

INTERNATIONAL STANDARD

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Second edition
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Expression of performance of electrochemical analyzers –

Part 3: Electrolytic conductivity

*Expression des qualités de fonctionnement
des analyseurs électrochimiques –*

*Partie 3:
Conductivité électrolytique*



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INTERNATIONAL ELECTROTECHNICAL COMMISSION

**EXPRESSION OF PERFORMANCE
OF ELECTROCHEMICAL ANALYZERS –****Part 3: Electrolytic conductivity**

FOREWORD

- 1) The IEC (International Electrotechnical Commission) is a worldwide organization for standardization comprising all national electrotechnical committees (IEC National Committees). The object of the IEC is to promote international co-operation on all questions concerning standardization in the electrical and electronic fields. To this end and in addition to other activities, the IEC publishes International Standards. Their preparation is entrusted to technical committees; any IEC National Committee interested in the subject dealt with may participate in this preparatory work. International, governmental and non-governmental organizations liaising with the IEC also participate in this preparation. The IEC collaborates closely with the International Organization for Standardization (ISO) in accordance with conditions determined by agreement between the two organizations.
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International Standard IEC 60746-3 has been prepared by subcommittee 65D: Analyzing equipment, of IEC technical committee 65: Industrial-process measurement and control.

This second edition cancels and replaces the first edition, published in 1985, and constitutes a technical revision.

This standard shall be used in conjunction with IEC 60746-1.

The text of this standard is based on the following documents:

FDIS	Report on voting
65D/85/FDIS	65D/87/RVD

Full information on the voting for the approval of this standard can be found in the report on voting indicated in the above table.

This publication has been drafted in accordance with the ISO/IEC Directives, Part 3.

Annex C forms an integral part of this standard.

Annexes A, B and D are for information only.

IEC 60746 consists of the following parts, under the general title *Expression of performance of electrochemical analyzers*:

Part 1: General

Part 2: pH value

Part 3: Electrolytic conductivity

Part 4: Dissolved oxygen in water measured by membrane covered amperometric sensors

Part 5: Oxidation-reduction potential or redox potential

Part 6: Conductivity effect of foreign ions in ultrapure waters, from combined conductivity and pH¹⁾

The committee has decided that the contents of this publication will remain unchanged until 2007. At this date, the publication will be

- reconfirmed;
- withdrawn;
- replaced by a revised edition, or
- amended.

A bilingual version of this publication may be issued at a later date.

¹⁾ Under consideration.

EXPRESSION OF PERFORMANCE OF ELECTROCHEMICAL ANALYZERS –

Part 3: Electrolytic conductivity

1 Scope

This part of IEC 60746 is intended

- to specify terminology, definitions and requirements for statements by manufacturers for analyzers, sensor units, and electronic units used for the determination of the electrolytic conductivity of aqueous solutions;
- to establish performance tests for such analyzers, sensor units and electronic units;
- to provide basic documents to support the applications of quality assurance standards ISO 9001 [1]¹⁾, ISO 9002 [2] and ISO 9003 [3].

2 Normative references

The following referenced documents are indispensable for the application 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.

IEC 60746-1, *Expression of performance of electrochemical analyzers – Part 1: General*

3 Definitions

For the purpose of this part of IEC 60746, the definitions of IEC 60746-1 apply, together with the following definitions.

3.1

electrolytic conductance

current divided by the potential difference in the case of ionic charge transport within an electrolytic solution filling a conductivity cell:

$$G = \frac{I}{U}$$

where

I is the current through the electrolyte, in amperes (A);

U is the potential difference applied across the electrodes, in volts (V);

G is the electrolytic conductance, in siemens (S).

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

1) Figures in square brackets refer to the bibliography.

3.2

electrolytic conductivity

formerly called specific conductance, is defined by the equation:

$$\kappa = \frac{j}{E}$$

where

j is the electric current density, in $\text{A}\cdot\text{m}^{-2}$;

E is the electric field strength, in $\text{V}\cdot\text{m}^{-1}$.

