
**Fine bubble technology — Water
treatment applications —**

Part 1:

**Test method for evaluating ozone fine
bubble water generating systems by
the decolorization of methylene blue**

Technologie des fines bulles — Traitement de l'eau —

*Partie 1: Méthode d'essai pour évaluer les diffuseurs à fines bulles
d'ozone par la décoloration du bleu de méthylène*

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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 of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 281, *Fine bubble technology*.

A list of all parts in the ISO 20304 series can be found on the ISO website.

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

Introduction

Ozone is used to improve water quality e.g. for purification and decomposition of hardly decomposable substances and decolorization. The conventional method often uses diffuser tubes. However, it has been found that with ozone fine bubbles, it is possible to use the strong oxidizing power of ozone more efficiently.

In recent years, the establishment of fine bubble generating technology has made ozone utilization efficiency higher than that of diffuser tube systems. Test results demonstrate that ozone fine bubble water generating systems are about 1,6 times more efficient than diffuser tube systems. With this efficiency increase, cost reduction has become possible.

Decolorization is mainly used for factory wastewater, regeneration and sewage water. It is also used on a regular basis for sewage treatment facilities, as advanced treatment technology, in the dye-house effluent, etc.

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Fine bubble technology — Water treatment applications —

Part 1:

Test method for evaluating ozone fine bubble water generating systems by the decolorization of methylene blue

WARNING — Persons using this document should be familiar with normal laboratory practice. This document does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability of any other restrictions.

1 Scope

This document specifies a test method to assess the performance of ozone fine bubble water generating systems used for decolorizing water-soluble dye in e.g. wastewater and industrial water. This document does not address the impact of ozone on health and environment.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 10678, *Fine ceramics (advanced ceramics, advanced technical ceramics) — Determination of photocatalytic activity of surfaces in an aqueous medium by degradation of methylene blue*

ISO 20480-1, *Fine bubble technology — General principles for usage and measurement of fine bubbles — Part 1: Terminology*

ISO 20480-2:2018, *Fine bubble technology — General principles for usage and measurement of fine bubbles — Part 2: Categorization of the attributes of fine bubbles*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 20480-1 and the following apply.

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

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

3.1

fine bubble water

water containing air fine bubbles

3.2

ozone fine bubble water

water containing ozone fine bubbles

3.3

absorbance

natural logarithm of the ratio of the light amount before and after transmission of the test water-soluble dye with the photometric amount defined in ISO 80000-7:2019, 7-32.1

3.4

half-life of absorbance

time required for the change in absorbance to reach 50 % of the initial concentration

4 Decolorization test by ozone fine bubble water

4.1 Principle

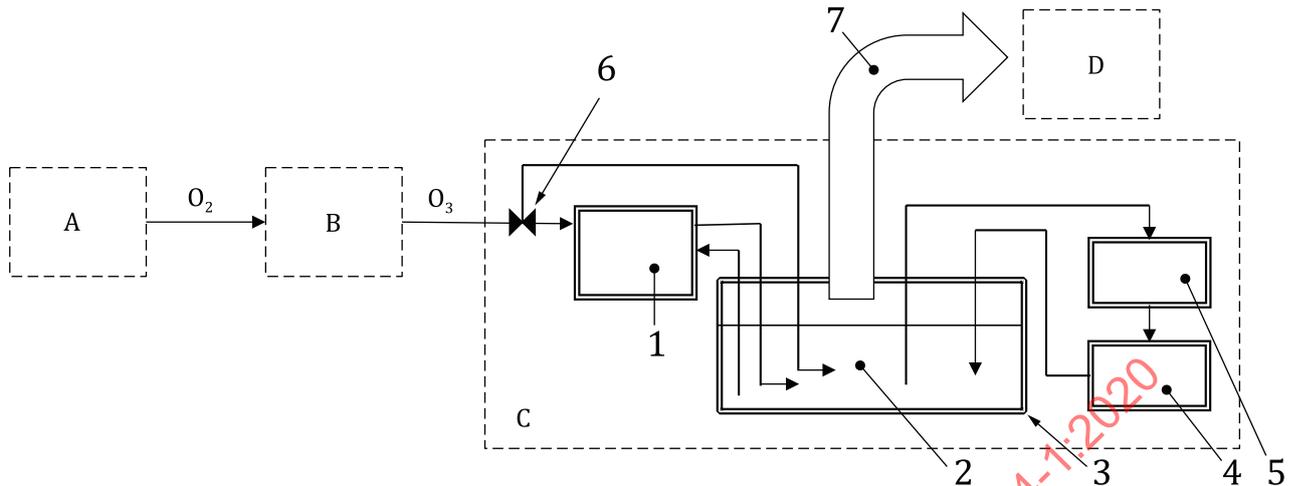
A measured quantity of ozone is sent to a water-soluble dye tank through a fine bubble water generating system. The absorbance in the tank is optically measured to determine the half-life of absorbance. Absorbance is measured using e.g. a colorimeter, spectrophotometer or absorbance meter. It is desirable to use an inline type absorbance measuring instrument. Examples of inline measuring instruments are shown in [Annex A](#).

