

TECHNICAL REPORT

IEC
TR 62456

First edition
2007-03

**An electrochemical reference system
for use in different solvent media –
The decamethylated ferricinium/ferrocene
redox couple**

IECNORM.COM: Click to view the full PDF of IEC TR 62456:2007



Reference number
IEC/TR 62456:2007(E)

Publication numbering

As from 1 January 1997 all IEC publications are issued with a designation in the 60000 series. For example, IEC 34-1 is now referred to as IEC 60034-1.

Consolidated editions

The IEC is now publishing consolidated versions of its publications. For example, edition numbers 1.0, 1.1 and 1.2 refer, respectively, to the base publication, the base publication incorporating amendment 1 and the base publication incorporating amendments 1 and 2.

Further information on IEC publications

The technical content of IEC publications is kept under constant review by the IEC, thus ensuring that the content reflects current technology. Information relating to this publication, including its validity, is available in the IEC Catalogue of publications (see below) in addition to new editions, amendments and corrigenda. Information on the subjects under consideration and work in progress undertaken by the technical committee which has prepared this publication, as well as the list of publications issued, is also available from the following:

- **IEC Web Site (www.iec.ch)**
- **Catalogue of IEC publications**

The on-line catalogue on the IEC web site (www.iec.ch/searchpub) enables you to search by a variety of criteria including text searches, technical committees and date of publication. On-line information is also available on recently issued publications, withdrawn and replaced publications, as well as corrigenda.

- **IEC Just Published**

This summary of recently issued publications (www.iec.ch/online_news/_justpub) is also available by email. Please contact the Customer Service Centre (see below) for further information.

- **Customer Service Centre**

If you have any questions regarding this publication or need further assistance, please contact the Customer Service Centre:

Email: custserv@iec.ch
Tel: +41 22 919 02 11
Fax: +41 22 919 03 00

TECHNICAL REPORT

IEC
TR 62456

First edition
2007-03

An electrochemical reference system for use in different solvent media – The decamethylated ferricinium/ferrocene redox couple

IECNORM.COM: Click to view the full PDF of IEC TR 62456:2007

© IEC 2007 — 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 Web: www.iec.ch



Commission Electrotechnique Internationale
International Electrotechnical Commission
Международная Электротехническая Комиссия

PRICE CODE

H

For price, see current catalogue

INTERNATIONAL ELECTROTECHNICAL COMMISSION

**AN ELECTROCHEMICAL REFERENCE
SYSTEM FOR USE IN DIFFERENT SOLVENT MEDIA –
THE DECAMETHYLATED FERRICINIUM/FERROCENE
REDOX COUPLE**

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 62456 which is a technical report, has been prepared by subcommittee 65D: Analysing 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/125/DTR	65D/127/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 publication may be issued at a later date.

IECNORM.COM: Click to view the full PDF of IEC TR 62456:2007

INTRODUCTION

The proposal of this technical report is justified by the difficulties met by electrochemists, electroanalysts, corrosionists, and biologists when electrode potentials measured in different non-aqueous or aqueous-organic solvents with reference to the familiar, commercially available, and very dependable, aqueous Saturated Calomel Electrode (SCE) are to be physically inter-compared on some "inter-solvental scale" of electrode potentials. These difficulties are caused by the occurrence of two basic extrathermodynamic factors, namely, the primary medium effect [1]¹ on electrode potentials and the liquid-junction potentials between different solvent media. This report details the use of the half-wave potential of the ferricinium/ferrocene redox couple or the decamethyl derivatized ferricinium/ferrocene redox couple as the basis of a reference electrode system useful to compare measured electrode potentials to the aqueous saturated calomel electrode when used in various solvent systems.

