# INTERNATIONAL STANDARD

ISO 16773-4

Second edition 2017-03

# 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





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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 <a href="https://www.iso.org/directives">www.iso.org/directives</a>).

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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  $\Omega$  to 1 000  $\Omega$ ) 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  $\Omega$  to 1 000  $\Omega$ ) 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 <a href="http://www.electropedia.org/">http://www.electropedia.org/</a>
- ISO Online browsing platform: available at <a href="http://www.iso.org/obp/">http://www.iso.org/obp/</a>

#### 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

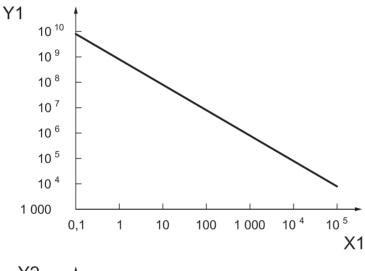
A metal covered with an undamaged coating generally has a very high impedance. The equivalent circuit for such a situation is shown in Figure 1.

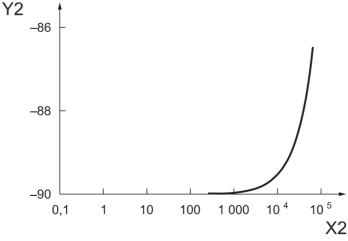


Figure 1 — Equivalent circuit for a purely capacitive coating

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 <u>Figure 2</u> 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  $\Omega$ 

X2 frequency, f, in Hz

Y2 phase angle,  $\varphi$ , 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.

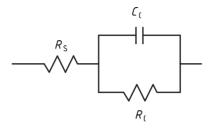
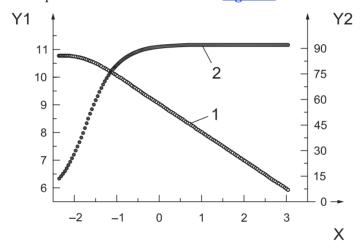


Figure 3 — Randles equivalent circuit

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



#### Key

- $X \log f(f \text{ in Hz})$
- Y1  $\log |Z|$  ( $Z \text{ in } \Omega$ )
- Y2  $|\varphi|$  (degrees)
- 1 impedance, Z
- 2 phase angle,  $\varphi$

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.

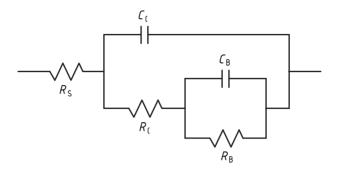
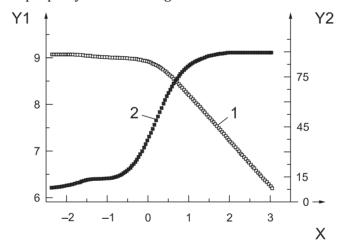


Figure 5 — Extended Randles equivalent circuit

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

In most cases of high-impedance coatings,  $R_{\rm B}$  and  $C_{\rm B}$  are the charge-transfer resistance  $R_{\rm ct}$  and double-layer capacitance  $C_{\rm dl}$ , 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.



- $X \log f(f \text{ in Hz})$
- Y1  $\log |Z|$  (Z in  $\Omega$ )
- Y2  $|\varphi|$  (degrees)
- 1 impedance, Z
- 2 phase angle,  $\varphi$

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:  $1\,000\,\mu m$  to  $3\,000\,\mu m$ .

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

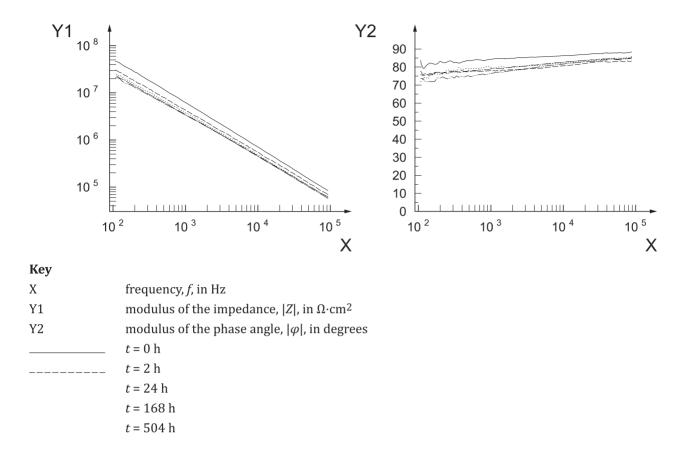


Figure A.1 — Bode plot for a high-build coating material under immersion conditions

#### 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:  $100~\mu m$  to  $200~\mu m$ .

Measurements were performed on one coat on steel, DFT 250  $\mu$ m, on an area of 10 cm² at 21 °C using concentrated artificial rainwater (see <u>Annex B</u>). A vertical three-electrode setup, with a saturated Ag/AgCl reference electrode, was used. Spectra were recorded after defined periods of immersion.

