

Practical Quality Assurance of On-Line Analytical Measurements

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ABSTRACT

Much has been presented about analytical instrumentation, its use in making on-line measurements, and plant control based on the results. This article presents a summary of practical recommendations for achieving good results and verifying them for parameters of conductivity, pH, ORP and dissolved oxygen. The old saying GIGO (garbage in: garbage out) certainly applies to analytical measurements. Means to assure quality of the input to improve the reliability and accuracy of the output are provided.

INTRODUCTION

On-line measurements are increasingly accepted as more reliable than laboratory measurements since they are not subject to discontinuous sampling conditions, grab sample contamination and manual errors of measurement. Furthermore, power plants are being run leaner, with fewer personnel available to make laboratory measurements. Presented here is a summary of practical recommendations for achieving good on-line results and verifying them for parameters of conductivity, pH, ORP and dissolved oxygen. Means to assure quality of the measurement are provided to improve the reliability and accuracy of chemistry control. The introduction of digital sensors for on-line monitoring brings significant new capabilities for ease of use, improved performance and higher quality measurements.

SAMPLING

On-line instruments have been optimized for accurate measurements of power plant samples. However, they can only measure the samples presented to them. Good measurements require that a representative sample reach the sensors. Effects of sample delay, continued reaction and air contamination must be minimized to obtain dependable results. Following are recommendations to maintain sample integrity.

Sample Source

Where two-phase flow (saturated steam/water droplet mixture) must be sampled, the sample should contain the same ratio of steam and water as the process line. A sample nozzle should be located near the center of the

process pipe, facing into the flow. The sample flow velocity should be nearly isokinetic – with the same flow velocity moving inside the nozzle as there is in the surrounding process pipe. Isokinetic sampling prevents pulling in excess steam at too high a sample velocity or accumulating too many water droplets at too low a sample velocity. It provides a representative sample of the two phases.

Sample Reaction

Where reducing agents such as hydrazine or reducing amines are used, the sample should be cooled as close to the sampling point as possible to prevent continued reaction. This is important for measurements of dissolved oxygen, reducing agent or ORP (oxidation reduction potential).

Corrosion Product Deposits

Corrosion product particles that accumulate inside sample tubing create a large active surface area along the length that can adsorb and desorb materials in the sample. A sample line with a lot of deposits can act like an ion chromatograph and delay the passage of ions through the line much longer than a simple calculation from flow rate, diameter and length would predict. In addition, it can change concentrations with changes in sample flow rates. It has been found that a flow velocity of 6 ft/s (2 m/s) gives the least accumulation of particles in horizontal sample lines and is recommended wherever possible. This high velocity is only practical using very small diameter tubing for the long lengths of the sample line. Some of the sample is then bypassed to drain and the rest divided for measurement by multiple sensors, some of which require quite low flow rates. Where main sample line flow velocities cannot be maintained at the highest recommended levels, regular cleaning may be needed.

Sample Flow

The appropriate sample flow rate at the sensor depends on the particular measurement. For example, cation (acid) conductivity requires a high flow rate to obtain good ion exchange. On the other hand, pH measurement in a low conductivity sample requires low flow rates to minimize electrostatic pickup and reference junction potentials to yield a stable measurement.

Filters

Placing a filter in the sample line upstream of optical analyzers can protect them from particulate contaminants and errors. However, the filter elements must be changed frequently to prevent a thick accumulation of sediment that slows the response to real sample changes. On the other hand, electrochemical measurements such as conductivity, pH, ORP and dissolved oxygen are not directly affected by particles. Some sensors for these parameters have flow housings designed with very small volume that encourages any particles to flow on through the housing and down the drain. In this way, the delays and maintenance of filters and the cleaning of bowl-shaped flow chambers are eliminated and better overall measurements result.

During initial startups when very high particulate concentrations are expected, all sample lines should be diverted to drain ahead of final flow regulation and sensors. Pressure regulators and flowmeters as well as sensors, with or without filters, should not be subjected to these heavy loads of corrosion products which could clog small orifices and fittings.

