A Multiparameter Instrumentation Approach to Makeup and Cycle Chemistry Measurements

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Abstract

Process analytical instrumentation for both makeup water treatment and cycle chemistry measurements has evolved to meet the increasing demands of these major parts of the plant. Makeup treatment at many locations is faced with deteriorating quality of raw water supplies, increasing use of membrane processes and specifications requiring higher purity. Newer cycle chemistry treatment schemes depend on lower and more accurate cation conductivity, controlled dissolved oxygen and reliable pH, sometimes with reduced budgets for sample conditioning. There is heightened interest in the detrimental effects of organics in the cycle. Described here is the use of multiparameter instrumentation specifically designed to give successful measurements in these processes. Parameters of specific, cation and degassed cation conductivity, pH, dissolved oxygen, ORP and TOC as well as the benefits of having them available within a common instrument platform are discussed. Commonality of instrumentation for makeup water treatment and for cycle chemistry monitoring can greatly simplify specification, installation, training, operation, calibration, maintenance and spare parts inventory within the plant.

Before discussing multiparameter instrumentation, it is appropriate to take a step back and review sampling, measurement and sensor details. The old adage "garbage in—garbage out" normally applied to computers is also fully applicable, perhaps more literally, to on-line analytical measurements. Samples must have integrity at the sensors and sensors must be proven appropriate for the specialized measurements required before there can be any confidence in the results. With reliable sensor signals then the capability for handling measurements on a common platform can have far reaching benefits.

Sampling

The need for isokinetic sampling when two-phases are present in order to obtain a representative sample is well understood but should be implemented more widely.

Once the sample is withdrawn, it should be cooled as quickly as possible to minimize the length of high temperature sample line where further reaction of reducing agents and other materials could take place. The flow velocity should be kept high to minimize deposition of solids. Accumulated solids in a sample line can provide a medium for ionic or dissolved gas adsorption and desorption which can cause delayed and inconsistent delivery of sample contaminants to the sensors. A dirty sample line takes on some characteristics of a chromatograph, which in this case is quite undesirable.

Sampling studies have shown that flow velocities near 6 ft/sec (2 m/sec) in horizontal lines yield a minimum of solids deposition.[1] Lower flow velocities should be avoided. To minimize waste of valuable pure water and heat, small diameter sample lines on the order of 1/8 inch (3 mm) ID are recommended to achieve this velocity. Of course fast flow velocities provide more timely measurement as well. Where sample lines have been used at low flow velocities for long periods of time, thorough acid cleaning is recommended. A long conditioning time is needed after cleaning to restore the sample line to steady state operation.

High pressure samples require pressure reduction before going to sensors. Extended needle valve-type pressure reducing devices designed for this purpose are generally used. Where grab samples as well as continuous measurements are needed, flow controls should be provided to maintain the sample flowrate in the main line and to the on-line analyzers, as required. While it is good practice to do primary cooling near the sample source, it is not always practical or economical. In any case, cooling again near the sensors is desirable to control temperature to the industry standard of 25 °C. However, even if sample temperature is controlled well, ambient influences after the cooler (such as passing through a cation column) may cause significant deviations. For this reason, and because the temperature coefficient of measured parameters is quite significant, accurate temperature compensation is essential. It goes without saying that sample lines should be tight with no leaks. However, sample contamination with traces of air frequently occur and cause

errors frequently occur and cause errors in low concentration dissolved oxygen measurements. Even though a sample may be under positive pressure, a liquid film at a loose compression fitting, rotameter or other component can allow ppb quantities of air to diffuse into the sample without exhibiting a leak externally. Such an air leak can be detected by varying the sample flowrate. A higher sample flowrate will dilute any air leak and cause a lower dissolved oxygen measurement. Insensitivity of dissolved oxygen reading to sample flow (within the operating range of the sensor) is a good indication of a tight sampling system.

Conductivity

Conductivity measurement responds to all ionic materials in a sample, whether they are intentionally added treatment chemicals, contaminating minerals or dissolved gases such as carbon dioxide (in the form of carbonic acid, bicarbonates or carbonates). Contaminants can be deionizer regenerant chemicals from inadequately rinsed resins, air with CO_2 not completely removed by deaerators, carry-over from drum boilers, or leaks from condensers or other heat exchangers. Conductivity is greatly influenced by temperature since all ions become more mobile and conductive at higher temperatures. In addition, in pure waters there is increasing ionization of the water itself with temperature. Because of these two effects, guidelines and specifications reference conductivity values at 25°C which dictates sample temperature control and/or accurate compensation.

