Analytical Measurements and Instrumentation for Process and Pollution Control

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PREFACE

A prerequisite for control of processes and environmental parameters is an understanding of the analytical factors that are involved in measurement, and applying such measurements as standards of comparison and regulation. Additionally, high-sensitivity techniques for measurement of various species are required. Making measurements in the industrial and real-world environment is important for a number of reasons:

1. such analytical data may be required for designing control equipment;
2. instrumentation may be required for process control and efficiency;
3. data may be required for submission to governmental enforcement agencies to comply with source measurement requirements;
4. as legal evidence of compliance; and
5. for protection of health and property for both workers and the public at large.

Analytical Measurements is organized in 14 chapters, each written by an expert in his or her respective field. Each of these sections examines selected significant analytical methods and documents the technique from the standpoint of current practice and the case study approach. An extensive listing of information sources accompanies many sections where applicable, with the intent of stimulating further information exchange for the reader or user of this volume. The book goes beyond a state-of-the-art review by structuring the information on instrumentation/control environments, problems according to concepts and how to proceed. The aim is to provide a how-to-do-it book—as well as what the method will do and where to find it.

This book should prove useful to engineers, scientists, chemists and students concerned with a wide variety of instrumentation and measurement problems in industrial process and environmental control fields. Acknowledgment is made to the experts who gave willingly of their time and knowledge to make this volume possible.

This volume was completed and published after the untimely death of Dr. Harlan J. Perlis who was co-editor at the inception of this project. Dr. Perlis is, and will be, sorely missed for his tireless interests and efforts in the field of instrumentation and control and his ceaseless activities, pioneering spirit and research.

Paul N. Cheremisinoff

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CHAPTER 1

pH MEASUREMENT INSTRUMENTATION

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ACIDS AND BASES

A common way to describe an aqueous solution of an acid or base is in terms of the weight of the material that is present in a given amount of solution. For example, specifying that one solution is 5% hydrochloric acid and that another is 8.5% boric acid describes the two solutions exactly. In this particular case, because the molecular weights of the two acids are in the ratio of 5:8.5, equal volumes of the two solutions contain the same number of molecules of acid. In spite of this, the two solutions differ markedly from each other in their properties. For example, the solution of boric acid can be used as an eyewash, whereas similar use of the solution of hydrochloric acid would be disastrous, even though the weight percents of the acids are similar. Clearly, something else must be considered to describe the solutions more precisely.

The difference between the two solutions mentioned above is related to the way in which each of the acids behaves when added to water. Adding any acid to water produces an excess of hydrogen ions, and both hydrochloric acid and boric acid do this, but to different extents. When hydrogen chloride is dissolved in water, almost all of the molecules dissociate to form hydrogen ions and chloride ions.

Since nearly all the molecules dissociate, hydrochloric acid is described as a strong acid. However, when boric acid is dissolved in water, almost all of the boric acid remains in molecular form; only a relatively small number of molecules dissociate to form hydrogen ions and the corresponding negative ions. Because of this, boric acid is described as a weak acid.

Thus, hydrochloric acid is unfit for use as an eyewash because it is a strong acid. A solution of it contains a high enough concentration of hydrogen ions to damage the eye. On the other hand, boric acid can be used as an eyewash because it is a weak acid. Even a fairly concentrated solution of it contains a relatively low concentration of hydrogen ions. What is necessary, then, to describe an acidic solution more precisely is a measure of the concentration of hydrogen ions in the solution.

For similar reasons, what is necessary to describe a solution of a base is a measure of the concentration of hydroxyl ions in the solution. Bases can be described in the same sort of terms as acids. Adding a base to water produces an excess of hydroxyl ions. Thus, sodium bicarbonate is a base. It is more properly described as a weak base because a relatively large amount of it produces only a small excess of hydroxyl ions. On the other hand, caustic soda (sodium hydroxide) is described as a strong base because it is totally dissociated in water. In fact, even water dissociates to a slight degree, forming both hydrogen and hydroxyl ions in small but equal amounts. Since the hydrogen ions and the hydroxyl ions are present in the same amount, pure water is neither acidic nor basic.