The unit of electrolytic conductivity, κ , is siemens per metre ($\text{S}\cdot\text{m}^{-1}$). Electrolytic resistivity is the reciprocal of electrolytic conductivity with the unit of ohmmeter ($\Omega\cdot\text{m}$)

NOTE In practical use, the most commonly employed conductivity unit is microsiemens per centimetre ($\mu\text{S}\cdot\text{cm}^{-1}$) or the corresponding resistivity unit, megohm per centimetre ($\text{M}\Omega\cdot\text{cm}$)

$$1 \mu\text{S}\cdot\text{cm}^{-1} = 10^{-4} \text{S}\cdot\text{m}^{-1}$$

3.3

cell constant of the sensor unit

an electrolytic conductor of a uniform cross-section X and length L is defined by the equation:

$$\kappa_{\text{cell}} = \frac{L}{X}$$

where κ_{cell} is the cell constant, in m^{-1} (see Note 1).

It is usual to measure electrolytic conductivity by means of cells without a uniform cross-section, in which case the κ_{cell} should be determined by means of a reference solution of known electrolytic conductivity.

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

$$\kappa = \kappa_{\text{cell}} \times G$$

where

κ is the electrolytic conductivity, in $\text{S}\cdot\text{m}^{-1}$;

G is the electrolytic conductance, in S ;

κ_{cell} is the cell constant, in m^{-1} .

NOTE 1 In practical use, κ_{cell} is generally expressed in cm^{-1} , κ in $\mu\text{S}\cdot\text{cm}^{-1}$ and G in μS (see 3.2).

NOTE 2 The cell constant will normally have a constant value over a stated range (see 4.1). Outside this range, it should be expected that polarization or other effects will produce errors (see 3.4 and annex D).

3.4

polarization

effect which occurs at electrode surfaces in an electrolytic solution when the current between the electrodes is such as to produce electrolysis and consequent partial insulation of the electrode surface

To avoid this uncertainty, different measuring methods can be applied (see 3.7, 3.8 and annex D):

- a.c. measurements with a frequency high enough to avoid polarization effects;
- four or six electrode measurements with separated current transporting and potential measuring electrodes;
- 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.

3.5

temperature coefficient

relative increase (or decrease) of the electrolytic conductivity of a solution per kelvin temperature change. The temperature coefficient is dependent on the reference temperature and the nature of the solution.

The following approximate equation can be applied for strong electrolyte solutions where $\kappa > 10^{-4} \text{ S} \cdot \text{m}^{-1}$ ($1 \mu\text{S} \cdot \text{cm}^{-1}$)

$$\kappa_t = \kappa_{tr} \times (1 + \alpha \Delta t)$$

where

κ_t is the electrolytic conductivity at temperature t ;

κ_{tr} is the electrolytic conductivity at reference temperature tr ;

Δt is the temperature difference $t - tr$;

α is the temperature coefficient.

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 the above equation, to obtain sufficient accuracy. The percentage temperature coefficient, which is the percentage relative deviation per kelvin from the reference value κ_{tr} , is often used so that

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

NOTE The manufacturer's literature should be consulted for details of sample temperature compensation technique(s) applied.

3.6

simulator

a series of non-inductive resistors (preferably step-variable, e.g., a decade resistance box), used for the performance tests of conductimetric electronic units, simulating two- and three-electrode sensors

NOTE The minimum step should preferably be $0,01 R$, where R is the reciprocal value of the nominal full range conductivity value. Analogously, the highest resistance value should correspond to the lower limit of the measuring range: if the range begins at zero, the resistance value should be at least $10 R$ for testing at 10 % of the range.

For multi-electrode sensor simulator design, the manufacturer must be consulted.

The temperature sensor may be simulated by another variable precision resistor, e.g., a variable decade resistance box.

3.7

cell capacitance

produced by the electrostatic field existing between the sensor's measuring electrodes due to the high dielectric constant of water. Its value is inversely proportional to the cell constant and expressed by the approximate relationship:

$$C_{\text{cell}} \Omega \frac{7}{K_{\text{cell}}}$$

where

C_{cell} is the cell capacitance, in picofarads (pF: $1 \text{ pF} = 10^{-12} \text{ F}$);

K_{cell} is the cell constant, in cm^{-1} ;

C_{cell} may disturb low conductivity measurements made with two- or three-electrode cells when too high a frequency is used. The effect can be reduced by means of phase discrimination within the electronic unit.

