Inferred pH in Steam Plant Water Chemistry Monitoring

INTRODUCTION

Inferred pH means pH calculated from straight and cation conductivity. The calculation can be applied to condensate, feedwater, and boiler water. Although not widely used in the United States, inferred pH is popular in Europe. Some plant chemists find inferred pH useful because it eliminates the need to measure pH directly, which without proper equipment can be a difficult task. This paper discusses the two models used to calculate inferred pH and the errors resulting if the actual conditions do not match the model.

BACKGROUND

The water used in high pressure steam plants is commonly treated with small amounts of chemicals for the purpose of reducing corrosion. The treatment chemicals can be divided into two types: volatile chemicals and solids.

The most common volatile treatment chemical is ammonia. When added to condensate and feedwater, ammonia elevates the pH and reduces waterside and steamside corrosion of ferrous metals. Because the condenser and feedwater heaters often contain copper alloys, ammonia levels must be carefully controlled, lest excessive amounts increase copper corrosion. Ammonia accumulates to some extent in the boiler, although much of it volatilizes with the steam and reappears in the condensate. In a once-through steam generator, all of the ammonia passes into the steam.

Ammonia is not the only volatile water treatment chemical used for corrosion control. Morpholine, which is an organic amine, is sometimes used in place of ammonia. Another common volatile treatment chemical is hydrazine, which is a chemical oxygen scavenger.

Solid treatment chemicals are fed only to boiler water, never to condensate and feedwater. Common boiler water treatment chemicals are sodium hydroxide and sodium phosphate salts. They are used to adjust boiler water pH to reduce corrosion and buffer the water against acid-forming contaminants. Boiler water chemicals by and large remain in the boiler. However, vaporous and mechanical carryover do introduce trace

amounts into the steam. Solid treatment chemicals are never used in plants with once-through steam generators.

In addition to treatment chemicals, trace amount of contaminants are always present in the system. As shown in Figure 1 contamination has several sources. Condenser tube leaks introduce cooling water. Leaks in the last stages of the low-pressure turbine housing and in the condenser shell introduce atmospheric carbon dioxide. And, in plants with condensate polishers, ionic leakage from the polishers and deterioration of the resins themselves introduce contamination. The contaminants are primarily ionic; although, some, like silica, are weakly ionized and others are not ionized at all. Contaminants accumulate in the boiler water, where mechanical and vaporous carryover transport trace amounts into the steam. In once-through units, all of the contaminants entering the steam generator are carried into the steam.
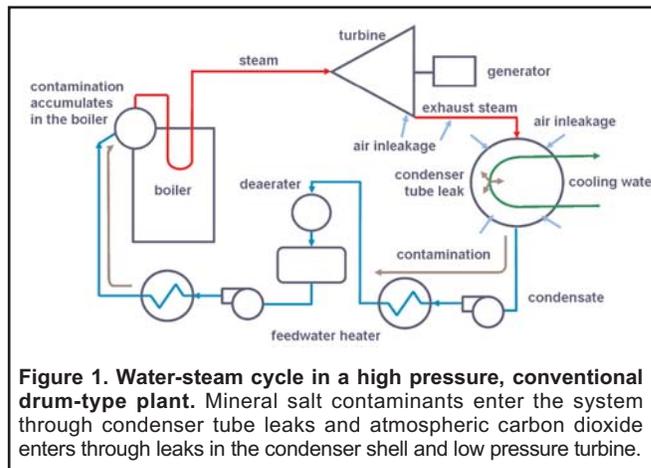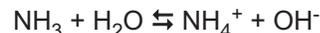

Figure 1. Water-steam cycle in a high pressure, conventional drum-type plant. Mineral salt contaminants enter the system through condenser tube leaks and atmospheric carbon dioxide enters through leaks in the condenser shell and low pressure turbine.

MEASURING AMMONIA

Ammonia is a weak base. It undergoes the following reaction with water:

$$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$$

As the equation implies, adding ammonia to water changes both the pH and conductivity. Figure 2 shows the relationship among concentration, pH, and conductivity for dilute aqueous ammonia solutions.

