

pH and CO₂ Determinations Based on Power Plant Conductivity Measurements

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ABSTRACT

Previous work has focused on major improvements in the accuracy of conductivity measurements and on the development and benefit of multi-parameter on-line analytical instrumentation [1–3]. This background as well as continuing work now provide additional parameters that can be derived from accurate specific, cation (acid) and degassed cation (acid) conductivity measurements.

INTRODUCTION

Described here are capabilities to read out pH in real time based on calculations from specific and cation conductivity values. On cycle chemistry samples, calculated pH can be more accurate and more reliable than high purity pH measured with a conventional glass electrode. It is recognized that this inferred measurement has major limitations well outside normal operating conditions, where the electrode will give a much more accurate reading. Availability of both types of pH measurement in multi-parameter instrumentation provides the best of both worlds: high accuracy by calculation within normal operating conditions and direct electrode pH measurement for confirmation when operation goes out of the normal range. Because specific and cation conductivity measurements are already required for most samples, the calculated pH value can be obtained at no additional cost.

A further capability is inferring CO₂ concentration from cation conductivity and degassed cation conductivity. Degassing the sample is the best means of monitoring condensate to determine how much of the cation conductivity value is due to non-volatile mineral contamination and how much is due to CO₂. Appropriate instrumentation can use these values along with known CO₂ conductivity data to derive the CO₂ concentration on-line. With the CO₂ removed, the remaining degassed cation conductivity can be interpreted as total non-volatile anions with readout as $\mu\text{g} \cdot \text{kg}^{-1}$ chlorides or sulfates.

With the decrease in personnel overseeing power plant cycle chemistry today, greater reliance on on-line instrumentation can be a necessity. The calculated pH approach can be of further help in this regard because conductivity sensors require much less maintenance than pH sensors.

This work describes some of the improvements in instrument reliability, ease of use and capabilities that raise confidence in these on-line measurements.

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. There are two reasons for the higher reliability of conductivity:

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 two-fold (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 this instability is frequently greater than ± 0.1 pH, depending on the electrode system used.

Inherent in the simple correlation above is the assumption that there is nothing else present but ammonia and water. Any traces of carbon dioxide and/or mineral contaminants must be negligible. Under many operating conditions, this is a reasonable assumption. However, as these trace contaminants grow in concentration during plant startup, unusual conditions, or upsets, their effects must be accommodated.

The effect of substantial amounts of carbon dioxide contamination was analyzed and graphed some years ago by NUS Corporation (now Scientech) with *Figure 1*, which has been reproduced in ASTM and EPRI documents. The data for this figure assume that only ammonia and carbon dioxide are present. When this is true, and when accurate pH and conductivity measurements can be made, then the ammonia and carbon dioxide concentrations can be determined. However, this still relies on the difficult high purity pH measurement.

Refinement of the conductivity and pH correlation has been used in various ways by several organizations [4–6]. The Westinghouse ChemAID expert cycle chemistry monitoring system provided extensive automated diagnostics including comparison of these measurements [7]. Boyd provided a similar correlation in a stand alone "pH

