SCHOTT Instruments with information on: Laboratory pH meters and electrodes in quality systems

This paper contains recommendations for companies that have established a quality system in accordance with ISO 9000 ff. standards.

The following text includes the following definitions:

- ☞ A "national standard" or a „reference standard“ are devices, e.g., measuring instruments, which are available at governmental or governmentally recognised institutions.
- ☞ A "working standard" is, e.g., a measuring instrument that is used routinely to calibrate or check measuring instruments.
- ☞ A "test equipment" is, e.g., a measuring instrument which is used frequently and which is checked at regular intervals using the working standard.

In each quality system, regular calibration of the test equipment is absolutely required and defined in the quality manual. The intervals and required accuracy (the uncertainty of measurement) can be defined by each company according to the demands specified by the company for the measurements. The ISO 10 012 standard, Part 1, can be used as a guideline.

The laboratory pH meters and the corresponding electrodes are also checked on a regular basis at defined intervals in accordance with these regulations.

The working standards used for these checks must also be calibrated at regular intervals using national reference standards. A reference standard is usually only available once in each department or company. All other test equipment is checked at the specified intervals using this reference standard.

Proper calibration of working standards while taking into account national standards is defined in different words in the relevant literature: *"The working standard (or the test equipment) is connected to a nationally recognised standard" or "... can be traced back to a national standard" or "refers, on the basis of a well-known, valid relationship, to a national standard."*

1. Checking the electrical characteristics of laboratory pH meters

1.1 pH and mV range: Checks performed using a voltage source with mV range as a reference standard: The pH meter is connected by electric means to the voltage source. The supplied voltages are read off in the mV range and evaluated while taking into account the permissible uncertainties of measurement defined in the quality manual. An electrical inspection of the pH range is advisable even in case of positive results in the mV range in order to check the perfect operation of the operating elements for proper slope, temperature and zero point adjustments. For the inspection of the pH range, the pH meter is adjusted, in accordance with the operating instructions, to 100% of slope, a temperature of 25°C and a zero point of pH = 7.0, with the zero point generally corresponding to an input voltage of 0 mV. A supplied voltage of +200 mV for instance then results in a reading of pH = 3.6 ± 0.1.

1.2 Temperature measuring range: Checks performed using calibrated electric resistors on the basis of IEC 751 standard: Calibrated fixed resistors can be used as well. The values of these resistors are then converted into temperature values in accordance with IEC 751 standard (e.g. Pt 100). In the case of the usual temperature simulators commercially available for this purpose, the temperature is directly adjusted and the reading compared with the setpoint values.

1.3 Dead-stop range with voltage output: Checks performed using a voltage meter. The voltage applied to the sockets is measured using a mV meter. Normally, this range is not subject to the usual calibration requirement.

2. Checking the pH electrode (using the example of a combination electrode)

Slope and electrode zero point: Required equipment includes a pH meter checked in accordance with Item 1, a thermostat and two temperature-stabilised buffer solutions.
For proper preparation of the test, the electrode is soaked as described in the operating instructions. Buffer solutions in accordance with DIN 19 266 are used for the test.
Buffer solutions and the electrode are thermostated at a temperature of 25 °C ± 1 K. The pH meter is switched over to the mV range. If buffer solutions with pH = 6.87 and pH = 4.01 in accordance with DIN 19 266 are used, the resulting readings for an correct functioning electrode will range from -37 ... +21 mV (pH = 6.87) and from +143 ... +207 mV (pH = 4.01). The voltage difference between the two readings, however, must amount to 165 ... 170 mV. The measured response time should not exceed 1 min. The response time is over when the value changes less than 1 mV in 10 sec.

3. Calibration of a pH measuring unit, consisting of a pH meter and an electrode

The individual inspections of the pH meter and electrode basically only provide information on proper operation of the pH meter and the electrode as individual equipment units but they do not provide any information on the correctness of the pH measurement to be performed. Prior to the pH measurements, the complete measuring system consisting of the pH meter including the

connected electrode must be calibrated using buffer solutions.
The result of this calibration is that the pH meter is adjusted in its electric characteristics to the characteristic parameters of the individual electrode. The electrode and pH meter must then be used in this combination for all subsequent measurements. Replacement of electrodes always requires that the calibration be repeated with buffer solutions. Calibration instructions can be looked up in the instructions for use specified for the pH meter and for the electrodes. The effect of the temperature must be taken into account in any case.

4. Recommendations for pH measuring systems in quality systems in accordance with ISO 9000 ff.

- The user must define the required accuracy (the permissible uncertainty of measurement) in his documents.
- These specifications then result in the requirements for the regular calibrations for the testing equipment, e.g., pH meters and electrodes.
- The regular calibrations are described in company-specific regulations.
  These regulations also define the type of the calibration methods, the permissible uncertainties of measurement, the intervals for the repetitions of the calibrations and the type of connection to national standards. Further information is provided, e.g., in ISO 9001, 4.11 "Test equipment".
- The required recording of results is defined on a company-specific basis. The method for correct recording of results can be based on the standards DIN 55 350, Part 18, or EN 45 001.
- Independent of the regular inspections, the user must make sure that the equipment units are always functioning perfectly when they are being used. Accordingly, for especially important measurements, it may be necessary to specify very short intervals of time for the inspections. In extreme cases, calibration using a reference standard may be required prior to each measurement.

5. A non-binding example for the definition of the requirements for a pH measurement and the measuring apparatus in the quality manual, could for instance be (see also DIN 19 268):

- The uncertainty of measurement for the pH measurement in a solution, Δ pH = ± 0.1 is permitted.
- Therefore a measuring uncertainty of Δ pH = 0.02 is deduced for the pH meter.
- This results in a demanded temperature accuracy with a maximum deviation of 1 K from the specified temperature for buffer solutions and measuring solutions.
- As an interval of time for the inspections of the electrical characteristics of the pH meter according to Item 1, a period of 3 months is specified.
- As an interval of time for the inspection of the electrodes, a period of 1 week is specified.
- The calibration of the pH meter and electrode in accordance with the manufacturer's instruction manual is carried out on a daily basis as a two-point calibration with buffer solutions in accordance with DIN 19 266.
- For the completed pH measurements, it could, for instance, be specified that they must be subjected to a plausibility check by an independent expert.

References to standards and literature

1. ISO 9000 to 9004
2. DIN 19 260 to 19 268
3. ISO 10 012, Part 1
4. DIN 55 350, Part 18
5. EN 45 001
6. DIN 38 404, Part 5
7. IEC 751
8. Kortüm: Lehrbuch der Elektrochemie, Weinheim
9. Brdicka: Grundlagen der physikalischen Chemie, Berlin
10. Roger G. Bates: Electrometric pH Determinations, New York, London
11. Schwabe: Fortschritte der pH-Meßtechnik, Berlin
12. Milazzo: Elektrochemie, Basel, Boston, Stuttgart

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