INTERNATIONAL STANDARD

ISO 16773-3

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

Part 3: Processing and analysis of data from dummy cells

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

Partie 3: Traitement et analyse des données obtenues à partir de cellules test

Reference number
ISO 16773-3:2016(E)

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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 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 16773-3:2009), 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 for dummy cells with low impedance values (10 Ω to 1 000 Ω) has been added;

c) a reference to ASTM G106 for the precision data of low impedance measurements has been added;

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 3: Processing and analysis of data from dummy cells

1 Scope

This part of ISO 16773 specifies a procedure for the evaluation of the experimental set-up used for carrying out EIS on high-impedance coated samples. For this purpose, dummy cells are used to simulate high-impedance coated samples. On the basis of the equivalent circuits described, this part of ISO 16773 gives guidelines for the use of dummy cells to increase confidence in the test protocol, including making measurements, curve fitting and data presentation.

NOTE Due to the nature of the measurements, investigations of high-impedance coated samples are more susceptible to artefacts coming from electromagnetic interferences. Therefore, this part of ISO 16773 considers the aspects for measuring high-impedance samples by using appropriate dummy cells in a Faraday cage. However, most manufacturers offer complementary dummy cells in the low and medium impedance range. This allows checking the setup in the respective low impedance range.

2 Description of the dummy cells

2.1 General

A set of four equivalent circuits (dummy cells) is used to check the overall experimental arrangement. The dummy cells are mounted separately. Two types of equivalent circuit, A and B, are used, as shown in Figure 1. The specific electrical components of these four cells are given in Table 1. Dummy cells with low impedance values (10 Ω to 1 000 Ω) are described in ISO/TR 16208.

NOTE In Clause 8, the results of an interlaboratory test are used to evaluate the precision of this method. During the interlaboratory test, the participating laboratories also measured a fifth dummy cell consisting of an equivalent circuit of type B with unknown component values.

2.2 Components of the dummy cells

Each dummy cell consists of a combination of resistors and capacitors which are soldered directly onto a printed-circuit board (see Figures 1 and 2). Such networks of resistors and capacitors (equivalent circuits) are often used in work on high-impedance coated specimens.

NOTE Because of the very high overall resistance of circuits A and B, the resistor simulating the electrolyte can be neglected. Typically, the values of resistances R_1 and R_2 are above 100 MΩ whereas the electrolyte resistance is around 100 Ω to 500 Ω. As a consequence, the electrolyte resistance is not significant in this kind of EIS application.

The values of the components of the four dummy cells are chosen in accordance with the following considerations.

- Dummy cell 1 should check the input resistance as well as the input capacitance of the measurement equipment.
- Dummy cells 2 to 4 should check the capability of the evaluation software and the impedance measurement equipment to distinguish between only slightly different resistor/capacitor combinations.

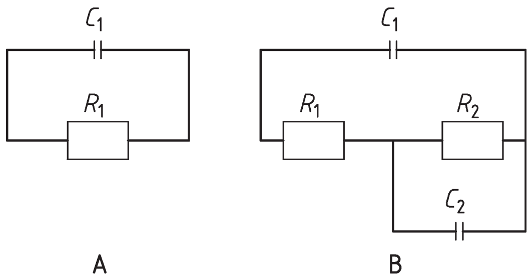


Figure 1 — Equivalent circuits of the dummy cells

Table 1 — Values of the components of the dummy cells

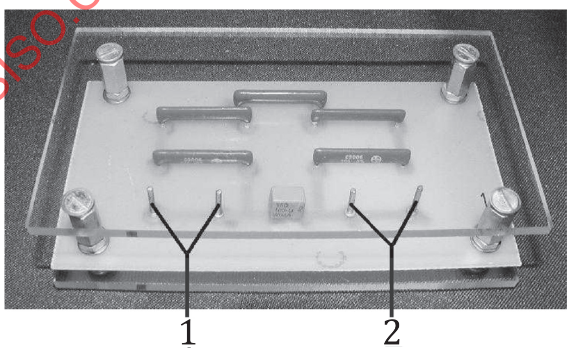
Dummy cell	Circuit	R_1 GΩ	R_2 GΩ	C_1 nF	C_2 nF
1	A	50	—	0,15	—
2	B	1	10	0,15	0,47
3	B	1	0,2	0,1	20
4	B	0,1	0,1	10	10

2.3 Accuracy requirements for the components

The accuracy required for resistors below 10^9 Ω is ±2 % and for resistors above 10^9 Ω it is ±5 %. The accuracy required for the capacitors is ±5 %. Such resistors and capacitors are available commercially.