The values are typical for a steam power plant. The graph also illustrates that only one measurement is needed to infer the other two. Thus, if the conductivity is measured, the pH and concentration are automatically known.
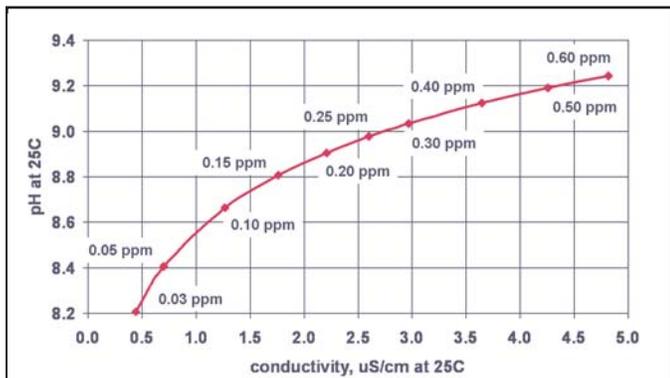

Figure 2. pH and conductivity of ammonia solutions. Every point on the line corresponds to a different concentration of ammonia.

Figure 2 can be used to infer pH from conductivity only if ammonia is the sole source of conductivity. If ionic contaminants are present, the pH value from Figure 2 will be in error. For example, assume the measured conductivity is 0.80 µS/cm of which 0.10 uS/cm comes from a neutral ionic contaminant. Because the conductivity from ammonia is 0.70 uS/cm, the true pH is 8.40. However, the inferred pH (using 0.80 uS/cm) is 8.46.

MEASURING CAUSTIC

Over the years two types of boiler treatment programs have evolved. One uses only sodium hydroxide (caustic). The other uses a mixture of sodium hydroxide and sodium phosphate salts.

Phosphate-based programs require monitoring pH, conductivity, and phosphate. pH and phosphate measurements are used to control the concentration of the treatment chemicals. Conductivity is used to monitor the total concentration of dissolved solids (treatment chemicals and contaminants). **pH cannot be inferred from conductivity in phosphate treated boilers.**
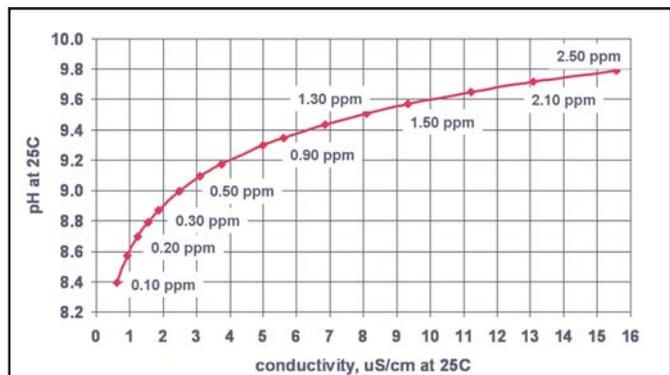

Figure 3. pH and conductivity of sodium hydroxide solutions. Every point on the line corresponds to a different concentration of sodium hydroxide.

Caustic-based treatments require measuring only pH and conductivity. pH indicates the caustic level and conductivity indicates the total concentration of dissolved solids (treatment chemicals and contaminants).

Inferred pH is possible only in caustic-based boiler treatments.

Sodium hydroxide is a strong base. It dissociates completely in water according to the equation:

$$NaOH(s) \rightarrow Na^+ + OH^-$$

As the equation shows, adding sodium hydroxide to water changes both the pH and the conductivity. Figure 3 shows the relationship among concentration, pH, and conductivity for sodium hydroxide levels typically found in caustic-only boilers. As was the case with ammonia, if the conductivity is known, the pH and sodium hydroxide concentration are automatically known. However, if electrolytes other than sodium hydroxide are present, the pH inferred from Figure 3 will be in error.

MEASURING CONTAMINANTS

pH can be inferred from conductivity only if the contribution of ionic contaminants is taken into account. Cation conductivity is the common method for detetermining contamination.

