# IEC TS 63165

Edition 1.0 2024-12

# TECHNICAL SPECIFICATION

## Requirements for industrial water quality analyzer system – Photometry

IEC TS 63165:2024-12(en)

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INTERNATIONAL
ELECTROTECHNICAL
COMMISSION

ICS 13.060.25

ISBN 978-2-8327-0089-1

CONTENTS

INTERNATIONAL ELECTROTECHNICAL COMMISSION

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# REQUIREMENTS FOR INDUSTRIAL WATER QUALITY ANALYZER SYSTEM – PHOTOMETRY

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The text of this Technical Specification is based on the following documents:

| Draft | Report on voting |
|---|---|
| 65B/1253/DTS | 65B/1274/RVDTS |

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

The language used for the development of this Technical Specification: is English.

This document was drafted in accordance with ISO/IEC Directives, Part 2, and developed in accordance with ISO/IEC Directives, Part 1 and ISO/IEC Directives, IEC Supplement, available at www.iec.ch/members_experts/refdocs. The main document types developed by IEC are described in greater detail at www.iec.ch/standardsdev/publications.

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- reconfirmed,
- withdrawn, or
- revised.

# REQUIREMENTS FOR INDUSTRIAL WATER QUALITY ANALYZER SYSTEM – PHOTOMETRY

## 1 Scope

This document applies to the industrial water quality analyzer system that uses a photometric method to determine the concentration of one or more chemical components in industrial water (water used in manufacturing, processing, cooling, washing, boiler, etc).

The objective of this document is to:

- specify the terminology and definitions related to the performance characteristics of a photometric industrial water quality analyzer system;
- unify the performance expression and verifying methods of such an analyzer system;
- specify the test procedures to be used in making statements on the performance characteristics of a photometric industrial water quality analyzer system.

## 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.

IEC 62443-3-3, *Industrial communication networks – Network and system security – Part 3-3: System security requirements and security levels*

IEC 62443-4-2, *Security for industrial automation and control systems – Part 4-2: Technical security requirements for IACS components*

## 3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

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

- IEC Electropedia: available at https://www.electropedia.org/
- ISO Online browsing platform: available at https://www.iso.org/obp

### 3.1
**photometry**
determination of the concentration of a dissolved substance in a solution by using the absorption of light by this substance

[SOURCE: ISO 14532:2014, 2.4.12]

### 3.2
**measurand**
particular quantity subject to measurement

[SOURCE: IEC 60050-311:2001, 311-01-03]

**3.3**
**measuring range**
range defined by two values of the measurand, or quantity to be supplied, within which the limits of uncertainty of the measuring instrument are specified

Note 1 to entry: An instrument can have several measuring ranges.

[SOURCE: IEC 60050-311:2001, 311-03-12]

**3.4**
**90 %response time**
**$T_{90}$**
time interval from the instant a step change occurs in the value of the property being measured to the instant when the change in the indicated value passes (and remains beyond) 90 % of its steady-state amplitude difference, i.e., $T_{90} = T_{10} + T_r$(or $T_f$). For cases where the rising and falling response times differ, the different response times should be specified

[SOURCE: IEC 60746-1:2003, 3.38]

**3.5**
**calibration**
set of operations which establishes, by reference to standards, the relationship which exists, under specified conditions, between an indication and a result of a measurement

Note 1 to entry: This term is based on the "uncertainty" approach.

Note 2 to entry: The relationship between the indications and the results of measurement can be expressed, in principle, by a calibration diagram.

[SOURCE: IEC 60050-311:2001, 311-01-09]

**3.6**
**calibration interval**
period between routine calibrations over which the performance of the analyser meets specified requirements

[SOURCE: ISO 14532:2014, 2.5.1.6]

**3.7**
**blank calibration solution**
solution prepared in the same way as the calibration solution but leaving out the analyte

[SOURCE: ISO 17294-1:2004, 3.3]

**3.8**
**calibration solution**
solution of known value of the property being measured, used for periodic calibration and for various performance tests

Note 1 to entry: The value should be expressed in SI units compatible with ISO 31.