Air Leaks

Dissolved oxygen samples at $\mu\text{g} \cdot \text{kg}^{-1}$ (ppb) levels are especially vulnerable to errors from air leakage. Although samples are pressurized and flowing, it has been observed that a loose rotameter, valve or compression fitting seal that leaves a path through a thin film of water can allow a trace amount of oxygen to diffuse into the sample. At $\mu\text{g} \cdot \text{kg}^{-1}$ levels no bubbles will be present, but a significant change in readings can occur.

Air can also pass through polymer sample tubing and have the same effect as a leak. Stainless steel should be used for all dissolved oxygen sample lines. But if flexible tubing is needed, it should be as short as possible and should be made of polyvinylidene fluoride (PVDF) or Nylon, which both have especially low gas permeability. The same precautions should also be used for low conductivity measurements where CO_2 from the air can contaminate a sample and raise the conductivity due to increased bicarbonate and hydrogen ion concentrations.

Grab Samples

Off-line samples are inevitably subject to contamination from the air and the container. Whenever possible, it is always preferable to take a portable instrument and sensor to the flowing sample rather than taking a grab sample to the laboratory. However, there are virtually no laboratory or portable instruments for conductivity and pH that have temperature compensation suitable for high purity measurements. They do not take into account the changing dissociation of water and ammonia or amines with temperature, which is a major factor at low concentrations.

Much better results can be obtained by using on-line pure water instrumentation in a portable mode which can duplicate the sample integrity of a permanent on-line measurement once it has been connected and run long enough to achieve steady sample line conditions. On-line instrumentation can also provide the appropriate high purity temperature compensation.

CONDUCTIVITY

Conductivity measurement represents the concentration of all ionic materials in the sample: treatment chemicals as well as contaminants. However, interferences can occur with this simple measurement of the conductance between two electrodes.

Interferences

Bubbles can cause erroneously low conductivity readings. If gas occupies some of the space that should be sampled, it will lower the conductivity measurement. This is particularly common with makeup water treatment in the wintertime. Cold water comes in under high pressure and with some dissolved air. As it passes through treatment, the pressure is lowered and it warms up, making any dissolved gases less soluble. Small bubbles can form at the surface of the conductivity sensor electrodes and will remain there unless a high enough flow velocity is available to carry them away. A further contribution to bubbles can occur downstream of a cation exchanger where dissolved bicarbonate is converted to CO_2 as a result of the lower pH after cation exchange. Repositioning or installing a longer conductivity sensor to reach a more turbulent part of the flow in the pipe is needed.

Particulate contamination of conductivity sensors can cause the opposite problem. Ion exchange resin beads and corrosion products are at least slightly conductive. If these particles accumulate between closely spaced electrodes of a sensor, they will cause erroneously high conductivity readings. This condition will continue to give high readings even if the sensor is removed from the pipe and shaken to remove water droplets, and is a good way to confirm this problem.

Sensor Selection

The vulnerability of interference from both bubbles and particulate contamination is greatly reduced if the spacing between sensor electrodes is wider. The spacing, along with the surface area across that space, establishes the cell constant that is specific for the instrument and range of measurement. In general, the higher the cell constant, the wider the spacing and the higher the resistance that must be measured by the instrument. Some instrumentation can use a 0.1 cm^{-1} cell constant even for accurate ultrapure water measurements while others must use lower cell constants with more electrode surface area spaced more closely together. See [Figure 1](#) for a visual comparison. In some situations the reliability of measurement can be improved significantly using a higher cell constant.

Accuracy

The accuracy of conductivity measurement is dependent on the measuring circuit, the cell constant and the temperature compensation. The measuring circuit is normally calibrated using precision resistances traceable to an internationally recognized standard such as NIST (National Institute for Standards and Technology). Modern conductivity instrumentation has internal auto-ranging to achieve maximum rangeability for a given cell constant and requires multiple resistances on each range to fully calibrate the circuit. In addition, the temperature measuring circuit is calibrated. This is all done during factory calibration and should be certified in a new instrument.

