contacting electrodes, frequently platinum, immersed in the test liquid. The second type of instrumentation is noncontacting or "electrodeless" and depends on inductive or capacitive effects to measure conductance. The remainder of this chapter is divided into two parts, which will include

the description of each type of instrumentation, commercial examples of each, and examples of applications.

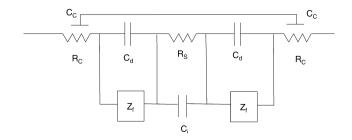
#### A. Immersed Electrode Measurements

#### 1. Conductivity Cells

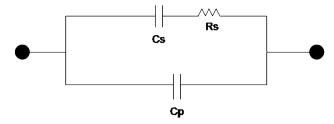
The conductivity cell can be represented schematically by the equivalent circuit shown in Fig. 2. Most measurements are made using two electrodes with the same geometric surface area, hence the same cell constant,  $\theta$ . The distance between the electrodes, the area, is also a known dimension.

The capacitance and resistance of the cell connectors and the contacts they make are shown as  $C_{\rm C}$  and  $R_{\rm C}$ , respectively. As the electrodes are assumed to be identical, the double-layer capacitances,  $C_{\rm d}$ , of the two electrodes are assumed to be equal. The ohmic resistance of the solution between the electrode surfaces is  $R_{\rm S}$ . An interelectrode capacitance term,  $C_{\rm I}$ , is included to account for the dielectric properties of the bulk solvent. And lastly, a frequency dependent faradaic impedance,  $Z_{\rm f}$ , which includes both charge-transfer resistance and Warburg impedance, is shown for each electrode (Coury, 1999).

When making low impedance connections to the cell, it is usually valid to ignore the contribution of  $C_{\rm C}$  and  $R_{\rm C}$ . Also, the complications imposed by Faradaic impedance can be minimized through experimental design. Conductance measurements are often made by applying an AC potential and then measuring the current. At high frequencies, the branch of the circuit containing  $Z_f$  can be neglected as it varies as the reciprocal of the square root of frequency. The circuit in Fig. 2 can be simplified to the circuit seen below in Fig. 3. In this diagram,  $C_p$  and  $C_{\rm S}$  represent the combined parallel and series capacitances, respectively.  $R_s$  is the ohmic resistance of the solution between the electrodes (Coury, 1999). If an AC potential is applied, alternating current will flow through  $R_{\rm s}$  and at the same time through  $C_{\rm p}$ . If  $C_{\rm p}$  can be kept small, the effect of  $R_s$  can be studied by itself. In practice,



**Figure 2** The electronic equivalent to a conductivity cell circuit. [Redrawn from Coury (1999).]



**Figure 3** The simplified version of the conductivity cell circuit shown in Fig. 2. [Redrawn from Coury (1999).]

the double-layer capacitances can be increased substantially by platinization, which greatly increases the effective surface area of the electrodes. Then  $C_{\rm p}$  becomes significant only with solutions of high resistance (low conductance), when large electrodes close together must be selected in order to keep the measurement within range. Hence, most commercial instruments for measuring electrolytic conductance operate on AC. Some use the 60 or 50 Hz power-line frequency for convenience; however, higher frequencies favor low impedance for double-layer capacitances; therefore, many instruments include built-in oscillators to provide excitation (typically) 1 or 2 kHz at 5 V (RMS). The most common contacting electrodes used to measure conductivity have two- or four-electrode cells.

#### Two-Electrode Cells

Figure 4 shows a simplified drawing of a two-electrode conductivity cell. Certain cells are primarily intended for precision physicochemical measurements, whereas others are more convenient for routine use or for titrimetry. For precise work, cells should be held at a constant temperature, as the conductance of most electrolytic solutions increases at the rate of about 2% per Kelvin (see Table 2). Cells are made with various cell constants, of which 1.0 and 0.1 are the most widely useful. Table 4 indicates the cell constants appropriate for various ranges of conductance (ASTM, 1992).

**Table 4** Recommended Cell Constants for Various Conductance Ranges

Conductance range (µS/cm)	Cell constant (cm <sup>-1</sup> )
0.05-20	0.01
1-200	0.1
10-2000	1.0
100-20,000	10.0
1000-200,000	50.0

Source: ASTM (1992).

The electrodes are usually fabricated from platinum, though graphite, titanium, and tungsten are also occasionally used. Platinum electrodes are best coated with a finely divided form of the metal, known as platinum black. This coating can be produced *in situ* by a few minutes of electrolysis in a solution of chloroplatinic acid containing a small amount of lead acetate. The electrolysis should be repeated with reversed polarity. After platinizing, the electrodes should be stored in distilled water.

#### Four-Electrode Cells

The innovative design of the four-electrode for contacting conductivity cells reduces the problem of polarization error and fouling. The technique using these cells, illustrated in Fig. 5, minimizes the effect of resistive electrode coatings caused by solution contaminants.

The current-carrying outer electrodes function similarly to the two-electrode cell in which the measured resistance depends not only on the solution but also the resistance of any coatings that might develop on the electrodes. Ohm's law is given for this situation by

$$V = I(R_{\text{solution}} + R_{\text{coating}}) \tag{29}$$

where V is the voltage across and I the current through the electrodes. Thus, with the two-electrode circuit, the measured resistance (or its reciprocal, conductance) is the sum of the solution and coating resistances. The alternating current is only applied to the outer rings. The

# Electrical Current

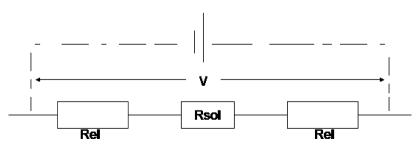
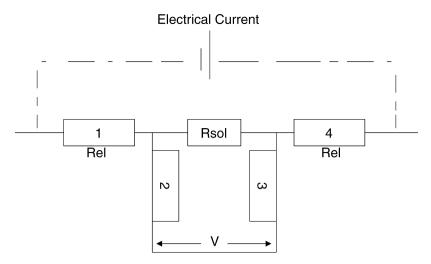


Figure 4 A schematic of a two-electrode conductivity cell (Redrawn from www.radiometer-analytical.com.)