3.8

leakage currents

a.c. currents at the measuring frequency flowing from the cell electrodes to local conductive parts in contact with the sample solution.

They effectively alter the cell constant causing measuring uncertainties and arise principally in symmetrical cells, i.e., with similar electrodes side by side.

4 Procedure for specification

See clause 5 of IEC 60746-1, plus the following.

4.1 Additional statements on sensor units

- a) Type, i.e., flow-through, dip or insertion unit, number of electrodes, if electrodeless whether inductive or capacitive cell (common types of cell are described in annex D).
- b) Cell constant, tolerance and corresponding range of measurement (see 4.3a)).
- c) Type of temperature compensator (for example, Pt100).
- d) Sensor dimensions, mounting and connection details.

4.2 Additional statements on electronic units

- a) Measuring frequency/frequencies.
- b) Cell constant adjustment range.
- c) Type of temperature compensator sensor to which the electronic unit can be connected and maximum permitted resistance of compensator plus connection leads.
- d) Reference temperature adjustment range; if fixed, state temperature.
- e) Range of temperature coefficient adjustment and details of sample temperature compensation that may be applied. If fixed, state value.
- f) Installation details.

4.3 Additional statements on complete analyzers

- a) Measuring ranges (rated and effective).

NOTE Some analyzers employ concentration units, for example, mass % NaCl, g NaOH per litre, etc. For such analyzers, the rated range should be specified on the measurement unit as well as the corresponding conductivity at the rated reference temperature.

- b) Reference temperature for the measurement.
- c) Installation details.

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

See annex A of IEC 60746-1.

6 Verification of values

See clause 6 of IEC 60746-1

6.1 General aspects

The parameters required to be set in the electronic unit for the specific combination of the electronic unit and sensor shall be established. These shall include

- the range to be measured and the units for display (if a display is fitted);
- the range and type of any transmitted output;
- the type of sample, i.e., a flow-through sample and its flow rate, or a static sample into which the sensor is immersed and its minimum depth;
- the type and range of sample temperature compensation for which verification is required, if applicable.

6.2 Calibration

For accurate calibration of a conductivity analyzer the following parameters are required for adjustment on the electronic unit:

- a) the cell constant (see 3.3 and 4.2 b));
- b) the reference temperature (see 4.2d));
- c) the temperature coefficient or appropriate algorithm (see 4.2e)).

NOTE The exact value of the cell constant can be determined using an appropriate calibration solution (see annex A).

6.3 Test solutions

Test solutions shall be applied in a manner suited to the design of the sensor.

For flow-through sensors, the solutions shall be applied at a flow rate within the manufacturer's stated rated range.

For sensors which can be immersed into test solutions, it is essential that the sensor unit is rinsed several times with water of negligible conductivity (in comparison with the range to be tested) after immersion in one solution prior to immersion in a fresh solution. A good procedure is to keep a second container of each test solution concentration to be used for the final rinse prior to immersion in each respective accurate test solution.

The immersion of sensor probes into containers of test solution exposed to air is not appropriate for measurements below $100 \mu\text{S}\cdot\text{m}^{-1}$.

NOTE De-ionized water in an open container absorbs CO_2 ; a typical equilibrium conductivity of approximately $0,9 \mu\text{S}\cdot\text{cm}^{-1}$ is eventually reached.

Examples of test solutions are tabulated in annex B.

For low-conductivity solutions below about $100 \mu\text{S}\cdot\text{cm}^{-1}$ (at 25°C), it is essential that flowing solutions of appropriate conductivities are generated by continuous injection of, e.g., NaCl solutions into a pure water stream at a controlled flow rate. Required concentrations may be determined by extrapolation of values in annex B.

Pure water can only be generated by a circulatory de-ionization system: standard test solutions shall be generated from such water.

6.4 Test procedures

The following test procedures shall be carried out as described in IEC 60746-1, using the appropriate test solutions.

