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Fine bubble technology — Evaluation method for determining surface tension of ultrafine bubble dispersions

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

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

Ultrafine bubble (UFB) dispersion in water has been used to take advantage of UFB's ability to slip into narrow space in various technologies such as desalting from the surface of concrete structure, scrubbing a stain on the floor of restroom, since the early period in the development of UFB technology. Recently some appliances such as showerhead and washing machine have installed a nozzle to generate UFBs. The mechanism of removing substances by UFBs is still under investigation, however, squeezing of bubbles between substrate and substances to be removed is presumed to play an important role. Surface tension is inferred to be one of the basic characteristics pertinent to such behaviour of UFBs.

The standardization of measuring method for surface tension is necessary to evaluate the performance of those products using UFBs. The application of measurement technique of surface tension to UFB dispersion in water requires however, special attention to the fact that the change in surface tension caused by UFBs is rather small compared to that caused by surface active agent. Furthermore, UFB dispersion in water is a mixture of water, UFBs and impurities in water, and hence its surface tension can behave in a different manner compared to that of pure material or homogeneous solution.

This document is intended to specify the evaluation method of surface tension of UFB dispersion in water using three measurement methods, Wilhelmy, du Noüy and the pendant drop method, which have been chosen from those widely used in industries. The standardized evaluation method also enables to measure the surface tension of liquid containing UFB dispersion in dilute surfactant water such as detergent or machining coolant, leading to an easy choice for surfactant matching to UFBs.

Fine bubble technology — Evaluation method for determining surface tension of ultrafine bubble dispersions

1 Scope

This document specifies evaluation methods for surface tension of ultrafine bubble (UFB) dispersion in water.

Three test methods, Wilhelmy, du Noüy and the pendant drop method, are adopted because of their advantages to detect small change in surface tension by UFB dispersion in water and the high accessibility to commercially available instruments.

This document can be used to measure the surface tension of liquid containing UFB dispersion in dilute surfactant water solution such as detergent or machining coolant as well as UFB dispersion in water.

NOTE Measurement data of liquid containing UFB dispersion in dilute surfactant water solution are summarized in Annex D.

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 304:1985, *Surface active agents — Determination of surface tension by drawing up liquid films*

ISO 19403-3:2017, *Paints and varnishes — Wettability — Part 3: Determination of the surface tension of liquids using the pendant drop method*

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

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 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
UFB dispersion
UFBD
liquid which contains ultrafine bubbles

[SOURCE: ISO 21255:2018, 3.2[1]]

4 Apparatus

4.1 General

Measuring instruments which are designed for the following established measuring methods, Wilhelmy, du Noüy and the pendant drop methods, are used with ordinary laboratory apparatus. The instrument for Wilhelmy and du Noüy method and that for the pendant drop method, which are usually commercially available, shall be in accordance with ISO 304:1985, Clause 5 and ISO 19403-3:2017, Clause 5, respectively.

In most cases, the instruments are computerized, and measurement and data analysis software are installed.

Measurement is conducted with measuring unit, a rectangular plate in Wilhelmy, a ring in du Noüy, and a needle in the pendant drop method. The measuring units should be chosen from those recommended by manufacturers of instruments.

A measuring cup for the Wilhelmy and du Noüy methods such as a petri dish and a syringe for the pendant drop method, which hold the sample liquid to be tested, should be made of glass to avoid adsorption of UFBs on the wall thereof.[1],[2]

Special attention should be paid to the cleanliness of apparatus to be in contact with the sample liquid because the change in surface tension by the presence of UFBs is expected to be small in the measurement.

NOTE Specifications for commercially available measurement instruments are provided in Annex A.

4.2 Wilhelmy method

When a plate for measurement is distorted, it should be turned back to normal shape or replaced with a brand-new one.

4.3 du Noüy method

When a ring for measurement is distorted, it should be turned back to normal shape or replaced with a brand-new one.

A special jig to restore the original shape can be provided from the manufacturer of tensiometer.

4.4 Pendant drop method

Outer diameter of needle for the pendant drop method d_o should be chosen based on the manufacturer's instruction. The relationship between d_o and σ/ρ the ratio of surface tension σ and sample density ρ illustrated in ISO 19403-3:2017, Clause 5, Figure 2, is an informative guide to find an appropriate needle size.

5 Procedure

5.1 Testing environment

Measurement should be carried out in an air-conditioned room.

The use of a heat regulating unit for a measuring instrument to keep the temperature of sample liquid constant is more desirable.

