

Electrochemical analyzers —

Part 3: Method for specifying performance of electrolytic conductivity analyzers

[IEC title: Expression of performance of electrochemical
analyzers — Part 3: Electrolytic conductivity]

UDC 621.35.083:541.133.082.7

Committees responsible for this British Standard

The preparation of this British Standard was entrusted by the Electronic Equipment Standards Committee (EEL/-) to Technical Committee EEL/8, upon which the following bodies were represented:

- British Telecommunications plc
- Department of Trade and Industry (National Physical Laboratory)
- Department of Trade and Industry (National Measurement Accreditation Service)
- Electricity Supply Industry in England and Wales
- GAMBICA (BEAMA Ltd.)
- Institution of Electronic and Radio Engineers
- Ministry of Defence

The following was also represented in the drafting of the standard, through subcommittees and panels:

- Water Research Centre

This British Standard, having been prepared under the direction of the Electronic Equipment Standards Committee, was published under the authority of the Board of BSI and comes into effect on 28 November 1986

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The following BSI references relate to the work on this standard:
Committee reference EEL/8
Draft for comment 82/26773 DC

ISBN 0 580 15253 7

Amendments issued since publication

Amd. No.	Date of issue	Comments

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National foreword

This Part of BS 6438 has been prepared under the direction of the Electronic Equipment Standards Committee. It is identical with IEC Publication 746-3:1985 “*Expression of performance of electrochemical analyzers — Part 3: Electrolytic conductivity*”, published by the International Electrotechnical Commission (IEC).

BS 6438-1 contains methods common to all analyzers and this Part should be read in conjunction with Part 1. The other Parts deal with certain aspects of a particular type of analyzer. Part 2, which deals with pH value, has been published, and other Parts, which will include dissolved oxygen content and oxidation reduction (REDOX) potential, are in preparation.

Terminology and conventions. The text of the International Standard has been approved as suitable for publication as a British Standard without deviation. Some terminology and certain conventions are not identical with those used in British Standards; attention is drawn especially to the following.

In Table B.I, Table B.II and Table B.III the comma has been used as a decimal marker. In British Standards it is current practice to use a full point on the baseline as the decimal marker.

Cross-reference

International Standard	Corresponding British Standard
IEC 746-1:1982 ^a	BS 6438 <i>Electrochemical analyzers</i> Part 1:1984 <i>Method for specifying performance common to all analyzers</i> (Identical)

^a Undated in the text.

A British Standard does not purport to include all the necessary provisions of a contract. Users of British Standards are responsible for their correct application.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 16, an inside back cover and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

1 Scope

This standard is applicable to analyzers, sensor units and electronic units used for the determination of electrolytic conductivity of aqueous solutions. IEC Publication 746-1: Expression of Performance of Electrochemical Analyzers, Part 1: General, includes further definitions of the scope and provides for the general aspects of all electrochemical analyzers, including electrolytic conductivity.

2 Object

This standard is intended to specify the terminology, definitions, requirements for statements by manufacturers and performance tests for analyzers, sensor units and electronic units used for the determination of electrolytic conductivity of aqueous solutions.

3 Definitions

See Clause 3 of IEC Publication 746-1, plus the following:

3.1

electrolytic conductance

the current divided by the potential difference is defined as electrolytic conductance in the case of ionic charge transport

$$G = \frac{I}{U} \quad (1)$$

where:

- I is the current through electrolyte, in amperes
- U is the potential difference applied across the electrodes in volts
- G is the electrolytic conductance

the unit of electrolytic conductance is the siemens (S)

electrolytic resistance is the reciprocal of electrolytic conductance with the ohm (Ω) as the unit of measurement

3.2

electrolytic conductivity

electrolytic conductivity, formerly called specific conductance, is defined by the equation:

$$\kappa = \frac{j}{E} \quad (2)$$

where:

- j is the electric current density, in A m^{-2}
- E is the electric field strength, in V m^{-1}

the unit of electrolytic conductivity is S m^{-1} .