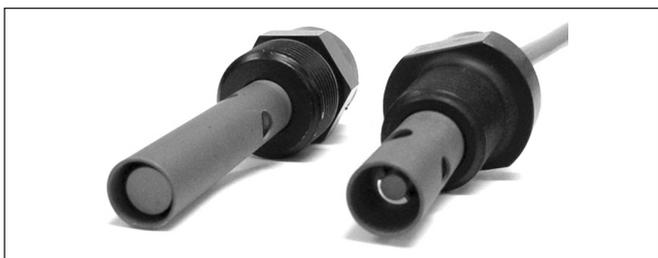


Figure 1:
Comparison of electrode spacing of 0.1 cm^{-1} and 0.01 cm^{-1} cell constant conductivity sensors.

To verify the measuring circuit later with an aging instrument, a user must have an appropriate procedure and precision resistances available to connect to the input to confirm that the measuring circuit is still accurate. Resistance standards are typically in the form of a certified resistance decade box or a certified ohmmeter. For more convenient verification or calibration, a manufacturer may provide instrument-specific, certified calibrators that can be connected in place of the sensor to check the measuring circuit, including all the resistance values needed, a compatible connector and instructions, as shown in [Figure 2](#).

Cell Constant

As noted above, the sensor's cell constant may have a nominal value of 0.1 cm^{-1} , but the precise cell constant is typically calibrated individually to achieve higher accuracy. This is done in a known solution or in comparison with another calibrated measuring system. Factory calibrations are usually certified and traceable to an ASTM standard [1].

Conductivity Temperature Compensation

Temperature compensation in low conductivity ranges has a huge influence on the measurement. Temperature for compensation of conductivity should therefore be calibrated within a few tenths degree C. Industry standards reference conductivity readings to $25 \text{ }^\circ\text{C}$. But even if samples are cooled very close to $25 \text{ }^\circ\text{C}$, by the time they pass through flow meters, valves, tubing and in some cases a cation exchange column, the sample temperature will be greatly influenced by the ambient temperature.

The temperature coefficient of pure water is about 5 % of the conductivity reading per $^\circ\text{C}$. It is non-linear with both temperature and conductivity level and varies with composition, so care should be taken that the temperature compensation algorithm used is capable of doing the job. Many algorithms show significant errors [2,3]. Be sure to select the appropriate algorithm in the instrument for pure makeup water, for ammonia/amine-treated water or for cation conductivity, depending on the measurement point. Each has a significantly different characteristic.



Figure 2:
Instrument-specific conductivity calibrators with certified resistances for all measuring ranges.

Laboratory conductivity instruments do not provide any high purity temperature compensation algorithms so their readings cannot be compared with on-line measurements except at 25 °C or if compensation in both instruments can be turned off.

Cation Conductivity

Cation conductivity is an excellent technique for sensing corrosive contaminants such as chlorides and sulfates by removing ammonia or amines and their higher background conductivities. Cation conductivity measurement inevitably involves a compromise between the quality of measurement and the sample flow rate. A high sample flow rate assures a timely measurement and turbulence within the cation resin that promotes thorough ion exchange. However, the higher flow rate also depletes the resin capacity faster, requiring more frequent replacement.

It has been found that a minimum flow velocity through the resin column of $0.3 \text{ m} \cdot \text{min}^{-1}$ (approximately $600 \text{ mL} \cdot \text{min}^{-1}$ in a 5 cm inner diameter column) will assure good results [4]: As the flow rate is decreased, greater channeling through the resin will occur, resulting in increasing traces of ammonia or amines and erroneously high cation conductivity readings. If the sample flow velocity is lower than recommended, the water quality may actually be better than is indicated. This could result in waste in delayed startups, premature condensate polisher regenerations and other decisions based on this key parameter.

pH

It is well known that pH measurement of low conductivity samples is difficult. Several precautions are recommended. The sensor should be designed with a stainless steel flow housing to provide electrical shielding of the sample and electrodes. Low sample flow rates are recommended to minimize any electrostatic charge buildup from poorly conductive water flowing along the glass electrode. A small volume flow housing will encourage corrosion product particles to exit through the outflow instead of collecting in the bottom of a large flow bowl and slowing response.

The reference electrode should be a flowing junction type which provides pressurization of the electrolyte, whether by gravity or by internal pressurization. The forced electrolyte flow maintains a relatively low resistance in the junction to minimize junction potential differences between the conditions of calibrating in buffer solution and measuring in low ionic strength sample.