2.4 Circuit description

Usually, the measurement of high-impedance coatings requires only a two-electrode set-up, but electrochemical workstations offer the possibility of connecting up three or four electrodes. To simplify the connection of the dummy cells to electrochemical workstations, each cell should have four connectors (as indicated in Figure 2), the connectors being connected internally in pairs. To avoid contamination (e.g. by fingerprints) of the printed-circuit board, each dummy cell is protected by acrylic plates mounted on top of and underneath the cell.



Key

1, 2 connector pairs

Figure 2 — Photograph of a dummy cell used in the interlaboratory test

3 Procedure

Perform all measurements in a Faraday cage in order to minimize electromagnetic interference.

NOTE The four dummy cells allow the suitability of a shielding technique (i.e. a Faraday cage) to be determined, as well as helping to find the location in the laboratory where electromagnetic noise levels are lowest.

Perform the measurements in accordance with the manufacturer's recommendations in the potentiostatic mode at a DC value of zero volts, using an amplitude of 20 mV (peak-to-zero).

A frequency range between 10^4 Hz and 10^{-2} Hz is sufficient for measurements with dummy cells 2 to 4. For dummy cell 1, a frequency range of 1 000 Hz to 5×10^{-3} Hz is recommended. About 30 min to 40 min are required for a single measurement (for dummy cell 1, about 1 h).

If the results of the measurements are not satisfactory when using an amplitude of 20 mV, increase the amplitude.

4 Data analysis

Using suitable software, e.g. that supplied by the manufacturer of the electrochemical workstation, analyse the results obtained from the dummy cell with equivalent circuit A (see Table 1). Record the result of curve fitting, the theoretical values of the circuit components and the excitation potential which was applied.

NOTE 1 Unfortunately, the curve-fitting error given for the data analysed differs from manufacturer to manufacturer, so direct comparison is not possible.

Prepare a Bode plot with the measured and simulated data.

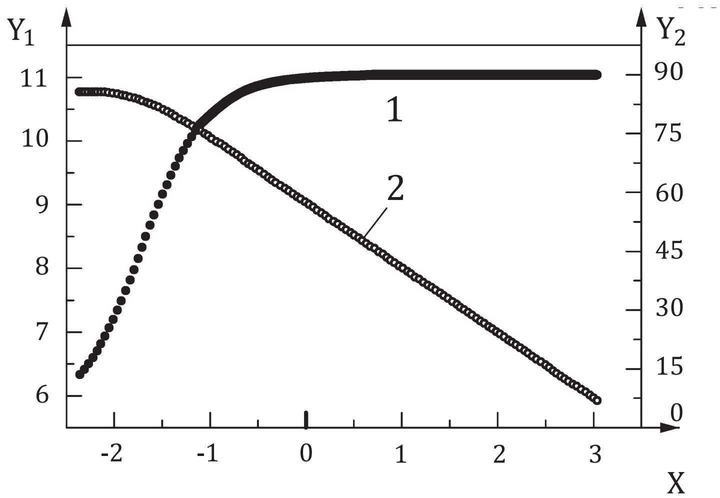
NOTE 2 Although the curve-fitting errors are not comparable, the Bode plot gives an indication of the quality of the measured data, especially at low frequencies.

Repeat the analysis with the results from cells 2 to 4 using equivalent circuit B (see Table 1).

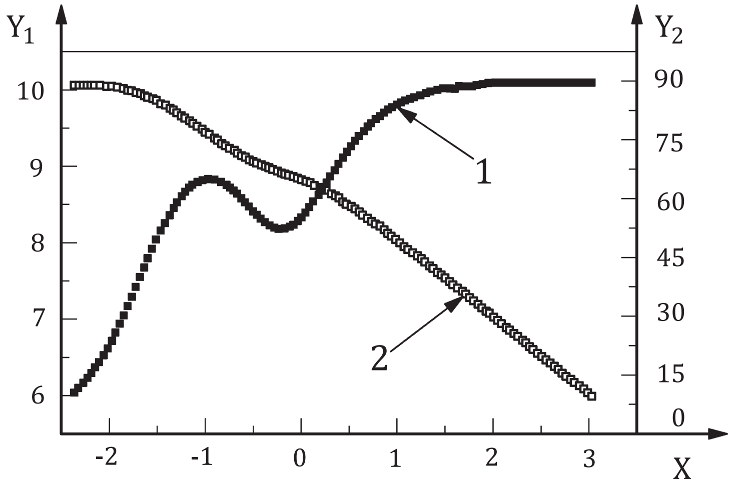
5 Presentation of the results

Present the measured data as Bode plots for comparison purposes.

