

# MEASUREMENTS

## EXTENDING THE VALUE OF RESISTIVITY TO OPTIMIZE MICROELECTRONICS WATER SYSTEM OPERATION

**M**icroelectronics ultrapure water (UPW\*) requirements continue to grow more and more demanding as line widths of circuits are narrowed. This trend is reflected in periodic updates to the International Technology Roadmap for Semiconductors (ITRS). Conductivity/resistivity measurement has marginal sensitivity to detect trace ionic impurities at levels that affect product yields in semiconductor manufacturing. As a result, resistivity measuring equipment is challenged by semiconductor facilities experts to achieve higher accuracy of resistivity calibration and measurement. This is an update on recent improvements in these areas.

Because the goal of the measurement is to know water purity, not its actual resistivity at temperature, temperature effects must be compensated very accurately to obtain the resistivity value referenced to 25°C, regardless of the water temperature. The resistivity of UPW is accepted as 18.18 Mohm-cm at 25.0°C and is well documented at other temperatures as shown in Table A (1). This precise data enables accurate temperature compensation, provided appropriate algorithms and very precise resistivity and temperature measuring devices are used. Temperature measurement and compensation accuracy is critical because the temperature coefficient of UPW resistivity is 5.3% per

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°C at 25°C and more than 7% per °C in cold UPW.

Because resistivity is non-specific, responding to all ionic contaminants, its sensitivity depends on the nature of the contaminant. Figure 1 shows the relative conductivity response to various common ions. It is clear that acids and bases will have much greater response than neutral salts. If contamination comes from cross-contamination during ion exchange regeneration because of incomplete resin separation, the contaminant is likely to be in the form of hydrochloric acid (HCl) or sodium hydroxide (NaOH). These reagents include the much higher equivalent ionic conductivities of hydrogen (H<sup>+</sup>) and hydroxide (OH<sup>-</sup>), which would be expected to boost the sensitivity considerably. There could also potentially be NaCl with more modest sensitivity.

However, a deeper consideration of the properties of pure water with traces of alkali contamination (e.g., NaOH) reveals that the concentration of the highly conductive H<sup>+</sup> will be suppressed and will be replaced by less conductive Na<sup>+</sup>, plus additional OH<sup>-</sup> ions. So, for the first traces of NaOH added, the resistivity

will actually increase. The resistivity of nearly pure water reaches a maximum of 18.28 Mohm-cm when it contains 0.76 parts per billion (ppb) of NaOH (0.44 ppb sodium) (2, 3). Additional NaOH will quickly lower the resistivity as shown in Figure 2 (4). This phenomenon creates an ambiguous region for sodium contamination less than about 1 ppb, and limits the sensitivity of resistivity measurement to alkali contamination. Of the potential contaminants from ion exchange in UPW, there is highest sensitivity to HCl, then NaCl, and lastly NaOH.

With quality resistivity instrumentation, it is possible to reliably sense a reduction from pure water at 18.18 to 18.00 Mohm-cm. Figure 2 shows that this reduction corresponds to 0.1 ppb of HCl, 0.2 ppb of NaCl or 2 ppb of NaOH (1 ppb sodium). Some microelectronics facilities have improved on that sensitivity, detecting smaller changes after especially careful calibration of the sensor to UPW and from experience with their UPW system operation. The rest of this article focuses on recent improvements to resistivity instrumentation and calibration to support that sensitivity.

