Standard Test Method for
On-Line pH Measurement of Water of Low Conductivity[1]

1. Scope

1.1 This test method covers the precise on-line determination of pH in water samples of conductivity lower than 100 µS/cm (see Table 1 and Table 2) over the pH range of 3 to 11 (see Fig. 1), under field operating conditions. pH measurements of water of low conductivity are problematic for conventional pH electrodes, methods, and related measurement apparatus.

1.2 This test method includes the procedures and equipment required for the continuous pH measurement of low conductivity water sample streams including the requirements for the control of sample stream pressure, flow rate, and temperature. For off-line pH measurements in low conductivity samples, refer to Test Method D5464.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]
D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D1293 Test Methods for pH of Water
D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
D3864 Guide for On-Line Monitoring Systems for Water Analysis

D4453 Practice for Handling of High Purity Water Samples
D5464 Test Method for pH Measurement of Water of Low Conductivity

3. Terminology

3.1 *Definitions*—For definitions of other terms used in this test method, refer to Terminology D1129 and Practice D3864.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *liquid junction potential, n*—a dc potential that appears at the point of contact between the reference electrode's salt bridge (sometimes called diaphragm) and the sample solution.

3.2.1.1 *Discussion*—Ideally this potential is near zero, and is stable. However, in low conductivity water it becomes larger by an unknown amount, and is a zero offset. As long as it remains stable its effect can be minimized by "grab sample" calibration (**3**).[3]

3.2.2 *streaming potential, n*—the static electrical charge that is induced by the movement of a low ionic strength solution having a high electrical resistivity or low electrical conductivity (such as pure water), across relatively non-conductive surfaces such as the pH electrode or other non-conductive wetted materials found in flowing sample streams.

4. Summary of Test Method

4.1 pH is measured by electrodes contained in an all stainless steel flow cell. The pH measurement half-cell is constructed of a glass membrane suitable for continuous service in low conductivity water. The reference half-cell is constructed in such a manner that the salt bridge uses either a flowing liquid electrolyte, or a pressurized gel electrolyte that resists significant dilution for periods up to several months of continuous operation.

4.2 This test method describes the apparatus and procedures to be used for the continuous on-line pH measurement of low conductivity water sample streams. The requirements for conditioning sample pressure and flow rate are defined, and arrangements for this associated equipment are illustrated.

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[3] The boldface numbers given in parentheses refer to a list of references at the end of this standard.

TABLE 1 Calculated Conductivity and pH Values at 25°C of Low Concentrations of NaOH in Pure Water [A]

NOTE 1—This table tabulates the theoretical conductivity and pH values of low levels of NaOH in pure water as calculated from available thermodynamic data.

NOTE 2—To illustrate the high sensitivity of the sample pH at these low concentrations to contaminants, the last column lists errors that would result if the sample were contaminated with an additional 1 mg/L through sample or equipment handling errors.

Sample Concentration, mg/L	Sample Conductivity, µS/cm	Sample pH	Δ pH Error from Additional 1 mg/L NaOH Contaminate
0.001	0.055	7.05	Δ 2.35
0.010	0.082	7.45	Δ 1.95
0.100	0.625	8.40	Δ 1.03
1.0	6.229	9.40	Δ 0.30
8.0	49.830	10.30	Δ 0.05

[A] Data courtesy of Ref (**1**).[B] This data developed from algorithms originally published in Ref (**2**).
[B] The boldface numbers in parentheses refer to a list of references at the end of this standard.

TABLE 2 Calculated Conductivity and pH Values at 25°C of Low Concentrations of HCl in Pure Water [A]

NOTE 1—This table tabulates the theoretical conductivity and pH values of low levels of HCl in pure water as calculated from available thermodynamic data

NOTE 2—To illustrate the high sensitivity of the sample pH at these low concentrations to contaminants, the last column lists errors that would result if the sample were contaminated with an additional 1 mg/L through sample or equipment handling errors.

Sample Concentration, mg/L	Sample Conductivity, µS/cm	Sample pH	Δ pH Error from Additional 1 mg/L HCl Contaminate
0.001	0.060	6.94	Δ2.38
0.010	0.134	6.51	Δ 1.95
0.100	1.166	5.56	Δ 1.03
1.0	11.645	4.56	Δ 0.30
8.0	93.163	3.66	Δ 0.05

[A] Data courtesy of Ref (**1**). This data developed from algorithms originally published in Ref (**2**).

4.3 The apparatus and procedures described in this test method are intended to be used with process-grade, pH analyzer/transmitter instruments.

5. Significance and Use

5.1 Continuous pH measurements in low conductivity samples are sometimes required in pure water treatment using multiple pass reverse osmosis processes. Membrane rejection efficiency for several contaminants depends on pH measurement and control between passes where the conductivity is low.

5.2 Continuous pH measurement is used to monitor power plant cycle chemistry where small amounts of ammonia or amines or both are added to minimize corrosion by high temperature pure water and steam.

5.3 Conventional pH measurements are made in solutions that contain relatively large amounts of acid, base, or dissolved salts. Under these conditions, pH determinations may be made quickly and precisely. Continuous on-line pH measurements in water samples of low conductivity are more difficult (**4, 5**).