Figure 4 shows how cation conductivity works when applied to ammoniated feedwater. The heart of the measurement is a column containing a hydrogen-form cation exchange resin. As the sample passes through the column, the resin converts ammonia to water and, thus, removes the background conductivity from ammonia. The resin also converts the mineral salt contamination into the equivalent amount of strong acid. Because the acid has greater conductivity than the salt, the conductivity attributable to the contaminant is moderately amplified.
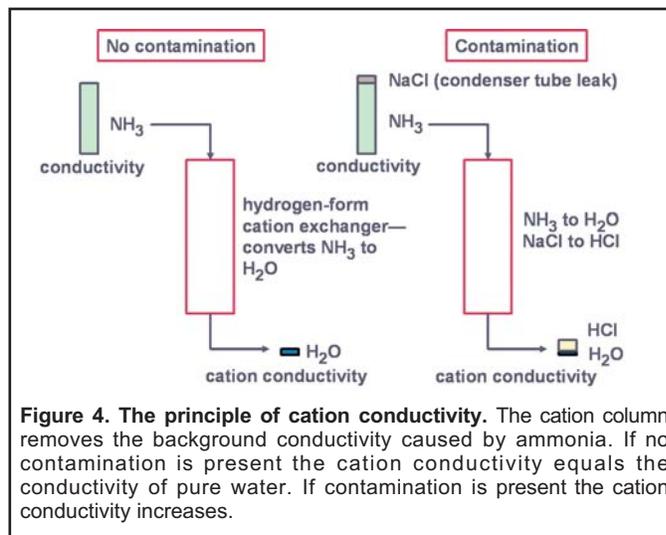

Figure 4. The principle of cation conductivity. The cation column removes the background conductivity caused by ammonia. If no contamination is present the cation conductivity equals the conductivity of pure water. If contamination is present the cation conductivity increases.

Cation conductivity in good quality condensate is typically less than 0.2 µS/cm. Cation conductivity in the effluent from a properly operated condensate polisher is usually less than 0.07 µS/cm. The theoretical lowest cation conductivity is 0.055 µS/cm at 25°C, which is the conductivity of pure water.

Cation conductivity is also used to monitor contamination in caustic-treated boiler water. The cation column converts sodium hydroxide to water and removes the background conductivity. Cation conductivity cannot be used to measure contamination in phosphate-treated boiler water because the phosphate salts are converted to phosphoric acid, which has high conductivity.

Both models for calculating inferred pH assume the ionic contaminant is sodium chloride, which means the effluent from the cation column is hydrochloric acid. As Figure 5 shows, the amount of sodium chloride contaminant can be readily calculated from the cation conductivity.
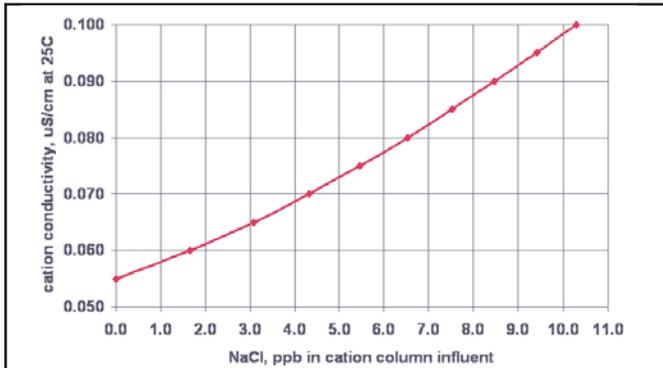

Figure 5. Concentration of hydrochloric acid as a function of conductivity. The x-axis is the concentration of sodium chloride in the sample entering the cation column. The y-axis is conductivity of hydrochloric acid in the column effluent. The graph allows conversion of cation conductivity to concentration of sodium chloride.

In power plant chemistry conductivity is often called straight conductivity or specific conductivity to distinguish it from cation conductivity.

AVT MODEL FOR INFERRED pH

The AVT or all-volatile treatment model for inferred pH assumes the alkalizing agent is ammonia and the contaminant is sodium chloride. There are four steps to the calculation.

