# How to Increase the Accuracy of Solution Conductivity Measurements

*Measuring the electrical conductivity of aqueous solutions can provide useful information about the amount of material dissolved in solution, i.e. chemical concentrations. The parameters of this widely used technique are straightforward, but do vary appreciably with the type of chemicals present. An understanding of these variations will enable the conductivity instrument user to obtain greater accuracy and repeatability. This paper will explain the basics of the measurement, discuss the variables, and then suggest methods for use and calibration that will enhance accuracy.*

ELECTRIC CURRENT will readily flow through certain solids and liquids when a voltage difference exists between two points thereon or in. The amount of current that will flow for a given voltage is predicted by Ohm's Law

$$E = IR \qquad \text{Eq.(1)}$$

Where E is the potential difference in volts, I is the current in amps, and R is the resistance to current flow in ohms offered by the conductor.

In metals this current will consist of free electrons moving through the atomic structure. These charge carriers have almost negligible mass and move quite freely. Any limitations on current flow (electrical resistance) are determined by the characteristics of the conducting medium more so than by the carriers themselves.

Electric current will also pass through certain liquids, via a different mechanism. The molecular structure of a liquid is not suitable for free electron movement, and another sort of charged particle must serve this purpose if any current is to flow at all. In solvents that will support conduction, ionization provides the needed carriers.

When most inorganic compounds are dissolved in water, their molecules separate into two equally and oppositely charged parts called ions. Sodium chloride, NaCl, will separate into sodium ions, Na+, and chloride ions, Cl-. When a voltage is applied across a volume of water containing dissolved NaCl, the positive sodium ions will move toward the negative voltage, the negative chloride ions will move toward the positive voltage, and current flow will occur. However, the current carriers in this case have very different characteristics than the electron carriers in metal.

Compared to electrons, ions are huge, and much more limited in number per unit volume. Limitations on current flow will be less due to the resistance of the conducting medium than to the availability of ionic carriers. Since this current controlling factor is an enabler rather than an impedance, measurements of solution current carrying ability are described in terms of conductivity, the opposite of resistivity

$$\text{Conductivity} = 1 \div \text{Resistivity} \qquad \text{Eq.(2)}$$

The unit of resistance is the ohm, and the unit of conductivity is its literal and figurative reciprocal, the mho. Europeans have recently changed the name of the conductivity unit to the siemen. The mho and the siemen are identical, and choice of usage depends on which scientist you care to honor.

Because commonly encountered dilute aqueous solutions have small conductivities, the units are most often expressed as the millionth part, which is micromho or microsiemen. A typical conductivity range for tap water, for instance, is 20 to 1,000 micromhos. The latter figure approaches the edge of comfortable drinkability, as is the case in much of Southern California. Sea water has a conductivity of about 65,000 micromhos (or microsiemens).

Since the primary limiting factor in liquid conductivity is the number of current carriers (ions) that are available, the technique immediately suggests itself as a means to deter-

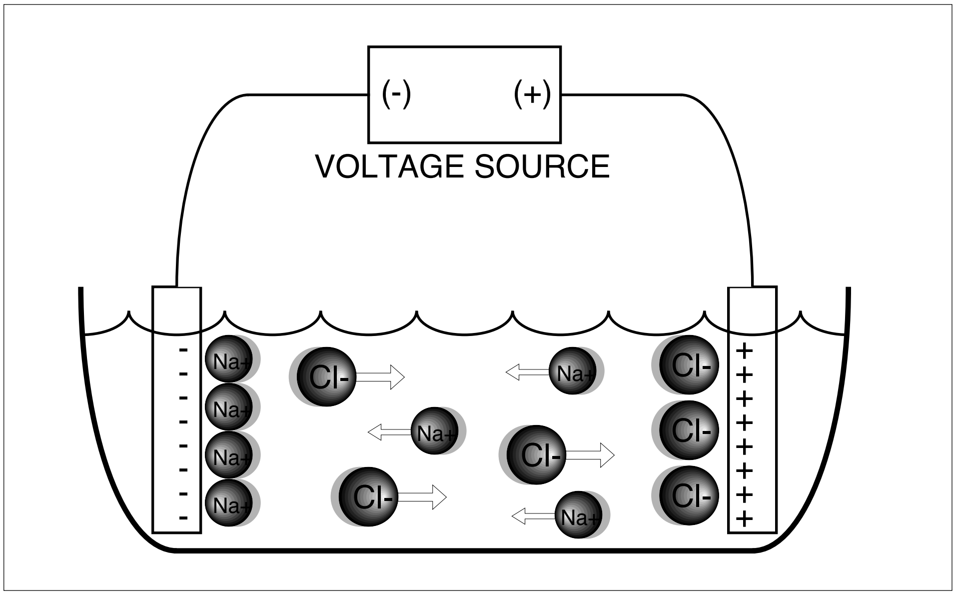


*Fig.(1)* Movement of ions in solution, under influence of applied voltage.

mine chemical concentration levels. That capability in fact makes it one of the most common analytical measurements encountered in water treatment and chemical processes.

The oldest and still most commonly used way to make a conductivity measurement in liquid is to immerse two conducting electrodes in solution, apply a known voltage across them, and measure the current which results. Since the object is to determine the number of ions per unit volume, the volume of fluid being measured must be defined in order to interpret the results accurately. This differs appreciably from the normal usage of resistance measurements.

In the typical case, resistance is measured between two points without regard for either the shape or the volume specific resistivity of the item being measured. This is because interest lies primarily in the item's total effect on current flow in a circuit, and not in determining the electrical properties of its material of construction. Another way of stating this is that the interest is in the measured resistance, not the specific resistivity. The relationship between resistance and specific resistivity is described by

$$R = \rho\ (L / A) \qquad \text{Eq.(3)}$$

Where R is the measured resistance in ohms, $\rho$ is the volume specific resistivity in units of Ω-cm, and the expression in brackets is the defined volume of conducting material. L is the distance between the electrodes in centimeters, and A is the cross sectional area of the uniform conductive path separating them in square centimeters.

When using conductivity for chemical analysis, the term of interest is specific conductivity, which is the inverse of specific resistivity, $\rho$, and is designated as $\kappa$. It is therefore necessary to relate specific conductivity to measured conductivity in a volume defined manner. This can be done by inverting Eq(3) and stating it in terms of $\kappa$

$$(1 / \rho) = \kappa = (1 / R)\ (L / A) \qquad \text{Eq.(4)}$$

The term (1 / R) is the measured conductivity. To convert to specific conductivity, the volume being measured, L/A, must always be considered. This leads to the concept of a probe constant or cell constant. A probe constant of 1 is defined as two electrodes, each 1cm$^2$, located 1cm apart, with all current flow contained within that 1cm$^3$ of fluid between them as shown in Fig.(2). The probe constant is expressed by

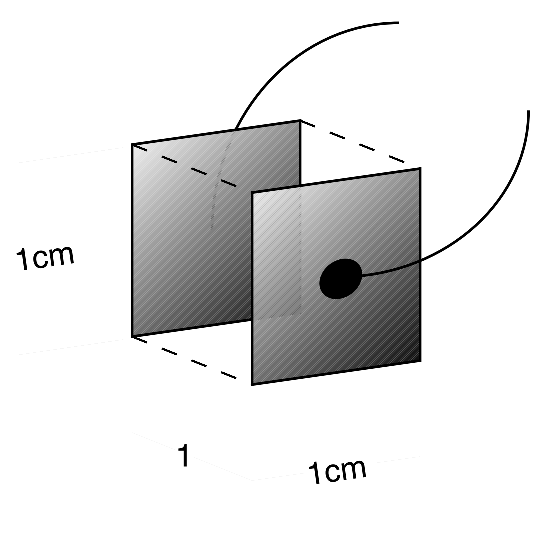


*Fig.(2)* A probe constant of 1 is obtained when the fluid to be measured is contained entirely within a 1cm cube with 1cm$^2$ electrodes on two opposing sides.

$$\text{Probe Constant} = \theta = L / A \qquad \text{Eq.(5)}$$

Bear in mind that A is the cross-sectional area of the intervening liquid volume, and not the area of the electrodes, as is often supposed. It is also common to see $\kappa$ used as the symbol for probe constant, probably because of the similarities between Eq.(4) and Eq.(5).

If the electrodes are moved to 10cm apart, the probe constant becomes 10. For a constant of 0.1, move them to 0.1cm apart. (The same effect can be achieved by inversely varying the area instead of the length.) It can be seen that the probe constant is a multiplier figure that can be used to scale the relationship between measured conductivity and the figure of actual interest, specific conductivity. In instrument terms, the probe constant is a scale multiplier.

An instrument set for a full scale range of 5,000 micromhos using a probe constant of 1 will have a range of 50,000 micromhos when using a probe constant of 10, and 500 micromhos if the probe constant is reduced to 0.1.

In practice, the separating geometries are usually more complex than the defining example, since the closed cube is not a practical sensor design, and the electric field between the electrodes will actively extend to all available fluid volumes between them. The relationship in Eq.(2) still holds, but L and A become complex mathematical expressions. For most if not all electrode arrangements, the formula for probe constant will be a scaled reciprocal of the formula for the capacitance between the electrodes.

### *From Theory to Practice*

As with many measurements, the idealized central premise is compromised by a number of side effects that must be taken into account. A major factor is polarization.

Ions travelling toward the electrodes will quickly form dense clouds near the electrode surfaces. They cannot physically cross the solid/liquid barrier, and the voltage is usually too low for significant electrolysis to occur (forming elemental sodium and chlorine gas for our example). But the cloud of negative ions will present a rising counter emf at the positive electrode, and vice-versa. The result is that current flow rapidly and exponentially drops to zero, invalidating the measurement.

