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Paints and varnishes — Determination of pH value —

Part 2:
pH electrodes with ISFET technology

Peintures et vernis — Détermination de la valeur pH —

Partie 2: Électrodes pH avec technique ISFET

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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).

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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.

INTERNATIONAL STANDARD **ISO 19396-2:2017(E)**

Paints and varnishes — Determination of pH value —

Part 2:
pH electrodes with ISFET technology

1 Scope

This document specifies a method for measuring the pH value of dispersions and coating materials using pH electrodes with ion-sensitive field-effect transistor (ISFET) technology. ISO 19396-1 specifies a method for measuring the pH value using pH electrodes with a glass membrane.

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.

[SOURCE: ISO 19396-1:2017, 3.1]

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

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.

[SOURCE: ISO 19396-1:2017, 3.2]

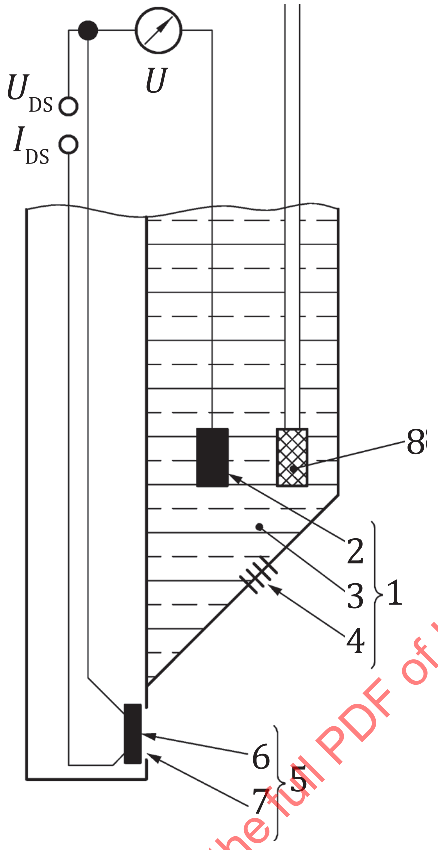
3.3
ISFET electrode

combined pH electrode with ISFET technology

potentiometric cell providing a voltage which depends on the *pH value* (3.2) of the measuring medium

Note 1 to entry: One of the two electrochemical cells is the ISFET; the second is a reference electrode.

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 and 7
6	ISFET (see Figure 4)
7	opening to the measuring medium (gate)
8	temperature sensor
U	pH proportional voltage
U_{DS}	voltage receiver/sender (drain/source)
I_{DS}	current receiver/sender (drain/source)

Figure 1 — Design of an ISFET electrode (schematic diagram)

3.4
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* (3.6).

[SOURCE: ISO 19396-1:2017, 3.5]

3.5
reference element

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

[SOURCE: ISO 19396-1:2017, 3.6, modified — Note 1 to entry has been deleted.]

3.6
reference electrolyte

aqueous salt solution (generally potassium chloride solution), whose chloride ion activity determines the potential of the *reference electrode* (3.4)

Note 1 to entry: At the *diaphragm* (3.7), 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.

[SOURCE: ISO 19396-1:2017, 3.7, modified — Note 2 to entry has been deleted.]

3.7
diaphragm

permeable material in the sides of the casing of *reference electrodes* (3.4), which enables the electrolytic contact between *reference electrolytes* (3.6) and measuring solution and simultaneously impedes the exchange of electrolyte

[SOURCE: ISO 19396-1:2017, 3.8, modified — Note 1 to entry has been deleted.]

3.8
measuring electrode

ion-sensitive field-effect transistor

ISFET

electrode providing a pH proportional signal with a suitable electronic circuit

3.9
temperature compensation

compensation of the temperature-dependent measuring signal only of the *buffer solutions* (3.13) 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.

[SOURCE: ISO 19396-1:2017, 3.11]

3.10
theoretical slope

k

change of the voltage of the pH electrode 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.

[SOURCE: ISO 19396-1:2017, 3.12]

3.11
practical slope

k'

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

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

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

[SOURCE: ISO 19396-1:2017, 3.13]

3.12
zero point

pH value (3.2), pH_0, of a pH electrode, 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 for the *ISFET electrode* (3.3) is set by calibrating the offset voltage.

[SOURCE: ISO 19396-1:2017, 3.14, modified — Note 1 to entry has been replaced, Note 2 to entry has been deleted.]

