# INSTRUMENTS

## UNIQUE TEMPERATURE COMPENSATION FOR CONDUCTIVITY AND RESISTIVITY MEASUREMENTS

Conductivity and resistivity measurements are the most common, reliable, sensitive, accurate, and low-cost means of monitoring water purity for typical mineral contamination. A critical part of this monitoring is to eliminate the temperature dependence. At higher temperatures, ions become more mobile and therefore more conductive. It is desirable to have a fixed threshold of conductivity or resistivity for control or alarm, regardless of the temperature at which the measurement is made. As a result, the industry convention is to compensate measurements to 25 °C (77 °F) and to establish contamination limits based on conductivity or resistivity values at that temperature. Precise temperature control is usually costly, and with accurate temperature compensation, it is not required. The choice of the correct compensation is discussed here.

There are three parameters required to make accurate temperature-compensated conductivity measurements: a conductivity measurement, a temperature measurement, and knowledge of the type of impurity. Modern instrumentation is capable of measuring the conductivity and temperature with one sensor device and one meter, but the compensation for a specific impurity depends upon the application or the industry convention. All this presumes that the instrumentation has the capability to compensate for that specific impurity.

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Conductivity temperature characteristics of natural waters, drinking water, cooling waters, and service waters are routinely and appropriately compensated with a simple coefficient of 2% per degree centigrade (%/°C). These are not critical applications, and most neutral contaminants at moderate concentrations have a coefficient near this value. In fact, this is the only compensation available in many conductivity instruments. However, for nonroutine applications such as high-purity water, acids, bases, organic solutions, and concentrated solutions, it is important to recognize and account for their much different, nonlinear temperature characteristics. Instrumentation specifications (and sometimes even performance) must be examined to determine whether appropriate compensation is provided.

In years past, analog instruments were limited by the ability to match temperature characteristics of a solution with those of an electrical circuit, usually a resistor/thermistor network. A unique temperature-compensator circuit was built into the cell and was appropriate for only one type of material in solution and over a limited temperature and/or concentration range. This often forced the user into an inventory of many cells with specialized temperature compensators to provide compensation for each application. The more the measuring conditions deviated from 25 °C and from the reference concentration or purity level, the more the accuracy of compensation deteriorated.

This measurement method was further challenged by the addition of significant leadwire resistance for long runs between sensor and instrument. The leadwire resistance added to the temperature signal resistance, causing direct errors. There was considerable room for improvement. Today, several manufacturers offer three- or four-wire temperature measurement as a means to accurately correct for leadwire resistance.

Microprocessor-based instrumentation brought with it the ability to select the temperature sensor solely for the accuracy of temperature measurement and to leave the nonlinear curve-match-

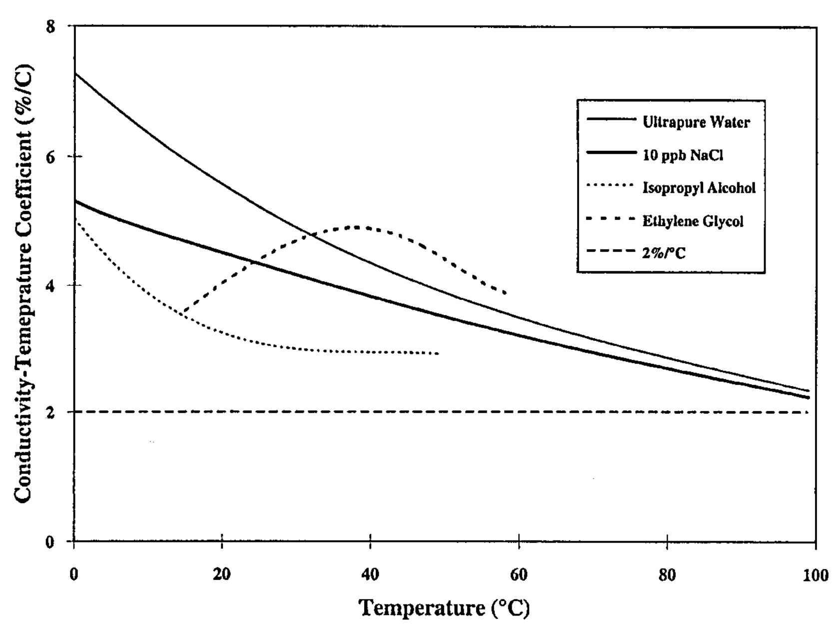


*Figure 1. Sensitivity of the conductivity of various fluids to temperature. Graph of %/°C versus temperature. Pure water, pure water with 10 parts per billion of sodium chloride, 75% isopropyl alcohol, 50% ethylene glycol, and linear (2%/°C).*