1. Calculate the concentration of sodium chloride from the cation conductivity at 25ºC using Figure 5.

2. Calculate the conductivity of sodium and chloride ions at 25ºC.

3. Subtract the conductivity of sodium and chloride from the straight conductivity. The result is the conductivity of ammonia at 25ºC.

4. Convert the conductivity of ammonia to pH using Figure 2.

Figure 6 shows the relation between conductivity and pH for dilute ammonia solutions at three different values of cation conductivity. The graph shows that cation conductivity has the greatest effect on inferred pH when the conductivity (and ammonia level) is low. As the conductivity increases, the cation conductivity correction becomes less important.

SOLIDS MODEL FOR INFERRED pH

The solids model for inferred pH assumes the alkalizing agent is sodium hydroxide and the contaminant is sodium chloride. The calculation proceeds as follows:

1. Calculate the concentration of sodium chloride from the cation conductivity at 25ºC using Figure 5.

2. Calculate the conductivity of sodium and chloride ions at 25ºC.

3. Subtract the conductivity of sodium and chloride from the straight conductivity. The result is the conductivity of the sodium hydroxide solution at 25ºC.

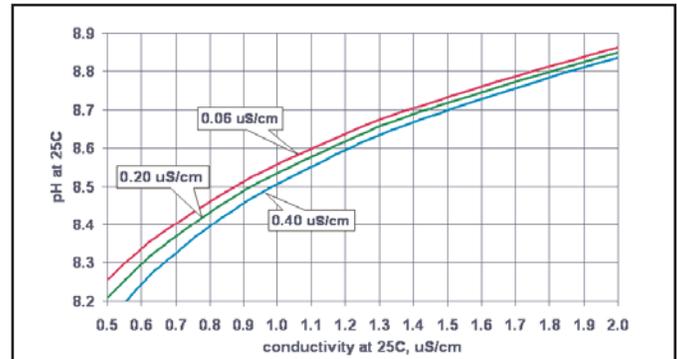4. Convert the conductivity of sodium hydroxide to pH using Figure 3.

Figure 6. pH and conductivity of ammonia solutions at different cation conductivities. The cation conductivity (from sodium chloride) for each line is shown. As the concentration (conductivity) of ammonia increases, the lines merge.

Figure 7 shows the relation between conductivity and pH for dilute sodium hydroxide solutions at three different values of cation conductivity. Clearly, cation conductivity has the greatest effect on inferred pH when the conductivity (and sodium hydroxide level) is low. As the conductivity increases, the cation conductivity correction becomes less important.
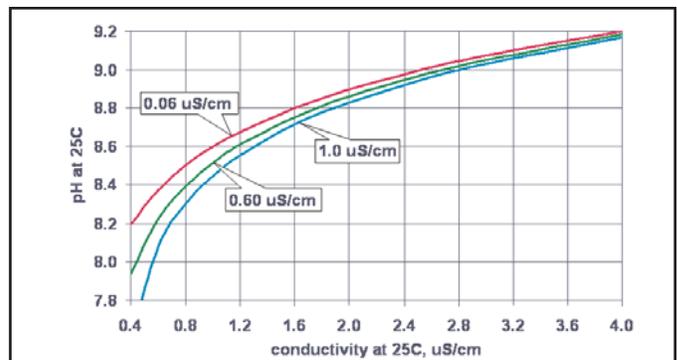

Figure 7. pH and conductivity of sodium hydroxide solutions at different cation conductivities. The cation conductivity (from sodium chloride) for each line is shown. As the concentration (conductivity) of sodium hydroxide increases the lines merge.

ERRORS IN INFERRED pH

There are three sources of error in inferred pH:

1. The straight conductivity, cation conductivity, or temperature are in error.

2. The composition of the sample does not match the model on which the temperature correction algorithms are based.

3. The composition of the sample does not match the model used to calculate inferred pH.

Measurement and temperature correction errors can lead to significant errors in the inferred pH. In most plants the error in the temperature-corrected straight conductivity is about 2%, and the error in the temperature-corrected cation conductivity can be as high as 10%. The resulting error in the inferred pH in ammoniated condensate is 0.04 at pH 8.2 (0.5 uS/cm) and drops to 0.01 or less above pH 8.9 (2.5 uS/cm).

