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Paints and varnishes — Determination of pH value —

Part 1: pH electrodes with glass membrane

Peintures et vernis — Détermination de la valeur pH —

Partie 1: Électrodes pH avec membrane de verre

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Foreword

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This document was prepared by Technical Committee ISO/TC 35, *Paints and varnishes*, Subcommittee SC 9, *General test methods for paints and varnishes*.

A list of all parts in the ISO 19396 series can be found on the ISO website.

Introduction

The pH value of aqueous products is of decisive importance for the product properties and durability.

Paints and varnishes — Determination of pH value —

Part 1:
pH electrodes with glass membrane

1 Scope

This document specifies a method for laboratory measurement of the pH value of polymer dispersions and coating materials using pH electrodes with a glass membrane. ISO 19396-2 specifies a method for measuring the pH value using pH electrodes with ion-sensitive field-effect transistor (ISFET) technology.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 1513, *Paints and varnishes — Examination and preparation of test samples*

ISO 4618, *Paints and varnishes — Terms and definitions*

ISO 15528, *Paints, varnishes and raw materials for paints and varnishes — Sampling*

ISO 80000-9:2009, *Quantities and units — Part 9: Physical chemistry and molecular physics*

3 Terms and definitions

For the purpose of this document, the terms and definitions given in ISO 4618 and ISO 80000-9 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— IEC Electropedia: available at http://www.electropedia.org/

— ISO Online browsing platform: available at http://www.iso.org/obp

3.1
pH
measure for the acidic or basic reaction of an aqueous solution or polymer dispersion

Note 1 to entry: Notation of pH: the p and the H are vertically on one line. The same is valid for pOH.

Note 2 to entry: The acidic reaction is determined by the activity of the existing "hydrogen ions". The basic reaction is determined by the activity of the existing hydroxide ions. The direct relationship between the activities of the "hydrogen ions" and the hydroxide ions is described by the ionic product of the water.

3.2
pH value
decadal logarithm of the hydrogen ion activity multiplied with (–1)

$$\mathrm{pH} = \mathrm{p}a_{\mathrm{H}^+} = -\lg\left(\frac{a_{\mathrm{H}^+}}{m^0}\right) = -\lg\left(\frac{m_{\mathrm{H}^+} \cdot \gamma_{m,\mathrm{H}^+}}{m^0}\right)$$

with $a_{H^+} = m_{H^+} \cdot \gamma_{m,H^+}$

where

a_{H^+} is the activity of the hydrogen ion, in mol/kg;

m^0 is the standard molality (1 mol/kg);

γ_{m,H^+} is the activity coefficient of the hydrogen ion;

m_{H^+} is the molality of the hydrogen ion, in mol/kg.

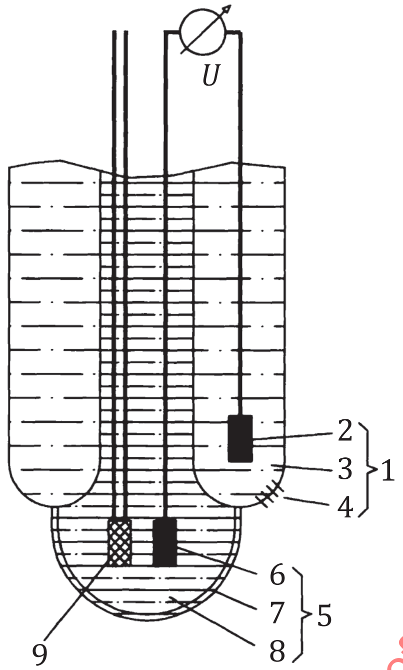
Note 1 to entry: The pH value is not measurable as a measure of a single ion activity. Therefore, pH (PS) values of solutions of primary reference material (PS, en: Primary Standard) are determined, which are approximate to it and can be attributed to it. This is based on a worldwide agreement; see ISO 80000-9:2009, Annex C.

3.3
potentiometric measuring chain
combination of electrochemical half cells

3.4
pH (combination) electrode
pH (single-rod) measuring chain
potentiometric measuring chain (3.3) providing a voltage which depends on the *pH value* (3.2) of the measuring solution

Note 1 to entry: One of the two electrochemical half cells is the pH measuring electrode, the second is a *reference electrode* (3.5) (see Figure 1). Both electrodes can be combined as a single-rod measuring chain in one unit.

Note 2 to entry: An integrated temperature sensor is recommended (see Figure 1).



Key

1	reference electrode, consisting of 2, 3 and 4	6	reference element
2	reference element	7	glass membrane
3	reference electrolyte	8	internal buffer
4	diaphragm	9	temperature sensor
5	pH measuring electrode, consisting of 6, 7 and 8	*U*	pH proportional voltage

Figure 1 — Design of a pH electrode with glass membrane and temperature sensor (schematic illustration)

Note 3 to entry: This document refers to pH electrodes with glass membrane. The electrode shaft should be made of material resistant to chemicals and solvents.

