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Fine ceramics (advanced ceramics, advanced technical ceramics) — Test method for determination of phenol oxidative decomposition performance of semiconducting photocatalytic materials by quantitative analysis of total organic carbon (TOC)

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Foreword

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This document was prepared by Technical Committee ISO/TC 206, *Fine ceramics*.

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

Since photocatalysts have a wide range of functions such as purification of air or water, antibacterial effect and self-cleaning, many application products that make use of said functions are developed. Photocatalyst-applied products for water purification are expected to exert oxidative decomposing performance against organic compounds composed of hydrocarbon, which is a water polluting substance. In line with this, there is a necessity for developing a testing method for measuring the oxidative decomposition against water polluting substances. This document stipulates a test method for measuring the performance of a semiconducting photocatalytic material irradiated with UV light in water for the oxidative decomposition of hydrocarbon such as phenol and the byproducts as intermediate produced by the photocatalysis, by the TOC method.

An examples of data evaluation is given in Annex D while the results of the interlaboratory tests are given in Annex E.

Fine ceramics (advanced ceramics, advanced technical ceramics) — Test method for determination of phenol oxidative decomposition performance of semiconducting photocatalytic materials by quantitative analysis of total organic carbon (TOC)

1 Scope

This document provides a testing method for testing phenol oxidative decomposition performance of semiconducting photocatalytic materials or made of a material adsorbed with photocatalyst to its surface for the purpose of purifying water polluting substances in water making use of photocatalytic performance as test piece. The test piece can be planar, spherical, flake or block shape. A test piece that can elute hydrocarbon or the like by immersion into water or phenol aqueous solution or by light irradiation, a semiconducting photocatalytic material that cannot maintain its shape or a powdery semiconducting photocatalytic material are excluded from the scope of application, since they cannot be evaluated.

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 8425, *Water quality—Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC)*

ISO 10523, *Water quality — Determination of pH*

ISO 10677, *Fine ceramics (advanced ceramics, advanced technical ceramics) — Ultraviolet light source for testing semiconducting photocatalytic materials*

ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories*

ISO 19722, *Fine ceramics (advances ceramics, advanced technical ceramics) — Test method for determination of photocatalytic activity on semiconducting photocatalytic materials by dissolved oxygen consumption*

ISO 20507, *Fine ceramics (advanced ceramics, advanced technical ceramics) — Vocabulary*

ISO 22197-1, *Fine ceramics (advanced ceramics, advanced technical ceramics) — Test method for air-purification performance of semiconducting photocatalytic materials — Part 1: Removal of nitric oxide*

ISO 80000-1, *Quantities and units — Part 1: General principles*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 19722 and ISO 20507 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
test piece
planar, spherical, flake or block shaped semiconducting photocatalyst materials for water purification prescribed in ISO 20507 using semiconducting photocatalyst

3.2
illuminated condition
test condition under which a test is conducted with light source lit

3.3
dark condition
measuring condition under which no light source is lit and no light is incoming from outside

Note 1 to entry: The purpose of this condition is for comparing the result with that conducted under the illuminated condition.

4 Symbols

Symbol	Designation	Unit
C	concentration of hydrocarbon	mg/l
ΔTOC_D	phenol concentration adsorbed to the test piece in the dark	mg/l
C_{Di}	phenol concentration measured from the test solution as the initial concentration in the dark condition	mg/l
C_{Df}	phenol concentration measured from the test solution after 6 hours in the dark condition	mg/l
ΔTOC_L	phenol concentration adsorbed to the test piece and decomposed by photocatalysis	mg/l
C_{Li}	phenol concentration measured from the test solution as the initial concentration under the illuminated condition	mg/l
C_{Lf}	concentration of residual phenol and byproduct measured from the test solution after 6 hours under an illuminated condition	mg/l
ΔTOC	decomposed phenol concentration as hydrocarbon on the test piece by the photocatalysis	mg/l
V	volume of test solution	ml
λ	wavelength	nm
I	ultraviolet (UV) light irradiation intensity	mW/cm^2

5 Principle

Organic compound in waste water is oxidatively decomposed to CO_2 and water by the photocatalysis, so called as photocatalytic mineralization. Under the photocatalytic mineralization, many kinds of byproducts are usually produced and the production mechanism including the changes of a molecular structure and the concentration of byproducts are depending on the characteristics of photocatalyst, such as the surface structure, crystal phase and the photocatalytic activity. Accordingly, estimation of photocatalytic activity by the decrement of initial concentration of organic compounds means mainly changing the original structure of the organic compound. Preferable estimation method of the

photocatalytic activity for waste water treatment should oxidatively decompose organic compound to CO_2 and water as photocatalytic mineralization. On the basis of the conception, total organic carbon analysis as measurement of the photocatalytic mineralization is most suitable method because no the byproducts production as reaction mechanism should be taken into account.

