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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 électrochimiques utilisant les techniques de bruit

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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

This standard was prepared by Technical Committee 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).

Corrosion of Metals and Alloys – Guidelines for corrosion test by electrochemical noise measurements

1. Scope

This standard is intended to assist in corrosion testing by electrochemical noise (EN) measurement. It covers test procedures and analysis methods for reliable measurement of EN.

2. Normative references

The following referenced documents are indispensable for the application 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 8044:1999, *Corrosion of metals and alloys – Basic terms and definitions.*
ISO 17475:2005, *Corrosion of metals and alloys – Electrochemical test methods-Guidelines for conducting potentiostatic and potentiodynamic polarization measurements*.

3. Terms and definitions

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

3.1

electrochemical noise

fluctuation typically at low frequencies (≤ 1 Hz) and low amplitude in current and potential generated by electrochemical and other reactions

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) to 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 time record

3.5

power spectral density of potential

***PSD*$_E$**

the power present in the potential noise as a function of frequency

3.6

power spectral density of current

***PSD*$_\text{I}$**

the power present in the current noise as a function of frequency

3.7

electrochemical noise impedance

***Z*$_\text{n}$**

the impedance determined as $Z_n = \sqrt{PSD_E / PSD_I}$ where all terms are a function of frequency; note that the noise impedance is real and positive

3.8

working electrode

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

3.9

counter electrode

electronic conductor in contact with the electrolyte, only to make an electrical connection to the electrolyte so that a current can be applied to the working electrode; usually made out of an inert material (e.g., platinum)

3.10

pseudo-reference electrode

electrode (e.g., platinum wire or sheet) used as reference electrode, but without defined potential and limited stability due to a lack of thermodynamic equilibrium; used for its simplicity, convenience and ease of operation

3.11

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

3.12

thermal noise

noise resulting from thermal vibrations of electrons and charge carriers; thermal noise is the absolute minimum of the noise that can be expected; also called Johnson noise

3.13

shot noise

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

3.14

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

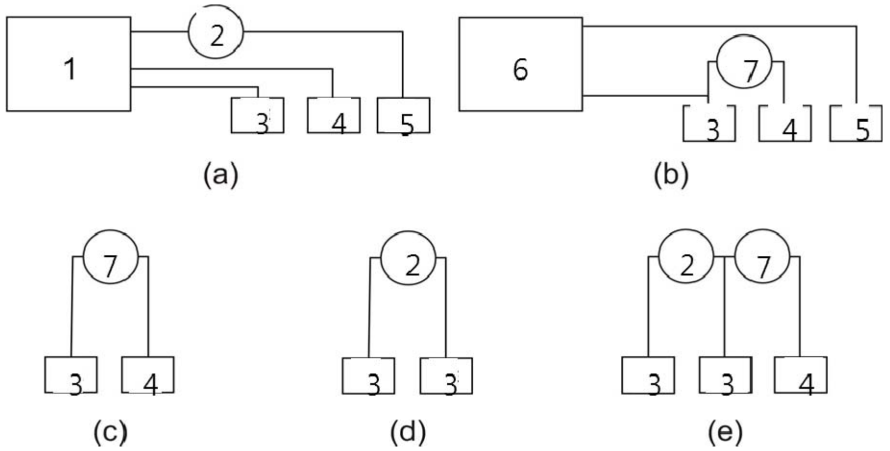
4.1 The source of EN in corrosion may result from partial faradaic currents, adsorption/desorption processes, surface coverage, and, in the case of localized corrosion, the initiation of pits, crevice corrosion and mechanical effects from cracking and several other processes. Special care has to be taken as a variety of other sources not related to corrosion may 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 aluminum during pitting corrosion and on coated carbon steel can be found in Annex B and C.

4.3 Electrochemical noise data may be analyzed in the time and/or frequency domains. Details of data analysis are described in Annex A.

5. Apparatus and measurement methods

Schematics of the most important EN measurement configurations can be seen in Figure 1.



Key:

1	potentiostat (see 5.1.3)
2	current measurement device (see 5.1.2, implies connection to PC or other device for recording or analysis)
3	working electrode (WE)
4	reference electrode (RE)
5	counter electrode (CE)
6	galvanostat (see 5.1.4)
7	potential measurement device (see 5.1.1, implies connection to PC or other device for recording or analysis)

Figure 1 - Configurations for measurements of: (a) potentiostatic current noise, (b) galvanostatic potential noise, (c) open-circuit potential noise, (d) current noise at open-circuit potential and (e) simultaneous current and potential noise.