(Courtesy EPRI, NP-35891).
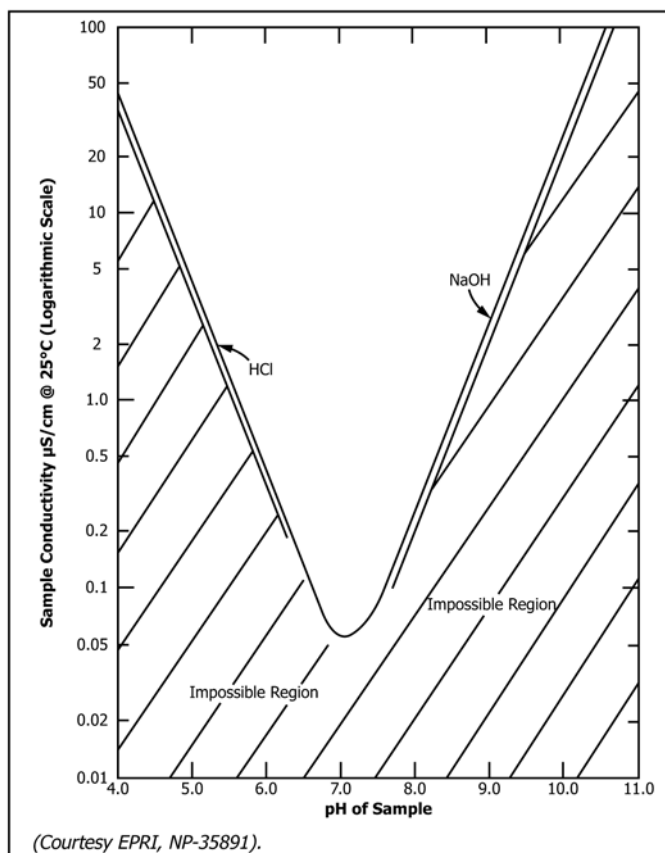
FIG. 1 Restrictions Imposed by the Conductivity pH Relationship

These low ionic strength solutions are susceptible to contamination from the atmosphere, sample stream hardware, and the pH electrodes. Variations in the constituent concentration of low conductivity waters cause liquid junction potential shifts (see 3.2.1) resulting in pH measurement errors. Special precautions are required.

6. Interferences

6.1 Sample systems for high purity, low conductivity waters are especially sensitive to contamination from atmospheric gases (especially carbon dioxide, see Appendix X1 and Table 3), and to accumulation of power plant corrosion particles in sample lines that can absorb or desorb contaminants. Excessive

TABLE 3 Calculated pH and Conductivity Values at 25°C of Water Solutions Containing Only Ammonia and Carbon Dioxide [A]

Ammonia mg/L	Carbon Dioxide 0 mg/L		Carbon Dioxide 0.2 mg/L		pH Shift Caused by 0.2 mg/L CO2 Contamination of Sample
	µS/cm	pH	µS/cm	pH	
0	0.056	7.00	0.508	5.89	Δ 1.11 pH
0.12	1.462	8.73	1.006	8.18	Δ 0.55 pH
0.51	4.308	9.20	4.014	9.09	Δ 0.11 pH
0.85	6.036	9.34	5.788	9.26	Δ 0.08 pH
1.19	7.467	9.44	7.246	9.38	Δ 0.06 pH

[A] Data extracted from Ref (**8**).

KCl electrolyte leakage from the pH reference half-cell can also affect the sample. Refer to Practice D4453 and Refs (6) and (7).

6.2 Streaming potentials that are developed by flowing, low conductivity water across non-conductive surfaces are dynamic in nature and will add to the potential (millivolt) generated by the pH sensor. This resultant pH error appears as a noisy, flow-sensitive and drifting pH signal. These effects are minimized by using a conductive flow cell, low sample flowrates and, in some cases, a symmetrical combination measurement/reference electrode (9).

6.3 Reference electrode liquid junction potentials are significant in low conductivity waters and shift the potential of the pH reference half-cell, resulting in both short and long-term pH measurement errors. The instability of liquid junction potentials depends on reference half-cell design, electrical conductivity of the sample water, time, and sampling conditions such as flow rate and pressure. Generally, reference electrodes with refillable liquid electrolyte flowing junctions provide more stable junction potential than non-refillable, sealed reference electrodes. Exposure of the pH electrodes to pH calibration buffer solutions, that have a higher ionic strength than the pure water sample stream, causes significant change in the liquid junction potential of sealed reference electrodes from what it is in a low conductivity sample, resulting in pH measurement errors that appear immediately after calibration in buffer solutions.

6.3.1 Liquid junction potentials must be stable to make a reliable calibration of the system. Sealed reference electrodes that have been exposed to the much higher ionic strength of buffer solutions require considerable rinse time to establish a stable liquid junction potential in high purity water. To determine the pH electrode's suitability in low conductivity water, a comparative low conductivity water sample calibration, or on-line calibration with low conductivity standards similar to the samples being addressed should be performed, as described in 9.5.

6.3.2 The severity of the error resulting from a liquid junction potential shift when the ionic strength of the sample changes, for example, measuring 1.0 mg/L ammonia (pH = 9.38 and conductivity = 6.58 S∕cm) followed by measuring 0.1 mg/L ammonia (pH = 8.65 and conductivity = 1.24 S∕cm) is not known and is a deficiency in the state-of-the-art. Table 4 and Fig. X1.1 provide a correlation between pH and specific conductivity of dilute ammonia.

