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Electrochemical impedance spectroscopy (EIS) on coated and uncoated metallic specimens —

Part 2:
Collection of data

Spectroscopie d'impédance électrochimique (SIE) sur des éprouvettes métalliques revêtues et non revêtues —

Partie 2: Recueil des données

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Foreword

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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).

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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 35, *Paints and varnishes*, Subcommittee SC 9, *General test methods for paints and varnishes*.

This second edition cancels and replaces the first edition (ISO 16773-2:2007), which has been technically revised. The main changes are the following:

a) the introductory element of the title, *Paints and varnishes*, has been omitted, because the scope is broadened to include metals and alloys and the main element of the title has been changed to: *Electrochemical impedance spectroscopy (EIS) on coated and uncoated metallic specimens*;

b) a reference to ISO/TR 16208 has been added;

c) considerations about the precise determination of the exposed area have been added as an informative annex;

d) a test report has been added.

ISO 16773 consists of the following parts, under the general title *Electrochemical impedance spectroscopy (EIS) on coated and uncoated metallic specimens*:

- *Part 1: Terms and definitions*
- *Part 2: Collection of data*
- *Part 3: Processing and analysis of data from dummy cells*
- *Part 4: Examples of spectra of polymer-coated and uncoated specimens*

Electrochemical impedance spectroscopy (EIS) on coated and uncoated metallic specimens —

Part 2:
Collection of data

1 Scope

This part of ISO 16773 gives guidelines for optimizing the collection of EIS data with focus on high-impedance systems. High impedance in the context of intact coatings refers to systems with an impedance greater than $10^9\ \Omega\cdot\text{cm}^2$. This does not preclude measurements on systems with lower impedance. For uncoated samples extra information can be found in ISO/TR 16208.

This part of ISO 16773 deals with the following:

— instrumental set-up: requirements and pit-falls;

— data validation: checking the measurement range and the accuracy of the data;

— performing an EIS measurement: specimen considerations and instrumental parameters;

— the experimental results: different methods of presenting EIS data.

These guidelines are intended to ensure the acquisition of EIS data that can be used to study the performance of the specimen. This part of ISO 16773 does not give guidelines for the interpretation of the data.

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

3 Terms and definitions

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

4 Principle

A so-called “confidence” test is described in order to check the suitability of the entire set-up and recommendations are given as to how to perform EIS experiments. For convenience, only potentiostatically controlled EIS measurements are described, although it is also possible to make EIS measurements under galvanostatic control.

A potentiostat is connected either to a dummy cell or to an electrochemical cell (with working, counter- and reference electrodes). A single-sinusoidal- or multi-sinusoidal-waveform potential, either in conjunction with a d.c. offset or not, is applied by the potentiostat to the dummy cell or to the electrochemical cell, and the resulting a.c. current is measured. Both potential and a.c. current data are collected and analysed for amplitude and phase shift. This can be done in a variety of ways, depending on the type of equipment used. All data are presented and compared graphically or computed for equivalent circuits. In the case of the dummy cell, the values of these equivalent components are compared to the actual cell components connected to the potentiostat and evaluated for coherence.

5 Electrochemical cell

5.1 General

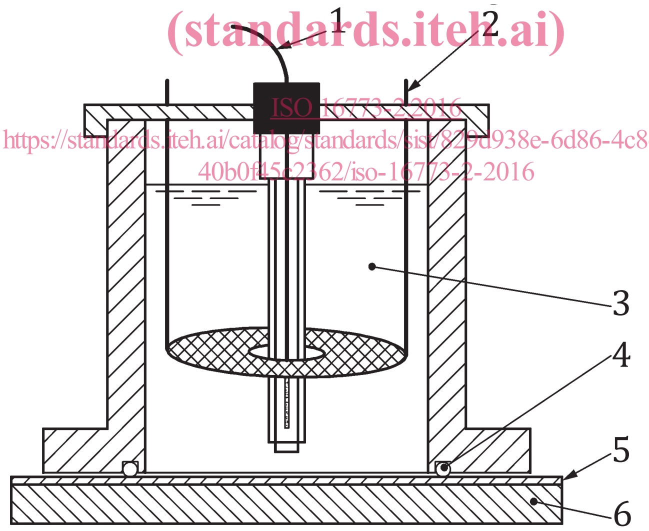
NOTE 1 Various types of measurement cell exist which are suitable for use with this part of ISO 16773. Most commonly used are two-electrode and three-electrode arrangements for measurements in an aqueous electrolyte.

