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Fine bubble technology — Evaluation method for determining gas content in fine bubble dispersions in water —

Part 2: Hydrogen content

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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

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Foreword

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

A list of all parts in the ISO 7383 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

Hydrogen has recently attracted considerable research attention across several fields, such as agriculture, food, environment, and medicine sciences, owing to its antioxidant capacity and zero-residual and ecofriendly properties. Hydrogen concentration is a crucial parameter to ensure its successful hydrogen application. At present, there are potential limitations regarding the application of hydrogen in living organisms, such as accessibility, availability, and biological intake. For example, hydrogen exhibits low solubility, with a saturation concentration of only 1,6 mg/l. Fine bubble and ultrafine bubble (UFB) technology have been used to address the low solubility of hydrogen in recent years. UFBs have a large surface area, high internal pressure, and negatively charged surfaces, which accelerate the dissolution of gas into liquids and maintain their stability in the liquids for relatively long periods. Therefore, UFBs can potentially expand the application of hydrogen molecules because of their unique characteristics.

An accurate hydrogen concentration measurement is required to develop an impact evaluation standard for the variety of hydrogen production equipment and hydrogen-rich water products. Normal techniques for measuring the hydrogen content in water include the electrochemical probe (membrane-type polarography) method, titration (oxidimetry) method using a methylene blue (MB)–platinum colloid reagent, and gas chromatography.

The electrochemical probe (membrane-type polarography) method is advantageous as it can be used for both in situ and real-time measurements. Detection limits are stated in the instruction manuals of instruments and, in most cases, are approximately 0,01 mg/l. The upper limit depends on the specifications of the instrument, but it is generally lower than 20 mg/l. Electrochemical probe methods can measure only the dissolved hydrogen concentration in hydrogen UFB dispersions under a steady state or flow state and are not suitable for static water samples. Additionally, the presence of UFBs in water can influence measurement results.

The titration (oxidimetry) method is straightforward and economical; however, its lower limit of detection is only 0,1 mg/l, and the titration range with acceptable accuracy is narrow. Moreover, hydrogen evaporation during measurements and the presence of UFBs in water can influence measurements. Thus, this method can be used only to approximate hydrogen concentrations in UFB dispersions.

Gas chromatography is the most accurate method for measuring the hydrogen content of gas. Its lower limit of detection is the lowest among all methods, and there are no upper measurement limits. However, few attempts have been made to apply this method to measuring hydrogen contents in water. Furthermore, appropriate sample preparation and UFB elimination methods have yet to be developed.

Therefore, a standard method for measuring total hydrogen contents in UFB dispersions has been established. For this document, the titration (oxidimetry) method is proposed as a rapid estimation method and gas chromatography is proposed as an accurate measurement method. The following procedure was used for gas chromatography. First, a bubble-elimination pretreatment is performed to drive both dissolved hydrogen and hydrogen in UFBs from the liquid phase into the headspace, followed by gas chromatography combined with theoretical calculations to determine the total hydrogen content in UFB dispersions. The establishment of this standard method will serve various hydrogen production enterprises, the corresponding customers, and research institutions, enabling them to have a common measurement standard when determining hydrogen contents, thereby facilitating comparisons and judgments of the quality and function of hydrogen products.

The standardized evaluation method for hydrogen content provides an important theoretical basis for future applications in several fields, with further potential for industry, commerce, government, consumers, and academic and research bodies. The establishment of standards will enable governments to establish policies, regulate the development of the hydrogen health industry, and promote research and development into products and technologies related to hydrogen agriculture, hydrogen medicine, and hydrogen-based environmental applications.

Fine bubble technology — Evaluation method for determining gas content in fine bubble dispersions in water —

Part 2:
Hydrogen content

1 Scope

This document specifies the evaluation methods for hydrogen content in ultrafine bubble (UFB) dispersions.

The titration (oxidimetry) method can be used as a quick method to estimate the hydrogen content in hydrogen UFB dispersions. The lower limit of detection is 0,1 mg/l, and the range with acceptable accuracy is between 0,2 mg/l and 1,6 mg/l. The existence of oxidizing or reducing substances in dispersions influences measurement accuracy.

The gas chromatographic method features a considerably high accuracy range and lower limit of detection. The existence of UFBs in water does not influence the measurement results. The existence of oxidizing or reducing substances in water does not affect the measurement accuracy either. However, the measurement procedure is time consuming.

NOTE This document only provides a method for determining hydrogen contents in UFB dispersions and does not involve the specific effects of hydrogen UFB dispersion application.

2 Normative references

There are no normative references in this document.

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:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

3.1
dissolved hydrogen
DH
hydrogen molecules, dissolved in a liquid

3.2
hydrogen UFB
hydrogen molecules, dissolved as ultrafine bubble (UFB)

3.3
titration
method or process of determining the concentration of a dissolved substance in terms of the smallest amount of a reagent of known concentration required to bring about a given effect in reaction with a known volume of the test solution

4 Principle and application

4.1 General

The following two methods can be employed for hydrogen content measurements in UFB dispersions, which are generated by cleaned UFB generation systems utilizing pure water, saline, or buffer solutions, and the gas in which can be pure hydrogen or a gaseous mixture containing hydrogen.