- a) Intrinsic uncertainty
- b) Linearity uncertainty

NOTE 1 Deviations from linearity of the sensor unit may be produced at high conductivities by polarization with too low a measuring frequency, and at low conductivities by cell capacitance with too high a frequency. Conductivity analyzers that incorporate frequency selection permit simple verification. For analyzers without frequency selection, polarization errors can be revealed by using test solutions at the upper range (approximately 80 % – 100 %). Capacitance uncertainties may be demonstrated by parallel connection of a capacitor of approximately the value given by the equation in 3.7 to the electronic unit input, i.e., to the cell electrodes (for four- and six-electrode cells, the inner voltage electrodes): if an increase of displayed value is observed, the capacitance uncertainty is about the same.

- c) Repeatability
- d) Output fluctuation
- e) Warm-up time
- f) Drift

NOTE 2 Drift is generally reported as a linear regression in two ways, short term over a period in the range of 1 h to 24 h and for a longer period in the range of 30 days to 100 days.

- g) Response times

NOTE 3 These are given in detail in annex C, where method A is the preferred and the only method appropriate to flow-through cells.

- h) Sample temperature

Errors caused by variation of the sample temperature shall be determined at two points near the lower and higher limits of the measuring range. Measurements shall be made at the reference sample temperature, then at the lowest temperature within the compensation range (see 4.2d) and 4.2e)), and repeated at the highest temperature within that range.

NOTE 4 For flowing samples, this may be achieved by passage of the solution through a stainless-steel heat exchanger prior to the sensor.

- i) Primary influence quantities

Response to the following influence quantities will generally need to be determined using two test solutions near the higher and lower ends of the range. Influence quantities should first be applied at the reference value then the two limits (upper and lower) of the rated range. Final measurement should be made when the quantity is returned to the reference value.

Variations in electrical supply characteristics usually affect the electronics unit only and may be tested with only one solution at the mid-point of the span. These tests may be carried out on the electronics unit alone, using resistors to simulate the mid-point of the range for conductivity and the temperature sensor.

- Ambient temperature
- Humidity
- Sample flow-rate
- Sample pressure
- Sample outlet pressure (if different from above)
- Vibration
- Supply voltage
- AC supply frequency, or
- DC supply ripple and impedance
- Electromagnetic compatibility

Additional influence quantities which may require verification for specific applications are listed in IEC 60746-1. In addition to those listed, the following parameters may require verification.

j) Range of cell constant adjustment (electronic unit)

Using a test solution near the mid-point of the range, verify the possibility of increasing and/or reducing the displayed value within a variation range not less than the manufacturer's stated adjustment range. Repeat with other test solutions near the lower and higher limits of the measuring range. An appropriate simulator may be used (see 3.6).

Annex A (informative)

Electrolytic conductivity values of potassium chloride calibration solutions and pure water

Table A.1 – Electrolytic conductivity values

Calibration solution	Molal concentration m (mol KCl per kg water)	Mass of KCl per kg water	Temperature °C	Conductivity $\mu\text{S}\cdot\text{cm}^{-1}$	Temperature coefficient
A	1	74,551 g	25	111 070	
B [1]	0,1	7,455 1 g	0	7 115,85	0,030 5
		(or 107,456 g solution A and 900 g water)	25	12 824,6	0,019 0
			50	19 180,9	0,013 5
C [1]	0,01	0,745 6 g	0	772,921	0,031 2
		(or 100,746 g solution B and 900 g water)	25	1 408,23	0,019 6
			50	2 123,43	0,013 8
D	0,001	0,074 6 g (or 100,075 g solution C and 900 g water)	25	146,87	
E [2]	0,000 5	0,037 3 g (or 100,075 g solution C and 900 g water)	25	73,87	
Intermediate conductivity values at temperatures within ± 20 °C of stated reference temperatures can be obtained with an accuracy of better than 1 % using the relationship: $\kappa_t = \kappa_{tr} (1 + \alpha \Delta t)$ where κ_t is the conductivity at temperature, t; κ_{tr} is the tabulated value of nearest reference temperature tr; α is the temperature coefficient at tr; $\Delta t = t - tr$ For the preparation of the solution, KCl of analytical grade dried for at least 2 h at 220 °C to 240 °C shall be used. De-ionized water, with negligible conductivity compared with the stated value and preferably lower than $1 \mu\text{S}\cdot\text{cm}^{-1}$ (at 25 °C) shall be used (see 6.3). Tabulated conductivity values include the contribution of water: for solutions D and E, the conductivity of the de-ionized water must be taken into account. NOTE In the absence of a low-conductivity standard solution, solution E is included.					