The rest of this section examines the errors arising from failure of the model to match the real sample. It is convenient to examine the errors in the AVT and solids models separately.

AVT Model

The AVT model assumes the contaminant is sodium chloride. In reality, sodium chloride is rarely the sole contaminant. Instead, contamination is a mixture of mineral salts, including sodium chloride, from condenser in-leakage and atmospheric carbon dioxide from air in-leakage. Because all mineral salts have roughly the same equivalent conductance, the presence of salts other than sodium chloride causes little if any error. Carbon dioxide, however, can cause a significant error.

Carbon dioxide is a weak acid. When it dissolves in condensate, it neutralizes a portion of the ammonia, forming ammonium carbonate. The pH drops and, unless a large amount of carbon dioxide is present, the conductivity drops as well. Table 1 shows how small amounts of carbon dioxide can alter the pH and conductivity of ammoniated condensate, particularly at low pH and conductivity.

Table 1: Effect of carbon dioxide on the pH and conductivity of ammonia solutions at 25ºC.

NH$_3$, ppm	CO$_2$, ppb	pH	uS/cm
0.07	0	8.54	0.943
	20	8.48	0.891
	40	8.42	0.839
	60	8.36	0.789
0.40	0	9.12	3.66
	20	9.11	3.63
	40	9.10	3.60
	60	9.09	3.56

Carbon dioxide also affects the cation conductivity. As the sample passes through the cation column, ammonium carbonate is converted to carbonic acid. Although carbonic acid is a weak electrolyte, it does contribute to the cation conductivity. In fact, in many plants, atmospheric carbon dioxide is probably the major source of cation conductivity.

Figure 8 shows the error in inferred pH caused by carbon dioxide. In Figure 8, the sodium chloride concentration is constant at 3.3 ppb, which is equivalent to 2 ppb chloride, while the carbon dioxide concentration ranges from 0 to 50 ppb. Each line on the graph corresponds to a different concentration of ammonia. The approximate pH for each concentration is also shown.

An examination of the graph reveals the following:

1. As the concentration of carbon dioxide increases (and the sodium chloride remains constant), the cation conductivity increases.

2. As the concentration of carbon dioxide increases, the error in the inferred pH increases.

3. As the concentration of ammonia (i.e., pH and straight conductivity) decreases, the error in the inferred pH caused by carbon dioxide increases.

Graphs similar to Figure 8 can be drawn for other concentrations of sodium chloride. However, the magnitude of the errors will be practically the same as those shown in Figure 8.
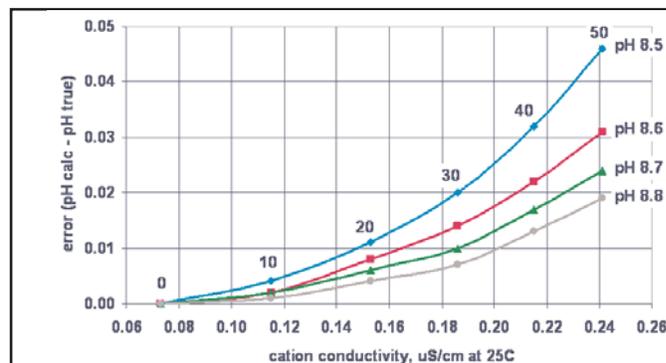

Figure 8. Error in the inferred pH when carbon dioxide is present. Each line on the graph corresponds to a different concentration of ammonia, and the approximate pH is shown next to the line. The numbers above the pH 8.5 line are the concentrations of carbon dioxide (0 to 50 ppb). In each case, the concentration of sodium chloride is 3.3 ppb.