4.2 Test environment conditions

The temperature of the test room should be $23\text{ °C} \pm 3\text{ °C}$ and the relative humidity should be $50\% \pm 10\%$. In addition, it should be taken care not to mix fine particles in the test environment.

4.3 Configuration of test equipment

The testing apparatus comprises a raw material gas supply unit, an ozone generator supply unit, a chemical reaction unit by ozone, and a discharged ozone treatment unit. The configuration of the test equipment is shown in [Figure 1](#). The ozone reaction unit is indicated by a double line in [Figure 1](#).

**Key**

- 1 fine bubble water generating system
- 2 fine bubble water with dissolved methylene blue
- 3 test tank
- 4 circulating pump
- 5 measurement instrument unit
- 6 valve
- 7 untreated O₃
- A raw material gas supply unit
- B ozone generator supply unit
- C chemical reaction unit by ozone
- D discharged ozone treatment unit

Figure 1 – Configuration of test equipment

4.4 Raw material gas supply unit (A unit)

The raw material gas supply unit (A unit) is shown in [Figure 1](#). [Figure 1](#) shows a material gas supply unit when using an oxygen cylinder or an oxygen gas generator. The oxygen concentration of the material gas supply should be 90 % or more.

4.5 Ozone generator supply unit (B unit)

The conditions for supply of ozone to the ozone reaction unit shall be as follows:

- a) The ozone flow rate shall be 0,5 l/min, the ozone yield shall be 3 g/h, it is important that the gas gauge pressure is set and maintained at a certain level of pressure. In addition, the numerical value of the gas gauge pressure shall be given in the test report, see [Clause 7](#).

NOTE The conversion between ozone mass concentration and volume fraction is standardized by ISO 13964:1998, 7.2. The results are reported as micrograms per cubic meter at the chosen reference conditions, or as volume fraction. For ozone, a volume fraction of $1,0 \times 10^{-6}$ at 0 °C, 101,3 kPa (standard condition) is equivalent to 2 141 µg/m³ and 1 995 µg/m³ at 20 °C, 101,3 kPa.

- b) The ozone generator supply unit (B unit) is shown in [Figure 1](#).

4.6 Chemical reaction unit by ozone (C unit)

This C unit is composed of a fine bubble water generating system, a test tank, a measuring instrument and a circulating pump. The installation of fine bubble water generating system shall be structured so that the reference water-soluble dye in the test tank does not leak out of the system in case of immersion.

a) The fine bubble water generating system is as follows.

- 1) The equipment has the function to discharge fine bubble water and to circulate it. A material that can withstand the oxidizing power of ozone shall be used.
- 2) The operation conditions and data of fine bubble water generating system should be provided by the system supplier.
- 3) [Figure 1](#) shows the chemical reaction unit (C unit) using the fine bubble water generating system which includes the configuration of the reaction apparatus and dissolution apparatus of the ozone reaction section.

b) Test tank

It is an aquarium that can be hermetically sealed so as not to leak ozone. It is made of a material that can withstand the oxidizing power of ozone. A colourless and transparent column is desirable to carry out the test while observing the change in colour. The column should have such an enough capacity that can reserve the ozone fine bubble water when it is generated. The reference test tank is made of glass with a capacity of 60 l or more, and the water depth at the time of test shall be $35 \text{ cm} \pm 1 \text{ cm}$.

