

ISO/TC 35/SC 9

Secretariat: BSI

Voting begins on:
2023-08-31

Voting terminates on:
2023-10-26

Electrochemical noise measurement for assessing the protection of metal afforded by organic coatings

iTeh STANDARD PREVIEW
(standards.iteh.ai)

ISO/DTR 5604

<https://standards.iteh.ai/catalog/standards/sist/da94eff8-a0ae-454f-9f34-9fe43b978c20/iso-dtr-5604>

RECIPIENTS OF THIS DRAFT ARE INVITED TO SUBMIT, WITH THEIR COMMENTS, NOTIFICATION OF ANY RELEVANT PATENT RIGHTS OF WHICH THEY ARE AWARE AND TO PROVIDE SUPPORTING DOCUMENTATION.

IN ADDITION TO THEIR EVALUATION AS BEING ACCEPTABLE FOR INDUSTRIAL, TECHNOLOGICAL, COMMERCIAL AND USER PURPOSES, DRAFT INTERNATIONAL STANDARDS MAY ON OCCASION HAVE TO BE CONSIDERED IN THE LIGHT OF THEIR POTENTIAL TO BECOME STANDARDS TO WHICH REFERENCE MAY BE MADE IN NATIONAL REGULATIONS.



Reference number
ISO/DTR 5604:2023(E)

iTeh STANDARD PREVIEW (standards.iteh.ai)

ISO/DTR 5604

<https://standards.iteh.ai/catalog/standards/sist/da94eff8-a0ae-454f-9f34-9fe43b978c20/iso-dtr-5604>



COPYRIGHT PROTECTED DOCUMENT

© ISO 2023

All rights reserved. Unless otherwise specified, or required in the context of its implementation, no part of this publication may be reproduced or utilized otherwise in any form or by any means, electronic or mechanical, including photocopying, or posting on the internet or an intranet, without prior written permission. Permission can be requested from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

	Page
Foreword.....	iv
Introduction.....	v
1 Scope.....	1
2 Normative references.....	1
3 Terms and definitions.....	1
4 Principles.....	2
4.1 Organically coated metal exposed to a corrosive environment – how a resistance measurement can indicate protection.....	2
4.2 Generation of electrochemical noise from bare and coated metal.....	3
4.3 Evaluation criteria.....	3
5 Apparatus.....	3
5.1 Test cell.....	3
5.2 Field or site work.....	3
5.3 Reference electrode.....	4
5.4 Working electrode.....	4
5.5 Electrolyte.....	4
6 Description of the measurement system.....	4
7 Electrode configurations.....	5
7.1 General.....	5
7.2 Bridge (laboratory use).....	5
7.3 Single substrate (laboratory use).....	6
7.4 No connection to the substrate as used in the laboratory.....	7
7.5 Field measurement.....	7
8 Dummy cell and checking/calibration.....	8
9 Measurement.....	8
10 Data analysis and data treatment.....	9
11 Summary.....	9
Annex A (informative) Description of an experiment with resistors simulation of a paint system.....	10
Annex B (informative) Data analysis and data treatment.....	12
Annex C (informative) Comparison of noise data from bare metal compared with organically coated metal.....	13
Bibliography.....	15

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 document 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).

ISO draws attention to the possibility that the implementation of this document may involve the use of (a) patent(s). ISO takes no position concerning the evidence, validity or applicability of any claimed patent rights in respect thereof. As of the date of publication of this document, ISO had not received notice of (a) patent(s) which may be required to implement this document. However, implementers are cautioned that this may not represent the latest information, which may be obtained from the patent database available at www.iso.org/patents. ISO shall not be held responsible for identifying any or all such patent rights.

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.

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.

Introduction

There are several test methods for assessing the protection afforded by organic coatings on metal, particularly on low carbon steel, using the available electrochemical measurements. The most commonly used technique is electrochemical impedance spectroscopy (EIS), which is detailed in the ISO 16773 series, and is well suited for laboratory use. However, there is a strong need for a non-intrusive technique that can be used on site to monitor or for quality control that is quick and is relatively simple to use and interpret.

