

INTERNATIONAL STANDARD

ISO
976

Third edition
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Rubber and plastics — Polymer dispersions and rubber latices — Determination of pH

*Caoutchouc et plastiques — Dispersions de polymères et latex de
caoutchouc — Détermination du pH*



Reference number
ISO 976:1996(E)

Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 976 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 3, *Raw materials (including latex) for use in the rubber industry*, in close collaboration with ISO/TC 61, *Plastics*, and ISO/TC 35, *Paints and varnishes*.

This third edition cancels and replaces the second edition (ISO 976:1986), as well as the second edition of ISO 1148 (ISO 1148:1980).

Annex A of this International Standard is for information only.

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Rubber and plastics — Polymer dispersions and rubber latices — Determination of pH

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

1 Scope

This International Standard specifies a method for the determination of the pH of polymer dispersions and rubber latices (natural and synthetic) by means of a pH-meter equipped with a combined glass and silver reference electrode.

The method is also suitable for prevulcanized latex and compounds containing polymer dispersions or rubber latices, including adhesives.

NOTE 1 The accuracy of the method decreases at pH values above 11.

Users should note that this edition of ISO 976 not only represents a revision of the previous edition, but also supersedes ISO 1148:1980, *Plastics — Aqueous dispersions of polymers and copolymers — Determination of pH*. This edition represents a harmonized version of the two standards.

One of the major changes in this new edition of ISO 976 is the use of a combined electrode rather than the separate electrodes used in the previous edition, the combined electrode being considered superior to the separate electrodes since the latter are prone to latex deposits blocking the electrolyte junction, thus adversely affecting repeatability. Although older-type twin electrodes are capable of giving accurate results, they should be progressively replaced because of this problem of cleaning and repeatability.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of

this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 123:1985, *Rubber latex — Sampling*.

ISO 842:—¹⁾, *Raw materials for paints and varnishes — Sampling*.

ISO 3696:1987, *Water for laboratory use — Specifications and methods of test*.

3 Reagents

Use commercially available analytical-grade buffer-solutions of known pH or, in the absence of commercial buffer solutions, prepare the solutions required (3.1, 3.2 and 3.3) using only reagents of recognized analytical grade and carbon-dioxide-free distilled water or water of equivalent purity (grade 3 as defined in ISO 3696).

3.1 Buffer solution of nominal pH 7.

Dissolve 3,40 g of potassium dihydrogen phosphate (KH_2PO_4) and 3,55 g of disodium hydrogen phosphate (Na_2HPO_4) in water and make up to 1 000 cm³ in a volumetric flask.

The pH of this solution is 6,87 at 23 °C.

Store the solution in a glass or polyethylene vessel that is resistant to chemicals.

1) To be published. (Revision of ISO 842:1984)

3.2 Buffer solution of pH 4.

Dissolve 10,21 g of potassium hydrogen phthalate ($\text{KOOCC}_6\text{H}_4\text{COOH}$) in water and make up to 1 000 cm³ in a volumetric flask.

The pH of this solution is 4,00 at 23 °C.

Store the solution in a glass or polyethylene vessel that is resistant to chemicals.

3.3 Buffer solution of nominal pH 9.

Dissolve 3,814 g of sodium tetraborate decahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) in water and make up to 1 000 cm³ in a volumetric flask.

The pH of this solution, when freshly prepared, is 9,20 at 23 °C.

Store the solution in a glass or polyethylene vessel that is resistant to chemicals and fitted with a soda-lime carbon dioxide trap. Replace the solution after 1 month.

NOTE 2 Alkaline buffer solutions are unstable; they absorb carbon dioxide from the atmosphere. When an alkaline buffer has been used for calibration, the accuracy can be verified by means of the buffer solution of pH 4.

3.4 Reference electrolyte: 3 mol/dm³ potassium chloride solution saturated with silver chloride.

4 Apparatus

General laboratory equipment, plus the following:

4.1 pH-meter, with an input impedance of at least $10^{12} \Omega$, a resolution of 0,01 pH-units and equipped for temperature compensation.

4.2 Combined electrode, in which the glass electrode is surrounded concentrically by the silver reference electrode. The reference electrolyte (3.4) is kept in electrical contact with the test sample by a chemically inert diaphragm, e.g. a retractable sleeve made of polytetrafluoroethylene or glass. This is supplied with the electrode by the electrode manufacturer.

A typical combined electrode is shown in figure 1.

The glass electrode used shall be one recommended by the manufacturer as suitable over the pH-range to be encountered (0 to 14 in the case of polychloroprene latices).

NOTES

3 Electrical contact between the electrolyte and the test sample is maintained through a thin film of electrolyte between the sleeve and the electrode.

4 The electrode functions linearly between pH 0 and the appearance of the alkaline error, which, depending on the sodium ion concentration, usually does not appear until the pH is over 11.

5 Combined electrodes of this kind are widely available, but in the event of difficulty obtaining them contact Mettler-Toledo at one of their offices worldwide or at the following address:

Mettler-Toledo et Cie, 30 boulevard de Douaumont, 75017 Paris, France; Phone +33 1 47 37 06 00, Fax +33 1 47 37 46 26.