5.1 Instrumentation

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.

5.1.1 Potential measuring instruments

The instrument should have an input impedance of at least 10^9 Ω to minimize current drawn from the system during measurement. A higher input impedance may 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 μV or lower for the typical range of 1 V.

5.1.2 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.

5.1.3 Potentiostat

Some measurement configurations use a potentiostat to control the potential of an electrode. The potentiostat must 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 [1]).

5.1.4 Galvanostat

Some measurement configurations use a galvanostat to apply a current to an electrode. The galvanostat must 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 [1]).

5.1.5 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 Signal processing and recording

5.2.1 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.

5.2.2 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 DC component of the signal. These must 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.

5.2.3 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.

5.2.4 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.

5.3 Measurement configurations (see Figure 1)

5.3.1 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 may 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.

5.3.2 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.

5.3.3 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 may be useful. This may be used for on-line corrosion monitoring.

5.3.4 Current noise measurement at open-circuit potential

The current noise between two identical working electrodes is monitored.

5.3.5 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.

6. Test cell

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

7. Measurement procedure

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.

7.1 In case 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 ten times lower than the PSD of your system of interest at all frequencies.

7.2 Measure the exposed surface area of the working electrode.

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

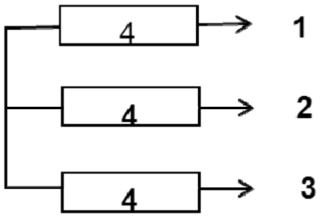
7.4 Add the test solution to the cell (after pre-conditioning if necessary). Control the temperature to ± 1 °C by immersing the test cell in a controlled-temperature water bath or by other convenient means.

7.5 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 care has to be taken that analyses requiring a stationary system will not be valid initially.

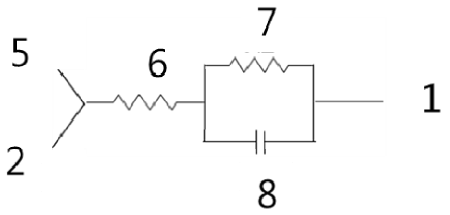
7.6 Obtain and record EN at a predetermined sampling frequency.

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 [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 standard.



(a)



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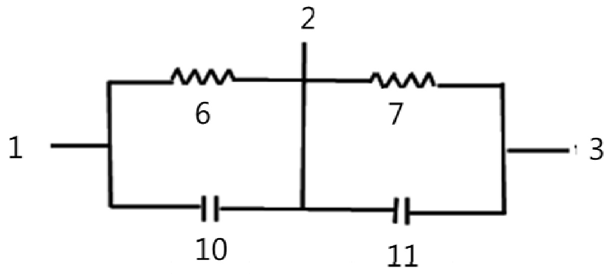


(c)

Key:

1	working electrode 1	5	working or counter electrode	9	working electrode
2	reference electrode	6	resistor 1	10	capacitor 1
3	working electrode 2	7	resistor 2	11	capacitor 2
4	resistor	8	capacitor		

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 may 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 providing 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 $f_{\text{max}} = f_s/2$ (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}.
Further disturbances at certain frequencies, coming from the measurement device or from external sources, can also be identified in the power spectra by the appearance of peaks at the corresponding frequencies.

8.7 Verification of the time domain noise data
The time domain data of the EN measurements should be plotted and checked for identification of problems such as quantization.

9. Test report

The test report should include the following information:

a) a reference to this International Standard;

b) a full description of the test material from which the specimens were taken, composition, method of manufacture of the specimens and details of the surface preparation, heat treatment, type of product;

c) the solution composition, pH, volume and temperature, and any variations with time;

d) area of the working electrode(s) exposed to the test solution;

e) description of cell and electrodes used;

f) type and/or manufacturer of the EN measurement device;

g) time of immersion prior to EN measurement;

h) sampling frequency and duration of EN measurement;

i) plots of time record and/or PSD of current and/or potential noise;

j) methods of trend removal and windowing.