This document gives the current state of the art for such a technique, which is electrochemical noise measurement (EN). The developments described in this document suggest that electrochemical noise measurement can be used as an alternative to and potentially even as the preferred process for field or on-site use.

For further information, a detailed description of the EN methodology when applied to bare metal can be found in ISO 17093. The differences associated with using the technique for organic coatings are described in this document, which is intended to complement ISO 17093.

The EN approach has been directly compared with methodologies such as EIS and DC resistance, with good agreement.^{[3][4]}

Furthermore, electrochemical noise applied to assess coatings has been reviewed in References [5] and [6], showing the potential for this technique.

iTeh STANDARD PREVIEW
(standards.iteh.ai)

ISO/DTR 5604

<https://standards.iteh.ai/catalog/standards/sist/da94eff8-a0ae-454f-9f34-9fe43b978c20/iso-dtr-5604>

Electrochemical noise measurement for assessing the protection of metal afforded by organic coatings

1 Scope

This document describes the principle of electrochemical noise measurement (EN), specifically focusing on the application of the technique to indicate the level of protection provided by an organic coating to the underlying metal. It discusses the principles behind the measurement method but also the type of electrochemical apparatus, the experimental set-up and electrodes configurations, the presentation of measured data, and analysis of results that have been used in the work done so far and reported in the references. This work has mainly been done in the laboratory, and there are some examples of work conducted in the field.

NOTE Electrochemical noise measurement for coatings is only used in few academical groups. A general application of the method cannot be guaranteed.

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 16773-1, *Electrochemical impedance spectroscopy (EIS) on coated and uncoated metallic specimens — Part 1: Terms and definitions*

ISO 17093, *Corrosion of metals and alloys — Guidelines for corrosion test by electrochemical noise measurements*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 16773-1, ISO 17093 and the following apply.

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

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <https://www.electropedia.org/>

3.1

electrochemical noise

EN

fluctuation typically at low frequencies (≤ 1 Hz) and low amplitude in current and potential, generated by electrochemical reactions and other processes on the surface, for example, bubble evolution

3.2

electrochemical potential noise

fluctuation in potential of an electrode relative to a reference electrode or fluctuation in potential between two similar electrodes

Note 1 to entry: The electrochemical potential noise is expressed in microvolts (μV) or millivolts (mV).

3.3
electrochemical current noise

fluctuation in current to one electrode or between two electrodes

Note 1 to entry: The electrochemical current noise is normally expressed in nanoamperes (nA).

3.4
electrochemical noise resistance

R_n
resistance obtained by dividing the standard deviation of potential noise by the standard deviation of current noise from the time record

3.5
working electrode

WE
coated metal in contact with the electrolyte, made out of the investigated material(s)

3.6
pseudo-working electrode

PWE
working electrode (3.5) other than coated metal

Note 1 to entry: A silver/silver chloride electrode (Ag/AgCl) in laboratory work or a noble metal like silver, platinum or gold can be used as part of a sensing probe in field work. PWEs are needed for configurations other than the standard bridge.

3.7
pseudo reference electrode

P_{Ref}
electrode used as a reference electrode in field work

Note 1 to entry: The metal itself (for single substrate configuration), platinum wire or sheet, copper, and silver.

3.8
electrode configuration

arrangement by which the electrodes are connected to the measuring device, i.e. bridge (Bridge), single Substrate (SS), no connection to the substrate (NOCS)

Note 1 to entry: The configuration used depends on the particular circumstances of the measurement.

3.9
zero resistance amperemeter

ZRA
electronic circuit which measures current but has itself no significant impedance

Note 1 to entry: For coatings, a ZRA capable of measuring low levels of current down to picoamperes (pA) is usually needed.

