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**The rH index in aqueous
and aqueous-organic media**

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INTERNATIONAL ELECTROTECHNICAL COMMISSION

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THE rH INDEX IN AQUEOUS AND
AQUEOUS-ORGANIC MEDIA

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IEC 62432, which is a technical report, has been prepared by subcommittee 65D: Analyzing equipment, of IEC technical committee 65: Industrial-process measurement and control.

The text of this technical report is based on the following documents:

Enquiry draft	Report on voting
65D/120/DTR	65D/123/RVC

Full information on the voting for the approval of this technical report can be found in the report on voting indicated in the above table.

This publication has been drafted in accordance with the ISO/IEC Directives, Part 2.

The committee has decided that the contents of this publication will remain unchanged until the maintenance result date indicated on the IEC web site under "http://webstore.iec.ch" in the data related to the specific publication. At this date, the publication will be

- reconfirmed,
- withdrawn,
- replaced by a revised edition, or
- amended.

A bilingual version of this Technical report may be issued at a later date.

INTRODUCTION

The fundamental rationale for the rH index, extended to cover the pure aqueous and the aqueous-organic media, has been recently described critically [1][1], but for the user's convenience, the essentials will be recalled in the present Technical Report together with the application domains, the recommended procedures and operational details.

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[1] Numbers in square brackets refer to the bibliography.

THE rH INDEX IN AQUEOUS AND AQUEOUS-ORGANIC MEDIA

1 Scope

This Technical Report concerns analyzers, sensor units and electronic units used for the determinations of the rH index in aqueous and aqueous organic media.

This Technical Report identifies the terminology, definitions, theory and methodology used for the determination of rH values or redox systems in aqueous solvent or aqueous-organic solvent mixtures.

2 General principles

2.1 Redox couples, redox equilibria, redox potentials, redox systems

An oxidation/reduction couple ("redox" couple) O|R, present in water or in an aqueous-organic solvent mixture involves the concurrence of an oxidant species O (ionic or uncharged) and a reductant species R (ionic or uncharged) of the same chemical element, thereby establishing an oxidation/reduction equilibrium (redox equilibrium) $O + n e = R$, and an electrochemical oxidation/reduction potential (redox potential) $E_{O|R}$ which is transmitted to the meter by an inert metal electrode (usually platinum or gold). This metal participates in the specific charge transfer which is going on throughout the solution and is called upon only to act as a donor or acceptor of electrons. When both the O and R species are at unit activity (standard state) the redox potential $E_{O|R}$ becomes the standard redox potential, symbolized as $E_{O|R}$.

In the environmental, hydrological, biomedical, winery, dairy-farming, and corrosion domains of interest for rH measurements, only seldom is a single O|R couple present alone in the solvent medium. Instead, an undefined number of redox couples O|R, O'|R', O"|R",...O^n|R^n overlap, thus determining a mixed redox potential of very complex (not to say impossible) interpretation: therefore it is better to speak of a "redox system", but this latter term is also legitimately applicable to a single redox couple.

NOTE   Some examples of familiar redox couples with related reaction equilibria and redox potential expressions, are given in Table 1.

Table 1 - Examples of familiar redox couples with related reaction equilibria and redox potential expressions

Redox couple	Redox equilibrium	Redox potential
ferric|ferrous	$Fe^{3+} + \mathbf{e} = Fe^{2+}$	$E_{Fe3+|Fe2+} = E_{Fe3+|Fe2+} + k \log(a_{Fe3+}/a_{Fe2+})$
H^+|H_2 (hydrogen electrode)	$2H^+ + 2\mathbf{e} = H_2$	$E_{H+|H2} = E°_{H+|H2} + k \log a_{H+} - (k/2)\log p_{H2}$
Cl_2|Cl^- (chlorine electrode)	$Cl_2 + 2\mathbf{e} = 2Cl^-$	$E_{Cl2|Cl^-} = E_{Cl2|Cl^-} - k \log a_{Cl^-} + (k/2)\log p_{Cl2}$
O_2|H_2O (oxygen electrode)	$O_2 + 4\mathbf{e} + 4H^+ = 2 H_2O$	$E_{O2|H2O} = E°_{O2|H2O} + k \log a_{H+} + (k/4)\log p_{O2} - (k/2)\log a_{H2O}$
MnO_4^-|Mn^{2+} (permanganate electrode)	$MnO_4^- + 5\mathbf{e} + 8H^+ =$ $Mn^{2+} + 4H_2O$	$E_{MnO4|Mn2+} = E°_{MnO4|Mn2+} + (k/5)\log(a_{MnO4|Mn2+}/a_{Mn2+}) +$ $+ (8k/5)\log a_{H+} - (4k/5)\log a_{H2O}$
Symbols: $\mathbf{e}$ = the electron; k = Nernstian coefficient = $2{,}303 RT/F$; a = activity; p = pressure.		