Annex A (informative) – Analysis of data

EN data are analyzed in the time and frequency domains. In the former, the fluctuation of the instantaneous potential or current is analyzed as a function of time and in the latter in terms of power at various frequencies after transforms. This Annex only describes standard methods of data analysis. The reader is referred to the bibliography [2-4] and open literature for further information on the many specialist methods that are being developed.

A.1. Data analysis in the time domain

A.1.1 Transient analysis

A simple way of data analysis in the time domain is to examine the time records for features characteristic of particular types of corrosion. Current and potential transients appear in localized corrosion such as pitting, crevice corrosion and stress corrosion cracking. A comprehensive analysis on the birth, growth and death of transient events is required for the identification of types of corrosion.

A.1.2 Noise resistance, R_n

The EN resistance is defined as the standard deviation of potential noise (S_E) divided by the standard deviation of current noise (S_I): $R_n=S_E/S_I$

This value may also be multiplied by the area of specimen exposed to solution to give units of Ohm m^2. Providing a number of assumptions are valid, it can be shown theoretically, and has been confirmed experimentally, that R_n is equivalent to the linear polarization resistance, and it can be used in the same way to estimate corrosion rate. However, this analysis should be checked for any systems that have not previously been studied. Noise resistance incorporates the solution resistance in the same way as the polarization resistance.

A.1.3 Mean

The mean potential over long term may be directly related to the changes in corrosion processes occurring. The mean current is expected to be zero when nominally identical electrodes are used, and non-zero values of mean current may provide information on the dissimilarity of the electrodes.

A.1.4 Variance, standard deviation and root mean square

The variance of a signal depends on the range of frequencies included in the signal. The variance of the current will often be found to increase as the rate of corrosion process increases and as the corrosion becomes more localized. The variance of the potential is often found to decrease as the rate of corrosion process increases but to increase as the corrosion becomes more localized. The variance, standard deviation and root mean square are related, and the interpretation of standard deviation and root mean square are essentially equivalent to that of the variance.

A.1.5 Kurtosis and skew

Kurtosis is a measure of the shape of the distribution compared with the normal distribution. A positive Kurtosis indicates a more spiky distribution, whereas a negative Kurtosis indicates a flatter distribution.

Skew or skewness is a measure of the symmetry of the distribution. A positive skew implies that there is tail in the positive direction, whereas a negative skew implies that there is tail in the negative direction.

Kurtosis and skew may provide information about localized corrosion, but the values of the parameters have a relatively large uncertainty and are not considered to be significantly different unless they show quite large differences.

A.1.6 Coefficient of variation
The coefficient of variation (the standard deviation divided by the mean) is a measure of the noisiness of the signal compared with mean value. More detailed examination is required for this parameter because in case the mean is close to zero, the coefficient of variation will be close to infinite, regardless of the standard deviation and will give false information about the localized corrosion.

A.2. Data analysis in the frequency domain

A.2.1 In this analysis, the power spectrum is usually estimated using transforms of time records, mainly performed using the Fourier transform or the Maximum Entropy Method (MEM).

A.2.2 The power spectral density (PSD) is a measure of the power of the signal as a function of frequency. The unit of PSD is represented by power per Hertz, V^2/Hz or A^2/Hz (the square root of the PSD, $V/\sqrt{Hz}$ or $A/\sqrt{Hz}$ may equivalently be reported).

A.2.3 In spectral estimation the signal should be stationary, and it is common to remove the drift, usually by subtracting a linear regression line from the data. It should be appreciated that trend removal can produce a low frequency plateau in MEM spectra.

A2.4. Windowing is often used in spectral estimation and done by multiplying the time series by a windowing function to select the time record for analysis. Windowing must be applied after trend removal in A.2.3.

A.2.5 In power spectrum estimation, the maximum frequency that can be analyzed is the Nyquist frequency and the frequency resolution, and hence the lowest frequency that can be analyzed, is limited by duration of the time record, that is, 1/(time record duration). The MEM algorithm produces a set of coefficients that allow calculation of the PSD outside the valid frequency range, but the results are not valid.

A.2.6 The results of the MEM are strongly dependent on the order used in the analysis (in essence the number of coefficients used for the model that is fitted to the measured data), and misleading results can be obtained if an inappropriate order is used. For this reason, spectra produced using the MEM algorithm should always be validated against spectra produced using the Fourier transform.