Note 2 to entry: For the purposes of this document, the value of this solution represents the conventional true value against which the indicated value is compared.

Note 3 to entry: The values of calibration solutions should be traceable to reference material according to international or national standards, or agreed upon by the manufacturer and the user, and the conventional true values shall be stated.

[SOURCE: IEC 60746-1:2003, 3.5]

### 3.9

**accuracy**

quality which characterizes the ability of a measuring instrument to provide an indicated value close to a true value of the measurand

Note 1 to entry: This term is used in the "true value" approach.

Note 2 to entry: Accuracy is all the better when the indicated value is closer to the corresponding true value.

[SOURCE: IEC 60050-311:2001, 311-06-08]

### 3.10

**precision**

**measurement precision**

closeness of agreement between independent test/measurement results obtained under stipulated conditions

Note 1 to entry: Precision can be expressed as a standard deviation or relative standard deviation (coefficient of variation).

[SOURCE: ISO 18158:2016, 2.4.3.3]

### 3.11

**span drift**

change in analyzer system output in response to a standard of 90 % of the measuring range(s) of the analyzer system over a stated period of unattended operation

[SOURCE: ISO 11042-2:1996, 3.5.4, modified – in the term “span instability (drift)” has been replaced by “span drift”, and in the definition, “instrument” has been replaced with “analyzer system”.]

### 3.12

**zero drift**

change in analyzer system output in response to a zero sample over a stated period of unattended operation

### 3.13

**memory effect**

effect of previous values of the measurand on the current measurement results

Note 1 to entry: This effect mainly occurs in the residue of solutions or water samples.

[SOURCE: ISO 9169:2006, 2.1.21, modified – the note has been added.]

### 3.14

**limit of detection**

measured quantity value, obtained by a given measurement procedure, for which the probability of falsely claiming the absence of a component in a material is β, given a probability α of falsely claiming its presence

Note 1 to entry: IUPAC recommends default values for α and β equal to 0.05.

Note 2 to entry: The abbreviation LOD is sometimes used.

Note 3 to entry: The term “sensitivity” is discouraged for ‘detection limit’.

Note 4 to entry: The LOD is the lowest concentration of measurand in a sample that can be detected, but not necessarily quantitated under the stated conditions of the test.

[SOURCE:ISO 6107:2021, 3.169, modified – “detection level” has been removed from the term.]

### 3.15
**limit of quantification**
lowest concentration of a measurand that can be determined with acceptable precision under the stated conditions of the test

Note 1 to entry: As such defined, LOQ is based on evaluation of precision. This does not encompass neither any eventual bias, nor laboratory measurement uncertainty at LOQ level`.

[SOURCE: ISO 6107:2021, 3.320]

### 3.16
**parallel measurements**
measurements by different analyzer systems with sampling the same industrial water over the same time period

[SOURCE: ISO 9169:2006, 2.1.22, modified – in the definition, “measuring” has been replaced with “analyzer”.]

### 3.17
**consistency of parallel measurements**
evaluation of the maximum difference among different analyzer systems by parallel measurements

### 3.18
**bias**
difference between the expectation of a measurement result and a test result by laboratory methods

### 3.19
**period of unattended operation**
maximum interval of time for which the performance characteristics remains within a predefined range without external servicing, e.g. refill, adjustment

[SOURCE: ISO 9169:2006, 2.2.11]

### 3.20
**rate of valid data**
ratio of valid data to total data during the period of unattended operation

### 3.21
**interference of ambient temperature**
relative deviation between the measured value and the reference value of the standard solution under different ambient temperature

### 3.22
**interference of supply voltage**
deviation between the measured value and the reference value of the standard solution under different supply voltage

### 3.23
**interference of colour and suspended particles**
accuracy of a measured value after adding a standard solution with a specific colour and suspended particles in comparison with the reference value

### 3.24
**ion interference**
accuracy of a measured value after adding a standard solution with a specific interfering ion in comparison with the reference value

**3.25**
**pH interference**
accuracy of a measured value of a standard solution at different pH level in comparison with the reference value

# 4 Procedure for specification

## 4.1 Procedure for specification

For an industrial water quality analyzer system, manufacturers should provide all the applicable characteristic parameters with tolerances.