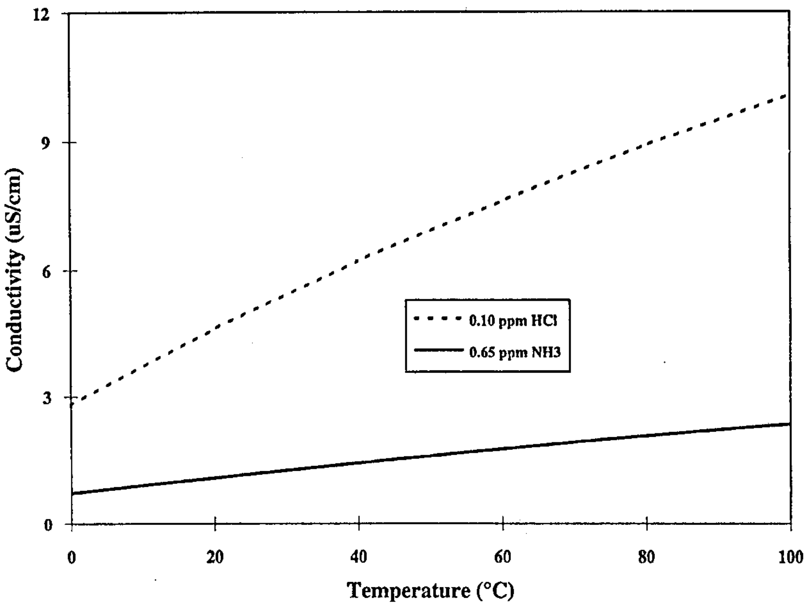


*Figure 2. Temperature characteristics of typical power plant samples (0.65 parts per million of ammonia and 0.10 ppm of hydrochloric acid.*

ing to microprocessor algorithms. Instruments with comprehensive algorithms can accurately compensate measurements over wide ranges of temperature and concentration; and a single, versatile instrument with several algorithms can be used in several industries and applications.

**Semiconductor Industry**

The temperature characteristics of pure water have been determined with greater accuracy in recent years (1-3). With this increased knowledge, more accurate temperature compensation can be provided in instrumentation monitoring pure water used to rinse the finest microelectronics wafers as well as pure water treatment systems in all industries. Of special concern are hot-deionized (DI) water rinse operations where temperature compensation is most critical (3). The reduced sensitivity at high temperatures makes hot-DI measurements more critical to accurate temperature compensation. Any small inaccuracy in the temperature or conductivity measurement is magnified under these conditions, thereby necessitating the use of three-wire temperature measurements and careful meter/sensor calibration.

Some rinse operations in the semiconductor industry use a hot mixture of isopropyl alcohol (IPA) and pure water to remove organic contaminants. Since IPA dissociates less efficiently than water ($K_{a,IPA} \sim 10^{-18}$, $K_w \sim 10^{-14}$), the resistivities of IPA solutions are higher and the temperature characteristics are very different than those for pure water alone. The different *temperature sensitivity* of IPA necessitates the use of a specialized compensation algorithm (4). The use of a standard "pure water with NaCl" algorithm for an IPA application results in meaningless compensated resistivity calculations.

In another semiconductor application, a mixture of ethylene glycol (EG) and pure water is used as a coolant in a heat-exchange loop where purity must be maintained. Purity requirements are closely controlled in order to maintain the effectiveness of radio frequency (RF) transmission from the source, through the coolant, to the semiconductor process. Like IPA, EG solutions have higher resistivities than water because of a lower ion concentration ($K_{a,EG} \sim 10^{-16}$) and lower ion mobilities. Likewise, the temperature dependences of their resistivities are also different than that of IPA and water. The use of the Thornton-Light temperature-compensation algorithm, because it is an inappropriate algorithm in this case, results in compensated resistivities ranging from negative values to several hundred Mohm-cm, regardless of the equipment supplier. In order to adequately detect small amounts of contamination by conductivity, another special algorithm was developed (4) for this specific application.

Representative curves for these applications are illustrated in Figure 1. Note that these high-purity applications cannot be satisfied with linear approximations over any appreciable temperature range.