The cell shall be constructed of materials that will not corrode, otherwise deteriorate or contaminate the solution (e.g. PMMA, PTFE or glass). A material compatibility test should be carried out.

The cell shall be leak-proof to ensure that the geometrical surface of the specimen does not change with time. Use an electrically insulating gasket material (O-ring, etc.) for the seal, i.e. with a through-thickness resistance much greater than that of the coating.

The cell should preferably be designed to allow the following items to be inserted into the electrolyte chamber: the working electrode, the reference electrode, the counter-electrode, a thermometer (for temperature control) and gas inlet/outlet tubes to modify the oxygen content of the electrolyte. When using an inert gas, a gas scrubber should be used.

An example of an electrochemical cell is shown in Figure 1.



Key

1	reference electrode
2	counter electrode
3	electrolyte
4	O-ring
5	coating
6	working electrode

Figure 1 — Example of an electrochemical cell

NOTE 2 Other designs can be suitable.

For uncoated metallic specimens, IR drop should be considered.

The components shown in Figure 1 are described in 5.2 to 5.4.

5.2 Electrodes

To perform EIS in aqueous solution, the more conventional set-up is composed of a three-electrode arrangement: a working electrode, a reference electrode and a counter-electrode.

Working electrode: A conductive substrate covered by the coating to be investigated. A large surface area is preferred to better take into account any defects and to decrease the impedance of the system to give a better signal-to-noise ratio.

Counter electrode: Inert material such as platinum with a large surface area oriented parallel to the working electrode in order to ensure a homogeneous current distribution.

Reference electrode: A low-impedance and low-noise reference electrode is recommended, according to supplier's user manual [when testing organic coatings, a salt bridge (e.g. Luggin capillary) is not required]. The potential of the reference electrode should be checked periodically to control the accuracy of the electrode and its stability with time. At very high frequencies, the presence of the reference electrode can induce some spurious effects.

NOTE 1 To improve the quality of the high-frequency signal, a platinum wire with a capacitor may be placed in parallel with the reference electrode. The capacitor ensures that the d.c. potential is coming from the reference electrode and a.c. potential from the platinum wire.

NOTE 2 For specific applications, it can be acceptable to use a pseudo-reference electrode consisting of an inert material such as a high-nickel alloy or a chloridized silver wire. Pseudo-reference electrodes are useful for measurements in the field, where a reference electrode can be easily broken.

5.3 Exposed area

The exposed area should be known, constant with time, and should be adequate for the investigation. The larger the exposed area the more sensitive the measurement is to single defects (pores) and the better the signal-to-noise ratio.

If an O-ring is used, the precise exposed area shall be determined under compression (see Annex C for a recommended technique).

NOTE For example, when using an O-ring with a diameter of 1,2 cm and an approximate exposed area of 1,13 cm^2, an error of up 37 % can occur. When using an O-ring with a diameter of 4,7 cm and an approximate exposed area of 18 cm^2, an error of up 8 % can occur.

It is recommended that the user selects the largest possible area without defects. A typical area is in the order of magnitude of 10 cm^2.

5.4 Electrolyte

The resistance of the solution should be low in comparison to the impedance of the investigated system. Different types of electrolyte can be used. Non-aggressive electrolytes can be employed to characterize the properties of the system without introducing corrosion. An aggressive solution may be selected to characterize the corrosion resistance of the system. The electrolyte should be chosen with the end use in mind.

NOTE 1 For the desired end-use, the pH value, the concentration and the composition of the electrolyte might be important parameters.

When the oxygen content is influencing the corrosion, the preconditioning has to be chosen in a way that a steady state is established.

NOTE 2 Purging with oxygen or an inert gas could be necessary to obtain steady state condition.

6 Procedure

6.1 Grounding

An EIS instrument consists of a potentiostat, a computer and a module or instrument specifically required for the impedance measurement.

