OPERATION AND
SERVICE GUIDE
O-670A
DEC. 1997

PORTABLE pH METER

MODEL	PRICE CODE NUMBER
100	56-0032

Refer to Bulletin A-301.

GENERAL INFORMATION

Model 100 pH meter is designed for measuring pH over the entire 0 to 14 range. The plus 700 to minus 700 millivolt range is useful for oxidation-reduction potential measurements as well as other electrochemical measurements. The instrument is shipped with batteries in place. It is only necessary to standardize with buffer and it is ready for use.

All controls and connections are on the front panel. The power switch has four positions. Two select the range and one is for battery test. A temperature knob permits compensation for sample temperature. Electrode asymmetry potential (electrode zero output) may be compensated with use of a buffer and adjustment of the calibration knob. The meter has scales for both pH and millivolts. Below the meter are connections for a glass or a combination electrode (BNC connector) and, if used, a reference electrode (pin jack). Access to the batteries is obtained by removing the rear cover.

OPERATION

1. Connect electrode.
2. Set solution temperature knob.
3. Turn on switch.
4. Standardize electode in buffer.
5. Immerse electrode tip into solution.
6. Read meter.

Periodically test the battery which should show a meter reading above 11.6 pH.

The standard electrode (56-0412) furnished with the instrument is a combination glass and reference electrode. Two electrodes are required in the solution to complete the electrical circuit and they are combined in this one unit. The round glass bulb on the end is the pH sensitive portion. There is a protective plastic cap over the glass bulb and a reference junction. There is a rubber sleeve and tape over a vent hole for the reference electrode.

To use the electrode, pull off the cap protecting the pH glass bulb. Slide off the rubber sleeve. Remove the tape over the reference electrode vent. Do not allow anything but filling solution to enter this vent hose because sample can destroy the reference. Connect the electrode to the instrument.

If the electrode is a guarded type it may be allowed to rest on the bottom of a shallow beaker of solution. If the electrode is not guarded, it must be supported to prevent the glass pH sensitive bulb from touching the beaker.

Turn the switch to BATT. The meter must read above 11.6. If not, replace the batteries. For a pH test proceed as follows:

1. Turn the switch to pH
2. Calibrate the electrode with buffer solution. For best accuracy, select a buffer with pH close to that expected for the sample.
3. Set the temperature knob to the buffer temperature.
4. Dip the electrode tip one to four centimeters below the surface of the solution.
5. Swirl the solution or stir with the electrode until a constant meter reading is obtained. Adjust the calibration knob to make the meter indicate the pH of the buffer.

The meter is now ready for a test. Rinse the electrode with distilled water, deionized water or the solution to be tested. Dip the tip of the electrode one to four centimeters below the surface of the sample solution, mix the solution and then read the meter.

The electrode will hold its calibration for a period of minutes to days, depending on the treatment it receives. After a few recalibrations, the user will learn the stability of the electrode in a specific application.

To store the electrode, slide the upper rubber sleeve over the vent and replace the plastic cap. Tape over the vent hole is necessary only if the electrode will be stored for several weeks between tests.

SLOPE CORRECTION

Electrodes may be encountered which do not produce the theoretical voltage change for a unit of pH change. This is called slope error. It may be determined by measuring two freshly prepared buffers of different pH. If the response if not correct, the slope error may be corrected by turning the temperature knob. A lower temperature setting will increase the meter movement. The difference between the actual solution temperature and the temperature knob setting may be considered the slope error. This slope error for a specific electrode may be applied to future measurements at other temperatures. Certain pH meter models have a slope correction knob calibrated in percent error. The slope error is frequently due to foreign ions in the reference electrode junction or solution.

BUFFER SOLUTION

Buffer solutions for calibrating the electrode are available from your pH meter dealer, or may be prepared from the instructions provided in many chemical handbooks. For best test accuracy, the buffer pH should be as close as possible to the sample pH. Buffer solution pH may change with time due to adsorption of carbon dioxide. Solution stored in plastic bottles for more than a year should be suspect and checked against fresh buffer. Deterioration is greatest for high pH buffers such as borate.