5.2 Temperature measurement

The temperature of the sample shall be determined immediately before the measurement.

When the measurement is replicated for the same sample liquid, the temperature of the sample should be monitored during the measurement.

Fluctuation of the sample temperature should be kept within 2 °C.

To prevent the contamination during the temperature measurement, attention shall be paid to the cleanliness of the sensor surface of the thermometer.

Temperature should be read with an accuracy of 0,1 °C.

5.3 Handling of the sample

A sample should be kept in an airtight container without air-liquid interface under constant temperature until immediately before testing.[1],[2]

To avoid the increase and decrease in the number of ultrafine bubbles during sampling, the following practical measures are recommended: pouring a sample liquid gently into a measuring cup and syringing a sample liquid slowly.

To keep the homogeneity of the sample liquid, gentle stirring with a motor-driven drum roller illustrated in ISO 20298-1:2018, Annex A,[3] is recommended.

5.4 Cleaning of the measuring unit

5.4.1 Cleaning of the plate and ring

Before every measurement, immersion cleaning with ethanol followed by heating to red heat with the alcohol lamp should be carried out.

A plate and a ring shall be kept in ambient temperature after heating to avoid deformation by quenching with the sample liquid.

5.4.2 Cleaning of the measuring cup and syringe

Immersion cleaning with neutral detergent followed by rinsing well with purified or distilled water should be carried out before measurement.

5.5 Determination

The horizontality of instrument shall be confirmed before determination.

As for the pendant drop method, vibrations and air flow shall be minimized. Special attention should be paid to the reduction in vibration of droplet during measurement when a small size of needle is chosen. Intense exposure to light from outside shall be avoided to keep the precision in optical profilometry of droplet.

Carry out the determination on the sample to be analysed according to the manufacturer's instructions for each instrument.

5.6 Measurement of blank water

To explicitly show the influence of UFBs on surface tension, the surface tension of blank water shall be determined with the methods described in 5.5 and subtract data thereof from those of the sample to be analysed.

NOTE Raw water for fine bubble generation can be used as blank water.

6 Calculation and expression of results

For the practical procedure, it is recommended to use the software supplied by the manufacturers of the instruments.

Alternatively, for Wilhelmy and du Noüy methods, calculation methods are specified in ISO 304:1985, Clause 7.

NOTE 1 The pendant drop method assumes the usage of software for optical profilometry of water drop and calculation of surface tension.

NOTE 2 The feature of the three measurement methods is demonstrated in Annex B.

NOTE 3 The influence of measuring condition on measurement results is demonstrated in Annex C.

7 Test report

The test report shall include the following information.

a) the test method used, together with a reference to this document, i.e. ISO 7392:2024 and information about the measuring instrument used:

— the name of the instrument and its manufacture's name, version of software;

— the specification of the needle used in the pendant drop method;

b) the nature of the water used:

— property of the water sample such as pH, electroconductivity, etc.;

c) the measuring conditions:

— the temperature of the water when the measurement was carried out;

— the retention time of a droplet in the measurement by the pendant drop method;

d) the result in accordance with Clause 6;

e) all circumstances that can have influenced the result.

Annex A
(informative)

Specifications for commercially available measurement instruments

Table A1 — Example of specifications for commercially available measurement instruments

	Wilhelmy	du Noüy	Pendant drop	Capillary-rise
Measurement range(mN/m) [a]	0 to 100	0 to 100	0 to 100	0 to 80
Surface tension of water (mN/m)	72,09 [b]	72,47 [b]	72,38 [c]	72,88 [a]
Standard deviation (mN/m)	0,01 [b]	0,07 [b]	0,12 [c]	1 [a]

[a] Catalogue value.

[b] Measured at ambient temperature of 21,1 °C ± 0,5 °C.

[c] Measured at ambient temperature between 21,2 °C and 21,7 °C.

Annex B
(informative)