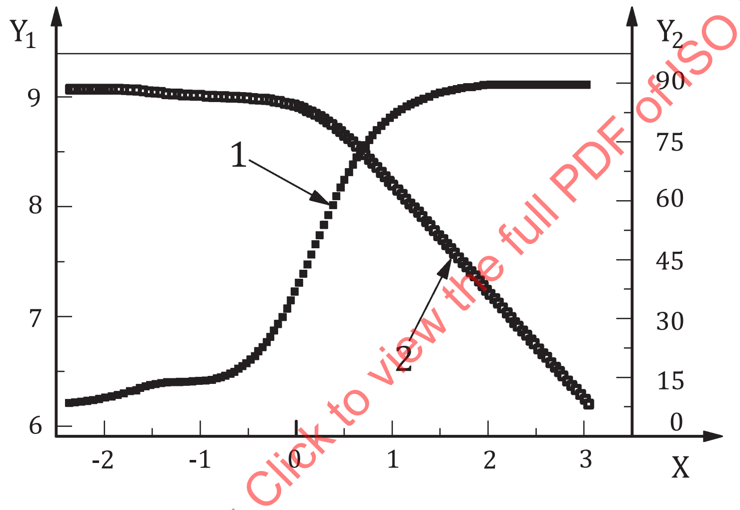
The Bode plots in Figure 3 show how the dummy-cell measurements should look. These diagrams were calculated using simulation software and can be used to compare with results from dummy-cell measurements.



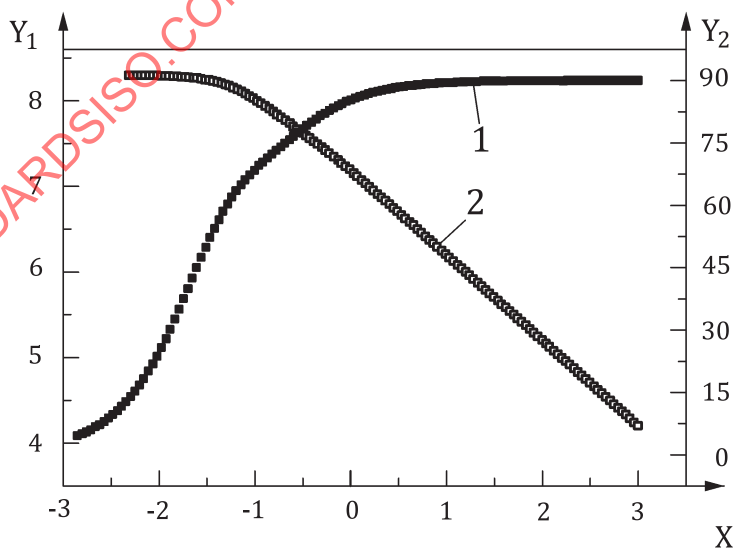
a) Cell 1



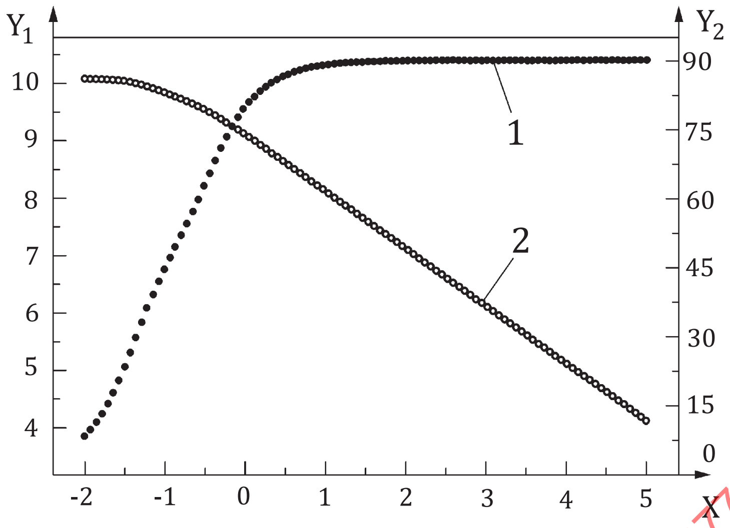
b) Cell 2



c) Cell 3



d) Cell 4



e) Cell 5 (values of components unknown)