The accuracy and repeatability of

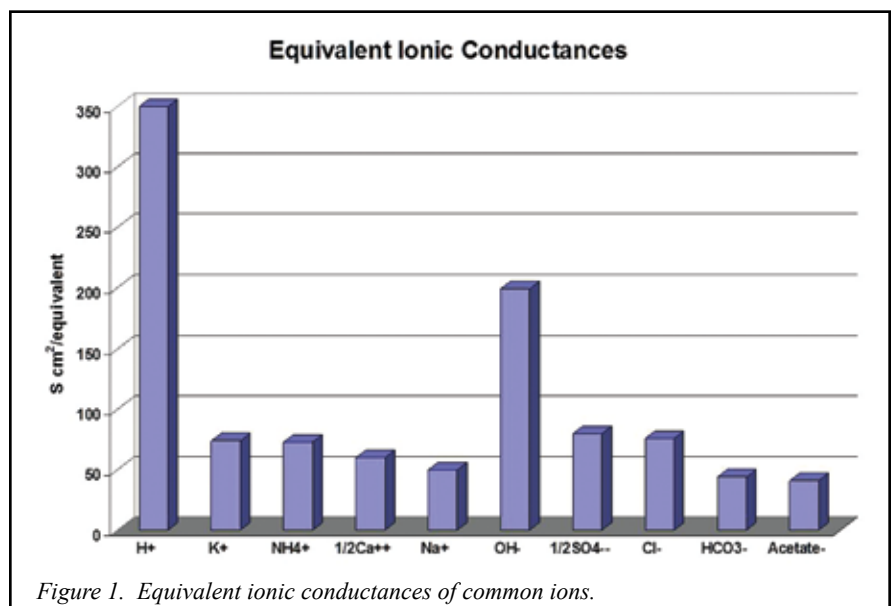


Figure 1. Equivalent ionic conductances of common ions.

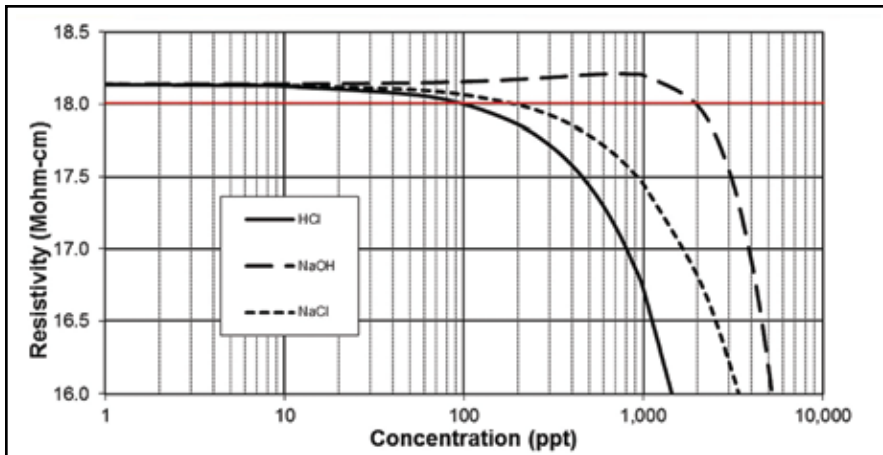


Figure 2. Resistivity of possible species from ion exchange resins<sup>4</sup>

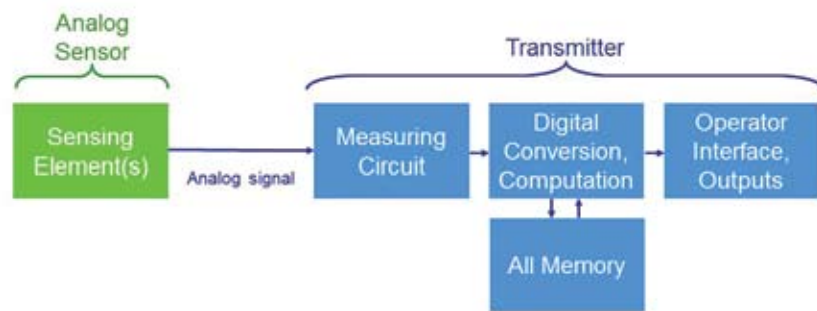


Figure 3. Traditional analog sensor configuration.

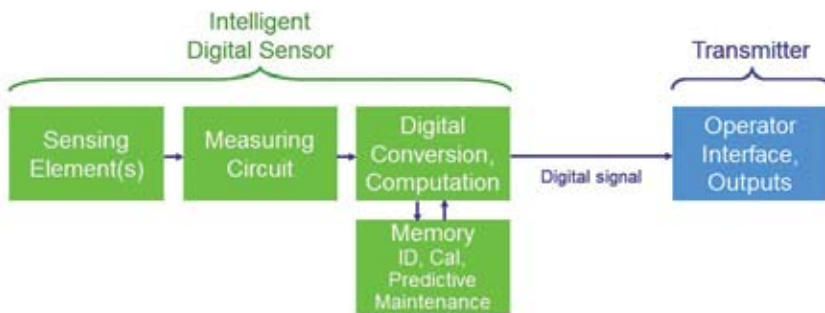


Figure 4. Digital sensor configuration.



