INTERNATIONAL STANDARD

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

Part 4: Examples of spectra of polymer-coated and uncoated specimens

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

Partie 4: Exemples de spectres d'éprouvettes revêtues de polymères et non revêtues

Reference number
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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).

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For an explanation on 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 the following URL: 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* in collaboration with ISO/TC 156, *Corrosion of metals and alloys*.

This second edition cancels and replaces the first edition (ISO 16773-4:2009), which has been technically revised with the following changes.

a) The introductory element of the title, *Paints and varnishes*, has been omitted, because the scope has been broadened to include metals and alloys. 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 and ASTM G106 for examples of spectra for low-impedance systems (range from, e.g. 10 Ω to 1 000 Ω) has been added.

c) Examples for uncoated specimens have been added.

A list of all parts in the ISO 16773 series can be found on the ISO website.

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

Part 4:
Examples of spectra of polymer-coated and uncoated specimens

1 Scope

This document gives some typical examples of impedance spectra of polymer-coated and uncoated specimens (see Annex A). Some guidance on interpretation of such spectra is also given. Further examples of spectra of low-impedance systems (range from, e.g. 10 Ω to 1 000 Ω) are given in ISO/TR 16208 and in ASTM G106. ISO 16773-2 gives guidelines for optimizing the collection of EIS data with focus on high-impedance systems.

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*

3 Terms and definitions

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

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

— IEC Electropedia: available at http://www.electropedia.org/

— ISO Online browsing platform: available at http://www.iso.org/obp/

4 Theoretical background

4.1 Basic considerations

A basic introduction to electrochemical impedance spectroscopy, especially in connection with corrosion, is given in ASTM G106.

It is not intended to limit the interpretation of EIS measurements to the models given below. Other interpretations may be valid. The choice of the proper model requires other experimental and theoretical considerations to be taken into account.

4.2 Examples of models

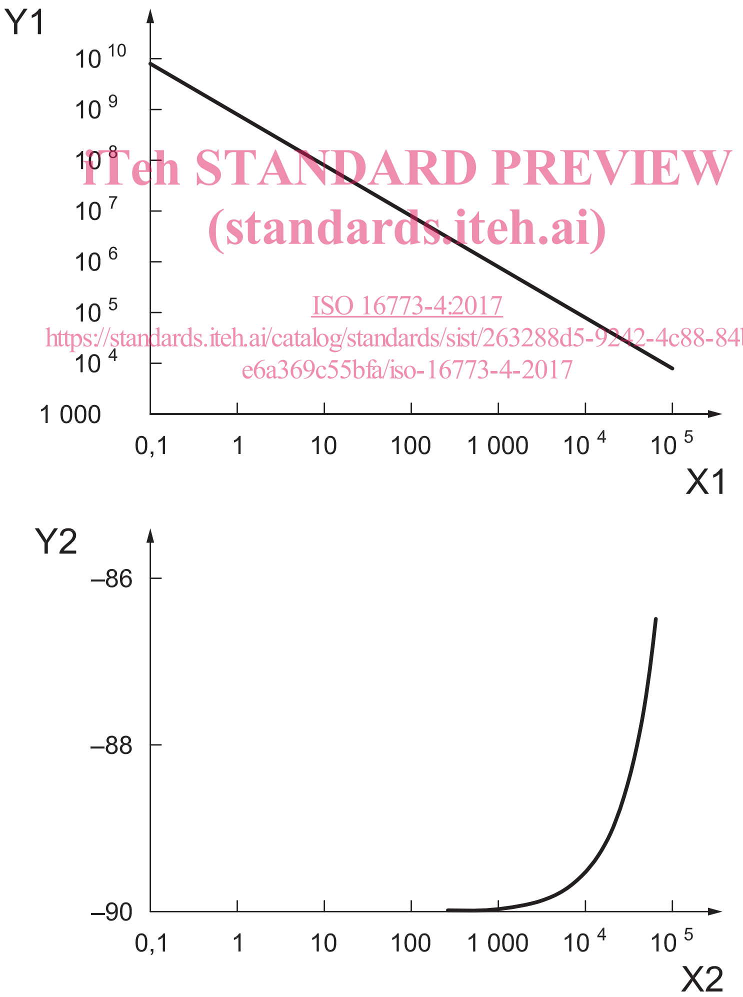
4.2.1 Purely capacitive coating

A metal covered with an undamaged coating generally has a very high impedance. The equivalent circuit for such a situation is shown in Figure 1.