The titration (oxidimetry) method is a quick, economical method with a lower limit of detection of 0,1 mg/l; it is recommended for use only as a rough estimation method.

NOTE The existence of oxidizing or reducing substances in the dispersions influences measurement accuracy.

Gas chromatography is a method with higher accuracy, but it is more expensive and time consuming; it is recommended to be used for more accurate hydrogen content measurements in UFB dispersions and as the reference for the validation titration method.

4.2 Titration (oxidimetry) method

The titration (oxidimetry) method involves a redox reaction of a MB oxidant in the presence of a colloidal platinum catalyst. MB generally reacts with an equimolar amount of hydrogen with platinum or palladium to produce colorless, reduced MB (leucomethylene blue, leucoMB), as shown below:

$$\text{MB (blue)} + 2H^+ + 2e^- \rightarrow \text{leucoMB (colorless)}.$$

The oxidimetry determination of the hydrogen concentration was performed by redox titration. The MB–platinum reagent was added dropwise to a 6 ml sample of a hydrogen UFB dispersion until the solution changed from blue to colourless.

If 6 ml of hydrogen dispersion reduces one drop (20 µl) of the MB–platinum reagent, the concentration of dissolved hydrogen is 0,1 mg/l.

4.3 Gas chromatography

After the hydrogen UFB dispersion is sealed in a vial, the rubber stopper made of butyl rubber and aluminium cap can effectively prevent the diffusion of hydrogen molecules. Through the change of the hydrogen UFB dispersions from a liquid phase to a solid phase by the freezing process, the hydrogen molecules that dissolve in the dispersions are transferred to the gas phase in the vial. Thereafter, the gas components in the vial were separated into electrical signals that were sent to signal processing devices (computer) to obtain peaks corresponding to the separated gas components. Resultantly, the molar concentration of the hydrogen released from the UFB dispersions can be measured. Finally, the total hydrogen content in the hydrogen UFB dispersion can be calculated.

5 Apparatus and materials

5.1 Titration (oxidimetry) method

5.1.1 Reagent

5.1.1.1 MB, $C_{16}H_{18}ClN_3S$ Mass mol: 319,86 g/mol.

Form: brownish-red powder

Grade: analytical pure

5.1.1.2 Ethanol, C_2H_6O · 98 % (GC) Mass mol: 46,07 g/mol.

5.1.1.3 Colloidal platinum, Pt concentration 2 g/kg.

5.1.2 Dropper or titrator

Plastic Pasteur pipette (dropper) commonly comes in 1 ml, 2 ml, 3 ml, and 5 ml which comes with a specific drop size of 10 µl, 20 µl, 25 µl, 35 µl, and 50 µl. For 2 ml plastic Pasteur pipette, one drop of the dropper should be approximately 17 mg or 0,02 ml in the MB–platinum reagent.

To reduce the dosing error, a pipettor covering a volume range of 0 µl to 20 µl can be used instead of a dropper; a commercial titrator can be used as well.

5.1.3 Clear vial

The vial had 6 ml graduated marks, and the colour change of the solution in the vial can be seen clearly.

5.2 Gas chromatography

5.2.1 Vial and clamping machine

5.2.1.1 Vial, made of borosilicate glass; the recommended volume of the vial was 100 ml. However, if the amount of water is less, volumes as low as 15 ml are also acceptable. In Annex D, the comparative results of the same water sample measured in different vials are displayed.

5.2.1.2 Rubber stopper, made of butyl rubber.

5.2.1.3 Cap, made of aluminium.

5.2.1.4 Clamping machine for a flip-top-cap.

5.2.2 UFBs elimination

5.2.2.1 4 °C-refrigerator.

5.2.2.2 –20 °C-freezer.

5.2.3 Carrier gases and column

5.2.3.1 Carrier gas, argon (Ar) or helium (He).

5.2.3.2 Standard hydrogen, can be obtained from a gas company or hydrogen generator (purity > 99,99 %).

5.2.3.3 Hydrogen calibration gases with 0,5 %, 1 %, 5 %, 10 %, 20 %, 50 % and 100 % hydrogen concentrations in air.

5.2.3.4 Gastight plunger syringe, 1 ml in volume.

5.2.3.5 Chromatographic column, molecular sieve 5A capillary/plot columns (Msieve-5A or MolSieve-5A).

5.2.4 Gas chromatograph

A thermal conductivity detector (TCD) should be equipped for gas chromatography for the detection of hydrogen gas present in an air mixture.