Specific Conductivity

Because conductivity responds to all ionic materials, specific (direct) conductivity measurement in high pressure boiler cycles is typically dominated by treatment chemicals such as amonia, phosphates, amines, etc. which should be at much higher concentrations than any contaminants. Therefore, specific conductivity, often with corroboration by pH, is generally used to monitor and control treatment chemical concentrations Where the sample conductivity is dominated by ammonia or amine concentration, the conductivity temperature characteristic is considerably different from that of pure makeup water—for which most instruments' pure water temperature compensation was designed. For this reason, proven specialized temperature compensation for this application is necessary for accurate specific conductivity measurement. The magnitude of errors with improper temperature compensation can be quite large.[2] Also to support good accuracy, the cell constant and the temperature element of the conductivity sensor should be individually calibrated and certified by the manufacturer. Any errors in the cell constant will cause proportional errors in the measurement. At the same time, errors in the temperature measurement will have a significant impact on the compensated reading. An automated system for factory calibration of both cell constant and temperature compensator in an ultrapure DI water loop is shown in Figure 1.

Figure 1 - Automated Factory Calibration System for Conductivity Sensors

It should be noted that some instrumentation with low resistance temperature elements requires temperature calibration by the user at installation to achieve rated accuracy. This can require a temperature bath, a certified thermometer and a lot of patience— for every point of measurement. Startup calibration is not necessary with instrumentation designed with 3- or 4-wire resistance measurement techniques which eliminate the effects of leadwire resistance.

Cation Conductivity

Cation or acid conductivity is the technique of continuously conditioning the sample by passing it through a cation exchange cartridge in the hydrogen form. It enhances the sensitivity to contaminants by two means:

• Ammonia or amines that are intentionally present at ppm levels are removed. This eliminates their high conductivity. The lower ppb concentrations and conductivity of contaminants can then be "seen" by the measurement.

• Contaminant corrosive salts are converted to their respective acids which are typically 3 times as conductive as the original salt.

This simplicity and detection sensitivity have made cation conductivity the most widely used measure of contamination in the cycle. In samples where carbon dioxide will be present it is sometimes worthwhile to add a degas unit to allow measurement of cation conductivity with the carbon dioxide removed. Carbon dioxide is acknowledged to be less corrosive but a cation conductivity measurement by itself cannot distinguish between carbon dioxide and more corrosive contaminants. Figures 2 and 3 illustrate typical conditioning for and response of specific, cation and degassed cation conductivity measurements.
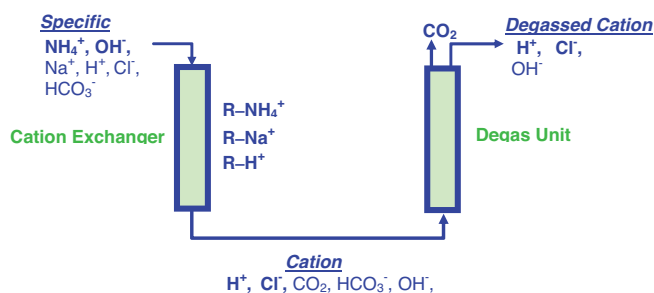
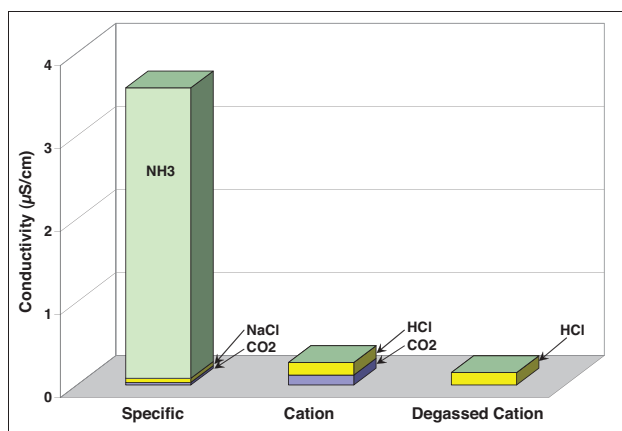Figure 2 - Specific, Cation and Degassed Conductivity Measurements (dominant ions in bold)