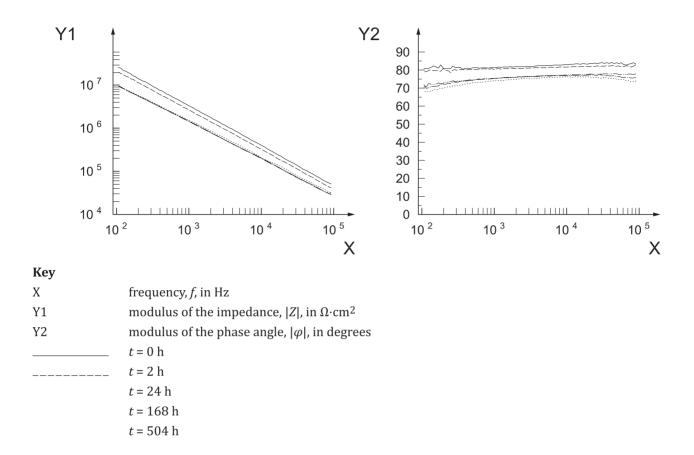


Figure A.2 — Bode plot for a surface-tolerant coating material under immersion conditions

#### 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:  $500~\mu m$  to  $1~000~\mu m$  as one coat.

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

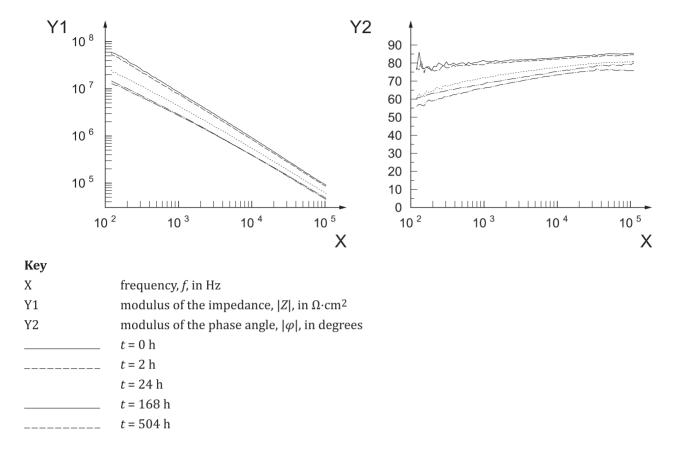


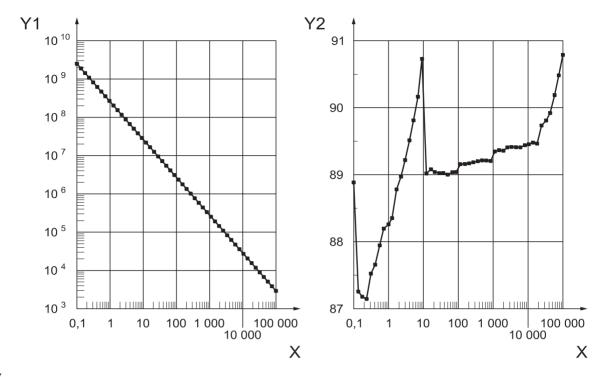
Figure A.3 — Bode plot for a solvent-free coating material under immersion conditions

#### 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<sup>2</sup> 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  $\pm$  3)  $\mu m$ . No ageing.

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



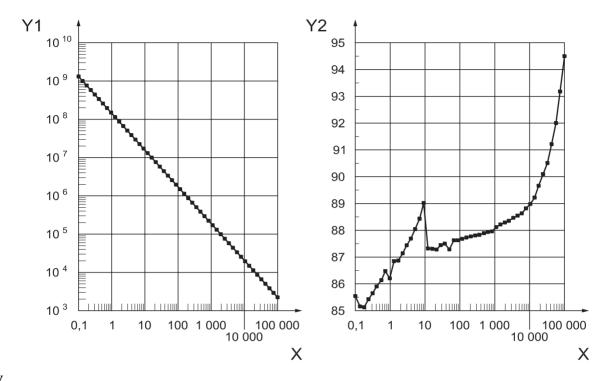
#### Kev

- X frequency, f, in Hz
- Y1 modulus of the impedance, |Z|, in  $\Omega \cdot \text{cm}^2$
- Y2 modulus of the phase angle,  $|\varphi|$ , in degrees

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

The spectra shown in <u>Figure A.5</u> 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.



- X frequency, f, in Hz
- Y1 modulus of the impedance, |Z|, in  $\Omega \cdot \text{cm}^2$
- Y2 modulus of the phase angle,  $|\varphi|$ , in degrees

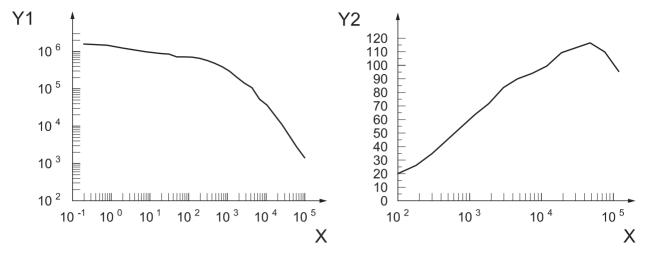
Figure A.5 — Bode plot for a powder coating after ageing

#### A.6 Example 5

Packaging materials are frequently coated with thin, unpigmented "clear coats". The spectra of a coating of this type were measured after chemical attack by citric acid and sorbic acid (see <u>Figure A.6</u>). Such thin coatings do not give high impedance values, but they give relatively high capacitance values. The phase angle plot indicates measurement anomalies in the high-frequency range. These anomalies can be attributed to non-steady state conditions, insufficient shielding (Faraday cage and/or cables) or shielding by the reference electrode.

Details: Epoxy-phenolic lacquer coating typical of that used for packaging. Two coats applied on tinplated steel by roller and stoved at 220 °C for 20 min. Total DFT:  $7 \mu m$  to  $8 \mu m$ .

Before measurement, the sample was immersed for 2 d at 25 °C in an electrolyte containing 5 g of citric acid per litre and 200 mg of sorbic acid per litre. Measurements were performed on an area of  $105 \text{ cm}^2$ . A vertical three-electrode setup, with a calomel reference electrode, was used.