In pure water, and in any aqueous solution, the product of the concentrations of hydrogen and hydroxyl ions is a constant, provided the temperature remains constant. At 25°C, for example, the product is 10^{-14} mol^2/l^2. Thus, the acidity or basicity of any aqueous solution can be described by specifying just the concentration of hydrogen ions and the temperature.

The hydrogen ion concentrations of commonly encountered solutions vary over a wide range, so that a logarithmic scale is convenient. Using such a scale introduces the concept of pH.

pH

pH may be described as the negative logarithm of the concentration of hydrogen ions in an aqueous solution. (The description is exact if the term *activity* is substituted for *concentration*.) In absolute terms, this means that pure water, which contains 10^{-7} mol/l of hydrogen ions, has a pH of 7. In relative terms, this means that a solution having a pH of 4 contains 10 times more hydrogen ions than a solution having a pH of 5. That is, a change of pH of one unit reflects a 10-fold change in hyrdogen ion concentration. A pH below 7 means that the solution is acidic. A pH above 7 means that the solution is basic. A pH of 7 means that the solution is neutral—neither acidic nor basic. The pH index is usually considered to range between pH 0 and pH 14. Values outside this range are only infrequently encountered in practice.

THE GLASS ELECTRODE—SILVER/SILVER CHLORIDE REFERENCE ELECTRODE PAIR

If two solutions of different pH values are separated by a glass membrane of certain composition, a potential is developed across the membrane. Experimentally, it is determined that the potential is a function of the difference in pH values between the two solutions. If the pH values are the same, the potential difference will be essentially zero. As the difference in pH of the two solutions is increased, the potential across the membrane increases by about 59 mV per pH unit difference at 25°C. This property of the glass membrane may be exploited to make pH measurements. A simple configuration is illustrated in Figure 1.

A connection to each solution is necessary to measure the difference in potential. To make the connections, a silver wire coated with silver chloride is dipped into each solution. Chloride ions are added to each solution in the same amount as, say, potassium chloride. Other things being essentially equal, reproducible and equal potentials are produced between each coated wire and the solution in which it is immersed because of the formation of two nearly identical silver/silver chloride half-cells. Thus, the potential difference between the two wires depends solely on the difference in pH between the two solutions. This potential may be measured by using a high-impedance millivolt meter with characteristics that are described later.

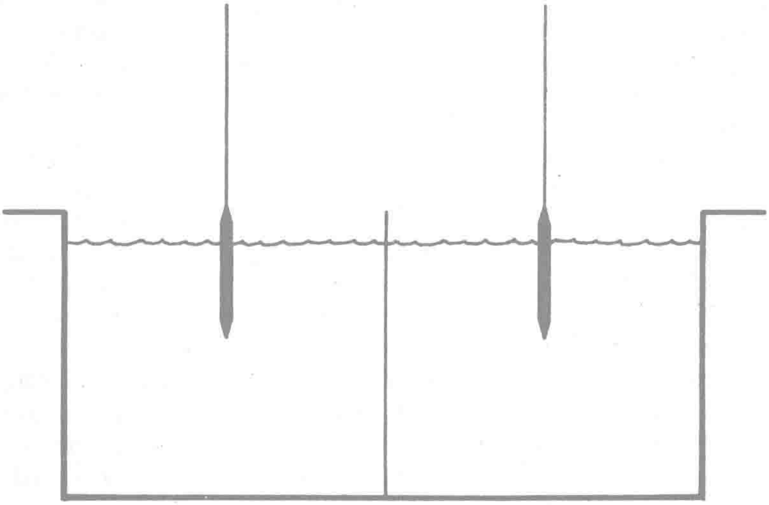

Figure 1. Cell for pH measurement showing two solutions separated by glass membrane. Probes into solutions are silver wires coated with silver chloride.

Of course, to make a useful measurement of pH, a sample of the solution to be tested is substituted for one of the solutions shown in Figure 1. Unfortunately, when this is done the potential between the coated silver wire and the solution may vary with the composition of the solution to be tested, independently of pH. If that happens, the potential difference between the two silver wires is no longer solely a function of pH. To deal with this problem, each of the coated silver wires is enclosed in an envelope so that the solution with which each wire is in contact remains of constant composition.