6.4 Temperature compensation of pH in low conductivity water is more significant and more involved than in conventional measurements.

6.4.1 All pH measurements must compensate for the changing output of the electrode with temperature. This effect is represented by a changing slope with units of millivolts per pH. This slope is proportional to absolute temperature according to the Nernst equation.

6.4.2 In addition, pH measurements in low conductivity water in the power industry must compensate for the change of the dissociation of water and ammonia or amines with temperature to report pH at 25°C. This is typically set into the

TABLE 4 pH versus Specific Conductivity At 25°C^A

NOTE 1—This table tabulates the theoretical pH and specific conductivity values of low levels of ammonium hydroxide in reagent water as calculated from available thermodynamic data.

Ammonia, mg/L NH$_3$	Ammonium Hydroxide, mg/L NH$_4$OH	pH	Specific Conductivity, µS/cm
0.10	0.21	8.65	1.24
0.15	0.31	8.79	1.72
0.20	0.41	8.89	2.15
0.25	0.51	8.96	2.54
0.30	0.62	9.02	2.91
0.35	0.72	9.07	3.25
0.40	0.82	9.11	3.57
0.45	0.93	9.15	3.88
0.50	1.03	9.18	4.17
1.00	2.06	9.38	6.58
1.50	3.09	9.49	8.47
2.00	4.11	9.56	10.08

^{A} Data courtesy of Ref (1). This data developed from algorithms originally published in Ref (2).

instrument by the user with a solution temperature coefficient in units of pH per °C. Most process pH instrumentation for use in power plants has a setting for solution temperature compensation which the user must enter to activate this compensation. Laboratory instrumentation typically does not have this capability (5, 9, 10, 11, 12, 13).

6.4.3 Further discussion of the temperature effects on pH measurements is presented in Annex A1.

6.5 The flow rate to the pH electrodes and related apparatus must be controlled in order to obtain repeatable results. A discussion of the flow sensitivity is presented in Annex A2.

7. Apparatus

7.1 A complete high purity water pH sensor assembly is required. The pH flow cell and connecting tubing should be constructed of stainless steel and be earth grounded. The sensor assembly design shall provide shielding to prevent noise pick-up and shall minimize air entrapment and corrosion particle accumulation. Sample discharge shall be near the top of the flow cell to purge any air bubbles rapidly and shall go downward to an open drain to prevent any back pressure on the electrode(s).

7.1.1 A single probe combination measuring and reference electrode with integral temperature compensator enables use of a very small volume flow cell which creates a high sample flow velocity that prevents power plant sample corrosion particles from accumulating.

7.1.2 Where separate measuring, reference and temperature compensator probes are used, a larger volume flow cell is necessary and the design should enable convenient periodic cleanout of accumulated corrosion particles.

7.2 Electrodes should have half-cells that quickly equilibrate to each other and the sample temperature. Refer to Ref (6).

7.3 Electrodes should be suitable for continuous service in low conductivity water (14).

7.4 Changes in liquid junction potential (3) with time and eventual degradation of the reference half-cell caused by

diffusion of low ionic strength sample water into the high ionic strength electrolyte of the half-cell, must be avoided in order to maintain an accurate and stable pH measurement. To achieve this, a liquid-electrolyte, flowing-junction reference system is preferred. A sealed reference half-cell (requiring no electrolyte replenishment) that is pressurized or otherwise constructed in such a manner that the salt bridge, while making diffusion contact to the sample, resists significant dilution for periods up to several months of continuous operation in low conductivity water measurements may also be used.

7.5 A sample stream conditioning manifold with capabilities similar to Fig. 2 shall be used immediately upstream of the pH sensor. The manifold provides proper sample stream pressure and flow rate control after primary sample cooling and pressure regulation. This manifold shall also provide a grab sample outlet for verification or calibration of the pH sensor. This manifold shall operate such that when a grab sample is being taken for calibration purposes, neither the sample flow rate nor pressure shall vary at the on-line pH sensor location.

8. Reagents

8.1 *Commercial Buffer Solutions*—Commercially available prepared buffers traceable to National Institute of Standards and Technology (NIST) standards should be adequate for the calibration procedures in 9.2 – 9.5. These commercial buffer solutions usually have pH values near 4, 7, 9, and 10 pH at 25°C. The exact pH of the buffer will change with temperature and this pH versus temperature data will be provided by the purveyor of the specific buffer. Refer to Method A in Test Method D1293 for the preparation of reference buffer solutions if desired.

8.2 *Buffer A*—Commercially available 7 pH buffer.

8.3 *Buffer B*—Commercially available 4 pH buffer.

8.4 *Buffer C*—Commercially available 9 pH buffer.

