INTERNATIONAL STANDARD

ISO 7875-1

Second edition
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Water quality — Determination of surfactants —

Part 1: Determination of anionic surfactants by measurement of the methylene blue index (MBAS)

Qualité de l'eau — Dosage des agents de surface —

Partie 1: Dosage des agents de surface anioniques par mesurage de l'indice au bleu de méthylène (indice SABM)

Reference number
ISO 7875-1:1996(E)

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 7875-1 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical, biochemical methods*.

This second edition cancels and replaces the first edition (ISO 7875-1:1984, of which it constitutes a technical revision.

ISO 7875 consists of the following parts, under the general title *Water quality — Determination of surfactants*:

— *Part 1: Determination of anionic surfactants by measurement of the methylene blue index (MBAS)*

— *Part 2: Determination of non-ionic surfactants using Dragendorff reagent*

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Introduction

Natural and synthetic anionic surface-active substances may be determined as methylene-blue active substances (MBAS); they are referred to as MBAS index, a summary parameter.

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Water quality — Determination of surfactants —

Part 1:
Determination of anionic surfactants by measurement of the methylene blue index (MBAS)

1 Scope

This part of ISO 7875 specifies a spectrometric method for the determination of anionic surfactants by measurement of the methylene blue index (MBAS) in aqueous media.

The method is applicable to drinking water, surface water as well as waste water, for example for the determination of the primary degradation of surfactants under investigation in test systems containing natural or synthetic waste water. It applies for both laboratory scale and technical waste-water treatment plants.

In the case of effluents originating from municipal waste-water treatment plants, the MBAS index comprises not only synthetic but also, to a considerable extent, natural anionic surface active substances

This method is applicable to a range of concentrations from 0,1 mg/l to 5,0 mg/l and the limit of detection is about 0,05 mg/l for solutions of standard surfactants in distilled water.

Under the experimental conditions, sulfonates and sulfates are the compounds chiefly measured, but some positive and negative interferences may occur (see clause 9).

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this part of ISO 7875. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this part of ISO 7875 are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 5667-2:1991, *Water quality — Sampling — Part 2: Guidance on sampling techniques.*

ISO 5667-3:1994, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of samples.*

3 Principle

Formation of salts from methylene blue and anionic surfactants in an alkaline medium. Extraction of these salts with chloroform and acid treatment of the chloroform solution. Elimination of any interferences by extraction of the anionic surfactant-methylene blue complex from alkaline solutions and shaking with acidic methylene blue solution.

Measurement of the absorbance of the separated organic phase at the maximum absorption wavelength of 650 nm. Evaluation by means of a calibration curve.

For reasons of purity and stability, the preferred standard is dodecyl benzene sulfonic acid methyl ester (tetrapropylene type, of relative molecular mass 340), although other calibration standards may be used (see the note to 4.11). The calibration standard is prepared from the standard dodecyl benzene sulfonic acid ester after saponification to the sodium salt. Calculation of the MBAS index as sodium dodecyl benzene sulfonate (see 8.1).

4 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity

4.1 Sodium chloride (NaCl).

4.2 Ethyl acetate ($C_4H_8O_2$), freshly distilled.

CAUTION — Ethyl acetate is flammable and toxic.

4.3 Chloroform ($CHCl_3$).

CAUTION — Chloroform is a suspected carcinogen.

If necessary [for example if it gives rise to high results in blank tests (7.2)] purify the chloroform by filtration through Al_2O_3 (neutral grade, W 200).

NOTE — Due to the toxicity of chloroform, it would be preferable to replace it by another solvent. Research work is continuing.

4.4 Ethanol (C_2H_5OH), 95 % (V/V).

4.5 Methanol (CH_3OH), freshly distilled.

In order to avoid high results in blank tests (7.2) store in a glass bottle.

4.6 Sulfuric acid (H_2SO_4), 0,5 mol/l solution.

4.7 Ethanolic sodium hydroxide (NaOH), 0,1 mol/l solution in ethanol.

Dissolve 4 g of sodium hydroxide pellets in ethanol (4.4) and dilute to 1 000 ml with the same ethanol.

4.8 Methylene blue, neutral solution.

NOTE — The solid methylene blue used should be the purest available.

Dissolve 0,350 g of methylene blue in water and dilute to 1 000 ml.

Prepare the solution at least 24 h before use.

This solution is stable for at least 2 weeks.

The absorbance of the chloroform phase of the blank test (see 7.2), measured against chloroform, shall not exceed 0,2 per 10 mm of optical path length at 650 nm. In the case of higher absorbances during the blank test, use other batches of methylene blue and/or purify the methylene blue solution by extraction as follows.

Place the methylene blue solution in a suitably large separating funnel. For each 100 ml of methylene blue solution, add 200 ml of buffer solution (4.10) and 200 ml of chloroform (4.3). Shake for 30 s and allow to separate . Run off the chloroform layer as completely as possible and rinse the aqueous layer without shaking with 60 ml of chloroform for each 100 ml of methylene blue solution. Repeat the extraction and rinse as before. Discard the chloroform extracts; collect for reuse after treatment.