The envelope that encloses one of the coated silver wires is simply the glass membrane itself in the form of a thin-wall bulb. Filling the bulb with a buffered solution that contains chloride ions provides an electrode that is sensitive only to the pH of the external stream.

The remaining coated wire is enclosed within an inert envelope and that envelope filled with a solution of constant composition, which contains a fixed concentration of chloride ions. To complete the circuit, the solution within the envelope must be in electrical contact with the external stream. Classically, this is done by providing a controlled leak in a thick-wall glass bulb, so that the filling solution slowly can be forced outward into the external stream. An external, elevated reservoir is used to provide a continuous supply of filling solution to the electrode.

Maintaining a positive (but very slow) flow outward ensures that none of the external stream will enter the electrode and contaminate the filling solution. Such an electrode is properly called a reference electrode because it is essentially insensitive to changes in the pH or composition of the external stream. This is true even if the thick-wall bulb is made of a glass that is sensitive to pH because the resistance of the leak is so much less than the resistance of the bulb. The leak is a "short circuit" path.

More recently developed reference electrodes establish a junction between the filling solution and external stream by means of a porous polymeric junction. Filling solution diffuses outward through the junction of the reference electrode and the stream diffuses inward (both at extremely slow rates). The two mingle in the junction area, providing electrical contact. Since the need to force filling solution from the electrode is eliminated, the external reservoir is no longer necessary, and maintenance requirements are drastically reduced.

A refinement of the nonflowing-junction reference electrode is the double-junction reference electrode. It consists of a small, conventional, nonflowing-junction electrode and a nonflowing-junction outer body. An "inert" electrolyte, typically potassium nitrate, fills the space between the inner electrode and the outer body, providing electrical continuity. With this arrangement, the stream does not come in physical contact with the filling solution or the internals of the inner electrode. Because of this isolation, the stream may contain components

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that otherwise would react with the filling solution or internals, such as sulfide, silver, lead or mercury.

Industrial versions of the glass pH-sensitive electrode and silver/silver chloride electrode are available for use at temperatures as high as 130°C and pressures as high as 150 psi.

OTHER ELECTRODES

While the glass pH-sensitive electrode and silver/silver chloride reference electrode are the most widely used in online industrial applications, others are available.

The most common alternative to the glass pH-sensitive electrode is the antimony electrode. It is useful in applications that are too harsh for the glass electrode, such as pH measurements in acidic fluoride media or in some ore-extraction processes. The electrode consists of a stick of antimony metal on which a coating of antimony oxide is present. It exploits the pH dependence of the antimony/antimony oxide couple.

The antimony electrode is limited in application compared to the glass electrode. The antimony electrode is not usable at pH values less than about 2 nor greater than about 12. In comparison, the glass electrode is usable over the range of 0 to 14. Further, the antimony electrode is sensitive to the presence of oxidizing and reducing agents in the stream being measured, whereas the glass electrode is virtually interference free. Other metal/metal oxide pH-sensitive electrodes have been devised but none has gained wide acceptance by the industrial community.

The most common alternative to the silver/silver chloride reference electrode is the Calomel electrode. It is based on the mercury/mercurous chloride couple. For the vast majority of online industrial applications, the Calomel electrode provides no substantial advantage over the silver/silver chloride electrode. Further, it is limited to applications in which the temperature does not exceed about 80°C.

The remainder of this discussion is based only on the glass pH-sensitive electrode and the silver/silver chloride electrode.

THE ELECTROCHEMICAL CELL

When the reference and the glass electrodes are immersed in a stream, an electrochemical cell is formed. The potential of the cell is related to the pH of the stream. At this point it is useful to discuss that relationship and see how the potential is measured.

