

# TECHNICAL REPORT

# IEC TR 62432

First edition  
2006-03

---

---

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

© IEC 2006 — Copyright - all rights reserved

No part of this publication may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and microfilm, without permission in writing from the publisher.

International Electrotechnical Commission, 3, rue de Varembé, PO Box 131, CH-1211 Geneva 20, Switzerland  
Telephone: +41 22 919 02 11 Telefax: +41 22 919 03 00 E-mail: [inmail@iec.ch](mailto:inmail@iec.ch) Web: [www.iec.ch](http://www.iec.ch)



Commission Electrotechnique Internationale  
International Electrotechnical Commission  
Международная Электротехническая Комиссия

PRICE CODE

**N**

*For price, see current catalogue*

## CONTENTS

|   |        |
|---|--------|
| FOREWORD.....   | 3      |
| INTRODUCTION.....   | 5      |
| 1 Scope.....  | 6      |
| 2 General principles .....  | 6      |
| 2.1 Redox couples, redox equilibria, redox potentials, redox systems.....   | 6      |
| 2.2 The rH value .....  | 7      |
| 2.3 rH Standards for use in water and aqueous-organic solvent mixtures .....  | 11     |
| 2.4 Electrodes for the operational rH cell.....   | 12     |
| 2.4.1 General .....   | 12     |
| 2.4.2 The glass electrode .....   | 12     |
| 2.4.3 The inert noble-metal electrode (Pt or Au) .....  | 12     |
| 2.5 rH Scales in diverse solvents .....   | 12     |
| 2.6 Pourbaix's diagrams for the triad rH – pH – $E_{O R}$ .....   | 13     |
| 3 Instrumentation .....   | 13     |
| <br>Bibliography.....   | <br>14 |
| <br>Figure 1 – Pourbaix's diagram for the triad rH – pH – $E_{O R}$ for some key redox systems .....  | <br>10 |
| <br>Table 1 .....   | <br>6  |
| Table 2 – Some reference aqueous solutions proposed as rH-metric standards rH <sub>S</sub> [8, 9] at 25 °C and for the calibration of the redox electrode at $E_{O R}$ .....  | 11     |
| Table 3 – Values of ( $E_{QH_Y} - E_{H +  H_2}$ ) [6] with corresponding rH <sub>S</sub> values, at various temperatures, valid for any solvent (water W, or aquo-organic mixture Z = W + S compatible with Quinhydrone) in non-alkaline solution ..... | 12     |
| Table 4 – Parallelisms between the aqueous pH-metric and rH-metric scales .....   | 11     |

## INTERNATIONAL ELECTROTECHNICAL COMMISSION

---

**THE rH INDEX IN AQUEOUS AND  
AQUEOUS-ORGANIC MEDIA**
**FOREWORD**

- 1) The International Electrotechnical Commission (IEC) is a worldwide organization for standardization comprising all national electrotechnical committees (IEC National Committees). The object of IEC is to promote international co-operation on all questions concerning standardization in the electrical and electronic fields. To this end and in addition to other activities, IEC publishes International Standards, Technical Specifications, Technical Reports, Publicly Available Specifications (PAS) and Guides (hereafter referred to as "IEC Publication(s)"). Their preparation is entrusted to technical committees; any IEC National Committee interested in the subject dealt with may participate in this preparatory work. International, governmental and non-governmental organizations liaising with the IEC also participate in this preparation. IEC collaborates closely with the International Organization for Standardization (ISO) in accordance with conditions determined by agreement between the two organizations.
- 2) The formal decisions or agreements of IEC on technical matters express, as nearly as possible, an international consensus of opinion on the relevant subjects since each technical committee has representation from all interested IEC National Committees.
- 3) IEC Publications have the form of recommendations for international use and are accepted by IEC National Committees in that sense. While all reasonable efforts are made to ensure that the technical content of IEC Publications is accurate, IEC cannot be held responsible for the way in which they are used or for any misinterpretation by any end user.
- 4) In order to promote international uniformity, IEC National Committees undertake to apply IEC Publications transparently to the maximum extent possible in their national and regional publications. Any divergence between any IEC Publication and the corresponding national or regional publication shall be clearly indicated in the latter.
- 5) IEC provides no marking procedure to indicate its approval and cannot be rendered responsible for any equipment declared to be in conformity with an IEC Publication.
- 6) All users should ensure that they have the latest edition of this publication.
- 7) No liability shall attach to IEC or its directors, employees, servants or agents including individual experts and members of its technical committees and IEC National Committees for any personal injury, property damage or other damage of any nature whatsoever, whether direct or indirect, or for costs (including legal fees) and expenses arising out of the publication, use of, or reliance upon, this IEC Publication or any other IEC Publications.
- 8) Attention is drawn to the Normative references cited in this publication. Use of the referenced publications is indispensable for the correct application of this publication.
- 9) Attention is drawn to the possibility that some of the elements of this IEC Publication may be the subject of patent rights. IEC shall not be held responsible for identifying any or all such patent rights.

The main task of IEC technical committees is to prepare International Standards. However, a technical committee may propose the publication of a technical report when it has collected data of a different kind from that which is normally published as an International Standard, for example "state of the art".

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]<sup>1</sup>, 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.

---

<sup>1</sup> 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.