TECHNICAL REPORT

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Sources of error in the use of electrochemical impedance spectroscopy for the investigation of coatings and other materials

Sources d'erreur dans l'utilisation de la spectroscopie d'impédance électrochimique pour l'étude des revêtements et autres matériaux

Reference number
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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 of 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 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*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Electrochemical impedance spectroscopy is described in detail in ISO 16773-1 to ISO 16773-4. It became apparent during use of these standards that sources of error and measurement artefacts that lead to incorrect interpretations are not dealt with comprehensively. This document supplements the ISO 16773 series of standards to deal with this issue.

Sources of error in the use of electrochemical impedance spectroscopy for the investigation of coatings and other materials

1 Scope

This document describes the main sources of error in the use of electrochemical impedance spectroscopy for the investigation of coatings and other materials. The sources of error listed here include all process steps from the set-up of the sample with the measuring cell right through to evaluation.

NOTE The sources of error discussed here do not represent a complete list.

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 4618, *Paints and varnishes — Terms and definitions*

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 4618, ISO 16773-1 and the following apply.

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

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

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

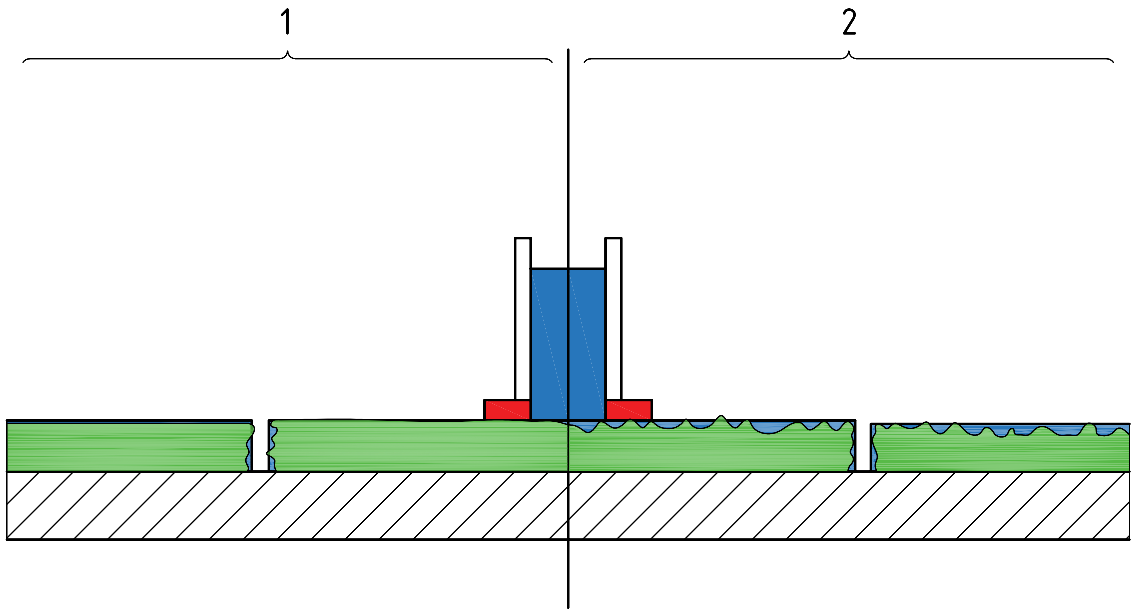
3.1
limit impedance
minimum or maximum impedance that can be measured using the impedance spectrometer

3.2
limit frequency
minimum or maximum frequency that can be set on the impedance spectrometer

4 Error in the make-up of the measuring cell

4.1 Roughness of the surface

A wet and rough surface could conduct stray currents to a scratch or artificial defect, see Figure 1. This could yield in a spectrum showing a much lower resistance than in reality. Examples of spectra are shown in Figure 2.