To overcome this, an alternating polarity voltage is applied. This can be a sine wave, square wave, trapezoid, or any number of forms. The purpose of using AC is to reverse the motion of the ions before they build up near the electrode surfaces in any quantity.

This simplified description does not address lesser but still serious problems with the reduced but not eliminated polarization that are overcome with various electronic tricks. Frequency manipulation, current sensing windows, peak detectors and other devices are used to make sure that the current monitored is representative of the ion population and not polarization.

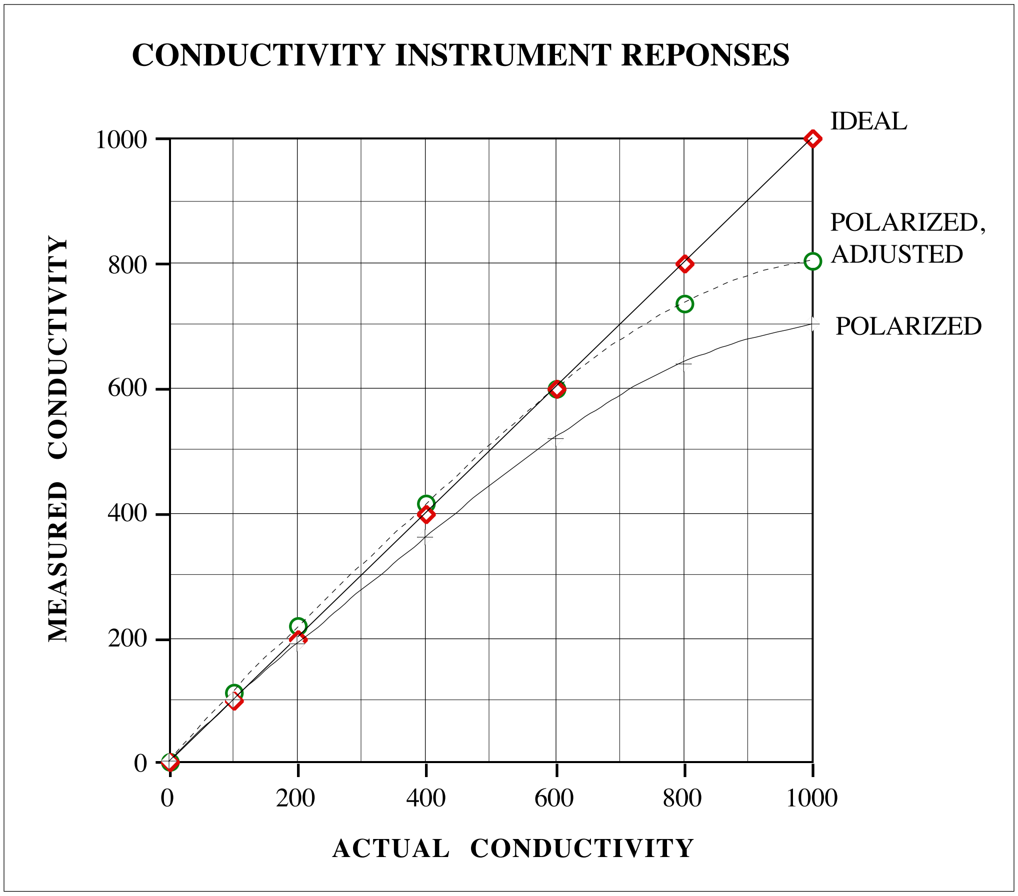


*Fig.(3)* This graph shows typical response for an instrument operating beyond its linear range and severely polarizing its electrodes. A normal reaction to this by users is to adjust for an accurate reading at some point near the center of range, in this case at 600 micromhos, and reduce the overall error somewhat. While the response below 600 looks reasonable when graphed, it might be noted that the error at 200 is 10% of the reading. By standardizing at 700 instead, the error at both 200 and 1,000 would be about 15% of reading. In some cases, response actually goes flat-line and there is no possibility of meaningful adjustment. The response labeled IDEAL is what might be expected if a black platinized sensor of the same probe constant were substituted for the plain metal sensor being polarized.

The problem is not fully appreciated by some instrument designers. It is an unfortunate fact that circuits can readily be designed that will work to extremely high conductivity ranges with dummy resistive loads or idealized sensors. The latter term refers to sensors whose electrode surfaces have been coated with black platinum. This spongy coating increases the effective surface area of the electrode by a factor of hundreds or more, making it less sensitive to the early stages of polarization. It also catalytically speeds up the small amount of electrolysis that occurs. The technique is not often used for on-line measurements because the platinized coating is soft and easily removed by abrasion in flowing streams of less than ideal fluids.

It is when a circuit is tied to plain metal electrodes with limited surface area that its design meets a real and practical test. Well designed instruments will give linear response with a 1 constant plain metal electrode sensor up to 20,000 to 100,000 micromhos. However, it is not uncommon to see some popular instruments with linear unity constant ranges limited to 5,000 micromhos or less unless a platinized sensor or a sensor with extremely large electrodes is used.

Such limited ranges not only cause the user to have to go to higher probe constants, with increased expense and reduced reliability due to small passageways, but they are inordinately sensitive to electrode fouling in use. Partial occlusion of an electrode surface with stream contaminants will produce a large decline in the reading.

An instrument which will not take a plain metal unity probe constant sensor to at least 10,000 micromhos in a linear manner will be hard pressed to deliver repeatable readings in on-line use. A further disadvantage of the limited linear ranging is that when temperature begins to rise, the range is reduced even further because the uncorrected conductivity level rises.

Non-linear response can be detected by measuring standard solutions across the range of interest and graphing the results. An increasing droop in response below the expected value of the solutions as the conductivity increases is an indication that polarization is creeping into the reading.

Another way to verify this is to obtain a platinized laboratory sensor with the same probe constant as the on-line sensor, and take measurements with it in the same solutions, connected to the instrument in place of the on-line sensor. A linear response with the platinized sensor absolutely confirms the sick instrument diagnosis.

*Measuring Concentration*

While the current that develops from the applied voltage is proportional to the number of ions in solution, the proportion varies for each kind of ion.

Ions are massive when compared to electrons, and thus have to bull their way through all the other large molecules in solution instead of flitting from atom to atom at near the speed of light.

Ions are hydrated, meaning that they have several polarized water molecules stuck to them which have to be dragged along for the ride. The technical names for the solution phenomena which retard movement of the ions are electrophoresis and assymetry effect.

In addition, electrons have a charge of 1, while ions frequently have charges of 2 and 3 or even higher, which in turn affects their speed in an applied electric field.

Chemical handbooks list mobility ratings for various ions, and no two are exactly the same. Further, these mobility figures vary with both temperature and chemical concentration.

As the temperature goes up, mobility increases, and the conductivity for a fixed concentration of the chemical rises. This is a large change, on the order of 2% of the 25°C conductivity value for each °C of temperature change. Automatic compensation for this effect is a definite requirement for accuracy.

Because the temperature effect is close to linear for some common solutions, the following equation is used to describe it. Keep in mind, however, that the real case is nonlinear, so this equation is just an approximation.

$$C_t = C_{25}\,(1 + \alpha\,(t - 25)) \qquad \text{Eq.(6)}$$

$C_t$ = conductivity at t °C
$C_{25}$ = conductivity at 25 °C
t = operating temp. in °C
$\alpha$ = temperature coefficient

The temperature coefficient is the amount of change in conductivity per °C , expressed as a decimal part of the conductivity at some reference temperature. In this case, as in most modern instruments, the reference temperature is 25°C. A typical value for $\alpha$ is 0.02, although it can vary from that figure by a factor of 2 or more in either direction and is actually a function of both temperature and chemical concentration.

As chemical concentration rises, the ions become so numerous as to impede one another's movements through the solution. This is analo-

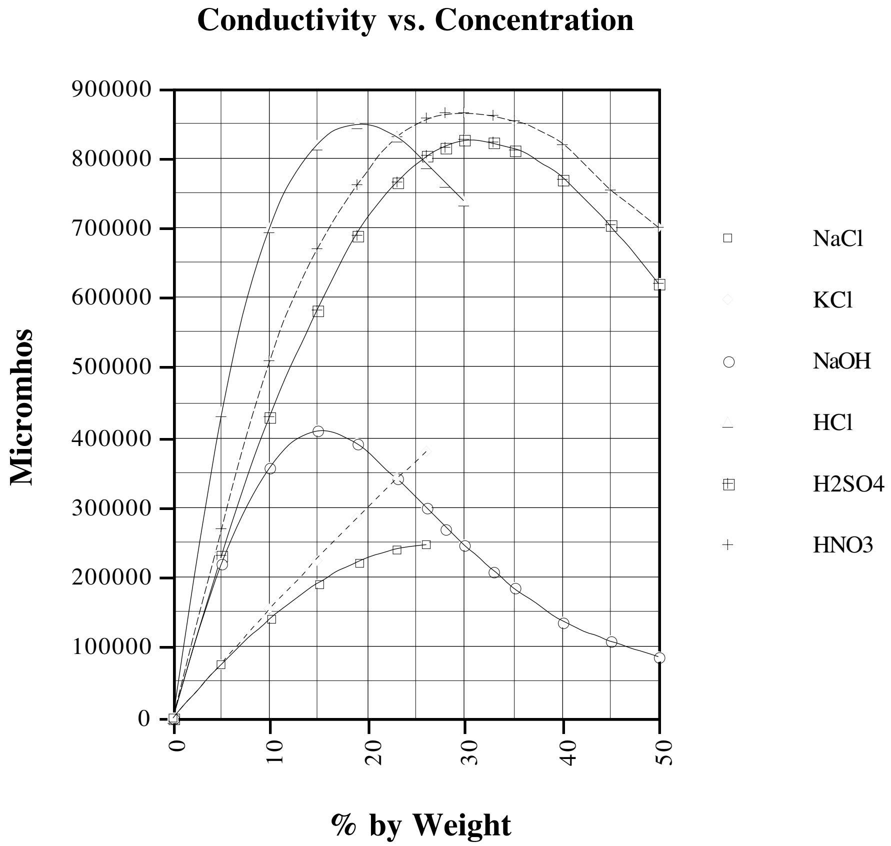


Fig.(4)

gous to an attempt to run through a crowd of people. The more of them, the slower your speed, regardless of the attraction coming from the destination. (Stated scientifically, electrophoresis and assymetry effect are more pronounced at higher concentrations.) The result is that conductivity begins to increase at a slower percentage rate than the increase in chemical concentration. At some point, it may reach a maximum and then actually decrease for further increases in concentration. Refer to the graph in Fig.(4) for examples.

