INTERNATIONAL STANDARD

ISO 19396-1

First edition
2017-08

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

Reference number
ISO 19396-1:2017(E)

Contents

Page

Foreword iv

Introduction v

1 Scope 1

2 Normative references 1

3 Terms and definitions 1

4 Principle 5

5 Apparatus and materials 5

6 Sampling 8

7 Procedure 8

7.1 Test conditions 8

7.2 Calibration 8

7.3 Number of determinations 9

7.4 Measuring the pH value 9

8 Evaluation 9

9 Precision 9

9.1 General 9

9.2 Repeatability limit, *r* 9

9.3 Reproducibility limit, *R* 10

10 Test report 10

Annex A (informative) **Recommended pH electrodes for different groups of coating materials, based on the results of interlaboratory tests** 11

Annex B (informative) **Determination of precision** 13

Bibliography 15

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

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.

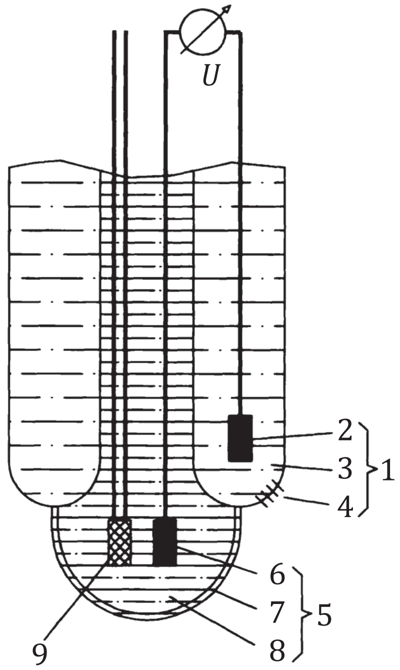
Note 1 to entry: The pH value is not measurable as a measure of a single ion activity. Therefore, pH (PS) values of solutions of primary reference material (PS, en: Primary Standard) are determined, which are approximate to it and can be attributed to it. This is based on a worldwide agreement; see ISO 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
2 reference element
3 reference electrolyte
4 diaphragm
5 pH measuring electrode, consisting of 6, 7 and 8
6 reference element
7 glass membrane
8 internal buffer
9 temperature sensor
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, d*U*/d*t*, 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.