Key

1 without UV-irradiation

2 after UV-irradiation

□ PMMA tube

■ seal

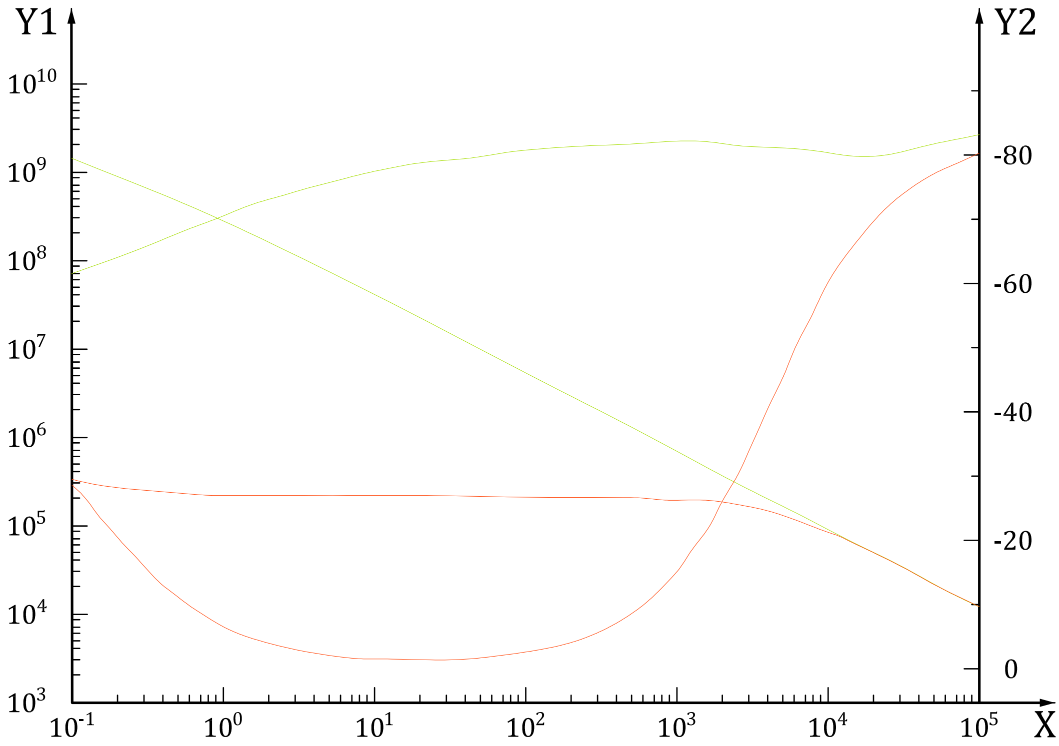
■ coating

■ electrolyte

▨ steel

Figure 1 — Conductive path from counter electrode to scratch due to surface roughness

The rough surface was measured on the unscratched area. Although the rough surface was dried with a tissue, the residual amount of water was sufficient to produce a conductive path via the scratch to the substrate. As result, the spectrum of the sample resulted in the incorrect identification of a defective coating. After 2 h of continuous immersion in the cell, the surface outside the cell had dried and the conductive path was interrupted, which resulted in a typical spectrum of an intact coating.



Key

X frequency, *f*, in Hz

Y1 impedance, *Z*, in Ω

Y2 phase angle, *φ*, in degrees

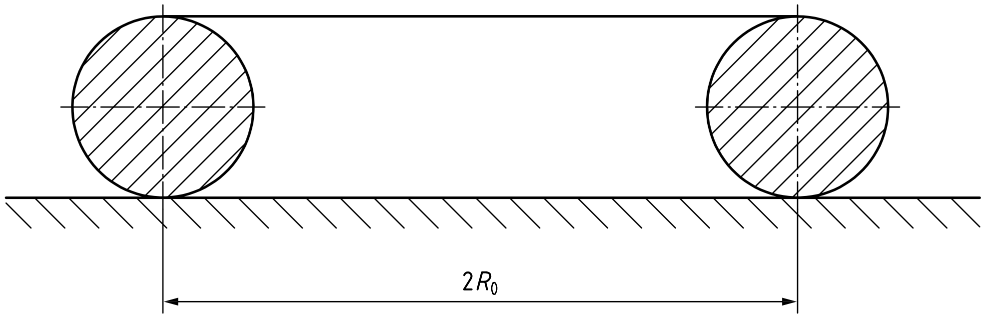
——— 2 h drying

——— wet

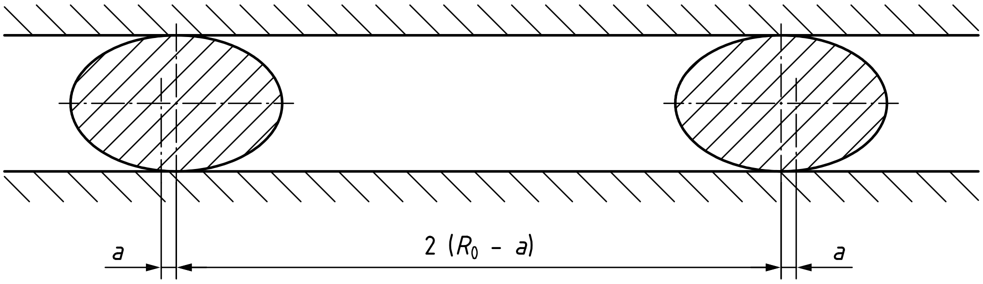
Figure 2 — EIS spectra of the initially wet coating and 2 h after drying

