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

*Corrosion des métaux et alliages — Lignes directrices pour essais de
corrosion par mesures de bruit électrochimique*

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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 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).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: [Foreword - Supplementary information](#)

The committee responsible for this document is ISO/TC 156, *Corrosion of metals and alloys*, in cooperation with the ECG-COMON (European Cooperative Group on Corrosion Monitoring of Nuclear Materials, <http://www.ecg-comon.org>).

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Corrosion of metals and alloys — Guidelines for corrosion test by electrochemical noise measurements

1 Scope

This International Standard is intended to assist in corrosion testing by electrochemical noise measurement. It covers test procedures and analysis methods for reliable measurement of electrochemical noise for both uncoated and organically coated metal.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 8044, *Corrosion of metals and alloys — Basic terms and definitions*

ISO 17475, *Corrosion of metals and alloys — Electrochemical test methods — Guidelines for conducting potentiostatic and potentiodynamic polarization measurements*

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3 Terms and definitions (standards.iteh.ai)

For the purposes of this document, the terms and definitions given in ISO 8044 and the following apply.

3.1 electrochemical noise <https://standards.iteh.ai/catalog/standards/sist/eb252da3-7c05-46bb-bcf0-136fbe6c1402/iso-17093-2015>

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 (typically in the range of μV to mV) of an electrode relative to a reference electrode or fluctuation in potential between two similar electrodes

3.3

electrochemical current noise

fluctuation in current (typically in the range of nA to μA) of one electrode or between two electrodes

3.4

electrochemical noise resistance

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

3.5

power spectral density of potential

PSD_E

power present in the potential noise as a function of frequency

3.6

power spectral density of current

PSD_I

power present in the current noise as a function of frequency

**3.7
electrochemical noise impedance**

Z_n
impedance determined as $Z_n = \sqrt{PSD_E / PSD_I}$ where all terms are a function of frequency

Note 1 to entry: The noise impedance is real and positive.

**3.8
working electrode**

electronic conductor in contact with the electrolyte, made out of the investigated material

Note 1 to entry: This definition differs from that of the same term given in ISO 8044:2015, 6.1.46, "test electrode in an electrochemical cell designed for polarization tests".

**3.9
auxiliary electrode**

electrode commonly used in applied polarization to balance the current passing to the working electrode

Note 1 to entry: It is usually made from a non-corroding material.

**3.10
Nyquist frequency**

frequency equal to one half of the sampling frequency ($f_s/2$); maximum frequency about which information can be obtained from the sampled data

**3.11
thermal noise**

noise resulting from thermal vibrations of electrons and charge carriers

Note 1 to entry: Thermal noise is the absolute minimum of the noise that can be expected; also called Johnson noise.

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**3.12
shot noise**

noise due to the quantized nature of the charge carriers that move in very short times causing current peaks

**3.13
dummy cell**

non-electrochemical cell with a well-defined noise level that usually does not deliberately generate noise above normal thermal noise levels

4 Principles

4.1 The source of EN in corrosion might result from partial faradaic currents, adsorption/desorption processes, surface coverage, and, in the case of localized corrosion, the initiation of pits, crevice corrosion, and mechanical effects from cracking and several other processes. Special care has to be taken as a variety of other sources not related to corrosion might cause fluctuations in current and potential.

4.2 Electrochemical noise can be measured potentiostatically, galvanostatically, or at the free corrosion potential (the various methods are described in [Clause 5](#)). Examples of two simple tests with EN measurements on aluminium during pitting corrosion and on organically coated carbon steel can be found in [Annexes B and C](#).

4.3 Electrochemical noise data can be analysed in the time and/or frequency domains. Details of data analysis are described in [Annex A](#).

5 Apparatus and measurement methods

5.1 Instrumentation

5.1.1 Accurate measurement of potential and current requires instruments that have appropriate input impedance (much higher than the system being measured in the case of potential and much lower in the case of current) and sensitivity (sufficient to minimize quantization noise). Suggestions are given in the following Clauses but these will not be sufficient for some systems.

5.1.2 Potential measuring instruments

The instrument should have an input impedance of at least 10^9 ohm for bare metal and 10^{11} ohm for coated metal to minimize current drawn from the system during measurement. The higher input impedance might be necessary for very high impedance systems (e.g. for EN measurements with coated metals). The sensitivity and accuracy of the instrument should be sufficient to detect a change of $10\ \mu\text{V}$ or lower for the typical range of 1 V.