8.5 *Buffer D*—Commercially available 10 pH buffer.
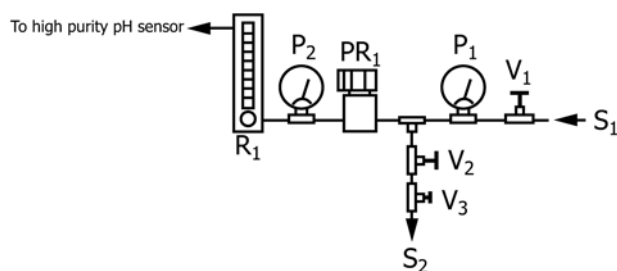
S₁ = sample inlet, 6.35 mm stainless steel tube fitting	PR₁ = secondary pressure regulator, 0 – 172.4 kPa (gage)
V₁ = high pressure sample inlet shut-off valve	R₁ = rotameter, with control valve, 0 – 600 mL/min
P₁ = sample inlet pressure gauge 0 – 689.4 kPa (gage)	P₂ = flow-cell pressure gauge, 0 – 182.4 kPa (gage)
V₂ = grab sample valve / on-off	
V₃ = tamper resistant flow rate value, max. 200 mL/min at specified system pressure	
S₂ = grab sample outlet	

FIG. 2 Schematic Sample System

8.6 *Purity of Water*—Reference to water shall mean water that meets or exceeds the quantitative specifications for Type II reagent water of Specification D1193, Section 1.1, unless otherwise specified.

9. Calibration

9.1 Perform initial and subsequent start-ups of the on-line pH sensor in accordance with manufacturer's instructions.

9.2 Perform a two point calibration of the pH measurement and reference electrodes after removing them from the on-line pH sensor flow chamber. Refer to Method B in Test Method D1293 for guidelines on the standardization of a pH meter and electrode assembly. Be certain to include the temperature compensator with the pH instrument in the automatic temperature compensation (ATC) mode. Use a quiescent sample of both buffer solutions and laboratory containers dedicated for this service only. For proper pH calibration buffers, see 8.1 – 8.5. Thoroughly rinse electrodes and glassware with reagent water between each buffer calibration.

9.3 Thoroughly rinse electrodes with reagent water or low ionic strength sample water and reinsert them into the on-line pH sensor flow cell in accordance with the manufacturer's instructions.

9.3.1 When using a sealed reference electrode, permit the pure water sample stream to flush the sensor flow cell for a minimum of 3 to 4 h at manufacturer's recommended flow rate to remove all traces of the high ionic strength pH buffer solutions before using measurements.

9.3.2 When using a reference electrode with refillable liquid electrolyte, allow the pure water sample stream to flush the flow cell for a minimum of 15 minutes before using measurements.

9.4 Connect the pH electrodes and automatic temperature compensator to the pH instrument in accordance with the manufacturer's instructions.

9.5 The technique for subsequent or routine calibrations of the on-line pH sensor depends on the type of reference electrode being used.

9.5.1 When using a sealed reference electrode, perform comparative-sample calibration in accordance with Test Method D5464 in lieu of conventional direct buffer calibration of this on-line high purity pH sensor. Test Method D5464 has the advantage of using a liquid electrolyte reference electrode with minimal change in junction potential between high ionic strength buffer solutions and high purity samples.

NOTE 1—If the comparative sample temperature is not maintained at 25°C and is not compensated for solution temperature effects, its temperature must be recorded and the proper temperature correction applied. See Annex A1 for a discussion of temperature effects on pH measurements.

9.5.2 When using a reference electrode with refillable liquid electrolyte, for subsequent or routine calibrations use direct two-buffer calibration as in 9.2 and 9.3.

NOTE 2—Periodic confirmation of the calibration of the temperature probe in the on-line pH sensor should be verified at least at one point in accordance with the manufacturer's instructions.

9.6 An alternative method of calibration may be considered which provides for the regular measurement of certifiable standards. This test method employs the use of a precision metering or syringe pump to inject a known standard solution of acid or base into a flowing deionized water stream meeting Type I water of Specification D1193. From the ratio of flowrates and the concentration of the standard solution, very dilute, known concentrations can be obtained and used for calibration or verification (15).

10. Procedure

10.1 Install a sample system manifold as shown in Fig. 2, using the components indicated in the equipment schedule. Wetted materials should consist of stainless steel, glass, PTFE, and ceramic. Use of dissimilar metals should be avoided to prevent galvanic corrosion of these metals. Galvanic corrosion could develop EMF potentials in the sample stream that could result in pH measurement errors. A discussion of contaminants in sample systems is presented in A3.1.

Note 3—PTFE is not suitable for radioactive samples and suitable materials should be substituted for all PTFE components in the radiation areas.

10.2 Flush all wetted components of the sample system manifold according to manufacturer's recommendations with water or low ionic strength sample water for 3 to 4 h, especially if on-line pH sensor assembly has been exposed to pH calibration buffers or other high ionic strength solutions.

10.3 Maintain sample stream flow rates at a fixed rate according to the manufacturer's recommendation. It is important to maintain both the sample stream flow rate and pressure at recommended levels to prevent pH signal drift and noise resulting from electrode sensitivities to variations in these two parameters and to achieve repeatability of the pH electrode output signal. Determination of the sample line flow rate for a given installation will depend on variables such as total length of sample line and its effect on representative sampling and lag times, size, and age of existing sample lines, and upstream sample pressure and temperature conditioning. A discussion on sample stream flow rates is presented in Annex A2.

10.4 Maintain sample stream temperature at 25 ± 1°C or confirm that the appropriate solution temperature compensation setting has been entered into the measuring instrument.

For more information, refer to 6.4. A discussion of sample stream temperature conditioning is presented in A3.2.3.