All buffer solutions change pH with a change in temperature. The pH of common buffer solutions is shown below.

TEMP °C	pH 4.01 phthalate	pH 7.00 phosphate	pH 9.18 borate
0	4.01	7.12	9.46
5	4.01	7.09	9.39
10	4.00	7.06	9.33
15	4.00	7.04	9.27
20	4.00	7.02	9.22
25	4.01	7.00	9.18
30	4.01	6.99	9.14
35	4.02	6.98	9.10
40	4.03	6.98	9.07
45	4.04	6.97	9.04
50	4.06	6.97	9.01
55	4.08	6.98	8.99
60	4.10	6.98	8.96
70	4.12	6.99	8.92
80	4.16	7.00	8.88
90	4.20	7.00	8.85

Sample pH will also change with temperature, depending on the composition. For accurate results it is important that buffer and sample be at the same temperature. Conversely, if an accuracy of only 0.2 pH is required, buffer pH drift with temperature generally may be ignored.

CALIBRATION SHUNT

A calibration shunt is available and it is used to eliminate the need for buffer in field tests. The shunt is a shorting cap for the instrument input. Satisfactory calibration is dependent on the stability of the reference electrode.

The procedure for calibrating the shunt is to first calibrate the electrode in pH 7.00 buffer. Without moving the calibration knob, the electrode is disconnected and the shunt is plugged into the electrode connector on the meter. The pH reading in the meter is the calibration value for that electrode and is retained for future field calibrations.

To standardize the meter in the field, connect the shunt to the meter electrode connector and set the meter pointer to the pH value found for the shunt above by turning the calibration knob. Remove the shunt and connect the electrode to the meter. The instrument is now ready for a pH test.

ELECTRODES

There are three types of electrodes available. These are glass, reference, and combination glass/reference. Combination electrodes are usually supplied with the instrument.

The glass electrode produces a voltage as a result of the pH difference across a thin glass membrane. This membrane is in the form of a bulb at the lower end of the tubular body of the electrode. A silver wire coated with silver chloride makes an electrical connection to buffer solution on the inside of the membrane. In use, the outside of the electrode is immersed in buffer or sample solution. Electric current passes through the thin pH glass wall. Electrical connection to the buffer or sample is made through a reference electrode. The reproducibility and stability of the pH reading is dependent on the reference electrode. Originally, these two electrodes were separate and many users prefer this arrangement. However, today the more common arrangement for laboratory applications is with the two electrodes combined in a combination electrode with the reference electrode surrounding the glass pH electrode. This arrangement has advantages in convenience and requires less sample.

GLASS ELECTRODES

These instructions are for either a glass pH electrode or the glass electrode portion of a combination electrode. For first time use or after long storage, soak the tip in tap water or buffer for five to thirty minutes, depending on the accuracy desired. The longer period is necessary if an accuracy of 0.001 pH is desired.

It is important that the water at the surface of the pH glass bulb have the same composition as the entire sample. Therefore, the bulb surface must be clean. Sample must flush away prior solution adequately to produce the desired pH accuracy.

If the electrode is used in oily solution, it will be necessary to periodically clean the electrode's pH sensitive surface with a towel. If detergent is necessary, the electrode should be rinsed thoroughly since a surface film will interfere with correct operation.

The output voltage of a glass electrode is approximately the same as a reference electrode at pH 7.0. The pH at which there is no voltage difference between the glass and reference electrode is zero potential. There are small differences in asymmetry potential between different electrodes. The previously described procedure of calibrating the electrode with buffer corrects any difference from standard.

For users who are involved with the electrochemistry of pH, the glass electrode becomes more negative with increasing pH.