4 Principles

4.1 Organically coated metal exposed to a corrosive environment – how a resistance measurement can indicate protection

Water and oxygen penetrate through an organic coating leading to electrochemical reactions occurring at the interface between the metal and the coating.^[Z] In aqueous corrosion, discrete anodic and cathodic areas arise, and these allow corrosion to proceed whenever there is an ionically conductive pathway between the substrate and the surrounding environment. However, if a high ionic resistance is introduced into the circuit between anodes and cathodes, e.g. by the coating, the rate of corrosion will decrease to a low value. This is one accepted mechanism by which the coatings can operate to prevent corrosion. Another mechanism, which can take place concurrently, is interface reactions when

aided by an oxidizing agent, e.g. oxygen, hydrogen peroxide or chemicals within the coating. These can result in the formation of a passive coherent, protective, chemically stable oxide layer which slows the corrosion rate. For this “passivity” to pertain for any length of time, the coating acts to prevent the arrival of incoming aggressive ions. In both mechanism routes, a high resistance (R) between the anodes and cathodes prevent aggressive ions arriving at the interface and the rate of the corrosion process is largely determined by the through film ionic resistivity of the coating system. Overall, the resistance whether measured by a DC technique as R_{dc} , by EIS as $R_{0,1Hz}$, or by electrochemical noise resistance as R_n , is believed to provide a quantitative measure for the extent to which the coating is protecting the underlying metal. However, the influence of e.g. binder type on coating resistance is not fully understood, therefore the above statement on coating resistance is not fully justified.

4.2 Generation of electrochemical noise from bare and coated metal

A metal in contact with any solution generates both current noise and potential or voltage noise, due to small random fluctuations which arise stochastically during electrochemical processes.^[8] The voltage noise can be easily measured with respect to a stable reference electrode. In the case of current noise, it is important to simulate the situation within the metal by using two identical but separated metal specimens and measuring the current in between using a zero resistance amperemeter (ZRA). The current noise is the level of fluctuation on the current value. It has been theoretically shown^[5] that the standard deviation of the voltage values, i.e. voltage noise, divided by the standard deviation of the current values, i.e. current noise, gives rise to a parameter called electrochemical noise resistance (R_n). In the case of bare metal, R_n has been shown to be equivalent to the resistance obtained using the linear polarization technique.

When a coating is present, R_n can be attenuated in the case of current noise and amplified in the case of potential noise, through the coating. The level of both potential and current noise that is sensed by the instrument can be converted to R_n . The largest value of resistance R_n is very likely the resistance of the coating system to the movement of ions (R_{paint}) and this in turn has a direct bearing on the rate of corrosion, as described in 4.1. An exception would be when the coating has broken down and corrosion is occurring, and in that case a low measured value will be indicative of failure.

<https://standards.iteh.ai/catalog/standards/sist/da94eff8-a0ae-454f-9f34-9fe43b978c20/iso-dtr-5604>

4.3 Evaluation criteria

The measurement of the electrochemical noise resistance (R_n) provides a manner of assessing the protection capability of the coating.

When $R_n > 1 \times 10^8 \Omega \cdot \text{cm}^2$ indicates good protection, $1 \times 10^6 \Omega \cdot \text{cm}^2$ to $1 \times 10^8 \Omega \cdot \text{cm}^2$ is the borderline and $R_n < 1 \times 10^6 \Omega \cdot \text{cm}^2$ affords poor protection.^[9] The rate of reduction of R_n with time will indicate the rate at which the coating system is breaking down.

5 Apparatus

The usual laboratory apparatus and, in particular, the following shall be used.

5.1 Test cell

The test cell is a leak proof cell constructed of material that will not corrode, deteriorate or contaminate the solution was used to contain the electrolyte. The electrode holder and mounting material for the electrodes were mounted so as to have no influence on the measurement.

5.2 Field or site work

Although in laboratory work leak proof cells can be permanently attached, in field work a different approach is used since a dismountable probe is needed. One solution is to hold the electrolyte solution in a filter paper pad cut to the size of the pseudo reference electrode (P_{Ref}) or pseudo working electrodes (PWE), whose area defines the measurement area.

5.3 Reference electrode

In the field a robust electrode, such as a silver/silver chloride (Ag/AgCl) or copper/copper sulfate (Cu/CuSO₄) is used.