10.5 Install the on-line sensor in accordance with the manufacturer's instructions.

10.6 Connect the pH signal output of the high purity water pH sensor to the pH signal input of the on-line pH analyzer/transmitter in accordance with the manufacturer's instructions.

10.7 After completion of the calibration procedures in 9.2 to 9.5, record data continuously or manually until the run is completed.

11. Precision and Bias

11.1 Neither precision nor bias data can be obtained for this test method from a collaborative study designed in accordance with the requirements of Practice D2777 since this test method is a continuous determination. This inability of D2777 procedures to obtain precision and bias data for continuous determinations is recognized and stated in the scope of Practice D2777.

12. Quality Control

12.1 Two-point instrument calibration in two pH standard buffer solutions near the anticipated measuring range must be performed according to the manufacturer's instructions periodically, depending on the stability of the electrodes and the pH control specification.

12.2 With power plant samples containing predominately ammonia or amines or both, and negligible carbon dioxide, an accurate correlation with specific conductivity can be made. See Fig. X1.1. Under these conditions, periodically verify pH readings corrected to 25°C by solution temperature compensation with the conductivity also referenced to 25°C. Some two-channel conductivity instrumentation includes an option for the calculation of pH of power plant samples based on specific and cation conductivity and will make a correction for the presence of minor amounts of carbon dioxide and other contaminants. If available, use this calculated value to verify the measured pH readings under normal plant operating conditions (16, 17).

13. Keywords

13.1 high purity; low conductivity; on-line; pH; calculated pH

ANNEXES

(Mandatory Information)

A1. TEMPERATURE EFFECTS ON PH MEASUREMENTS OF LOW CONDUCTIVITY WATER (5, 9, 10, 11, 12, 13)

A1.1 There are two types of temperature effects on pH measurement of low conductivity water (10, 12).

A1.1.1 *Standard Nernst equation temperature compensation* accounts for the thermodynamic response of the glass pH electrode output slope in millivolts per pH which is proportional to absolute temperature. Nernst electrode temperature compensation converts the millivolt signal to pH units at the temperature of the sample. It does not compensate the pH of the sample to a reference temperature.

A1.1.1.1 Standard Nernstian compensation is provided by the automatic temperature compensation (ATC) feature of virtually all pH meters and the temperature element provided with the pH electrodes or sensor assembly.

A1.1.1.2 pH meters with manual temperature compensation can accomplish the same result as long as the operator measures the sample temperature and sets that temperature into the pH meter.

A1.1.2 *Solution Temperature Effect (STE)* is due to the temperature influence on the ionization of water and other materials present in the sample. Ionic concentrations undergo changes with temperature change. Small (mg/L) amounts of acidic or alkaline materials can have a substantial effect on this pH temperature influence. Compensation for this is typically accomplished by establishing a reference temperature and a linear solution temperature coefficient (STC) that approximates the influence. The reference temperature is usually 25°C and the coefficient is nominally –0.03 pH/°C for very dilute alkaline solutions typical of power plant cycle chemistry samples. Because of this effect, cycle chemistry guidelines for pH are referenced to 25°C to eliminate variable sample temperature effects.

A1.1.2.1 To avoid solution temperature effect errors, it is necessary to develop a solution temperature coefficient (STC) that matches the specific sample pH across the operating temperature range. For example, once the STC is developed, the technician can measure the pH in the lab at 22°C and then calculate what the referenced pH must be at 25°C by applying the STC.

A1.1.2.2 The STC may be derived empirically by measuring the pH of a known solution under carefully controlled conditions at two or more temperatures covering the anticipated sample range as well as the reference temperature. From that, the best slope in pH/°C can be determined.

A1.1.2.3 Temperature data for normalizing pH measurements to 25°C have been determined for the following:

(1) Pure water.

(2) Matrix No. 1—4.84 mg/L sulfate, that represents an acidic solution at pH 4.0 at 25°C.

(3) Matrix No. 2—0.272 mg/L ammonia and 20 g/L hydrazine, that represents average conditions for steam cycle all-volatile reducing chemistry control (pH 9.0 at 25°C).

(4) Matrix No. 3—1.832 mg/L ammonia, 10 mg/L morpholine, and 50 g/L hydrazine, that represents conditions for all-volatile reducing chemistry control at high pH with amines (pH 9.6 at 25°C).

(5) Matrix No. 4—3 mg/L phosphate with a sodium-to-phosphate molar ratio of 2.7 with 0.3 mg/L ammonia, that represents "average" conditions for phosphate chemistry control.

A1.1.2.4 pH values for these solutions and temperature corrections are given in Table A1.1 and Table A1.2. The temperature corrections for the basic solutions are essentially the same, and approximately twice the correction for pure water

A1.1.2.5 pH instrumentation with a setting and algorithm for the STC correction enables continuous on-line pH measurements to be more error-free (5).

A1.1.2.6 The STC correction in pH instruments must be disabled during buffer calibration because the temperature coefficient of buffer solutions is different from the coefficient of the sample. In most instruments this is done automatically. As a result, if the buffer solution is not at the reference temperature, the pH measured in a buffer solution with the STC active will normally differ from the buffer value entered during calibration. pH measurement with the STC active is only correct back in the sample.