Figure 1 — Equivalent circuit for a purely capacitive coating

The model includes a resistor representing the resistance R_S, of the solution and, connected in series with it, a capacitor representing the capacitance C_C, of the coating.

In practice, the resistance of a perfect coating can often not be seen in the given frequency range. Any deviation from the graph given in the Bode plot in Figure 2 indicates either a modified model or the input limits of the impedance device (see ISO 16773-2:2016, Annex A).



Key

X1 frequency, *f*, in Hz
Y1 impedance, *Z*, in Ω
X2 frequency, *f*, in Hz
Y2 phase angle, *φ*, in degrees

Figure 2 — Bode plot for a perfect coating

4.2.2 Randles equivalent circuit

The Randles equivalent circuit includes the resistance of the solution R_S, the capacitance of the coating C_C and the ohmic resistance of the coating R_C, as shown in Figure 3.

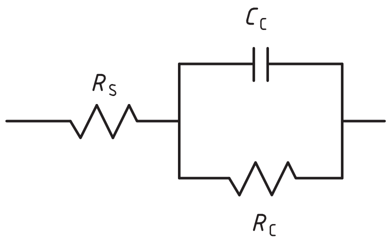
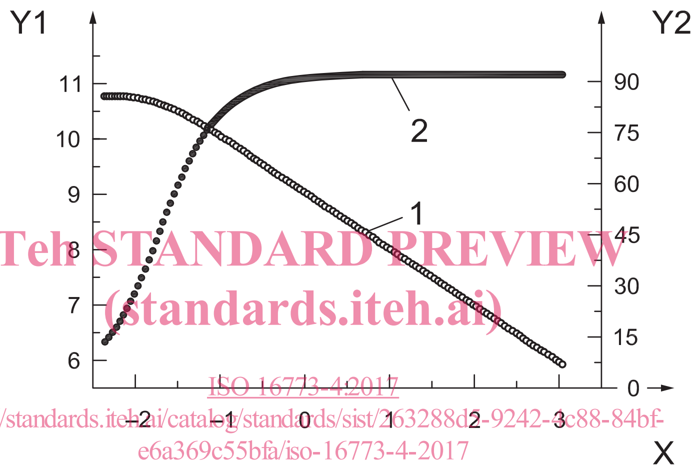


Figure 3 — Randles equivalent circuit

The Bode plot for a Randles equivalent circuit is shown in Figure 4.



Key

X log*f* (*f* in Hz)

Y1 log|*Z*| (*Z* in Ω)

Y2 |*φ*| (degrees)

1 impedance, *Z*

2 phase angle, *φ*

Figure 4 — Bode plot for a Randles equivalent circuit

4.2.3 Extended Randles equivalent circuit

Quite often, fitting experimental data to the model shown in Figure 3 results in systematic errors. In such cases, the literature shows that it is possible to use the model shown in Figure 5 to obtain a better fit.