3.13
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.

[SOURCE: ISO 19396-1:2017, 3.15]

3.17
stability of measured value

change of the measurement signal over time, $\mathrm{d}U/\mathrm{d}t$, under unchanged measurement conditions

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

[SOURCE: ISO 19396-1:2017, 3.16]

4 Principle

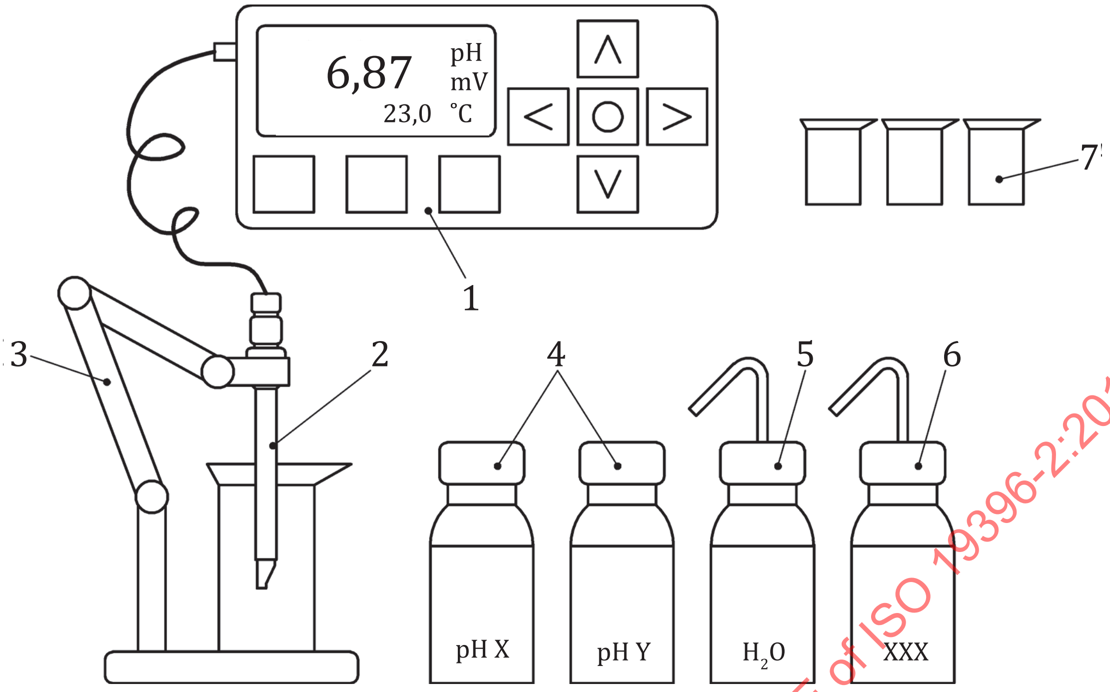
This document comprises the description of the ISFET electrode, its calibration and cleaning, as well as the procedure of pH measurement. The specified method and measuring conditions are based on the results of an interlaboratory test (see also Annex A).

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 suitable for ISFET electrodes, an ISFET electrode, at least two buffer solutions, containers for the buffer solutions and the material to be measured. For cleaning the ISFET electrode, a spray bottle with deionized water or a suitable cleaning solution and a small brush are recommended. In addition, it can be helpful to use a stand, a stirring tool, a thermostat, as well as data recording and analysis systems.



Key

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

Figure 2 — Example of a pH measuring apparatus

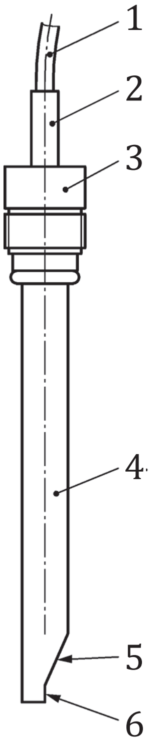
5.2 pH meter.

The pH meter shall at least have the following functions:

- pH value, with reading accuracy 0,01;
- pH proportional voltage of the ISFET 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 ISFET electrode).