TABLE A1.1 pH as a Function of Temperature for Different Matrixes [A,B]

Temperature °C	Matrix No. 1 pH	Matrix No. 2 pH	Matrix No. 3 pH	Matrix No. 4 pH
0	4.004	9.924	10.491	10.388
1	4.004	9.882	10.451	10.345
2	4.004	9.840	10.411	10.303
3	4.004	9.800	10.372	10.261
4	4.004	9.759	10.333	10.219
5	4.004	9.719	10.294	10.178
6	4.004	9.680	10.256	10.138
7	4.004	9.640	10.218	10.098
8	4.004	9.602	10.181	10.058
9	4.004	9.563	10.144	10.019
10	4.004	9.525	10.108	9.981
11	4.004	9.488	10.072	9.943
12	4.004	9.451	10.036	9.905
13	4.004	9.414	10.001	9.868
14	4.005	9.378	9.966	9.831
15	4.005	9.342	9.932	9.795
16	4.005	9.307	9.898	9.759
17	4.005	9.272	9.864	9.723
18	4.005	9.237	9.831	9.688
19	4.005	9.203	9.798	9.654
20	4.005	9.169	9.765	9.619
21	4.005	9.135	9.732	9.583
22	4.006	9.102	9.700	9.552
23	4.006	9.069	9.669	9.519
24	4.006	9.036	9.637	9.486
25	4.006	9.002	9.604	9.451
26	4.006	8.972	9.576	9.421
27	4.006	8.940	9.545	9.390
28	4.007	8.909	9.515	9.358
29	4.007	8.878	9.485	9.327
30	4.007	8.847	9.456	9.296
31	4.007	8.817	9.426	9.266
32	4.007	8.787	9.397	9.236
33	4.008	8.757	9.369	9.206
34	4.008	8.728	9.340	9.177
35	4.008	8.699	9.312	9.148
36	4.008	8.670	9.284	9.119
37	4.009	8.641	9.257	9.091
38	4.009	8.613	9.229	9.063
39	4.009	8.585	9.202	9.035
40	4.010	8.557	9.175	9.007
41	4.010	8.529	9.149	8.980
42	4.010	8.502	9.122	8.953
43	4.010	8.475	9.096	8.925
44	4.011	8.448	9.070	8.900
45	4.011	8.422	9.044	8.874
46	4.011	8.396	9.019	8.848
47	4.012	8.370	8.994	8.823
48	4.012	8.344	8.969	8.757
49	4.012	8.318	8.944	8.772
50	4.013	8.293	8.919	8.748

[A] See A1.1.2.3 Matrix No.

    1: 4.84 mg/L $SO_4^=$,

    2: 0.272 mg/L NH_3 + 20 µg/L N_2H_4,

    3: 1.832 mg/L NH_3 + 10.0 mg/L morpholine + 50 µg/L N_2H_4, and

    4: 3.0 mg/L PO_4 at 2.7 Na^+: $PO_4^{\pm p}$ + 0.30 mg/L NH_3.

[B] Values calculated by John Riddle, NUS Corporation, Pittsburgh, PA.

TABLE A1.2 Temperature Corrections of pH Measurements for Different Matrixes [A,B]

Temperature, °C	Pure Water Temperature Correction	Matrix No. 1 Temperature Correction	Matrix No. 2 Temperature Correction	Matrix No. 3 Temperature Correction	Matrix No. 4 Temperature Correction
0	− 0.477	− 0.002	− 0.923	− 0.887	− 0.937
1	− 0.455	− 0.002	− 0.881	− 0.847	− 0.894
2	− 0.433	− 0.002	− 0.838	− 0.807	− 0.851
3	− 0.412	− 0.002	− 0.798	− 0.767	− 0.809
4	− 0.390	−0.002	− 0.757	− 0.728	− 0.768
5	− 0.369	−0.002	− 0.717	− 0.690	− 0.727
6	− 0.349	− 0.002	− 0.678	− 0.652	− 0.686
7	− 0.328	−0.002	− 0.639	− 0.614	− 0.647
8	− 0.308	− 0.002	− 0.600	− 0.577	− 0.607
9	− 0.288	− 0.002	− 0.561	− 0.540	− 0.568
10	− 0.269	− 0.002	− 0.524	− 0.504	−0.530
11	− 0.249	− 0.002	− 0.486	− 0.468	− 0.491
12	− 0.230	− 0.002	− 0.449	− 0.432	− 0.454
13	− 0.211	− 0.002	− 0.412	− 0.397	− 0.417
14	− 0.193	− 0.002	− 0.376	− 0.362	− 0.380
15	− 0.174	− 0.001	− 0.340	− 0.327	−0.343
16	− 0.156	− 0.001	− 0.305	− 0.293	− 0.308
17	− 0.138	− 0.001	− 0.270	− 0.260	− 0.272
18	− 0.120	− 0.001	− 0.235	− 0.226	− 0.237
19	− 0.102	− 0.001	− 0.201	− 0.193	− 0.202
20	− 0.085	− 0.001	− 0.167	− 0.160	− 0.168
21	− 0.068	− 0.001	− 0.133	− 0.128	− 0.132
22	− 0.051	− 0.001	− 0.100	− 0.096	− 0.100
23	− 0.034	− 0.000	− 0.067	− 0.064	− 0.057
24	− 0.017	− 0.000	− 0.034	− 0.033	−0.034
25	0.000	0.000	0.000	0.000	0.000
26	0.015	0.000	0.030	0.029	0.030
27	0.031	0.000	0.062	0.059	0.062
28	0.047	0.001	0.093	0.089	0.093
29	0.063	0.001	0.124	0.119	0.124
30	0.078	0.001	0.154	0.149	0.155
31	0.094	0.001	0.185	0.178	0.185
32	0.109	0.001	0.215	0.207	0.215
33	0.124	0.002	0.245	0.236	0.245
34	0.139	0.002	0.274	0.264	0.274
35	0.153	0.002	0.303	0.292	0.304
36	0.168	0.002	0.332	0.320	0.332
37	0.182	0.003	0.361	0.348	0.361
38	0.196	0.003	0.389	0.375	0.389
39	0.210	0.003	0.417	0.402	0.417
40	0.224	0.004	0.445	0.429	0.444
41	0.238	0.004	0.472	0.456	0.471
42	0.252	0.004	0.500	0.482	0.498
43	0.265	0.004	0.527	0.508	0.525
44	0.278	0.005	0.553	0.534	0.551
45	0.292	0.005	0.580	0.560	0.577
46	0.305	0.005	0.606	0.585	0.603
47	0.318	0.006	0.632	0.611	0.629
48	0.330	0.006	0.658	0.636	0.654
49	0.343	0.006	0.684	0.661	0.679
50	0.356	0.007	0.709	0.685	0.704