Electrical grounding considerations between the instruments, the specimen and the environment are important, both for the safety of the operator and the acquisition of as accurate and noise-free EIS data as possible.

a) The safety of the operator is important. The chassis of the EIS instrument should be connected to ground to avoid a potentially lethal electrical shock if the instrument malfunctions. The chassis is normally grounded through the connection to the a.c. mains. Under no circumstances should this connection to ground be bypassed.

b) In most cases, the coated specimen is tested in the laboratory in an electrochemical cell such as that described in 5.1 in which the specimen is electrically isolated from ground, or “floating”. This is the simplest case with no special consideration needed for connection of the instrument to the specimen.

c) If, however, the coated specimen is grounded, then the grounding considerations become more complex. This could happen if EIS is used to test coated structures in a field, such as vessels or pipelines. If the coated specimen is grounded, then the EIS instrument should be electrically isolated from ground to obtain accurate EIS data. This is not a trivial consideration and is generally taken into account during the design of the EIS system. Floating the EIS system by bypassing the protective ground connection to the mains is a safety hazard and is not acceptable.

d) When connecting up the various instruments and computers, it is possible to inadvertently ground a floating instrument through the connection to a grounded instrument. This can give rise to noise through “ground loops” or even result in improper operation.

6.2 Shielding

Shielding is very important for noise considerations in EIS measurements of high-impedance specimens. Proper shielding will ensure that the cell electrodes and cables will not pick up electromagnetic radiation from the surroundings. The electrochemical cell should be placed inside a Faraday cage and the Faraday cage connected to an appropriate ground connection of the potentiostat. If the potentiostat has an externally mounted electrometer, the electrometer should also be put inside the Faraday cage. The manufacturer’s manual should be consulted to ensure proper wiring.

6.3 Cell cable ground contacts

The connections between the cell cables and the cell should be clean and the length of the cables should be as short as possible to minimize stray capacitance.

6.4 Local conditions

The following conditions in the vicinity of the EIS experiment can affect the quality of the measurement.

a) The incoming a.c. power to the EIS instrument can be noisy or exhibit large voltage transients, both of which can result in noise in the electrochemical data. If severe, the user may install an a.c. line conditioner. The raw potential and current data are usually averaged by the EIS instrument and are not as susceptible to line noise as d.c. experiments.

b) Electromagnetic noise from electrical devices (e.g. computer monitors) in the local vicinity of the EIS experiment can also contribute to noise in the experiment. Again, data processing will discriminate against this noise. Instruments or appliances that operate intermittently (e.g. freezers, ovens, ultrasonic cleaners, magnetic stirrers, water baths) are particularly troublesome because they can introduce noise in the electrical circuit when they are activated. These devices should be operated on a different circuit, if possible. Because of the low current levels which are typically observed in EIS experiments on coated specimens, the specimen should always be contained in a Faraday cage that is connected to the appropriate instrument ground.

c) The relative humidity in the environment can also be of concern. If the relative humidity is high, then micro-condensation can occur in the electronics of the EIS instrument, providing a low-impedance leakage path. At the low current levels typically encountered in EIS experiments on coated specimens, this can result in errors in the current measurement.

6.5 Measurement equipment characteristics

An electrochemical cell has impedance values that can range from 1 mΩ to more than 1 TΩ (10^{12} Ω). The measured impedance of coated specimens can range up to 10^{12} Ω.

A specimen with high impedance will exhibit very low current flow during the EIS experiment. Therefore, the instrument used to measure the EIS of coated specimens needs to be capable of measuring these low currents. The test described in 6.6 is useful to make sure an EIS instrument is capable of measuring coated specimens.

All equipment should be able to measure the dummy cell described in 6.6.1.

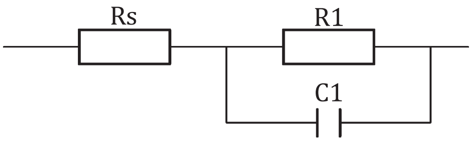
Sometimes, it might be desirable to perform an open-lead test in order to find the limits of the entire set-up under the given conditions. A method of estimating the maximum measurable impedance with the open-lead test is given in Annex A.

NOTE EIS measurements on high-impedance coatings are not limited to the above-mentioned cell designs.

6.6 Confidence test

6.6.1 General

In order to obtain confidence in the entire experimental set-up, it is recommended that a confidence test be carried out prior to measurements of real specimens. Confidence can be obtained by carrying out reference tests using hard-wired dummy circuits with known values for capacitance and resistance. These values should be in the order of magnitude which can be expected for the actual coated specimen under investigation. As high-impedance coatings easily reach values of several gigaohms, combined with low capacitance of about 100 pF, it is recommended that the circuit in Figure 2 be used as a reference.