Table A.2 – Electrolytic conductivity of pure water

Temperature °C	Conductivity $\mu\text{S}\cdot\text{cm}^{-1}$	Temperature °C	Conductivity $\mu\text{S}\cdot\text{cm}^{-1}$
0	0,010 74	50	0,174 4
10	0,022 55	60	0,251 7
20	0,042 01	70	0,349 2
25	0,055 44	80	0,467 0
30	0,072 02	90	0,605 9
40	0,114 9	100	0,763 1
NOTE Data are selected from [3].			

Annex B (informative)

Electrolytic conductivity values of aqueous sodium chloride solutions

Conductivity values have been interpolated from the data developed by G.F. Hewitt [4,5] with a stated accuracy of $\pm 0,25$ %.

For the preparation of the solutions, de-ionized water with negligible conductivity compared with the stated value shall be used and sodium chloride of analytical grade dried for at least 2 h at 220 °C to 240 °C.

Tabulated values are for a temperature of 18 °C. Values for other temperatures can be calculated from the equation

$$\kappa_t = \kappa_{18} [1 + \alpha(t - 18)]$$

where α is the temperature coefficient (table B.2 corrected by table B.3).

Table B.1 – Conductivity of sodium chloride solutions at 18 °C

Molal concentration m (mol NaCl ^a per kg water)	Conductivity $\mu\text{S}\cdot\text{cm}^{-1}$	Molal concentration m (mol NaCl ^a per kg water)	Conductivity $\mu\text{S}\cdot\text{cm}^{-1}$	Molal concentration m (mol NaCl ^a per kg water)	Conductivity $\mu\text{S}\cdot\text{cm}^{-1}$
2×10^{-4}	21,5	1×10^{-2}	1 016	1,0	73 290
4×10^{-4}	42,91	2×10^{-2}	1 983	1,2	86 270
6×10^{-4}	64,14	4×10^{-2}	3 853	1,4	96 240
8×10^{-4}	85,30	6×10^{-2}	5 669	1,6	106 700
1×10^{-3}	106,4	8×10^{-2}	7 444	1,8	116 600
2×10^{-3}	210,7	1×10^{-1}	9 190	2,0	125 400
4×10^{-3}	415,9	2×10^{-1}	17 430	2,5	145 700
6×10^{-3}	618,0	4×10^{-1}	32 720	3,0	163 800
8×10^{-3}	817,8	6×10^{-1}	47 150	3,5	179 000
		8×10^{-1}	60 650	4,0	190 900
				4,5	200 000
				5,0	206 800
				5,5	211 800
				6,0	215 400
a 1 mol NaCl = 58,443 g					

Table B.2 – Temperature coefficients for low-concentration sodium chloride solutions

Temperature °C	Temperature coefficient α	Temperature °C	Temperature coefficient α
0	0,021 1 ₈	80	0,026 1 ₈
10	0,021 9 ₈	90	0,026 4 ₃
20	0,022 7 ₇	100	0,026 6 ₀
30	0,023 5 ₃	110	0,026 6 ₉
40	0,024 2 ₃	120	0,026 7 ₄
50	0,024 8 ₆	130	0,026 7 ₅
60	0,025 3 ₉	140	0,026 7 ₈
70	0,025 8 ₄	150	0,026 8 ₄

Table B.3 – Tentative corrections to sodium chloride solution temperature coefficients