- X frequency, f, in Hz
- Y1 modulus of the impedance, |Z|, in  $\Omega \cdot \text{cm}^2$
- Y2 modulus of the phase angle,  $|\varphi|$ , in degrees

Figure A.6 — Bode plot for a thin lacquer coating, as used in the packaging industry, after chemical ageing

### A.7 Example 6

Temperature has an enormous effect on impedance spectra. Figure A.7 shows the temperature dependence of the impedance of a clear coat.

Details: Pure epoxy-vinyl coating without pigments. Same binder as used for marine anti-corrosion primers. Spray application in two coats on sand-blasted steel prepared to surface preparation grade Sa 3 (see ISO 8501-1) (24 h drying between coat 1 and coat 2) followed by one week's curing at 80 °C. Total DFT 170  $\mu m$ .

The temperature was cycled between 20 °C and 90 °C, each cycle lasting 10 h. Measurements were made at temperatures ranging from 20 °C to 90 °C on an area of  $14 \text{ cm}^2$  with the sample immersed in a vertical position in a saline solution containing 30 g of NaCl per litre, using a two-electrode setup with a Pt counter-electrode.

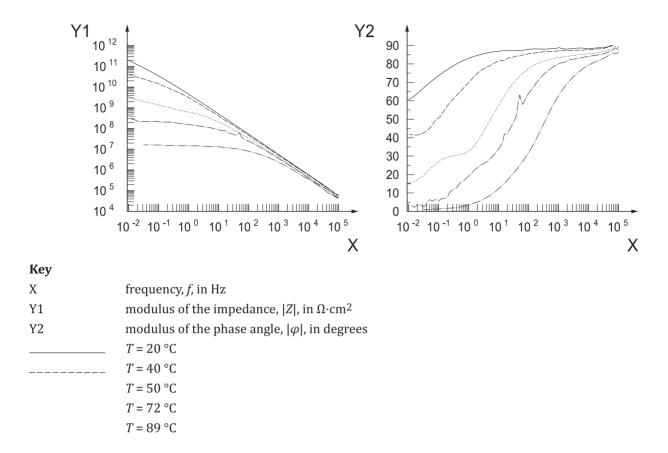


Figure A.7 — Bode plot for an epoxy coating at various temperatures

#### A.8 Example 7

This example concerns a combined coating system with a high-solids primer and a waterborne topcoat after immersion for 0,5 h, 300 h and 1 200 h (see <u>Figures A.8</u>, <u>A.9</u> and <u>A.10</u>). This coating system gives very similar spectra to those given by the dummy cells used in ISO 16773-3.

Details: Coating system made up of high-solids epoxy-polyamine primer and waterborne acrylic urethane topcoat. Used for repair and maintenance of structures, mainly if good surface preparation is not possible.

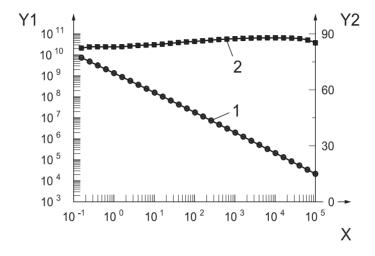
- Primer: 82 % solids content, pigmented with aluminium.
- Topcoat: 82 % solids content, pigmented with micaceous iron oxide.

Two coats applied by brush (primer 70  $\mu$ m, topcoat 50  $\mu$ m) on freshly galvanized steel (degreased prior to painting).

Measurements were performed at ambient temperature (about 23 °C) in a  $0.5 \text{ mol/l Na}_2SO_4$  solution on an area of  $13 \text{ cm}^2$ .

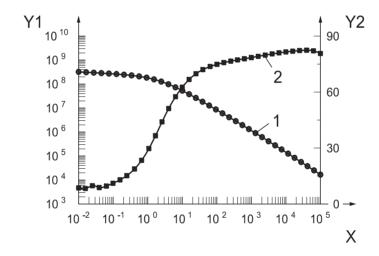
A horizontal cell design with a three-electrode setup, including a saturated calomel electrode (SCE), was used. The electrochemical impedance measurements were performed at the open-circuit potential. The frequency range scanned was from  $10^5$  Hz down to  $10^{-2}$  Hz and the signal amplitude was 20 mV rms (root mean square; for explanation, see also IEC 80000-6:2008, Item No. 6-57).

In <u>Figure A.9</u>, a typical behaviour of the phase angle during immersion that could not be described by a constant phase element or by any ordinary capacitor can be observed.



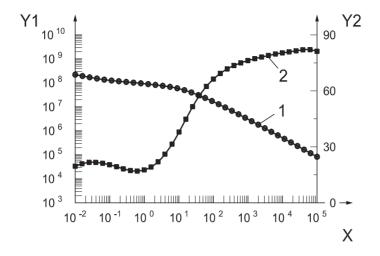
- X frequency, f, in Hz
- Y1 modulus of the impedance, |Z|, in  $\Omega \cdot \text{cm}^2$
- Y2 modulus of the phase angle,  $|\varphi|$ , in degrees
- 1 impedance, Z
- 2 phase angle,  $\varphi$

Figure A.8 — Bode plot for primer/topcoat system in Example 7 after 0,5 h immersion



- X frequency, f, in Hz
- Y1 modulus of the impedance, |Z|, in  $\Omega \cdot \text{cm}^2$
- Y2 modulus of the phase angle,  $|\varphi|$ , in degrees
- 1 impedance, Z
- 2 phase angle,  $\varphi$

Figure A.9 — Bode plot for primer/topcoat system in Example 7 after 300 h immersion



- X frequency, f, in Hz
- Y1 modulus of the impedance, |Z|, in  $\Omega \cdot \text{cm}^2$
- Y2 modulus of the phase angle,  $|\varphi|$ , in degrees
- 1 impedance, Z
- 2 phase angle,  $\varphi$

Figure A.10 — Bode plot for primer/topcoat system in Example 7 after 1 200 h immersion

### A.9 Example 8

Measurements on free films are not as easy to make as those on attached films because the preparation of the free film can cause defects which might be misinterpreted. This example concerns a free film measured at elevated temperatures in deionized water (see Figure A.11).