Key

R1 50 GΩ

C1 150 pF

Rs 50 Ω

Figure 2 — Dummy cell for confidence test

6.6.2 Use of interlaboratory test cells for confidence test

Because significant knowledge has been gathered during the performance of a related interlaboratory test, similar circuits with similar values, as used in the interlaboratory test, could be used for the confidence test.

NOTE Details are given in ISO 16773-3.

6.6.3 Error estimate and accuracy

Data for error estimate, accuracy, reproducibility and repeatability are not currently available. They will be provided after the completion of an interlaboratory test.

6.7 Specimens

6.7.1 Preconditioning of specimens

Proper preparation and preconditioning of coated specimens is critical for successful and reliable EIS data.

6.7.2 Environmental control

The coating should be applied and cured in accordance with the manufacturer's recommendation unless otherwise agreed upon between the participating parties.

The film thickness should be as uniform as possible. The exact film thickness should be measured and reported (e.g. in accordance with ISO 2808).

Temperature and humidity control during the application, curing, conditioning and impedance measurement of organic coatings is crucial for a proper determination of the coating resistance.

NOTE The standard temperature and relative humidity for application, conditioning and testing of organic coatings is specified in ISO 3270, i.e. (23 ± 2) °C and a relative humidity of (50 ± 5) %.

The temperature of the specimens during the impedance measurements should be held constant to within ±2 °C, preferably within ±1 °C. Relative values for comparison between specimens outside these guidelines are acceptable if all the specimens are run under the same conditions.

When the coating capacitance is the main parameter of interest, control of relative humidity during specimen conditioning is very important.

For reliable measurements, temperature control should be equal to or better than ±1 °C. For conditioning prior to measurement, an accuracy of ±2 °C is sufficient for most cases. Each specimen should be kept under controlled conditions in order to prevent post-curing, degradation or any unintended irreversible modification of the coating.

6.8 Evaluation of laboratory and field coating specimens

Impedance measurements can be used to further characterize coating degradation during a weathering test. Impedance is measured on separate specimens after different elapsed times during the test and on completion of the test. Such weathering tests can be salt spray exposure in accordance with ISO 9227, exposure in a humidity chamber in accordance with ISO 6270-1, or cyclic tests such as those described in ISO 20340:2009, Annex A. Other test methods are also used.

When the coated panels are removed from the test chamber for impedance measurements, they typically go through a change in temperature and humidity. Some drying-out can occur if they are removed for more than a few minutes. Further, the coating is exposed to an electrolyte in the electrochemical cell, which can be different from the fluid in the test chamber. Therefore, special attention should be given to the precise procedure and timing when changing, removing and replacing specimens for measurement. The procedural details should be reported with the results.

If the impedance measurement is done in an aggressive electrolyte (e.g. an organic solvent), the exposure of the coating to the electrolyte can be considered as an additional component of the weathering test.

In the case of cyclic weathering tests, impedance measurements will depend upon the specific cycle the test panels are in. To allow comparison of impedance measurements to reveal trends and changes, sequential impedance measurements should be taken at the same time and in the same part of the cycle.

Stray currents can occur when impedance is measured on a wet surface, even when the measured area is some distance from a scribe or other artificial holidays. These stray currents can simulate a damaged coating, even if the coating is in excellent condition. Therefore, it is recommended that preventive measures, such as drying the non-measured area as completely as possible, be taken to avoid stray currents or other potential sources of error.

6.9 Number of specimens and repeatability of results

Coatings are materials with certain inherent properties: holidays, inhomogeneous film thickness, and non-uniform distribution of pigments, fillers and other constituents. It is therefore necessary to test more than one panel. In most cases, a minimum of three replicate specimens is necessary for reliable results. It should be checked if the uniformity between the different specimen plates is sufficient. It is quite common to find repeatability better than 10 % between the capacitance of replicate specimens, but this depends on the type of coating and the conditions of measurement. More replicates might be necessary to overcome uniformity problems.

NOTE The accuracy of the determination of the exposed area might have a significant impact on the repeatability of coating parameters determined by EIS.

Such checks should be the responsibility of the operator and should also be agreed between the parties involved.