SILVER CHLORIDE REFERENCE ELECTRODE

When a new electrode is first being placed in service, wet the entire outside surface except top cap in tap water. Remove the lower cap which is for storage only. Clean the junction. Remove the upper rubber sleeve and the tape over the vent hole which is for shipping or long term storage. The vent hose must remain open during tests. Soak the electrode tip in water for five to thirty minutes depending upon the accuracy required. This soaking is necessary to allow the KCl flow from inside the electrode to become constant.

Periodically, it will be necessary to refill the reservoir with solution. Use only 4M potassium chloride saturated with silver chloride. For one to three hours after addition of solution the pH signal may be low and drifting up. Periodic standardization with buffer will be necessary during this period. The internal solution should be maintained within one centimeter of the vent hole.

For short storage of the electrode (up to one week), the electrode may be placed in a beaker containing about two centimeters of water. Leave the vent hose open. For long storage (over one week), the electrode should be filled with KCl to just below the filling hole and all rubbers should be placed in the original positions as when the electrode was received. The electrode may then be placed back in the box and stored.

Silver-silver chloride is a widely used reference electrode because it is rugged and simple. Its voltage is reliable over a broad temperature range. If the electode is allowed to run dry it can be refilled with little chance of being damaged. It has the disadvantage of being sensitive to flow or pressure of sample against the junction. If the sample is stirred, the pH meter reading may fluctuate as much as 0.3 pH. Certain ions such a proteins or heavy metals may change the electrode voltage.

The silver-silver chloride cell in the electrode consists of a silver wire coated with silver chloride. The silver chloride on the wire is in equilibrium with the surrounding potassium chloride solution. Consequently, for stable operation, the electrode must be filled with potassium chloride saturated with silver chloride.

CALOMEL REFERENCE ELECTRODE

All operating and service instructions are the same as for the silver chloride reference electrode with the exception of the filling solution. Saturated potassium chloride solution must be used. Do not use solution containing silver chloride.

The calomel electrode is considerably more stable than the silver-silver chloride electrode. The effect of solution motion is only 1/10th of that for the silver-silver chloride electrode. There is no interference from proteins or heavy metals. It does have a limited temperature range. If allowed to run dry, a bubble may enter the calomel cell and this can be removed by drawing a vacuum on the electrode vent. Silver ion must not be in the filling solution and only pure potassium chloride solution should be used to fill the calomel electrode.

DOUBLE JUNCTION ELECTRODE

Another reference electrode which has excellent stability and freedom from ion interference is the double junction type with silver-silver chloride electrode cell. It consists of a silver-silver chloride electrode of normal construction with its junction attached to a reservoir of potassium chloride solution. This solution has a junction to the sample. The advantage of this design is in the silver cell similar to the unit inside the pH electrode. Consequently, the temperature coefficient is similar to that of the pH electrode. Since the potassium chloride in contact with the sample contains very little silver, there is little problem with foreign ions. The disadvantages are the added complexity and greater price.

COMBINATION ELECTRODE

A combination electrode consists of a glass electrode and a reference electrode in a single probe. It has the advantage of requiring less sample and also of being easier to clean than two separate electrodes. Since either a silver-silver chloride or a calomel cell may be used, it is important that the correct procedure be followed for maintaining the electrode. Make certain that only filling solution containing silver is used with a silver chloride reference. Also make sure that filling solution containing silver never enters a calomel reference reservoir.

SEALED COMBINATION ELECTRODE

Sealed combination electrodes have the usual construction for the glass cell. The reference cell contains potassium chloride saturated with silver chloride and thickened with a gel. The junction is porous ceramic. There is no vent hole for the reference cell. The gel reduces the solution flow rate sufficiently so it will last for many months, depending upon the type of service.

If temperature changes occur during a series of tests, solution may be drawn into the reference junction. This may cause the calibration to drift. For this reason a sealed electrode should be carefully evaluated for any application requiring accuracy better than 0.2 pH. Such evaluation should include electrode response tests with two buffers of different pH, before and after sample tests.