5.3 ISFET electrode.

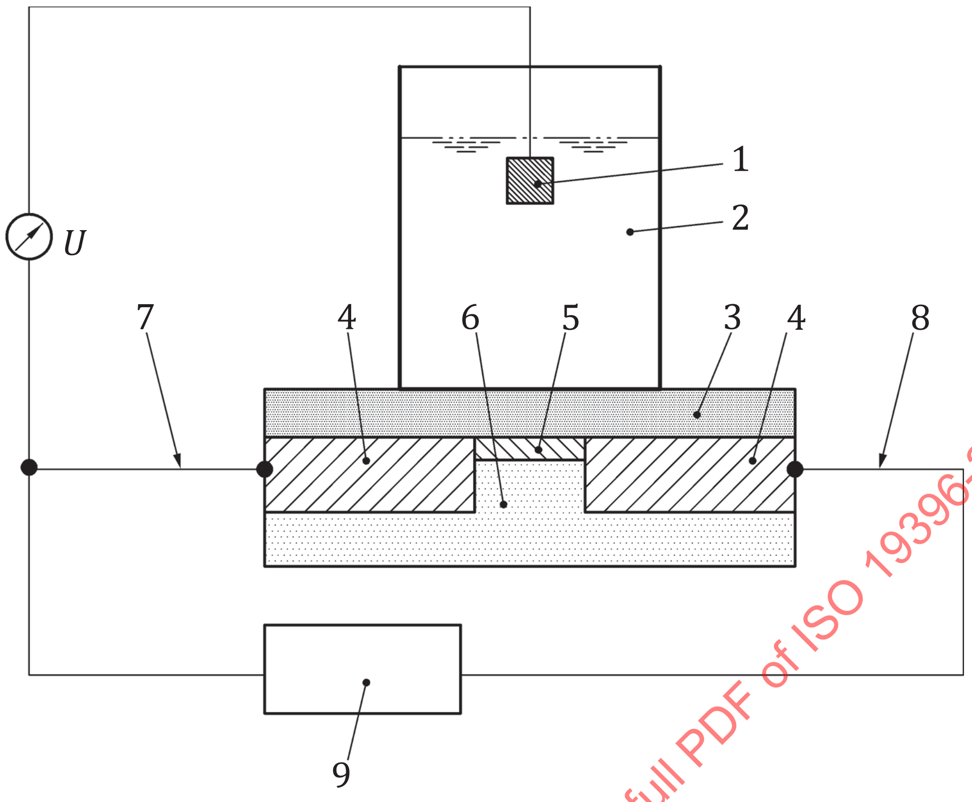
In regard to the pH electrode with ISFET technology, the ISFET and the reference electrode are combined in one unit (see Figure 3). An integrated temperature sensor is recommended.



Key

1	connecting cable	4	electrode shaft
2	bend protection	5	diaphragm
3	electrode head	6	ISFET

Figure 3 — Example of an ISFET electrode



Key

1	reference electrode	6	p-semiconductor
2	measuring medium	7	sender (source S)
3	pH-sensitive oxide film	8	receiver (drain D)
4	n-semiconductor	9	regulating circuit (U_{DS} = const. I_{DS} = const.)
5	contact to the measuring medium (gate)	U	pH proportional voltage

Figure 4 — Functional principle of the ISFET technology

As an example, an ISFET with npn-type doping is illustrated in Figure 4. Instead of a common electric contact at the gate, there is an ion-sensitive film (usually metal oxides, such as Ta_2O_5, Al_2O_3), which is in contact with the measuring medium. The activity of the H^+ ions of the measuring medium provides for a potential on the surface of the ion-sensitive film. Using a regulating circuit, current and voltage at the ISFET are constantly maintained in order to avoid the nonlinear characteristic curve of the ISFET. Between the ISFET and the reference electrode voltage forms which is proportional to the pH voltage U.

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.

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. Refer to the manufacturers' specifications on calibration.

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 of the ISFET electrode (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 ISFET electrode, rinse it with water (preferably deionized water).

Put the sample in a suitable, clean, and dry container and immerse the ISFET electrode. The diaphragm shall be covered completely.

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

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

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

After completing the measurements, clean the ISFET electrode and store it 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 A.

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, is 0,2 with a given probability of 95 %.

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 have been obtained on identical material by operators on succeeding days during shift operation using the standardized test method. The reproducibility limit, *R*, in accordance with this document, is 0,4 with a given probability of 95 %.

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 19396-2);

c) the ISFET electrode used;

d) the test temperature;

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

f) any deviation from the test procedure specified;

g) the date of the test.