Even with these precautions, there is always some small error between buffer calibration and reading in low conductivity waters. In cycle chemistry samples where specific and cation conductivity measurements are made on

the same sample, the pH can be calculated from these conductivity values with excellent accuracy.

Calculated pH

The correlation of pH and conductivity of ammonia has been used for decades to compare cycle chemistry measurements. For a given ammonia concentration in water, there is a definite pH and conductivity value which can be calculated from dissociation and conductance data. Because conductivity measurement is typically more reliable than high purity pH measurement, specific conductivity is often used as the primary variable to control ammonia feed although pH is also measured. Under normal operating conditions calculated pH from conductivity is more accurate than direct electrode pH measurement for two reasons:

- (1) Conductivity is linear with concentration whereas pH is logarithmic. pH therefore has less resolution. For example, a change of only 0.3 pH represents a 100 % change in both concentration and conductivity in cycle chemistry ranges.
- (2) pH reference electrode junction potential is notoriously less stable in low conductivity samples and that instability is frequently greater than ± 0.1 pH, depending on the electrode system used.

Specific conductivity is the primary value establishing the calculated pH while cation conductivity is used to trim for the presence of small amounts of mineral and/or carbon dioxide contamination. The algorithm assumes that the primary specific conductivity (and pH) influence is ammonia or amines and that the contaminants have lower concentrations. Generally, the pH must be within 7.5–10.5 and specific conductivity must be greater than cation conductivity, especially at low conductivity levels. Also, the pH calculation should not be used with phosphate-treated water.

pH calculation algorithms provide very accurate determinations when the sample composition complies with the conditions above. Its excellent performance is acknowledged by its use in plants around the world, especially in Europe. However, it is also important to be aware of the errors that can be produced when operation goes well outside normal operating conditions. For example, a failure causing an acid leak during condensate polisher regeneration could raise both the specific and cation conductivities to the point where they are nearly equal. In a situation where both go up to $40 \mu\text{S} \cdot \text{cm}^{-1}$, the calculated pH would show a value of 10 (assuming it was too much ammonia) though the real pH would be 4 (because of the acid leak!) Therefore, it is always recommended to also measure pH with a glass electrode for protection during upsets.

In practice, the calculated pH provides an excellent reference for a final 1-point calibration of the electrode pH measurement when normal operating conditions prevail. This final trim calibration eliminates the unknown change in reference junction potential between the buffer solution and low conductivity sample.

pH Temperature Compensation

All pH instrumentation provides temperature compensation for the variable output of pH electrodes with temperatures shown in Figure 3. This electrode temperature compensation makes the conversion from an electrode millivolt signal to a pH value at the temperature in which the measurement is made.

Solution temperature compensation, on the other hand, yields a value of pH compensated to 25 °C and is used almost exclusively in power cycle chemistry and pure makeup water measurements. This is because it is significant only with dilute alkaline samples where the changing dissociation of water and base is most pronounced. Figure 4 illustrates the temperature influence. Other samples have enough buffer content that the pH is stabilized over temperature and there is negligible change. Because of this, general-purpose pH instruments, including those in the lab, do not provide solution temperature compensation, so it must be done by manual calculation.

The block diagram in Figure 5 shows how a pH instrument compensates for these two temperature effects. Instruments have a default setting for the solution temperature coefficient of zero. A value must be entered into the instrument to make it active. The solution temperature coefficient of cycle chemistry samples is -0.033 pH per °C and of pure makeup waters is -0.017 pH per °C (the slopes of the curves in Figure 4 at 25 °C).

Oxidation Reduction Potential

Oxidation reduction or redox potential (ORP) is being used increasingly to monitor AVT(R) (all-volatile treatment reducing) conditions, usually where copper alloys require it. ORP responds to both oxidizing and reducing conditions and is closely related to the corrosion conditions in the sample. Very low ORP values due to excessive reducing agent feed is used to warn of the condition, which aggravates flow-assisted corrosion.

Because ORP responds to all oxidizing and reducing species, each plant will have different characteristics with different backgrounds of ferrous/ferric, cuprous/cupric, and other trace minerals in the samples. Both pH and dissolved oxygen also influence the ORP. The ORP level can

vary considerably from plant to plant, but once a baseline is established in normal operation, deviations from that can be used as on-line checks to regulate reducing agent feed.