5.4 Working electrode

In almost all the work described in the references the configurations were not just the standard bridge (see 6.2) where two nominally identical and separate coated samples are needed, and the two working electrodes will be the metal under the coating in each sample. The two most common alternatives are single substrate (see 6.3) configuration, where the reference becomes the metal under the coating, two standard reference electrodes (SRE) become the working electrodes, and no connection to the substrate (NOCS) configuration which requires three SREs (see 6.3) or P_{Ref} (field work).

5.5 Electrolyte

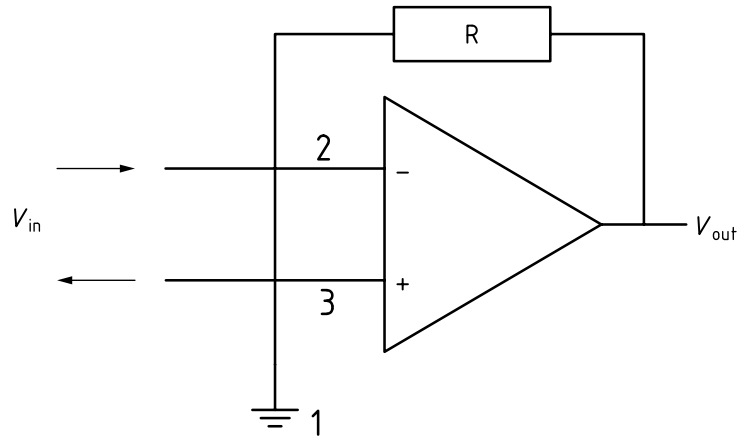
The test solution most commonly used in the references is e.g. NaCl solution, $c = 0,6$ mol/l, because it typically has a corrosivity similar to sea water. This solution has a low resistance in comparison with the resistance of the investigated system. Sometimes other electrolytes more in keeping with the likely exposure environment were used. In all cases though the electrolyte is normally conductive enough to not become the limiting factor.

6 Description of the measurement system

This clause describes how the experiments were normally done in the work which generated the results in the referenced papers and presented in [Annex A](#), [Annex B](#) and [Annex C](#).

A measurement system consisting of an electrochemical cell connected to instrumentation and software for the characterization of materials using standard precision electrical measurement techniques was employed. Decisions were made as to the length of time that the data are gathered and what frequency. Typically, data was obtained at 0,5 s (2 Hz), collecting 512 data points over 256 s with the measurement repeated twice. Experiments done many years ago showed this to be optimal for coatings work

A potentiometer with a very high input impedance (i.e. $10^{11} \Omega$ to $10^{14} \Omega$) to minimize the current drawn from the working electrode(s) during measurement was used to measure the potential difference between the reference and working electrodes, along with a zero-resistance amperemeter, ZRA with high sensitivity to measure currents as low as picoampere (see [Figure 1](#)).

**Key**

1	ground
2 and 3	working electrode
R	resistor
V_{in}	voltage in
V_{out}	voltage out

NOTE This figure shows the operational amplifier which is the basis for the zero-resistance amperemeter (ZRA) with an indication of connection to working electrodes (key references 2 and 3).

Figure 1 — Schematic representation of an operational amplifier

7 Electrode configurations

[ISO/DTR 5604](https://standards.iteh.ai/catalog/standards/sist/da94eff8-a0ae-454f-9f34-9fe43b978c20/iso-dtr-5604)

<https://standards.iteh.ai/catalog/standards/sist/da94eff8-a0ae-454f-9f34-9fe43b978c20/iso-dtr-5604>

7.1 General

There are three common electrode configurations which have been used for coated metal and these are described in [7.2](#) to [7.4](#). The first one is the standard arrangement (as shown in [Figure 2](#)). The other two have been developed specifically for coatings particularly to make application of the method in the field possible (see [Figures 3](#) and [4](#)).

7.2 Bridge (laboratory use)

This arrangement, shown in [Figure 2](#), was one of the three methods used in the references for laboratory-based investigations. It involves a bridge between the two nominally identical and electrically separated working electrodes both covered with the same coating at the same thickness applied at the same time and hence nominally identical. The current between these can be measured via a ZRA and simultaneously the potential of these electrodes, joined together internally in the equipment, can be measured with respect to a low noise standard reference electrode.