[A] See A1.1.2.3 Matrix No.
    1: 4.84 mg/L $SO_4^=$,
    2: 0.272 mg/L NH_3 + 20 µg/L N_2H_4,
    3: 1.832 mg/L NH_3 + 10.0 mg/L morpholine + 50 µg/L N_2H_4, and
    4: 3.0 mg/L PO_4 at 2.7 Na^+: $PO_4^{±p}$ + 0.30 mg/L NH_3.
[B] Values calculated by John Riddle, NUS Corporation, Pittsburgh, PA.

A2. FLOW SENSITIVITY OF PH ELECTRODES IN LOW CONDUCTIVITY WATER

A2.1 pH electrodes exhibit some flow sensitivity when exposed to a flowing low conductivity water sample stream. This flow sensitivity manifests itself by alterations of the pH electrode's output signal in relationship to changes in sample flow rate which are not necessarily representative of actual solution pH changes. It is always recommended, therefore, to maintain a fixed sample stream flow rate in low conductivity water applications.

A2.2 pH variations due to sample pressure are often mistaken for flow sensitivity. It is believed that sample stream pressure variations affect the pH reference half-cell's liquid junction potential resulting in pH measurement errors. This phenomenon is more noticeable in low conductivity water applications, therefore it is always recommended to maintain a fixed sample stream pressure (atmospheric discharge) in these applications.

A3. PH SENSOR AND SAMPLE LINE INSTALLATION (18)

A3.1 Contaminants

A3.1.1 Pure water sample streams in power plant boiler waters often contain suspended corrosion particles. These are fine insoluble particles of iron oxides and other by-products of metallic corrosion that are present throughout the system. The microscopic particles have an unfortunate tendency to adhere to the walls of horizontal sample tubing and accumulate in sensor flow cells. Along with the occasional ion exchange resin beads and bead particles, plus biological growths, these "crud" layers act as chemical sponges, trapping ionic impurities by absorption and adsorption. These impurities acting as an ionic reservoir and, hiding in a sample line, will act to mask real changes in the sample by trapping ions when conductivity rises and slowly bleeding them back when the water becomes cleaner. Sudden flow variations, temperature change or vibration, can release large amounts of this coating, replete with its load of ions, to give false indication of an increase in chemical levels. This situation must be avoided to enable accurate measurement, and sample flow rates are a major key to doing so.

A3.2 Flow Rates

A3.2.1 Data from Ref (19) indicates that as much as 80 % of the suspended particles can be deposited in a long horizontal sample line during the first few hours of operation while maintaining a turbulent flow rate with a Reynolds number of 4000. For normal sample flow rates, this works out to only a few grams of coating, but that constitutes a huge ion storage matrix. EPRI data indicates that 1.8 m/s is an optimum practical sample velocity to achieve minimum deposition.

A3.2.2 With flow velocity as the controlling factor, tubing size becomes important. A rate of 1.8 m/s corresponds to 850 mL/min for 6.35 mm tubing with 3.175 mm inside diameter, and 3400 mL/min for 9.525 mm tubing with 6.35 mm inside diameter. The smaller line will require 1 340 000 L per year less sample throughput than will the larger one. It is therefore recommended that 6.35 mm tubing be used for all sample handling where pressure is available and blockage is not a problem. It has a pressure drop of 18 bar per 100 m at 40°C and 1.8 m/s. Compression fittings are best for connections, as fillet welding can reduce bore diameter of the small tubing by half the fitting entry, restricting flow, and perhaps plugging entirely if resin beads are encountered. The tubing should be AISI 300 series stainless, preferably AISI type 304 or type 316. New tubing may take several weeks to wash out all the oil and other impurities left from fabrication.