4.9 Methylene blue, acidic solution.

Dissolve 0,350 g of methylene blue in 500 ml of water and add 6,50 ml of sulfuric acid (ρ = 1,84 g/ml). Dilute with water to 1 000 ml after mixing.

Prepare the solution at least 24 h before use.

The absorbance of the chloroform phase of the blank test (see 7.2), measured against chloroform, shall not exceed 0,02 per 10 mm of optical path length at 650 nm. In the case of higher blank absorbances, either wash the methylene blue solution twice with chloroform for purification (see 4.8) or use other batches of methylene blue.

4.10 Buffer solution, of pH 10.

4.10.1 Dissolve 24 g of sodium hydrogencarbonate ($NaCO_3$), and 27 g of anhydrous sodium carbonate (Na_2CO_3) in water and dilute to 1 000 ml.

4.10.2 Alternatively, especially for very hard water, the buffer solution prepared in 4.10.2.3 may be used.

4.10.2.1 Disodium tetraborate ($Na_2B_4O_7 \cdot 10H_2O$), 0,05 mol/l solution.

Dissolve 19 g of disodium tetraborate decahydrate in 1 000 ml of water.

This solution is stable for at least 2 weeks if stored in a stoppered glass bottle.

4.10.2.2 Sodium hydroxide (NaOH), 0,1 mol/l solution.

Dissolve 4 g of sodium hydroxide pellets in 1 000 ml of water.

This solution is stable for at least 2 weeks if stored in a glass bottle with a polyethylene stopper.

4.10.2.3 Borate, alkaline solution.

Mix equal volumes of disodium tetraborate solution (4.10.2.1) and sodium hydroxide solution (4.10.2.2).

This solution is stable for at least 1 week if stored in a glass bottle with a polyethylene stopper.

4.11 Dodecylbenzene sulfonic acid methyl ester (tetrapropylene type) ($C_{19}H_{32}O_3S$), stock standard solution.

Weigh, preferably from a weighing pipette, to the nearest 0,1 mg, 400 mg to 450 mg of dodecylbenzene sulfonic acid methyl ester, into a round-bottomed flask, and add 50 ml of ethanol sodium hydroxide solution (4.7) and some anti-bumping granules. Attach the reflux condenser and boil for 1 h. After cooling, rinse the condenser and the ground-glass joint with about 30 ml of ethanol (4.4) and add the rinsings to the contents of the flask. Neutralize the

solution with sulfuric acid (4.6) against phenolphtalein (4.12) until it becomes colourless. Transfer the solution to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

This standard solution is stable for at least 6 months.

NOTE — Although the dodecylbenze sulfonic acid methyl ester is preferable as it is a guaranteed nonhygroscopic standard, the calibration graph (see 7.3) may alternatively be established with the aid of commercially available sodium salt of dodecane-1 sulfonic acid ($C_{12}H_{25}NaO_3S$), dodecane-1 sulfuric acid ($C_{12}H_{25}NaO_4S$) or dioctyl sulfosuccinic acid ($C_{20}H_{37}NaO_7S$).

4.12 Phenolphtalein, indicator solution.

Dissolve 1,0 g of phenophtalein in 50 ml of ethanol (4.4) and add, while stirring continuously, 50 ml of water. Filter off any precipitate that forms.

5 Apparatus

Ordinary laboratory equipment and the following.

5.1 pH-meter, with suitable electrodes made from glass.

5.2 Spectrometer with selectors for discontinuous variation, capable of measurement at 650 nm, equipped with cells of optional path lengths 10 mm and 50 mm.

5.3 Gas-stripping apparatus (see figure 1), which is commercially available of capacity 1 litre.

The diameter of the sintered disc shall be the same as the internal diameter of the cylinder.

NOTES

1 To make cleaning easier, the apparatus should preferably be equipped with a spherical connection under the stripping funnel. The fixing member should also be divisible.

2 During preliminary cleaning, all glassware should be washed thoroughly with water and then with ethanolic hydrochloric acid about 10 % (*m/m*) and subsequently rinsed with water.

6 Sampling and samples

Instructions for sampling are given in ISO 5667-2 and ISO 5667-3.

Do not withdraw samples through a foam layer. Use clean glass bottles, previously washed with methanol (4.5) for sampling and storage. Cooling to 4 °C is recommended for preservation over short periods. Consider the addition of a preservative if the sample is to be kept for more than 24 h. The addition of 1 % (*V/V*) of a 40 % (*V/V*) formaldehyde solution is suitable for periods up to 4 d while saturating with chloroform is suitable for periods up to 8 d.

NOTE — Test samples should normally be free of suspended matteer which can be separated by centrifugation; however, it should be appreciated that, as a result of such a separation, surfactant adsorbed on suspended matter will not be determined.