A.2.7 Parameters such as the PSD at low frequency, the roll-off slope and the transition frequency of power spectra are sometimes used to obtain the information about the type of corrosion occurring, but there is still no consensus regarding their validity.

A.2.8 Electrochemical noise impedance can be calculated as $Z_n = \sqrt{PSD_E / PSD_I}$, where PSD_E and PSD_I are the power spectral densities of potential and current, when using two working electrodes connected through a ZRA. When identical working electrodes and a true reference electrode are used, it is comparable to the modulus of the electrochemical impedance of each electrode measured by conventional methods. No reliable estimation of phase angle is possible.

Annex B (informative) – Example of EN measurements on pitting corrosion of aluminum

An example of a rather simple test on EN measurements, adopted from a round-robin experiment performed in the 1990s by Goellner et al. [5], is shown in the current Annex. This test assumes a three electrode EN measurement setup, in which current and potential noise are measured simultaneously (see Clause 5.3.5). The EN signals of aluminum coupons are recorded in the passive state (in borate buffer solution, pH = 6,4), during metastable pitting corrosion (in 0,1 M NaCl solution) and in the repassivated state (in 0,5 M $NaNO_3$ solution, inhibitor). In the following Clauses detailed instructions on how to perform this test and examples of results are given.

B.1. Testing procedure and specimen preparation

B.1.1 Before the experiment the EN measurement device and the reference electrode should be assessed according to Clauses 7.1 and 8.

B.1.2 Preparation of the test solutions (please note the higher initial concentrations of the solutions; only after putting them together you will get the desired concentrations):
a) borate buffer solution (pH = 6,4): 3,81 g $Na_2B_4O_7$ ($\cdot 10\ H_2O$) and 30,92 g H_3BO_3 in 1 L deionized water,
b) 1 M NaCl solution: 58,44 g NaCl in 1 L deionized water,
c) 4 M $NaNO_3$ solution: 340 g $NaNO_3$ in 1 L deionized water.

B.1.3 Preparation of the specimens (WEs 1 and 2): embed two aluminum coupons (99,8 % purity, with metal wire attached to the specimens) in epoxy resin, wet grind with emery paper (25 µm grain size), rinse with deionized water and alcohol.

B.1.4 Fill beaker with solution a (*V* = 0,405 L) and prepare the reference electrode setup with Haber-Luggin capillary (see Figure B.1).

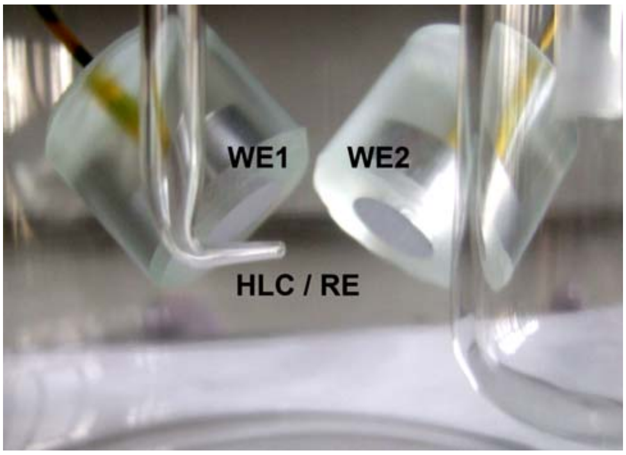


Figure B.1- EN measurement setup (WE = working electrode(s), RE = reference electrode, HLC = Haber-Luggin capillary).

B.1.5 Immerse both specimens into solution a according to Figure 3 immediately after preparation of the specimens.

B.1.6 Start EN measurement 1 h after immersion of the specimens: EN measurement with a sampling frequency of 1 Hz (or as close as possible to 1 Hz).

B.1.7 Stop EN measurement after 10 min.

B.1.8 Add solution b (V = 0,045 L).

B.1.9 Start EN measurement 4 min after addition of solution b.

B.1.10 Stop EN measurement after 10 min.

B.1.11 Add solution c (V = 0,643 L).

B.1.12 Start EN measurement 4 min after addition of solution c.

