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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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Foreword

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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.

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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

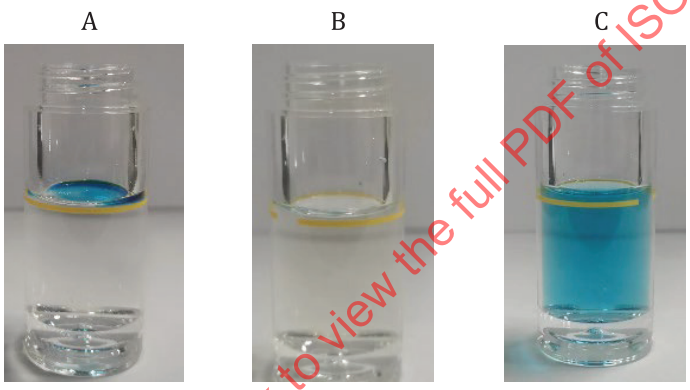
The size and concentration of the hydrogen UFB dispersion are measured using a nanoparticle tracking analysis (NTA) instrument (see ISO 19430). The instrument used was a ZetaView®[1)], allowing a measuring range from 50 nm to 1 000 nm. The wavelength of the laser light source was 488 nm. Alternative 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.

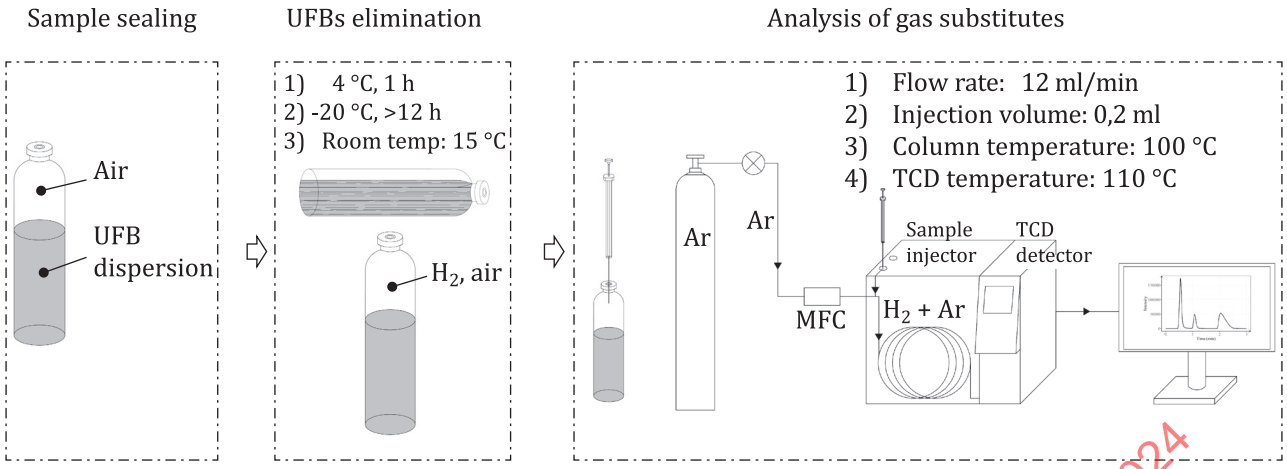


Figure 2 — General view of gas chromatography system

6.2.2 Sample sealing

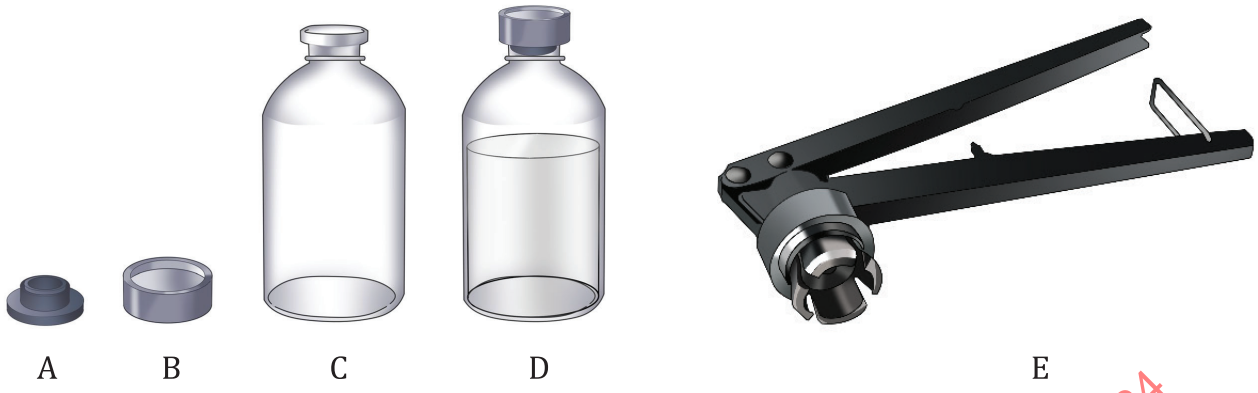
A freshly-prepared hydrogen UFB dispersion was placed in a sealed vial.