4.2 O-ring — Considerations about the precise determination of the exposed area

If an O-ring is used to seal the cell, the exposed area is smaller than the theoretically assumed area because the O-ring will be compressed, and therefore, the exposed area will be reduced (see Figure 3).



a) Ideal situation, uncompressed



b) Real situation, compressed

Key

R_0 radius of the uncompressed O-ring

a difference in the radius of the O-ring due to compression

Figure 3 — Uncompressed and compressed O-ring

This behaviour can be visualized easily by using two transparent PMMA (poly methylene methacrylate) plates which were compressed with 4 screws. The screws were gently tightened only by hand and without any tools.

Figure 4 shows the set-up and Figure 5 and Figure 6 show the compressed O-rings of 1,2 cm and 5 cm diameter, respectively.

Figure 4 — Compression of O-ring using 4 screws

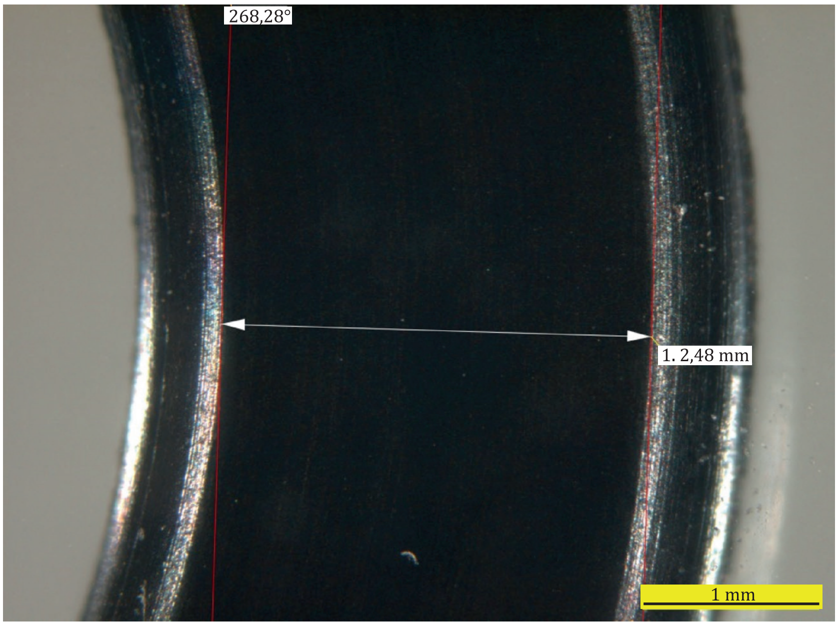


Figure 5 — Compressed O-ring of 1,2 cm diameter

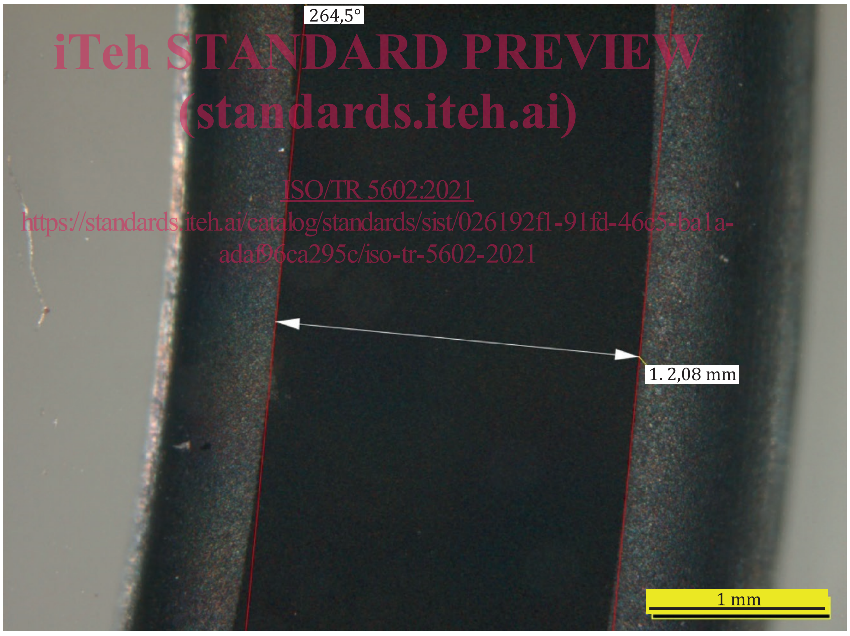
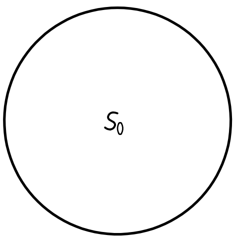