An ORP electrode is very similar to a pH electrode except that a platinum element replaces the pH-sensitive glass membrane. The platinum provides an inert electrical contact to the sample that responds with a voltage to the sample's tendency to contribute or remove electrons

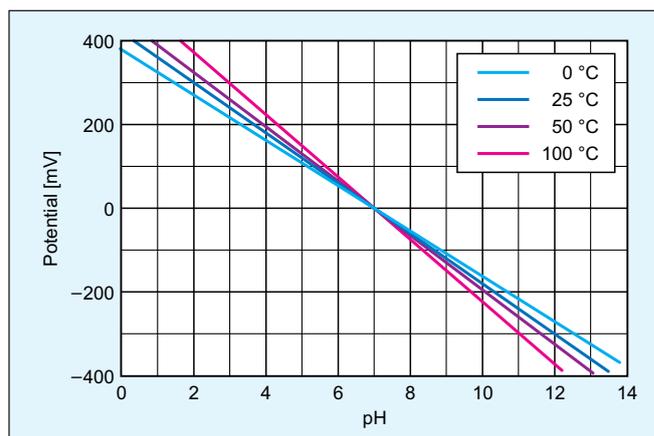


Figure 3: pH electrode output vs. temperature (Nernst response).

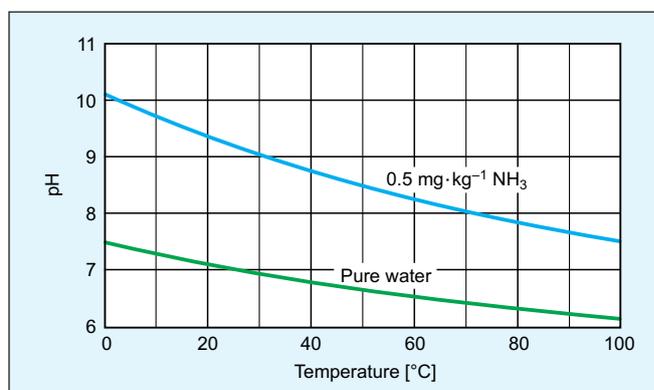


Figure 4: pH vs. temperature (solution ionization effect on pH).

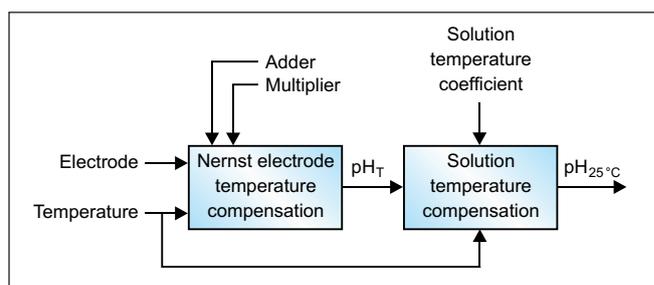


Figure 5: pH instrument measurement and temperature compensation.

based on the oxidizing and reducing conditions present. The reference electrode is identical to that used for a pH measurement and simply completes the voltage measuring circuit through the sample.

To be responsive, the platinum element must be kept clean. If fine corrosion products accumulate on its surface, even though they are not very visible, the response will deteriorate. Periodic cleaning with a soft cloth wetted with dilute acid can restore response although it will cause a temporary upset in the measurement.

The operation of an ORP measuring system should be verified by immersing the electrode in an ORP standard solution. These can be purchased or can be made up from pH buffer solution saturated with quinhydrone [5]. ORP measurements are normally just verified, not calibrated, in these solutions since they have tolerances of ± 20 to 30 mV. Measuring in absolute millivolts provides a definite reference point and gives an indication of the health of the electrode.

Dissolved Oxygen

Dissolved oxygen is another important parameter influencing corrosion. The reliability of dissolved oxygen measurements depends on consistent sensor maintenance according to manufacturer recommendations. Membrane and electrolyte replacement are needed periodically.