5.1.3 Current measuring instruments

The instrument should be capable of measuring current to a resolution of 10^{-9} A or better with a voltage burden (the voltage between the terminals, also known as a voltage drop or burden voltage) of less than 1 mV (the low voltage burden is only required when the current measurement is made between two corroding working electrodes). A low voltage burden ammeter is often termed a zero resistance ammeter (ZRA) in corrosion literature.

5.1.4 Potentiostat

Some measurement configurations use a potentiostat to control the potential of an electrode. The potentiostat shall have low noise characteristics, which should be tested by using a dummy cell with comparable properties to the system under investigation (see [Clause 8](#) or Reference [1]).

5.1.5 Galvanostat

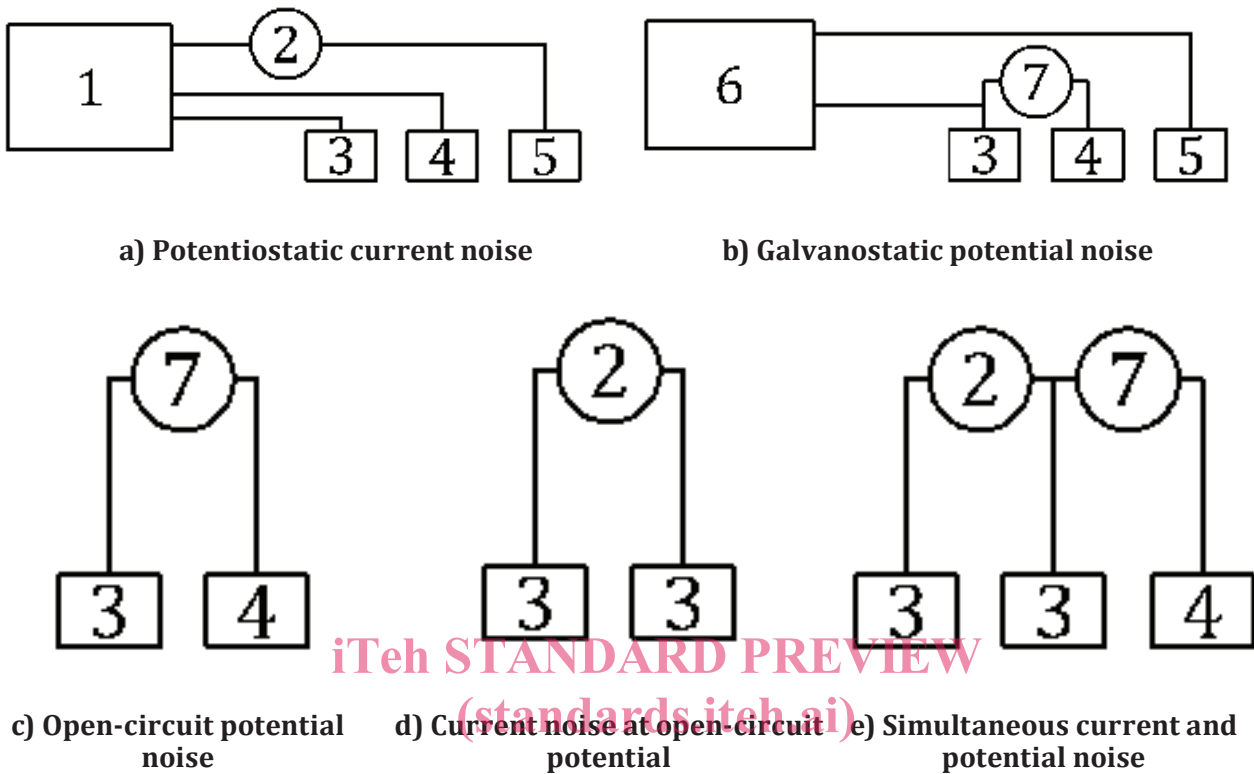
Some measurement configurations use a galvanostat to apply a current to an electrode. The galvanostat shall have low noise characteristics, which should be tested by using a dummy cell with comparable properties to the system under investigation (see [Clause 8](#) or Reference [1]).

5.1.6 Grounding, shielding, and isolation

It is very important to ensure correct grounding and shielding of the measurement system. In particular, there should be a single well-defined connection to ground in order to avoid ground loops and to minimize induced interference. Isolated or differential measuring devices will commonly be required to avoid short-circuit connections to ground and ground loops, especially in plant monitoring conditions.

5.2 Measurement configurations

Schematics of the most important EN measurement configurations can be seen in [Figure 1](#).