**Power Industry**

Recognition and accommodation of the need for specialized temperature compensation in the power industry has been documented (5). Power plant "specific" conductivity measurements generally involve pure water with traces of ammonia, ethanolamine (ETA), or other amines. "Cation" conductivity measurements involve trace amounts of acids in pure water. The effects with these basic and acidic materials are subtle in that they affect not only the normal solute temperature coefficient but also the dissociation of the water itself. A cation/ammonia/ETA compensation algorithm accounts for these effects, providing a substantial improvement in accuracy with samples where temperature is not controlled very close to 25 °C.

Makeup water and nuclear boiling water reactor (BWR) plant water are untreated, with the probability that neutral mineral traces will be the most common contaminants. In these cases, the standard Thornton-Light high-purity water temperature-compensation algorithm is appropriate (3). Figure 2 shows representative curves for these applications.

Because of the increased memory capacities available in current instruments, a single model can contain all of these algorithms and help reduce inventory of instruments and spare parts. The selection of the appropriate temperature- compensation mode can be made in the field upon installation in a particular application.

**Pharmaceutical Industry**

With the continuing revision of *United States Pharmacopeia 23 (USP 23)* water specifications, there is a need to provide limits on a variety of USP-identified contaminating ions (6). The least conductive of these ions at the allowed levels are chloride ($Cl^-$), ammonia (as $NH_4^+$), and innocuous ions that are always present (hydrogen [$H^+$], hydroxide [$OH^-$], bicarbonate [$HCO_3^-$], and counterions to chloride [$Cl^-$]). Since a conductivity measurement cannot differentiate among the different ions, it cannot compensate correctly for all possible compositions. In addition, the complex temperature properties of $CO_2/HCO_3^-$ were studied in detail to help with determination of their influence, particularly for offline, atmosphere-equilibrated samples. As temperature rises, the conductivity of $HCO_3^-$ increases, but the solubility of $CO_2$ decreases and the equilibrium between them shifts (7).

Because of these complexities, it is now proposed to measure uncompensated conductivity and temperature separately, with worst-case conductivity limits established across the temperature range. With an instrument capable of full field configuration, continuous uncompensated conductivity and separate temperature must be readily available to satisfy this need.

**Water Treatment Deionizer Regeneration**

Cation- and anion-exchange resins are typically regenerated with 2% to 8% by weight solutions of acid and caustic. Since these reagents are purchased at much higher concentrations, they must be diluted accurately to provide consistent regeneration and deionizer performance. Conductivity provides a means of continuously monitoring the accuracy of this dilution. However, the temperature characteristics of acid and caustic are much different than those for conventional water measurements and again require unique compensation algorithms. The dilution of these concentrated reagents is exothermic with considerable temperature rise, so accurate temperature compensation is especially important. These algorithms also include the nonlinear conductivity-to-concentration conversion for direct percent-by-weight readout (8).

**Special Applications**

In unique situations where new materials are being used without carefully documented temperature characteristics, it is possible to customize the compensation with a user-determined linear coefficient. If uncompensated conductivity and temperature are measured over the range of the application, the data can be plotted and the slope at 25 °C determined. A setting of linear compensation in units of percentage of reading %/°C of change can then be entered into the instrument for compensation.

**Temperature Measurement**

The accuracy of the temperature measurement is critical to providing accurate compensation. This can be appreciated from the temperature coefficient of cold pure water, which rises to more than 7%/°C. (See the low-temperature end of Figure 1 for pure water.) With a precise, traceable platinum resistance temperature detector (RTD) built into the conductivity cell and used in a circuit that corrects for leadwire resistance, the full accuracy of the temperature measurement can be realized and applied to the selected compensation. An RTD has a further benefit over a thermistor in that it can give much higher accuracy at elevated temperatures with greater mechanical stability.

**Conclusions**

There are many applications for conductivity measurements in a water treatment or process system. For maximum measurement flexibility, it is advantageous to use an instrument with the capability to compensate for numerous fluids and impurities. This allows users the opportunity to have a single instrument that can meet all requirements from a menu-selectable keypad, as opposed to requiring one instrument for pure water, another for cation conductivity, another with special %/°C coefficient, one for *USP 23* (no compensation), and so forth. Since these algorithms are microprocessor-controlled, their implementation can be kept a simple integral part of standard modest-cost, high-accuracy instrumentation.■

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