6 Materials

6.1 Chemicals and implements

6.1.1 Reagent

Reagent is phenol and the assay is > 99 wt%.

6.1.2 Purified water

Water used for the preparation of all solutions shall be distilled or deionised water.

6.1.3 Purified air

Air prepared by removing dusts and volatile organic compounds from atmospheric air using a filter or the like, or synthetic air filled in a high-pressure container as provided in ISO 22197-1.

6.1.4 Purified water saturated with dissolved oxygen

Purified water prepared in accordance with the preparation procedure provided for in ISO 19722 by saturating water with dissolved oxygen at ±1 °C of water temperature during the test.

7 Test device and instrument

7.1 Test vessel

Use a silica glass for the window glass plate for this test. The test vessel and O-ring used in this test shall be near-UV irradiation resistant and chemical resistant against phenol. For example, preferred material for an O-ring is fluorocarbon polymer, and preferred material for other parts is polytetrafluoroethylene.

The test vessel shall be inclined to avoid fogging the inner side of window glass by test solution because the fogged window glass induces extinction. Therefore, the test vessel shall be structured to maintain the test piece immersed under the test solution even when the test vessel is inclined as shown in Annex A. Moreover, a weir shall be provided so as to avoid the test piece from falling off or swept away by the circulation of the test solution. The height of the weir shall have a clearance of 5 mm + 0 mm, –1 mm from the window plate.

The size of window glass shall be larger than the size of the place for folding the test piece

7.2 Reserve container

Provide a reserve container for maintaining the condition of the test solution to be supplied to the test vessel and for taking water for TOC measuring (see Annex B). Preferably, the volume capacity of the reserve container is 500 ml ± 10 ml and it is made of borosilicate glass having chemical resistance against phenol. Since the test solution is stirring in the reserve container during the test, the reserve container shall have sufficient volume and structure that allows stirring. To maintain the temperature of the test solution within the predetermined range during the test, a water jacket shall be provided for fixing the reserve container that can circulate the thermostatic water. Provide a reserve container with a lid provided with an O-ring for keeping airtightness. The O-ring is preferably made of fluorocarbon polymer. This lid shall be provided with a through-hole for piping, a through-hole for air inflow, an air exhaust and a through-hole for fixing a thermometer. Diameter of the through-hole for air exhaust shall

be determined after conducting a test without using a test piece under a dark condition and under an environmental condition for conducting a test, and if the resulted variation of phenol concentration by TOC measuring is 1,5 % or less, such diameter is allowed. For example, around 3 mm + 0 mm, –1 mm of diameter of the through-hole for air exhaust is allowed.

For reference, specification of the reserve container, lid and water jacket are not limited to the above-mentioned examples, in other words, if they are of material and structure that satisfy the conditions specified here, they are allowed.

7.3 UV irradiation light source

Use the light source that is provided in ISO 10677. It is recommended to use UV fluorescent lamp having 351 nm of the maximum optical intensity that can irradiate UV ray.

7.4 UV radiometer

A radiometer with a detector whose sensitivity peak is at λ = 351 nm shall be used to measure the UV-light intensity. The radiometer shall be calibrated to closely match the characteristic of the UV light irradiation light source as specified in ISO 10677 or be corrected to ascertain sensitivity within the wavelength range to be adsorbed by the test piece.

7.5 UV light intensity

Adjust I to 2 mW/cm^2 ± 0,1 mW/cm^2 through the window glass when the light receiving portion of an UV illuminometer is positioned at the centre of the test piece.

7.6 pH meter

Measure pH of the test solution using the pH meter specified in ISO 10523.