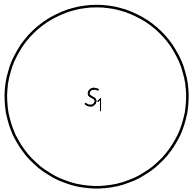
Figure 6 — Compressed O-ring of 5 cm diameter

The exposed area can be calculated as illustrated in Figure 7.



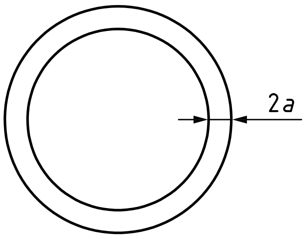
$$S_0 = \pi \cdot R_0^2$$

a) O-ring not compressed — Contact surface of the specimen with testing solution



$$S_1 = \pi \cdot (R_0 - a)^2$$

b) O-ring compressed — Contact surface of the specimen with testing solution



$$\Delta S = S_0 - S_1 = \pi \cdot R_0^2 - \pi \cdot (R_0 - a)^2$$

c) Reduction of contact surface of specimen due to O-ring compression

Key

S_0 geometric area with the O-ring uncompressed

S_1 exposed area with the O-ring compressed

ΔS difference $S_0 - S_1$

R_0 radius of the uncompressed O-ring

a difference of the radius of the O-ring due to compression

Figure 7 — Calculation of the exposed area

The error dS between exposed area S_1 and geometric area S_0 can be approximated depending on the O-ring radius, R_0, and the measured contact, $2a$, using Formula (1):

$$dS = \frac{\Delta S}{S_0} \cdot 100 = \frac{2 \cdot a \cdot R_0 \cdot a^2}{R_0^2} \cdot 100 \qquad (1)$$

Some examples for calculation of the error of the exposed area are shown in Table 1.

Table 1 — Approximate error estimation of contact surface of specimens in corrosion cells

Radius of the uncompressed O-ring R_0 mm	Difference in the radius of the O-ring due to compression a mm	$R_0 - a$ mm	Geometric area with the O-ring uncompressed (theoretical surface) S_0 mm²	Exposed area with the O-ring compressed (real surface) S_1 mm²	Error of the exposed area dS %
6	0,8	5,2	113	85	25
12	0,8	11,2	452	394	13
24	0,8	23,2	1 809	1 690	7
30	0,8	29,2	2 826	2 677	5
6	1	5	113	79	31
12	1	11	452	380	16
24	1	23	1 809	1 661	8
30	1	29	2 826	2 641	7
6	1,25	4,75	113	71	37
12	1,25	10,75	452	363	20
24	1,25	22,75	1 809	1 625	10
30	1,25	28,75	2 826	2 595	8

4.3 Faulty cell make-up

4.3.1 Optically detectable leaks

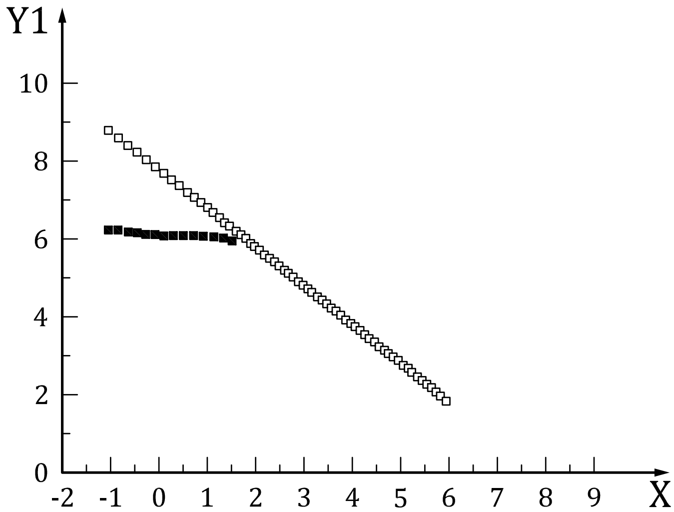
Optically detectable leaks in the measuring cell are obvious and are not dealt with here.