Solids Model (Boiler water only)

The solids model assumes the alkalizing agent is sodium hydroxide and the contaminant is sodium chloride. In reality, sodium chloride will not be the sole contaminant. Condenser leakage introduces a host of other mineral salts that accumulate in the boiler. However, most mineral salts contribute about the same to the straight and cation conductivity as sodium chloride, so other salts cause only a small error. Carbonates, arising from air in-leakage are not likely to introduce an error, either. Carbonates decompose in high pressure boilers, allowing carbon dioxide to escape with the steam. Ammonia, from feedwater treatment, may cause an error. Although ammonia is volatile, and most escapes with the steam, some remains behind in the boiler water. Ammonia does not affect the cation conductivity, but it does affect the pH and straight conductivity.
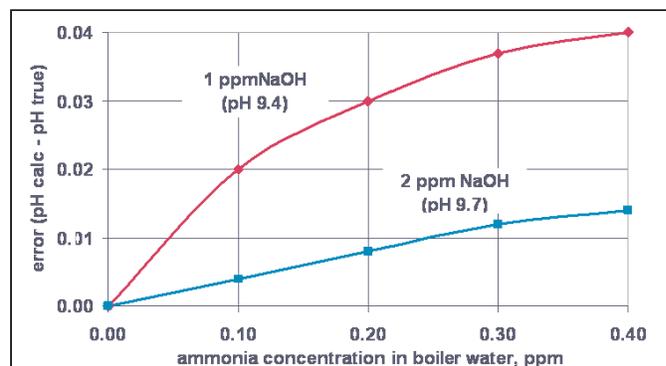

Figure 9. Error in inferred boiler water pH when ammonia is present. The error caused by ammonia increases as the caustic level decreases.

Figure 9 shows the error in the inferred pH at two sodium hydroxide concentrations for different concentration of ammonia. The sodium hydroxide levels shown are

typical for caustic-only treated boilers. In the calculation, the boiler water was also assumed to contain 0.1 ppm of sodium chloride.

As mentioned earlier, the solids model for inferred pH cannot be used for boiler water treated with phosphates. Figure 10 shows the error if the model is applied to a boiler on equilibrium phosphate in which free caustic (sodium hydroxide) is present.
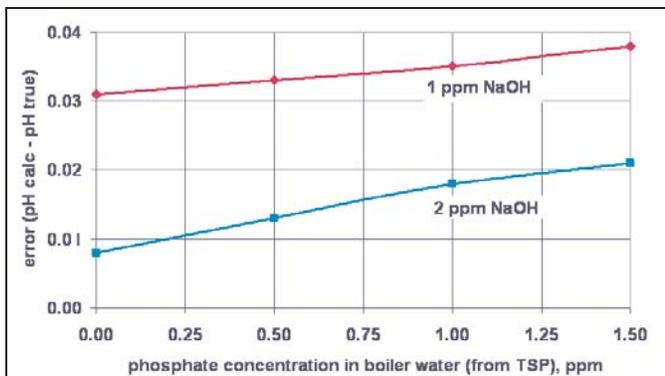

Figure 10. Error in inferred pH for a boiler on equilibrium phosphate treatment. The error for boiler water containing 1 ppm and 2 ppm of free caustic (sodium hydroxide) is shown. Small amounts of phosphate produce relatively little error. The water also contains 0.2 ppm each of ammonia and sodium chloride.

Figure 11 shows the error if the model is applied to a boiler on coordinated phosphate treatment. Errors will be similar for a boiler on congruent control. The errors when the model is applied to coordinated and congruent phosphate boilers are considerably higher than for equilibrium phosphate. The reason is the greater similarity between equilibrium phosphate and sodium hydroxide only control. In equilibrium phosphate, phosphate levels are usually fairly low, and typically a ppm or so of sodium hydroxide is also present. In coordinated and congruent control, phosphate levels are generally higher and no free caustic is allowed. Because there is little similarity between the actual boiler water and the inferred pH model, errors are high.
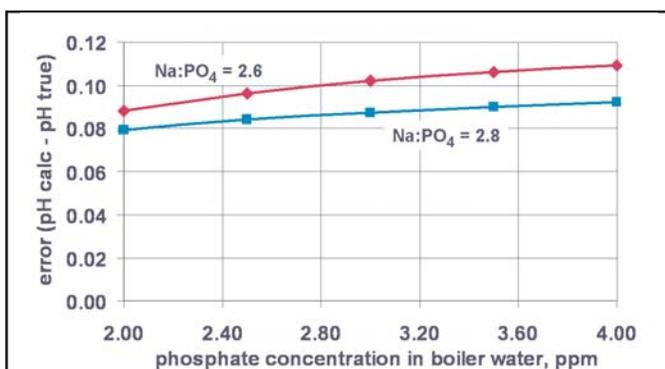

Figure 11. Error in inferred pH for a boiler on coordinated phosphate treatment. The error for boiler water containing two different values of sodium to phosphate molar ratio. The water also contains 0.2 ppm each of ammonia and sodium chloride.