The output of the cell is a potential that is directly proportional not only to pH, but to temperature as well. Typically, the filling solutions of the electrodes are chosen so that the potential is within a few millivolts of zero when the pH of the stream is near 7, regardless of the temperature. In a practical sense, picking an exact pH at which the potential will be exactly zero is impossible because the properties of the electrodes will vary slightly from one set to another.

At 25°C, as the pH of the stream decreases below 7, the potential of the cell becomes more positive by about 59 mV per unit. Similarly, as the pH of the stream increases above 7, the potential becomes more negative by about 59 mV per unit. At 50°C, the behavior is similar, except that the potential changes by about 64 mV per pH unit. The temperature dependence is linear from 0°C–100°C. Finally, because of the presence of the glass membrane, the internal resistance of the cell ranges as high as 10^3 megohms.

pH ANALYZERS

These characteristics place some definite constraints on the design of a pH analyzer, although such a device is basically nothing more than a millivolt meter with a scale that is graduated in pH units. First, since essentially no current should be drawn from the cell (to avoid "loading" it), the input impedance of the analyzer must be at least 10^6 megohms. Such values are achieved in present-day analyzers through the use of field-effect transistor input amplifiers.

Further, the output of the analyzer should consistently indicate the correct value of pH regardless of the temperature of the stream. Thus, a means of compensating for the effect of temperature on the sensitivity of the electrodes must be provided. In practice, this is accomplished by placing a temperature-sensitive resistive element in thermal contact with the stream and using the resistive element to adjust the gain of the analyzer.

Finally, some means of adjusting the offset of the analyzer must be provided to compensate for minor differences between sets of electrodes. Commonly, a wide range of offset adjustment is provided in conjunction with a span control, so that an arbitrary range of pH may be selected for display. This type of system is shown in Figure 2.

For many years, this single-ended input configuration was typical of all industrial online pH analyzers. In some applications, it is a satisfactory approach. However, it tends to be sensitive to stray electrical currents in the stream. The reference electrode effectively is tied to circuit ground at the analyzer. Thus, unless the circuit ground is extremely well isolated from earth ground, an iR drop will be produced across the reference electrode in response to the stray currents within the stream being measured. The iR drop adds to or subtracts from the pH potential, thereby producing an erroneous reading. This problem is eliminated in many modern pH analyzers by measuring the potential of the cell in a different way, as shown in Figure 3. In this case, each electrode is connected to a separate

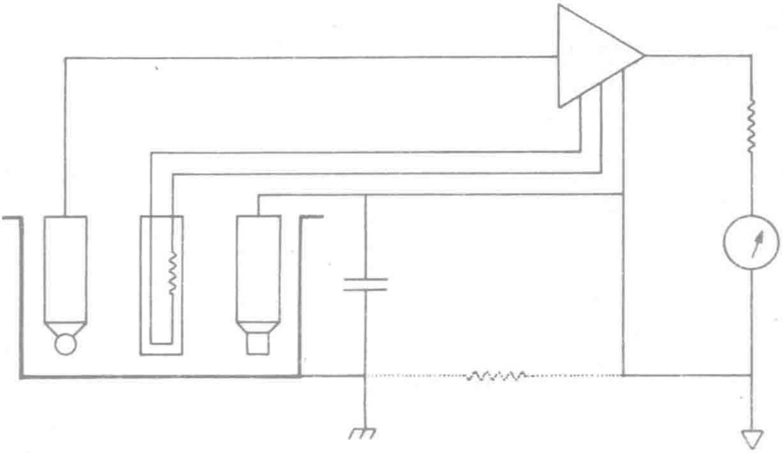

Figure 2. Single-ended-input pH analyzer. From left to right, elements of cell are glass electrode, thermocompensator and reference electrode. Dotted path depicts leakage resistance.

high-input impedance amplifier. No current can pass through the reference electrode and no iR-drop is produced, even if circuit ground is tied directly to earth ground. The potential of each electrode is measured with respect to a metallic rod that is immersed in the stream. The potential of the metallic rod is affected by many factors, including stray currents in the stream, but this is of no consequence because of the way in which the outputs of the amplifiers are combined. The output of the first amplifier is the potential of the glass electrode with respect to the rod: $e_g - e_{rod}$. The output of the second amplifier is the potential of the reference electrode with respect to the rod: $e_g - e_{rod}$. By subtracting the second output from the first, the desired potential, $e_g - e_r$, is obtained. This potential is directly related to pH.

