
**Determination of pH value —
Technical buffer solutions for the
calibration of technical measuring
installations**

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

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Foreword

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

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Determination of pH value — Technical buffer solutions for the calibration of technical measuring installations

1 Scope

This document specifies requirements for technical buffer solutions. These buffer solutions are preferably used for the calibration and adjustment of technical pH measuring equipment as well as pH measuring installations in laboratories. Measuring methods are given to determine pH values and buffer capacities of such buffer solutions based on pH reference buffer solutions in accordance with ISO 23496.

NOTE [Annex A](#) gives examples of technical buffer solutions.

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 23496, *Determination of pH value — Part 3: Reference buffer solutions for the calibration of pH measuring equipment*

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

DIN 19268:2007, *pH measurement — pH measurement of aqueous solutions with pH measuring chains with pH glass electrodes and evaluation of measurement uncertainty*¹⁾

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".

[SOURCE: ISO 23496:2019, 3.1]

1) A measuring chain in the sense of this standard is generally represented by a combined electrode.

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_{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: 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.

[SOURCE: ISO 23496:2019, 3.2]

4 pH values and buffer capacities of technical buffer solutions

4.1 General

The reference buffer solutions given in ISO 23496 are the basis for practical pH measurement. The pH values of these reference buffer solutions are traceable to primary standards, the pH values of which have been determined by national metrology institutes by means of measurements using primary methods^[1]. The accuracy and reproducibility have been confirmed by international interlaboratory tests^[2].

The reference buffer solutions in accordance with ISO 23496 are diluted solutions (ionic strength $\leq 0,1$ mol/kg). Consequently, they have a relative low buffer capacity. This complicates the handling in practice, since the pH value can change due to the addition of acid or bases (e.g. CO₂ from the air, carryovers of other solutions). For the calibration of combined pH electrodes in industrial environment, thus, further buffer solutions are required, which have a higher buffer capacity.

The pH values of these technical buffer solutions shall be measured in accordance with DIN 19268, so that the traceability of the pH values to the reference buffer solutions in accordance with ISO 23496 is provided for.

The uncertainty budget illustrated in DIN 19268 shall be considered as a simplified illustration without consideration of influences during application. Temperature and diffusion potentials of the diaphragm are the parameters with the most significant influence^{[3][4]}.

In comparison to reference buffer solutions, technical buffer solutions are solutions which have higher ionic strength and, consequently, a higher buffer capacity. The pH values of technical buffer solutions are measured based on reference buffer solutions in accordance with ISO 23496 and show measurement uncertainties due to this measurement.

pH values of technical buffer solutions with pH <10 at 25 °C shall have an expanded measurement uncertainty of $U \leq 0,03$ ($k = 2$) and pH values of technical buffer solutions with pH ≥ 10 at 25 °C shall

have an expanded measurement uncertainty of $U \leq 0,05$ ($k = 2$). Technical buffer solutions according to this document shall have a buffer capacity of $\beta \geq 0,05 \text{ mol}\cdot\text{l}^{-1}$.

4.2 Measurement of the pH values of technical buffer solutions

The pH values of technical buffer solutions are measured by means of combined electrodes with transference. This is done by using the combined electrode:

Reference electrode || buffer | pH measuring electrode

The pH value of a technical pH buffer solution shall be determined in accordance with DIN 19268. For measuring the pH value of the technical pH buffer solution, the pH measuring equipment shall be adjusted in accordance with DIN 19268:2007, 4.3.4. In case the pH value of the technical buffer solution is out of the pH range of the reference buffer solutions in accordance with ISO 23496, the pH measuring equipment shall be adjusted in accordance with DIN 19268:2007, 4.3.3 or 4.3.5.

The following shall be taken into account:

- the alkali error should be as low as possible for the used glass electrode in the pH range of the measurement in consideration of the measuring temperature. The respective instructions given by the manufacturer of the glass electrodes shall be considered;
- a combined pH electrode with liquid reference electrolytes shall be used for measurement;
- the KCl solution of the reference electrode to be used should have a minimum concentration of $3,0 \text{ mol}\cdot\text{l}^{-1}$, in order to keep the diffusion voltages reproducible;
- the used diaphragm should have a high electrolyte outflow, e.g. a ground-joint diaphragm, a platinum diaphragm or a capillary diaphragm;
- the pH value shall be measured isothermally, i.e. the temperature of the reference buffer solutions and the technical buffer solution to be determined shall match to $\pm 0,5 \text{ K}$;
- a temperature equilibration between solution and combined electrode shall be achieved, especially for saturated KCl solution. This can be realized by sufficiently deep immersion of the combined electrode;
- the liquid level of the KCl solution within the reference electrode shall be at least 5 cm higher than the measuring solution;
- the refill opening of the reference electrode shall be open;
- in case the pH values of a technical buffer solution are to be determined for more than one temperature, the measuring process shall be carried out for any of the temperatures.