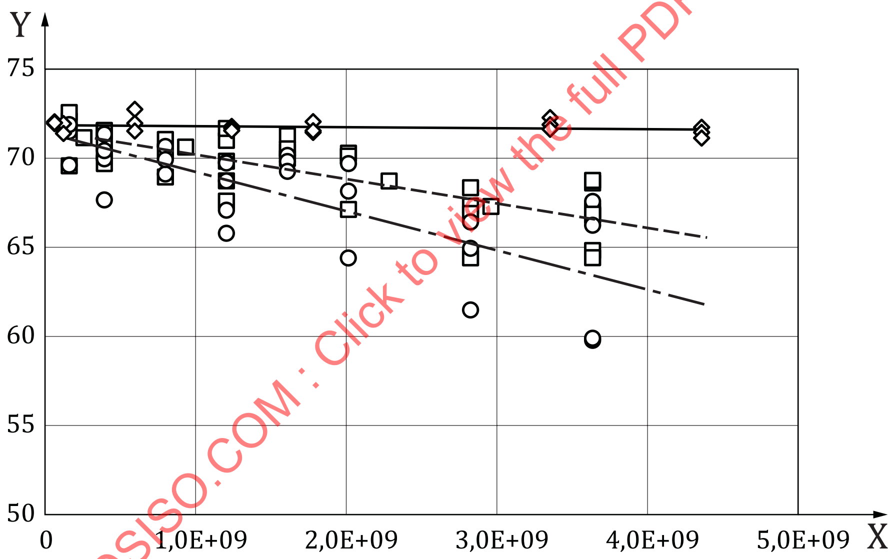
Feature of the measurement methods

B.1 Sensitivity to the number concentration of UFBs

Surface tension was measured at twelve different levels of the number concentration of UFBs. The UFBs were generated by a commercially available cavitation with a swirl type generator. Each symbol in Figure B.1 denotes the mean of three to five measurements of the surface tension. The number concentration was measured by the particle tracking analysis method.

The magnitude of lowering in the surface tension increased with the increase in the number concentration of UFBs in the following order, pendant drop, Wilhelmy, and du Noüy method.

According to the trend shown in Figure B.1, the pendant drop method seems to have little ability to detect the change in surface tension. The change in measurement results of the pendant drop method resulting from the measuring condition is provided in B.2.



Key

X number concentration of UFBs, in 1/ml

Y surface tension, in mN/m

□ Wilhelmy method

○ du Noüy method

◇ pendant drop method

- - - - linear regression of the Wilhelmy method

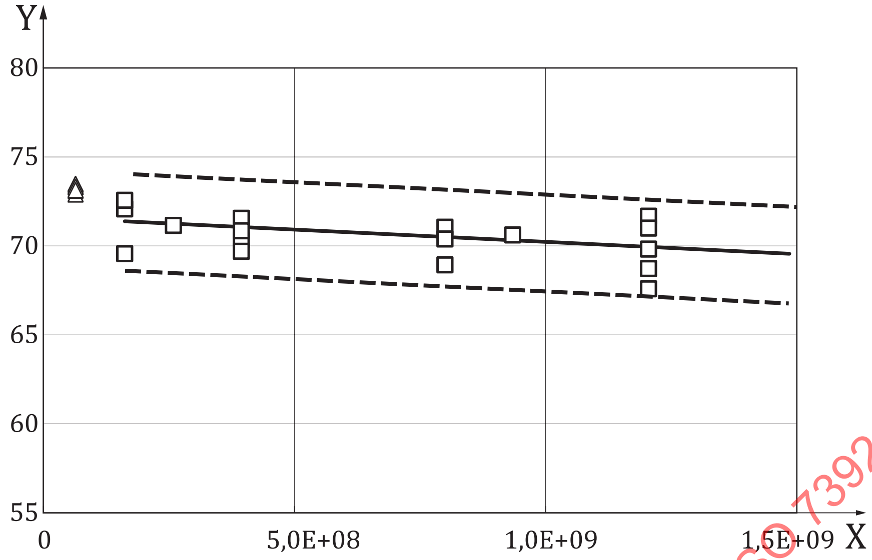
- · — · · linear regression of the du Noüy method

——— linear regression of the pendant drop method

SOURCE: Reference [4], reproduced with the permission of the publisher.

Figure B.1 — Differences in surface tension among measurement methods

To extract the trend in low number concentration area, data by the Wilhelmy method for the UFBD of concentration less than $1,5 \times 10^9$ in Figure B.1 were replotted in Figure B.2. With the increase in the number concentration of UFBs, the surface tension indicates a downward trend compared to that of water designated by open triangles as is the case in high number concentration area shown in Figure B.1.