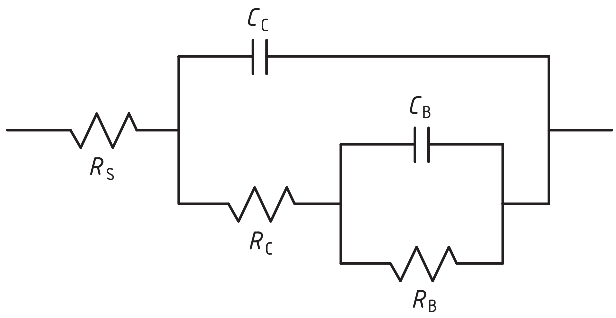
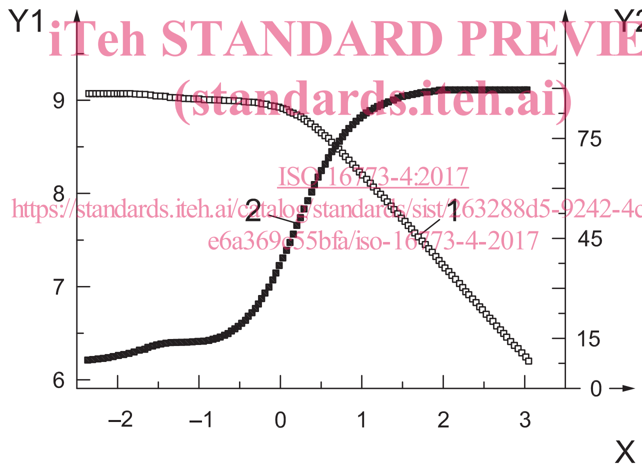


Figure 5 — Extended Randles equivalent circuit

NOTE This model is not necessarily the most appropriate and other models are not excluded.

In most cases of high-impedance coatings, R_B and C_B are the charge-transfer resistance R_{ct} and double-layer capacitance C_{dl}, respectively, in the extended Randles circuit corresponding to properties of the coating rather than to corrosion processes in the underlying metal.

The Bode plot shown in Figure 6 clearly shows the additional contribution of these two added elements. Again, the Bode plot does not go high enough in frequency to measure the solution resistance. In practice, this is not a problem because the solution resistance is a property of the test solution and the test cell geometry and not a property of the coating.



Key

X log*f* (*f* in Hz)
Y1 log|*Z*| (*Z* in Ω)
Y2 |*φ*| (degrees)
1 impedance, *Z*
2 phase angle, *φ*

Figure 6 — Bode plot for an extended Randles equivalent circuit

Annex A
(informative)

Examples

A.1 General

This annex contains a collection of spectra obtained from materials described briefly in the relevant clause. The examples were obtained from various laboratories using a range of different equipment and materials.

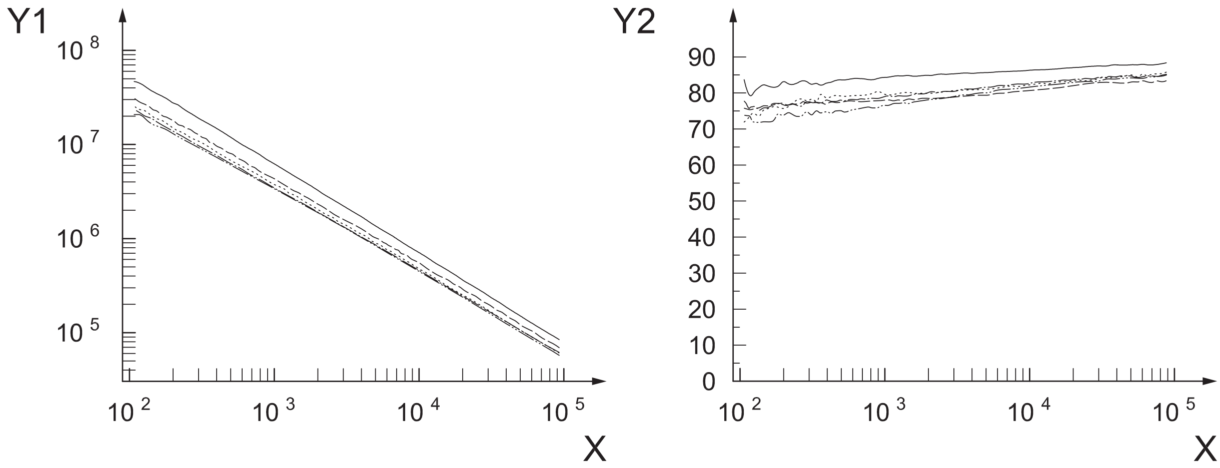
This collection of spectra is not intended to imply that all the materials mentioned necessarily give spectra similar to those shown or that the spectra given here are free of experimental errors. The collection does not represent the complete range of coating materials.