So far only the single solute case has been addressed. Conductivity is highly sensitive to ions in solution, but it is not selective. If more than one chemical is in solution, there is no way for a conductivity measurement to distinguish which of them causes a change in reading, unless their contributions to same are vastly different.

A numerically good example of this would be 5% acetic acid and 5% hydrochloric acid in the same solution. Conductivity would readily follow changes in the hydrochloric levels, but would not see the acetic at all. This is because 5% hydrochloric reads about 430,000 micromhos while 5% acetic acid is a little less than 1,800 micromhos. (Acetic is a weak acid and does not ionize fully.

The bottom lines are that in order to use conductivity to accurately measure chemical concentration, several things are needed:

- A chart showing the relationship between concentration and conductivity for the chemical of interest.

- Temperature compensation for the non-linear response of the specific solution.

- Either a single solute or the case where only the solute of interest is changing, or the solute of interest is much higher in conductivity than any others present.

In solutions containing multiple chemicals (assuming no reactions between them) the total conductivity is roughly equal to the sums of the individual conductivities. This rule of thumb is accurate for dilute solutions, and increasingly less so as concentrations rise.

Even at total concentrations of 1% it is readily observable that the whole of conductivity is less than its parts, and at 20% the difference is pronounced. These figures are for example only. There is no fixed starting point or relationship for which it can be said that the sum is any particular amount less than its component parts except for an explicitly defined mix.

### *Leak Detection & Water Quality*

Often it is necessary not to know exactly what is in solution, only whether a certain level of ions from any source has been reached (single point control). This is true in cooling towers and boilers, where the recirculating water must be dumped when its salt level increases due to evaporation or steam loss. Too high a dissolved solids level will cause scaling, foaming, heat transfer inefficiency, and corrosion.

Many processes use heat exchangers to vary the temperature of strong, and often dangerous chemicals. They need to know immediately if the low conductivity heating or cooling fluid is being contaminated with even small amounts of process chemical, so that flow can be shut down before damage is done.

In both these cases, measurement inaccuracies of 5% or greater can often be tolerated without problem. For these applications, linearity and exact temperature compensation are less important, and distinctions between types of chemicals is unimportant.

### *Neutralization Indicator*

Though not often used for this purpose, conductivity makes an excellent linear indicator of the progress of a batch neutralization. Whenever a strong acid is neutralized with a strong base, or vice-versa, somewhat less highly conductive salts are produced as the highly conductive main products react. The result is a linear decrease in conductivity toward a knee, where it will start to rise again as the neutralizing chemical exceeds the concentration of the chemical being neutralized.

A drawback to this use is that there is no way to tell whether the reading is on the acid or base side of neutral. However, a backup indicator of pH, which doesn't work accurately in strong acids and bases, will serve to tell which side it is on and thus enable the accuracy which the conductivity reading can give.

### *Accuracy of Conductivity Measurements*

Major items affecting the accuracy and repeatability of conductivity measurements are:

(1) Electronic stability and linearity of the instrument.
(2) Linearity of instrument/sensor with solutions (polarization).
(3) Accurate temperature measurement and correction for temperature effects in solution.
(4) Knowledge of the relationship between conductivity and concentration for the solution of interest.

The suggestions that follow assume a need for precision which justifies both the cost and time they will require. They are not proposed as standard procedures for using conductivity instruments, since many applications do not demand absolute accuracy, and single point control is not affected by non-linearities away from the setpoint. No pass or fail values are given for the error sources described, since that will be a function of the accuracy required by the individual user.

### *Electronic Stability & Linearity*

While it would be heartening to recommend a simple reference to the instrument manufacturer's specifications, this would fall short of verifying the actual on-line characteristics. Practically all instrument specs refer to electronic response to resistor simulations for both the conductivity and temperature sensors. Because no polarization occurs with resistors, optimum spec figures can be obtained from circuit designs that are ill suited to working with the solid/solution interface problems.

However, it is advisable to look at the published linearity tolerance, which should be no more than a few tenths of a percent across the range. Another important figure is stability with changes in ambient temperature. The instrument should exhibit zero and span changes of no more than 200ppm (of full scale) from 0° to 60°C. If there are no published ambient figures, it is advisable to put a resistive load on the instrument to simulate full scale of the range of interest, and put it through a temperature change while carefully monitoring the output. A simple way to get the high end temperature condition is to place a cardboard box over the instrument and a 100 watt standard light bulb (lit, of course). Monitor the temperature to make sure it does not exceed 60°C and cause damage.

Check for stability at both full scale and at zero deflection (open sensor leads). There may have to be a resistor in place of the temperature compensation element if there is no manual TC setting available. Make sure that the resistor has a low temperature coefficient value, less than 50 ppm, or attach leads so that it can be located outside the box and not see the temperature swings. Carbon resistors with broad tolerances can have temperature coefficients as large as several hundred ppm, well in excess of what needs to be monitored in the instrument.

Next, use precision resistors to check the linearity across the range of interest at four or more points. To determine the required resistance to achieve a given reading, divide the micromho value desired into one million times the probe constant. Thus, 1,000 micromhos requires a resistance of 1,000 ohms, 2,000 micromhos corresponds to 500 ohms, 4,000 micromhos to 250 ohms, and so on. An instrument that will not achieve the required accuracy and repeatability with resistors has no chance of improvement with a sensor in solution.

### *Linearity in Solution Measurements*

After verifying that the basic electronics are satisfactory, check for linearity with the sensor that will be used on-line. This can be done in one of two ways — using solutions of known conductivity value, or direct comparison with a platinized sensor with an accurately known probe constant similar to the on-line sensor's.

In either case, cover a conductivity range which reflects the temperature effects on the solution conductivity, since this increases the dynamic range that the instrument has to deal with. For example, if the range of interest is 0 to 5,000 micromhos at 75°C, then extend the tests to 10,000 micromhos. Conductivity will increase about 2% per°C, so an increase of 50°C will double the nominal full scale value. Despite what the corrected reading appears as on the display, the instrument will be seeing double that, or 10,000 micromhos, in its input stages.

### *Lead Wire Resistance*

Wires are not perfect conductors. Even heavy gauge copper wires offer some small amount of resistance to the passage of electric current, as illustrated in the table below.

Wire Resistance Values

| Wire Gauge | Ohms/1000 Ft. |
|---|---|
| 8 | 0.654 |
| 10 | 1.018 |
| 12 | 1.619 |
| 14 | 2.575 |
| 16 | 4.094 |
| 18 | 6.510 |
| 20 | 10.35 |
| 24 | 16.46 |
| 26 | 41.62 |
| 28 | 66.60 |

*From data published by the General Electric Company for solid round copper conductors.*

Since conductivity measurement is in essence also a resistance measurement, the series resistance of the lead wires between sensor and instrument will cause errors. At 100 micromhos, with a 1 probe constant, the solution resistance is 10,000 ohms and lead resistance is not a serious factor. But at 100,000 micromhos the solution resistance drops to 10 ohms and now lead resistance can cause gross errors.

This problem can be solved in several ways. Some instruments offer automatic lead resistance compensation circuitry, typically using 4 leads from sensor to instrument. In cases where the raw measurement is being fed to a computer for scaling and temperature compensation, the lead resistance can be compensated for with a calculation. A very few microprocessor instruments have this last feature built into their programming. Inserting a figure for lead length allows automatic correction for same.

In the majority of cases however, the only available solution is to tailor either wire gauge size and/or lead length in a manner that keeps lead resistance below some predetermined maximum allowable level. The calculations necessary to do this are straightforward but laborious. For convenience, the equation below will specify directly the required wire gauge based on inputs of allowable error as percent of full scale conductivity, probe constant, maximum conductivity, maximum temperature, and lead wire length.

$$\text{Wire Gauge} = 9.943 \,\text{Log}_{10} \left[ 5\text{x}10^{8}\theta \ \%E \,/\, d\,(\kappa_{25}\,(1 + \alpha\,(t - 25)))(100 - \%E) \right] + 9.9$$

Eq.(9)

%E = Allowable error in reading, expressed as % of full scale conductivity

d = Distance in feet between instrument and sensor (formula takes into account 2 leads)

$\kappa_{25}$ = Full scale conductivity value at 25℃ and $\theta$ = Probe Constant

t = Maximum operating temperature, ℃ and $\alpha$ = Temperature coefficient, decimal

*Cable Resistance Example*

Assume the application calls for a full scale of 2000 micromhos, max. temperature of 75°C, a 100 foot cable run, and an allowable error of 1% of full scale. Not knowing $\alpha$, assume it to be 0.02. Plugging these values into Eq.(9) tells us that 21 gauge lead wire is needed.

If the lead length is doubled to 200 feet and all other factors remain the same, the formula answer mandates 18 gauge wire in order to keep lead resistance error below the stipulated 1%. In practice, since careful calibration can split the error to both sides of ideal response, a 2% figure for error could have been used.

*Conductivity Standard Solutions*

Standard solutions present several problems. First is simply obtaining them. While available, they are less common than pH buffers and a ready source can be difficult to locate.