The bottom area and the water surface area of the test tank should be equal.

Validation or calibration of measuring equipment shall be as follows:

- 1) Ozone concentration meter, see ISO 1431-3;
- 2) Photometric instrument, calibration and measurement confirmation of inline type measuring instrument using a standard solution;
- 3) pH meter, adjusted with standard calibration solution.

c) Water

The water quality shall be determined in accordance with ISO 20480-2:2018, 4.2.

d) Methylene blue

Methylene blue powder specified in ISO 10678 shall be used.

NOTE The maximum absorption wavelength is 664 nm.

e) Methylene blue standard stock solution

Weigh 0,15 g of methylene blue powder and dissolve in 1 l of water.

f) Test coloured water

Prepare the test coloured water using 1 l of methylene blue stock solution, adjusted to 60 l. The pH of the test coloured water shall be $8 > \text{pH} > 5$. At the start of the test, it is recommended to set the water temperature to $20 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$ and neutral range of pH.

g) Circulating pump for absorbance measurement

A pump with performance of about 7 l/min (flow rate 23 cm/s), that circulates water by sending the test water into the test tank to the measuring device is required.

- h) Measuring unit. A measuring instrument for measuring the amount of visible light transmitted through a certain distance in water shall be as follows.
- 1) The measurement wavelength shall be 664 nm.
 - 2) The measurement time is the time at which at least 5 cycles can be measured when a series of measurement cycles is performed until the methylene blue concentration becomes transparent from the initial high concentration. At least 100 points of light intensity measurement are performed during one cycle measurement, and the data are recorded together with the measurement time.

It is necessary to be able to synchronize the measurement start signal with the fine bubble generation start signal including the artificial method.

- 3) In order to minimize the dynamic behaviour of the fine bubble and the effect of decreasing the number concentration value, it is desirable to perform the sampling in as short a time as possible, or to measure by flow. Return the sampled sample to the test tank.
- 4) The methylene blue concentration measurement of the test water shall be carried out considering one of the following measures because the fine bubble contained in the test water may affect the methylene blue concentration measurement.

— Measure the absorbance of the test water and the absorbance of ozone fine bubble water without methylene blue and record each. The difference between these two values is subtracted from the output absorbance of the methylene blue concentration measuring instrument at the time of the test and corrected.

— The ozone fine bubble is introduced, and the transmittance in the test water tank is confirmed that the decolorization is advanced enough and the transmittance in the test water tank has become almost saturated. Then, it is used to estimate and correct the final value as a reference to the asymptotic change of the measured value by the measuring instrument. The uncertainty of the estimation is assessed, and the uncertainty of the correction is considered.

4.7 Discharged ozone treatment unit (D unit)

See [Figure 1](#).

4.8 Calibration procedure

Prepare five levels of known concentration of methylene blue solution in water wherein two levels shall be above and three levels shall be below the starting concentration in the measurement (see [4.9](#)). For each level of concentration, take three replicates of absorbance measurement. Establish a calibration curve of absorbance to concentration by using least-square regression analysis.

4.9 Test procedure

The routine test procedure is as follows.

- a) Install the test equipment, connect it, and confirm operation.
- b) Perform calibration of the photometer.
- c) Add 59 l of water to the test tank, add 1 l of methylene blue standard stock solution, and stir to obtain the coloured test water.
- d) Measure the coloured test water with a photometer and measure the initial absorbance.

- e) Activate the ozone generator and adjust the ozone flow rate to 0,5 l/min; the ozone yield is 3 g/h. It is important that the gas gauge pressure is set and maintained at a certain level of pressure. In addition, the numerical value of the gas gauge pressure shall be given in the test report (see [Clause 7](#)).
- f) Connect an ozone pipe to the fine bubble water generating system.
- g) Start operation of the ozone generator and fine bubble water generating system. Measurement of the photometer and operation of the discharge ozone treatment section are started before the start of the test.
- h) When the absorbance obtained is less than 1, the test is terminated and the operation of each test apparatus is stopped.
- i) Confirm the environmental ozone concentration around the equipment during and after the test.