**Figure 5** A schematic of a four-electrode conductivity cell (Redrawn from www.radiometer-analytical.com.)

resistance of the electrode coating does not affect  $E_{\rm VME}$ , the measured voltage between the inner electrodes, because no current is drawn through them. With an independently measured value of the current, I, through the current-carrying electrodes, the resistance of the solution can be calculated from Eq. (29) and the potentiometrically measured voltage:

$$R_{\text{solution}} = \frac{E_{\text{VME}}}{I} \tag{30}$$

It is essential for both two- and four-electrode cells, that the source voltage must be from an alternating-current supply, as direct current could cause unwanted electrochemical reactions and polarization at the electrodes. Table 5 lists

the advantages and disadvantages of the two- and fourelectrode cells (www.radiometer-analytical.com).

# 2. Circuitry

The traditional circuit for measuring resistance is the Wheatstone bridge (Fig. 6). The bridge circuit consists of four resistors, an AC voltage source, and a detector. This circuit is well adapted to static measurements, but as the bridge must be balanced to give a reading, it is not readily applicable to continuous measurements. The Wheatstone bridge circuit is used to measure medium resistance values (1  $\Omega$  to 1 M $\Omega$ ). However, the two-ganged multiple-point switch shown selects between several ranges (only two are shown, but there may be more).

 Table 5
 Advantages and Disadvantages of Two- and Four-Electrode Cells

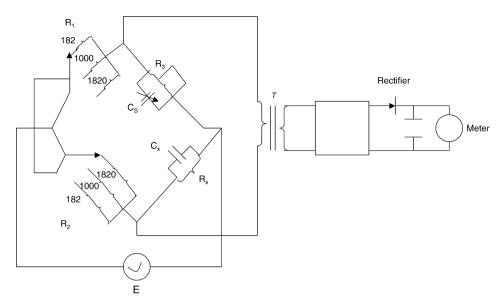
Advantages Disadvantages Two-Electrode Cell Easy to maintain Field effects cell must be positioned in the center of the measuring vessel Use with sample changer (no carryover) Only cells with no bridge between the plates Polarization in high conductivity samples **Economical** Calibrate using a standard with a value close to the measuring Recommended for viscous media or samples with value, measurement accurate over two decades suspension Four-Electrode Cell Linear over a very large conductivity range Unsuitable for micro samples, depth of immersion 3-4 cm Calibration and measurement in different ranges Unsuitable for use with a sample changer Flowthrough or immersion type cells

is compensated

Source: Coury (1999).

Ideal for high conductivity measurements

Can be used for low conductivity measurements if cell capacitance



**Figure 6** An AC Wheatstone bridge for measuring conductance. The two-pole and three-pole position switch permits choice of 0.1, 1.0, or 10 as ratios multiplying the readings of the variable resistor,  $R_3$ . [From Braunstein and Robbins (1971).]

In commercial models, accuracies on the order of  $\pm 0.1\%$  are possible (Nilsson and Riedel, 2001). At balance, when the meter shows a null, it is easily demonstrated that the resistance of the test cell is given by

$$R_x = \frac{R_1 R_3}{R_2} \tag{31}$$

or the conductance by

$$L_{x} = \frac{R_2}{R_1 R_3} \tag{32}$$

Note that  $R_3$  is a calibrated variable resistor or a bank of decade resistors, so that its reading a balance, multiplied by the  $R_1/R_2$  ratio, gives the resistance of the test cell directly. In some bridges a switch is included to interchange the positions of  $R_x$  and  $R_2$ , which permits a dial reading (on  $R_3$ ) directly proportional to conductance rather than resistance:

$$L_{x} = \frac{R_3}{R_1 R_2} \tag{33}$$

For precise results, it is necessary to include a small variable capacitor to cancel the effects of the cell capacitance, as without this the balance point of the bridge would not be sufficiently sharp. A detailed discussion of the capacitive effect has been published (Braunstein and Robbins, 1971). A number of electronic circuits have been developed to give an output voltage proportional to the conductance of a sample without the need for balancing a bridge. Such an instrument is needed for continuous monitoring of flow streams; such an example would be the output of a detector for liquid chromatography. If is also useful for

conductometric titrimetry with constant inflow or reagent, the voltage signal being displayed against time on chart recorder or computer (Ahmon, 1977; Daum and Nelson, 1973; Muha, 1977). A self-balancing bridge controlled by a microcomputer has been reported (Kiggen and Laumen, 1981).

#### 3. Commercial Instruments

Commercial instruments for the measurement of conductance come in the form of meters, probes, and sensors. The majority of instruments in today's market for the measurement of electrolytic conductance are self-contained electronic units provided with digital readout. Top-of-theline instruments include a temperature-sensing probe and automatic temperature compensation based on a range of value of the temperature coefficient. They may also have an option of displaying the temperature of the solution. Provision is usually made for entering the cell constant pertaining to the cell in use, so that the displayed readings are directly expressible in terms of Siemens per centimeter. Some instruments offer a selection of operating frequencies, with lower frequencies for solutions of low conductivity, where cell constants are low (0.1 cm<sup>-1</sup>, e.g.) requiring higher interelectrode capacitance.

## 4. Applications

One of the most common applications of conductivity is the measurement of ions in water sources. Figure 7 shows specific conductances for a number of materials.

Water itself is a very poor conductor; its specific conductance due to dissociation into  $H_3O^+$  and  $OH^-$  ions is

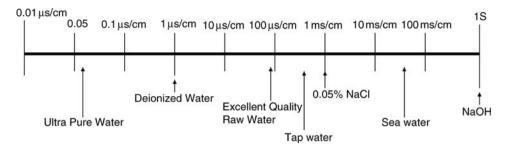


Figure 7 Specific conductance ranges for some typical solutions. [Compiled from Ewing (1985) and www.analyzer.com.]