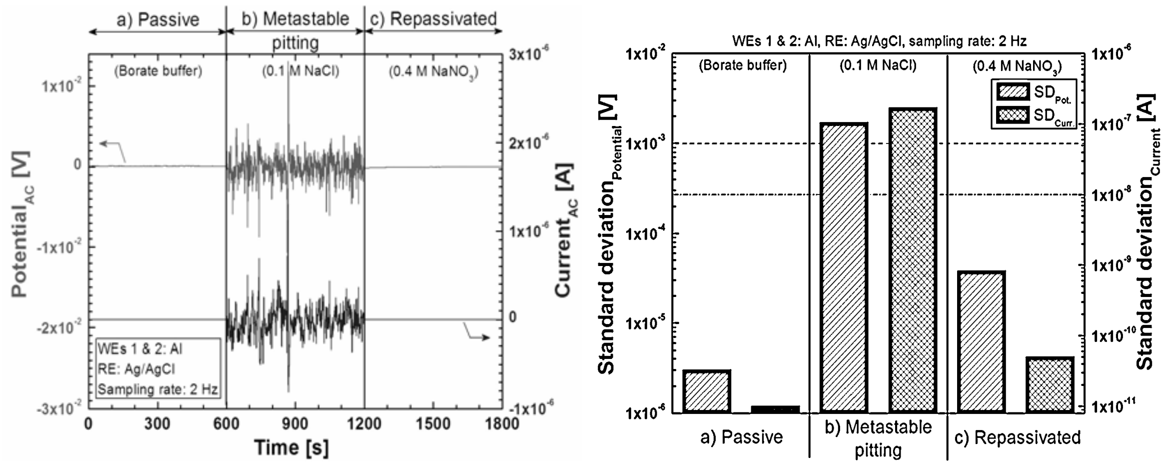
B.1.10 Stop EN measurement after 10 min.

B.2. Data analysis and reporting

The three time records of the current and potential noise measured in the three solutions should be plotted (preferably after removal of the DC component of the signals) and the standard deviation over each of the three sections should be calculated. A frequency domain analysis (see Annex A.2.) would complete the evaluation, although in this specific case no major additional information about the corrosion process would be gained. The results should be reported according to Clause 9. The standard deviation of section b (metastable pitting) should be above 10^{-3} V for the potential and 10^{-8} A for the current and at least an order of magnitude higher than the standard deviations of sections a and b (passive regions).

B.3. Typical results

Figure B.2 shows typical results of the described experiment. The corresponding test information can be found in Table B.1.



(a) (b)

Figure B.2 - Time records (a) of the potential and current signals (without DC component of the signals, achieved by high-pass filtering with a cut-off frequency of 0,01 Hz) measured according to the procedure described in Annex B.1. and the corresponding standard deviations (b).

Table B.1 - Example of a test report (according to Clause 9).

a) Measurements according to:	ISO xxxxx
b) Test material:	Al (99,8 % purity), rod material, wet grinded with emery paper (25 µm grain size)
c) Test solutions:	$T = 23$ °C (±1 °C), a) Borate buffer solution (pH = 6.4) b) 0,1 M NaCl solution c) 0,5 M $NaNO_3$ solution
d) Area of the specimen(s) exposed to the test solution:	WE area $A = 9 \cdot 10^{-5}$ m^2
e) Cell and electrodes:	RE = saturated silver/silver chloride electrode (E = 0,199 V vs. standard hydrogen electrode), cell arrangement: see Figure B.1
f) Type and manufacturer of the EN measurement device:	Simultaneous measurement of current (zero resistant ammeter) and potential (high impedance voltmeter) with a three electrode setup; device manufacturer: IPS, Germany (software: EcmNoise)
g) Time of immersion prior to EN measurement:	t = 1 h
h) Sampling frequency and duration of EN measurement:	f_s = 2 Hz, t = 3 x 10 min
i) Plots of time record and standard deviation of current and potential noise:	See Figure 4
j) Method of trend removal:	High-pass filtering with a cut-off frequency of f = 0,01 Hz

Annex C (informative) − Example of EN measurements on organically coated carbon steel

Four examples of EN noise data collected from organically coated steel with a range of protective properties are shown in this Annex. ENM was used to rank the level of protection afforded by these organic coatings.

C.1. Testing procedure and specimen preparation

C.1.1 Before the experiment the EN measurement device should be tested according to Claus 8 particularly for its current sensitivity. This is because a much lower level of current flows between working electrodes when coated with organic coatings.