The correct procedures for using a plastic body sealed electrode is to stir the solution with the electrode. First stir the buffer and calibrate to buffer pH. Next stir some ion free water (distilled or deionized). Finally stir the sample and read the meter. The reason for this procedure is that the reference junction is inside the electrode guard behind the glass bulb and good circulation in this cavity is necessary.

ACCESSORIES & ELECTRODES

Electrode, glass, general purpose. For use with pH meters 100, 140	56-0413 56-0402
Sealed, disposable, plastic sheathed, non-breakable, silver-chloride reference with ceramic junction. For use with pH meters 100, 140	56-0403
Refillable version of 56-0412. For use with pH meter 100	56-0306
8 mm, economy glass combination, refillable. For use with pH meter model PA-10	56-0404 56-0405
Sealed, disposable, plastic sheathed, non-breakable, silver-chloride with ceramic junction. For use with pH meter PA-10	56-0406 56-0407 56-0408 56-0409
Glass, 8 mm, refillable calomel. For pH meter model PA-10	56-0330
NOTE: All electrodes supplied with BNC connectors unless specified otherwise	56-0404
Buffer solution - 7.00 pH 2 oz.	
Buffer solution - 7.00 pH pint	
Electrode filling solution; silver-silver chloride electrode	
Carrying case for PA-10 meter	
Electrode stand for models 100, 140	
Electrode holder for use with 56-0408	
Battery charger for model 100 meter, complete with 6 batteries and meter connector - must be ordered with meter	
Adaptor for 230 Volt supply. For use with pH meter 140 56-0400 56-0412	

ELECTRODE TEMPERATURE

The pH calibration of all glass electrodes is dependent on temperature. Therefore, it is necessary to compensate for temperature of the electrode. A temperature control knob is on the front panel for this compensation. For measurements within one pH of the buffer and between 10° and 40°C, the temperature correction error is below 0.1 pH. Consequently, for this type of measurement, the temperature control may be left at 25°C. For measurements at greater than one pH from the buffer and requiring accurate results, the temperature compensation knob must be adjusted. Set this knob to the temperature of the buffer when standardizing the electrode.

For best accuracy, the buffer temperature and the sample temperature must be the same. One method of accomplishing this for field work is to immerse the bottle of buffer in the sample for a few minutes.

All glass electrodes have a temperature coefficient proportional to the absolute temperature. The voltage produced by the electrode is greater at higher temperature. For example, if an electrode is calibrated with buffer at pH 7.0 and a temperature of 25°C, each one pH change will produce an electrode output change of 64 millivolts.
The meter temperature knob adjusts the number of millivolts change at the input connector required to make a one pH change on meter. The instrument temperature compensation knob is essentially a slope control or in electronic terms, an amplifier gain control.

MAINTENANCE

Case exterior finish may be maintained by cleaning with a damp rag wetted with detergent. Spray type window cleaning materials are also effective but must never be allowed to wet the electrode connector.

The electronics are entirely solid state which essentially eliminates maintenance. All wearing parts such as potentiometers are standard type and available.

In the center of the meter there is an adjustment screw for the pointer. This has been set to zero millivolts with the power switch at millivolts and the instrument input shorted. Do not adjust this screw with the power off.

A quick method of determining whether faulty performance is due to the instrument or the electrode is as follows. Place a shorting cap on the input BNC or short the input with a wire. Turn the calibration knob from end to end of travel. The meter should move from pH 5 to pH 9. This test proves that the amplifier has the correct input voltage range. Disconnect the shorting cap. After an initial meter pointer movement, the pointer should drift down at a rate of less than 0.1 pH in 10 seconds.

Adjust the meter to pH 7.0 with the shorting cap in place. Replace the shorting cap with the electrode. If it has a silver chloride reference, the meter reading should be between pH 6.2 and 7.2. If it has a calomel reference the meter reading should be between pH 6.8 and 7.5.