Details: A non-commercial epoxy-amine clear coat of DGEBA-MCDEA [diglycidyl ether of bisphenol A cured with 4,4'-methylene-bis (3-chloro-2,6-diethylaniline)] prepared by moulding. Thickness 2 mm. Measurements performed on an area of  $12,5~\rm cm^2$  of the film in a double cell, with the film in between, during exposure to deionized water at  $100~\rm ^{\circ}C$ . Horizontal cell design with two-electrode setup.

The discontinuity of the phase angle plot at 50 Hz is likely due to insufficient shielding.

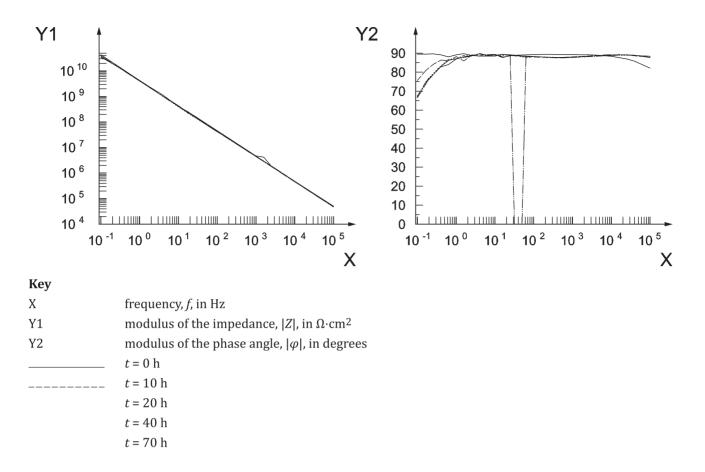


Figure A.11 — Bode plot for a free film

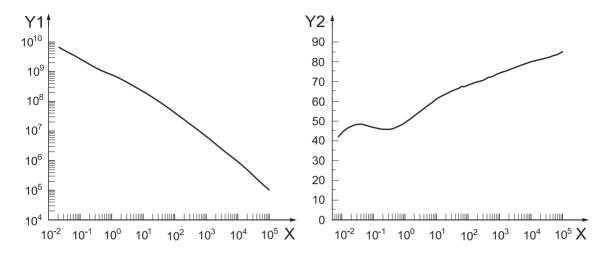
#### A.10 Example 9

Marine coatings are often associated with cathodic protection which can lead to cathodic disbonding. It is therefore necessary to test coatings for compatibility with cathodic protection over a long period so that any degradation of the coating can be detected.

This example concerns a double coat of epoxy-vinyl containing calcium ferrite pigment (see Figure A.12). It was sprayed onto sand-blasted steel prepared to surface preparation grade Sa  $2\frac{1}{2}$  (see ISO 8501-1). The total DFT was 250  $\mu$ m.

The coating was aged for 556 d in artificial seawater (prepared in accordance with ASTM D1141) at a cathodic potential of -1,53 V (SCE) using an Mg-alloy anode.

The measurements were performed on an area of  $64 \text{ cm}^2$  at -1 V and ambient temperature in artificial seawater using an SCE and a platinized Ti counter-electrode. The frequency range scanned was from 100 kHz down to 10 mHz with a 10 mV rms perturbation-signal amplitude (see ISO 16773-1).



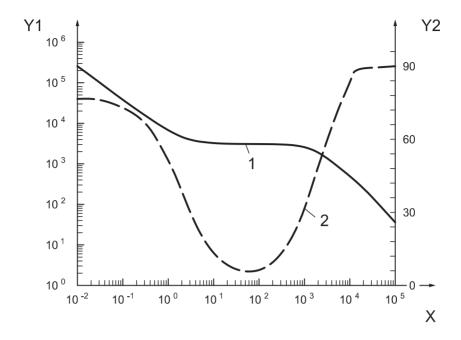
- X frequency, f, in Hz
- Y1 modulus of the impedance, |Z|, in  $\Omega \cdot \text{cm}^2$
- Y2 modulus of the phase angle,  $|\varphi|$ , in degrees

Figure A.12 — Bode plot for a marine coating aged under immersion conditions with cathodic protection

#### A.11 Example 10

Sol-gel coating technologies are discussed as a possible alternative to anti-corrosive coatings in aerospace or automotive industries.

The DFT of the sol-gel coating was in accordance with the recommendation of the manufacturer between 2  $\mu m$  and 3  $\mu m$ . Measurements were performed at 23 °C in 3,5 % (by mass) NaCl solution on an area of 16 cm<sup>2</sup>. A three-electrode setup, with an Ag/AgCl reference electrode, in a vertical plastic tube was used. A spectrum was recorded immediately after immersion (see Figure A.13).