INSTRUMENTATION

Figure 12 shows the configuration of the sensors and cation column for measuring inferred pH. The analyzer is not shown. The inferred pH calculation is available only with the 1056 dual conductivity analyzer. To configure the analyzer to measure inferred pH, open the expert menu, select pHCalc in the Configure screen, and choose AVT or Solids. Sensor assignment is important. Sensor 1 must be straight conductivity, and sensor 2 must be cation conductivity. Use 1.9% per ºC temperature correction for straight conductivity and the cation temperature correction for cation conductivity.
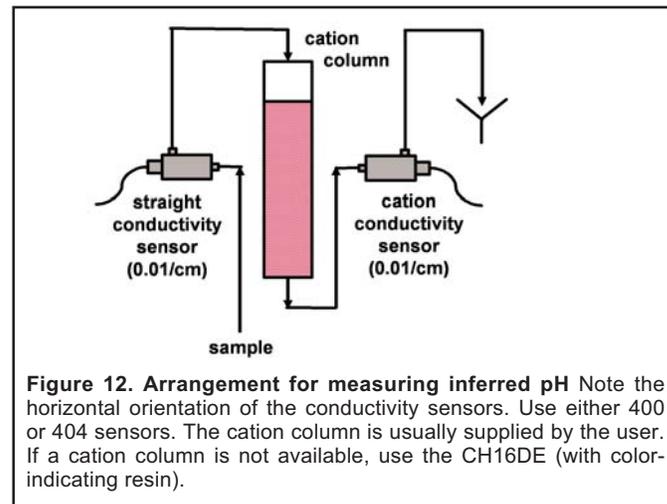

Figure 12. Arrangement for measuring inferred pH Note the horizontal orientation of the conductivity sensors. Use either 400 or 404 sensors. The cation column is usually supplied by the user. If a cation column is not available, use the CH16DE (with color-indicating resin).

CONCLUSIONS

The usefulness of the inferred pH method is subject to debate. Some plant chemists use nothing but inferred pH. Others find it useful only for checking the accuracy of a direct pH measurement. No matter which camp one falls in, it is important to understand the limitations of the technique.

Obviously, the closer the match between the sample and model, the more accurate is the inferred pH. Because failure of cation conductivity to fully account for ionic contamination is the main source of error, the most accurate inferred pH is to be found in plants with full in-stream condensate polishers. If the polisher is properly regenerated and operated, the cation conductivity will be less than 0.07 μS/cm. Under these conditions, the inferred pH is highly accurate.

Errors in the temperature-corrected straight and cation conductivity cannot be ignored. No temperature correction algorithm is perfect. Even if the uncorrected conductivity is perfect, the corrected conductivity will always have an error, and the error generally increases the further the temperature is from 25ºC. Because errors in the measured conductivity affect the inferred pH, the best accuracy occurs when the temperature is close to 25ºC.

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MODEL 1056

- LARGE DISPLAY; can be customized to show conductivity and cation conductivity as well as inferred pH.
- INTUITIVE MENU IN SIX LANGUAGES means an instruction manual is hardly needed.
- EASY TO WIRE
- ADVANCED DIAGNOSTICS AND HELP SCREENS aid troubleshooting

MODEL 400

MODEL 400VP

MODEL 404

- INITIAL CALIBRATION NOT REQUIRED. Factory-measured cell constant ensures out-of-the-box accuracy.
- RUGGED TITANIUM ELECTRODES for long life.
- AVAILABLE WITH VARIOPOL (VP) quick disconnect fitting.

EMERSON
Process Management