4.3 Magnetic stirrer and magnetic bar.

4.4 Electrode holder.

5 Sampling

Carry out the sampling of the rubber latex or polymer dispersion in accordance with one of the methods specified in ISO 123 or ISO 842.

6 Procedure

In order to reduce thermal and electrical hysteresis effects, ensure that the temperatures of the test samples, electrode, demineralized or distilled rinsing water and buffer solutions are as close to one another as possible. The temperatures of the test samples and buffer solutions shall not differ by more than 1 °C. The temperature for the determination shall be 23 °C ± 3 °C (27 °C ± 3 °C in tropical countries).

NOTE 6 The pH variation over the range of 20 °C to 30 °C is negligible. In addition, the temperature compensator in the instrument should be set at the actual temperature.

6.1 Maintenance of the electrode

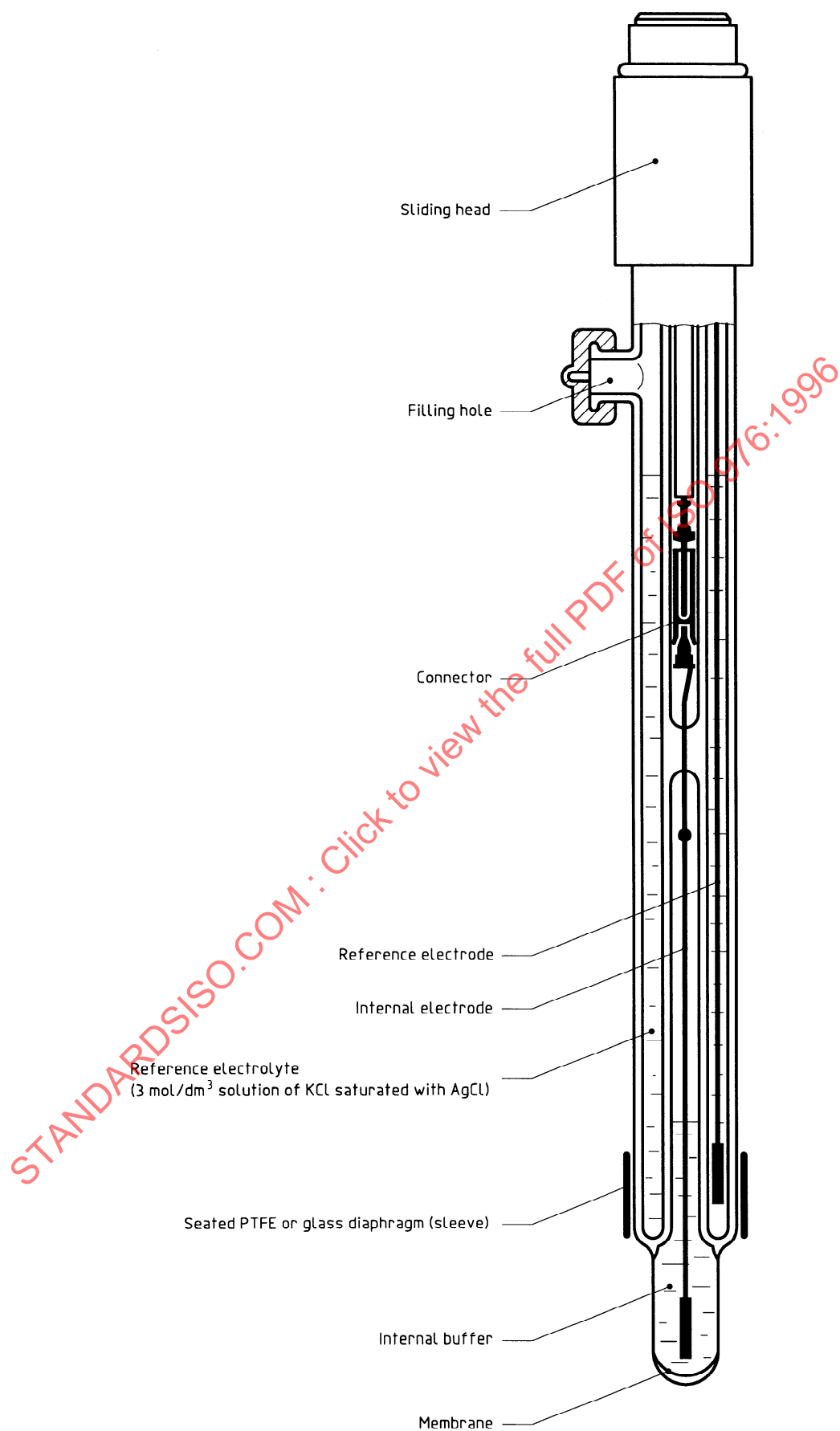
The combined electrode (4.2) shall be maintained following the manufacturer's instructions, paying particular attention to the following points:

6.1.1 Refill the electrode with the reference electrolyte (3.4) through the filling hole, first removing the filling cap if one is fitted.