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).



Key

A rubber stopper
B aluminium cap
C empty vial
D sealed vial
E clamping machine

Figure 3 — Vial and clamping machine for the flip-top cap

6.2.3 UFBs elimination

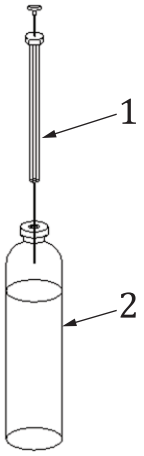
Preferably, the freeze–thaw method is used to eliminate UFBs in water, as described in ISO 24261-2.

To avoid the vial from cracking during the freezing process, a step-by-step freezing method is preferable. The vial should be kept horizontal when freezing. First, place the vial containing the UFB dispersion horizontally in a 4 °C-refrigerator for 1 h. Second, transfer the vial to a –20 °C-freezer for more than 12 h to ensure that all the liquid change into a solid acid state. Finally, thaw the sample at room temperature, such as approximately 15 °C. After the temperature stabilizes, use a manual airtight injection needle to accurately draw a specific amount of headspace gas.

The elimination efficiency should be investigated by measuring bubble number densities using NTA before and after the freeze–thaw process.

6.2.4 Analysis of gas substitutes

The flow rate of argon gas (carrier gas) was controlled using a mass flow controller, and the sample to be analysed was obtained in a gastight plunger syringe. The outgassing from the sample was mixed with the carrier gas and sent to the gas chromatography column using the injector. The TCD of the gas chromatograph enabled the conversion of the separated gas components into electrical signals, which were sent to the signal processing devices (computer) to obtain peaks corresponding to the separated gas components. Resultantly, the molar concentration of the gas released from the sample was measured, and afterward, the hydrogen content in the UFB dispersion was analysed.



Key

1 gastight plunger syringe

2 sealed vial

Figure 4 — Illustration of how to draw gas from the vial using gastight plunger syringe

Standard hydrogen can be obtained from a gas company or hydrogen generator. The calibration gases contain 0,5 %, 1 %, 5 %, 10 %, 20 %, 50 % and 100 % hydrogen in air.

A gastight plunger syringe was used to accurately draw a 0,2 ml of headspace gas (see Figure 4).

Capillary column and packed column can both be used. The packed column allows a large sample load capacity. The injection volume is typically 1 ml. The capillary column allows a small injection volume of the gas sample, and the gas flow rate is lower than that of the packed column type.

When using the capillary columns, the recommended run conditions used are as follows:

a) carrier gas: argon gas, constant flow rate mode, 12 ml/min flow rate measured at the column outlet;

b) injection volume: 0,2 ml;

c) column: MSieve 5 A, 30 m length, 0,53 mm o.d., 50 µm i.d.;

d) column temperature: 100 °C;

e) TCD temperature: 110 °C.

When using the packed column, the recommended run conditions used are as follows:

a) carrier gas: argon gas, constant flow rate mode, 30 ml/min flow rate measured at column outlet;

b) injection volume: 1 ml;

c) column: MolSieve 5 A, 1,83 m length, 3,1 mm o.d., 2 mm i.d., mesh size 180 µm to 250 µm;

d) column temperature: 60 °C;

e) TCD temperature: 120 °C.

7 Results and calculation

7.1 Titration (oxidimetry) method

The dissolved hydrogen concentrations determined by the titration (oxidimetry) method are described in Reference [3]. For a detailed example of the titration (oxidimetry) method applied in testing laboratories, please refer to Annex A.

7.2 Gas chromatography

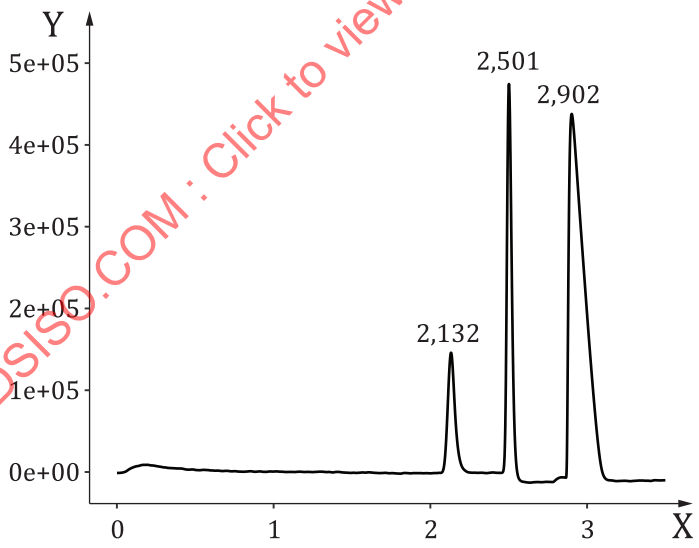
7.2.1 General

To accurately determine the total amount of hydrogen in the hydrogen UFB dispersion, a standard curve for the relationship between the hydrogen concentration and the hydrogen peak area of the gas chromatography shall be established. Further, these five parameters, the gas volume of the headspace, headspace gas pressure, percentage of hydrogen in the headspace gas, volume of solution in the sample, and measurement temperature, should be determined accordingly.