4.3.2 Optically non-detectable causes

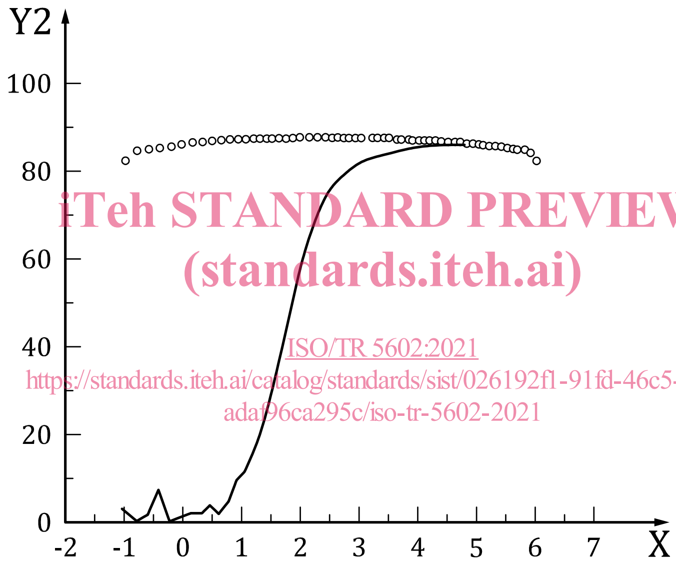
The behaviour shown in Figure 8 was observed in a non-reproducible manner for a very well-documented coating (cathodic e-coat) that is in familiar use in measurement technology. This behaviour occurred with varying amounts of pressure on the measuring cell at different locations on the same test panels; however, a direct relationship was not detected.

If the behaviour shown in Figure 8 is observed in a measuring cell, the measuring cell is not suitable.

Generally, every measurement set-up is tested for errors with a familiar system before this measuring cell is used on an unfamiliar system.



a) Magnitude of impedance as a function of frequency



b) Phase angle as a function of frequency

Key

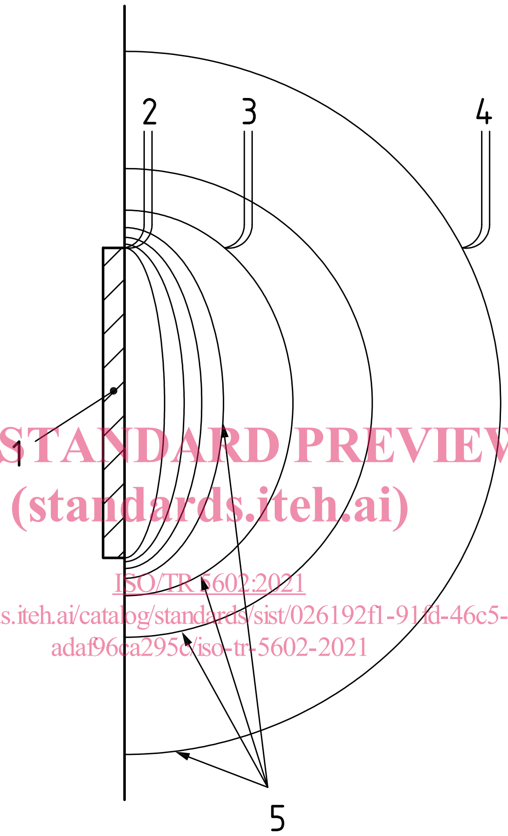
X	logarithm of the frequency, log *f*, in Hz
Y1	logarithm of the modulus of the impedance, log |*Z*|, in Ω·cm^2
Y2	absolute value of the phase angle, *φ*, in degrees
■	wrong sealing
□	sealing correct
———	wrong sealing
○	sealing correct

Figure 8 — Possible influence of a faulty cell set-up

4.4 Reference electrodes

4.4.1 General information on the distance between the reference and working electrodes

RE1, RE2 and RE3 as shown in Figure 9 are the various positions where the reference electrode RE can be placed to measure the potential. At distances very close to the working electrode, the equipotential lines are close together and small variations in the position of the reference electrode can lead to large variations in the ohmic drop. This applies in particular to uncoated samples. In some cases, it is preferable not to use a Luggin capillary, and instead to place the reference electrode far from the working electrode and measure and compensate for the ohmic drop.



Key

1 working electrode (WE)
2 reference electrode 1 (RE 1)
3 reference electrode 2 (RE 2)
4 reference electrode 3 (RE 3)
5 equipotential lines

Figure 9 — Equipotential lines shown at close proximity to the working electrode

The influence of the reference electrode distance is negligible for measurements on coated (high-resistance) samples. See Figure 10.