These characteristics should include performance characteristics, functional characteristics, ambient conditions, safety instructions, etc., which should be listed in the illustrative materials such as the product/user manual, or product nameplate.

These statements shall cover the aspects described in 4.2 to 4.5.

## 4.2 General

### 4.2.1 Rated operating conditions

Statements shall be made on rated operating conditions and limit conditions of operation in such a way that the following requirements are met, unless otherwise specified.

The apparatus, while functioning, shall show no damage or degradation of performance when performance characteristics or influence quantities, or both, are within the operation condition range during a specified time.

### 4.2.2 Storage and transportation conditions

The ambient conditions such as temperature, humidity, and the exposure to sunshine during storage shall be clearly identified by the manufacturer.

The condition requirements such as vibration, sunshine, and tipping/tilt during transportation shall be identified by the manufacturer.

The apparatus shall show no permanent damage or degradation of performance while inoperative when it has been stored or transported within required conditions during a specified time.

### 4.2.3 Safety of people, environment and equipment

Explanation and warning of safety related situations, such as high temperature, toxic solutions, special light, radiation, etc., shall be clearly specified.

### 4.2.4 Construction materials

Construction materials in contact with the sample shall be stated and verified to not contaminate the sample.

## 4.3 Performance characteristics requiring statements of rated values

**4.3.1** The manufacturer shall state minimum and maximum rated values for property to be measured (range or ranges).

**4.3.2** Minimum and maximum rated values for output signals corresponding to the rated values as given in 4.3.1.

## 4.4 Performance characteristics

Table 1 shows some typical performance characteristics.

**Table 1 – Performance characteristics**

| Contents | | |
|---|---|---|
| Measuring range | Response time | Accuracy |
| Precision | Span drift | Zero drift |
| Memory effect | Limit of detection | Limit of quantification |
| Period of unattended operation | Interference | Reagent consumption |
| There are two kinds of timing for calibration: calibration before every determination / measurement or calibration at regular intervals. Generally, the calibration is executed at regular intervals of days, weeks, or months. The recommended maximum calibration interval for ensuring the stable performance should be declared, so that users can make a reasonable calibration work plan, including material, cost, personnel and other resources. | | |

## 4.5 Functional characteristics requiring statements

### 4.5.1 Measured component

The name of the component of the determinant shall be clearly stated.

### 4.5.2 Analysis principle

The basic analysis method and principle in areas such as photo-electricity, chemistry, and associated signal conditioning shall be specified.

### 4.5.3 Detection wavelength

One or more typical operating wavelengths applied in the determination shall be clearly stated and their accuracy corrected.

### 4.5.4 Automatic calibration

It has to be verified whether the analyzer system has periodic automatic calibration and standard verification function.

### 4.5.5 Sample conditions

Rated ranges of sample conditions shall be stated at the analyzer inlet for an analyzer system. These shall include flow rate (if appropriate), pressure and temperature.

### 4.5.6 Explosion-proof

The analyzer system should be explosion-proof in some applications, so the analyzer system manufacturer should declare the explosion-proof grade of the analyzer system.

### 4.5.7 Ingress protection

The analyzer system shall be waterproof and dustproof, and the analyzer system manufacturer shall declare the IP protection level of the analyzer system.

# 5 Functional requirements of analyzer system

## 5.1 Internal and external interface

### 5.1.1 Electrical interface

The water quality analyzer system shall have one or more data exchange interfaces, so as to ensure that the device can support the functions such as digitalized data transmission, control and configuration.