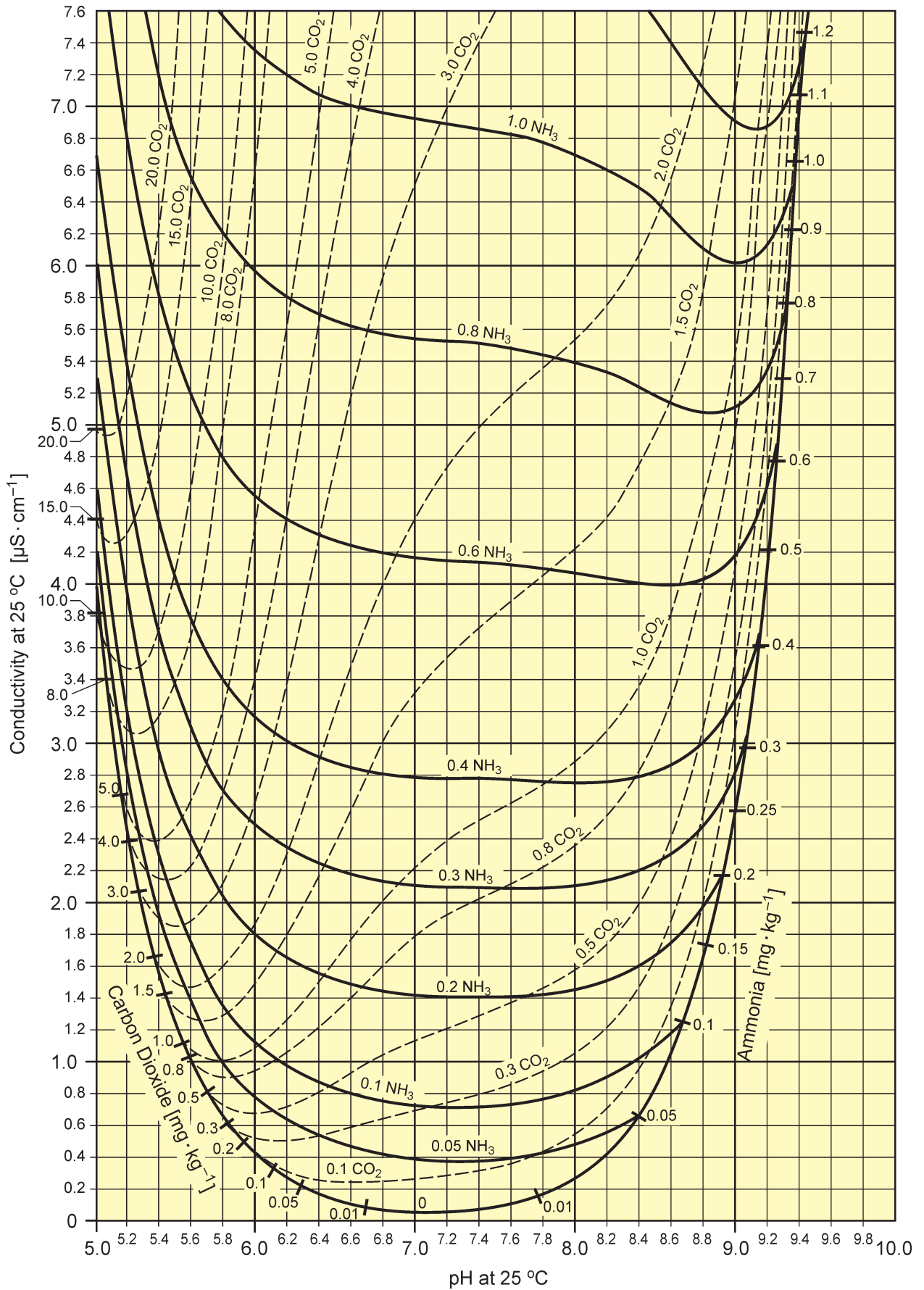


Figure 1: Conductivity vs. pH of carbon dioxide and ammonia (NUS Corp.).

Calculator" program [8]. In these cases the specific and cation conductivity values are used as the input to calculate pH.

Specific conductivity is the primary influence while cation conductivity is used to trim for the presence of small amounts of mineral and/or carbon dioxide contamination. These algorithms still assume 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.

Figure 2 illustrates that the specific conductivity is dominated by hydroxide and ammonium (or amine) ions, which are at the highest concentrations and are shown in bold. Hydroxide ion conductivity is 3 times that of other ions (except hydrogen, which is suppressed at the high sample pH). *Figure 2* also illustrates the operation of the cation exchange resin to remove the ammonium (or amine) and mineral cations (e.g., sodium), leaving hydrogen ion to dominate the conductivity of the cation exchanged sample. Hydrogen ion is about 7 times as conductive as other ions (except hydroxide, which has a suppressed concentration at the low pH in the sample at this point) so it makes little difference just what the mix of anions is among chlorides, bicarbonates, sulfates, or others.

pH calculation algorithms provide very accurate determinations when the sample composition complies with the conditions above. This 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 deionizer 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)! Although very unusual, this condition was experienced in a Danish power plant, where they have since recognized the need to monitor both calculated pH and direct electrode pH [9].

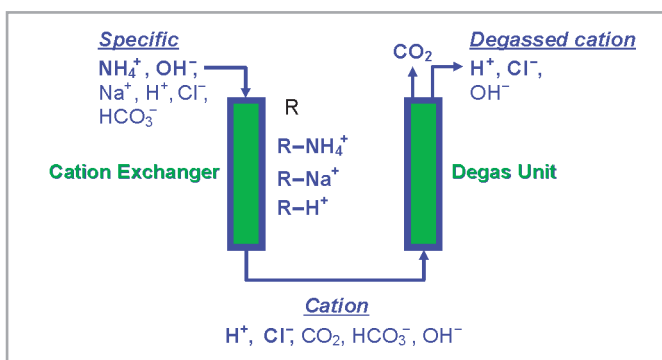


Figure 2: Specific, cation and degassed cation conductivity measurements.