7.2.2 Calibration curve for hydrogen concentration measurement

Both capillary columns and packed columns can be used. As the capillary column has a small injection volume, it can reduce and avoid headspace volume changes, thereby reducing experimental errors. The calibration curve for the hydrogen concentration is shown in Figures 4 and 5 as an example of using the capillary column.

The calibration curve was used for standard hydrogen gas with known percentages of 0,5 %, 1 %, 5 %, 10 %, 20 %, 50 %, and 100 % hydrogen in air. Thus, the area of the hydrogen signal was converted to the percentage concentration using the non-linear equation in the calibration curve.



Key

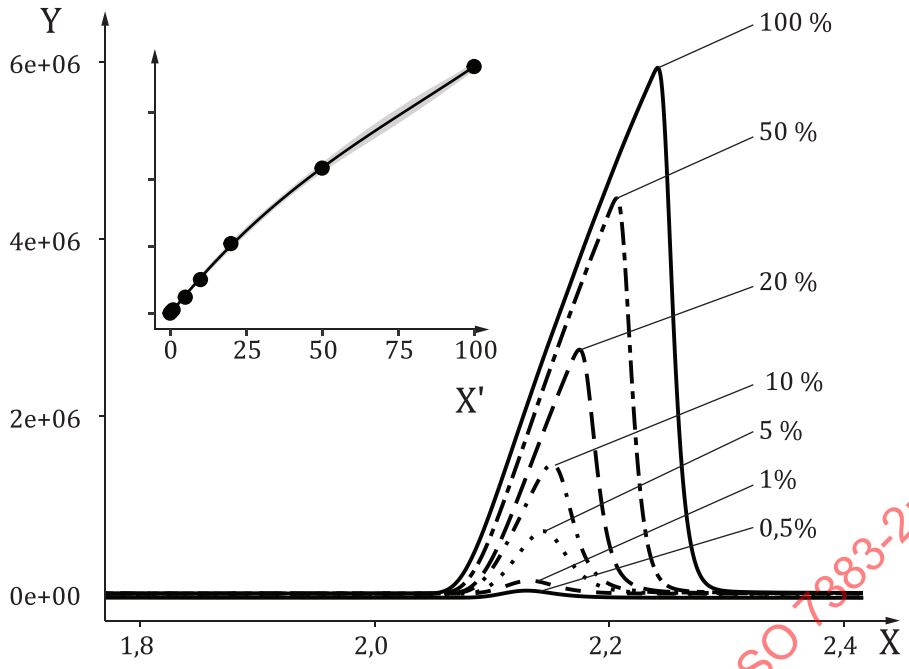
X retention time (min)

Y detection response (a.u.)

NOTE The gas chromatography signals of hydrogen, oxygen and nitrogen molecules are shown from left to right

Figure 5 — Gas chromatography spectra of a standard sample with 1 % hydrogen, 21 % oxygen, and 78 % nitrogen

Figure 6 shows an example of calibration curve.



Key

X retention time (min)

Y detection response (a.u.)

X' standard concentration (%)

NOTE The formula for standard curve is $\boldsymbol{Y = 11{,}305\,2X^3 - 3\,023{,}59X^2 + 558\,840X}$; correlation coefficient: 0,999 9

Figure 6 — Calibration curve obtained for standard hydrogen gas using the capillary column

7.2.3 Volume of the water sample in the vial

The weighing method was used to accurately calculate the volume of the solution in the vial.

The water sample volume is calculated from Formula (1):

$$V_w = \frac{(M_a - M_b)}{\rho} \quad (1)$$

where

M_a is the mass of the vial containing a specific amount of the UFB dispersion;

M_b is the mass of an empty vial;

ρ is the density of ultrapure water.

7.2.4 Volume of the headspace above the UFB dispersion in the vial

The weighing method was used to accurately calculate the volume of gas in the headspace of the vial.

The gas volume in the headspace is calculated from Formula (2):

$$V_g = V_t - V_w = \frac{M_T - M_b}{\rho} - V_w \quad (2)$$

where

V_t is the volume of the vial;

M_T is the mass of the vial filled with ultrapure water;

M_b is the mass of an empty vial;

ρ is the density of ultrapure water;

V_w is the volume of the water sample in the vial.