Figure 5. 0.01 cm<sup>-1</sup> constant (left) and 0.1 cm<sup>-1</sup> constant (right) resistivity sensors comparing electrode length and spacing.

resistivity measurement are paramount in achieving sensitive on-line contamination detection. The challenges of improving the accuracy of resistivity measurement have existed for decades and significant progress has been made in two areas to meet these challenges as described here. These areas of progress are 1. the development of digital resistivity sensors; and 2. improvements in calibration approach. Both have been optimized for pure water measurement accuracy.

### Advances in Sensors

**Conventional analog** resistivity measuring equipment consists of a remote transmitter with an AC resistance measuring circuit, a sensor immersed in the water sample, and a cable connecting the two devices. The AC circuit measures the resistance through the volume of fluid between the electrodes of the sensor, and then converts the resistance (ohms) to a resistivity value (ohm-cm) according to the sensor cell constant (cm<sup>-1</sup>) illustrated in Equation 1, where:

$$\text{Resistivity} = \frac{\text{Resistance}}{\text{Cell Constant}} \quad \text{Eq. 1}$$

With conventional analog resistivity measuring equipment, even using identical models of a manufacturer's transmitter and sensor, there are still a number of variables in every installation. These include the signal wiring distance between sensor and transmitter, cable routing, wire termination, and slight differences in transmitter measuring circuits—all differences between factory calibrated equipment and the performance of equipment after installation. Most of these differences are because of added resistance and capacitance caused by the cable (length, routing, and connections). Any water system installation differs considerably from factory calibration conditions, and each of the above differences contributes a small amount to the uncertainty of the measurement with conventional equipment.

Of particular note is the change of transmitters and their measuring circuits from factory calibration to the unit installed in the water system. The small but significant uncertainty of the measuring circuits must be added to the

uncertainty of the sensor calibration. Contributions to the total error occur both in the resistivity and in the temperature measurements. In addition, the use of various length cables between sensor and transmitter and their terminations add yet more sources of uncertainty. These challenges are mitigated to some extent by the use of 4-wire resistance measurements and supplier-specific measuring techniques to reduce the cable impact but the various sources of error can accumulate to an estimated uncertainty of  $\pm 0.35$  Mohm-cm.

**Digital advances.** A major breakthrough in resistivity measurement is the development of self-contained, intelligent, digital sensors that eliminate all of these sources of error. Digital sensors have the measuring circuit built into the sensor body with a digital signal sent over virtually any distance to the transmitter. Figures 3 and 4 provide a comparison of traditional analog and new digital sensor configurations. (An intermediate design was the Smart Sensor, with identification and calibration memory stored in the analog sensor connector.) A fully digital sensor has zero signal degradation because of cable length, routing, and connection resistance and capacitance. Electrical noise problems are virtually eliminated.

With a digital sensor the same measuring circuit is always used to calibrate the sensor elements since they are inseparable and this holds true for both resistivity and temperature. The measuring circuits and all wiring are extremely compact, fixed, and sealed within the sensor body. The factory calibration of the total measurement system is unaltered after installation so factory accuracy can always be achieved in the field. The remaining uncertainty with digital sensors is estimated at  $\pm 0.2$  Mohm-cm, which is a 43% improvement from that of analog sensors.

Beyond the improvements in accuracy, digital sensors also contain the memory for their identity and all calibration data. This information is automatically communicated to the transmitter without attention by a technician. This configuration enables a more reliable plug-and-measure installation as well as assuring full performance integrity if the sensor

is moved to another location.

Yet another benefit of the digital sensor design is its extremely wide rangeability. The same sensor that provides high accuracy in UPW has been found to measure at ranges as high as seawater with only modest reductions in accuracy. This enables significant simplification of equipment and spare parts in water treatment systems.

A requirement of UPW monitoring is immediate response and minimal interference. Fast, interference-free resistivity measurement is provided with short, widely-spaced electrodes in the sensor cell. Electrode dimensions are governed by the cell constant required for the measuring circuit. The compact measuring circuit in intelligent digital sensors has the ability to give uncompromised performance in UPW with a  $0.1 \text{ cm}^{-1}$  cell constant with short, widely spaced electrodes. On the other hand, many analog sensor measuring circuits require the closer electrode spacing required by  $0.01$  to  $0.05 \text{ cm}^{-1}$  cell constant sensors to perform adequately in UPW.