### 5.1.2 Liquid interface

The analyzer system's liquid interfaces are shown in Table 2. It should be noted that no liquid interface is necessary for in-situ photometric analyzers.

**Table 2 – Liquid interfaces**

| Liquid interface | Direction | Description |
|---|---|---|
| Water samples | Input | The general sample size ranges from 1mL to hundreds of millilitres. |
| Waste liquid with reagents | Output | The waste liquid after the reaction of digestion and chromophore, is complicated and cannot be discharged directly. It has to be collected and treated |
| Waste liquid without reagents | Output | The waste liquid does not contain reagents. The main components are water samples or pure water, which are used for cleaning, soak and other functions, and can be discharged directly<br>The waste liquid without reagents can be collected with the waste liquid with reagents together, but this will increase the burden of the waste liquid with reagents collection and treatment |
| Reagent | Input | There is generally a variety of reagents, such as masking agents, oxidants, reducers, colour agents, etc., including one or more standard liquids |

## 5.2 Automatic verification

The industrial water quality analyzer system shall have the automatic verification function, that is, it can be independent or equipped with peripheral equipment to complete the automatic verification functions.

Standard verification: the analyzer system automatically executes standard verification periodically. Values of the standard shall be near the upper and lower limits of the measuring range and at least one other point within the range.

The automatic verification items should be carried out during the idle status phase of the online cycle test to ensure the continuity of the actual water sample data.

## 5.3 Access and control protocol

### 5.3.1 General

The water quality analyzer system for industrial monitoring generally has the function of remote access and control. The analyzer system can be connected by a digital communication interface, and the functions should be achieved, such as data and state queries, parameter settings and process execution, etc.

### 5.3.2 Data record

Record the real-time and historical data of the analyzer system. The data content is defined in Table 3.

**Table 3 – Definition of measurement data content**

| Name | Description |
|---|---|
| Time | Start time of measurement |
| Component code | The measured component representation as an abbreviation or mnemonic |
| Measurement value | The concentration of the measurand component |
| Data label | See Table 4 for the labels of the measurement data |

Table 4 shows the description for different data labels.

**Table 4 – Labels of the measurement data**

| Label name | Description |
|---|---|
| Normal | Measurement data is normal and valid |
| Above the upper limit | Measurement data exceeds the upper limit of the analyzer system |
| Below the lower limit | Measurement data is lower than the lower limit of the analyzer system |
| Error | Analyzer system failure |
| Under maintenance | The data was produced during the maintenance or commissioning of the analyzer system |
| Standard verification | Two methods of manual and automatic for introducing a standard |

### 5.3.3 Status and information query

The status and information of the analyzer system shall be checked, see Table 5.

**Table 5 – Status and information query content**

| Status&information | Content |
|---|---|
| Device info | Device identification, serial number, device time, reagent available, standard concentration |
| Status of analyzer system | Service, failure, normal |
| Alarm | Lack of reagents, lack of sample, lack of blank water, lack of standard, analyzer system leakage, abnormal calibration, over range, heating abnormal, low reagent, beyond the upper limit, under the lower limit |
| Running log | Power on/off, modification of parameters, on-line/offline, manual operation, online execution |

### 5.3.4 Parameter setting

The parameters listed in Table 6 shall be set.

**Table 6 – Parameter setting**

| Items | Content |
|---|---|
| Measurement and calibration | Measurement cycle, measurement range, time setting, calibration interval calibration parameters, linear correlation coefficient |
| Digestion settings | Digestion time, digestion temperature, digestion procedure |
| Display settings | Unit significant digits (display resolution) |
| Cycle settings | Verification items: calibration, standard verification<br>Verification properties: time, cycle, concentration of standard and so on |

### 5.3.5 Remote control

Remote control operations listed in Table 7 should be supported.