7.2.5 Pressure of the gas in the vial headspace

Even though hydrogen gas moves from the liquid phase to the gas phase in the vial, oxygen from the air in the gas phase also moves into the liquid phase. This exchange keeps the gas pressure in the headspace of the vial close to the atmospheric pressure outside.

7.2.6 Hydrogen content in the vial head space

By assuming an ideal gas equation under a constant volume and temperature, the total number of moles (n) of mixed gas was calculated by substituting the volume of the headspace in the vial and the gas constant at calculated pressure and measurement temperature.

The unit conversion from % to mol/m^3 is shown in Formula (3). It was assumed that the gas was ideal, and the gas pressure (P) was 101,325 kPa. C_i (mol/m^3 or %) is the concentration of the gas component, n (mol) is the molecular number, V (m^3) is the gas volume, and T (K) is the gas temperature at the surface. Subscription 0 indicates the standard condition (101,325 kPa, 273 K), and the subscription of C_i indicates the unit of the concentration.

$$C_{i,\mathrm{mol/m^3}} = \frac{\mathrm{n}_i}{\mathrm{V}} = \frac{\mathrm{n}_i}{\mathrm{n}}\frac{\mathrm{n}}{\mathrm{V}} = \frac{C_{i,\%}}{100}\frac{\mathrm{P}}{\mathrm{RT}} = \frac{C_{i,\%}}{100}\frac{\mathrm{P}_0}{\mathrm{RT}_0}\frac{P}{\mathrm{P}_0}\frac{\mathrm{T}_0}{\mathrm{T}} = \frac{C_{i,\%}}{100}\frac{1000}{22{,}4}\frac{P}{\mathrm{P}_0}\frac{\mathrm{T}_0}{\mathrm{T}} = C_{i,\%}\frac{10}{22{,}4}\frac{P}{\mathrm{P}_0}\frac{\mathrm{T}_0}{\mathrm{T}} \quad (3)$$

where

C_i is the concentration of each gas component (mol/m^3 or %);

n is the number of moles of the gas (g · mol^{-1});

P_0 is the standard atmospheric pressure (101,325 kPa);

T_0 is the standard condition temperature (273,15 K);

P is the pressure of the gas in the headspace of the vial (kPa);

V is the volume of the headspace above the UFB dispersion (ml);

R is the gas constant (R = 8,314 16 × 10^{-2} m^3 · Pa · K^{-1} · mol^{-1});

T is the measurement temperature (K).

7.2.7 Hydrogen content in the vial water sample

The vial water sample exhibits a specific hydrogen content, divided into two components: the first component is the amount of hydrogen that has been transferred from the water to gas phase, represented as C_g.

The second component is the small quantity of dissolved hydrogen that remains in the water when equilibrium is reached, denoted as C_w. This second component can be determined using the partial pressure of hydrogen in the gas phase in conjunction with Henry's law. Therefore, to calculate the total hydrogen

content in the water sample, consider both the association with each number concentration of UFBs and the dissolved hydrogen formula as shown in Formulae (4) to (6):

$$C_t = C_g + C_w \tag{4}$$

$$C_g = C_{i,mol/m^3} \frac{V_g}{V_w} \times M_{H_2} \tag{5}$$

$$C_w = P_{H^2} \times H_s^{cp} \times M_{H_2} \tag{6}$$

where

C_g is the amount of hydrogen transferred from the water to the gas phase;

C_w is the dissolved hydrogen remaining in the water at equilibrium;

H_s^{cp} is the Henry constant for hydrogen at a certain temperature ($7{,}698\times10^{-9}$ $mol \cdot l^{-1} \cdot Pa^{-1}$);

M_{H_2} is the molar mass of hydrogen ($2{,}015\ 88\ g \cdot mol^{-1}$).

Annex B and Annex C provide detailed examples of how to utilize gas chromatography with both capillary and packed columns, respectively, to measure and calculate the hydrogen content in hydrogen UFB dispersion.

7.2.8 Hydrogen content in association with each number concentration of UFBs and dissolved hydrogen

The measurement results of 17 samples with different number concentrations of hydrogen UFBs are shown in Table 1.

For UFBs elimination effects, the freeze–thaw method is effective. The elimination rate is above 99 %.