Consistent with the "garbage in – garbage out" principle of computations in general, accurate conductivity measurements are required to determine accurate pH values. It has been recognized that very poor accuracy of specific and cation conductivity temperature compensation is a major issue with most conductivity instruments [1,2]. To resolve this, either the sample must be controlled very close to 25 °C or the instrumentation must have specialized temperature compensation algorithms proven to be accurate for these sample types. Units described here have that confirmation.

A unique benefit of multi-parameter, multi-channel instrumentation is its ability to measure specific and cation conductivities, compute pH from them, and simultaneously measure from a pH electrode. This kind of instrumentation covers both situations: it provides highly accurate calculated pH measurement under normal conditions and can give a warning based on a pH electrode measurement when conditions become abnormal.

The multi-parameter instrument can also display and alarm on the difference between the calculated and the measured pH values. This kind of diagnostic can identify the need for pH electrode maintenance or calibration, or warn of conditions outside the range for accurate pH calculation as well as conditions exceeding cycle chemistry guidelines.

The availability of both calculated and electrode pH measurements allows fine tuning of the calibration of the electrode measurement. When operation is within the conditions for accurate computation of pH, this value can be used for a one-point calibration of the electrode system. The electrode system should previously have been calibrated at two points using buffer solutions to set up the span response. Buffer calibration can then be done at less frequent intervals since the span does not change rapidly. But the final trim can easily be done more frequently and will greatly enhance the accuracy, reliability and diagnostic capability of the electrode measurement, as well as save considerable time in calibration.

CALCULATED CARBON DIOXIDE & ANIONS

Carbon dioxide in steam and condensate can come from the decomposition of organics not removed in makeup water treatment. Carbon dioxide can also be an indication of condenser leakage or inadequate deaeration. Although there is not a consensus on the severity of its threat for corrosion, carbon dioxide is known to be far less corrosive than chlorides or sulfates. For this reason, plants that experience significant amounts of carbon dioxide and therefore high cation conductivity values need to distinguish bicarbonate from more corrosive anions. Ion chromatography is the most specific means to determine this, but it is too expensive and operator-intensive to be used in most fossil fuel plants.

Degassed cation conductivity can provide similar, though less specific information, and is certainly more affordable.

Figure 2 and *Figure 3* illustrate the basic operation and provide examples of the kind of sample composition experienced with specific, cation and degassed cation conductivity samples. The bicarbonate species dominates the high pH specific conductivity sample. This shifts to a carbon dioxide/bicarbonate equilibrium at the lower pH after the cation exchanger. The degasifier then removes carbon dioxide gas, which causes the bicarbonate equilibrium to shift to replace the lost carbon dioxide, allowing removal of both species.

Studies have been made to show the performance of degasification using "reboilers," which operate by raising the sample temperature near the boiling point, where carbon dioxide is driven off [10,11]. One evaluation compared performance of reboiler, nitrogen sparger, and membrane systems for carbon dioxide removal [12]. Although not a precise measurement, degassed cation conductivity does serve a very useful purpose.

Carbon dioxide concentration can be inferred from the difference between cation conductivity and degassed cation conductivity [13]. Because carbon dioxide is the only volatile species in the sample after the cation exchanger, the drop in conductivity can be wholly attributed to its loss in the degasifier. Instrumentation can combine the measurements by interpolating ASTM standard tables in its memory to provide display and output signals for carbon dioxide.

Yet another parameter that can be obtained is the anion concentration in the degassed cation conductivity sample. If the degassed cation conductivity is assumed to be all due to chlorides or sulfates, a conversion to concentration can be done. Instrumentation including ASTM conversion tables in memory easily makes the conversion to display, alarm and output ppb concentrations of chlorides or sulfates [13].

MULTI-PARAMETER INSTRUMENTATION

Cycle chemistry surveillance may include measurements of conductivity, cation conductivity, calculated pH, degassed cation conductivity, carbon dioxide, pH by elec-

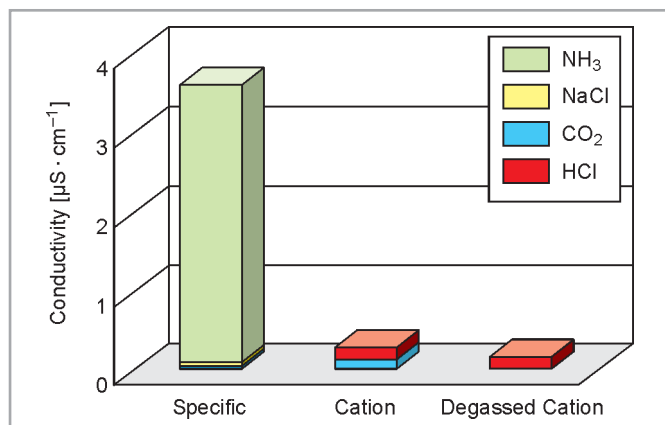


Figure 3: Typical specific, cation and degassed cation conductivity response.