For an acceptable approach to the solution of the above problem, superseding earlier attempts [2], Strehlow and co-workers [3], [4] proposed to use the redox couple ferricinium|ferrocene (in terms of its "half-wave potentials", or "formal redox potentials", obtainable from voltammetric experiments in different solvents with the same supporting electrolyte and against the same working reference electrodes), for which, based on an extended experimental evidence, they assessed an "invariancy of potential" to within about ± 15 mV in a dozen different solvents, assuming the above redox couple to be unaffected by solvent interactions. Principles and reasons for this choice were expounded in detail [3], [4] and need not be repeated here. Strehlow's idea was later reassessed in nearly the same terms by Gritzner and Kútá [5], but various authors later demonstrated the existence of specific interactions of the ferricinium|ferrocene couple with some of the solvent media considered, thus partially impairing the intersolvental invariancy of the above redox potentials. However, recently [6], [7], [8], [9], and [10], it was shown that such residual solvent effects could be drastically abated by permethylation of the aromatic rings of the redox couple. For instance, the decamethyl-derivatized ferricinium|ferrocene couple, being chemically and electrochemically reversible, with half-wave potentials quite unaffected by the working solvent, lends itself as the best reference-potential redox couple known so far (besides other advantages with respect to the unmethylated parent couple, such as a more general chemical stability, and a more advantageous potential window compared to the operating reference electrode SCE is more advantageously placed). Therefore, what remains to be done by the user is to calibrate the aqueous SCE electrode (which, in common practice, is the reference electrode blindly and invariably used in contact with the non-aqueous solvents studied) versus the half-wave potential of the decamethylferricinium|decamethylferrocene $[\text{Me}_{10}\text{Fec}^+|\text{Me}_{10}\text{Fec}]$ couple in the solvent studied, along the lines explained below, and to apply the consequent corrections to the measured potentials (see Table 1). The resulting corrected potentials will finally become intersolventally comparable.

An additional bonus to the present methodology is provided by the parallel decamethyl-derivatized cobalticinium|cobaltocene $[\text{Me}_{10}\text{Coc}^+|\text{Me}_{10}\text{Coc}]$ redox couple because it also was shown to be chemically and electrochemically reversible and its half-wave potential E^* differs by a constant value from that of $[\text{Me}_{10}\text{Fec}^+|\text{Me}_{10}\text{Fec}]$, in terms of $E^*[\text{Me}_{10}\text{Coc}^+|\text{Me}_{10}\text{Coc}] = E^*[\text{Me}_{10}\text{Fec}^+|\text{Me}_{10}\text{Fec}] - 1,407$ V, at 298,15 K.

¹ Figures in square brackets refer to the Bibliography.

**AN ELECTROCHEMICAL REFERENCE
SYSTEM FOR USE IN DIFFERENT SOLVENT MEDIA –
THE DECAMETHYLATED FERRICINIUM/FERROCENE
REDOX COUPLE**

1 Scope

The scope of this technical report is to present the background considerations which led to this compilation of potentials of the aqueous saturated calomel electrode compared to the cyclovoltametric data for a glassy carbon electrode in various solvent media. A tabulation of working potentials of this electrode pair in various solvent media is presented. A comparison of the cyclovoltametric scans for the ferricinium/ferrocene and deamethyl derivatized ferricinium/ferrocene redox couple system is presented and important features are discussed.

2 Tabulation of working potentials

Clause 2 gives an explanation of the basis for the tabulation of working potentials of the aqueous saturated calomel electrode compared to the ferricinium/ferrocene redox couple and the decamethyl derivatized ferricinium/ferrocene redox couple in various solvent media, as well as an identification of the voltametric range of these couples in various solvent media.

2.1 Working potentials of an SCE

Table 1 compiles the working potentials of the aqueous saturated calomel electrode compared to the ferricinium/ferrocene redox couple and the deamethyl derivatized ferricinium/ferrocene redox couple in various solvent media.