7.7 TOC measuring device

Measure the total organic carbon in accordance with TOC analysis by combustion oxidizing and infrared system [Non-Purgeable Organic Carbon (NPOC) analysis] as provided in ISO 8425, using TOC automatic measuring instrument. For reference, pH resulted after oxidizing treatment as provided in ISO 8425 shall not necessarily be 2, rather, 3 or 4 is acceptable if non-organic carbon can be removed.

8 Arrangement of test method

8.1 Measuring device setup

The test device comprises a test vessel, a light source, a reserve container, a liquid feeding pump and a thermostatic bath/cryostat as shown in Annex C. It is for evaluating the phenol oxidative decomposition performance using a semiconducting photocatalyst material by TOC analysis. Decrease of phenol contained in the test solution is measured by a test piece, irradiating light necessary for expression of semiconducting photocatalyst performance to the test piece and continuously supplying and circulating test solution. In this test, a lid for fixing the window glass plate for avoiding the test solution from leaking is provided, since the test vessel shall be inclined. The lid is also for limiting evaporation of the test solution. This is a semi-closed system where an air exhaust is provided which is necessary for air inflow. An example of the measuring device setup is shown in Annex C.

8.2 Test solution feeding device

The test device as shown in Annex C has a liquid feeding pump and piping for controlling the flowing amount of the test solution circulated continuously at a predetermined speed from the reserve container

to the test vessel. Material for piping shall be chemical resistant against phenol and UV resistant. For example, a thermoplastic elastomer is recommended.

A liquid feeding pump shall be able to feed and circulate predetermined amount of the test solution at a constant speed for a long time and shall be chemical resistant against phenol. Furthermore, no material that may be eroded by phenol or that may be adsorbed with phenol shall be used in any part of the liquid feeding pump structure. For example, a peristatic type pump is recommended, which compresses the liquid feeding tube formed of phenol resistant and UV resistant material by a roller to feed liquid.

8.3 Instruments for air flow

For air inflow of dissolved oxygen supplying air, hollow tubular instrument made of material that does not adsorb phenol nor elute impurities shall be used. For example, a disposable pipet made of borosilicate glass that is replaces for every test (volume of 3 ml ± 1 ml), or cylindrical gas injection pipet with diameter 10 mm ± 1 mm and height 18 mm ± 1 mm are good. Air inflow amount may be an inflow amount that can maintain the concentration of dissolved oxygen under the water temperature during the test. It is better if air inflow amount is controllable within the range from 400 ml/min to 600 ml/min.

9 Test material

9.1 Test piece

Sample size of the test piece shall be as follows:

Width — 49 mm + 0 mm, –1 mm

Length — 199 mm + 0 mm, –1 mm

The size of a test piece shall be able to be put at the place for folding the test piece as shown in Annex A. The thickness of the test piece is not especially specified, it is acceptable if 5 mm + 0 mm, –1 mm of clearance is secured between the uppermost surface of the test piece and the inner surface of the window glass plate. If a test piece of different thickness is used, the clearance should be adjusted using an accessory plate. Material for an accessory plate is preferably PTFE that has UV irradiation resistance and chemical resistance against phenol.

If the test piece is flake shape or the like, set it at the place for holding the test piece in the test vessel, and then flatten it and a secure 5 mm + 0 mm, –1 mm of clearance between the uppermost surface of the test piece and the inner surface of the window glass plate. If the test piece falls off by inclination of the test vessel or be swept away by the circulation of water, use an offset preventing structure at the place for holding the test piece.

9.2 Pre-treatment of the test piece

If any of the followings possibly occur, do proper pre-treatment. After any pre-treatment, the test piece shall be dried well for the test. At this time, adsorption of organic substances or other effect shall be avoided to the extent possible.

a) If the resulted pH varies beyond the range from 5 to 8 during the test under a dark condition, wash the test piece with purified water. Repeat washing with purified water until pH stays between the range from 5 to 8, measuring pH after each washing.

b) If elution of any organic substance from the test piece is suspected in a test under a dark condition, wash the test piece with purified water. In addition, irradiate light by an UV fluorescent lamp for more than 5 h in the atmosphere or in water as provided for in ISO 22197-1. Elution of organic substances from the test piece is allowed if C_{Df} value results in 95 % or more of C_{Di} value after conducting the procedure of the measurement 10.4 a) to d) and f).