4.3 Measurement of the buffer capacity

The buffer capacity is a measure for the change in pH value of the technical buffer solutions when reacting with a strong base or acid and is described by [Formula \(1\)](#).

$$\beta = \frac{1}{V_0} \cdot \frac{\Delta n}{\Delta \text{pH}} \quad (1)$$

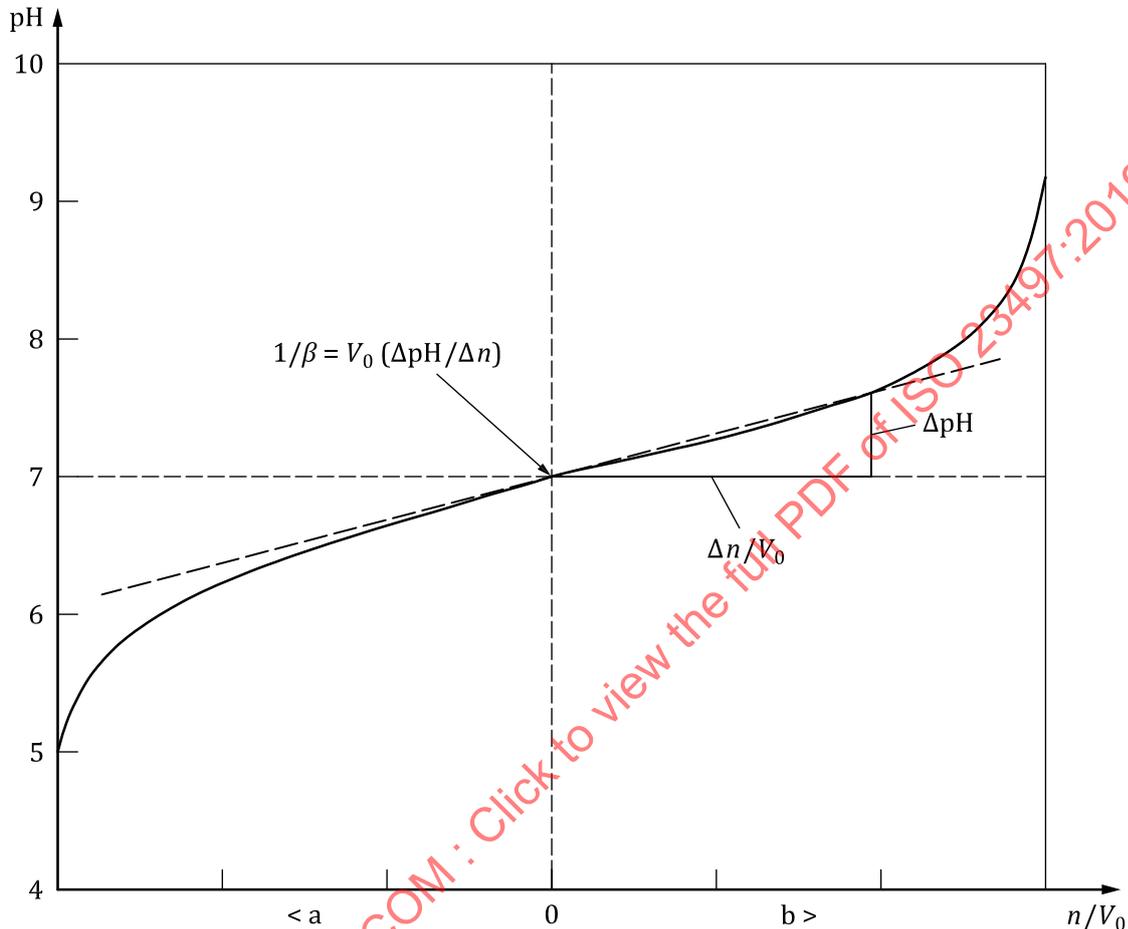
where

V_0 is the volume of the technical buffer solution, in litres;

Δn is the amount of substance of the added acid or base, in moles;

ΔpH is the change of the pH value caused by the addition of the acid or base.