**Table 7 – Remote control content**

| Items | Content |
|---|---|
| Service | Cleaning, initialization |
| Calibration | Blank calibration, range calibration |
| Measurement | Measurement start, measurement stop |
| Verification | Standard verification, 24 h zero drift, 24 h span drift |
| Other | System time setting, etc. |

### 5.3.6 Network security management

The network protocol used for remote access and control of the analyzer system should have high security network authentication, such as setting the remote user's address, port, identity account and password to ensure the security of remote access. The analyzer system optionally equipped with a network system has the ability for the user to authorize or forbid the remote access, view the current remote connection and remote access records.

The system shall conform to cybersecurity requirements, referring to IEC 62443-4-2.

The system shall conform to certain functions of security level 2, referring to IEC 62443-3-3.

Table 8 lists the mandatory and recommended security functions.

**Table 8 – Security functions**

| Type | Function |
|---|---|
| Mandatory requirements | System requirement (SR) 1.2 – Software process and device identification and authentication |
| | SR 1.3 – Account management |
| | SR 1.12 – System use notification |
| | SR 2.6 – Remote session termination |
| Recommended enhancements | SR 1.7 – Strength of password-based authentication |
| | SR 1.11 – Unsuccessful login attempts |

### 5.3.7 Analyzer system self-recovery

The analyzer system shall have the self-recovery function.

For some recoverable faults, the analyzer system should have the self-recovery function. For example, when the analyzer system identifies the photoelectric detection unit signal beyond a reasonable range, the photoelectric detection unit of the analyzer system can automatically adjust and restore to a reasonable range.

After identifying a component of the analyzer system which shows a fault alarm, the analyzer system can control the device to perform specific actions and try to restore the status. The analyzer system can attempt to restore communication by means of a reconnection mechanism.

### 5.3.8 Fault diagnosis information output

According to the alarm state and process parameters output by the analyzer system, and supplemented by manual analysis, the remote fault analysis of the analyzer system will be carried out.

## 5.4 Additional information

The operation and maintenance plan of the analyzer system is referred to in Annex B.

# 6 Verification of values

## 6.1 Test preparation

### 6.1.1 General

Operation and calibration conditions shall be clearly stated when verifying the analyzer system’s performance characteristics.

### 6.1.2 Operational conditions

Tests shall be performed with the analyzer system in stable condition after warm-up time, and the working conditions meeting the requirements. Working conditions are as follows:

a) ambient conditions: temperature, humidity, supply voltage and frequency;

b) sample conditions: flow rate, pressure, temperature, pH, colour and suspended particles.

### 6.1.3 Calibration

Preparation or analysis of the calibration solution shall meet the requirements of international standards. National standards or regulatory authority guidance can apply.

## 6.2 Testing procedures

### 6.2.1 Precision

The standard solution of 80 % of the measuring range is measured 6 times, and the relative standard deviation $S_\mathrm{r}$ is calculated. Use 2,77 × $S$ of the measuring range ($s$) as the decision value of repeatability with normal distribution assumptions under 95 % probability.

The relative standard deviation is calculated as in Formula (1):

$$S_\mathrm{r} = \frac{\sqrt{\frac{1}{n-1}\sum_{i=1}^{n}\left(x_i - \bar{x}\right)^2}}{\bar{x}} \times 100\% \qquad (1)$$

where

$S_\mathrm{r}$ is the relative standard deviation of the analyzer system;

$n$ is the number of measurements;

$x_i$ is the result of the $i^\mathrm{th}$ measurement, expressed in mg/L;

$\bar{x}$ is the mean result of measurements, expressed in mg/L.

### 6.2.2 Accuracy

Measure the standard solution of 20 % ,50 %, 80 % of the measuring range for 6 times, respectively. Calculate the relative error according to the standard concentration for each standard solution. The largest relative error is the value of accuracy.