Figure 5 illustrates the typical difference in electrode geometry and makes it clear that the long, thin passage of low constant sensors (left) causes slower, laminar flow inside them that requires much longer rinsing during startups and could trap air bubbles between electrodes. The higher cell constant sensor (right) has shorter and more widely spaced electrodes with much less restriction. It allows better rinsing with more turbulent sample flow through the sensing area and has less chance of trapping bubbles or contamination. The higher cell constant sensor promotes faster resistivity response that can be very important in water recycle and reclaim systems. The smaller inner electrode containing the temperature sensor has less thermal mass, giving faster temperature response, which is especially important with temperature cycling in heated UPW systems.

To summarize the improvements, an intelligent digital sensor is calibrated as a system, including the cell constant, temperature sensor and respective measuring circuits. Calibration results are stored in on-board memory and everything is contained within the sealed sensor body. The measuring circuit in this type of sen-

sor provides excellent performance and wide rangeability with the wide electrode spacing of a  $0.1 \text{ cm}^{-1}$  cell constant.

Experience with the digital sensor has shown stability as well as accuracy. At one large microelectronics facility, continuous digital resistivity measurements all fell between 18.193 and 18.206 Mohm-cm throughout a two-week test period—a span of only 0.013 Mohm-cm or 0.07% of the measurement.

### Sensor Calibration

There is a long history of cutting-edge resistivity sensor calibration through several generations of automated UPW calibration systems. These systems have used UPW as the medium to calibrate production sensors against laboratory-calibrated sensors. The laboratory standard sensors were, in turn, traceable to ASTM International, or other recognized standard solutions, and verified by the known resistivity of UPW as a function of temperature as in Table A. The critical temperature measurement was calibrated based on National Institute of Science and Technology (NIST)-traceable resistance temperature detectors (RTDs) in the same loop.

Recognizing the improvements available with digital sensors, the factory sensor calibration system was reviewed for possible improvements to further reduce errors of measurement. In early 2013, an instrument maker<sup>a</sup> changed the procedure for calibrating production resistivity sensors. It was recognized that the production UPW loop had excellent reliability in maintaining water purity and was in fact more consistent than the process of transferring calibration through laboratory sensors. Instead of performing the calibration of production sensors by comparison to laboratory sensors, the production sensors are now calibrated directly to UPW as the more stable standard. The water purity is verified by laboratory sensors that still provide traceability to ASTM standard solutions (5, 6). Temperature is calibrated in the same manner as with the previous system, based on NIST-traceable standards.

The UPW system has given very consistent results over the period it has been used as the basic standard—more consistent that the method depending

on periodic laboratory standard sensor calibration. As a result, the new calibration procedure is producing improved cell constant precision.

### Conclusion

Progress is being made in resistivity measurement through better calibration capability using UPW as the standard coupled with intelligent digital sensor technology that guarantees this accuracy will be delivered in the water system or any other process. These are two major steps toward meeting the on-line trace contaminant sensitivity needed in microelectronics manufacturing. Work continues to advance the capabilities of this important water quality measurement. □

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### Endnote

\*In the text, the term UPW refers to semiconductor-grade water produced in microelectronics facilities. Its quality parameters are defined under the International Technology Roadmap for Semiconductors (ITRS).

\*METTLER TOLEDO Thornton, Billerica, Mass., is the instrument manufacturer referred to in the text.

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**TABLE A**  
**Pure Water Resistivity versus Temperature<sup>1</sup>**

Temperature (°C)	Resistivity (Mohm-cm)
0.0	86.19
5.0	60.48
10.0	43.44
15.0	31.87
20.0	23.85
25.0	18.18
30.0	14.09
35.0	11.09
40.0	8.849
45.0	7.154
50.0	5.853
55.0	4.840
60.0	4.042
65.0	3.407
70.0	2.896
75.0	2.482
80.0	2.142
85.0	1.862
90.0	1.630
95.0	1.436
100.0	1.274