0.055 µS/cm at 25°C (Light, 1997; Morash, et al., 1994; Thornton and Light, 1989) Water of this theoretical purity can be produced using commercially available nuclear-grade ion-exchange resins. It is used extensively in the semiconductor, power, and pharmaceutical industries. The conductivity measurement is extremely sensitive to traces of ionic impurities. The presence of 1 ppb (1  $\mu$ g/L) of sodium chloride will increase the conductivity by 4% from 0.0550 to 0.0571 µS/cm at 25°C. The resistivity, which is the unit more commonly used for measurement of ultrapure water, will correspondingly decrease from 18.2 to 17.5 M $\Omega$ /cm at 25°C. Ordinary distilled or deionized water with a conductivity of about 1 μS/cm falls far short of this purity. The conductivity and resistivity of ultrapure water over the range of 0-100°C are shown in Table 6 (Light, 1997; Morash, et al., 1994; Thornton and Light, 1989). Table 7 gives the conductivity of different types of water at 25°C (www.topac.com/conductivityprobes.html).

Water purification equipment is often provided with conductance monitors that can be configured to shut down a still or initiate regeneration of the ion-exchange bed of a demineralizer if the conductance becomes too high.

Quantitative analysis for many common acids, bases, and salts may be carried out rapidly by conductivity measurements as well. Table 8 is an extensive compilation of equivalent conductivities over the range of commonly useful concentrations (MacInnes, 1951).

**Table 6** Conductivity and Resistivity of Theoretically Pure Water

Temperature $(^{\circ}C)$	Conductivity $(\mu S/cm)$	Resistivity $(M\Omega/cm)$
0	0.01162	86.09
25	0.0550	18.18
50	0.1708	5.855
75	0.4010	2.494
100	0.7768	1.287

Source: Light (1997), Morash et al. (1994), Thornton and Light (1989).

This table used in conjunction with  $\kappa = G\theta$  and Eq. (3), permits accurate calculation of concentration of many of the most common binary electrolyte solutions. Solutions of strong electrolytes show a nearly linear increase of conductance with concentration up to about 10% or 20% by weight. At higher concentrations the conductance decreases again, due to such interactions as complexation reactions, formation of dimers or higher polymers, or increased viscosity. Figure 8 shows the relation between conductance and concentration for a few representative solutes.

Conductance measurements can be useful in following the kinetics of reactions that involve a change in ionic content or mobility. For example, see a report by Queen and Shabaga (1973) on the kinetics of a series of solvolytic reactions. Kiggen and Laumen (1981) have used similar measurements to observe diffusion processes in solution.

#### Conductometric Titrimetry

Conductometric titrimetry is widely applicable for titration reactions involving ions. Figure 9 shows an example of the type of curve that result in the titration of a strong acid with a strong base.

Any type of titration can be carried out conductometrically if a substantial change in conductance takes place before and/or after the equivalence point. Conductometric titration has been used in acid-base, precipitation and complex formation titrations, and displacement titrations.

**Table 7** Conductivity of Different Types of Water at 25°C

Water	μS/cm
Ultrapure water	0.055
Distilled water	0.5 - 5
Rain water	20-100
Mineral water	50-200
River water	250-800
Tap water	100-1500

Source: www.topac.com/conductivitypro bes.html

**Table 8** Equivalent Conductances of Some Electrolytes at 25°C

	Concentration (M)							
Electrolyte	0.0000	0.0005	0.001	0.005	0.01	0.02	0.05	0.10
NaCl	126.45	124.50	123.73	120.65	118.51	115.76	111.06	106.74
KCl	149.86	147.81	146.95	143.55	141.27	138.34	133.37	128.96
LiCl	115.03	113.15	112.4	109.4	107.32	104.65	100.11	95.86
HCl	426.16	422.74	421.36	415.80	412.00	407.24	399.09	391.32
NH <sub>4</sub> Cl	149.7				141.28	138.33	133.29	128.75
KBr	151.9			146.09	143.43	140.48	135.68	131.39
KI	150.3	_	_	144.37	142.18	139.45	134.97	131.11
NaI	126.94	125.36	124.25	121.25	119.24	11.70	112.79	108.78
NaO <sub>2</sub> CCH <sub>3</sub>	91.0	89.2	88.5	85.72	83.76	81.24	76.92	72.80
NaO <sub>2</sub> CCH <sub>2</sub> CH <sub>3</sub>	85.92	84.24	83.54	80.90	79.05	76.63		_
NaO <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>3</sub>	82.70	81.04	80.31	77.58	75.76	73.39	69.32	65.27
KNO <sub>3</sub>	144.96	142.77	141.84	138.48	132.82	132.41	126.31	120.40
KHCO <sub>3</sub>	118.00	116.10	115.34	112.24	110.08	107.22		_
$AgNO_3$	133.36	131.36	130.51	127.20	124.76	121.41	115.24	109.14
NaOH	248	246	245	240	237	233	227	221

Source: MacInnes (1951).

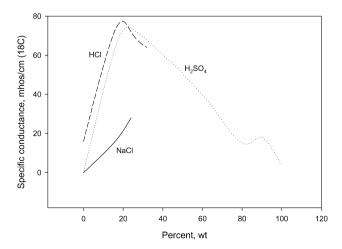
Conductometric titrimetry is rarely used for redox titrations because the needed conditions cannot be met.

The concentration of electrolytes not participating in the titration reaction should be kept small in order to keep the background conductance low and improve sensitivity. Conductance  $(G = \kappa/\theta)$  is usually plotted against the titration parameter  $\lambda$ , the degree of conversion. For the case of strong acids and bases, the plot of G vs.  $\lambda$  shows a plot yielding straight lines of positive and negative slopes. It is where these slopes intersect that is the equivalence point. A different type of plot is obtained when titrating a weak acid with a strong base. The equivalence point on these graphs is sometimes hard to

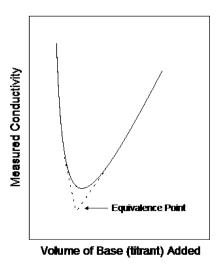
distinguish, especially at low acid concentrations with high pKa values. In these cases the curves lie lower and start to rise at smaller  $\lambda$  value making the inflection point harder to discern (see Fig. 10) (Dahmen, 1986).