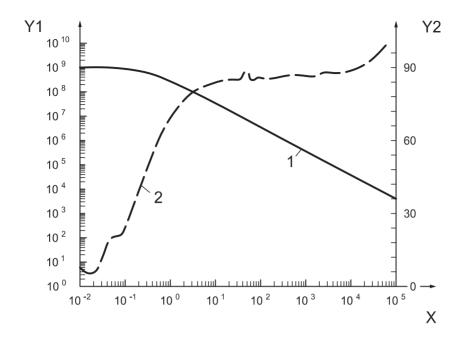
- X frequency, f, in Hz
- Y1 modulus of the impedance, |Z|, in  $\Omega \cdot \text{cm}^2$
- Y2 modulus of the phase angle,  $|\varphi|$ , in degrees
- 1 impedance, Z
- 2 phase angle,  $\varphi$

Figure A.13 — Bode plot for a sol-gel coating material under immersion conditions

### A.12 Example 11

Heavy-duty corrosion protection is achieved by applying a multi-layer system consisting of a zinc-rich epoxy primer, an epoxy mid-coat and a polyurethane topcoat.

The DFT of the coating system was in accordance with the recommendation of the manufacturer between 240  $\mu$ m and 330  $\mu$ m. Measurements were performed at 23 °C in 3,5 % (by mass) NaCl solution on an area of 16 cm<sup>2</sup>. A three-electrode setup, with an Ag/AgCl reference electrode, in a vertical plastic tube was used. A spectrum was recorded immediately after immersion (see Figure A.14).



- X frequency, f, in Hz
- Y1 modulus of the impedance, |Z|, in  $\Omega \cdot \text{cm}^2$
- Y2 modulus of the phase angle,  $|\varphi|$ , in degrees
- 1 impedance, Z
- 2 phase angle,  $\varphi$

Figure A.14 — Bode plot for a coating system with a zinc primer

#### **A.13 Example 12**

Electrolytic tinplate and tin-free steel substrates are widely used for the production of food packaging containers. Substrates are typically in accordance with EN 10202 (double reduced, steel grade 620, fine stone finish, continuous annealing).

The electrolytic tinplate was coated with  $2.0~{\rm g/m^2}$  tin and passivation 311. Measurements were performed at 23 °C in a sodium hydrogen/dihydrogen phosphate buffer solution with a pH of 6,5. An exposed area of  $2.3~{\rm cm^2}$  was measured using a two-electrode setup with an amplitude of 20 mV.

See Figure A.15 and Figure A.16.

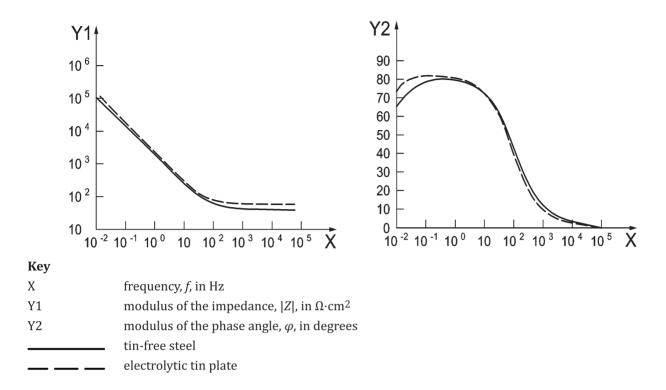
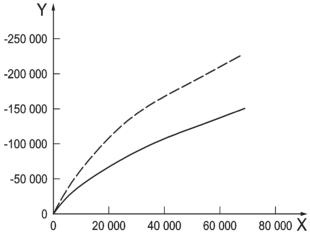


Figure A.15 — Bode plot for electrolytic tin plate and tin-free steel



Key	
X	real part of the impedance, $z'$ , in $\Omega \cdot \mathrm{cm}^2$
Y	imaginary part of the impedance, $z''$ , in $\Omega \cdot \mathrm{cm}^2$
	tin-free steel
	electrolytic tin plate

Figure A.16 — Nyquist plot for electrolytic tin plate and tin-free steel

#### A.14 Example 13

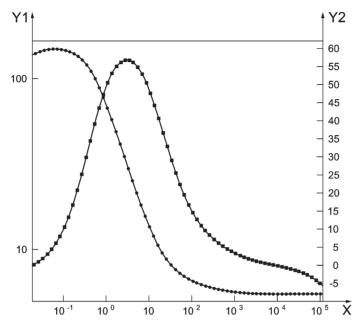
Cold-rolled steel is used as construction material in the automotive industry.

Measurements were performed at 22 °C in a 3,5 % (by mass) sodium chloride solution. An alkaline degreased exposed area of 7  $\rm cm^2$  was measured with a three-electrode setup, using a pseudo-reference

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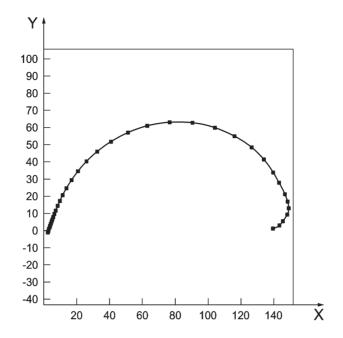
electrode (Ag/AgCl wire), with an amplitude of 10 mV rms. The measurement was started after stabilization of 15 min at OCP.

See Figure A.17 to Figure A.21.