Key

X	number concentration of UFBs, in 1/ml
Y	surface tension, in mN/m
□	UFBD
△	water
———	linear regression for UFBD
- - - -	prediction limits for UFBD

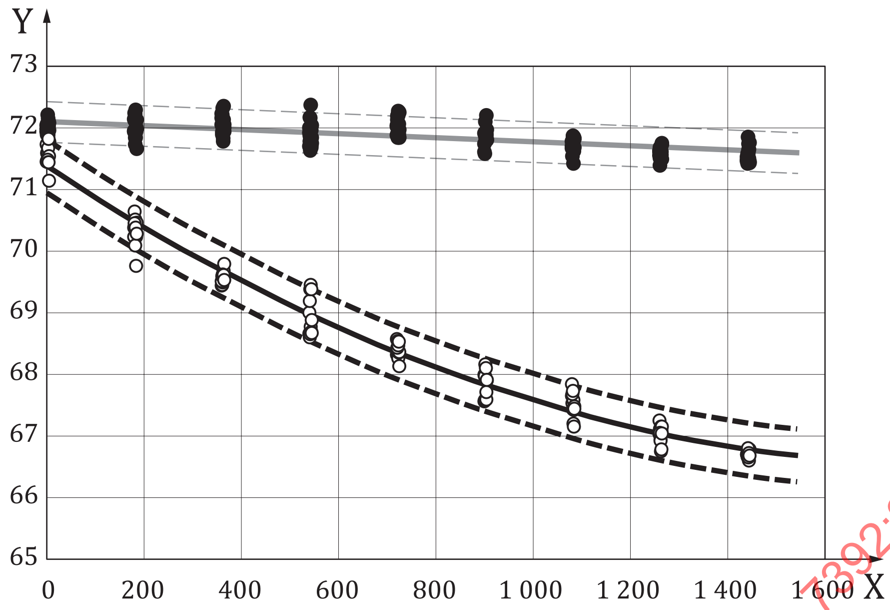
Figure B.2 — Surface tension of UFB dispersion of low concentration area (measurement results by the Wilhelmy method)

B.2 Time evolution of the surface tension by the pendant drop method

Song and Springer[5] reported that the surface tension of water measured by the pendant drop method decreased with the increase in retention time of droplet and that the use of a small needle resulted with a larger uncertainty.

Figure B.3 exhibits the difference in decreasing trends between water and UFBD of the number concentration of 4,36 × 10^9 using a needle of 1,65 mm in outer diameter. Decreasing rate of the latter is measurably larger than that of the former and the difference in surface tension between them increased with the increase in the retention time of droplet.

The decrease in surface tension even after the retention of 1 440 sec is not large as those by the Wilhelmy and du Noüy methods as shown in Figure B.1.



Key

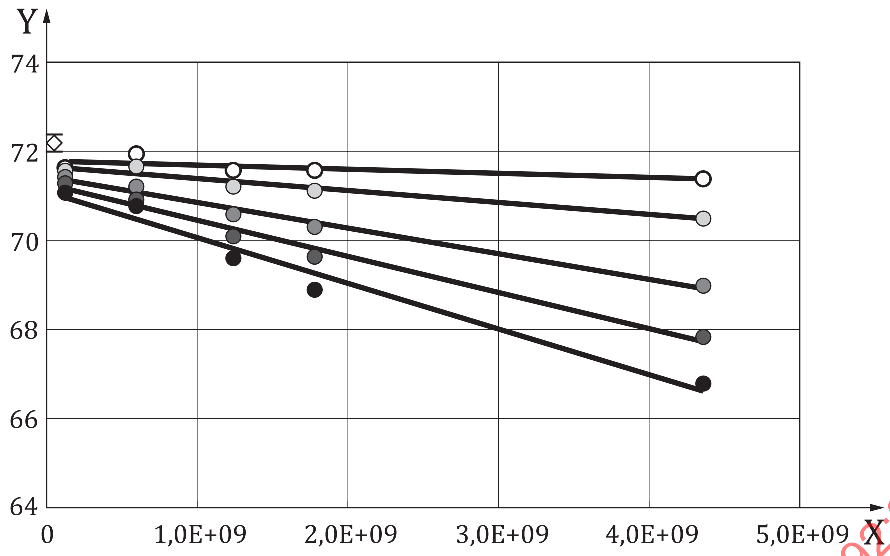
X	droplet retention time, in sec
Y	surface tension, in mN/m
●	water
○	UFBD
——— (grey)	linear regression for water
- - - -	prediction limits for water
———	regression for UFBD
■■■■	prediction limits for UFBD

SOURCE: Reference [4], reproduced with the permission of the publisher.

Figure B.3 — Dependence of the surface tension by the pendant drop method on the retention time of droplet of water and UFBD

Time evolutions in surface tension of UFBDs of another four different number concentrations from $1,23 \times 10^8$ to $1,78 \times 10^9$ were measured (not shown here) in the same manner as in Figure B.3. The surface tension at specific retention time from 0 sec to 1 440 sec was replotted against the five different number concentrations of UFBs in Figure B.4.