Specimens undergoing a rapid change, caused by weathering or other effects producing degradation, can show a larger fluctuation and therefore a lower repeatability.

Most measurement cells contain an electrolyte that is the medium between the coating and the counter-electrode. This means that the dominant process in the first 24 h is the absorption of electrolyte by the coating. To follow this process, the impedance of the coating should be measured more frequently at the beginning, the exact frequency depending on the system.

The accuracy, reliability and repeatability of the experimental set-up should be determined on the dummy cell.

7 Instrumental parameters

7.1 General

Before running an impedance experiment, enter those parameters necessary to set up the instrument for the measurement. Most computer-controlled instruments have software that provides the set-up of these parameters. At this point, assume these parameters have been set correctly and the signals applied to the electrode are consistent with the required set-up. Although different manufacturers each have their specific way(s) of setting these parameters, this part of ISO 16773 focuses only on those parameters that are relevant to the test and need to be specifically controlled.

This part of ISO 16773 describes only the standard method based on single-sine techniques. It does not apply to other ways of collecting EIS spectra, such as multi-sine-waveform techniques. In addition, it is limited to impedance spectra produced in the potentiostatic operating mode. This means that the potential will be controlled at the working electrode and the current measured as a function of the perturbation in the potential.

7.2 Conditioning potential and conditioning time

If the test is performed on a dummy cell, the conditioning potential and conditioning time need not be entered. They provide electrochemical treatment to the specimen before the actual measurement is started. They are sometimes also referred to as delay timing or equilibration timing.

7.3 Frequency spectrum

Most of the coating information will be found between 100 kHz and 0,01 Hz.

The frequency spectrum is the range of frequencies that is applied to the cell. In most high-impedance coating applications, high frequencies (above 10 kHz) will not be used, since most of the characteristic information of the coating will be found below this frequency. Therefore, the recommended high-frequency limit is 100 kHz.

The low-frequency limit will vary with the application. As a general comment, the minimum frequency should be low enough so that the impedance assumes a constant value. Precise work on high-impedance coatings might require frequencies as low as 0,000 1 Hz for determination of the limiting resistance and other characteristics. For screening work, low-impedance coatings, or other specialized applications, a low-frequency limit of 0,01 Hz or higher might be adequate.

If the equipment allows the selection of the direction of the frequency scan, preference should be given to scanning from high frequency to low frequency for coating measurements. The spectrum obtained from a dummy cell should be completely independent of scan direction.

7.4 Data point spacing and points per decade

The standard procedure in electrochemical impedance spectroscopy is to take the frequency spectrum with logarithmic data point spacing. Therefore, it is also necessary to apply the number of data points within each decade of frequency points. At least 5 points should be taken per decade to provide a minimum data point resolution. This resolution is needed to allow accurate equivalent-circuit modelling with the data after the experiment.

7.5 D.C. potential control

D.C. potential control is always used with impedance measurements to control the electrochemical reactions at the surface of an electrode while performing the impedance measurement. Most EIS instruments allow the d.c. potential to be specified with respect to the open-circuit potential or as an absolute voltage versus the reference electrode. In most cases, the d.c. potential applied during an EIS measurement on a coating is the open-circuit potential.

The dummy cell does not require this potential to be controlled at a specific offset value. It should be fixed at 0 V. Since the open-circuit potential (U_{OC}) of a dummy cell is 0 V, the d.c. voltage can also be specified as “0 V vs. U_{OC}”.

For a coated metal specimen that is in excellent condition, it is difficult to obtain a stable value of the open-circuit potential. The non-electroactive nature of the coating causes the specimen to behave like a capacitor, for which an open-circuit potential is undefined. This capacitance, combined with instrumental effects, can lead to drift in the value of the open-circuit potential.

For coatings in good condition, the EIS experiment should be performed at the open-circuit voltage of the bare, uncoated substrate in the electrolyte. The open-circuit voltage of the substrate should be measured in the electrolyte as a separate experiment. The value of the open-circuit potential is then used during the EIS measurement and specified “vs. the reference electrode”.

As the coating deteriorates upon exposure to the electrolyte, the specimen will assume more resistive characteristics. This condition can be recognized by a more stable value for the open-circuit potential. When this occurs, the d.c. potential during the EIS measurement can be defined with respect to the stable open-circuit potential for convenience.