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**Determination of pH value —  
Reference buffer solutions for  
the calibration of pH measuring  
equipment**

*Détermination de la valeur pH — Solutions tampons de référence  
pour l'étalonnage des appareils de mesure du pH*

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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](http://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](http://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 of 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 [www.iso.org/iso/foreword.html](http://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*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at [www.iso.org/members.html](http://www.iso.org/members.html).

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# Determination of pH value — Reference buffer solutions for the calibration of pH measuring equipment

## 1 Scope

This document specifies reference buffer solutions for the calibration of pH measuring equipment.

## 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 4793, *Laboratory sintered (fritted) filters — Porosity grading, classification and designation*

ISO 19396-1, *Paints and varnishes — Determination of pH value — Part 1: pH electrodes with glass membrane*

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

## 3 Terms and definitions

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

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

— ISO Online browsing platform: available at <https://www.iso.org/obp>

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

### 3.1

#### pH

measure for the acidic or basic character of an aqueous solution

Note 1 to entry: Notation of pH: the "p" and the "H" are upright on one line.

Note 2 to entry: The acidic character is determined by the activity of the existing "hydrogen ions".

### 3.2

#### pH value

decadal logarithm of the hydrogen ion activity multiplied with (-1)

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

where

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

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

$\gamma_{m,\text{H}^+}$  is the activity coefficient of the hydrogen ion;

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

Note 1 to entry: Molality is understood as moles per kilogram solvent.

Note 2 to entry: The pH value is not measurable as a measure of a single ion activity. Therefore, pH(PR) values of solutions of primary reference material 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.

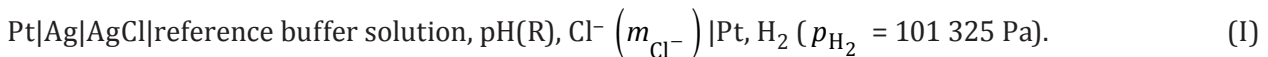
## 4 Basic information

### 4.1 General

Reference buffer solutions are prepared using primary or secondary reference materials. The pH values of the reference buffer solutions are determined using the methods described in 4.2 and 4.3. The pH value of a reference buffer solution and the associated uncertainty of measurement are documented in a calibration certificate as the result of calibration. pH values of primary reference buffer solutions form the basis of pH measurements in practice and are generally determined by national metrology institutes. Secondary reference buffer solutions are commercially available. The reference buffer solutions prepared according to the methods described in Clause 5 serve as a material measure of the pH value.

### 4.2 pH values of primary reference buffer solutions

The pH value based upon the activity of single ions according to the formula in 3.2 cannot be measured. The pH value is assigned to reference buffer solutions outlined in Table 1. This is achieved using an electrochemical method of measurement that is based on the thermodynamic dependence of the potential of the platinum/hydrogen electrode on the hydrogen ion activity. Through the use of cells without transference, diffusion voltages arising from liquid junctions do not appear and therefore do not need to be considered when calculating the voltage of the cell. The cell (I) for this purpose shall consist of a platinum/hydrogen and a silver/silver chloride electrode, immersed in the reference buffer solution to which chloride in a low concentration ( $m_{\text{Cl}^-}$ ) has been added.



The pH value of the reference buffer solution is calculated according to Formula (1):

$$\text{pH} = \lim_{m_{\text{Cl}^-} \rightarrow 0} \left[ \frac{(E - E^0)}{k} + \lg \left( \frac{m_{\text{Cl}^-}}{m^0} \right) \right] + \lg \gamma_{\text{Cl}^-} \quad (1)$$

where

$E$  is the voltage of cell (I);

$E^0$  is the standard potential of the Ag/AgCl electrode;

$k$  is the Nernst slope ( $k = RT(\ln 10) / F$ );