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Key

- 1 potentiostat (see 5.1.4)
- 2 current measurement device (see 5.1.3, implies connection to PC or other device for recording or analysis)
- 3 working electrode (WE)
- 4 reference electrode (RE)
- 5 auxiliary electrode (AE)
- 6 galvanostat (see 5.1.5)
- 7 potential measurement device (see 5.1.2, implies connection to PC or other device for recording or analysis)

Figure 1 — Configurations for measurements

5.2.1 Potentiostatic current noise measurement

The current to a potentiostatically controlled working electrode using an inert counter electrode is measured. This is usually used to study individual current transients in localized corrosion, since the controlled potential minimizes fluctuation of current on the passive surface, and permits the potential to be held at a value at which the localized corrosion process occurs. The current can be measured in the lead to the counter electrode, as shown in [Figure 1a](#), or by using a current amplifier that is internal to the potentiostat.

5.2.2 Galvanostatic potential noise measurement

The potential of one galvanostatically controlled working electrode relative to a low-noise reference is measured. This is also used to study individual potential transients in localized corrosion. If an AC current is used, this can also permit the simultaneous estimation of impedance.

5.2.3 Open-circuit potential noise measurement

The potential of one working electrode relative to a low-noise reference electrode or the potential difference between two identical working electrodes is measured in open-circuit conditions. The use of two working electrodes typically reduces the DC component of the measured noise and permits higher sensitivity to be obtained without using very high resolution analogue to digital convertors. It does, however, lose information about the DC potential, which might be useful. This can be used for online corrosion monitoring.

5.2.4 Current noise measurement at open-circuit potential

The current noise between two identical working electrodes is monitored.

5.2.5 Simultaneous current and potential noise measurement

Two identical working electrodes are connected by low voltage burden ammeter, which records the fluctuating current between two electrodes. The potential fluctuations of this coupled electrode pair are recorded with a voltmeter. This is the most common method for measuring coated substrates.

5.3 Signal processing and recording

5.3.1 Digital techniques are used in most EN measurements because of limitations in the accuracy for recording time record and data analysis with analogue methods. Amplifiers are used to convert the current to a voltage and to condition the measured potential. The current and/or potential outputs from amplifiers are filtered and converted to a digital form for recording or analysis.

5.3.2 Filters are used to prevent aliasing that occurs in the conversion of continuous analogue data to discrete signals. To avoid aliasing, it is necessary to remove frequencies above the Nyquist frequency, which reappear as false indications at a low frequency. In most EN measurements, power line frequency noise is a typical example of aliasing to a low frequency. Optionally, high-pass filters can be used to remove the direct current (DC) component of the signal. These shall have a very low knee (or cut-off) frequency (0,01 Hz or less) to avoid removing significant information, and it should be appreciated that this will result in a long settling time when the cell is first connected.

5.3.3 Quantization errors or noise are present due to the finite resolution of analogue to digital converters and can be reduced by increasing the resolution of the converter.

5.3.4 Another unavoidable noise originates from fundamental physical processes of electronic devices. Two forms of noise, shot noise and thermal noise, are present in electrochemical noise measurement devices. In addition, electronic devices produce $1/f$ noise at low frequency.

6 Test cell

The test cell should be prepared according to the general requirements given in ISO 17475.

7 Measurement procedure

7.1 Electrochemical noise measurements can be used in a wide range of applications, and the optimal procedure will vary from case to case. However, the following indicate some factors that should be considered.

7.2 In cases where the conventional, capillary type reference electrode is used, evaluate the electrode in accordance with ISO 17475 and check the noise produced by the reference electrode by measuring the potential noise between two reference electrodes. The noise level of reference electrodes should give a PSD that is at least 10 times lower than the PSD of the system of interest at all frequencies.

7.3 Measure the exposed surface area of the working electrode.

7.4 Assemble the cell with the working electrode(s), reference electrode, and counter electrode (if used).

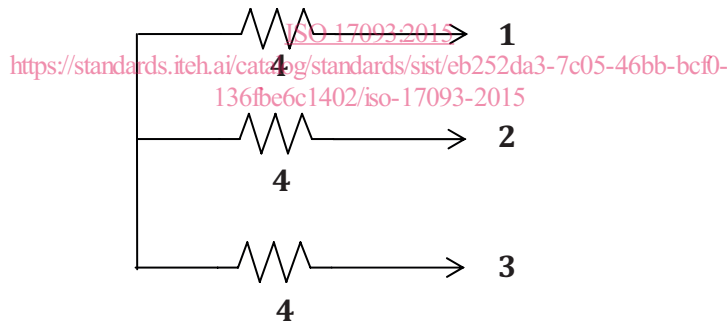
7.5 Add the test solution to the cell (after pre-conditioning, if necessary). Control the temperature to ± 1 °C by immersing the test cell in a controlled-temperature water bath or by other convenient means.