Key

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

Y_1 log|*Z*| (*Z* in Ω)

Y_2 |*φ*| (degrees)

1 phase angle *φ*

2 impedance *Z*

Figure 3 — Bode plots of the simulated impedance spectra of the dummy cells and the unknown cell

6 Acceptance criteria for the measurement system

The EIS system shall be capable of measuring and extracting the values of the resistors and capacitors in the dummy cells. Deviations of the fitted values of the electronic components from the real values (see Table 1) should not exceed the accuracy limits of the components used in the dummy cells. Excessive errors in the values indicate experimental problems with the EIS system or inaccurate operation of the system.

NOTE Guidance is given in ISO 16773-2.

7 Test report

If a test report is required for the documentation of dummy-cell measurements, it shall contain at least the following information:

a) all details necessary to identify the dummy cell tested and its accuracy of electronic components;

b) a reference to this part of ISO 16773, i.e. ISO 16773-3;

c) the temperature and relative humidity during the conditioning and test, if different from those specified in ISO 16773-2: 2016, 6.7.2;

d) the test method used including excitation conditions and test duration, in particular:

1) frequency range, and

2) amplitude;

e) the results obtained from fitting of the respective equivalent circuit to the measured data, as indicated in Clause 4;

f) any deviations from the procedure specified;

g) any unusual features (anomalies) observed during the test;

h) the date of the test.

8 Repeatability and reproducibility

For the determination of the precision data of high impedance measurements, an interlaboratory test was carried out, details see below. For the precision data of low impedance measurements, refer to ASTM G106.

Fourteen laboratories, mainly in Europe and the USA, participated in an interlaboratory test. The purpose of the interlaboratory test was to obtain an estimate of the repeatability and reproducibility of the procedure. Each laboratory made measurements with the four dummy cells (see Table 1) and with a fifth cell (circuit B) with unknown components. After measurement and curve fitting, the results were as shown in Tables 2 to 6.

In cases where the measurements were acceptable (see Clause 6), it was found that the repeatability was very good, the deviations between measurements being better than the accuracy of the circuit components.

The reproducibility of the measurements made with cells 1 to 5 can be estimated from Tables 2 to 6.[1)] It can be seen that not every laboratory was able to make measurements with cell 1 with sufficient accuracy. Cell 2 gave no problems for any of the laboratories. Cells 3 and 4 were more difficult for some laboratories, although the majority were able to measure the correct values.

1) The amplitude in all tables is the peak-to-peak amplitude.

Table 2 — Reproducibility of measurements with cell 1

Laboratory	R GΩ	C pF	Amplitude mV	Error in R %	Error in C %	Total error %
1	28	195	50	44,0	30,0	74,0
2	44	180	50	12,0	20,0	32,0
3	50	155	20	0,0	3,3	3,3
4	50	150	20	0,0	0,0	0,0
5	52	170	20	4,0	13,3	17,3
6	52	155	20	4,0	3,3	7,3
7	52	155	20	4,0	3,3	7,3
8	52	160	20	4,0	6,7	10,7
9	54	155	20	8,0	3,3	11,3
10	54	155	20	8,0	3,3	11,3
11	54	210	14	8,0	40,0	48,0
12	56	160	20	12,0	6,7	18,7
13	58	155	20	16,0	3,3	19,3
14	N.A.[a]	N.A.[a]	20	N.A.[a]	N.A.[a]	N.A.[a]
Mean value	50,46	165,77				
Standard deviation	7,53	18,35				
Median	52	155				

[a] N.A. = Not available.