C. 1.2 Test solution used here was 0,5 M NaCl solution

C.1.3 Specimens were prepared by affixing PVC tubes (1,9 cm^2 internal diameter) on the coating surface using epoxy glue. Specimens were left for 24 hours before the experiment for epoxy glue to fully dry.

C.1.4. PVC tubes were filled with test solution 24 hours before the experiment. In the case of coated metal an equilibrium time is required for text solution to penetrate the coating if the coating is dry and non-degraded. The equilibrium time increases with coating thickness and barrier properties [6]. For dry coatings, repetitive EN measurement is recommended until steady results are obtained.

C.1.5 The two working electrodes and a saturated calomel electrode (SCE) were connected to the EN measurement device in salt bridge configuration as shown in Figure C.1.

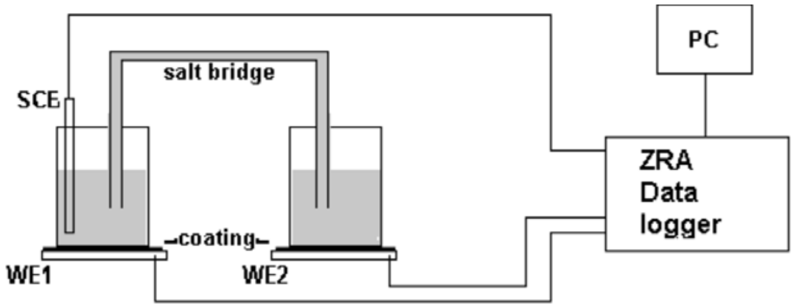


Figure C.1 - EN measurement setup (WE1 & WE2 = working electrode(s), SCE = saturated calomel electrode as the reference electrode).

C.1.6 EN data was collected with sampling frequency of 2 Hz for 512 seconds (1024 data points).

C.2. Data analysis and reporting

The raw data was treated for DC trend removal using moving average method and tested for normal (Gaussian) distribution of data points. Standard deviation of current and potential data was calculated and used to derive the noise resistance according to Claus A.1.2.

C.3. Typical results

Figures C.2-C.5 show typical results acquired from coated steel with a range of noise resistance from 2x10^{10} Ω to 8x10^{7} Ω. Note that the unit of current and potential axis are mA and mV, respectively.

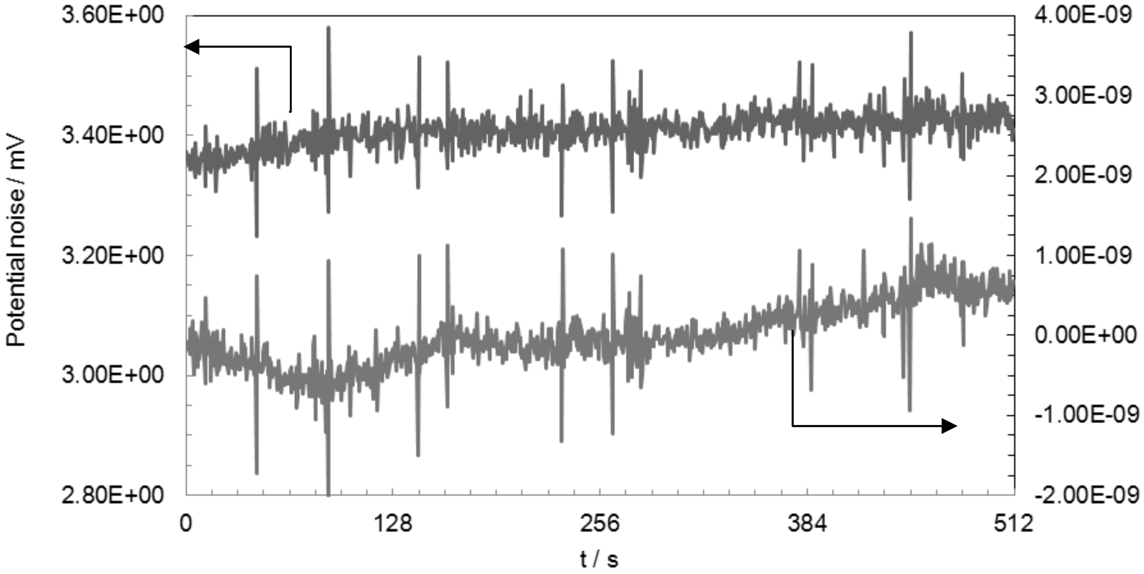


Figure C.2 - Time records of the potential and current signals from steel coated with a zinc phosphate pigmented vinyl paint with thickness of 90 µm, R_n=7.6x10^{7} Ω.cm^{2}.