Figure B.4 indicates that the difference of surface tension between water and UFBD becomes prominent with the increase in retention time.



Key

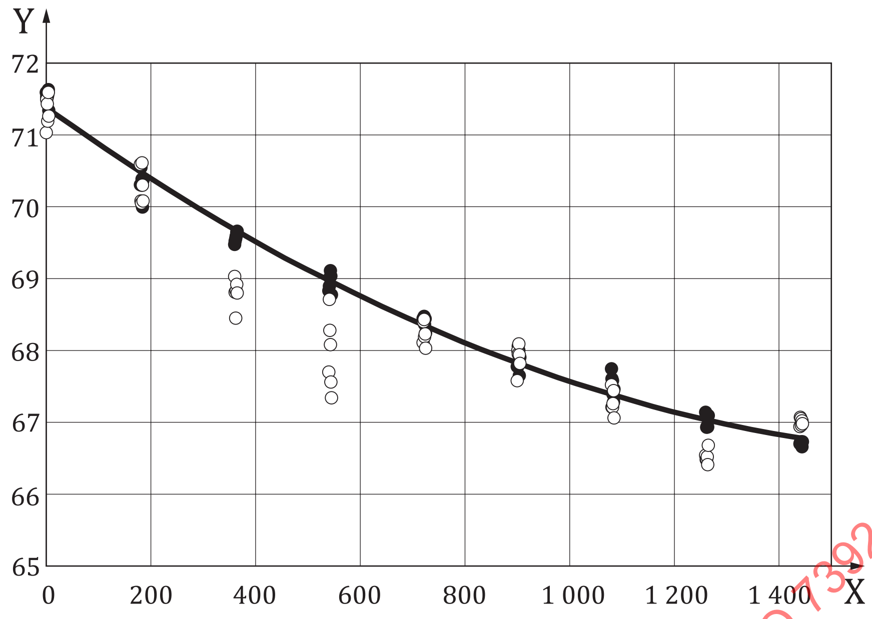
X	number concentration of UFBs, in 1/ml
Y	surface tension, in mN/m
○	retention time of droplet, 0 sec
● (light grey)	180 sec
● (grey)	540 sec
● (dark grey)	900 sec
●	1 440 sec
◇	surface tension of water
▬	linear regression

SOURCE: Reference [4], reproduced with the permission of the publisher.

Figure B.4 — Dependence of surface tension by the pendant drop method on the retention time of droplet of water and UFBD

Figure B.5 demonstrates the influence of outer diameter of the needle on the surface tension of UFBD. The sample water was the same one as that in Figure B.3 and its number concentration was 4,36 × 10^9 1/ml. Measurement results with a needle of 0,52 mm in outer diameter were compared to those with a needle of 1,65 mm.

Decreasing the trend of a 0,52 mm needle is similar to that of a 1,65 mm one, indicating that the influence of the needle diameter is relatively small. At some retention times, however, variation in the surface tension increased significantly. It is suggested that droplet at a needle of 0,52 mm is more sensitive to the vibration of the measuring instrument.



Key

X	droplet retention time, in sec
Y	surface tension, in mN/m
●	outer diameter of the needle, 1,65 mm
○	outer diameter of the needle, 0,52 mm
▬▬	regression for the needle of 1,65 mm

Figure B.5 — Dependence of the surface tension by the pendant drop method on the outer diameter of the needle

B.3 Selection of the measuring method

An appropriate method should be chosen from the three methods specified in this document according to the characteristics of the sample such as the number concentration of UFBs. The comparison of the surface tension between different samples shall be done by the measurement with the same measuring method. Particularly in the pendant drop method, measuring conditions such as retention time of droplet, the outer diameter of the needle should be selected to suit a sample to be measured.

B.4 Comparison among the three measuring methods

Table B.1 summarizes the feature of the three methods. Figures in the first row represent the surface tension calculated for UFBD of a specific number concentration, 1×10^9 1/ml. The calculation was done by using the results of regression analysis in Figures B.1 and B.4. The figures in the table seemingly indicate the sensitivity of the measuring methods for UFBD. However, attention should be paid to the influence of the measurement error listed in the second row. The inclination of ring plane in the du Noüy method is recognized as the cause of negative bias in the measurement result.[6] The vibration of droplet causes a fluctuation as shown in Figure B.5. Under these circumstances, comparison result in the first row does not necessarily indicate that the du Noüy method is the most sensitive to the influence of UFB on surface tension.