They can be prepared with considerable accuracy using a precise “recipe”, reagent grade chemicals, distilled water, a scale accurate to within a thousandth of a gram or better, and a good volumetric flask of one or two liters. If no scale is available, precise solutions can be purchased from a lab chemical supply house and diluted using good volumetric glassware. This discussion concludes with a listing of information that will allow accurate solutions to be prepared from a wide choice of chemicals.

Because they are simple salt solutions, conductivity standards do not have the stability of pH buffers and are easily contaminated, particularly at low values.

Last, and far from least, they, like all conductive solutions, are temperature sensitive and automatic temperature correction is a source of considerable error if not done properly.

Despite these drawbacks, however, they can give good results if certain precautions are taken. Make sure that the instrument has been calibrated at full scale with a precision resistor before doing these tests.

(1) Allow the solutions to temperature equilibrate in a location that is as close to 25°C (77°F) as possible, in order to minimize automatic temperature compensation errors.

It may be preferable to simulate 25°C with a resistor in place of the automatic compensation element or select manual compensation at 25°C, and monitor the solution temperature with a lab thermometer. Reference to the solution chemical’s temperature response will then allow slight corrections to be calculated and applied to the measured readings.

Automatic compensation can be used if enough time is taken to insure temperature equilibration, and the proper $\alpha$ value is selected. If $\alpha$ for the standard solution is not known, it can be determined by heating the solution slightly and adjusting the instrument’s $\alpha$ setting, assuming that it has one. If it does not, then use manual simulation or consider using a precision lab sensor comparison instead (next section).

(2) Metal sensors go through a passivation stage in solution, as various oxides form on their electrode surfaces. Before making measurements, clean the electrode surfaces well with strong detergent or degreasing agent, rinse extremely well with running water, then soak the sensor for at least 24 hours in a solution whose conductivity is near the middle of the range of interest.

The apparent probe constant of a plain metal electrode sensor will increase slightly during the first 24 hours in solution as the oxides are formed. Detergents and degreasers have high conductivities, and small amounts may be carried over in crevices of the sensor body even with good rinsing. If this or their chemical constituents are problematic, then clean the surfaces by wiping with a high purity solvent such as MEK or trichlorethane. Spray cans of circuit board cleaning solvent work well for this purpose. Whatever method is used, it is most important to insure there is no grease on the electrode surfaces from handling or production.

(3) Start with the lowest conductivity solutions first to reduce contamination from carryover traces on the sensor. A small amount of strong solution can seriously contaminate a weaker one, but a weak solution carryover to a stronger one can do no more than dilute the stronger with a nearly negligible amount of liquid. For best results, pour some of the stronger solution over the sensor to rinse it before taking a measurement.

(4) Use a lab mixer to keep the solution in constant motion. If not available, then stir the solution well with the sensor until there is no observable difference between the mixing and stationary modes. A gradual change in reading with a non-stirred sample may indicate leaching of a previous solution from sensor crevices, lack of temperature equilibration between sensor and sample, or air bubbles forming on electrode surfaces.

(5) With some designs part of the current flow will be outside the sensor body and the conductivity reading will fall as the sensor is moved closer to the sides or bottom of a non-conducting fluid container. Move the sensor around in the container to see what effect positioning has on the reading, and locate it in a region where several inches of movement in any direction has no observable effect on the reading. In some cases, this may require a large container and a large amount of fluid, as well as a holding device to suspend the sensor in a fixed location. It may, in fact, be impractical to test certain sensor designs on the bench if their electrode geometry is too open (such as two pins projecting from the end of an insulator, with no shroud around them). These sensors must be calibrated on-line in their actual working configuration, and standard solutions will be difficult or impossible to apply.

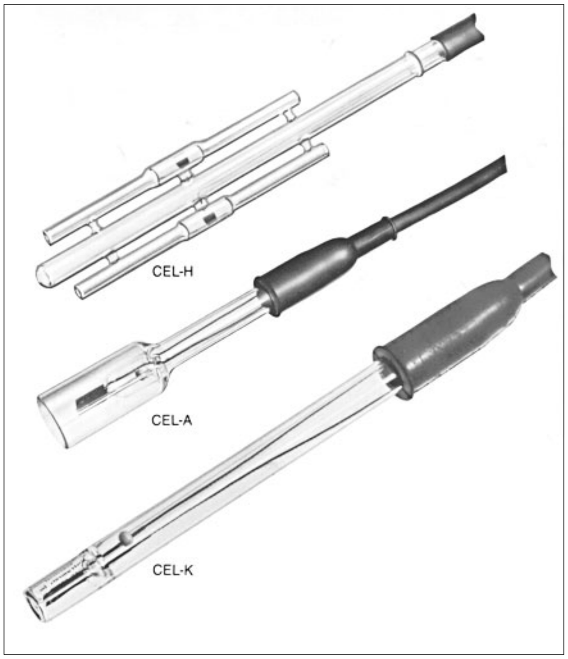


Fig.(5) Precision laboratory sensors with platinized electrodes. These were manufactured by the former Beckman Instruments and similar units are now available from Rosemount Analytical, located in Irvine, California.

(6) Don’t allow bubbles to form on the electrode surfaces or be trapped inside the sensor. Solution mixing helps here, but it may be necessary to give the sensor a vigorous shake from time to time before taking readings. (This also turns out to be a common and little recognized problem on-line.)

(7) Never mix used conductivity standard solutions with the remaining unused portions. Discard the solutions after use. With great care their integrity can be maintained for a time, but contamination happens easily and there is no warning flag to tell the user that the standard is no longer accurate.

Carefully plot the measured values against the known solution values to determine the amount of non-linearity. This should take the form of measured values that are increasingly lower than the known at some point. Errors alternating to both high and low sides indicate problems with the technique, and the test should be repeated with greater care.

Since calibration at mid-scale will split the top end error to both sides of ideal (see Fig.(3)) a droop that is double the allowable error can be tolerated.

### *Comparisons With Precision Platinized Sensors*

A much easier way to check on-line linearity is by using a laboratory type platinized sensor whose probe constant is similar to that of the on-line sensor. It is best to use identical probe constants, but acceptable results can still be obtained with a platinized probe constant that is no more than ten times smaller or larger. Larger is preferable since it avoids the polarization threshold.

The great advantages here are that no temperature compensation is needed (and indeed should not even be attempted) and there is no need for precision in making the test solutions. Simply add salt until a 10% or so increase is noted, then connect each sensor alternately to the instrument and take readings from each with no more than 2 minutes between them to avoid temperature drift.

Since the intent is only to compare responses, it is useful but not necessary to know the constant of the platinized sensor to a high degree of accuracy.

While it is probable that a poor instrument will produce non-linear readings at some point even with a platinized sensor, such a device will give distinctly low comparison readings with the plain metal electrodes, possibly even getting into flat-line response.

In other words, it will fail the comparison test miserably, so the fact that the referee readings are also non-linear will be unimportant.

A rough rule of thumb for the platinized sensors would be to use 0.1 constants to no more than 1,000 micromhos, 1 constants to a maximum of 10,000 micromhos, and so forth. Plot the comparative readings as outlined previously in order to check for non-linearity (polarization droop).

One of the better sources for lab type sensors with highly accurate constants is Rosemount Analytical, located in Irvine, California. They acquired Beckman Instruments, who had previously acquired Industrial Instruments of Cedar Grove, New Jersey. They offer a variety of platinized sensor types with probe constants certifiable to 1/2% and 1/4% accuracy. Prices range from about $300 to over $700, depending on style and accuracy. Yellow Springs Instruments of Yellow Springs, Ohio is another source.

For really top-drawer calibration, a research grade bridge or instrument can be purchased to go with the accurate sensor. This isn’t a requirement, but it does offer a solid base to determine the absolute values of test solutions. Price of an instrument of this caliber is about $7,000. Sources are Rosemount, and Radiometer of Copenhagen. The latter have offices in the United States. Yellow Springs Instruments also offers lab instruments to go with their sensors.

A lab instrument/sensor combination of high accuracy offers the ability to make precise adjustments of on-line instruments from grab samples.

Some manufacturers are offering plain metal electrode sensors with probe constants that are tested to a high degree of accuracy and marked on the sensor. This offers potential problems because of polarization effects.

If the instrument and sensor are being operated into a non-linear region, then the highly accurate probe constant which was measured at a lower conductivity value offers nothing except a false sense of security. This approach will be more successful for solutions under 100 micromhos, where polarization effects are less prevalent because of the low ionic density. At higher ranges, an “accurate” determination of the plain metal electrode cell constant is of dubious value.

There is an area of application where knowing the probe constant to a high degree of accuracy is particularly important, and that is in high purity water solutions of less than 10 micromhos. This is because temperature correction is large, non-linear and done in two parts — one for the solutes, and another for the self-ionized portion of the water.

The latter is always a part of any conductivity reading, but since it is small (less than 1 micromho at 100°C) it can be ignored in the higher ranges. Even in the region of 10 to 100 micromhos it can be corrected as an assumed part of the solute TC with reasonable accuracy.

The accurate correction for this portion that is needed below 10 micromhos, where it becomes significant, utilizes a presumed value for the probe constant in its calculations, and a small error in in this presumption will translate to much larger errors in the temperature corrected reading.

Knowing the probe constant accurately is only useful if the instrument contains some provision for inputting that information into its correction scheme. Some instruments do not, and simply assume that an accurate probe constant is being used.

Accurately standardizing the reading to correct for probe constant deviations will not alleviate the temperature compensation error described.

### *Temperature Compensation*

After assuring non-polarized operation, the greatest remaining source of error in a conductivity measurement is improper correction for temperature effects. There are three distinct sources of this problem—incorrect readings from the temperature element, a poor temperature correction scheme, and a lack of knowledge about the temperature characteristics of the solution.