If it is suspected that the instrument calibration is not correct, use the following procedure to calibrate the pH scale. The basic adjustment will be positioning the temperature compensator knob on its shaft. The voltage output of any pH electrode is directly proportional to the absolute temperature. At a higher sample temperature, the voltage change per solution pH change is higher and the temperature compensator will reduce this voltage change on the meter. A theoretically perfect electrode will produce 0.05916 volts change for each 1,000 pH change at 25°C. Calibration of a pH meter involves injecting known voltage into the instrument BNC electrode connector and adjustment of the temperature compensator to produce the correct meter reading. Make certain that the source of calibration voltage has adequate accuracy because some of the commonly used pH calibration boxes have considerably less accuracy than the pH meter being calibrated. The procedure is to turn on the power, inject 0.00 volts and adjust the meter to pH 7.00 by means of the calibration knob. Inject +0.414 volts and make the meter read 0.00 pH by turning the temperature knob. Repeat, then finally loosen the set screw for the temperature knob, set to 25°C and tighten the set screw.

ELECTRODES

Of all the parts of this instrument, the electrodes will require the most service. The two most critical service details are the cleanliness of the pH sensitive glass bulb and the cleanliness of the reference electrode junction. To clean, use a wet paper towel and wipe the glass bulb or junction several times. Detergent may be used to clean electrodes severely contaminated with oil or grease. During this process, the electrode must be held vertical to ensure filling solution flow out of the junction.

The refillable electrodes have a 3 millimeter hole in the side about 15 millimeters below the plastic cap. The solution level should be maintained within 10 millimeters of this hole. Except for the calomel electrode, only 4 molar potassium chloride saturated with silver chloride should be used to fill this reservoir. The calomel electrode requires saturated potassium chloride solution.

The procedure for refilling a reference electrode is to first open the vent hole. With the electrode held at an angle, touch the tip of the filling solution bottle against the vent hole and squeeze the bottle but allow for displaced air at vent. If sample is allowed to enter the vent hole of the electrode, it may become permanently damaged. Evidence of this would be that an electrode which has operated correctly would fail to come to the buffer pH on the 0-14 scale even though the standardization knob were at one end of its travel.

If sample is allowed to enter the vent hole of the electrode, the filling solution should be removed and the interior flushed with filling solution. The solution may be drawn out by capillary action using a paper towel. Hold the electrode horizontal with the vent hole on the bottom. Roll the edge of a paper towel to a point and insert the point in the vent hole. After rinsing the electrode refill it with the correct type of filling solution.

Sometimes potassium chloride crystals will accumulate inside the reference electrode junction and fill the bottom of the electrode. This is due to evaporation during prolonged storage. The crystals may interfere with filling solution flow and cause pH signal drift. To clean out the crystals, first remove the filling solution by wicking it out with a paper towel as described above. Refill the electrode with distilled water, completely eliminating bubbles. Place the electrode on its side with the vent up. Gravity will circulate the water past the salt deposit where it will become heavier with dissolved salt. In about an hour all of the salt will be dissolved. Wick out the water and replace with the correct filling solution.

Samples containing materials which react with silver may produce an error on the signal from the silver-silver chloride reference electrode. Evidence of this would be a slowly drifting pH reading when the electrode is in sample, but a steady reading when the electrode is in buffer. Examples of interfering materials are proteins and some heavy metal plating solutions. A glass/calomel electrode is recommended for these applications.

BATTERY

Periodically test the battery by turning the switch to BATT and the meter should read above pH 11.6. If the reading is below 11.6, replace all cells at the same time with extra service type AA batteries. This type should gave steel case to prevent leakage from dead batteries into instrument electronics. Alkaline batteries will provide a similar life at the low drain of this instrument.

Recommended Replacement Batteries

Eveready	1015 zinc carbon
Burgess	930
Eveready	E91 alkaline
Burgess	AL9

The rechargeable battery option consists of nickel cadmium AA cells and a connector in the bottom of the instrument. To recharge the battery, plug the charger into the bottom side connector and charge overnight. New cells should provide approximately 300 hours of service before requiring recharge. After a large number of recharge cycles, the service life will decrease to a point at which it will be too short for the application. Replace the rechargeable cells with Eveready C450.