The third row exhibits the rough estimate of required measuring time, which is an operation time of measuring device for a single measurement. In the pendant drop method, the retention time of droplet before measurement accounts for the majority of the measuring time.

The rough estimate of minimal required volume of the sample is shown in the last row. The pendant drop method requires as small as a sample of tens of µl. This is an advantage over the remaining two methods for the applicability to a sample of limited amount such as liquid containing pharmaceutical under development and biological matter.

Table B.1 — Feature of the three measuring methods

	Wilhelmy	du Noüy	Pendant drop
Surface tension of UFBD (mN/m) [a]	70,23	69,18	70,45 [b]
Source of error	–	inclination of ring plane	vibration of droplet
Required measuring time	tens of s	tens of s	hundreds of s
Minimal required volume of sample	tens of ml	tens of ml	tens of µl

[a] Surface tension of UFBD at the number concentration of 1 × 10^9 1/ml calculated from the data in Figures B.1 and B.4.

[b] Droplet retention time of 900 s.

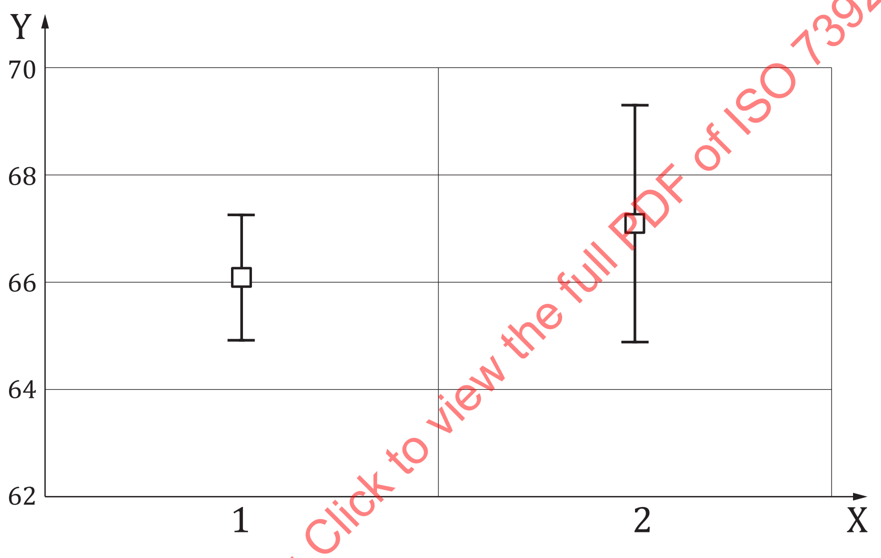
Annex C
(informative)

Measurement results under various measuring conditions

C.1 Measurement using different instruments on the same measuring principle

The surface tension of the same UFBD, of which number concentration was $3,64 \times 10^9$ 1/ml, was measured with two different surface tensiometers using the Wilhelmy method by the same operator.

The difference between the tensiometers was approximately 1 mN/m as shown in Figure C.1 and the student's t-test did not demonstrate a statistically significant difference.



Key

X surface tensiometer by the Wilhelmy method

Y surface tension, in mN/m

1 surface tensiometer A

2 surface tensiometer B

NOTE The error bar denotes standard deviation.

Figure C.1 — Difference in surface tension between different tensiometers of the Wilhelmy method

C.2 Measurement by the different measurers using the same instrument

The sensitivity of the measuring method to the proficiency of the measurer was evaluated. The surface tension of water was measured with the same surface tensiometer by three different measurers who are in different proficiency levels. The specific resistance of water ranged between 14,1 MΩ cm and 15,0 MΩ cm.

The surface tension was measured by the Wilhelmy and du Noüy methods. One-way analysis of variance for the data by both methods was carried out. In the du Noüy method, no significant difference between the three measurers was detected. Meanwhile in the Wilhelmy method, the difference was detected, but the magnitude of the change was in the order of 0,1 mN/m, which is close to the resolution of the tensiometer.