# Ion Chromatography

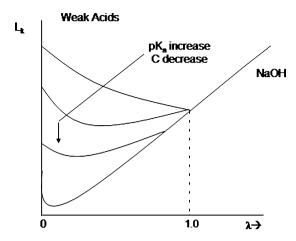
Conductance detectors are routinely used with ionexchange and similar types of chromatography, including ion chromatography (IC). This latter analytical tool has been developed during the last several decades, and has rapidly established for itself a major position in analytical instrumentation. IC can be used for the analysis of



**Figure 8** Conductance vs. concentration for selected electrolytes. [Adapted from Rosenthal (1957).]



**Figure 9** Titration of a strong acid with a strong base. [Adapted from Shugar and Dean (1990).]



**Figure 10** Conductometric titration of weak acids. [Adapted from Dahman (1986).]

chloride, nitrate, sulfate, and hydrogen carbonate in drinking and boiler water; nitrate in food products; fluoride in toothpaste; ammonium, potassium, nitrate, and phosphate in soil and fertilizers; bromide, sulphate, and thiosulphate in fixing baths, and sodium and potassium in body fluids and infusion solutions (Franklin, 1985; Meyer, 1997). Dionex corporation has recently been able to detect perchlorate ions in water as well. As one can see, subsequent development has broadened the application of IC beyond simple anion analysis of inorganic ions. Organic ions, such as acids found in fruit juices (i.e., citric acid) can also be detected (Meyer, 1997). Table 9 lists the four major classes of compounds amenable to IC analysis (Franklin, 1985; Meyer, 1997).

IC is a special form of liquid chromatography (covered in another chapter) and so modern HPLC equipment, with proper accessories, can be used for IC. IC was first reported, by Small et al. (1975). Figure 11 shows, schematically, the arrangement of parts in a typical ion chromatograph.

The unique contribution of these authors was the use of a "suppressor column", which is a second ion-exchange column to react with the ions of the eluent. They also used a sensitive small-volume conductivity cell as a detector to measure only the conducting analyte ions in the sample. Conductivity is a nonspecific measurement and cannot distinguish between the eluent and sample ions. Sensitivities in the  $\mu g/L$  (ppb) range may be achieved. Detection of inorganic ions can be accomplished with either chemical or electronic suppression.

Detection using a chemical suppressor has also been called dual-column chromatography. Figure 12 shows the principle of chemical suppression of background conductivity, which is due to the buffers and other salt solutions used as the mobile phase. Chemical suppression is not always necessary. If the background is low, nonsuppressed IC can be used; however, the limits of detection are usually higher.

The column used for separation is packed with far fewer ionic groups than would be found in an ion-exchange column, allowing for the use of a mobile phase of low ionic strength. Mobile phase conductivity is reduced by the suppressor column, which contains oppositely charged ions. The suppressor column must exchange large amounts of weakly concentrated mobile phase; therefore, a high exchange capacity resin is essential to its function. Because the suppressor column needs to be regenerated from time to time, it is easier to use a hollow-fibre or membrane suppressor. Both allow for suppression, without the need for regeneration (Haddad et al., 2003). A packed fibre may be used to reduce extra column volume. Using these fibers and membranes, gradient elution is possible. Typical ion chromatograms are shown in Fig. 13.

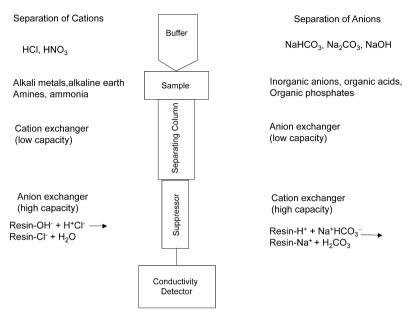
IC with chemical suppression is more sensitive than electronic suppression, but requires more sophisticated equipment.

Conductivity detection with electronic suppression can also be termed single-column IC. A suppressor is not essential if the eluents are carefully chosen to have a low equivalent conductance and sufficient chromatographic strength (i.e., phthalate solutions) and the background

**Table 9** Compounds Amenable to Chromatographic Analysis

Major classes	Examples	Primary detectors
Inorganics	Sulfate, sulfite, thiosulfate, sulfide, nitrate, nitrite, borate, phosphate, hypophosphite, pyrophosphate, tripolysulfate, trimetaphosphate, selenate, selenite, arsenate, arsenite, chlorite, perchlorate, chlorate, hypochlorite, carbonate, cyanide, fluoride, bromide, other halides, potassium, sodium	Conductivity, amperometry
Metals	Alkalis, alkaline earths, gold (I and II), platinum, silver, palladium, iron (II and III), copper, nickel, tin, lead, cobalt, manganese, cadmium, chromium, aluminum	Conductivity, colorimetry
Organics	Organic acids (citric), amines, amino acids, carbohydrates, alcohols, saccharin, sugars, surfactants (anionic or cationic)	Conductivity, amperometry, fluorescence

Source: Franklin (1985) and Meyer (1997).



**Figure 11** Typical ion chromatograph setup. [Adapted from Meyer (1997).]

current is electronically compensated (Haddad et al., 2003). However, the noise is higher than with chemical suppression. Temperature stability also requires attention so as not to change ion mobility. This method is preferred when sensitivity is not an issue because working with the one column simplifies the method (Meyer, 1997). Cation determinations are carried out in a similar manner by using a cation-exchange resin in the separator column. The sample cations are eluted with a strong acid, which in turn is eliminated in the suppressor column by using an anion-exchange resin in the hydroxide form.

Conductivity is the most used detector for IC. A host of improvements have been made in cell design and detector

circuitry, driven by the needs of this new analytical method. These include miniaturization of cell volume, improved electronic suppression and stabilization techniques, and better temperature control and regulation. One of the latest improvements to the ion chromatograph has been the development of reagent-free IC. Solvents used for the mobile phase no longer have to be made because the system runs on deionized water alone. The solvents needed for separation are made by the eluent generator which is coupled to the self-regenerating suppressor. What eluent is generated is dependent upon whether the separation is for anions or cations, KOH and MSA respectively. Along with the reagent-free system, Dionex is continually developing new forms of suppressors such

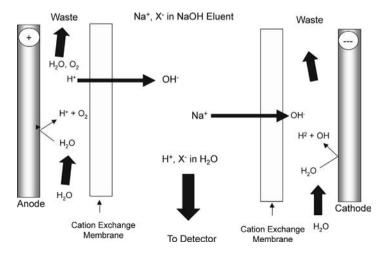


Figure 12 Principles of chemical suppression. [Redrawn from Haddad et al. (2003).]