Table 1 — Hydrogen content in different UFB dispersions with two methods

No.	Number concentration (/ml)	C_t ($mg \cdot l^{-1}$)[a]	V_w (ml)	V_g (ml)	$C_{i,\%}$ (%)	C_t ($mg \cdot l^{-1}$)[b]
1	$2{,}2\times10^6$	1,4	73,11	50,13	2,325	1,397
2	$2{,}2\times10^6$	1,4	73,3	50,5	2,253	1,360
3	$5{,}0\times10^6$	1,4	73,83	49,82	2,386	1,411
4	$5{,}0\times10^6$	1,4	74,06	50,13	2,294	1,361
5	$1{,}1\times10^7$	1,4	73,15	50,26	2,664	1,603
6	$1{,}1\times10^7$	1,4	73,65	49,88	2,535	1,505
7	$1{,}5\times10^7$	1,4	74,14	49,67	2,853	1,675
8	$1{,}5\times10^7$	1,4	74,7	48,05	2,745	1,549

V_w : Volume of the UFB dispersion (ml)

V_g : Volume of the headspace (ml)

$C_{i,\%}$: Percentage of hydrogen in the headspace measured using gas chromatography (%)

[a] C_t ($mg \cdot l^{-1}$): Hydrogen content measured by titration method ($mg \cdot l^{-1}$).

[b] C_t ($mg \cdot l^{-1}$): Hydrogen content measured by gas chromatography ($mg \cdot l^{-1}$).

[c] Below detection limit of ZetaView.

NOTE Samples 1 to 15 used a capillary column, the injection volume was 0,2 ml. Samples 16 and 17 used packed column, the injection volume was 1 ml. The measurement temperature is 15 °C.

Table 1 *(continued)*

No.	Number concentration (/ml)	C_t ($mg \cdot l^{-1}$)[a]	V_w (ml)	V_g (ml)	$C_{i,\%}$ (%)	C_t ($mg \cdot l^{-1}$)[b]
9	$2{,}0\times10^7$	1,4	74,38	49,55	3,169	1,851
10	$2{,}0\times10^7$	1,4	74,69	47,72	2,984	1,673
11	$2{,}5\times10^7$	1,4	73,67	49,19	3,164	1,852
12	$2{,}5\times10^7$	1,4	73,45	50,15	3,000	1,794
13	[c]	0,6	75,37	47,82	1,739	0,969
14	[c]	1,0	75,06	49,46	2,977	1,720
15	[c]	1,4	75,72	48,72	2,696	1,522
16	$1{,}4\times10^7$	1,4	100	24,5	7,189	1,616
17	$9{,}8\times10^6$	1,4	100	24,5	6,615	1,487

V_w : Volume of the UFB dispersion (ml)

V_g : Volume of the headspace (ml)

$C_{i,\%}$: Percentage of hydrogen in the headspace measured using gas chromatography (%)

[a] C_t ($mg \cdot l^{-1}$): Hydrogen content measured by titration method ($mg \cdot l^{-1}$).

[b] C_t ($mg \cdot l^{-1}$): Hydrogen content measured by gas chromatography ($mg \cdot l^{-1}$).

[c] Below detection limit of ZetaView.

NOTE Samples 1 to 15 used a capillary column, the injection volume was 0,2 ml. Samples 16 and 17 used packed column, the injection volume was 1 ml. The measurement temperature is 15 °C.

8 Error of measurement

8.1 Titration (oxidimetry) method

With regard to the titration method, the stirring and titration times shall be carefully controlled during the process as they can affect the diffusion of dissolved hydrogen gas in water to air.

Measurement uncertainties associated with the titration method include:

a) uncertainty in water sample weighing;

b) uncertainty in MB standard preparation;

c) uncertainty in hydrogen loss through stirring and prolonged titration duration.

8.2 Gas chromatography

For gas chromatography, it is recommended to avoid repeated pouring when transferring the sample into the vial to prevent the diffusion of hydrogen gas from water to air. When using a pipettor to draw water samples, negative pressures can result in the loss of hydrogen gas from the water sample. Therefore, it is recommended to use the pouring method in combination with weighing to determine the water sample volume. Additionally, when sampling in the headspace of the vial, it is advisable to keep the position of the gastight syringe needle tip fixed to minimize errors.

Measurement uncertainty in the gas chromatographic method includes:

a) uncertainty in water sample weighing;

b) uncertainty in hydrogen UFB dispersion preparation;

c) uncertainty in hydrogen gas calibration standard preparation;

d) uncertainty in gastight syringe sampling;

e) uncertainty in gas chromatographic measurement.

8.3 Relative standard deviation of the gas chromatograph

The relative standard deviation (RSD)RSD calculation is shown in Formulae (7) and (8):

$$s=\sqrt{\frac{1}{N-1}\sum_{i=1}^{N}(x_i-\bar{x})^2} \tag{7}$$

$$RSD=\frac{s}{\bar{x}} \tag{8}$$

where

s is the sample standard deviation;

RSD is the relative standard deviation;

$X_1, \ldots, X_N$ is the sample data set;

$\bar{x}$ is the mean value of the sample data set;

N is the size of the sample data set.