3.5
reference electrode
electrode providing a constant potential which is independent from the *pH value* (3.2) of the measuring medium

Note 1 to entry: At present, the most commonly used type is the silver/silver chloride reference electrode, whose potential is stabilized by a constant concentration of potassium chloride (KCl) in the *reference electrolyte* (3.7).

3.6
reference element
galvanic cell which dips into the *reference electrolyte* (3.7) and transmits the reference potential to the pH meter

Note 1 to entry: The reference elements of the pH measuring electrode and of the reference electrode should be aligned so that identical temperature characteristics are given.

3.7
reference electrolyte
aqueous salt solution (generally potassium chloride solution), whose chloride ion activity determines the potential of the *reference electrode* (3.5)

Note 1 to entry: At the *diaphragm* (3.8), the reference electrolyte has contact with the measuring solution. Potassium chloride solution is used as reference electrolyte, because K^+ ions and Cl^- ions have almost the same ion mobility and, therefore, only slight diffusion potentials result.

Note 2 to entry: The reference electrolyte should flow out of the diaphragm in order to ensure a constant reference potential. Therefore, it shall be refilled occasionally. For *reference electrodes* (3.5) or *pH electrodes* (3.4) with thickened/gel or solidified electrolyte, refilling of the electrolyte can be omitted. Such reference electrodes or pH electrodes are called low-maintenance.

3.8
diaphragm
permeable material in the sides of the casing of *reference electrodes* (3.5), which enables the electrolytic contact between *reference electrolytes* (3.7) and measuring solution and simultaneously impedes the exchange of electrolyte

Note 1 to entry: For types of diaphragms, see 5.3.

3.9
measuring electrode with glass membrane
electrode providing a potential which is a function of the *pH value* (3.2)

3.10
pH glass membrane
membrane made of special glass, on whose interface to the solution an electrical potential (electrode function) results, which is proportional to the *pH* (3.1) of the solution

3.11
temperature compensation
compensation of the temperature-dependent measuring signal only of the *buffer solutions* (3.15) with known temperature dependency

Note 1 to entry: By this, the temperature dependency of the *pH value* (3.2) of the measuring medium cannot be compensated. Therefore, the temperature is always recorded together with the pH value.

3.12
theoretical slope
k
change of the voltage of the *pH electrode* (3.4) with temperature

$$k = -\frac{R \cdot T}{F} \cdot \ln 10 = -2{,}303 \cdot \frac{R \cdot T}{F}$$

where

- T is the thermodynamic temperature, in Kelvin (measuring temperature, in °C + 273,15 °C);
- R is the gas constant 8,314 J mol^{-1} K^{-1};
- F is the Faraday constant 96 485 C mol^{-1}.

Note 1 to entry: At 23 °C, k = −58,57 mV.

3.13
practical slope
k'
slope of a *pH electrode* (3.4), which is obtained by measuring the pH proportional voltages of the pH electrode in at least two reference *buffer solutions* (3.15)

$$k' = \frac{\Delta U}{\Delta \mathrm{pH}}$$

Note 1 to entry: The slope obtained during calibration is a characteristic for the quality of the pH electrode.

3.14
zero point
pH value (3.2), pH_0, of a *pH electrode* (3.4), for which the pH proportional voltage of the pH electrode is $U = 0$ mV at a given temperature

Note 1 to entry: The zero point can also be indicated in terms of a voltage (offset voltage).

Note 2 to entry: The zero point obtained during calibration is a characteristic for the quality of the pH electrode.

3.15
buffer solution
solution with a *pH value* (3.2) of known measurement uncertainty

Note 1 to entry: The buffer solution is used for calibration and adjustment of pH meters. Buffer solutions have a pH value that is largely non-sensitive to dilution and acid or alkali addition.

3.16
stability of measured value
change of the measurement signal over time, dU/dt, under unchanged measurement conditions

Note 1 to entry: The stability of measured value is specified in accordance with the reproducibility requirement of the measurement.