Sample leaks

As noted earlier, in sampling for dissolved oxygen measurement it is especially critical to have a tightly sealed sample line. $\mu\text{g} \cdot \text{kg}^{-1}$ levels of air can be easily aspirated into a sample or just diffused through a film of water at a loose seal of a compression fitting, rotameter gasket, valve, etc. The quick way to check for an air leak is to increase the sample flow rate. The dissolved oxygen reading should remain relatively constant. If it decreases, that is an indication of a leak, because the increased amount of sample dilutes it to a greater extent. Fittings may need to be tightened or replaced. If a reading goes up with an increased flow rate, it indicates the flow was too low in the first place and that the sensor was consuming more oxygen from the surface of the membrane than was being replenished by the sample flow turbulence.

Calibration

Ampoule colorimetric systems can be used for rough grab sample verification but are not accurate enough at low $\mu\text{g} \cdot \text{kg}^{-1}$ levels for any kind of calibration. Air calibration is still generally the best method for establishing the span response of dissolved oxygen sensors. Response of sensors is extremely linear so calibration at the high air level will track back to $\mu\text{g} \cdot \text{kg}^{-1}$ levels very well.

Just as it is sometimes difficult to get a leak-free sampling system for dissolved oxygen, it is also quite difficult to achieve zero dissolved oxygen for a zero point calibration. Sulfite solutions come close but cannot be relied on if a true zero is needed. The best method is to use 99.999 % pure nitrogen and allow it to flow slowly through the sensor flow housing, allotting enough time for all oxygen in the sensor to diffuse out or react.

Digital Sensors

A new development in on-line analytical measurement technology promises to improve the quality of measurements in a number of ways. Just as consumer electronics are becoming ever smaller, high quality analytical sensors are now being constructed with the microelectronics measuring circuit integral to the sensor body. In addition, the electronics package provides analog to digital conversion to enable transmission of a digital signal back to readout, control and/or data acquisition instrumentation.

Digital sensors have improved control of measurement conditions. This is largely due to elimination of the analog sensor-to-transmitter cable length, which has been effectively reduced to a few centimeters – the wiring distance between the sensing elements and the measuring circuit. Analog signal degradation due to cable resistance and capacitance is eliminated. This is particularly advantageous for conductivity where measurements are made using alternating current (AC) and the signal is vulnerable to capacitance effects. Eliminating these impediments enables much greater control over the measuring technique. The range of measurement has been pushed beyond previous limits so that a single UniCond^{®1} conductivity sensor can measure accurately from ultrapure water up to waters with a conductivity of 50 000 $\mu\text{S} \cdot \text{cm}^{-1}$. In cooling water and makeup water treatment, this universal sensor can eliminate confusion about what cell constant to use, what process fitting must be accommodated, what calibration data to enter, what spare parts to maintain and other decisions where multiple sensor types would normally be required. The installed reliability is therefore increased.

In addition to greater rangeability, the accuracy of measurement is also improved. Because the sensor and measuring circuit are always paired together, they are calibrated as a single unit with a single limit of error. There is no error contribution from pairing separate sensors and measuring instruments. The instrument for a digital sensor only displays a precise digital value; it is not making a measurement.

¹ UniCond is a registered trademark of Mettler-Toledo Thornton



Figure 6:
Cutaway view of the digital sensor for conductivity revealing its integral measuring circuit.

Parameters of pH, ORP and dissolved oxygen as well as conductivity are available with digital sensors as shown in Figure 6. In fact, a single digital sensor for pH with a platinum solution ground element provides simultaneous measurements of pH, ORP and temperature. In all cases, the on-board memory with Intelligent Sensor Management™ maintains sensor identity, factory and user calibration data and diagnostic information. This allows calibration in the laboratory before installation in the process with no special handling to prevent operator error. The sensors configure the multiparameter instrument for measurement as soon as they are connected, communicating the parameter and calibration data as well as settings that have been entered previously by the user. Spare parts for the instrument are greatly reduced because a single model works with all parameters without hardware or configuration changes.

Transmission of digital signals from the sensors to the instrument preserves the integrity of the measurements. This trend for improving the quality of analytical measurements using on-board measurement and digital conversion is anticipated to receive wide industry acceptance within the next few years.

CONCLUSION

With on-line measurements being used for more and more decision-making, instrument performance must be commensurate with this responsibility. Instrument design, selection, installation, operation and maintenance must all be optimized to achieve results to support excellence in chemistry management and control over the long term.

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