Electrolytic resistivity is the reciprocal of electrolytic conductivity with units of ohm meter ($\Omega \text{ m}$). In the case of an electrolytic conductor of a uniform cross-section A and length l and an electrolytic conductance G (see Sub-clause 3.1), we have

$$\kappa = \frac{Gl}{A} \quad (3)$$

it is usual to measure electrolytic conductivity by means of cells without a uniform cross-section, in which case the quotient $1/A$ should be determined by means of a reference solution of known electrolytic conductivity. The quotient $1/A$ is called the cell constant

at the electrode surfaces polarization phenomena can occur which influence the measured quantity. To avoid this error, different measuring methods can be applied

- 1) A.C. measurements with a frequency high enough to avoid polarization effects.
- 2) Four electrode measurements with separated current transporting and potential measuring electrodes.
- 3) Inductive or capacitive measurements by coupling between the electrolytic conductor and the electrical measuring circuit through non-conductive media.

in each case the relationship between the electrolytic conductivity and the measured output quantity is established by the cell constant

3.3

cell constant of the sensor unit

the relationship between electrolytic conductance and electrolytic conductivity is defined by the equation:

$$\kappa = K_{\text{cell}} \cdot G \quad (4)$$

where:

- κ is the electrolytic conductivity, in S m^{-1}
- G is the electrolytic conductance, in siemens
- K_{cell} is the cell constant, in m^{-1} in place of cell conductance

NOTE The cell constant will normally have a constant value over a stated range (see Sub-clause 4.1). Outside this range it should be expected that polarization effects will produce errors.

3.4

temperature coefficient

the relative increase (or decrease) of the electrolytic conductivity of a solution per degree kelvin temperature change. The temperature coefficient is strongly dependent on the application

the following equation can be applied:

$$\kappa_{t_r} = \frac{\kappa_t}{(1 + \alpha \Delta t)} \quad (5)$$

where:

κ_t is the electrolytic conductivity at temperature t

κ_{t_r} is the electrolytic conductivity at a reference temperature t_r

Δt is the temperature difference $t - t_r$

α is the temperature coefficient

the unit of temperature coefficient is K^{-1}

in practice, this formula is sufficiently accurate over a small temperature range. For large temperature ranges it is usually necessary to add higher terms of a polynomial series such as $\beta(\Delta t)^2 + \gamma(\Delta t)^3 + \dots$, to equation (5), to obtain sufficient accuracy. The percentage temperature coefficient, which is the percentage relative deviation per degree kelvin from the reference value κ_{t_r} , is often used so that:

$$\alpha(\%) = 100 \alpha \quad (6)$$

NOTE In practice, the manufacturers' literature should be consulted when solving the temperature dependence of conductivity measurements.

3.5

common mode input voltage

a voltage that is applied to both input terminals at the same time

3.6

input common mode rejection ratio (CMRR)

the ratio of the input voltage range to the maximum change in input offset voltage over this range

4 Procedure for statement

See Clause 4 of IEC Publication 746-1, plus the following:

NOTE Warm-up time statement is not required for sensor units. For complete analyzers, statement on warm-up time refers only to electronic units and is validated as in IEC Publication 746-1.