9 Test report

9.1 Testing results

The following information shall be reported based on the testing results:

a) number concentration of the UFB dispersion before and after the elimination process;

b) volume of the UFB dispersion;

c) volume of the headspace of the vial containing UFB dispersion;

d) the temperature and pressure of the experiment setting;

e) hydrogen content in the vial head space;

f) hydrogen content in the vial water sample.

9.2 Testing conditions

a) date, and time of measurement;

b) a reference to this document, i.e. ISO 7383-2:2024;

c) identification of measuring instruments;

d) identification of measurement officer;

e) identification of the apparatus and materials.

Annex A
(informative)

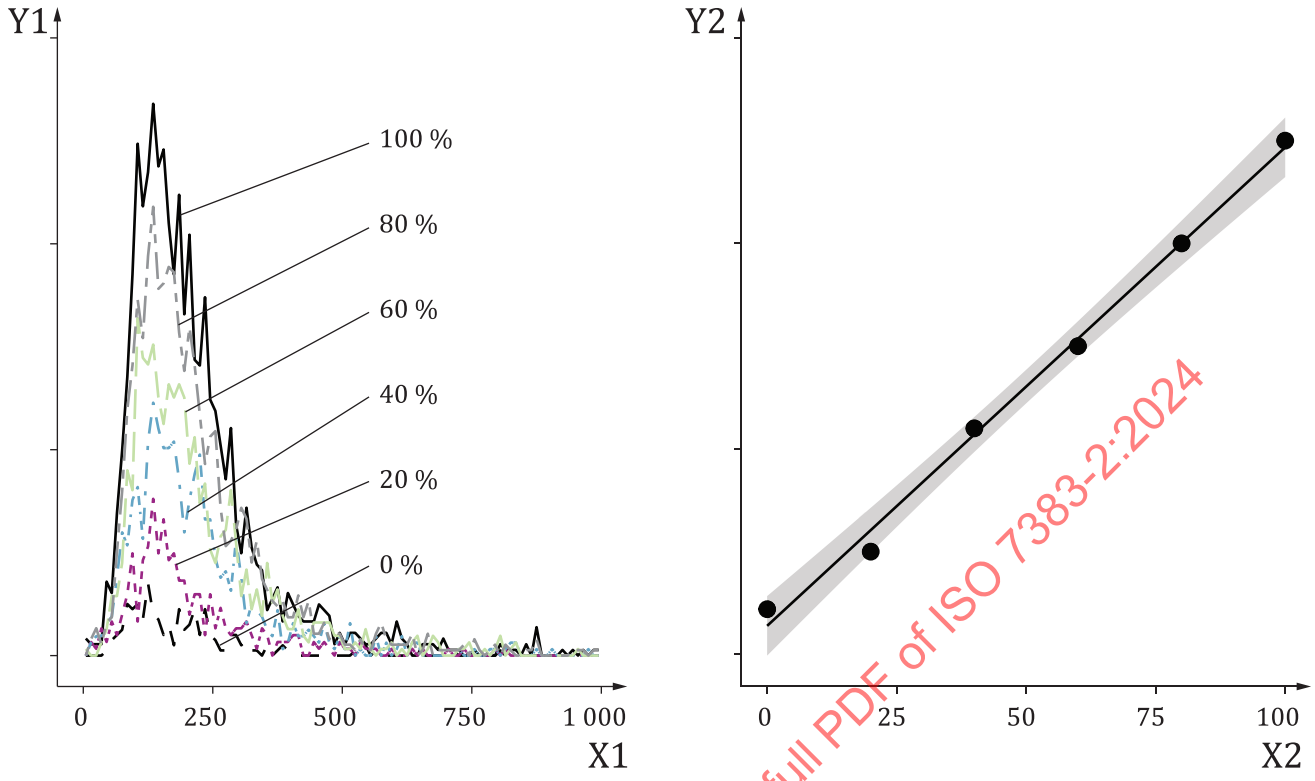
Example of test result at testing laboratory by titration (oxidimetry) method

The following test result was acquired and reported.

The results of analysing samples from no. 1 to no. 12 in Table 1 are an example of the hydrogen content measurement of the hydrogen UFB dispersion by titration method and gas chromatography.

Hydrogen water samples with different UFB concentrations were obtained by mixing hydrogen-rich water and hydrogen UFB water in varying proportions. UFB concentrations and bubble size distributions were analysed using a nanoparticle tracking instrument (see Figure A.1).

The dissolved hydrogen contents of hydrogen UFBs with different concentrations (see Figure A.2) were found to be similar when determined using the titration method. At UFB concentrations lower than $2{,}0 \times 10^7$ particles/ml, measurements by titration (oxidimetry) were close to the real value (sample nos. 1 to 8). However, at UFB concentrations higher than $2{,}0 \times 10^7$ particles/ml, the bubbles themselves affected the accuracy of the measurement results (sample nos. 9 to 12).