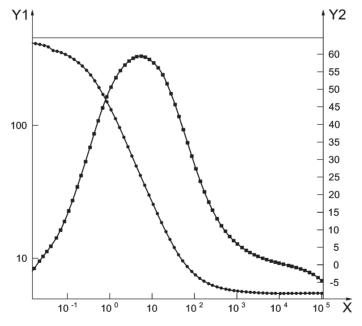
Key	
X	frequency, f, in Hz
Y1	impedance, $ Z $ , in $\Omega$
Y2	negative phase angle, $\phi$
<del></del>	impedance, $Z$
	phase angle, $\phi$

Figure A.17 — Bode plot for alkaline degreased cold rolled steel



- X real part of the impedance, z', in  $\Omega$
- Y imaginary part of the impedance, -z'', in  $\Omega$

Figure A.18 — Nyquist plot for alkaline degreased cold rolled steel



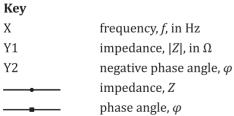
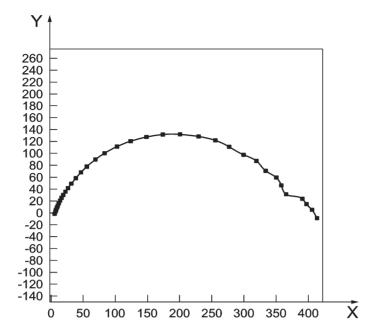


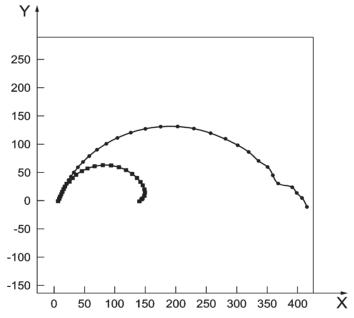
Figure A.19 — Bode plot for alkaline degreased cold rolled steel — After 1 h waiting time

#### ISO 16773-4:2017(E)



- X real part of the impedance z', in  $\Omega$
- Y imaginary part of the impedance -z'', in  $\Omega$

Figure A.20 — Nyquist plot for alkaline degreased cold rolled steel — After 1 h waiting time



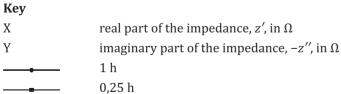


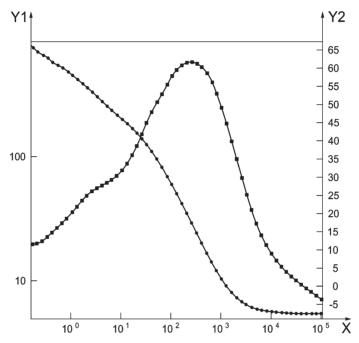
Figure A.21 — Nyquist plot for alkaline degreased cold rolled steel — Comparison 0,25 h and 1 h

#### **A.15 Example 14**

Coil-galvanized steel is used as construction material, e.g. in the automotive industry and household appliances.

Measurements were performed at 22 °C in a 3,5 % (by mass) sodium chloride solution. An alkaline degreased exposed area of 7 cm $^2$  was measured with a three-electrode setup, using a pseudo-reference electrode (Ag/AgCl wire), with an amplitude of 10 mV rms. The measurement was started after stabilization of 15 min at OCP.

See Figure A.22 to Figure A.26.



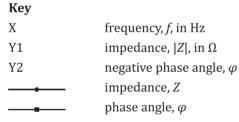
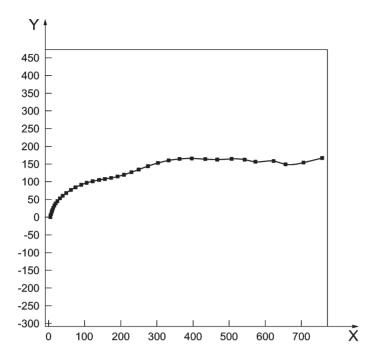
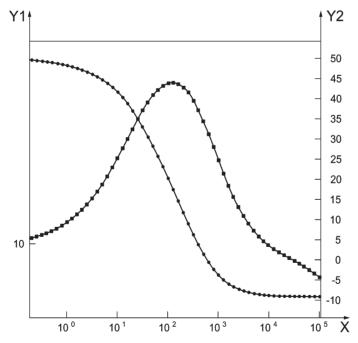


Figure A.22 — Bode plot for alkaline degreased coil-galvanized steel



- X real part of the impedance, z', in  $\Omega$
- Y imaginary part of the impedance, -z'', in  $\Omega$

Figure A.23 — Nyquist plot for alkaline degreased coil-galvanized steel



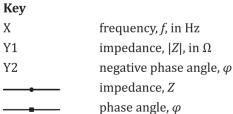
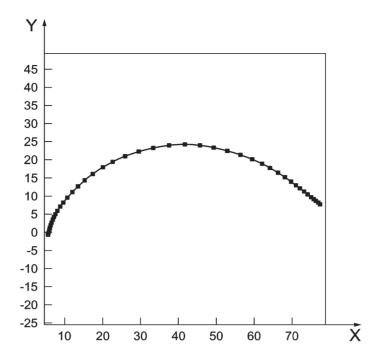


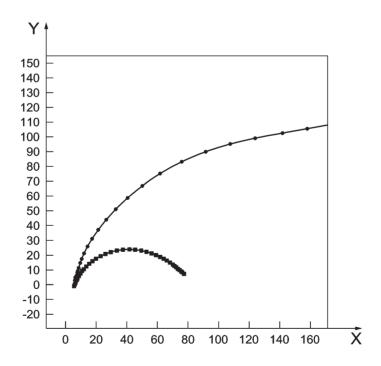
Figure A.24 — Bode plot for alkaline degreased coil-galvanized steel — After 2 h waiting time