Table 1 – Working potentials of the aqueous SCE compared to the half-wave potential of the decamethyl derivatized ferricinium/ferrocene redox couple in various solvent media

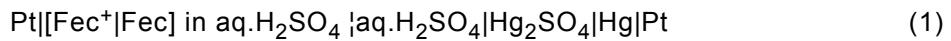
Solvent	E_{SCE} / V^a	References
Water	0,144	[7]
Methanol	0,124	[7]
Propylene carbonate	0,069	[7]
Methyl pyrrolidinone	–0,055	[8] to [10]
Acetone	0,021	[8] to [10]
Acetonitrile	0,119	[8] to [10]
Methylene chloride	0,060	[8] to [10]
Dimethyl formamide	0,008	[8] to [10]

^a Values to be added to the potentials measured in the solvent studied versus the aqueous SCE to get them referred to the solvent-invariant half-wave potential of the $[Me_{10}Fec^+|Me_{10}Fec]$ redox couple.

NOTE Table 1 gives values for the aqueous SCE at 298K working potential (including insolvental liquid junction potentials) when compared to the decamethyl derivatized ferricinium/ferrocene redox couple

Ferrocene [Fec] is the dicyclopentadienyl ferrous complex; oxidation to the corresponding ferric complex (ferricinium, $[Fec^+]$) is a simple, chemically and electrochemically reversible one-electron process. The metal ion is buried at the centre of a nearly spherical, big complex; hence, these substances undergo negligible chemical or steric changes when oxidation or reduction occurs.

The half-wave potentials of $[\text{Fec}^+|\text{Fec}]$ were first measured polarographically by Strehlow [3], [4] in concentrated aqueous sulfuric acid solutions with respect to the Hg_2SO_4 electrode in the cell (1):



combined with cell (2):



It is readily shown that

$$E_2 - E_1 = E^\circ_{\text{Hg}_2\text{SO}_4} - E^\circ_{\text{H}_2} - E^*_{\text{Fec}^+|\text{Fec}} + k \text{ pH} \quad (3)$$

Now, since in Equation (3) the constant term ($E^\circ_{\text{Hg}_2\text{SO}_4} - E^\circ_{\text{H}_2} - E^*_{\text{Fec}^+|\text{Fec}}$) is determinable, pH is here a true pH = $-\log(a_{\text{H}^+})$ in superacid H_2SO_4 solutions, a quantity not attainable by the conventional IUPAC procedure, which is reliable only in the range $1 < \text{pH} < 13$, due to the increasing effect of residual liquid junction potentials at extreme pH. This interesting scheme can also be applied to other ultra-concentrated acid solutions (HCl, HBr, HI).