A3.2.3 *Sample Temperature Conditioning*—Sample cooling is to be done upstream of sensor manifolds. Most samples are cooled to near 25°C to improve measurement accuracy in accordance with Ref (20). Ref (19) recommends cooling to 25°C ± 1°.

APPENDIX

X1. EFFECTS OF CO_2 ON PH MEASUREMENTS OF HIGH PURITY WATER

X1.1 High purity water will rapidly absorb carbon dioxide when exposed to the atmosphere. Carbon dioxide levels in the atmosphere are near 400 ppm by volume. Pure water by definition does not contain carbon dioxide. However, in practice CO_2 is present in trace levels in most low conductivity water samples. High purity water on-line pH sensor assemblies and related sample system hardware should be designed and installed in such a manner as to prevent the intrusion of carbon dioxide from the atmosphere. See Fig. X1.1 for the theoretical pH and conductivity values of ammonia solutions at various carbon dioxide levels. Also see Table 3 for the theoretical pH shift caused by 0.2 mg/L CO_2 contamination of a high purity water sample. This information is provided to give the user an indication of the level of pH measurement error introduced by the presence of CO_2. The user should determine the actual effects of CO_2 contamination for the user's specific operating
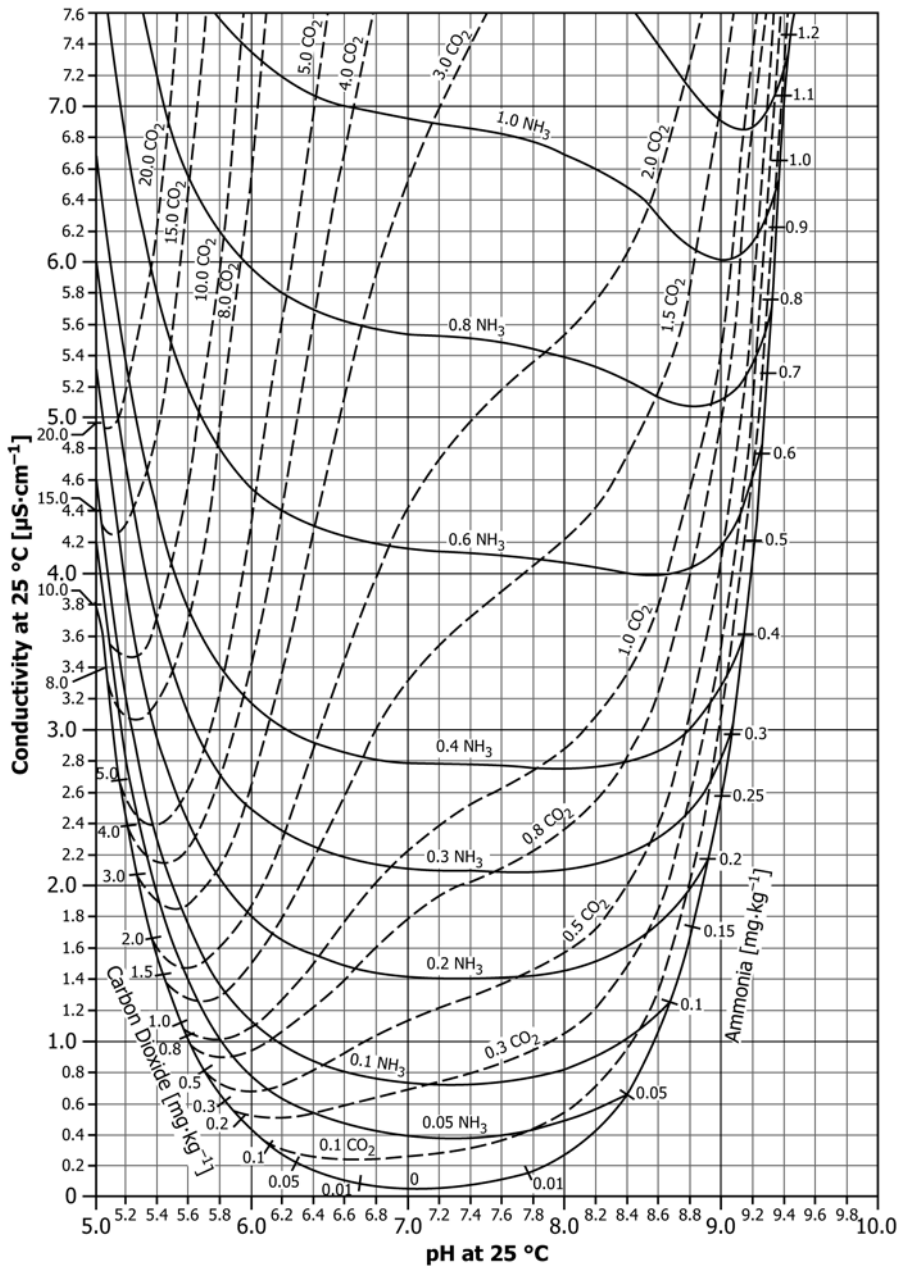
NOTE 1—Calculated by NUS Corporation, Pittsburgh, PA; graphics enhanced by *PowerPlant Chemistry* journal.

FIG. X1.1 pH and Conductivity of Ammonia Solutions at Various Carbon Dioxide Levels

conditions as they may differ from application to application.

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