The calculation method is as in Formula (2):

$$R_e = \frac{\bar{x} - C}{C} \times 100\% \qquad (2)$$

where

$R_e$ is the relative error of the standard solution;

$\bar{x}$ is the mean result of measurements, expressed in mg/L;

$C$ is the concentration of the standard solution, expressed in mg/L.

### 6.2.3 Zero drift

a) Off-line zero drift

Prepare the standard solution of 10 % of the measuring range. Continuously measure the standard solution for 24 times in 1 h cycle, calculate the average of the first three determined off-line drift test values as the initial value, and calculate the maximum relative deviation between the follow-up determined values and the initial value as the zero drift.

The calculation method is as in Formula (3):

$$ZD = \frac{\max\{x_i - \overline{C}\}}{A} \times 100\% \tag{3}$$

where

$ZD$ is the zero drift of the analyzer system;

$x_i$ is the measured data of each hour, expressed in mg/L;

$\overline{C}$ is the mean measured concentration of the first three readings, expressed in mg/L;

$A$ is the measuring range, expressed in mg/L.

b) On-line zero drift

Using the standard solution of 10 % of the measuring range as a check sample, the 24 h on-line zero drift verification is carried out, then the actual water samples are tested continuously, which are represented by the relative error ($RE_1$); the calculation Formula (4) is as follows:

$$RE_1 = \frac{x_{z1} - x_{z2}}{B} \times 100\% \tag{4}$$

where

$RE_1$ is the relative error;

$x_{z1}$ is the 24 h zero drift verification value, expressed in mg/L;

$x_{z2}$ is the previous 24 h zero drift verification value, expressed in mg/L;

$B$ is the measuring range of the analyzer system, expressed in mg/L.

### 6.2.4 Span drift

a) Off-line span drift

The standard solution is continuously measured for 24 times in 1 h cycle at the standard solution of 90 % of the measuring range; the mean value of the first three measurements is calculated as the initial value, and then the variation between the follow-up measured value and initial value is calculated. The largest proportion of such variation accounting for the measuring range is the value of span drift.

Quantities of data: $x_1$, $x_2$, $x_3$……$x_{24}$, total of 24.

$$RD = \frac{\max\{x_i - \overline{C}\}}{A} \times 100\% \tag{5}$$

where

$RD$ is the span drift of the analyzer system;

$\overline{C}$ is the mean measured concentration of the standard solution,expressed in mg/L;

$A$ is the measuring range, expressed in mg/L.

b) On-line span drift

Using the standard solution of 90 % of the measuring range as a check sample, the 24 h on-line span drift verification is carried out, then the actual water samples are tested continuously,which are represented by the relative error ($RE_2$); the calculation formula is as follows:

$$RE_2 = \frac{x_{z1} - x_{z2}}{B} \times 100\% \tag{6}$$

where

$RE_2$ is the relative error;

$x_{z1}$ is the 24 h span drift verification value, expressed in mg/L;

$x_{z2}$ is the previous 24 h span drift verification value, expressed in mg/L;

$B$ is the current range value of the analyzer system, expressed in mg/L.

### 6.2.5 Bias

The bias is represented by the measuring error, and the calculation formula is as follows:

$$RE = \frac{x_i - x_l}{x_l} \times 100\% \tag{7}$$

where

$RE$ is the measuring error;

$x_i$ is the value of the measurement result by the analyzer system, expressed in mg/L;

$x_l$ is the manual analysis value of a water sample that has been manually collected and precipitated for 30 min, expressed in mg/L.

### 6.2.6 Linearity

The linearity is checked by the correlation coefficient of the standard curve.

Test method: use the standard solution of 0 %, 10 %, 20 %, 40 %, 60 % and 80 % of the measuring range as sample.The linearity test is carried out from the lower concentration to the higher concentration,and the correlation coefficient is calculated with the linear regression.

### 6.2.7 Standard verification

The verification uses the standard solution of 50 % of the measuring range. The purpose of the standard verification is to evaluate the accuracy of the analyzer system.