Table 3 — Reproducibility of measurements with cell 2

Laboratory	R_1 GΩ	C_1 nF	R_2 GΩ	C_2 nF	Amplitude mV	Error in R_1 %	Error in C_1 %	Total error %	Error in R_2 %	Error in C_2 %	Total error %
1	1,01	0,15	10,4	0,46	14	1	0	1	4	2	6
2	0,995	0,16	10	0,48	20	0,5	7	7	0	2	2
3	1,005	0,18	10,7	0,47	20	0,5	20	21	7	0	7
4	1,01	0,155	10,6	0,465	20	1	3	4	6	1	7
5	1,005	0,15	10,7	0,46	20	0,5	0	0	7	2	9
6	1,01	0,16	10,2	0,47	20	1	7	8	2	0	2
7	1,01	0,15	10,3	0,46	20	1	0	1	3	2	5
8	1	0,15	10,4	0,465	20	0	0	0	4	1	5
9	1,01	0,155	10,4	0,47	20	1	3	4	4	0	4
10	1,01	0,15	10,5	0,46	20	1	0	1	5	2	7
11	1	0,2	10,2	0,44	20	0	33	33	2	6	8
12	1,005	0,16	10,3	0,47	20	0,5	7	7	3	0	3
13	1,09	0,18	10,2	0,4	50	9	20	29	2	15	17
14	0,87	0,18	9,1	0,45	50	13	20	33	9	4	13
Mean value	1,00	0,16	10,29	0,46							
Standard deviation	0,04	0,02	0,40	0,02							

Table 4 — Reproducibility of measurements with cell 3

Laboratory	R_1 GΩ	C_1 nF	R_2 GΩ	C_2 nF	Amplitude mV	Error in R_1 %	Error in C_1 %	Total error %	Error in R_2 %	Error in C_2 %	Total error %
1	1,000	0,101	0,200	20,0	14	0	1	1	0	0	0
2	0,970	0,103	0,195	19,0	20	3	3	6	2,5	5	8
3	1,010	0,100	0,220	24,0	20	1	0	1	10	20	30
4	1,000	0,099	0,200	20,0	20	0	1	1	0	0	0
5	1,005	0,101	0,200	20,0	20	0,5	1	1	0	0	0
6	0,990	0,100	0,200	19,0	20	1	0	1	0	5	5
7	1,000	0,100	0,200	21,0	20	0	0	0	0	5	5
8	1,000	0,101	0,200	20,0	20	0	1	1	0	0	0
9	0,980	0,100	0,400	30,0	20	2	0	2	100	50	150
10	1,000	0,101	0,200	20,0	20	0	1	1	0	0	0
11	1,000	0,170	0,200	20,0	20	0	70	70	0	0	0
12	1,000	0,102	0,195	21,0	20	0	2	2	2,5	5	8
13	6,000	0,120	1,200	0,5	50	500	20	520	500	98	598
14	4,000	0,110	1,000	31,0	50	300	10	310	400	55	455
Mean value	1,57	0,11	0,34	20,39							
Standard deviation	1,51	0,02	0,33	6,90							

Table 5 — Reproducibility of measurements with cell 4

Laboratory	R_1 GΩ	C_1 nF	R_2 GΩ	C_2 nF	Amplitude mV	Error in R_1 %	Error in C_1 %	Total error %	Error in R_2 %	Error in C_2 %	Total error %
1	0,100	10	0,1	10	14	0	0	0	0	0	0
2	0,105	9,9	0,1	10,9	20	5	1	6	0	9	9
3	0,205	11,5	0	0	20	105	15	120	100	100	200
4	0,100	9,9	0,1	9,6	20	0	1	1	0	4	4
5	0,100	9,7	0,1	9,7	20	0	3	3	0	3	3
6	0,095	9,85	0,105	9,2	20	5	1,5	6,5	5	8	13
7	0,100	9,7	0,1	9,7	20	0	3	3	0	3	3
8	0,100	10	0,1	9,5	20	0	0	0	0	5	5
9	0,100	9,7	0,1	9,7	20	0	3	3	0	3	3
10	0,100	9,7	0,1	9,6	20	0	3	2	0	4	4
11	0,105	10	0,1	10,5	20	5	0	5	0	5	5
12	N.A.[a]	N.A.[a]	N.A.[a]	N.A.[a]	20	N.A.[a]	N.A.[a]	N.A.[a]	N.A.[a]	N.A.[a]	N.A.[a]
13	0,180	10	0,19	3	50	80	0	80	90	70	160
14	0,130	9,9	0,17	4	50	30	1	31	70	60	130
Mean value	0,12	9,99	0,11	8,11							
Standard deviation	0,03	0,47	0,04	3,43							

[a] N.A. = Not available.