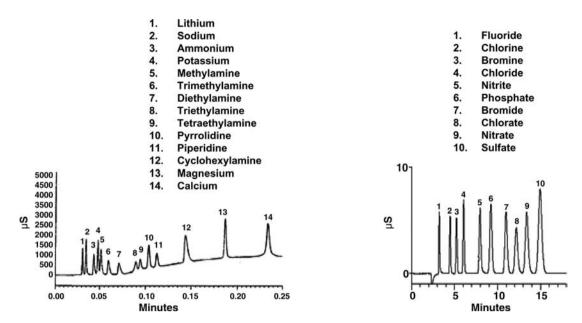


Figure 13 Chromatograms of cation and anion inorganic standards.

as the Atlas Electrolytic Suppressor, The SRS—Ultra Self-Regenerating Suppressor, the MMS III or micromembrane suppressor, and the AMMS-ICE, the anion ion exclusion suppressor. Discussion of these improvements (suppressors) and others pertaining to IC has been presented in several review papers (Haddad et al., 2003; Hatsis and Lucy, 2003; Lopez-Ruiz, 2000; Rabin et al., 1993).

# B. Electrodeless (Noncontacting) Measurements

Conductance measurements can be without physical contact between the solution and any metallic conductors. Information is transferred from the solution to the electronic sensing circuits by electromagnetic induction. Two techniques are available: high frequency AC (radiofrequency) or low frequency.

In the first of these two techniques, the sample cell, made of glass or plastic, is surrounded by two metallic bands cemented onto the glass and separated from each other by a few millimeters. The two bands constitute the two electrodes of a capacitor, with a dielectric of glass. This capacitor is small in terms of microfarads, but offers very low impedance at radiofrequency. This is symbolized (in Fig. 2) by the sum of the double-layer capacitances. The high-frequency current passes easily through these impedances, but at the same time, both series resistances,  $R_{\rm C}$ , become essentially infinite (i.e., open circuit). In this way the resistance of the cell becomes the desired  $R_{\rm s}$ , paralleled by the very small value  $C_{\rm p}$ . This approach, sometimes called oscillometry,

has been treated extensively by Pungor and several instruments have been on the market (Pungor, 1965).

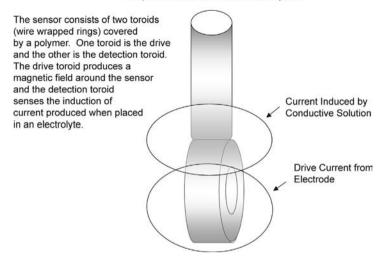
# 1. Cell Design

The low-frequency method (20–50 kHz) of electrodeless conductivity, often called "inductive conductivity" has become popular, especially in chemical processes and industrial solution applications. This system utilizes a probe consisting of two encapsulated toroids in close proximity to each other, as shown in Fig. 14.

One toroid generates an alternating electric field in the solution, whereas the other acts as a receiver to pick up a signal from the field. The transformer core consists of the solution itself. The efficiency with which alternating current is transferred from the primary to the secondary depends on the conductivity of the solution. Several configurations are possible. One form is designed for immersion. The toroids are covered with a chemically resistant fluorocarbon or other high-temperature thermoplastic material. Any precipitates or coatings adhering to this probe generally have little or no effect on the measured conductance. A configuration in which the probe does not come in contact with the solution illustrated in Fig. 15. The unit is installed around a section of nonconducting pipe, such as a capillary in capillary electrophoresis, which contains a solution being separated. A complete liquid loop must exist for this arrangement to work.

In either case, the generating toroid is energized from a stable audiofrequency source, typically 20–50 kHz. The pick-up toroid is connected to a receiver that measures

#### Simplified Electrodeless Conductivity Cell



**Figure 14** Simplified representation of an electrodeless conducutivity measuring circuit. [From Light (1997).]

the current through this secondary winding. The current is then amplified and sent to an analog recorder or to a computer. This current is a direct function of the conductance of the solution in the loop, in a manner completely analogous to the traditional measurement with contacting electrodes (Light and Licht, 1987).

The useful range of commercially available instruments extends from  $0-100 \,\mu\text{S/cm}$  to  $0-2 \,\text{S/cm}$ , with relative accuracy of a few tenths of a percent of full-scale, after

temperature compensation. A temperature sensor is incorporated into the toroid probe, and a compensation circuit corrects all reading to the standard reference temperature of 25°C.

#### 2. Circuitry

The circuitry of a contactless detection system varies from detector to detector. Several different types include the

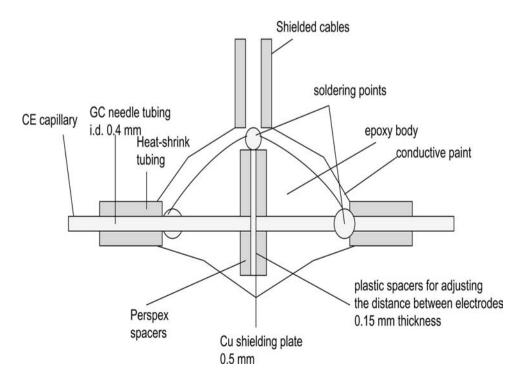


Figure 15 Electrodeless capacitative cell on a CE capillary. [From Macka et al. (2003).]

oscillator-based detector, bridge-based detector, and the single-electrode detector. In the oscillator-based detector, the electrodes are driven by an oscillator with a capacitive coupling to the measurement electrodes. The conductance between the electrodes determines the frequency of oscillation, which is then amplified before the signal is sent out to the processor (Alder et al., 1984; Vairneau et al., 2000). The second circuit design is relatively novel and is being investigated by Treves Brown et al. (2000). Three capacitors are used to isolate two arms of an AC bridge. This circuit for a conductivity cell would be applicable for capillary zone electrophoresis (CZE), isoelectric focusing, miniature flow injection analysis, and also stacking methods such as isotachophoresis (ITP). The last type of circuit, the single-electrode detector, was reported in 1999 (Prest et al., 1999). An electrode measures the potential at a single point in the separation forming a potential divider. Preparation of a device for use with the singleelectrode detector was reported previously (Prest et al., 1999).