A.2 Example 1

This example shows how a smaller than usual thickness of a high-build coating material can be used to investigate the influence of immersion time on EIS measurements (see Figure A.1).

Details: Two-component epoxy coating, typically used for (maritime) steel constructions, above and below the water level. Airless spray application. Dry film thickness (DFT) recommended by the manufacturer: 1 000 µm to 3 000 µm.

Measurements were performed on one coat on steel, DFT 200 µm, on an area of 10 cm^2 at 21 °C using concentrated artificial rainwater (see Annex B). A vertical three-electrode setup, with a saturated Ag/AgCl reference electrode, was used. Spectra were recorded after defined periods of immersion.



Key

X	frequency, *f*, in Hz
Y1	modulus of the impedance, |*Z*|, in Ω·cm^2
Y2	modulus of the phase angle, |*φ*|, in degrees
————————	*t* = 0 h
– – – – – – – –	*t* = 2 h
....	*t* = 24 h
—..—..—..—	*t* = 168 h
——..——..——	*t* = 504 h

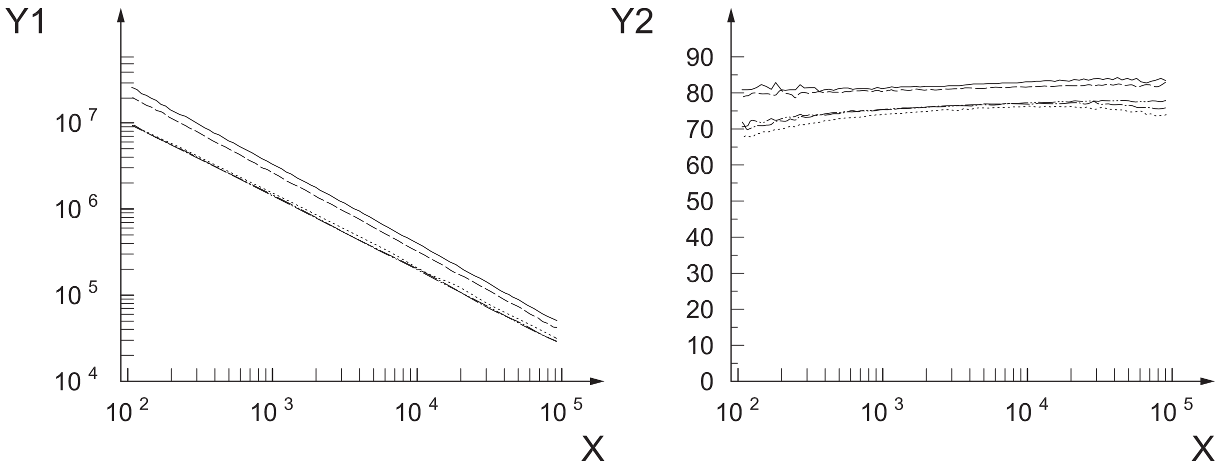
Figure A.1 — Bode plot for a high-build coating material under immersion conditions

A.3 Example 2

This example concerns a surface-tolerant coating material which does not require the same amount of surface pretreatment as that in Example 1 (see Figure A.2). Usually, de-rusting with mechanical tools is used rather than grit blasting.

Details: Surface-tolerant two-component epoxy coating for (maritime) steel constructions, above and below the water level, can be applied on corroded steel, grit-blasted steel and old (undamaged) paint coatings. Application by airless spray, conventional spray, brushing or rolling. DFT recommended by the manufacturer: 100 µm to 200 µm.