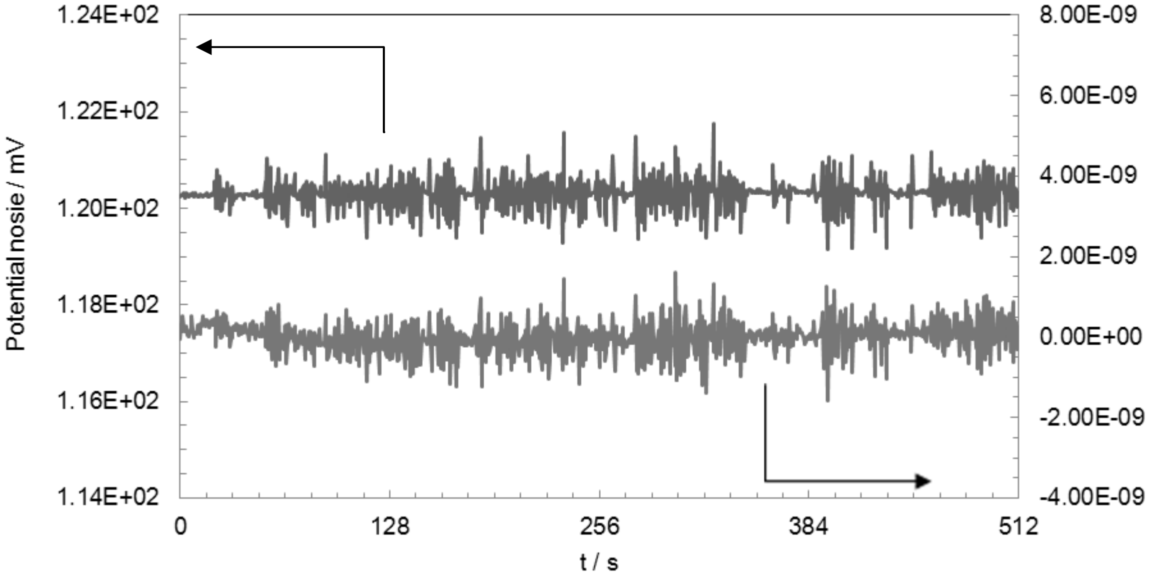


Figure C.3 - Time records of the potential and current signals from steel coated with a maintenance alkyd paint pigmented with calcium diphosphate pigment with thickness of 90 µm, R_n=7.7x10^{8} Ω.cm^{2}.