7.6 Record the open-circuit specimen potential, i.e. the free corrosion potential. The period of exposure at open circuit prior to noise measurement will depend on the purpose of the experiment. The measurement can also be started immediately on exposure, but it should be appreciated that analyses requiring a stationary system will not be valid initially.

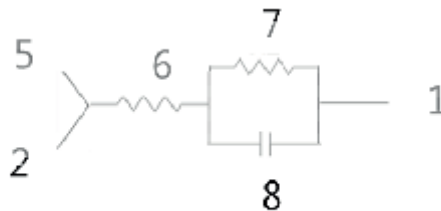
7.7 Obtain and record EN at a predetermined sampling frequency.

8 Evaluation of instrument noise

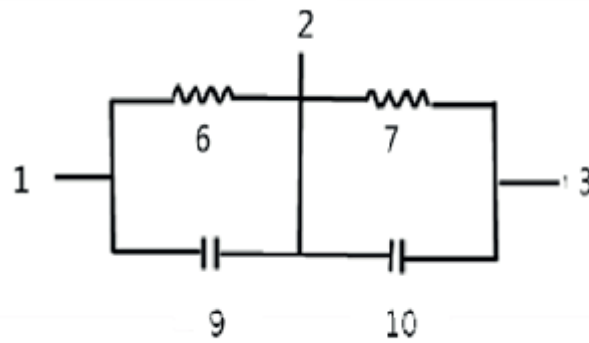
8.1 The EN measurement system should be evaluated for background noise and signal fidelity using dummy cells, such as those shown in Figure 2 (also see Reference [1]). The values of resistance and capacitance should be chosen to be similar to those of solution resistance, polarization resistance, and double layer capacitance expected in the corrosion system to be investigated. The objective of measurements with a 'passive' dummy cell (i.e. one that does not deliberately generate noise above normal thermal noise levels) is to check the instrument noise level with a low noise source, so that this can be compared with measured noise. Calibration of the measurement precision of instruments requires specialized instrumentation and is beyond the scope of this International Standard.



(a)



(b)



(c)

Key

1 and 3	working electrode	5	working or auxiliary electrode
2	reference electrode	8, 9, and 10	capacitors
4, 6, and 7	resistors		

Figure 2 — Dummy cells for evaluation of instrument noise

8.2 Duration of the instrument noise evaluation measurement should be at least twice the period of the lowest frequency of interest, and the sampling frequency should be at least twice the highest frequency of interest, using at least two different sampling frequencies.

8.3 The range setting should be selected to maximize the sensitivity. Avoid using the automatic setting of the measurement parameters (sensitivity, gain, offset correction, etc.), such as “autorange” or use it initially to find the range selected by the instrument, then deselect “autorange” and use this range or the next higher range (to allow for drift) for the EN measurements (with some instruments, the “autorange” setting might cause artefacts in the EN signals when automatically switching ranges).

8.4 For the dummy cell illustrated in [Figure 2a](#), validation of the EN data can be done in the frequency domain by calculating the PSD of the potential and current fluctuations for time records sampled at different sampling frequencies f_s : firstly to check whether an anti-aliasing filter was included in the data acquisition system before the analogue-to-digital converter, secondly to check the good overlap of the PSDs recorded with different sampling frequencies, and thirdly to compare the experimental PSD to the theoretical PSD of the thermal noise, respectively $6 kT R$ for the potential thermal noise and $2 kT/R$ for the current thermal noise generated by the dummy cell with three resistors of resistance R . Details on the calculation of PSDs are described in Reference [1].

8.5 For dummy cells that include capacitance, such as those shown in [Figures 2b](#) and [2c](#), the PSD of thermal noise produced will be frequency dependent. Both potential and current noise baselines are a function of source resistance, and the dummy cell used to evaluate baseline noise should have comparable impedance to the real cell. Please note that it is difficult to achieve baseline noise levels that are comparable to the thermal noise of a resistor; and higher levels are acceptable provided they are significantly lower than the noise to be measured in the system to be investigated.

8.6 Validation of the measured PSDs

The presence of anti-aliasing filters is revealed by a PSD decrease at high frequency, close to the maximum frequency $f_{\max} = f_s/2$ (also known as Nyquist frequency). If the PSD is flat up to f_{\max} , there is no anti-aliasing filter in the data acquisition system and the PSD amplitude is overestimated since it contains the power of the signal at frequencies higher than f_{\max} .