Figure 3 – Typical Specific, Cation and Degassed Cation Conductivity Response

Although cation conductivity is widely applied, there has been little standardization of the cation exchange cartridge which can add many variables to the measurement. In particular, the sample flow velocity through the cartridge must be high enough to promote good exchange with little ion leakage. Incomplete exchange would add significant flow-dependent errors to this important measurement. Reasonable guidelines for the technique have been defined.[3]

As described for specific conductivity above, the temperature influence on cation conductivity is different from deionized makeup water. This dilute acid sample requires another specialized temperature compensation algorithm to meet this need. Unfortunately, not all instrumentation available for this application performs adequately. Figure 4 illustrates an evaluation of the cation conductivity temperature compensation in five widely used instruments. Instrument E (Thornton) showed more than an order of magnitude better accuracy than the best of the others.[4] Errors in compensation can have very adverse practical implications. One installation in Asia with a commonly used but inadequate cation conductivity instrument that was included in the evaluation cited, significantly delayed acceptance of an entire condensate polishing system. The system performance could not be proven until the poor temperature compensation issue was resolved.[5]
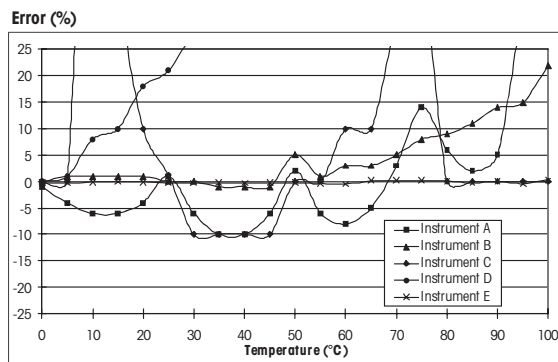

Figure 4 - Cation Conductivity Temperature Compensation Evaluation at 0.1 µS/cm

Degassed Cation Conductivity

Where carbon dioxide concentrations are a significant interference with detection of more corrosive contaminants, degassing the sample can be very helpful. A degassed cation conductivity measurement is more likely to meet turbine manufacturers' requirements, especially during startups. In-depth theoretical and physical evaluations have been made on the performance of various degassing methods, including heating to near boiling, nitrogen sparging and membrane transfer. Results appeared to be reasonably good for all the methods.[6,7]

Specification and Installation of Conductivity Instrumentation

The following issues must be addressed for efficient startup and reliable, accurate conductivity measurements:

- Small inside diameter sample line and low volume flow chamber to ensure high flow velocity to carry through any corrosion product particles in the sample.

- Conductivity sensors that are ISO 9001 factory-certified with individual cell constant and temperature element calibrations traceable to NIST or ASTM standards. No on-site calibration required at installation to achieve rated accuracy.

- Conductivity signal handling capability to meet accuracy specifications for the length of required sensor-to-instrument cable runs.

- Field-selectable, proven temperature compensation algorithms designed specifically for the application: a) Ammonia/amine compensation for specific conductivity in the cycle, b) Cation compensation for cation and degassed conductivity, c) Standard non-linear high purity compensation for specific conductivity in deionized makeup water.

- For cation conductivity—correct sample flow velocity through the cation resin; inclusion of degassifier if needed to eliminate carbon dioxide interference.

pH Measurement

pH is much more specific than conductivity since it responds only to the hydrogen ion, H^+. It measures acidity or alkalinity of water which provides additional information when trying to identify a source of contamination. pH is defined as, $pH = -\log_{10}[H^+]$ and $[H^+] = 10^{-pH}$, a logarithmic measure of hydrogen ion concentration.