### *Temperature Measurement Accuracy*

Most auto TC elements are built into the conductivity measuring sensor. In addition to the basic tolerance of the element, which can be surprisingly large in some cases, there is the problem of the effect of sensor mass on response to stream temperature.

The element may be buried in the main body of the sensor, or contained in a thermowell projecting into the stream. In either case, the mass of the sensor will slow response to changes in stream temperature, since it is built of materials with low thermal conductivity (plastics, epoxy, stainless steels). If the stream being measured has rapid swings in temperature, there is a good chance that the TC element is reading incorrectly a majority of the time.

A plot of sensed temperature versus actual would reveal that the element sees each swing, but at a truncated level out of time phase with the fluid changes. The larger and more rapid the swings, the more serious this problem. It is therefore a good idea to make tests on-line with a rapid response temperature sensing device to see what the relationship is between sensor TC element response and the actual stream temperature.

The John Fluke Company, best known for its excellent line of digital voltmeters, also sells temperature sensing modules which can be plugged into any DVM to give a readout in °C or °F. A variety of sensors are offered which give both rapid and accurate readings. Cost of the Fluke Model 80TK thermocouple module is in the neighborhood of $100.

The heat sink influence of the sensor can also be considerable, especially for units that are inserted into a pipe or the wall of a vessel. Since the back part of the sensor is at a different temperature than the front, heat is constantly being pumped in or out of the temperature element through its leads and through contact with other parts of the sensor.

The differential this creates between actual stream temperature and measured will increase as solution temperature increases. Its pattern is similar to the graph shown in Fig.(3) which illustrates polarized electrode response, except that the measured temperature droop will be more linear.

It also tends to be repeatable. This allows the differential to be effectively corrected by calibration, if and only if the temperature adjustment is a gain, or two-point adjustment, rather than a simple zero adjust.

Take readings from both the TC element and the referee device at increasing temperatures. If the differential becomes pronounced, it may be necessary to insulate the back of the sensor, use a separate thermowell for the temperature element, or select a sensor design with more rapid temperature response.

### *Correction Schemes and the Data That Enables Them*

Many, perhaps most, instruments offer only a single value linear correction that assumes $\alpha$ from Eq.(6) to be exactly 0.02, or 2% per °C, for a reference temperature of 25°C. Fortunately, this is nearly true for many common salt solutions at ambient temperature levels. Unfortunately, it is exactly true for none, and quickly loses validity for wide swings in concentration and/or temperature. An error of only a half percent per °C in the $\alpha$ assumption will give a corrected reading in error by 25% at 75°C. Temperature correction coefficients vary from a half percent per °C to almost 4%, and very pure water approaches 10%.

Reference literature on $\alpha$ values is both scarce and, in many cases, suspect. In reviewing literature for this paper, two currently published data sources for NaCl temperature coefficients were found that offer graphs of the change in the $\alpha$ value across the range of 0 to 100°C.

One shows $\alpha$ increasing from 0°C to 100°C in a perfectly linear manner. The other gives an equally impressive graph showing that $\alpha$ falls from 0 to 100°C, and further, that it does this in a distinctly non-linear manner. Their $\alpha$ values differ by more than 0.014 at 100°C which translates to a huge correction error.

Neither references a concentration for which the values are supposed to apply, and neither explicity states the reference temperature for compensation. While most instruments use 25°C as a reference, scientific work and published data frequently use both 18° and 20°C.

As with the probe constant, knowing precise values for $\alpha$ across wide ranges of temperature and concentration means nothing if there is no way to input that information to the instrument. While a number of instruments offer the ability to dial in a value for $\alpha$ to be used in a linear correction scheme, few can handle $\alpha$ values that are non-linear with temperature. Variations of $\alpha$ with concentration require sophisticated digital calculating ability to perform iterative circular reference solutions for the temperature correction.

### *Limited Range = Higher Accuracy*

That being the case, high accuracy can only be obtained in instances of limited ranges of temperature and concentration changes, or by characterizing the temperature response of a specific solution in great detail and doing the correction in a computer.

It should be noted that a small but definite part of the temperature effect is due to thermal expansion and contraction of sensor parts, causing a small but very real change in the probe constant. Any characterization of a particular fluid should also include the sensor and instrument so that all appropriate factors enter into the picture.

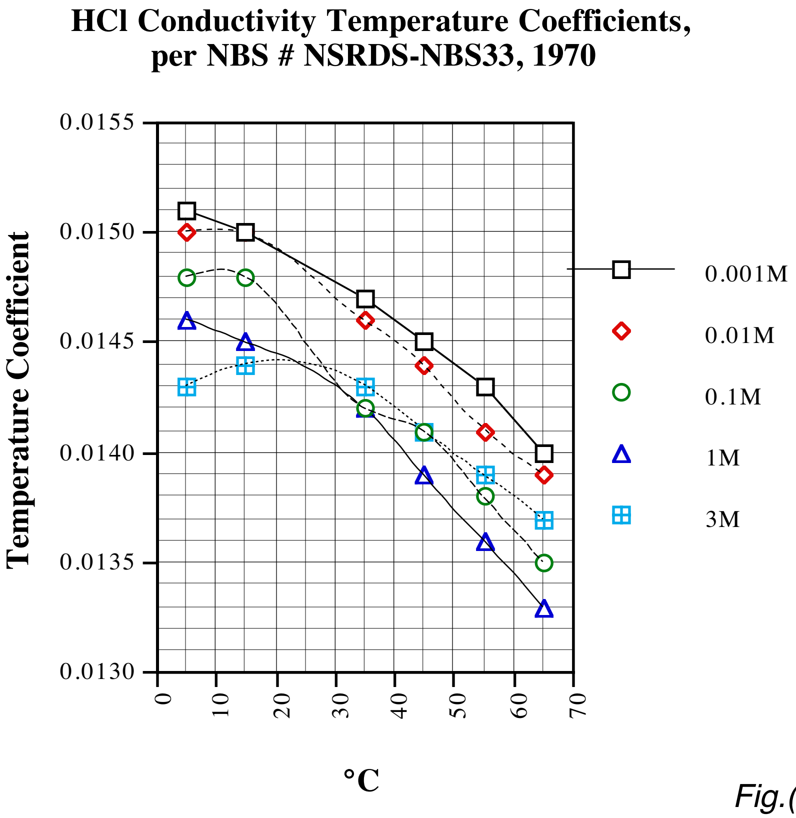


*Fig.(6)*

A good method of obtaining accurate temperature compensation is to measure and plot the temperature responses of the actual solution to be measured over the expected ranges of temperatures and concentrations. Once this is done, it is relatively simple to obtain linear assumptions for α, or to derive a polynomial function for it which can be used in a computer correction scheme.

On-site temperature characterizing is advisable even for single chemical solutions because of the data sourcing problems. For multi-chemical solutions this is absolutely necessary, since there will be about zero chance of finding relevant published data.

If the sensor plumbing allows, there is a simple way to do this. Valve isolate the sensor and monitor the temperature of the trapped sample accurately. This can be done with either a separate temperature measurement, or by monitoring the temperature element in the sensor.

If the trapped sample is already hot, allow it to cool slowly and record the temperature/conductivity reading pairs at intervals. If the line is at ambient temperature, obtain a heating element that can be placed in contact with the piping (wrap-around strips work nicely) and heat the sample from the outside, taking care not to build up excessive pressure in the trapped fluid or melt plastic piping. The same sort of manipulation can be done to the cold side with strapped-on ice packs.

In the event that the sensor is not accessible enough for this technique, the tests will have to be done on the bench. In either case, make sure that automatic temperature compensation is disabled, and that 25°C is being simulated.

In theory only two points bracketing the temperature range of interest are needed to calculate α, but it's a good idea to take several as a self-check. Even with care it is easy to get slightly erroneous readings, especially if the temperature changes rapidly and the monitoring element has any time lag in its response. Temperature elements built into sensors often show a lag because of the considerable mass they are buried in.

Bench checks with low conductivity solutions are difficult because of contamination by carbon dioxide from the atmosphere. Absolutely pure water has a 25°C conductivity value of 0.054 micromhos, but will rise to a little more than 2 micromhos within minutes of exposure to atmosphere. Bench testing is not advisable for solutions under 20 micromhos unless they are known to already be carbon dioxide saturated by exposure to atmosphere in the circulating system.

Attention should also be given to the chemistry of the solution to insure that it is not undergoing some reactive change during the test which will invalidate the conductivity data. Tests should always be done as quickly as possible to minimize changes due to chemical reaction, evaporation and the like.

The following formula calculates an assumed linear α:

$$\alpha = (C_{t1} - C_{t2}) / [C_{t2}(t_1 - 25) - C_{t1}(t_2 - 25)] \qquad Eq.(7)$$

Where $t_1$ and $t_2$ are two different solution temperatures and C is the measured conductivity value at the temperature indicated by the subscript. For using the formula, it does not matter which of the two temperatures is higher.

Because α is likely to be non-linear, greater accuracy will be obtained if one of the temperature values is close to 25°C and the other is near the expected center of the operating temperature range.

If computer correction is possible, then $\alpha$ should be calculated at numerous points across the entire temperature range. The results can be entered into a number of commercially available personal computer programs to obtain a curve fit equation, most likely a polynomial of the 2nd to 5th order.

The graph in Fig.(6) is for hydrochloric acid, using data published by the National Bureau of Standards, applied to Eq.(7). A concentration of 1 molar HCl is approximately 3.65% by weight.

This level of detail about the behavior of the temperature coefficient allows accurate temperature corrections to be made, and thus accurate conductivity readings to be obtained, even in the absence of non-linear correction capability.

An example will help to illustrate the degree of improvement offered by this attention to detail.