5.2.5 Measurement device for UFB size and concentration

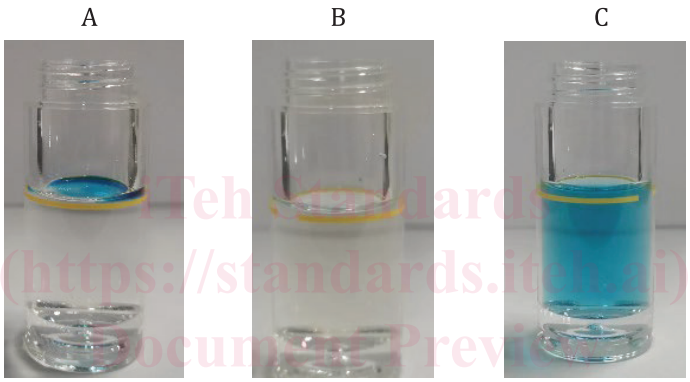
The size and concentration of the hydrogen UFB dispersion are measured using a nanoparticle tracking analysis (NTA) instrument (see ISO 19430). The instrument used was a ZetaView®[1)], allowing a measuring range from 50 nm to 1 000 nm. The wavelength of the laser light source was 488 nm. Alternative instruments with similar or superior characteristics can also be used. The measuring temperature was approximately 15 °C.

6 Procedure

6.1 Titration (oxidimetry) method

MB (0,3 g) was dissolved in 98 % ethanol (98,9 g) to obtain a solution of MB in ethanol. An aqueous suspension of 2 % colloidal platinum (0,8 g) was added to the solution, and the mixture was stirred to produce 100 g of the MB–platinum reagent.

The MB–platinum reagent was added dropwise to a 6 ml sample of hydrogen UFB dispersions until the solution changed from blue to colourless (see Figure 1). Thereafter, the MB–platinum reagent was added using a dropper. To prevent uneven dropper volume, a pipettor covering a volume range of 0 µl to 20 µl was used to add the MB–platinum reagent to the water sample (20 µl each time).



Key

A MB–platinum reagent added dropwise to sample
B solution changed from blue to colourless
C titration endpoint

Figure 1 — Image of the titration process

6.2 Gas chromatography

6.2.1 General

The total procedure consisted of three steps: sample sealing, UFBs elimination, and the analysis of gas substitutes. The setup is shown in Figure 2. The detailed processes are as follows.

1) ZetaView® is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

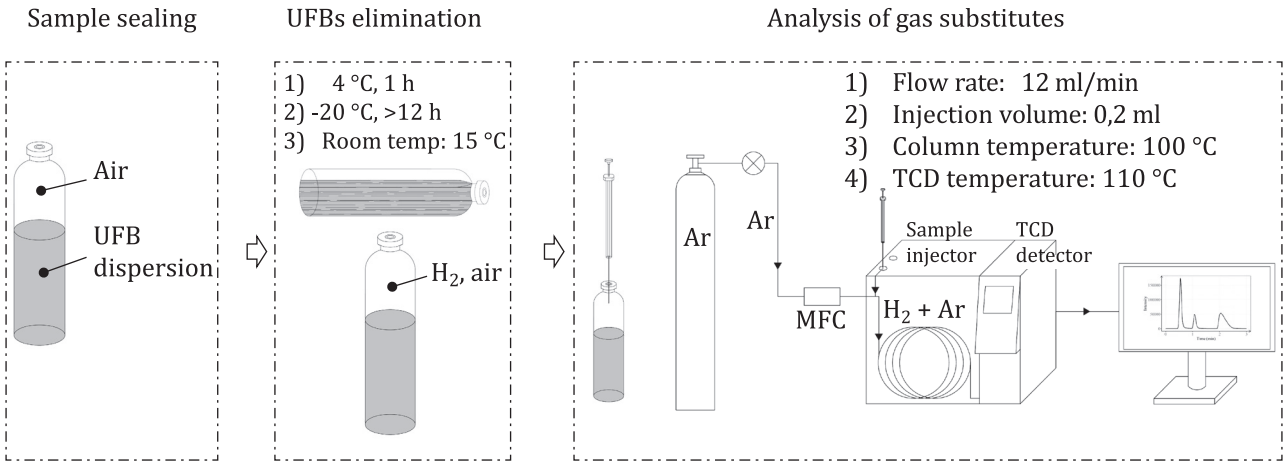


Figure 2 — General view of gas chromatography system

6.2.2 Sample sealing

A freshly-prepared hydrogen UFB dispersion was placed in a sealed vial.

If the sample is a freshly-prepared dispersion with microbubbles and you wish to exclude the hydrogen content within these microbubbles from your measurement, the sample shall be allowed to settle until the water changes from its initial milky appearance to clear before sealing it in the vial. This will ensure that the hydrogen content within the microbubbles is not included in the total hydrogen content measurement.

The ratio of liquid volume to headspace volume in the vial was set in the range from 2:1 to 4:1 based on the volume expansion after the liquid underwent a phase transition to a solid phase. For example, the amount of liquid contained in a 100 ml vial should be less than 80 ml.

Thus, 70 ml to 80 ml of the UFB solution was added into the vial using a graduated cylinder. The accurate volume of the liquid and the volume of the headspace were measured using an analytical balance.

Thereafter, the rubber stopper, aluminium cap, and clamping machine described in 5.2.1 were used to seal the sample in the vial (see Figure 3).