Temperature Effects on pH

As noted previously for conductivity, pure waters have unique temperature characteristics due to changing ionization with temperature and this applies also to pH. This ionization effect must be compensated—with what is called pH solution temperature compensation, a capability provided only in instrumentation intended for pure water measurements. This compensation must be activated when commissioning the instrument, typically with a manually set temperature correction near 0.032 pH/°C for cycle chemistry samples, to counteract the opposite negative coefficient. Similar to conductivity, pure water pH specifications are referenced to the industry standard of 25 °C. Laboratory instruments do not provide solution temperature compensation so any lab measurements must be corrected manually.

This solution temperature compensation should not be confused with conventional electrode temperature compensation which is included in virtually all pH instrumentation. Conventional compensation compensates for the universal output change of all electrodes with temperature. It provides the conversion from an electrode millivolt signal to a pH value at the temperature at which the measurement is made. Solution temperature compensation discussed previously yields a value of pH compensated to 25 °C, unique for the type of sample. Both types of compensation are needed for cycle chemistry measurements.

pH Electrodes

pH is derived from a millivolt signal developed at the outer surface of a glass measuring electrode membrane. This signal depends on the glass/solution ionic equilibrium in which it is immersed and is directly proportional to the pH. To complete the measuring circuit, the reference electrode makes electrical contact with the sample.
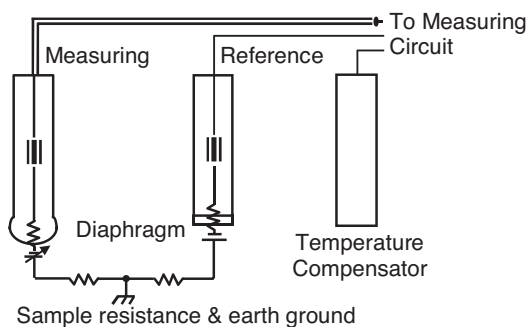

Figure 5 - pH Electrode Schematic (functions may be built into a single probe)

Some pH electrode systems include the measuring and the reference electrodes arranged concentrically, plus the temperature compensator, into a single compact probe body. They are shown separately in Figure 5 to also illustrate their electrical functions.

The reference electrode which completes the measuring circuit contains the critical diaphragm or reference junction. This is made of porous ceramic, polymer, fibers, or a very narrow passage and provides electrical continuity. It should ideally maintain a constant voltage of its own—a true reference. It also acts as a physical barrier to the conductive salts contained inside the reference electrode so they are not depleted too rapidly and are not contaminated by the process sample.

The most reliable reference diaphragms for pure waters are of the flowing type where a small quantity of electrolyte solution or gel slowly bleeds out through the junction. The electrolyte flow may be driven by gravity from an elevated reservoir or it may be driven by a closed prepressurized gel electrode. This positive flow of electrolyte is critical to maintaining consistent diaphragm potential in both pure water and in calibrating buffer solutions. Without this, an accurate calibration cannot be made. A good source for additional high purity pH measuring information is available.[8]

Specification and Installation of High Purity pH Instrumentation

The following areas can be critical to successful pH measurment:

- Instrumentation with adjustable solution temperature compensation in addition to conventional electrode temperature compensation.

- Grounded, closed, low volume stainless steel flow chamber to minimize electrostatic interference, air contamination and accumulation of suspended corrosion products.

- Flowing diaphragm reference electrode—solution or pressurized gel.

- Low, constant sample flowrate with discharge to atmospheric pressure to provide very low, constant back pressure on the reference diaphragm.

Dissolved Oxygen Measurement

Dissolved oxygen (DO) measurement and control is essential to minimize corrosion and the subsequent deposition of metal oxide corrosion products in critical components in the power cycle. In greatly simplified terms, there are two basic cycle chemistry strategies for DO. Copper alloys usually require very low ppb levels of DO to prevent attack. This is typical of Phosphate and All Volatile Treatment (Reducing) regimes. In other, especially clean systems, ferrous alloys benefit from more moderate levels of DO in the 50-150 ppb range where the more durable and less soluble hematite iron oxide is formed. In both cases DO levels are critical to staying within low corrosion rate conditions.