Measurements were performed on one coat on steel, DFT 250 µm, on an area of 10 cm^2 at 21 °C using concentrated artificial rainwater (see Annex B). A vertical three-electrode setup, with a saturated Ag/AgCl reference electrode, was used. Spectra were recorded after defined periods of immersion.



Key

X	frequency, *f*, in Hz
Y1	modulus of the impedance, |*Z*|, in Ω·cm^2
Y2	modulus of the phase angle, |*φ*|, in degrees
———————	*t* = 0 h
– – – – – – – – – –	*t* = 2 h
....	*t* = 24 h
——..——..——..——	*t* = 168 h
——..——..——	*t* = 504 h

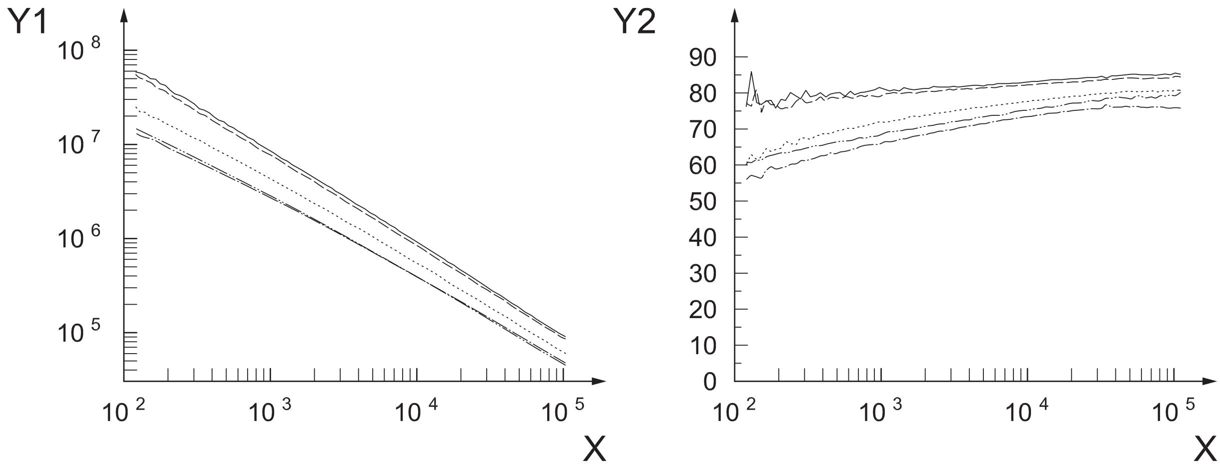
Figure A.2 — Bode plot for a surface-tolerant coating material under immersion conditions

A.4 Example 3

This example represents a high-build, solvent-free coating material with high abrasion resistance, applied as a single coat (see Figure A.3).

Details: Solvent-free two-component epoxy coating for grit-blasted metals, concrete and fibreglass in aggressive environments. High abrasion resistance and corrosion protection. Application by airless spray or brush. DFT recommended by the manufacturer: 500 µm to 1 000 µm as one coat.

Measurements were performed on one coat on steel, DFT 230 µm, on an area of 10 cm^2 at 21 °C using concentrated artificial rainwater (see Annex B). A vertical three-electrode setup, with a saturated Ag/AgCl reference electrode, was used. Spectra were recorded after defined periods of immersion.