### 6.2.8 Retest of the retained sample

The retained water sample should be retested by the analyzer system when the result exceeds the alert limit.

### 6.2.9 Interference of colour and suspended particles

According to the property of the measured object, potassium chloroplatinate, cobalt chloride, hydrazine sulfate and hexamethylene tetramine are added into the standard solution as mixed solution. The standard solution of 50 % of the measuring range is to be measured. The mixed solution is measured 3 times and the accuracy based on 3 measured values is calculated. The larger accuracy is the value of interference of colour and suspended particles.

### 6.2.10 Interference of ion

The specified ion is added into the standard solution as a mixed solution. The standard solution of 50 % of the measuring range is to be measured. The mixed solution is measured 3 times and the accuracy based on 3 measured values is calculated. The larger accuracy is the value of interference of the ion.

### 6.2.11 Interference of pH

The pH adjust solution is added into the standard solution. The pH adjusted standard solution to be measured is 50 % of the measuring range. The standard solution is measured 3 times and the accuracy based on 3 measured values is calculated; the larger accuracy is the value of interference of pH.

### 6.2.12 Limit of quantitation

The zero sample is measured 7 times, and the standard deviation is calculated based on 7 measured values. Ten times of the standard deviation is the limit of the quantity. The calculation formula is as follows:

$$\mathrm{LOQ} = 10 \times \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(x_i - \bar{x})^2} \tag{8}$$

where

LOQ is the limit of quantification, expressed in mg/L;

$n$ is the time of measurement;

$x_i$ is the $i^{\text{th}}$ measured value,expressed in mg/L;

$\bar{x}$ is the mean of measured values of standard solution, expressed in mg/L.

### 6.2.13 Memory effect

The standard solution of 20 % concentration of the measuring range is measured 3 times, and then the standard solution whose concentration value is 80 % and 20 % of the measuring range, respectively, is measured for three times. Calculate the accuracy of the first measured values of the last two standard solutions; the larger accuracy is the value of memory effect.

### 6.2.14 Rate of valid data

The water sample is continuously measured based on 1 h cycle without any maintenance (including reagent change, calibration, repair, etc.) until the analyzer system cannot maintain normal measurement or the indication error is more than 10 % in 3 measurements. In the meantime, the rate of valid data shall exceed 90 %; the total operation time (hour) is defined as minimum maintenance cycle. The rate of valid data is defined as the ratio of valid data to all data. The calculation formula is as follows:

$$D = \frac{D_\mathrm{e}}{D_\mathrm{t}} \times 100\% \tag{9}$$

where

$D$ is the rate of valid data;

$D_\mathrm{e}$ is the valid data;

$D_\mathrm{t}$ is the total data.

### 6.2.15 Consistency of parallel measurements

In a period of unattended operation, multiple series of data $C_{i,j}$ ($I$ being the number of analyzer systems, $j$ the number of times) by 3 different sets of analyzer system are acquired, and the relative standard deviation $CM_j$ at the $j^\mathrm{th}$ time and the consistency of parallel measurements are calculated by the following formulae:

$$CM_j = \frac{\sqrt{\frac{1}{t-1}\sum_{i=1}^{t}\left(C_{i,j} - \frac{1}{t}\sum_{i=1}^{t} C_{i,j}\right)^2}}{\frac{1}{t}\sum_{i=1}^{t} C_{i,j}} \times 100\% \tag{10}$$

$$CM = \sqrt{\frac{\sum_{j=1}^{m}\left(\mathrm{CM}_j\right)^2}{m}} \tag{11}$$

where

$CM_j$ is the relative standard deviation of the $j^\mathrm{th}$ time by three analyzer systems;

$t$ is the total number of analyzer systems;

$C_{i,j}$ is the data of the $j^\mathrm{th}$ time of the $i^\mathrm{th}$ analyzer, where $i$ = 1, 2, 3, $j$ = 1, 2, …, $m$;

$CM$ is the conformity of the analyzer system;

$m$ is the total series of data.