7 Procedure

7.1 Concentration and separation of the surfactant

For all types for water with known matrices and/or free of interferences, proceed according to 7.4. For determination of the total amount of MBAS in the presence of solids, also proceed according to 7.4, although quantitative recovery is not guaranteed due to sorption effects. For analysis of the amount of dissolved MBAS, use the following concentration and separation procedure.

Dimensions in millimetres

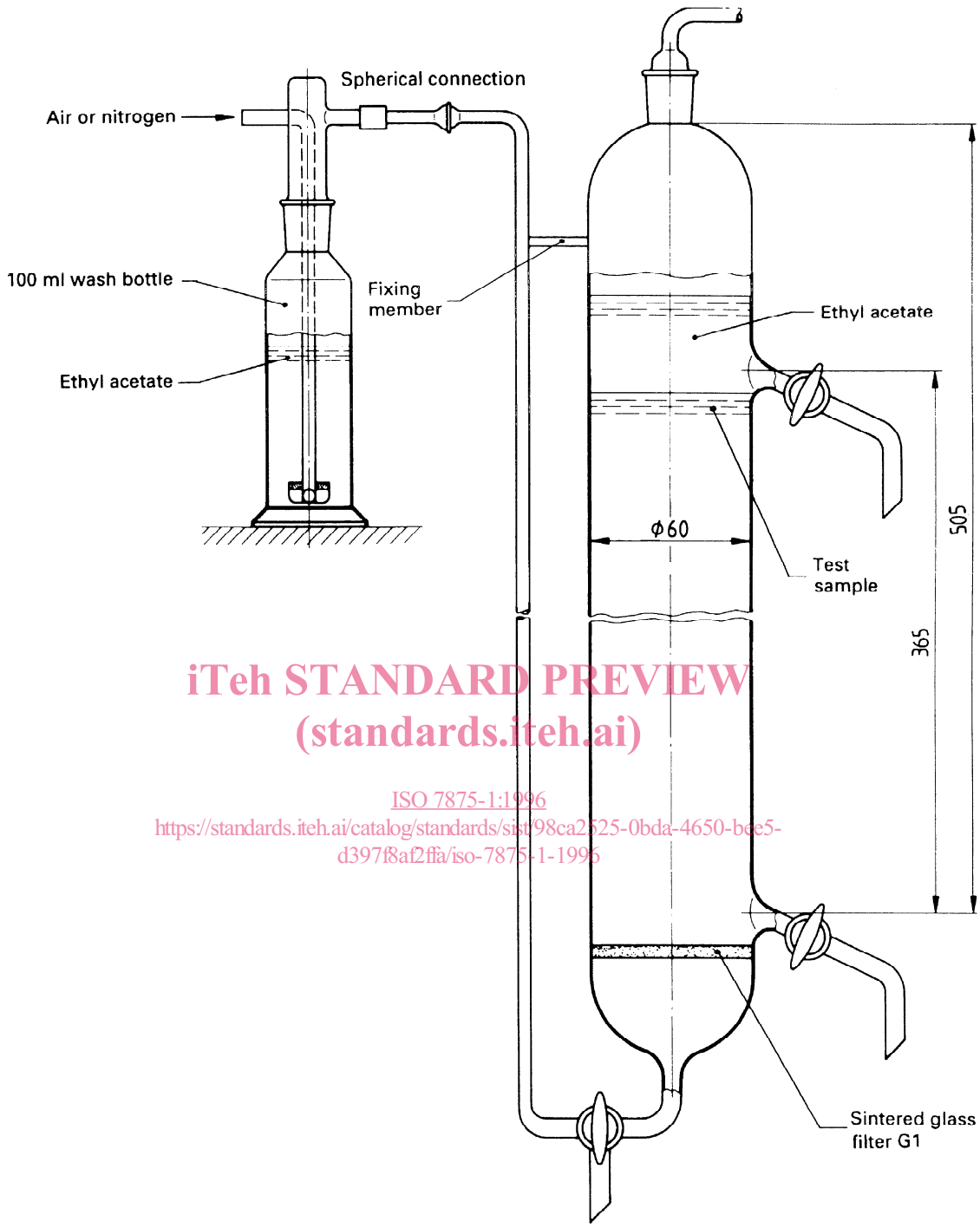

Figure 1 — Gas-stripping apparatus (see note to 5.3)

Non-surfactant methylene blue active substances can cause errors in the determination of the methylene blue index. In surface water and other types of water with unknown composition, or known to contain interfering compounds, separate the surfactants by stripping (solvent sublation). Stripping is also recommended for concentrating small amounts of surfactants from water samples. Separate suspended matter by centrifugation, but note that adsorbed surfactant on suspended matter will not be determined.

Place a measured quantity of the test sample, up to 1 000 ml, in the gas-stripping apparatus (5.3).

Install the stripping apparatus in well-ventilated hood to carry off ethyl acetate vapour.