4 Principle

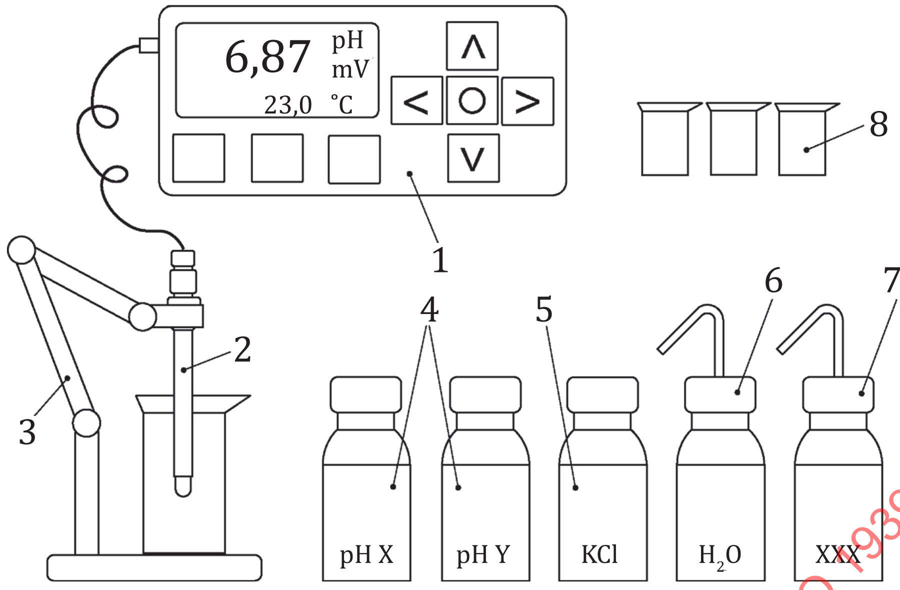
This document comprises the description of suitable pH electrodes and their calibration and cleaning, as well as the procedure of pH measurement. The specified methods and measuring conditions are based on the results of several interlaboratory tests (see also Annex B).

5 Apparatus and materials

Ordinary laboratory and glass apparatus, together with the following:

5.1 pH measuring apparatus.

A pH measuring apparatus (see Figure 2) for pH measurement of polymer dispersions and coating materials consists of a pH meter, a pH electrode, at least two buffer solutions, containers for the buffer solutions and the material to be measured. For cleaning the electrode, a spray bottle with deionized water or a suitable cleaning solution is recommended. In addition, it can be helpful to use a stand, a stirring tool, thermostats, as well as data recording and analysis systems.



Key

1 pH meter
2 pH electrode with temperature sensor
3 stand
4 buffer solutions
5 storage solution (e.g. KCl solution)
6 deionized water
7 cleaning solution (depending on the product)
8 measuring containers

Figure 2 — Example of a pH measuring apparatus

5.2 pH meter.

The pH meter shall at least have the following functions:

— pH value, with reading accuracy 0,01;

— pH proportional voltage of the pH electrode, with accuracy at least 1 mV;

— adjustment of the offset and indication of zero point or offset;

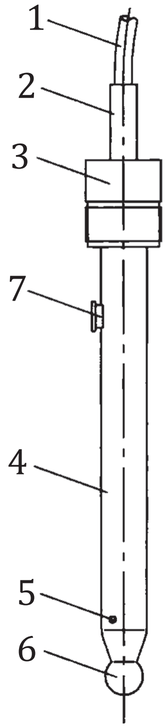
— adjustment of the practical slope;

— indication of the measuring temperature;

— temperature compensation: manually or automatically with connected temperature sensor (external or integrated in the pH electrode).

5.3 pH electrode.

In regard to the pH electrode, the two electrochemical half cells pH measuring electrode with glass membrane and reference electrode are combined in one unit (see Figure 3). An integrated temperature sensor is recommended (see Figure 1).



Key

1 connecting cable (alternatively plug head)
2 bend protection
3 electrode head
4 electrode shaft
5 diaphragm
6 glass membrane
7 refill opening (closable e.g. by slide)

Figure 3 — Example of a pH electrode with glass membrane

For measuring the pH value of polymer dispersions and coating materials, the following combined pH electrodes with glass membrane are suitable (see Figure 4).

Type A Solid electrolyte electrode with perforated or annular-gap diaphragm; the type of calotte and spherical glass membrane is illustrated.

Type B Liquid electrolyte electrode, refillable, with annular-gap diaphragm (e.g. glass cutting).

Type C Liquid electrolyte electrode, refillable, with capillary diaphragm (e.g. ceramic, platinum wire, and fibre), attached at the side in the electrode shaft; the type of calotte and spherical glass membrane is illustrated.

Type D Liquid electrolyte electrode, refillable, with protruding ceramic diaphragm, which can be protected by imposing a dialysis membrane. The dialysis membrane is disposed of after measuring. This way the diaphragm does not have contact with the paint. Without the dialysis membrane the electrode behaves like type C.

NOTE 1 Type D is recommended for coating materials with high ionic strength, such as electrodeposition paints.

Type A Type B Type C Type D

Figure 4 — pH electrodes

NOTE 2 Recommended pH electrodes for different groups of coating materials are based on the results of the interlaboratory tests; see Annex A.

5.4 Buffer solutions.

Buffer solutions with specifications on precision, durability, and temperature dependency.

NOTE Buffer solutions may change during storage in closed and, especially, in open containers.