Oxygen has a temperature-dependent solubility in water at atmospheric pressure as shown in Figure 6. The entire curve would be shifted upwards if the pressure over the water were increased. Working in the opposite direction, deaerators depend on partial vacuum and/or elevated temperatures to produce lower solubility and remove dissolved gases. Both temperature and pressure effects must be accommodated in the calibration of DO measurements.
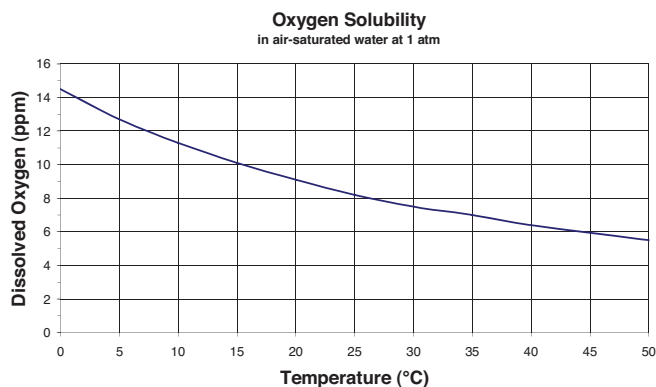

Oxygen Solubility
in air-saturated water at 1 atm

Figure 6 - Solubility of Oxygen in Water

DO Sensors

Dissolved oxygen sensors are electro-chemical devices that take advantage of the gas permeability of polymeric membranes to separate the electrochemistry of the sensor from the sample. This separation enables a sensor to provide a controlled environment for the electrodes and electrolyte while allowing oxygen to enter from the sample and react. Figure 7 is a simplified illustration of a DO sensor.

The diffusion rate of oxygen through a membrane is proportional to the partial pressure of oxygen in the sample. The oxygen which permeates the membrane reacts at the cathode, producing a current in direct proportion to the quantity of oxygen. That current is the measurement signal which matches the oxygen partial pressure and the concentration of DO, at constant temperature. The guard ring electrode prevents any residual oxygen in the electrolyte at the sides from diffusing to the cathode by reducing it first. It greatly improves the speed of downscale response which can be very important during plant startup. To derive a concentration measurement from partial pressure with varying temperature, the signal is compensated, based on the relationship in Figure 6. Further guidance for DO measurement is available.[9]
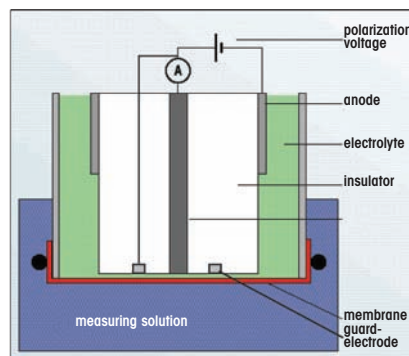

Figure 7 - Dissolved Oxygen Probe with Guard Ring Electrode for Fast Downscale Response

Specification and Installation of Dissolved Oxygen Instrumentation

Details of the particular probe technology include membrane material and thickness, electrode size and materials, electrolyte type and concentration, and method of electrode polarization. These technical details combine to determine the performance, maintenance requirements and life of the probe. Key capabilities include:

- Ability to operate at low sample flowrates without compromising accuracy, to conserve high purity water.

- Rapid downscale response to track plant startups.

- Operation with simple, minimal maintenance.

- Installation in a tight sampling system with rotameter down stream to eliminate air leaks.

Total Organic Carbon

The most common source of organic contamination is makeup water, either from raw surface water or from deionization resin deterioration. Some contaminants could be chlorinated and could break down into highly corrosive chlorides in the steam cycle. If these can be detected and controlled in the makeup water treatment system, many problems can be avoided downstream. Since organics are mostly non-conductive, direct conductivity measurement is not responsive and a TOC measurement is needed.

The most common TOC measuring technique is based on ultraviolet oxidation of organics in the sample with conductivity measured both before and after the UV exposure. The first measurement accounts for any conductive contaminants already in the sample while the second measurement detects the increased conductivity due to generated carbon dioxide. The conductivity measurements and their difference are compared using a correlation curve to produce a consistent TOC measurement.
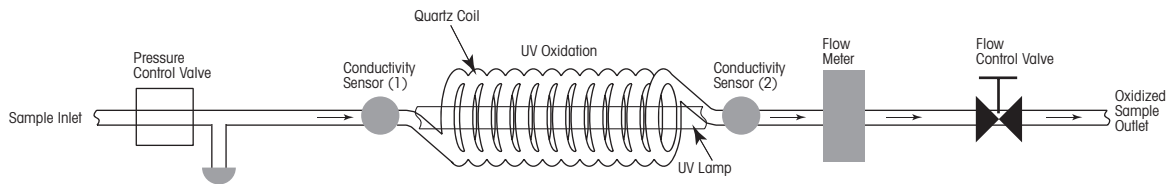
Figure 8 - Flow path of a direct conductivity TOC sensor