### *HCl Auto TC Example*

Chemical: Hydrochloric acid, HCl

Concentration: 10,000-20,000 ppm (1% - 2% by Weight)

Temperature Range: 50-60°C

Instrument Auto TC: Accepts dialed in values for $\alpha$ for use in a linear correction scheme.

For calculation, assume a concentration of 18,100 ppm, which is, conveniently enough, a 0.5 molar solution. Temperature is 55°C.

Per the data in NBS publication #NSRDS-NBS 33, *Electrolytic Conductance and the Conductances of the Halogen Acids in Water*, page 24, (also published in CRC Handbook of Chemistry and Physics, 67th Edition, page D-165), HCl conductivity values at that concentration are:

0.5M, 25°C = 180,350 μmhos

0.5M, 55°C = 254,000 μmhos

The referenced listing gives what is called equivalent conductivity values, which allow more ready comparison of conductance efficiency between various chemicals. To convert to specific conductivity, multiply by 1000 times the molarity.

Solving Eq.(6) for the corrected conductivity value, $C_{25}$, gives:

$$C_{25} = C_t / (1 + \alpha (t - 25)) \qquad \text{Eq.(8)}$$

If this correction scheme is applied to the example with the “standard” $\alpha$ value of 0.02, the instrument reading would be:

$$C_{25} = 254{,}000 / (1 + 0.02\,(55 - 25))$$

$$C_{25} = 158{,}750\ \mu\text{mhos}$$

This result is in error by -12%.

Now make the same calculation, first referring to $\alpha$ values in Fig.(6). The traces for 0.1M and 1M are parallel to one another in the region of 50 to 60°C. Since 0.5M is roughly half-way between them, a line drawn there gives an $\alpha$ range of 0.01385 to 0.01355. The middle value of this range is 0.0137. Using this $\alpha$ value in the correction gives:

$$C_{25} = 254{,}000 / (1 + 0.0137\,(55 - 25))$$

$$C_{25} = 180{,}014\ \mu\text{mhos}$$

This result is in error by only two-tenths of a percent to the low side (-0.2%), a sixty-fold improvement.

Despite the fact that approximations are still being used, temperature compensation has been reduced to a negligible error contributor. It will remain negligible only if the temperature and concentration excursions remain limited.

It is a straightforward exercise to continue the error calculations across wider ranges of concentration and temperature to see how broad a range can be covered while still maintaining the required accuracy.

If multiple chemical process solutions are reasonably consistent in makeup, then an $\alpha$ analysis can be done in the same manner as shown for HCl.

### *Summary of Conductivity Measurement Error Reduction Techniques*

✔ Do a one-time test to make sure the instrument selected is capable of meeting the accuracies being sought. Verify the electronic stability and linearity of the instrument with resistive loads over the ambient temperature range of 0-60°C ( or whatever it is likely to see in service). If the instrument will not perform properly with resistors, attempts to achieve on-line accuracy will be a total waste of time and effort. A bad instrument can be adjusted for accuracy at one point only, and will not maintain that for long, nor give acceptable accuracy even over limited range excursions. Systems operating in polarization can offer only single point control, not analytical accuracy.

✔ Determine the linear measurement range of the instrument/ sensor combination by measurements of known value solutions over the range of interest, or by comparison with platinized sensor responses with the instrument over the same range.

✔ If the purpose of the measurement is to determine chemical concentrations, make certain that accurate data is used to make the correlation to conductivity. Although some of the published data in this area was obtained with great care and precision, there is no guarantee of that, and it almost never states the possible error spread. In the case of multiple chemical solutions, on-site measurement often will be the only source of data.

✔ Characterize the temperature response of the measured fluid over the entire ranges of interest of concentration and temperature. Calculate $\alpha$ values using Eq.(7) and plot them for reference when calibrating the instrument for service over a specified chemical and temperature range.

✔ Make sure the sensor does not trap or collect air bubbles on its surfaces when on-line. This is a common and little appreciated problem because you cannot see through most piping. To test for surface bubbles, rap the back of an on-line sensor sharply with a screwdriver handle and look for a step change up in the conductivity reading. If it jumps suddenly, odds are good that the rap dislodged bubbles from the electrode surfaces.

✔ Air entrapment is often an unrecognized problem when using lab type platinized sensors for comparison or calibration. Air permeates the spongy coating and is usually not detectable by visual inspection. It is best to presoak the platinized sensor for a at least 24 hours in the fluid that will serve as the test solution. Run the conductivity up by adding salt and stirring, but do not remove the platinized sensor even momentarily during the test run. Offsets as large as 5% can occur, especially in low constant sensors where the distance between electrodes is short and surface occlusion therefore directly affects the effective volume between electrodes. Heating the sample to start will drive off much of the gas, but you must then allow it to cool to avoid temperature gradients during comparison tests. To verify results, take them several times over a period of several hours. Continue until variations are less than ±0.5%.

✔ When calibrating by collecting grab samples, be aware of the effects of temperature on the accuracy of the lab reading. If the lab test is done at some temperature other than 25°C or the on-line temperature, then correction effects can enter because of the non-linear nature of the temperature coefficient, $\alpha$. The best way to do grab sample checks is with a portable instrument, a constantly flowing sample straight from the process line next to the on-line sensor, and real-time access to the on-line instrument's reading. For samples below 20 micromhos this technique is mandatory if large errors are to be avoided.

✔ Limit the ranges of temperature and conductivity as much as possible. Smaller dynamic ranges limited to the areas of true interest allow much more precise calibration. Large errors often result from needless attempts to align for maximum accuracy at all points on the scale when in practice only a small percentage of the scale will be used.

✔ If the process coats surfaces with any sort of material, sensor cleaning will have to be done at regular intervals. Coatings typically cause the reading to fall off with time.

❄

# APPENDIX 1 - CONDUCTIVITY OF STANDARD SOLUTIONS

*The data listing which follows was taken from the* CRC Handbook of Chemistry and Physics, 31st Edition*, page 1994. The listing for sodium chloride is particularly useful, as it is a saturated solution (add salts until excess crystals remain at all times) and thus offers a very accurate standard which can be prepared with no equipment save reagent grade NaCl, deionized water and a beaker. Other chemicals are listed, and will be added to in succeeding appendices to offer alternatives whenever a particular ionic presence cannot be tolerated by the on-line system, and thus even the small carryover from testing an on-line sensor must be avoided. An example of this would be high purity solutions in the semiconductor industry, where both sodium and chlorides are objectionable.*

Conductivity values are given in micromhos. Solutions are as follows —

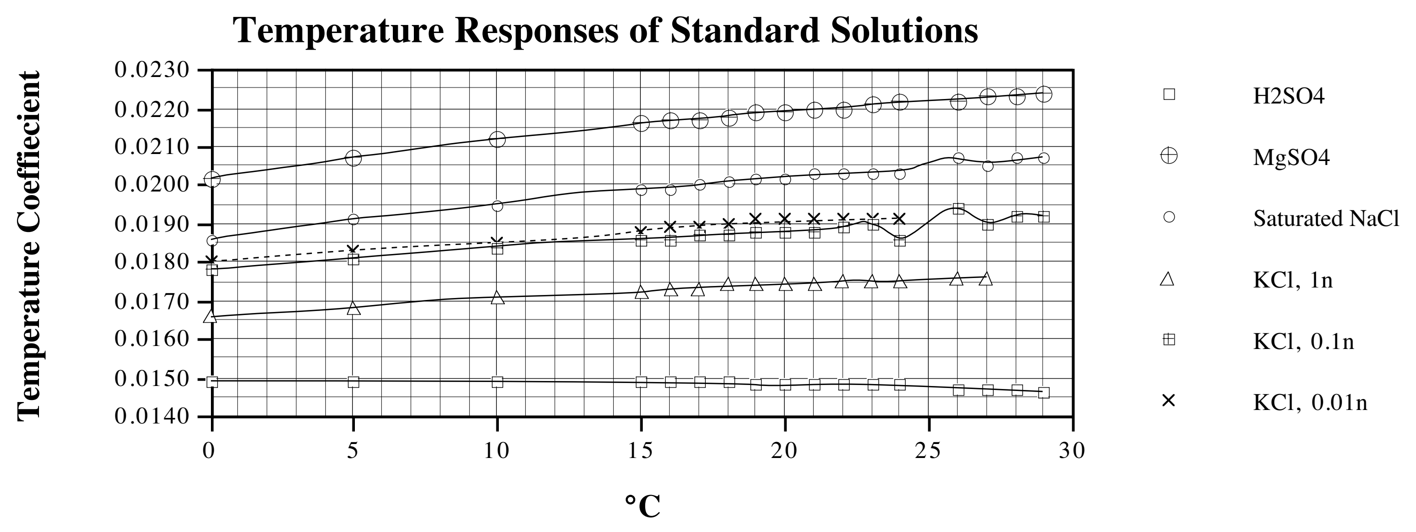
$H_2SO_4$ — maximum conductivity (18°C); dissolve 378 g. of 97% acid in pure water and dilute to 1 liter. Density at 18°C = 1.223.

$MgSO_4$ — maximum conductivity (18°C); dissolve in 1 liter of distilled water 552 g. of $MgSO_4{\cdot}7H_2O$. Density at 18°C = 1.190.

NaCl — solution saturated at all temperatures given. An excess of NaCl in distilled water, about 450 g. per liter. $D_{18}$ = 1.2014.