X real part of the impedance, z', in  $\Omega$ 

Y imaginary part of the impedance, -z'', in  $\Omega$ 

Figure A.25 — Nyquist plot for alkaline degreased coil-galvanized steel — After 2 h waiting time



Key X

real part of the impedance, z', in  $\Omega$ 

Y imaginary part of the impedance, -z'', in  $\Omega$ 0,25 h

2 h

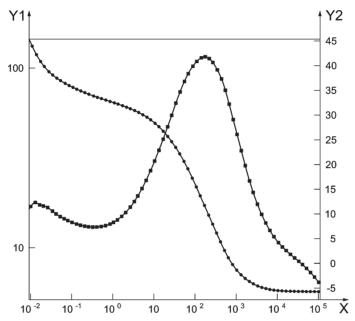
Figure A.26 — Nyquist plot for alkaline degreased coil-galvanized steel — Comparison 0,25 h and 2 h  $\,$ 

#### **A.16 Example 15**

Electro-galvanized steel is used as construction material in the automotive industry.

Measurements were performed at 22 °C in a 3,5 % (by mass) sodium chloride solution. An alkaline degreased exposed area of 7 cm $^2$  was measured with a three-electrode setup, using a pseudo-reference electrode (Ag/AgCl wire), with an amplitude of 10 mV rms. The measurement was started after stabilization of 15 min at OCP.

See Figure A.27 to Figure A.31.



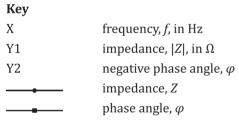
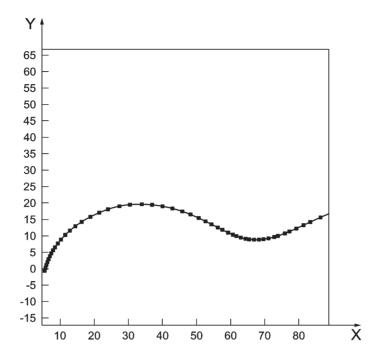
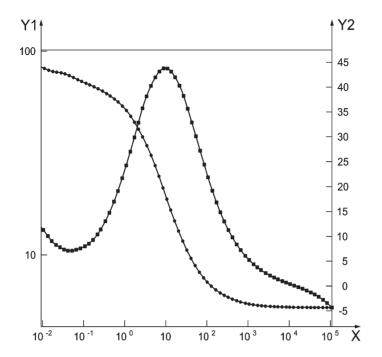


Figure A.27 — Bode plot for alkaline degreased electro-galvanized steel



- X real part of the impedance, z', in Ω
- Y imaginary part of the impedance, -z'', in  $\Omega$

Figure A.28 — Nyquist plot for alkaline degreased electro-galvanized steel



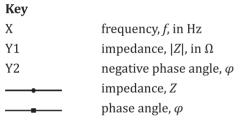
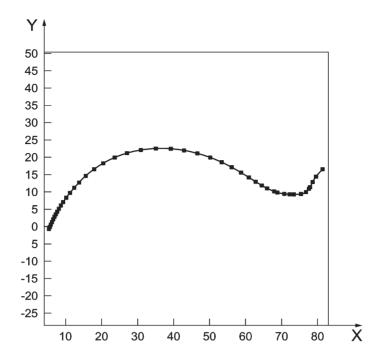
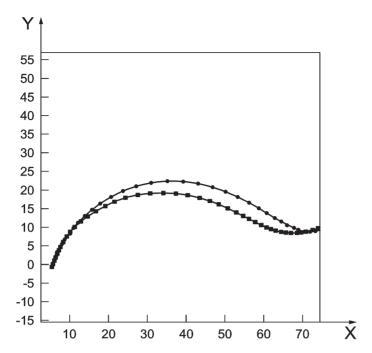


Figure A.29 — Bode plot for alkaline degreased electro-galvanized steel — After 6,5 h waiting time



- X real part of the impedance, z', in Ω
- Y imaginary part of the impedance, -z'', in  $\Omega$

Figure A.30 — Nyquist plot for alkaline degreased electro-galvanized steel — After 6,5 h waiting time



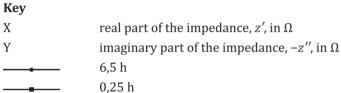


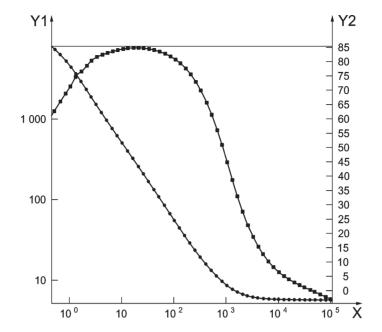
Figure A.31 — Nyquist plot for alkaline degreased electro-galvanized steel — Comparison 0,25 h and 6,5 h

#### A.17 Example 16

Aluminium alloy 6014 is used as construction material in the automotive industry.

Measurements were performed at 22 °C in a 3,5 % (by mass) sodium chloride solution. A degreased exposed area of 7 cm $^2$  was measured with a three-electrode setup, using a pseudo-reference electrode (Ag/AgCl wire), with an amplitude of 10 mV rms. The measurement was started after stabilization of 15 min at OCP.

See Figure A.32 to Figure A.36.