Key

X frequency, *f*, in Hz

Y1 modulus of the impedance, |*Z*|, in Ω·cm^2

Y2 modulus of the phase angle, |*φ*|, in degrees

——————— *t* = 0 h

– – – – – – *t* = 2 h

·············· *t* = 24 h

——————— *t* = 168 h

– – – – – – *t* = 504 h

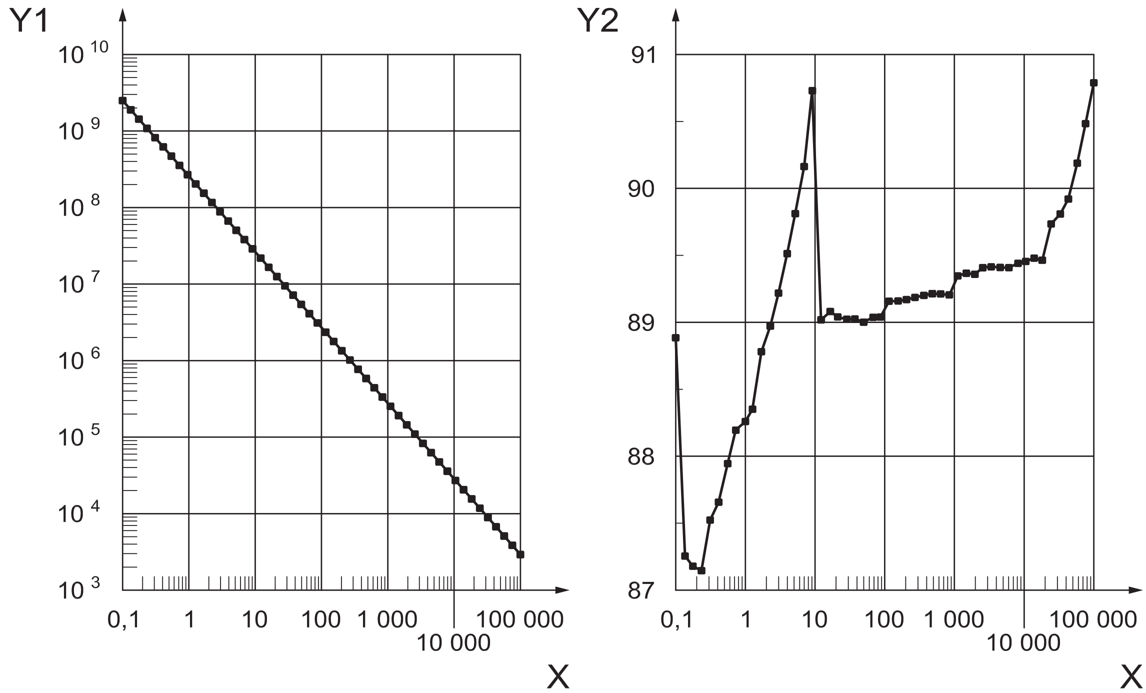
Figure A.3 — Bode plot for a solvent-free coating material under immersion conditions

A.5 Example 4

This example concerns a representative powder coating applied by spray on aluminium (see Figure A.4). The quite large measurement area of 16,5 cm^2 allowed a three-electrode setup to be used, but the open-circuit potential was not delivered with the spectra. The discontinuities in the phase-angle plot are due to potentiostat current range changes combined with the low capacitance of the system being examined, indicating incorrect setting of the measurement device.

Details: Polyester powder coating material sprayed on chromatized aluminium frames as a single coat with a DFT of (93 ± 3) µm. No ageing.

Measurements were performed at 25 °C in 3 g/l Na_2SO_4 solution on an area of 16,5 cm^2. A three-electrode setup, with an Ag/AgCl reference electrode, in a vertical plastic tube was used.



Key

X frequency, *f*, in Hz

Y1 modulus of the impedance, |*Z*|, in Ω·cm²

Y2 modulus of the phase angle, |*φ*|, in degrees

Figure A.4 — Bode plot for a powder coating before ageing

The spectra shown in Figure A.5 were obtained after ageing through eight thermal cycles, the coating remaining continuously in contact with the electrolyte.

One cycle consists of heating from 25 °C to 75 °C in 1 h, holding at 75 °C for 4 h and then cooling to room temperature. The time between each cycle was about 24 h. The temperature during the measurements was 25 °C.