KCl — normal solution, 74.59 g. per liter of solution at 18°C. Dissolve 74.555 g. (weighed in air) KCl, dilute to 1 liter. $D_{18}$ = 1.04492. 1N KCl = 71.3828 g. KCl per kg. solution — 0.1N KCl = 7.43344 g. KCl per kg. solution — 0.01N KCl = 0.746558 g. KCl per kg.

| TEMP., °C | $H_2SO_4$ | $MgSO_4$ | NaCl | KCl, 1N | KCl, 0.1N | KCl, 0.01N |
|---|---|---|---|---|---|---|
| 0 | 518,400 | 28,770 | 134,500 | 65,410 | 7,150 | 776 |
| *5* | *579,200* | *34,020* | *155,500* | *74,140* | *8,220* | *896* |
| 10 | 640,800 | 39,630 | 177,900 | 83,190 | 9,330 | 1,020 |
| *15* | *702,800* | *45,550* | *201,400* | *92,520* | *10,480* | *1,147* |
| 16 | 715,100 | 46,760 | 206,200 | 94,410 | 10,720 | 1,173 |
| *17* | *727,500* | *47,990* | *211,100* | *96,310* | *10,950* | *1,199* |
| 18 | 739,800 | 49,220 | 216,000 | 98,220 | 11,190 | 1,225 |
| *19* | *752,200* | *50,460* | *220,900* | *100,140* | *11,430* | *1,251* |
| 20 | 764,500 | 51,710 | 225,900 | 102,070 | 11,670 | 1,278 |
| *21* | *776,800* | *52,970* | *230,900* | *104,000* | *11,910* | *1,305* |
| 22 | 789,000 | 54,240 | 236,000 | 105,940 | 12,150 | 1,332 |
| *23* | *801,300* | *55,510* | *241,100* | *107,890* | *12,390* | *1,359* |
| 24 | 813,500 | 56,790 | 246,200 | 109,840 | 12,640 | 1,386 |
| *25* | *825,700* | *58,080* | *251,300* | *111,800* | *12,880* | *1,413* |
| 26 | 837,800 | 59,370 | 256,500 | 113,770 | 13,130 | .......... |
| *27* | *849,900* | *60,670* | *261,600* | *115,740* | *13,370* | .......... |
| 28 | 862,000 | 61,970 | 266,900 | ............ | 13,620 | .......... |
| *29* | *874,000* | *63,280* | *272,100* | ............ | *13,870* | .......... |
| 30 | 886,000 | 64,590 | 277,400 | ............ | 14,120 | .......... |



# APPENDIX 2 - PREPARING ACCURATE LOW RANGE CONDUCTIVITY STANDARDS

*The data listing which follows was taken from* Handbook of Electrochemical Constants, *Parsons; Academic Press/Butterworths, 1959. It gives a formula and a listing of plug-in values for same which will allow accurate correlation between conductivity and low concentrations of a wide variety of solutes. No guarantees of accuracy are available, but it appears from a number of actual trials that attention to detail will give results to within 1% of the absolute. The formula is valid only for concentrations between 0.001 and 0.1 normal. Density correction is a minor factor for most calculations, but a good source of density values can be found in current copies of the* CRC Handbook of Chemistry and Physics, *Section D, "Concentrative Properties of Aqueous Solutions: Conversion Tables". This section also contains a considerable listing of conductivity values, generally but not entirely of high accuracy.*

$$\textit{Conductivity at } 25^\circ\mathrm{C} = 1{,}000\,\Lambda\,N\,(1 - a\sqrt{\Lambda} + b\,\Lambda)$$

$\Lambda$ = Equivalent Conductivity
N = Concentration as Normality
"a" and "b" are constants from the tables which follow

Normality = Molarity / Valence = (ppm) (Solution Density at *25°* C) ÷ 1,000 (Equivalent Weight)

| Chemical | Eq.Wt. | $\Lambda$, 25C | a | b | Valid ppm Range |
|---|---|---|---|---|---|
| $\mathrm{AgMnO_4}$ | 226.81 | 122 | 0.72 | 2 | 20 - 23,000 |
| $\mathrm{AgNO_3}$ | 169.87 | 133.3 | 0.68 | 0.35 | 16 - 17,000 |
| $\mathrm{Ag_2SO_4}$ | 155.90 | 142 | 1.30 | -3.5 | 15 - 16,000 |
| $\mathrm{AlBr_3}$ | 88.90 | 139 | 1.64 | 2.2 | 8 - 9,000 |
| $\mathrm{AlCl_3}$ | 44.45 | 137.6 | 1.65 | 2.0 | 4 - 5,000 |
| $\mathrm{AlI_3}$ | 135.90 | 137.6 | 1.66 | 3.1 | 13 - 14,000 |
| $\mathrm{Al(NO_3)_3}$ | 71.00 | 129.5 | 1.72 | 2.2 | 7 - 8,000 |
| $\mathrm{BaAc_2}$ | 127.72 | 104.2 | 1.59 | 1.7 | 12 - 13,000 |
| $\mathrm{BaBr_2}$ | 148.58 | 141.1 | 1.28 | 1.78 | 14 - 15,000 |
| $\mathrm{Ba(BrO_3)_2}$ | 196.57 | 118 | 1.44 | 1.4 | 19 - 20,000 |
| $\mathrm{BaCl_2}$ | 104.13 | 139.5 | 1.28 | 1.74 | 10 - 11,000 |
| $\mathrm{BaI_2}$ | 195.58 | 141 | 1.28 | 2.7 | 19 - 20,000 |
| $\mathrm{Ba(MnO_4)_2}$ | 187.61 | 119 | 1.42 | 1.4 | 18 - 19,000 |
| $\mathrm{Ba(NO_3)_2}$ | 130.68 | 132 | 1.34 | 1.2 | 13 - 14,000 |
| $\mathrm{Ba(OH)_2}$ | 85.68 | 256 | 0.88 | 0.6 | 8 - 9,000 |
| $\mathrm{CaBr_2}$ | 99.95 | 133.0 | 1.32 | 2.1 | 9 - 10,000 |
| $\mathrm{CaCl_2}$ | 55.50 | 135.6 | 1.3 | 1.8 | 5 - 6,000 |
| $\mathrm{Ca_2Fe(CN)_6}$ | 73.03 | 118 | 5.47 | 11 | 7 - 8,000 |
| $\mathrm{Ca_3[Fe(CN)_6]_2}$ | 90.71 | 138 | 3.87 | 7.2 | 9 - 10,000 |
| $\mathrm{Ca(NO_3)_2}$ | 82.05 | 130.0 | 1.35 | 2.0 | 8 - 9,000 |
| $\mathrm{CaSO_4}$ | 68.07 | 104 | 2.9 | 3.6 | 6 - 7,000 |
| $\mathrm{CdBr_2}$ | 136.11 | 97 | 1.73 | 0.95 | 13 - 14,000 |
| $\mathrm{CdCl_2}$ | 91.66 | 104 | 1.65 | 0.9 | 9 - 10,000 |
| $\mathrm{CdI_2}$ | 183.11 | 77 | 2.02 | 1.38 | 18 - 19,000 |
| $\mathrm{CdSO_4}$ | 104.23 | 105 | 2.89 | 3.7 | 10 - 11,000 |
| $\mathrm{CoAC_2}$ | 1.28 | 90.1 | 1.74 | 1.4 | 11 - 12,000 |
| $\mathrm{CoBr_2}$ | 109.38 | 126 | 1.35 | 1.9 | 10 - 11,000 |
| $\mathrm{CoCl_2}$ | 64.92 | 124.5 | 1.37 | 1.2 | 6 - 7,000 |
| $\mathrm{Co(NO_3)_2}$ | 91.47 | 122.4 | 1.39 | 2.0 | 9 - 10,000 |
| $\mathrm{CoSO_4}$ | 77.50 | 100 | 2.07 | 1.65 | 7 - 8,000 |
| $\mathrm{CsCl}$ | 168.4 | 154.6 | 0.62 | -0.7 | 16 - 17,000 |
| $\mathrm{CsOH}$ | 74.96 | 271 | 0.45 | 0.5 | 7 - 8,000 |
| $\mathrm{CuAc_2}$ | 90.82 | 60 | 2.36 | 2.2 | 9 - 10,000 |
| $\mathrm{CuBr_2}$ | 71.73 | 134 | 1.31 | 1.6 | 7 - 8,000 |
| $\mathrm{CuCl_2}$ | 67.22 | 131 | 1.33 | 1.5 | 6 - 7,000 |
| $\mathrm{Cu(NO_3)_2}$ | 93.78 | 128.8 | 1.38 | 1.7 | 9 - 10,000 |
| $\mathrm{CuSO_4}$ | 79.80 | 113 | 2.79 | 3.3 | 7 - 8,000 |
| $\mathrm{FeCl_2}$ | 63.38 | 137 | 1.34 | 1.05 | 6 - 7,000 |
| $\mathrm{FeSO_4}$ | 75.97 | 99 | 2.08 | 1.7 | 7 - 8,000 |