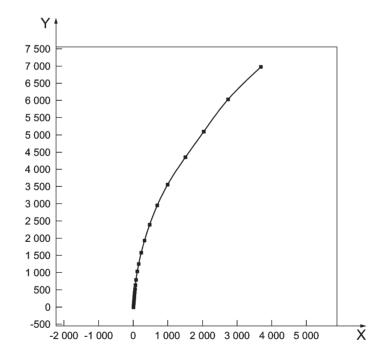


Key

X frequency, f, in Hz

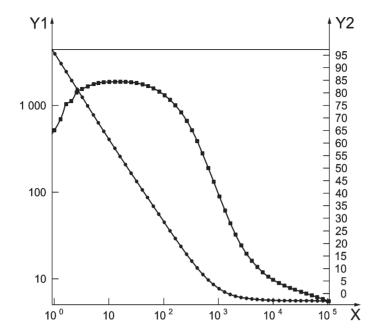
Y1 impedance, |Z|, in  $\Omega$ Y2 negative phase angle,  $\varphi$ impedance, Zphase angle,  $\varphi$ 

Figure A.32 — Bode plot for degreased aluminium alloy 6014



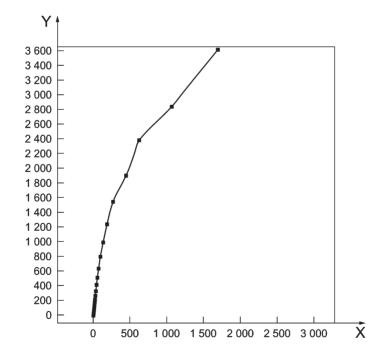
- X real part of the impedance, z', in  $\Omega$
- Y imaginary part of the impedance, -z'', in  $\Omega$

Figure A.33 — Nyquist plot for degreased aluminium alloy 6014



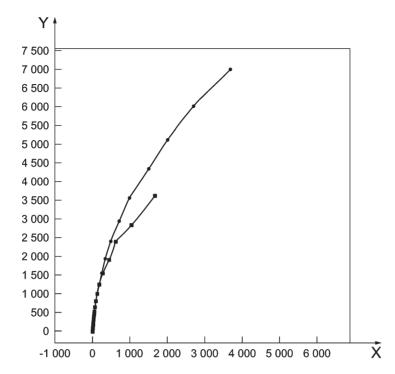
Key	
X	frequency, f, in Hz
Y1	impedance, $ Z $ , in $\Omega$
Y2	negative phase angle, $\phi$
	impedance, $Z$
	phase angle, $\phi$

Figure A.34 — Bode plot for degreased aluminium alloy 6014 — After 7 h waiting time



- X real part of the impedance, z', in Ω
- Y imaginary part of the impedance, -z'', in  $\Omega$

Figure A.35 — Nyquist plot for degreased aluminium alloy 6014 — After 7 h waiting time



Key

X real part of the impedance, z', in  $\Omega$ Y imaginary part of the impedance, -z'', in  $\Omega$ 0,25 h

7 h

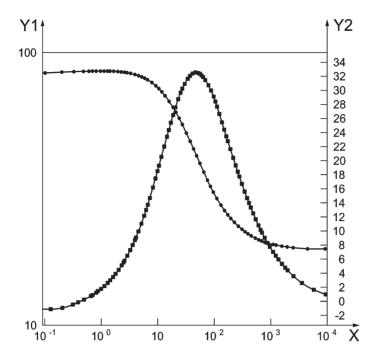
Figure A.36 — Nyquist plot for degreased aluminium ally 6014 — Comparison 0,25 h and 7 h

#### **A.18 Example 17**

Low-carbon steel is used as construction material in civil engineering.

Measurements were performed at 22 °C in an electrolyte with  $K_2SO_4$ , c = 0.1 mol/l and  $H_2SO_4$ , c = 0.02 mol/l. A degreased and polished area of 0.78 cm<sup>2</sup> was measured with a three-electrode setup, using a pseudo-reference electrode (Ag/AgCl wire), with an amplitude of 10 mV rms.

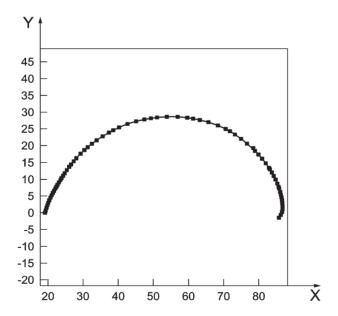
See Figure A.37 and Figure A.38.



X Y1 Y2

frequency, f, in Hz impedance, |Z|, in  $\Omega$  negative phase angle,  $\varphi$  impedance, Z phase angle,  $\varphi$ 

Figure A.37 — Bode plot for low-carbon steel



- X real part of the impedance, z', in Ω
- Y imaginary part of the impedance, -z'', in  $\Omega$

Figure A.38 — Nyquist plot for low-carbon steel

# **Annex B**

(informative)

# Composition of concentrated artificial rain water

The composition of the concentrated artificial rain water given in <u>Table B.1</u> corresponds to rain at Dutch coastal sites concentrated 50 times.

Table B.1 — Composition of concentrated artificial rain water

Chemical	Concentration		
Chemicai	mg/l		
Ammonium chloride	7,23		
Ammonium nitrate	0,85		
Ammonium sulfate	15,14		
Calcium nitrate	17,71		
Iron chloride	0,99		
Potassium nitrate	3,03		
Copper sulfate	0,05		
Magnesium chloride	12,71		
Sodium bicarbonate	0,17		
Sodium chloride	28,03		
Sodium fluoride	0,31		
Sodium sulfate	19,20		
Nickel chloride	0,02		
Nitric acid	3,74		

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- [6] ASTM G106, Standard Practice for Verification of Algorithm and Equipment for Electrochemical Impedance Measurements
- [7] EN 10202, Cold reduced tinmill products Electrolytic tinplate and electrolytic chromium/chromium oxide coated steel
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