After the test, water treatment shall be applied to appropriately treat the dissolved ozone and release it after checking that the dissolved ozone concentration is 0,05 mg/l or less (not detectable is below the lower limit of determination). It is desirable to process the dissolved ozone concentration by the following method.

- 1) Pass water through activated carbon.
 - 2) Send air to the fine bubble device to release and eliminate ozone completely, after degassing.
 - 3) Input the reducing agent.
 - 4) Leave the ozone as it is.
- j) Collect and analyse photometric data.

5 Expression of test results of the decolorization effect

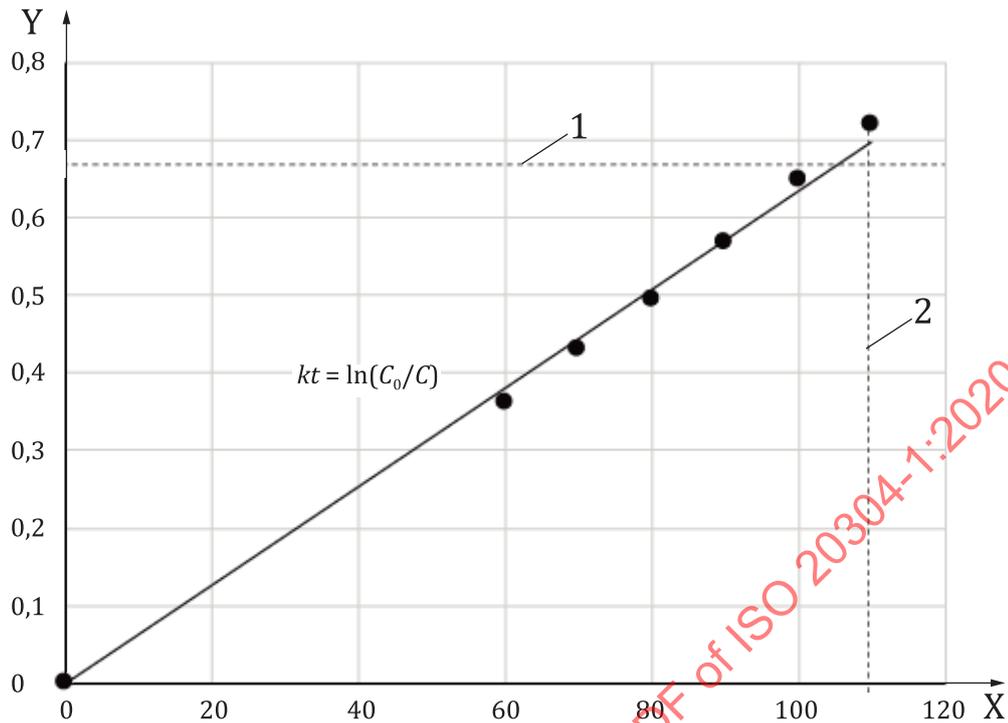
5.1 Evaluation object

Depending on the measurement data of the photometer, the absorbance at the elapsed time is read and the result is represented by a graph, see [Annex B](#). Since the circulation process is unstable at the beginning of the test, the data are taken after 1 min elapse from the start of fine bubble water generating system operation. After that, the time required from the value obtained by operating until the absorbance is less than 1, to the half-life $t_{1/2}$ is evaluated.

5.2 Functional processing

The performance of the fine bubble water generating system is evaluated by the value of the concentration (C) after the elapsed time (t) for the methylene blue initial concentration (C_0). The procedure is as follows.

- a) Create a graph of absorbance on the vertical axis and time on the horizontal axis. An example of the graph is shown in [Figure 2](#).
- b) Read the time $t_{1/2}$ at which it is more than half of the initial concentration ($C_0/C = 2$).
- c) Create a graph of $kt = \ln(C_0/C)$ for data from $t = 0$ s after the start of operation to $t_{1/2}$.
- d) Evaluate the performance of the device for the slope k .