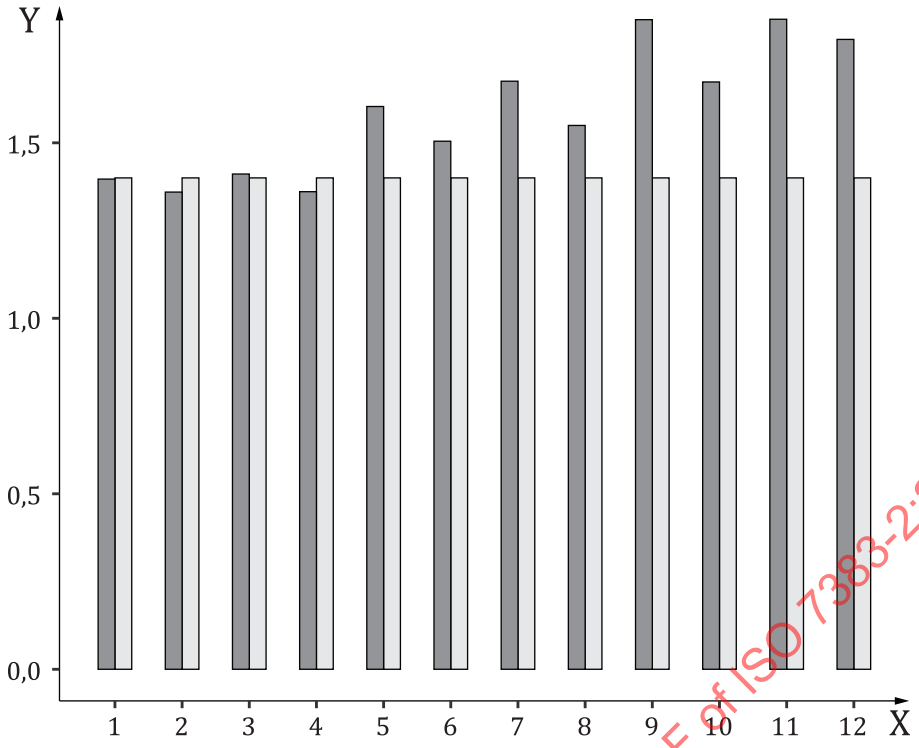


a) b)

Key

X1 size (min)
Y1 concentration (E6 particle/ml)
X2 ratio of UFB water (%)
Y2 concentration (E7 particle/ml)

Figure A.1 — UFB concentrations in water samples after mixing hydrogen UFB water and hydrogen-rich water in different proportions



Key

X analyzing a sample from No. 1 to No. 12 in Table 1

Y hydrogen content in the sample (mg/l)

results measured by titration (oxidimetry)

results measured by gas chromatography

Figure A.2 — Hydrogen content in UFB dispersions with different UFB number concentrations measured by titration (oxidimetry) and gas chromatography

Annex B
(informative)

Example of test result at testing laboratory by gas chromatography using the capillary column

The following test result was acquired and reported.

The result of analysing sample no. 12 in Table 1 is shown in Figures B.1 and B.2 as an example of the hydrogen content measurement of the hydrogen UFB dispersion by gas chromatography using a capillary column. The number concentration of UFB was $2,5 \times 10^7$/ml. The volume of the water sample was 73,45 ml. The volume of the headspace in the vial was 50,15 ml. The estimated dissolved hydrogen concentration by the titration method was 1,4 $\text{mg}\cdot\text{l}^{-1}$. Figure 5 shows the gas chromatography spectra of the gas in the headspace of the vial. Capillary column MSieve 5 Å (MS 5 A) was used. Figure B.2 shows the results of the UFB size distribution measured by NTA. The measurement temperature was 15 °C.

The concentration of hydrogen in sample no. 12 is determined as follows.

According to the calibration curve obtained for standard hydrogen gas and the peak area of the hydrogen content of sample no. 12 shown in Figure B.1, the hydrogen content, $C_{i,\%}$, was 3,000 (%).

Furthermore, the total hydrogen content in the headspace of the vial, $C_{i,\text{mol/m}^3}$, can be calculated as follows:

$$C_{\text{i,mol/m}^3} = C_{i,\%}\frac{10}{22,4}\frac{P}{P_0}\frac{T_0}{T} = 3\frac{10}{22,4}\frac{273,15}{288,15} = 1,269\,5\ \text{mol/m}^3.$$