CALIBRATION AND MAINTENANCE

Once a pH analyzer is in service, it must be calibrated periodically. This may be accomplished in at least two ways. First, a "grab sample" of the stream being measured is taken, and the pH indicated by the online analyzer at the time of sampling is noted. The pH of the sample is determined by means of a laboratory instrument, and the online analyzer is adjusted accordingly. Care must be taken to ensure that neither the composition nor the temperature of the sample changes before it is analyzed.

A better way to calibrate a pH analyzer is by means of buffer solutions. A single buffer (with pH value as near as possible to that of the stream being

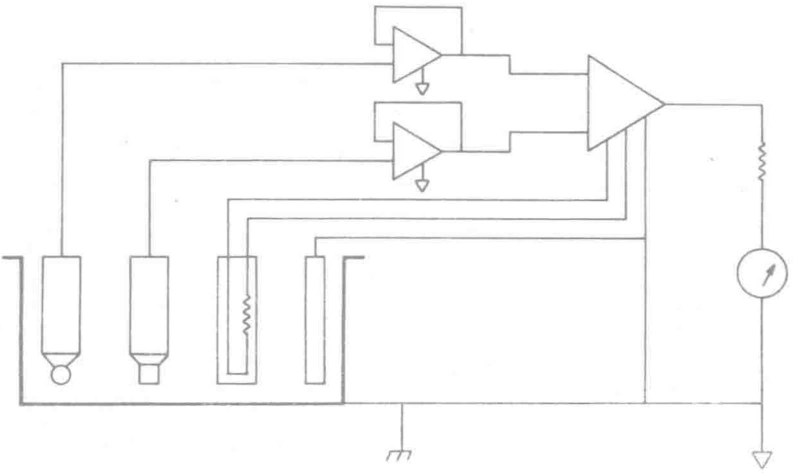

Figure 3. Differential-input pH analyzer. From left to right, elements of cell are glass electrode, reference electrode, thermocompensator and solution ground post.

measured) serves to calibrate the analyzer. However, good practice dictates that a second buffer be used to establish that the electrodes are in proper working order.

In some applications, simply performing periodic calibration is sufficient maintenance. However, many streams contain materials that either abrade or coat the electrodes. These must be dealt with if the analyzer is to produce reliable results.

In cases of electrode abrasion, simply reducing the velocity of the stream may be helpful. If that is not possible, a somewhat crude, but often effective, solution is to slip pieces of gum-rubber tubing over the electrodes. If the tubing extends just beyond the tips of the electrodes, relatively stagnant zones are produced, which tend to reduce abrasion.

Several means exist for dealing with electrode coating. In the case of a particularly tenacious coating, boiling the tips of the electrodes in concentrated hydrochloric acid for a few minutes or letting the tips stand in hydrofluoric acid for a few seconds may be the only soluton. The latter method should be used only as a last resort, however, since the hydrofluoric acid removes a part of the already thin-glass pH-sensitive membrane. An electrode that is subjected to such treatment should be calibrated using at least two buffers to ensure that it still performs properly.

Generally, less-stringent means can be used to eliminate electrode coatings. In some cases where a submersion-style probe is employed, a water jet may be useful for periodically spray cleaning the electrodes. Conveniently automated by means of a timer and valve, this device is particularly useful if a soft, mushy coating is involved.

A second method for cleaning electrodes is an automated brush assembly, which periodically brushes the coating from the electrodes. However, if the coating is particularly abrasive, the glass pH-sensitive electrode may require more frequent replacement than would otherwise be the case.

The final method included in this discussion is the ultrasonic cleaner. While details of the device vary from manufacturer to manufacturer, each consists of an ultrasonic transducer, which is placed within the electrode chamber, and a remote exciter. Such devices are useful in a wide variety of applications involving organic or inorganic coatings, but at least some periodic manual cleaning is generally required.

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