#### 3. Commercial Instruments

The electrodeless conductivity technique using low-frequency cells has been known since 1951 (Relis, 1951). Such instruments are manufactured commercially for analysis and control in the chemical process industries such as dairy and fermentation and in other continuous monitoring applications. Contactless detectors have several advantages over contacting such as improved stability, accuracy, and freedom from maintenance. Advancements in design and accuracy have become very important in the development of detectors for capillary electrophoresis (CE) and chip-based separations.

## 4. Applications

Numerous applications of electrodeless conductivity have been published for the chemical, pulp and paper, aluminum, mining, and food industries (Calvert et al., 1958; Fulford, 1985; Gow et al., 1966; Muscow, 1968; Muscow and Ballard, 1984; Ormod, 1978; Queeney and Downey, 1986; Timm et al., 1978). Similar instrumentation has been used for *in situ* measurements of the salinity of seawater (Hinkelmann, 1957). Another application in which contactless conductivity measurements has made a debut is CE.

#### Capillary Electrophoresis

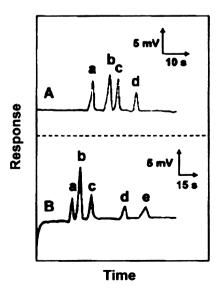
Conductivity detection following separation found a foothold in CE. The traditional contacting conductivity detectors were used originally by direct galvanic contact of the run buffers and sensing electrodes on column or at the end of the capillary. However, the development of more creative contactless detection techniques was to

follow. The contactless detector has several advantages over the contacting mode. There is the absence of passivation and bubble formation associated with the electrode–solution contact, effective isolation from high voltages, a simplified construction and alignment of the detector (even at different locations), and the use of narrower capillaries (Pumera et al., 2002). Contactless detection for conventional CE systems is based on a two-electrode cell with tubular or semitubular electrodes placed over the capillary. Zemann et al. (1998) describe a capacitively coupled conductivity detection system (CCCD). In their design, two cylindrical conducting surfaces are placed around the polyimide coated capillary. The electrodes can be made of conducting silver varnish painted on the capillary or of two syringe cannulas. Figure 16 illustrates the ion separations using CCCD.

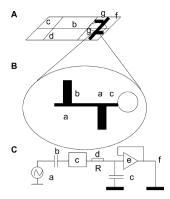
The detector can be placed anywhere along the length of the capillary and it is not necessary to burn a window in the polyimide coating, thus weakening the strength of the capillary (Zemann et al., 1998). Moving away from inorganic ions, several papers have been published recently using contactless conductivity to detect mono- and disaccharides and high voltage contactless conductivity detection of amino acids following separation by CE (Carvalho et al., 2003; Tanyanyiwa et al., 2003). Detection of the carbohydrates was based upon indirect principles; however, the amino acids could be detected directly or indirectly.

# Microchips

The idea of separations and lab on a chip has become very popular. It minimizes costs of solvents, systems, and system components, as well as minimizes time. At



**Figure 16** Electropherograms of cation and anion inorganic standards. [From Macka et al. (2003).]



**Figure 17** Microchip device used for ion separation with contactless conductivity detection. [From Pumera et al. (2002).]

one time, conductivity detection for microchips also relied on a galvanic contact of the run buffer and electrode; however, this technique has also turned toward contactless detection. One type of detector (see Fig. 17) is comprised of two external metallic film electrodes placed on the cover of a plastic such as polymethyl methacrylate.

The low-cost plastic microchips and easily constructed detectors allow for the possibility of designing disposable CE-conductivity microchips (Pumera et al., 2002). Figure 18 displays a diagram of the chip-based separation and detection of inorganic ions.

Wang et al. (2002a, b) has also separated and detected low-explosive ionic components and degradation products from chemical warfare agents using microchip CE-contactless conductivity.

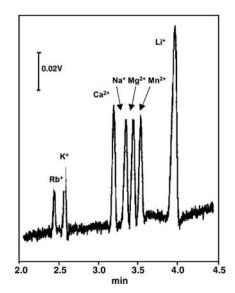
Theoprax has software which uses conductivity measurements to create a pH-spectra. Another company,

JAHM, has developed a database of 2200 materials and 16,000 sets of temperature-dependent data for elastic modulus, including thermal expansion and thermal conductivity to name a few.

#### III. SUMMARY

The theory behind conductivity is well studied and measurements such as resistance, ionic mobility, concentration, and diffusion can be calculated through measuring the conductivity of a solution. Measurement takes place using contacting cells, such as the two- or four-electrode cells, and contactless measurements using toroids. Contacting and contactless cells can take the form of meters, probes, sensors, or flowthrough cell detectors. Table 10 is a limited list of some of the companies and the products and instrumentation they sell for conductivity measurements.

Conductivity measurements are not only important in the lab, but in various industries as well. Applications range from water distillation, titrimetry, dairy and brewing industries, electrochemical reactions, IC, and CE to name a few. Aside from software designed to run the instrumentation for these various applications there is also a small amount of conductivity modeling software available. Most of this modeling software focuses on the assessment of soil and ground water conductivity estimates. Theoprax-Research has designed software that takes analytical conductivity measurements and converts this data into pH-spectra to study the interaction between different molecules in dependence on the degree of dissociation of their functional groups. All of



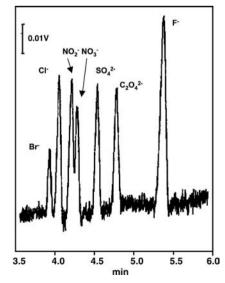


Figure 18 Example of cation and anion chip-based separation. [From Pumera et al. (2002).]