trode, ORP and/or dissolved oxygen – all of which may be handled with multi-parameter instrumentation. In fact, it is the multi-parameter capability that enables combinations of measurements to be accomplished in a single unit. The instrument described here accepts inputs from any combination of four analytical sensors and can derive multiple measurements from each one. For example, a single conductivity sensor may provide input for specific conductivity, calculated pH, and temperature measurements. Each measurement can become a display line on the instrument.

Figure 4 illustrates the type of display available. Its screen can display multiple pages to allow all measurements to be shown, with access by manual paging or automatic scrolling. The six-character labels on the left of each line are for user-defined identification. The first page shows specific and cation conductivity followed by calculated pH and then by a direct electrode pH measurement. The second page shows degassed cation conductivity, difference in pH between the calculated value and the electrode measurement, calculated carbon dioxide, and sample temperature. Another page on this same instrument might include ppb chlorides as a measurement. This is just an example; there is complete flexibility on measurement selection and their order on display pages. Alarms and relays can be assigned to any measurements and would be especially important on the pH difference measurement. Eight analog outputs may be assigned to the measurements and digital signals are also available.

The simplicity of having a variety of sensor types coming into a single instrument to provide a common-format display, alarms and outputs can be quite beneficial. It provides especially clear operator interface. Commonality can help eliminate confusion and inadvertent false readings taken from a variety of instrument types. When an overall installation is considered, the simplicity extends to common specification, panel design, installation, startup, training, calibration, maintenance and spare parts, as well as operation. Each one of these areas can represent a very significant savings in time and documentation.

The integrity of multiple measurements in compact instrumentation also lends itself very well to tight panel spacing and portable verification systems [14]. It is also used widely in trailer-mounted mobile makeup water treatment systems, where its durability is appreciated.

CONCLUSION

While the concept and practice of calculating pH, carbon dioxide and anion concentrations from conductivity measurements has been available for a number of years, it typically required a separate computer diagnostic system. A previous instrument that could calculate pH was limited to only two conductivity sensors and analog outputs. The new capability described here provides especially convenient mix-and-match flexibility in the choice of four parameters to meet the particular needs of a monitoring location.

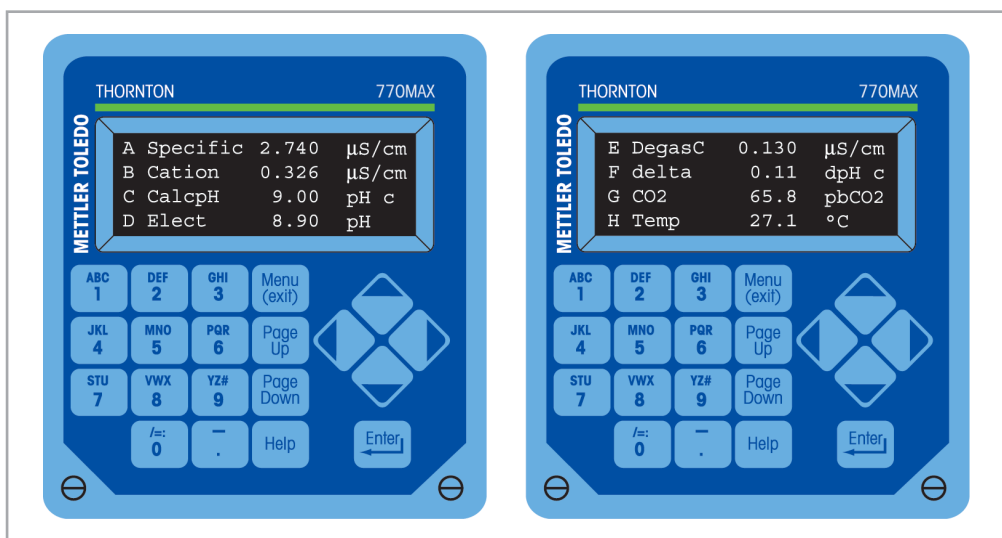


Figure 4:
Two-page display of a multi-parameter instrument configured with sensors for specific, cation and degassed cation conductivity plus a direct pH electrode.

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