**Key**

X elapsed time, in s

Y $\ln(C_0/C)$ 1 $\ln(2) = 0,693$ 2 $t_{1/2}$, in s**Figure 2 — Example of test result of the decolorization effect****5.3 Uncertainty evaluation**

The uncertainty of measurements should be composed of repeated measurement uncertainty, calibration uncertainty and other uncertainties (e.g. operators and temperature). See ISO/IEC Guide 98-1 and ISO/TS 21749:2005, Clause 5.

6 Measurement of size and number concentration classification using air

Fine bubble size usually refers to the equivalent hydrodynamic diameter but could be different in several techniques. Number concentration is the total number (or equivalent) of bubbles per unit volume. Typical examples for the expression of attributes for fine bubbles are given in ISO 20480-2:2018, Clause 5.

7 Test report

The test report may be prepared in a tabular form and should contain the following items. However, some items can be omitted or added as agreed between the interested parties.

- a) A reference to this document, i.e. ISO 20304-1;
- b) laboratory name;
- c) date of examination, place, test environment (temperature, humidity);

- d) description of the fine bubble water generating system tested (identification, operation setting conditions, main system parameters, pressure value, water temperature, water quality, pH);
- e) graph showing the decolorization effect test result (refer to [Figure 2](#));
- f) description of the decolorization effect test (slope k , uncertainty, ozone generation concentration);
- g) description of test equipment used, description of the test procedure;
- h) characteristics of fine bubble (size of fine bubble and number concentration), see [Clause 6](#).

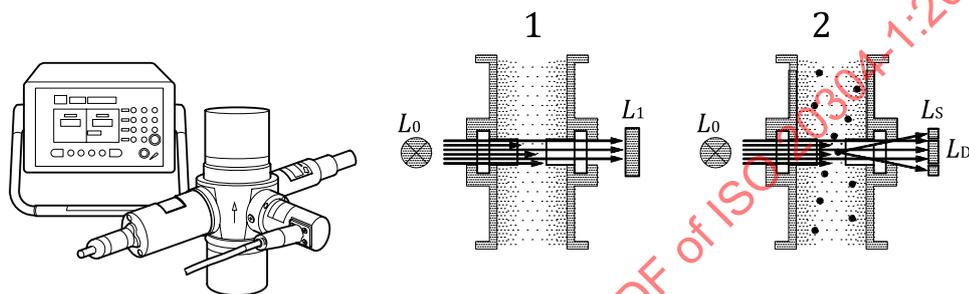
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Annex A (informative)

Examples of in-line measuring instruments

This annex describes examples of in-line measuring instruments conforming to this document.

- a) An example of in-line absorbance and turbidity measurement system for process is shown in [Figure A.1](#).



Key

- 1 measuring absorbance
- 2 measuring scattered light
- L_0 lamp lights intensity
- L_1 detector lamp lights intensity
- L_s scattered lights intensity
- L_D transmitted lights intensity

Figure A.1 — Example of in-line absorbance and scattered light analyser

- b) In-line process system for measuring absorbance and scattered light. A system to measure concentration and scattered light of process fluid or gas using visible light, near infrared light and ultraviolet (UV) light.
- c) In-line process system for measuring absorbance and scattered light measures process fluid or gas concentration and turbidity using visible lights near infrared radiation or UV. It is mounted in each part of piping, fermenter, reactor, tank, and container of plants. It allows real-time and accurate analysis. Its documented usages include detection of component concentration, process measurement of solid, liquid and gas, and analysis of trace pollutant and quality, and other measurements.
- d) In-line process system for measuring absorbance and turbidity is composed of three major assemblies listed below:
- 1) in-line flow cell equipped with light unit and detector assemblies;
 - 2) digital or analogue convertor;
 - 3) sensor and cables for connecting the convertor.
- e) Light from the light source converges within the sensor and is sent out to the process flow. The generated light passes through the process medium exactly through the filter and is measured by the opposite high precision absorption detector or scattered light detector.

- f) As the result, photovoltaic current generated from the process sensor is accurately amplified and analysed to be transmitted to process control system of each plant after conversion. Various measurement units are available.

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