 Table 10
 List of Some Companies and Their Products for Conductivity Measurement

Company and location	Website	Product description	
Aanderaa, Norway	www.aanderaa.com	Submersible conductivity/temperature sensors	
Applied Microsystems, Canada	www.appliedmicrosystems.com	Various conductivity/temperature sensors for underwater measurements	
Topac, USA	www.topac.com	Conductivity, salinity, resistivity, portable and handheld meters, probes, cells, kits	
QA Supplies, USA	www.qasupplies.com	Conductivity testers and meters	
LTH Electronics Ltd, UK	www.lth.co.uk	Contacting and electrodeless conductivity instruments and sensors for measuring food quality in dairy, brewing, and so on	
ESA, USA	www.esainc.com	HPLC and CE instruments and supplies	
Dionex, USA	www.dionex.com	Conductivity detectors, suppressors, ion chromatography systems	
Honeywell, USA	http://content.honeywell.com	Toriodal conductivity cells, analyzers, transmitters for measuring conductivity in electrical utilities, water, pulp and paper, pharmaceuticals, and metal finishing	
Aquarius Tech, Australia	www.aquariustech.com	Conductivity controller, monitor, and data log for automatic dosing and control for commercial and process water treatment	
GLI International, USA	www.gliint.com	Contacting and electrodeless analyzers, transmitters, and sensors	
JUMO, USA	www.jumoprocesscontrol.com	Analytical instruments, transmitters, electrodes, handheld meters, inductive conductivity transmitters, conductivity cells for measuring electrolytic conductivity	
ICM, USA	www.icmmeters.com	Bench top and field conductivity meters	
OI Analytical, USA	www.oico.com	Ion analyzers for flow injection analysis, and segmented flow analysis, electrolytic conductivity detector for GC	
Quadrex Corp., USA	www.quadrexcorp.com	SRI portable GC detectors such as FID/DELCD, NP/DELCD, HID, and TCD	
Foxboro Co., USA	www.foxboro.com	Contacting and electrodeless conductivity analyzers, transmitters and sensors	
Analytical Sensors, Inc. USA	ww.asi-sensors.com	Glass body and epoxy body conductivity sensors, ion selective electrodes	
Unidata America, USA		Precision water conductivity, electrode conductivity	
Yellow Springs Instrument Co., USA		Handheld and bench top instruments	

the instrumentation, software, and applications have one common interest—measurement of the total ionic content of an aqueous solution; hence, the measurement of electrolytic conductance.

# **REFERENCES**

- Ahmon, M. (1977). One-chip conductivity meter monitors salt concentration. *Electronics* 15:132–133.
- Alder, J. F., Fielden, P. R., Clark, A. (1984). Simultaneous conductivity and permittivity detection with a single cell for liquid-chromatography. *Anal. Chem.* 56:985–988.
- ASTM D1125-91. (1992). Standard test methods for electrical conductivity and resistivity of water. *Annual Book of ASTM*

- Standards. Vol. 11.01. American Society for Testing and Materials.
- Atkins, P. W. (1998). Molecules in motion. *Physical Chemistry*. 6th ed. New York: W.H. Freeman and Company, pp. 737–744.
- Braunstein, J., Robbins, J. D. (1971). Electrolytic conductance measurements and capacitive balance. *J. Chem. Educ.* 48:52–59.
- Brett, C. M. A., Brett, A. M. O. (1993). *Electrochemistry Principles, Methods, and Applications*. New York: Oxford Science Publishing, pp. 26–31.
- Calvert, R., Cornelius, J. A., Griffiths, V. S., Stock, D. I. (1958). The determination of the electrical conductivities of some concentrated electrolyte solutions using a transformer bridge. *J. Phys. Chem.* 62:47–53.
- Carvalho, A. Z., da Silva, J. A. F., do Lago, C. (2003). Determination of mono- and disaccharides by capillary

- electrophoresis with contactless conductivity detection. *Electrophoresis* 24:2138–2143.
- Coury, L. (1999). Conductance measurements part 1: theory. *Curr. Separations* 18(3):91–96.
- Dahmen, E. A. M. F. (1986). Non-faradaic methods of electrochemical analysis. *Electroanalysis Theory and Applications in Aqueous and Non-aqueous Media and in Automated Chemical Control*. Techniques and Instrumentation in Analytical Chemistry. Vol. 7. New York: Elsevier, pp. 11–25.
- Daum, P. H., and Nelson, D. F. (1973). Bipolar current method for the determination of solution resistance. *Anal. Chem.* 45:463–470.
- Frankenthal, R. P. (1963). In: Meites, L., ed. *Handbook of Analytical Chemistry*. New York: McGraw-Hill, pp. 5–30.
- Franklin, G. O. (1985). Development an applications of ion chromatography. *Am. Lab.* 17(6):65–80.
- Fulford, G. D. (1985). Use of conductivity techniques to follow Al<sub>2</sub>O<sub>3</sub> extraction at short digestion times. In: Bohner, H. O., ed. *Light Metals*. Warrendale, Pennsylvania: The Metallurgical Society of America, AIME, p. 265.
- Gow, W. A., McCreedy, H. H., Kelly, F. J. (1966). Can. Mining, Metallurgy Bull. July.
- Haddad, P. R., Jackson, P. E., Shaw, M. J. (2003). Developments in suppressor technology for inorganic ion analysis by ion chromatography using conductivity detection. *J. Chromatogr.* A 1000:725–742.
- Hatsis, P., Lucy, C. A. (2003). Improved sensitivity and characterization of high-speed ion chromatography of inorganic ions. *Anal. Chem.* 75:995–1001.
- Hinkelmann, H. (1957). Ein verfahren zur elektrodenlosen messung der elektrischen leitfähigkeit von elektrolyten. Z. Agnew. Phys., Einschl. Nukl. 9:505.
- Kiggen, H. J., Laumen, H. (1981). Self-balancing high precision ac wheatstone bridge for observing diffusion processes in electrolyte solutions. Rev. Sci. Instrum. 52:1761–1764.
- LaCourse, W. R. (1997). Amperometric detection in HPLC. Pulsed Electrochemical Detection in High Performance Liquid Chromatography. Techniques in Analytical Chemistry. New York: John Wiley and Sons, pp. 60–63.
- Light, T. S. (1997). Measurement of electrolytic conductance. Ewing's Analytical Instrumentation Handbook. 2nd ed. Galen Wood Ewing. New York: Marcel Dekker Inc., pp. 1099–1122.
- Light, T. S., Licht, S. L. (1987). Conductivity and resistivity of water from the melting to the critical point. *Anal. Chem.* 59(19):2327-2330.
- Lopez-Ruiz, B. (2000). Advances in the determination of inorganic anions by ion chromatography. *J. Chromatogr. A* 881(1–2):607–621.
- MacInnes, D. A. (1951). *The Principles of Electrochemistry*. New York: Dover, p. 339.
- Macka, M., Hutchinson, J., Zemann, A., Shusheng, Z., Haddad, P. (2003). Miniaturized movable contactless conductivity detection cell for capillary electrophoresis. *Electrophoresis* 24:2144–2149.
- Meyer, V. (1997). Ion chromatography. *Practical High-Performance Liquid Chromatography*. 2nd ed. New York: John Wiley, pp. 190–196.