2.2 The rH value

The notional definition of the rH index [2,3] for a given redox system in a given (aqueous or aqueous-organic) medium is

$$rH = -\log p_{H2} \tag{1}$$

where p_{H2} is that pressure of hydrogen gas that would equalize the potential $E_{H^+|H2}$ of the hydrogen gas electrode to the redox potential $E_{O|R}$ of the system being studied (thus zeroing the pd of the cell resulting from the combination of these two electrodes). **rH is an index of the reducing power of the redox system under consideration.** The Nernstian expression for $E_{H^+|H2}$ is (with $k = 2,303 RT/F$):

$$E_{H^+|H2} = E_{H^+|H2} - k\,pH + (k/2)\,rH \tag{2}$$

where $E_{H^+|H2}$ is the standard electrode potential (which varies with the solvent but it is conventionally put equal to zero at any temperature in pure aqueous medium [4, 5]). If the hydrogen gas electrode works at $p_{H2} = 1$ bar (i.e. under standard state conditions), then rH = 0 at any pH of the solution (see Figure 1, which describes the pertinent Pourbaix's E_{Redox} *vs.* pH diagram), and this is **the nominal zero of the rH-metric scale** to which corresponds **the nominal maximum reducing power** of a redox system

One redox system of paramount importance is the **equimolal (quinone[Q] + hydro-quinone[H₂Q]) system**, commonly called the "quinhydrone", of symbol QHY, whose electrode potential is expressed by

$$E_{QHY} = E_{QHY} - k\,pH \tag{3}$$

On consideration of equations (2) and (3), the potential difference E_4 of the cell (4) below, where the quinhydrone electrode is combined with the hydrogen electrode and the two solutions are at equal activity of the H^+ ion:

$$Pt|H2\,(p_{H2})|H^+ \,\vdots\, H^+ \text{ saturated with QHY}|Pt \tag{4}$$
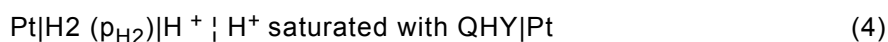
is clearly independent of pH. (In common practice, the two electrode compartments are kept separated by a porous glass frit or a closed stopcock, as indicated by the ¦ symbol, to avoid the mutual diffusion of hydrogen gas and quinhydrone which would produce an irreversible chemical reaction and formation of a useless mixed electrode potential). Therefore, equating $E_{H^+|H2}$ to E_{QHY} in accord with the equation (1), *i.e.* putting $E_4 = 0$, gives the related rH_{QHY} value:

$$E_4 = E_{QHY} - E_{H^+|H2} = E_{QHY} - E_{H^+ H2} - (k/2)\,rH_{QHY} = 0 \tag{5}$$

from which

$$rH_{QHY} = 2\,(E_{QHY} - E_{H^+|H2})\,/\,k = rH_S \tag{6}$$

As equation (6) shows, since the difference $(E_{QHY} - E_{H^+ H2})$ is a well defined and accurately known quantity which is a function of temperature but is **invariant upon passing from pure water medium to most water-rich aqueous-organic media** [1], the **quinhydrone redox system constitutes the key standard rH_S** for reference in rH measurements, according to the operational equation (27) described later on. In the context of this invariancy, at 298,15 K, $(E_{QHY} - E_{H^+ H2}) = 0,699\,75$ V [6] and, therefore:

$$(rH)_{QHY} = \mathbf{rH_S} = 2 \times 0,699\,75\,/\,0,059\,159\,7 = 23,66 \tag{7}$$