NOTE When $CM_j$ > 10 %, $CM$ > 10 %.

### 6.2.16 Interference of ambient temperature

The high temperature and low temperature stability of the analysis system should be tested according to IEC 60068-2-1, IEC 60068-2-2.

In a thermostatic chamber, the standard solution of 80 % of the measuring range is measured 3 times with the temperature of 20 °C, 5 °C, 20 °C, 40 °C and 20 °C. The mean value of 9 measured values is calculated with 20 °C as the reference value, the relative errors of the mean value with 5 °C and 40 °C with the reference value are calculated; the larger relative error is the value of interference of ambient temperature. The calculation method is according to the following formula:

$$W_t = \max\left\{\frac{X_1 - \overline{X}}{\overline{X}}, \frac{X_2 - \overline{X}}{\overline{X}}\right\} \times 100\% \quad (12)$$

where

$W_t$ is the interference of ambient temperature;

$X_1$ is the mean value of 3 measured values at 5 °C, expressed in mg/L;

$X_2$ is the mean value of 3 measured values at 40 °C, expressed in mg/L;

$\overline{X}$ is the mean value of 9 measured values at 20 °C, expressed in mg/L.

### 6.2.17 Interference of supply voltage

The standard solution of 80 % of the measuring range is measured 3 times in the rated supply voltage; The same standard solution is measured 3 times in a voltage 10 % higher and 10 % lower than the rated voltage, respectively. The relative errors of the mean value in the voltage 10 % higher and 10 % lower than the rated voltage with the mean value of the rated voltage are calculated; the larger relative error is the value of the interference of supply voltage. The calculation method is as follows:

$$V = \max\left\{\frac{|X - W|}{W}, \frac{|Y - W|}{W}\right\} \times 100\% \quad (13)$$

where

$V$ is the relative error caused by voltage change;

$W$ is the average of the 3 measured values in voltage;

$X$ is the average of the 3 measured values in the voltage 10 % higher than the rated voltage;

$Y$ is the average of the 3 measured values in the voltage 10 % lower than the rated voltage.

### 6.3 Additional information

In the testing procedures, the verification plan, assurance operations and data audit are referred to in Annex A.

# Annex A
(informative)

# Automatic and manual verification during work

## A.1 Verification plan

The verification plan of the analyzer system is shown in Table A.1.

**Table A.1 – Verification plan**

| Item | Recommended cycle | Mode |
|---|---|---|
| 24 h zero and span drift (including accuracy) | Daily | Automatic |
| Bias | Monthly | Manual |
| Standard verification | Weekly | Automatic |
| Zero and range calibration | Weekly | Automatic |
| Retest the retained sample | Excess, abnormal | Manual |
| Limit of quantitfication (LOQ) | Semi-annually | Manual |
| Precision | Semi-annually | Manual |
| Linearity | Monthly | Manual |

NOTE 1 All verifications are executed during the interval between water sample tests.

NOTE 2 Automatic means the analyzer system executes on time automatically; manual means manually operating the analyzer system.

## A.2 Assurance operations and data audit

a) Calibration

The standards used to calibrate the analyzer system should be prepared with certified standards or standard substances.

Measuring vessels for quantification, such as analyzer balance, standard thermometer, multimeter, pipette and volumetric flask, shall be calibrated periodically.

b) Immediate maintenance

When the verified result of the analyzer system is close to the required limit, the analyzer system shall be maintained in time.

When the test results of standard verification cannot meet the requirement, the analyzer system should be maintained.

c) Calibration and standard verification

When the reagents and components of the analyzer system have been replaced, the calibration and standard verification should be carried out, and the results should meet the requirements.

After the standard verification, the 24 h zero and span drift should be carried out. If the verification result cannot meet the requirements, the analyzer system shall be maintained again.