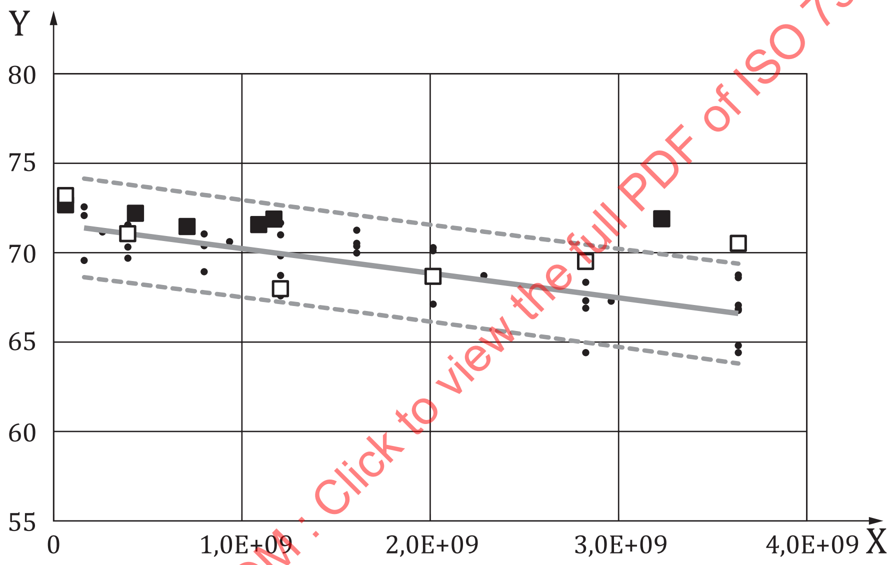
Consequently, the influence of the measurer's proficiency on the measurement results by both, the Wilhelmy and du Noüy methods are considered to be statistically small.

C.3 Measurement by the same method at different institution (details of an interlaboratory test)

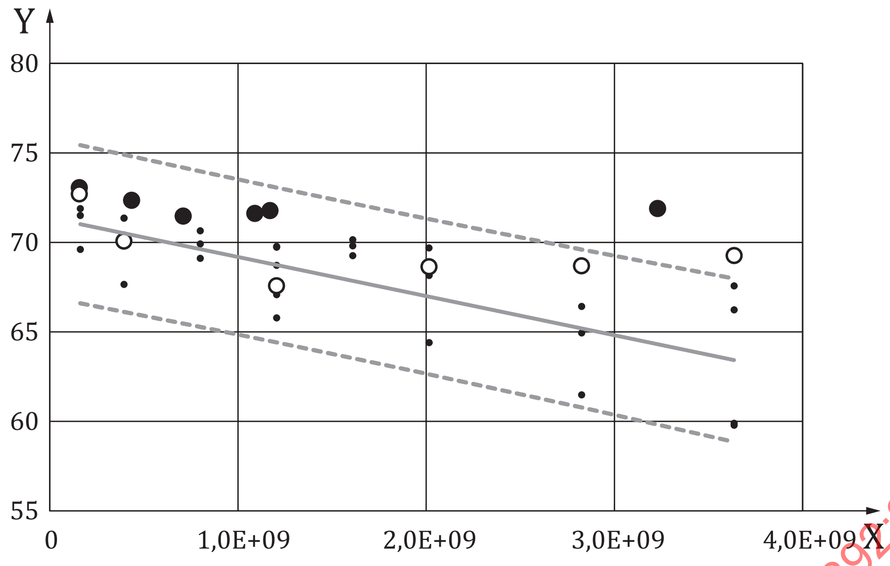
The data of the surface tension by the Wilhelmy and du Noüy methods in Figure B.1 are replotted as bullet point symbols in Figure C.2 a) and b), respectively. Linear regression and 95 % prediction interval obtained from the statistical analysis are overlaid on the plots.

A domestic interlaboratory test was conducted in Japan and two laboratories, designated by labs A and B, participated in the test. The UFBD sample was generated in lab A. The water sample was transported to lab B as carry-on baggage in public transportation to suppress the influence of temperature change and vibration on the properties of sample water as far as possible. The measurement of the surface tension and number concentration of UFBs were carried out in both labs on the same day. The surface tension was measured by the Wilhelmy and du Noüy methods. The product name of the surface tensiometer and its manufacturer are the same between the labs.