5.5 Storage solution for the pH electrodes.

pH electrodes shall be stored in a medium which inhibits the leaching of the reference electrode system, e.g. KCl solution, c = 3 mol/l.

NOTE An inappropriate storage medium is deionized water (zero offset caused by leaching of the reference electrode).

6 Sampling

Take a representative sample of the product to be tested as described in ISO 15528.

Examine the samples of coating materials in accordance with ISO 1513 and prepare for further testing.

Sampling, transport of samples, and sample preparation have influence on the pH value.

7 Procedure

7.1 Test conditions

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 ± 2) °C [(27 ± 2) °C in tropical countries].

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.

The sample to be measured shall be homogenous.

7.2 Calibration

Carry out at least a two-point calibration. The pH values of the buffer solutions shall cover the measuring range of the samples and the difference between the values of the two buffer solutions shall be ΔpH ≥ 2.

NOTE The pH value of basic buffer solutions changes relatively fast, by absorbing CO_2 from the air and thereby the measurement uncertainty increases.

Adjust the pH meter with the data (slope and zero point or offset) obtained during calibration.

Discard used buffer solutions after use.

7.3 Number of determinations

Carry out the determination in duplicate.

If the second measurement does not deviate by more than pH = 0,2 from the first measurement, the determination is completed.

If the two measurements deviate by more than pH = 0,2 from each other, two new measurements shall be carried out.

7.4 Measuring the pH value

Before using the pH electrode, rinse it with water (preferably deionized water).

Put the sample in a suitable clean and dry container and immerse the pH electrode. The diaphragm shall be covered completely. When using a pH electrode with liquid electrolyte, take into account that the level of the electrolyte inside the pH electrode is higher than the level of the sample.

For pH electrodes with liquid electrolyte, the refill opening shall be open during calibration and measuring.

Moderately move the pH electrode in the sample to be measured prior to measuring, so it is uniformly washed round with the sample material.

Stop moving the pH electrode, wait for 2 min and document the result.

Clean the pH electrode and carry out the second measurement subsequently.

After completing the measurements, clean the pH electrode and store it in the storage solution (5.5) in accordance with the manufacturer's specifications.

8 Evaluation

Express the mean value from the duplicates, rounded to one decimal place, as result.

9 Precision

9.1 General

For details on the determination of precision, see Annex B.

9.2 Repeatability limit, *r*

The repeatability limit, *r*, is the value below which the absolute difference between two test results (each the mean of three valid determinations) can be expected to lie when this method is used under repeatability conditions. In this case, the test results are obtained on identical material by one operator in one laboratory within a short interval of time using the standardized test method. The repeatability limit, *r*, in accordance with this document, calculated with a probability of 95 %, is given in Table 1.

Table 1 — Repeatability limit (*r*)

Samples	*r*
For all samples	0,3
Without electro-deposition coating	0,2

9.3 Reproducibility limit, *R*

The reproducibility limit, *R*, is the value below which the absolute difference between two single test results (each the mean of three valid determinations) can be expected to lie when this method is used under reproducibility conditions. In this case, the test results are obtained on identical material by different operators in different laboratories using the standardized test method. The reproducibility limit, *R*, in accordance with this document, calculated with a probability of 95 %, is given in Table 2.

Table 2 — Reproducibility limit (*R*)

Samples	*R*
For all samples	0,4
Without electro-deposition coating	0,3

10 Test report

The test report shall contain at least the following information:

a) all details necessary to identify the product under test (manufacturer, product designation, batch number, etc.);

b) a reference to this document (i.e. ISO 19396-1);

c) which type of pH electrode has been used for measuring;

d) the test temperature;

e) the test result, as specified in Clause 8;

f) any deviation from the test procedure specified;

g) any unusual features (anomalies) observed during the test;

h) the date of the test.

Annex A
(informative)

Recommended pH electrodes for different groups of coating materials, based on the results of interlaboratory tests

A.1 General

Table A.1 gives an overview of the coating materials and the recommendations, which types of pH electrodes have proven to be suitable for which group.

Table A.1 — Coating materials and recommendations for types of pH electrodes

Group of coating material	NV[c] %	Rheological flow	Suitability of the types of pH electrodes[a]				Remarks
			Type A	Type B	Type C	Type D	
Primer	48,2	Yield point, slight structural viscosity, rheopex, medium viscosity	1	2	1	2	Measuring results show broad distribution
Water-soluble base coat paint with inter-ference effect pigments	19,2	Small yield point, structural viscosity, low viscosity	1	2	1	2	Uncritical
Water-soluble base coat paint with aluminium effect pigments	18,5	Small yield point, structural viscosity, low viscosity	1	2	1	2	Uncritical
Wood stain	11,9	Small yield point, structural viscosity, low viscosity	1	2	1	2	Uncritical