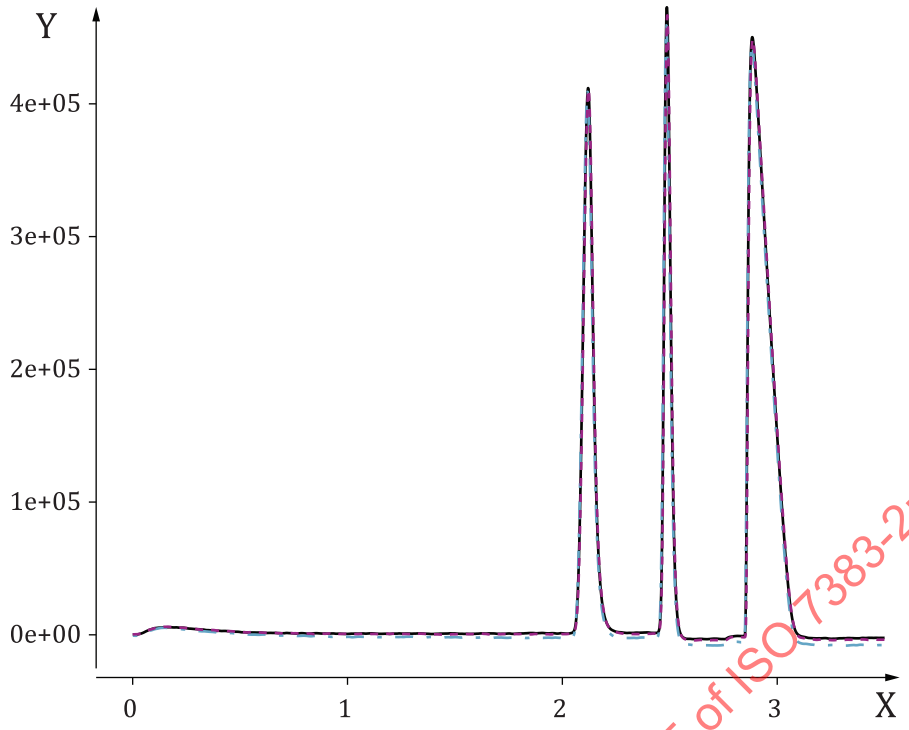
Thereafter, the total hydrogen content in sample no. 12 can be calculated as follows:

$$C_{\text{g}} = C_{\text{i,mol/m}^3}\frac{V_{\text{g}}}{V_{\text{w}}}\times M_{\text{H}_2} = 1,269\,5\frac{\text{mol}}{\text{m}^3}\times\frac{50,15}{73,45}\times 2,015\,88\ g\cdot\text{mol}^{-1} = 1,747\ \text{mg}\times L^{-1}.$$

$$C_w = P_{H^2}\times H_s^{cp}\times M_{H_2} = 0,03\times 101,325\ \text{kPa}\times 7,698\times 10^{-9}\cdot mol\cdot l^{-1}\cdot Pa^{-1}\times 2,015\ g\cdot mol^{-1}$$

$$= 0,047\ mg\cdot l^{-1}$$

$$C_t = C_g + C_w = 1,747\ mg\cdot l^{-1} + 0,047\ mg\cdot l^{-1} = 1,794\ mg\cdot l^{-1}$$

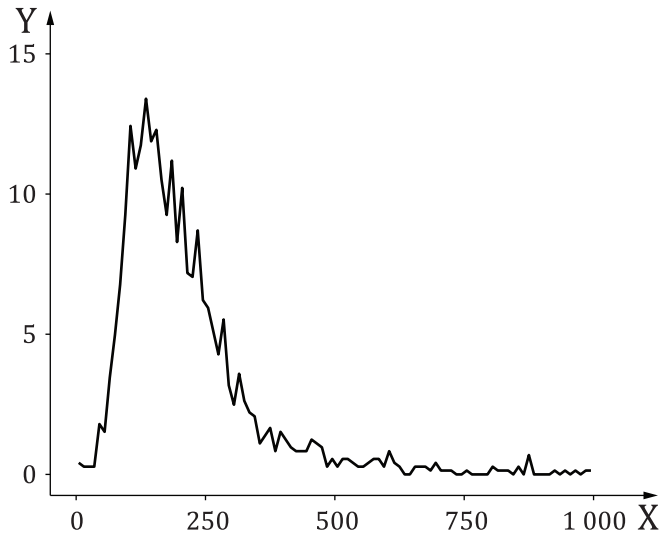


Key

X	retention time (min)
Y	detection response (a.u.)
———	first measurement
– – –	second measurement
- - - - - -	third measurement

NOTE The gas chromatography signals of hydrogen, oxygen, and nitrogen molecules are shown from left to right (capillary column).

Figure B.1 — Gas chromatography spectra of sample no. 12 in Table 1



Key

X size (nm)

Y concentration (E6 particle/ ml)

Figure B.2 — Size distribution of sample no. 12 in Table 1

By the titration (oxidimetry) method, the hydrogen content in sample no. 12 in Table 1 was estimated to be 1,4 mg/l.