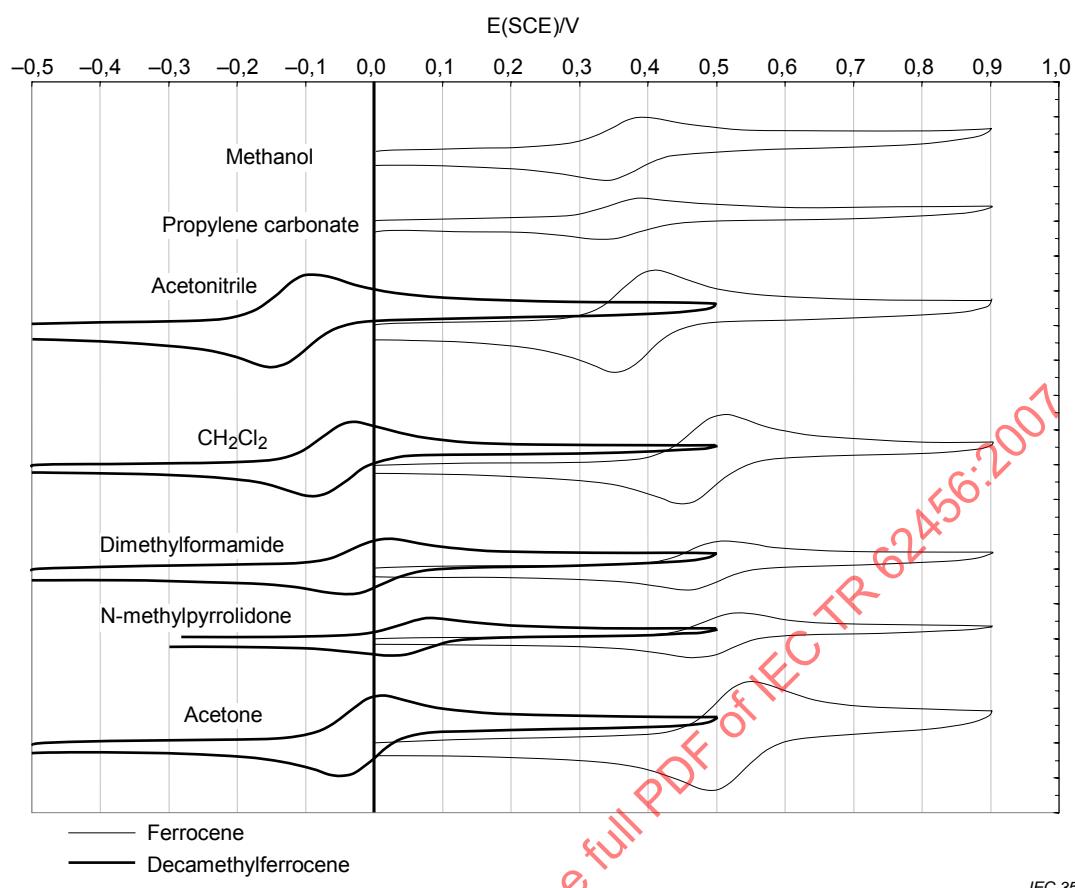
However, definitely, the most interesting and important opportunity is to use the $\text{Fec}^+|\text{Fec}$ couple in its improved decamethylated form [6], [7], [8], [9], and [10], $\text{Me}_{10}\text{Fec}^+|\text{Me}_{10}\text{Fec}$, as one tool of invariant potential across different solvents, i.e. entering into an “intersolvental” scale of electrode potentials. In this context, to attain the solvent-invariant potential of the $[\text{Me}_{10}\text{Fec}^+|\text{Me}_{10}\text{Fec}]$ redox couple, the pertinent half-wave potential or formal redox potential can be obtained in voltammetric experiments on a stationary, solid working electrode (such as glassy carbon or platinum, which can be reproducibly polished according to a severe protocol) compared to the same operating aqueous SCE reference electrode in the same supporting electrolyte, and with careful compensation of the residual ohmic drops. The half-wave potential values sought can be obtained, either

- as the average of the anodic and cathodic peak potentials in cyclic voltammetry experiments (typically resulting in symmetric peak signals); or
- from the waves obtained in “stationary” experiments (i.e., performed at very low scan rates, as in the case of polarography) or, more realistically, from the convolutive analysis of the above-mentioned peak signals [6], [7], [8], [9], and [10].

Accumulation of data for completion of Table 1 is under way.

2.2 Cyclovoltametric characteristics

The cyclovoltametric behaviour of the ferricinium/ferrocene and decamethyl derivatized ferricinium/ferrocene redox couples in various solvent media is shown in Figure 1.



IEC 353/07

Figure 1 – Synopsis of cyclovoltametric characteristics obtained for redox couples $\text{Fe}^{3+}/\text{Fe}^{2+}$ (thin curves) and $\text{Me}_{10}\text{Fe}^{3+}/\text{Me}_{10}\text{Fe}^{2+}$ (thick curves) at 298 K, and $0,2 \text{ V s}^{-1}$ scan rate, on a glassy carbon electrode, versus the operational reference aqueous SCE electrode, in different solvents with constant 0,1 M TBAP (tetra butyl ammonium perchlorate) supporting electrolyte