| Chemical | Eq.Wt. | $\Lambda$, 25C | a | b | Valid ppm Range |
|---|---|---|---|---|---|
| HBr | 80.92 | 429.4 | 0.37 | 0.35 | 8 - 9,000 |
| $HBrO_3$ | 128.92 | 408 | 0.37 | -5 | 12 - 13,000 |
| HCNS | 59.09 | 404 | 0.38 | 0.37 | 5 - 6,000 |
| HCl | 36.46 | 426.0 | 0.37 | 0.38 | 3 - 4,000 |
| $HClO_3$ | 84.46 | 408 | 0.36 | 0.4 | 8 - 9,000 |
| $HClO_4$ | 100.46 | 417 | 0.37 | 0.4 | 10 - 11,000 |
| $H_2CrO_4$ | 59.01 | 207 | 0.97 | 2.2 | 5 - 6,000 |
| HI | 127.91 | 428 | 0.37 | 0.42 | 12 - 13,000 |
| $HIO_3$ | 175.91 | 391.2 | 0.38 | -4.7 | 17 - 18,000 |
| $HMnO_4$ | 119.95 | 410 | 0.38 | 0.2 | 11 - 12,000 |
| $HNO_3$ | 63.01 | 420 | 0.37 | 0.36 | 6 - 7,000 |
| KAc | 98.15 | 115.4 | 0.75 | 1.3 | 9 - 10,000 |
| KBr | 119.01 | 151.7 | 0.62 | 0.62 | 11 - 12,000 |
| $KBrO_3$ | 167.01 | 129.4 | 0.69 | 0.48 | 16 - 17,000 |
| KCNS | 97.18 | 140.0 | 0.65 | 0.63 | 9 - 10,000 |
| KCl | 74.56 | 149.8 | 0.63 | 0.64 | 7 - 8,000 |
| $KClO_3$ | 122.55 | 138.7 | 0.66 | 0.4 | 12 - 13,000 |
| $K_2CrO_4$ | 97.10 | 156 | 1.22 | 1.3 | 9 - 10,000 |
| KF | 58.10 | 128 | 0.70 | 0.5 | 5 - 6,000 |
| $K_4Fe(CN)_6$ | 92.09 | 169 | 2.48 | 3.6 | 9 - 10,000 |
| $K_3Fe(CN)_6$ | 109.75 | 167.8 | 1.56 | 1.8 | 10 - 11,000 |
| $K_2Fe(CN)_5NO$ | 147.07 | 136.4 | 1.32 | 1.9 | 14 - 15,000 |
| KI | 166.01 | 150.8 | 0.63 | 0.62 | 16 - 17,000 |
| $KIO_3$ | 214.00 | 115 | 0.53 | 0.4 | 20 - 22,000 |
| $KMnO_4$ | 158.04 | 136 | 0.67 | 0.5 | 15 - 16,000 |
| $KNO_3$ | 101.11 | 144.5 | 0.64 | 0.36 | 10 - 11,000 |
| KOH | 56.11 | 271 | 0.45 | 0.4 | 5 - 6,000 |
| $K_2SO_4$ | 87.14 | 151.4 | 1.24 | 1.14 | 8 - 9,000 |
| LiBr | 86.85 | 121.4 | 0.72 | 0.5 | 8 - 9,000 |
| LiCl | 42.39 | 115 | 0.75 | 0.78 | 4 - 5,000 |
| $LiClO_3$ | 90.39 | 104.1 | 0.81 | 0.3 | 9 - 10,000 |
| $Li_2CrO_4$ | 64.93 | 123.6 | 1.46 | 1.5 | 6 - 7,000 |
| LiI | 133.84 | 117.7 | 0.74 | 0.8 | 13 - 14,000 |
| $LiNO_3$ | 68.94 | 111 | 0.77 | 0.45 | 6 - 7,000 |
| LiOH | 23.95 | 236.5 | 0.48 | 0.5 | 2 - 3,000 |
| $Li_2SO_4$ | 54.97 | 119.2 | 1.48 | 1.4 | 5 - 6,000 |
| $MgBr_2$ | 92.07 | 129 | 1.34 | 2.2 | 9 - 10,000 |
| $MgCrO_4$ | 70.15 | 125 | 2.64 | 3.2 | 7 - 8,000 |
| $Mg_2Fe(CN)_6$ | 65.14 | 172 | 4.75 | 13 | 6 - 7,000 |
| $Mg(NO_3)_2$ | 74.16 | 129.0 | 1.35 | 1.8 | 7 - 8,000 |
| $Mg(OH)_2$ | 29.17 | 257 | 0.87 | 2.1 | 2 - 3,000 |
| $MgSO_4$ | 60.19 | 116 | 2.75 | 3.7 | 6 - 6,000 |
| $MnBr_2$ | 107.38 | 128 | 1.34 | 1.7 | 10 - 11,000 |
| $MnCl_2$ | 62.92 | 126 | 1.36 | 1.6 | 6 - 7,000 |
| $MnSO_4$ | 75.50 | 109 | 2.84 | 3.8 | 7 - 8,000 |

| Chemical | Eq.Wt. | $\Lambda$, 25C | a | b | Valid ppm Range |
|---|---|---|---|---|---|
| $NH_4Br$ | 97.95 | 155 | 0.62 | 0.60 | 9 - 10,000 |
| $NH_4CNS$ | 76.12 | 140.8 | 0.65 | 0.5 | 7 - 8,000 |
| $NH_4Cl$ | 53.49 | 150.5 | 0.63 | 0.49 | 5 - 6,000 |
| $NH_4IO_3$ | 192.94 | 117 | 0.74 | 0 | 19 - 20,000 |
| $NH_4Pic$ | 246.14 | 104.4 | 0.80 | 0.9 | 24 - 25,000 |
| $(NH_4)_2SO_4$ | 66.07 | 149.9 | 1.25 | 1.1 | 6 - 7,000 |
| NaAC | 82.03 | 91.1 | 0.89 | 0.34 | 8 - 9,000 |
| NaBr | 102.90 | 126.0 | 0.70 | 0.5 | 10 - 11,000 |
| $NaBrO_3$ | 150.90 | 106.1 | 0.79 | 0.60 | 15 - 16,000 |
| NaCNS | 81.07 | 110.5 | 0.77 | 0.75 | 8 - 9,000 |
| $Na_2CO_3$ | 53.00 | 124.1 | 1.47 | 1.6 | 5 - 6,000 |
| NaCl | 58.44 | 126.5 | 0.70 | 0.74 | 5 - 6,000 |
| $NaClO_3$ | 106.44 | 115 | 0.75 | 0.6 | 10 - 11,000 |
| $NaClO_4$ | 122.44 | 110 | 0.77 | 0.6 | 12 - 13,000 |
| $NaCrO_4$ | 161.97 | 132 | 1.38 | 1.5 | 16 - 17,000 |
| NaF | 41.99 | 106 | 0.79 | 0.6 | 4 - 5,000 |
| $Na_4Fe(CN)_6$ | 75.98 | 155 | 2.74 | 4.7 | 7 - 8,000 |
| $NaHCO_3$ | 84.01 | 96.0 | 0.85 | 0.6 | 8 - 9,000 |
| NaI | 149.89 | 127.0 | 0.70 | 0.80 | 14 - 15,000 |
| $NaNO_3$ | 84.99 | 123 | 0.72 | 0.36 | 8 - 9,000 |
| NaOH | 40.01 | 246.5 | 0.47 | 0.3 | 4 - 4,000 |
| NaPic | 251.09 | 81 | 0.97 | 0.7 | 25 - 26,000 |
| $Na_2SO_4$ | 71.02 | 129.0 | 1.39 | 1.50 | 7 - 8,000 |
| $Na_2S_2O_3$ | 79.06 | 135.0 | 1.36 | 1.60 | 7 - 8,000 |
| $NiAc_2$ | 88.40 | 89.5 | 1.75 | 1.3 | 8 - 9,000 |
| $NiBr_2$ | 109.27 | 127 | 1.34 | 1.6 | 10 - 11,000 |
| $NiCl_2$ | 64.81 | 123.3 | 1.37 | 1.7 | 6 - 7,000 |
| $Ni(NO_3)_2$ | 91.36 | 124.5 | 1.37 | 1.8 | 9 - 10,000 |
| $NiSO_4$ | 77.39 | 100 | 2.7 | 1.6 | 7 - 8,000 |
| $PbCl_2$ | 139.05 | 145.0 | 1.26 | -7 | 13 - 14,000 |
| $Pb(NO_3)_2$ | 165.60 | 135.7 | 1.32 | 0.89 | 16 - 17,000 |
| RbBr | 165.37 | 148 | 0.63 | 0.2 | 16 - 17,000 |
| RbCl | 120.92 | 153 | 0.62 | 0.7 | 12 - 13,000 |
| RbI | 212.37 | 145.3 | 0.64 | 0.65 | 21 - 22,000 |
| RbOH | 102.48 | 272 | 0.45 | 0.5 | 10 - 11,000 |
| $SmBr_3$ | 130.02 | 140.2 | 1.63 | 2.9 | 12 - 14,000 |
| $SmCl_3$ | 85.57 | 139.8 | 1.64 | 3.0 | 8 - 9,000 |
| $SmI_3$ | 177.02 | 138.5 | 1.64 | 3.4 | 17 - 18,000 |
| $SrAC_2$ | 102.86 | 101 | 1.63 | 2.0 | 10 - 11,000 |
| $SrBr_2$ | 123.72 | 136.0 | 1.30 | 1.8 | 12 - 13,000 |
| $SrCl_2$ | 79.27 | 136.0 | 1.30 | 1.74 | 7 - 9,000 |
| $Sr(NO_3)_2$ | 105.82 | 131.8 | 1.34 | 1.5 | 10 - 11,000 |
| TlCl | 239.82 | 150.3 | 0.63 | -1.3 | 23 - 25,000 |
| $TlClO_3$ | 287.82 | 137.6 | 0.65 | 0.45 | 28 - 30,000 |
| TlOH | 221.38 | 276.1 | 0.45 | 0.45 | 22 - 23,000 |
| $YBr_3$ | 137.59 | 141 | 1.63 | 2.8 | 13 - 14,000 |
| $YCl_3$ | 65.09 | 136 | 1.67 | 3.5 | 6 - 7,000 |
| $YI_3$ | 156.54 | 143.8 | 1.60 | 2.6 | 15 - 16,000 |
| $ZnAc_2$ | 91.73 | 88 | 1.77 | 1.2 | 9 - 10,000 |
| $ZnBr_2$ | 112.60 | 159 | 1.23 | 0.7 | 11 - 12,000 |
| $ZnCl_2$ | 68.14 | 130 | 1.48 | 2.3 | 6 - 7,000 |
| $Zn(NO_3)_2$ | 94.69 | 125 | 1.37 | 2.2 | 9 - 10,000 |
| $ZnSO_4$ | 80.72 | 105 | 2.90 | 4.2 | 8 - 8,000 |