- Morash, K. R., Thornton, R. D., Saunders, C. C., Bevilacqua, A. C., Light, T. S. (1994). Measurement of the resistivity of highpurity water at elevated temperatures. *Ultrapure Water* 11(9):18.
- Muha, G. M. (1977). A simple conductivity bridge for student use. *J. Chem. Educ.* 54:677.
- Musow, W. (1968). On-line causticity sensor and programmable monitor applied to slaked lime addition and control. Canadian Pulp and Paper Association, Montreal.
- Musow, W., Ballard, A. (1984). Toroidal conductivity sensor technology applied to cyanidation of flotation tailings circuits. Instrument Society of American, 12th Annual Mining and Metallurgy Industries Symposium, Vancouver.
- Nilsson, J. W.; Riedel, S. A. (2001). Simple resistive circuits. *Electric Circuits*. 6th ed. New Jersey: Prentice Hall, pp. 77–78.
- Ormod, G. T. W. (1978). Electrodeless conductivity meters in the measurement and control of the amount of lime in alkaline slurries. NIM-SAIMC Symposium in Metallurgical Process Instrumentation, Nat. Inst. Metallurg., Johannesburg.
- Prest, J. E., Baldock, S. J., Bektas, N., Fielden, P. R., Treves Brown, B. J. (1999). Single electrode conductivity detection for electrophoretic separation systems. *J. Chromatogr. A* 836:59–65.
- Pumera, M., Wang, J., Opekar, F., Jelinek, I., Feldman, J., Lowe, H., Hardt, S. (2002). Contactless conductivity detector for microchip capillary electrophoresis. *Anal. Chem.* 74:1968–1971.
- Pungor, E. (1965). Oscillometry and Conductometry. Oxford: Pergamon.
- Queen, A., Shabaga, R. (1973). A simple automatic conductance bridge for measuring the rates of chemical reactions in solution. *Rev. Sci. Instrum.* 44:494–496.
- Queeney, K. M., Downey, J. E. (1986). Applications of a microprocessor-based electrodeless conductivity monitor. Adv. Instrum. 41(Pt 1):339.
- Rabin, S., Stillian, J., Barreto, V., Friedman, K., Toofan, M. (1993). New membrane-based electrolytic suppressor device for suppressed conductivity detection in ion chromatography. *J. Chromatogr.* 640:97–109.
- Relis, M. J. (1951). Method and apparatus for measuring the electrical conductivity of a solution. U.S. Patent 2,542,057.
- Robinson, R. A., Stokes, R. H. (1959). Electrolyte solutions. London: Butterworth.
- Rosenthal, R. (1957). Electrical conductivity measurements. In: Considine, D. M., ed. *Process Instruments and Controls Handbook*. New York: McGraw-Hill, pp. 6–159.
- Shugar, G. J., Dean, J. A. (1990). *The Chemist's Ready Reference Handbook*. New York: McGraw-Hill, pp. 20.10–20.17.
- Small, H., Stevens, T. S., Bauman, W. C. (1975). Novel ion exchange chromatographic method using conductimetric detection. *Anal. Chem.* 47:1801.
- Tanyanyiwa, J., Schweizer, K., Hauser, P. C. (2003). High-voltage contactless conductivity detection of underivitized amino acids in capillary electrophoresis. *Electrophoresis* 24:2119–2124.
- Thornton, R. D., Light, T. S. (1989). Ultrapure Water 6(5):14.
- Timm, A. R., Liebenberg, E. M., Ormrod, G. T. W., Lombard, S. C. (1978). Nat. Inst. Metallurg., Report 2003, Johannesburg.
- Treves B., B. J., Vairieanu, D.-I., Fielden, P. R. (2000). Conductivity detectors for microscale analytical chemistry. MicroTec Conference, Hanover, Germany, Sept 25–27.

- Vairneau, D.-I., Fielden, P. R., Treves Brown, B. J. (2000). A capacitively coupled conductivity detector for electroseparations. *Meas. Sci. Technol.* 11:244–251.
- Wang, J., Pumera, M., Collins, G. E., Mulchandani, A. (2002a). Measurements of chemical warfare agent degredation products using an electrophoresis microchip with contactless conductivity detector. *Anal. Chem.* 74(23):6121–6125.
- Wang, J., Pumera, M., Collins, G. E., Opekar, F., Jelinek, I. (2002b). A chip based capillary electrophoresis-contactless

conductivity microsystem for fast measurements of low explosive ionic components. *Analyst* 127(6):719–723. www.analyzer.com (accessed August, 2003) www.radiometer-analytical.com (accessed August 2003) www.theoprax-research.com (accessed November, 2003). www.topac.com/conductivityprobes.html (accessed August 2003) Zemann, A. J., Schnell, E., Volgger, D., Bonn, G. K. (1998). Contactless conductivity detection for capillary electrophoresis. *Anal. Chem.* 70:563–567.