Temperature °C	Molal concentration NaCl m				
	0,01	0,1	0,2	0,5	1,0
0	–0,000 1	–0,000 4	–0,000 9	–0,001 2	–0,001 0
50	–0,000 1	–0,000 4	–0,000 7	–0,000 6	–0,000 4
100	–0,000 1	–0,000 2	–0,000 4	–0,000 6	+0,000 4

Annex C

(normative)

Alternative procedures for measuring response times: delay (T_{10}), rise (fall) (T_r , T_f) and 90 % (T_{90}) times

C.1 Procedure A

A recorder is connected to the output terminals of the analyzer. The inlet of the flow-through sensor is fitted with a two-way stopcock to supply alternate test solutions. An insertion sensor may be suitably mounted within, e.g., a tube, preferably plastic, fitted with an inlet equipped with a two-way stopcock, and outlet. A test solution representing the minimum rated value (or approximately 2-5 % above) is supplied until a constant reading on the recorder is obtained. The two-way stopcock is switched to supply a test solution representing the maximum rated value (or approximately 2-5 % below) and a mark is made on the recorder chart. The maximum value test solution is supplied until a constant reading is obtained. The stopcock is switched back to the minimum value solution and a second mark is made on the recorder chart: the minimum value solution is supplied until a constant reading is obtained.

For flow-through sensors, the flow rate of the solutions shall be adjusted to the maximum specified by the manufacturer for the equipment. The temperature of solutions and sensor unit shall be constant within $\pm 0,5$ °C and shall be reported with other results.

The values for delay time (T_{10}) and 90 % time (T_{90}), for both increasing and decreasing step changes, rise time (T_r) and fall time (T_f), are determined from the chart speed. The larger of the two delay, rise or fall 90 % times are reported.

C.2 Procedure B

Procedure B is similar to procedure A except that the sensor unit is immersed alternately in two tanks, one containing a stirred test solution representing the minimum rated electrolytic conductivity value and the other containing a stirred test solution representing the maximum rated electrolytic conductivity value. When transferring the sensor unit from one tank to the other, the sensor unit is shaken but neither wiped nor rinsed. The sensor unit is left in the tanks until constant readings are obtained.

Annex D (informative)

Conductivity cells

D.1 Multiple electrode sensors

Lower conductivity range sensors are designed with two electrodes in contact with the solution, those for the lowest range of cell constants with large, concentric, metal electrodes. Sensors with larger cell constants require a reduction in area and an increase in separation (see 3.3), which is often achieved with two rings of conductor inset into an insulating tube. Two-electrode sensors offer no electrical isolation from the bulk of the sample. To overcome this problem three-electrode sensors use two outer guard electrodes connected together forming the low input to the electronics unit. To measure the very highest conductivities these guard electrodes themselves have to be isolated from the analyzer signal path leading to four-electrode and six-electrode designs with two outer guard electrodes, two current-sourcing electrodes and two voltage-sensing electrodes as the innermost conductors.

For a full description of these techniques, the reader should consult specialist texts [6,7]. All these designs may be specified and receive performance verification by procedures in this standard.

D.2 Inductive conductivity sensors

This type of sensor, often called electrodeless, is generally only suitable for conductivities above $100 \mu\text{S}\cdot\text{cm}^{-1}$ and offers complete electrical insulation from the sample. The sensor consists of an electrical transformer with the primary winding excited by the electronics unit. The secondary is effectively a shorted turn of sample solution within an insulating tube. As the solution conductivity rises, the shorted turn draws more current from the primary winding. For a comprehensive explanation of the theoretical aspects, the reader should refer to specialist texts.

Inductive conductivity sensors may be specified and tested by procedures in this document but verification tests are generally easier to carry out with actual solutions than with a simulation circuit.

D.3 Capacitive conductivity sensors (also termed electrodeless)

The measurement cell is mounted between the plates of a capacitor in a resonance circuit. The current flowing in the circuit is a function, not generally linear, of sample conductivity. The method is rarely used for process analyzers.

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Q2 Please tell us in what capacity(ies) you bought the standard (tick all that apply). I am the/a:

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safety engineer ☐
testing engineer ☐
marketing specialist ☐
other

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(tick all that apply)

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consultant ☐
government ☐
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nearly ☐
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