The fastest responding instruments using this technique have an especially high intensity UV lamp with continuously flowing sample through the sensor which operates without any moving parts, membranes or chemicals. Figure 8 shows the flow path of this kind of TOC sensor. Response time is particularly fast, taking less than 60 seconds for the sample to pass from the inlet to the final conductivity sensor.

This technology does have application limitations. It is used only on pure water samples with conductivity 2 µS/cm and TOC of 0.05 - 1000 ppb. Also, alkalinity should be much less than the TOC concentration since the carbon dioxide oxidation product would otherwise be neutralized by alkaline materials and would not produce the expected increase in conductivity. For these reasons this technology is recommended primarily for makeup water treatment systems. However, there are preliminary indications that measurement after a cation column to eliminate alkalinity can open up this technique to cycle chemistry applications—particularly condensate return from cogeneration.

Multiparameter Approach

Sensors for the above parameters utilize conductometric, potentiometric and polarographic or galvanic principles. These sensors look and operate quite differently from each other and require quite different measuring circuits. However, since all are needed to meet cycle chemistry requirements there are real advantages to having a common instrument platform to specify, install, startup, train on, operate and maintain. In addition, a multi-channel capability can save considerably on panel space, number of cutouts and wiring, for both new and retrofit installations. Figure 9 illustrates the input/output and configuration flexibility of a multiparameter, multichannel instrument. This instrument has inputs for up to 4 Smart sensors which have their own calibration data retained in memory. Two flow inputs are also available. Up to 16 measurement parameters may be derived from these channels, allowing the possibility of sample temperature and computed parameters to be displayed. The 4-line display can scroll through 4 screens to show all the measurements, as needed. Alarm setpoints, relays and up to 8 analog outputs may be freely assigned to the measurements. The flexibility is much like a small PLC but with analytical measuring capability.
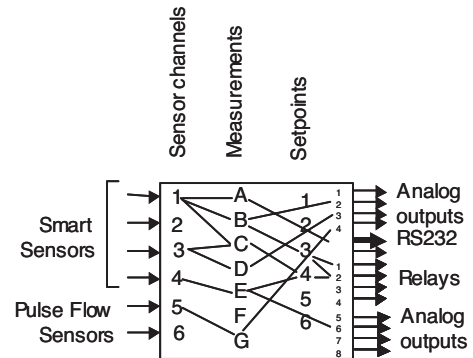

Figure 9 – Multiparameter Instrument Configuration

Figure 10 - Portable Verification System including cation Conductivity, pH, DO and TOC Measurements and Data Acquisition (courtesy Waters Equipment)

This comprehensive and compact instrument platform is being used widely to monitor and control makeup water treatment systems, including flowrate, pressure and tank level as well as analytical parameters. With its growing complement of parameters described above, its full potential for cycle chemistry monitoring is also being realized. Its compact size makes it especially convenient for use in portable verification systems such as that shown in Figure 10 which can be wheeled to sample panels around the plant to check on panel-mounted equipment.

Computed Parameters

The multiparameter instrument approach can provide much more than commonality of measurement functions. There is true synergism as the different parameters are used together to derive computed parameters on-line. These computed parameters provide greater insight to the various process operation, whether for makeup water treatment or for cycle chemistry monitoring. Their availability in real time along with conventional measurements increases the value.

% Salt Rejection

Reverse osmosis performance can be monitored by % rejection calculated from the conductivity values of product and feed water. It indicates the relative health of the membrane and quickly detects any flaws, leaks or significant deterioration in the membrane system.