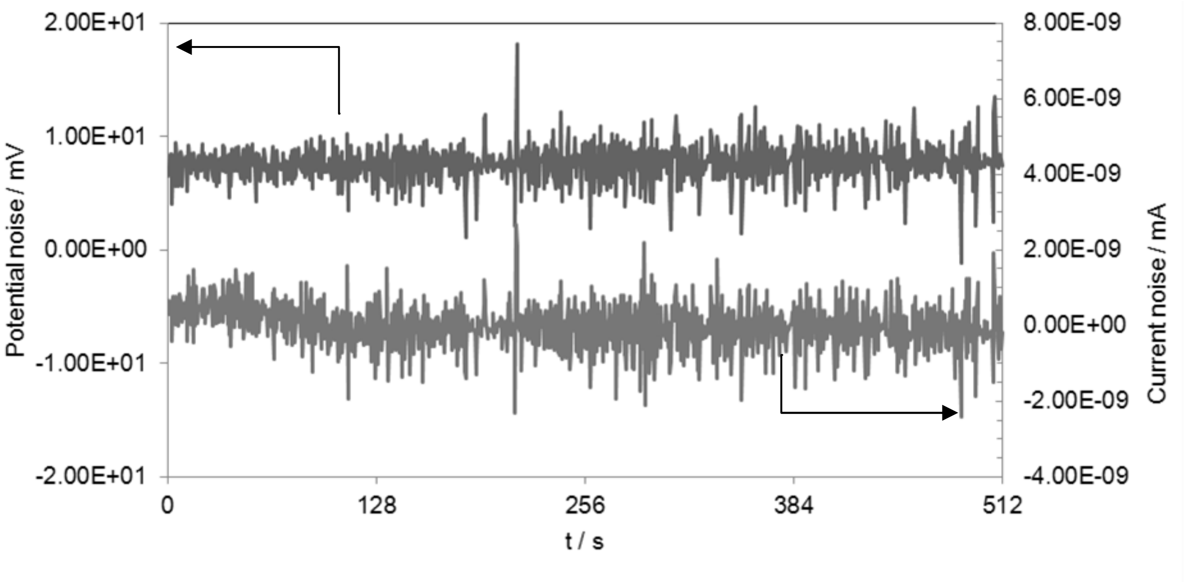


Figure C.4 - Time records of the potential and current signals from steel coated with a soya based alkyd varnish with thickness of 90 µm, $R_n=2.7\times10^9\ \Omega.cm^2$.

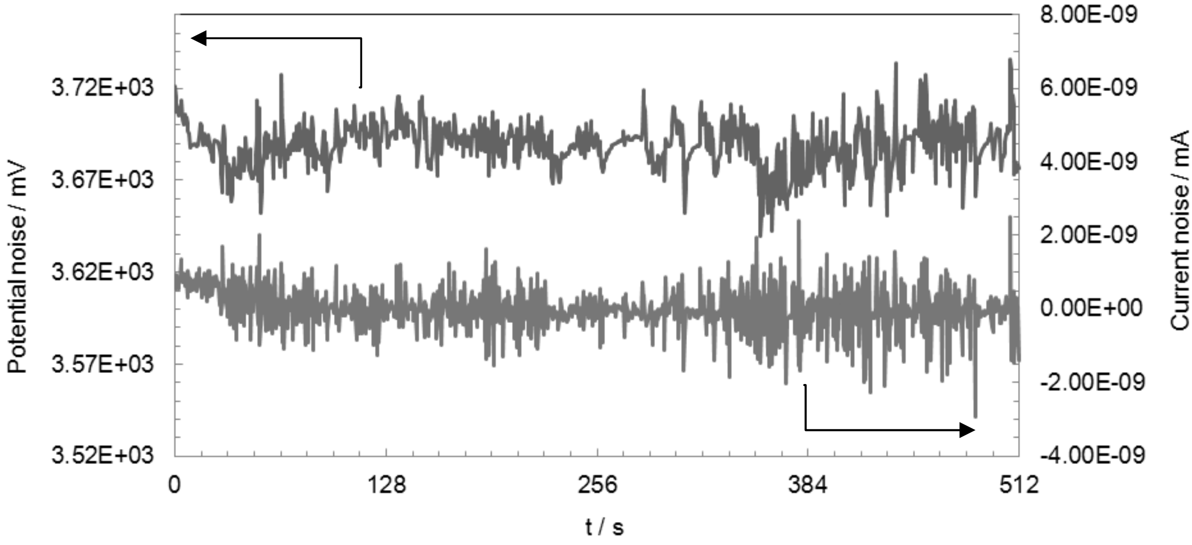


Figure C.5 - Time records of the potential and current signals from steel coated with an epoxy coating with thickness of 150 µm, assigned $R_n=2\times10^{10}\ \Omega.cm^2$.

Table C.2 - Example of a test report (according to Clause 9).

a) Measurements according to:	ISO xxxxx
b) Test material:	Mild steel Q-panel coated with organic paint
c) Test solutions:	0,5 M NaCl solution at ambient temperature T = 20 °C (±2 °C)
d) Area of the specimen(s) exposed to the test solution:	WE area $A = 11.4 \cdot 10^{-2}$ m^2
e) Cell and electrodes:	RE = saturated calomel electrode (E = 0,244 V vs. standard hydrogen electrode), cell arrangement: simultaneous current and potential noise measurement using standard salt bridge connection (see Figure C.4)
f) Type and manufacturer of the EN measurement device:	Simultaneous measurement of current (ZRA) and potential using Gill AC (potentiostat, galvanostat, ZRA) manufactured by ACM instruments, UK
g) Time of immersion prior to EN measurement:	t = 24 hr
h) Sampling frequency and duration of EN measurement:	f_s = 2 Hz, t = 512 sec
i) Plots of time record and standard deviation of current and potential noise:	See Figures C.2-C.5
j) Method of trend removal:	Moving average

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