In both test methods, the measured data of both labs other than those at largest number concentration of UFBs are plotted within prediction interval. These results indicate relatively good reproducibility of measurement between different places, measuring apparatuses and measurers.



a) Wilhelmy method



b) du Noüy method

Key

X number concentration of UFBs, in 1/ml

Y surface tension, in mN/m

• measured value in Figure B.1

□ Wilhelmy method in lab A

■ Wilhelmy method in lab B

○ du Noüy method in lab A

● du Noüy method in lab B

—— linear regression

- - - prediction limits

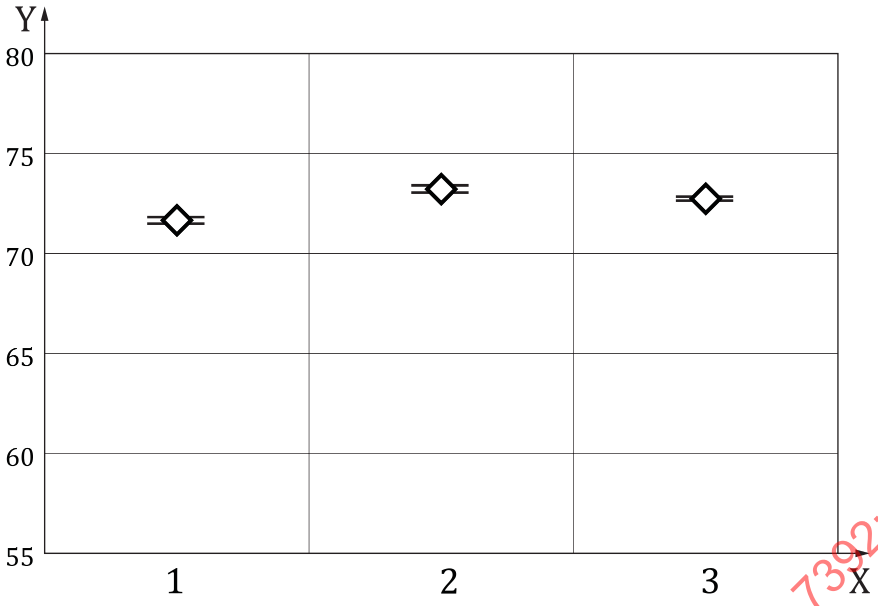
Figure C.2 — Results of the interlaboratory test

C.4 Repeatability of measurement

The repeatability of measurement was one of the parameters influencing the reliability of measurement. It is defined as the precision of measurement replicated through the same procedure, by the same operator using the same apparatus under the same testing conditions during a short time as far as possible.

The surface tension of water prepared by a commercially available production system was measured by the Wilhelmy method. Specific resistance of water ranged between 14,1 MΩ cm and 15,0 MΩ cm.

Figure C.3 exhibits the repeatability of measurement by the three methods, Wilhelmy, du Noüy and pendant drop. These methods show good repeatability. Standard deviations of the methods are less than 0,2 mN/m, which correspond to 0,3 % of the surface tension of water at 20 °C approximately.



Key

X	test method
Y	surface tension, in mN/m
◇	measured value
1	pendant drop method
2	Wilhelmy method
3	du Noüy method

SOURCE: Reference [4], reproduced with the permission of the publisher.

NOTE The error bar denotes standard deviation.

Figure C.3 — Repeatability of the measurement method

Annex D
(informative)

Variation in surface tension of surfactant solution diluted with UFBD

D.1 General

The measurement method specified in this document can be applied to the evaluation of surface tension of surfactant solution diluted with UFBD. As an example, three types of surfactants, anionic, cationic and non-ionic one, were evaluated in the following. The surface tension of surfactant solution diluted with UFBD was compared to a control of surfactant solution diluted with water. The water was prepared by commercially available production system and its specific resistance of water was approximately 18,0 MΩ cm. The UFBs were prepared with two types of generators which are based on different principles of UFB generation. The generation principles of type 1 and type 2 are pressurized dissolution and Venturi with swirling liquid flow, respectively. The measurement by the Wilhelmy method was conducted at ambient temperature of (25 ± 2) °C.

The characterization of UFBD prepared with type 1 and type 2 generator was conducted with the particle tracking analysis method one day after the generation. The results are tabulated in Table D.1.

Table D.1 — Characteristics of UFBD

UFB generator		**Type 1**	**Type 2**
Number concentration	1/ml	$6{,}01 \times 10^{7}$	$5{,}86 \times 10^{8}$
Standard error	1/ml	$6{,}95 \times 10^{6}$	$3{,}35 \times 10^{7}$
Mean diameter	nm	93,7	92,9
Standard error	nm	11,2	1,3

D.2 Anionic surfactant

Sodium dodecylbenzenesulfonate (LAS), of which critical micelle concentration is 1,2 mmol/kg, was evaluated. LAS is one of the major constituents of detergent for domestic use. The surface tension of surfactant diluted with UFBD decreased compared to that diluted with water at concentrations lower than the critical micelle concentration as illustrated in Figure D.1.