Slightly withdraw the seated sleeve to eliminate any latex deposits and allow a drop of the electrolyte to appear before reseating the sleeve.

Prior to calibration and measurement, remove the cap on the electrolyte filling hole to allow the reference electrolyte to be at atmospheric pressure.

6.1.2 When it is not in use, keep the electrode with the junction immersed in the electrolyte.

**Figure 1 —Typical combined electrode**

6.2 Calibration of the pH-meter

6.2.1 Switch on the pH-meter (4.1) and allow the electronic circuit to stabilize. Calibrate the pH-meter following the manufacturer's instructions. Where not available, proceed as follows:

6.2.2 Select two commercial buffer solutions (see clause 3), one of nominal pH 7 (i.e. close to the zero point of the electrode) and the other differing from the first by about 3 pH-units and of a higher or lower pH corresponding to the sample to be tested. In the event that commercial buffer solutions are not available, use the appropriate prepared buffer solutions (3.1 and 3.2 or 3.3).

6.2.3 Allow the temperature of the buffer solutions, the test sample and the electrode to equilibrate at the specified temperature (see beginning of this clause). Record the temperature and adjust the temperature correction on the pH-meter to correspond.

6.2.4 Rinse the electrode with distilled or demineralized water (see clause 3) and then with the buffer solution of nominal pH 7, so that the liquid runs down the length of the electrode.

6.2.5 Introduce an adequate volume of the same buffer solution into a suitable clean, dry glass or inert plastic vessel and immerse the electrode in it, taking care that the level of reference electrolyte in the electrode remains about 5 cm higher than the level of the buffer solution (so as to prevent any contamination of the electrode).

Stir gently and allow the reading to stabilize. Adjust the pH-meter, using the zero-point adjustment control, so that the reading corresponds to the pH of the buffer solution. Withdraw the electrode and discard the portion of buffer solution.

6.2.6 Rinse the electrode with water, followed by the chosen buffer solution [pH 4 (3.2) or pH 9 (3.3)] as described in 6.2.4.

NOTE 7 Commercial buffer solution with a pH in the range 9 to 11 may also be used, if available, instead of the prepared solution of pH 9 (3.3).

6.2.7 Immerse the electrode in a quantity of the chosen buffer solution as described in 6.2.5. Allow the reading to stabilize before adjusting the meter to the pH of the buffer solution, using the gradient adjustment control and without touching the zero-point control.

Ensure that the electrode gradient is in the range $-55,6$ to $-61,5$ mV/pH-unit, i.e. between 95 % and 103 % of the theoretical value ($-58,57$ mV/pH-unit at $23\text{ }^{\circ}\text{C}$).

If the electrode is outside this range, carry out the maintenance procedure specified in 6.1.

Discard the portion of buffer solution.

6.3 Measurement of the pH of the test sample

6.3.1 Mix the test sample thoroughly to ensure that it is homogeneous.

6.3.2 Rinse the electrode and measuring vessel, first with distilled or demineralized water, and then with some of the sample to be tested, as described in 6.2.4. Transfer an adequate volume into the vessel (an additional clean, dry vessel may be used) and immerse the electrode in it as described in 6.2.5. Stir gently.

Allow the pH-meter reading to stabilize and record the pH.

Clean the electrode by rinsing with distilled or demineralized water to remove any latex before it dries.

6.3.3 Repeat the operations specified in 6.3.2 with a fresh portion of the test sample:

- If the new reading does not differ from the first by more than 0,1 pH-units, the determination is complete.
- If the two readings differ by more than 0,1 pH-units, make two further determinations, having first carried out all the checks necessary to detect any sources of error.

If a series of consecutive determinations is to be made, recalibrate the pH-meter in accordance with 6.2 at 30-min intervals or more frequently, depending on the change found at each successive check.

7 Expression of results

Calculate the mean of the two readings that agree, and round to the nearest 0,1 of a pH-unit.

Express the results in units of pH at $23\text{ }^{\circ}\text{C}$ if the determination was carried out at this temperature. Otherwise, specify the temperature of the determination.

8 Test report

The test report shall contain the following information:

- a) a reference to this International Standard;

- b) sufficient information to identify the sample;
- c) the pH of the rubber latex or polymer dispersion, expressed to the nearest 0,1 pH-units, and the temperature of the determination;
- d) any particular features noted during the test;
- e) any departure from the procedures specified in this International Standard or the International Standards to which it refers, as well as any operation considered as optional.
- f) the date and place of the test.

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Annex A

(informative)

Precision of the method

Following the procedure accurately, it is possible to attain the following precision:

A.1 Repeatability

0,1 pH-units

A.2 Reproducibility

0,2 pH-units

NOTE 8 The work to generate the precision data was initiated before the publication of ISO/TR 9272:1986, *Rubber and rubber products — Determination of precision for test method standards*. Consequently, the precision data are not expressed in the recommended format.

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