The buffer capacity β is determined by adding a specific amount of substance Δn (e.g. 0,01 mol) of a strong acid (e.g. HCl) or base (e.g. NaOH) as a concentrated solution (e.g. 1,0 mol/l) to a specific volume V_0 of the buffer and measuring the pH value of the buffer prior to as well as after the addition. The observed change of the pH value can be positive or negative, depending on whether the pH value increases or decreases due to the addition. However, the absolute value of β is given. The measurements shall be carried out at $(25 \pm 1)^\circ\text{C}$. See [Figure 1](#).



Key

- a acid
- b base

Figure 1 — Graphical determination of the buffer capacity β

EXAMPLE

- a) Initial solution $V_0 = 100$ ml acetate solution. After measuring the pH value add 5 ml 1 mol/l NaOH (corresponding to 0,005 mol NaOH) and measure the pH value again.
Difference $\Delta\text{pH} = +0,48$.
- b) Initial solution $V_0 = 100$ ml acetate solution. After measuring the pH value add 5 ml 1 mol/l HCl (corresponding to 0,005 mol HCl) and measure the pH value again.
Difference $\Delta\text{pH} = -0,48$.

In accordance with a) and b) the buffer capacity is $\beta = 0,104 \text{ mol}\cdot\text{l}^{-1}$.

The recording of a complete titration curve of the technical buffer solution is recommended (abscissa n/V_0 , positive: addition of alkali; negative: addition of acid; ordinate pH). The sought buffer capacity β of the technical solution equals the reciprocal first derivative in point $(n/V_0 = 0; \text{pH} = \text{pH value of the technical buffer solution})$.

Annex A (informative)

Examples of technical buffer solutions

Tables A.1 to A.3 give the composition, pH value at 25 °C, temperature dependency of the pH value, reproducibility and buffer capacity of several technical buffer solutions described in the literature^[5].

Table A.1 — pH value, buffer capacity β and composition of several technical buffer solutions

Buffer solution	pH (at 25 °C)	Buffer capacity β mol·l ⁻¹	Composition or preparation specifications ^{a,b} (at 25 °C)
0,1 mol·l ⁻¹ HCl	1,09	0,26	0,1 mol·l ⁻¹ HCl
Glycine	3,06	0,11	Fill up 20 g glycine + 10 g NaCl + 50 ml 1 mol·l ⁻¹ HCl to 1 000 ml
Acetate	4,65	0,10	Fill up 100 ml 1 mol·l ⁻¹ NaOH + 200 ml 1 mol·l ⁻¹ acetic acid to 1 000 ml
Citric acid – Phosphate	6,79	0,09	Fill up 55,4 g Na ₂ HPO ₄ · 12 H ₂ O + 4,79 g citric acid monohydrate to 1 000 ml
Boric acid – NaOH	9,23	0,07	1 000 ml 0,2 mol·l ⁻¹ boric acid (H ₃ BO ₃) + 550 ml 0,2 mol·l ⁻¹ NaOH
0,1 mol·l ⁻¹ NaOH	12,75	0,33	0,1 mol·l ⁻¹ NaOH

^a The solutions are prepared at 25 °C, although the volumetric flasks used in accordance with ISO 1042 are calibrated at 20 °C. The errors in the pH values due to this may be ignored because dilution has little effect on the buffer solutions.

^b Fully desalinated water shall be used. For solutions of pH >7 CO₂-free water shall be used.

Table A.2 — pH values of the technical buffer solutions given in Table A.1 as a function of temperature

Temperature °C	0,1 mol·l ⁻¹ HCl	Glycine ^a	Acetate ^b	Citric acid – Phosphate	Boric acid – NaOH	0,1 mol·l ⁻¹ NaOH
0	1,08	—	4,67	6,89	9,48	—
10	1,09	3,10	4,66	6,84	9,37	13,37
20	1,09	3,07	4,65	6,80	9,27	12,96
25	1,09	3,06	4,65	6,79	9,23	12,75
30	1,10	3,05	4,65	6,78	9,18	12,61
40	1,10	3,04	4,66	6,76	9,09	12,29
50	1,11	3,04	4,68	6,76	9,00	11,98
60	1,11	3,04	4,70	6,76	8,92	11,69
70	1,11	3,04	4,72	6,76	8,88	11,43
80	1,12	3,05	4,75	6,78	8,85	11,19
90	1,13	3,07	4,79	6,80	8,82	10,99

^a Values according to Reference [5].

^b Values according to Reference [6].