4.1 Statements on sensor units

4.1.1 Cell constant.

4.1.2 Temperature compensation range, if applicable.

4.1.3 Type of temperature compensation system, if any, with electrical characteristics and limiting values.

4.1.4 Whether flow-through type, immersion type or other.

4.1.5 Flow range, in the case of a flow-through type sensor unit.

4.1.6 Materials in contact with the sample.

4.1.7 Pressure working range.

4.1.8 Temperature working range.

4.1.9 Sensor dimensions.

4.2 Additional statements on electronic units

4.2.1 Measuring frequency.

4.2.2 Temperature compensation range, if applicable.

4.2.3 Type of temperature compensation element of the sensor unit to which the electronic unit can be adapted.

4.2.4 Possibility of adjustment for reference temperature of the sample.

4.2.5 Maximum allowable common mode input voltage.

4.2.6 Input common mode rejection ratio (CMRR).¹⁾

4.2.7 Maximum voltage across the sensor.

4.3 Additional statements on complete analyzers

4.3.1 Conductivity measuring ranges (rated and effective).

4.3.2 Reference temperature for the sample.

4.3.3 Temperature coefficient or temperature coefficient range used in the temperature compensation.

4.3.4 Adjustment range for cell constant.

4.3.5 Electrolytic conductivity and/or composition of solution used for temperature compensation.

5 Recommended standard values and ranges of influence quantities affecting the performance of electronic units

See Clause 5 of IEC Publication 746-1.

¹⁾ This applies only in the case of certain four-electrode conductivity measuring systems.

6 Verification of values

See Clause 6 of IEC Publication 746-1, plus the following:

6.1 General

During measurements with more than one test solution, the sensor unit treatment described in Sub-clause 6.1.1 is to be used for:

- linearity error, if applicable;
- repeatability error;
- stability error;
- temperature effect on the sensor unit.

When using a sensor unit of one manufacturer and an electronic unit of another manufacturer, the specific test methods for the electronic unit shall be agreed upon between the user and the manufacturer of the electronic unit.

6.1.1 In the above-mentioned cases, the sensor unit shall be rinsed several times with water having a conductivity negligible within the rated operating range, then rinsed with new solution and only then shall it be immersed in a beaker filled with fresh solution. This procedure shall be repeated each time, in the event that several series of measurements are prescribed.

In the case of flow-through systems, the verification of values shall be carried out under flow conditions as specified by the manufacturer.

6.2 Calibration solutions and test solutions

For calibration solutions, see Appendix A.

For test solutions, see Appendix B.

6.3 Test procedures

In the case of special applications where these tests are not appropriate, test procedures shall be agreed upon between manufacturer and user.

6.3.1 Operating error

See Sub-clause 6.7.1 of IEC Publication 746-1.

6.3.2 Linearity error (if linearity is claimed)

6.3.2.1 Sensor unit

Using an appropriate electronic unit, perform the test as indicated in Sub-clause 6.3.2.2.

6.3.2.2 Analyzer

The sensor unit is exposed to at least five calibration solutions representing approximately uniformly distributed conductivities, including approximately the minimum and maximum rated values for the analyzer.

The first order least square fit is calculated and the maximum deviation from the regression line is determined. This maximum deviation is the linearity error and is expressed in terms of percentage of the rated range.

NOTE For reasons of efficiency, this test may be combined with the test for repeatability error (see Sub-clause 6.3.3.2).

6.3.3 Repeatability error

6.3.3.1 Sensor unit

Using an appropriate electronic unit, perform the test as indicated in Sub-clause 6.3.3.2.

6.3.3.2 Analyzer

The sensor unit is exposed sequentially to test solutions representing as nearly as possible the minimum, the maximum and the median rated conductivities.

The steps are repeated six times on each test solution in turn, at reference temperature, with no rinsing between the six readings, at intervals of about ten times the instrument's 90 % time. The standard deviation is calculated for each set of six recorded values for each solution. The average of the three standard deviations is calculated and reported as repeatability error. The temperature of all solutions and the sensor unit should be the same within ± 0.2 °C and reported along with the repeatability error.

6.3.4 Stability error

6.3.4.1 Sensor unit

Using an appropriate electronic unit, perform the test as indicated in Sub-clause 6.3.4.2.

6.3.4.2 Analyzer

The sensor unit is exposed to test solutions representing as nearly as possible the mid-scale rated conductivity value and the indicated value is recorded.

This is repeated after the specified time interval and the stability error is calculated and reported as a percentage value in terms of the rated range. The temperature of all solutions and the sensor unit shall be the same within ± 0.2 °C and reported along with the stability error.

6.3.5 Output fluctuation for the analyzer

For this test, the analyzer output shall be displayed on a recorder with a 90 % time less than the 90 % time of the analyzer.