% Rejection = [1 – product conductivity / feed conductivity] x 100   (1)

% Recovery

Where water is scarce, "percent recovery" of water is a very important parameter. This computation is available with multi-channel flow instrumentation as:

% Recovery = [product flow / (product flow + reject flow)] x 100   (2)

Deionization Capacity

Ion exchange loading can be determined by measuring conductivity and flowrate going into a DI bed. The calculation totalizes or integrates the conductivity as total dissolved solids (TDS) multiplied by flowrate to yield a value in grains or equivalents of cumulative ionic load. Deionization capacity measurement can be useful both for predicting when an ion exchange bed will exhaust and for tracking the long term performance of the resin.[10]

DI Capacity = Flowrate x TDS dt   (3)

Calculated pH

pH measurement in low conductivity samples are notoriously difficult to make and to calibrate. Specific conductivity is often used as a check on pH measurements, with the knowledge of the ammonia concentration vs. conductivity vs. pH relationship. However, the presence of carbon dioxide or other contaminants may distort this simple relationship. This distortion can be corrected using the cation conductivity measurement. Calculated pH using this correction has been accepted and used by European plants, the VGB and various expert cycle chemistry monitoring systems for a number of years.

Specific Conductivity at 25 °C
Cation conductivity at 25 °C   } Calculated pH at 25 °C

There are limitations that the pH must be greater than 8 and the specific conductivity must be significantly greater than the cation conductivity. It is also not applicable for samples containing phosphates. But when these conditions are met, the calculation is more accurate than an electrode pH measurement. When these conditions are not met, gross errors can result. Multiparameter instruments that provide both calculated pH and electrode pH measurement provide the best of both worlds:

1) More accurate and reliable pH measurement by calculation under normal operating conditions.

2) A convenient reference for more accurately calibrating the pH electrode.

3) A differential pH alarm to warn when calibration is needed or abnormal conditions are occuring.[11] Figure 11 illustrates an example of the display of these parameters.

The most common TOC measuring technique is based on ultraviolet oxidation of organics in the sample with conductivity measured both before and after the UV exposure. The first measurement accounts for any conductive contaminants already in the sample while the second measurement detects the increased conductivity due to generated carbon dioxide. The conductivity measurements and their difference are compared using a correlation curve to produce a consistent TOC measurement.
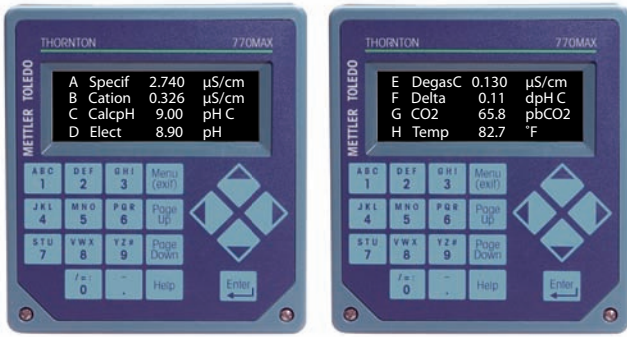
Figure 11 - Two Screen pages of a Single Instrument Display Specific, Cation and Degassed Cation Conductivity and Electrode pH, plus Computed pH, pH difference, and CO$_2$

Calculated Carbon Dioxide

Where degassed cation conductivity is measured, it can be related to the cation conductivity and the carbon dioxide content can be inferred using the ASTM standard for this determination.[12] The display pages of a single instrument in Figure 11 show typical readouts of these parameters.

$$\left. \begin{array}{l} \text{Cation Conductivity at 25 °C} \\ \text{Degassed Cation Conductivity at 25 °C} \end{array} \right\} \quad \text{Computed } CO_2 \quad (5)$$

While this multiparameter instrument platform appears to be somewhat complex, it should be remembered that it configures itself for simple direct measurements as soon as its sensors are plugged in. Additional functions or parameters may be configured through straightforward menus at any time as the need arises.

Conclusion

With fewer personnel to operate today's generating stations, on-line chemistry instrumentation becomes more critical. A confusing array of unreliable, user un-friendly and error-prone instrumentation cannot be tolerated. A practical approach to improving installed reliability and accuracy is the use of a high-performance multiparameter instrument platform. Its commonality of installation, functions, calibration and maintenance plus the availability of on-line computed parameters can be a great benefit to overextended plant personnel. Equally important are good sampling practices and appropriate sensor design, installation and maintenance. Consistent manufacturer support in all of these areas helps to assure success.

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