TC 147

International Standard ISO 7875/1

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Water quality — Determination of surfactants — Part 1: Determination of anionic surfactants by the methylene blue spectrometric method

Qualité de l'eau — Dosage des agents de surface — Partie 1: Dosage des agents de surface anioniques par la méthode spectrométrique au bleu de méthylène

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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

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Water quality — Determination of surfactants — Part 1: Determination of anionic surfactants by the methylene blue spectrometric method

0 Introduction

Anionic and non-ionic surface active substances, generally called surfactants, are used in synthetic products for general cleaning purposes.

ISO 7875 consists of the following parts:

Part 1: Determination of anionic surfactants by the methylene blue spectrometric method.

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

1 Scope

This part of ISO 7875 specifies a methylene blue spectrometric method for the determination of anionic surfactants in aqueous media.

2 Field of application

This part of ISO 7875 applies to the determination of low concentrations of methylene blue active substances (MBAS), i.e. anionic surface active material, in influents and effluents of sewage plants, waste water, surface water, and drinking water. Under the experimental conditions, sulfonates and sulfates are the compounds chiefly measured, but some positive and negative interferences can occur (see clause 10).

The range of this method is 0,1 to 5,0 mg/l and the limit of detection about 0,05 mg/l for solutions of standard surfactants in distilled water.

3 References

ISO 5667, *Water quality — Sampling —*

Part 2: Guidance on sampling techniques.

Part 3: Guidance on the preservation and handling of samples.[1)]

4 Principle

Formation in an alkaline medium of salts from methylene blue and anionic surfactants. Extraction of these salts with chloroform and acid treatment of the chloroform solution. Elimination of any interferences by extraction of the anionic substance-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, relative molecular mass 340), although other surfactants may be used as standards (see the note to 5.1). The calibration standard is prepared from the standard dodecyl benzene sulfonic acid ester after saponification to the sodium salt. Calculation of the MBAS as sodium dodecyl benzene sulfonate (see 9.1).

5 Reagents

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

5.1 Sodium chloride (NaCl).

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

CAUTION — Ethyl acetate is flammable and toxic.

5.3 Chloroform ($CHCl_3$).

CAUTION — Chloroform is a suspected carcinogen.

If necessary [for example, if it gives rise to high results in blank tests (8.2)] purify the chloroform by filtration through Al_2O_3 (neutral grade, W 200).

NOTE — Due to the toxicity of chloroform, it would be desirable to replace it by another solvent. Research work to this end is going on.

1) At present at the stage of draft.

5.4 Ethanol (C_2H_5OH), 95 % (*V*/*V*).

5.5 Methanol (CH_3OH), freshly distilled in order to avoid high results in blank tests (8.2) and stored in a glass bottle.

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

5.7 Ethanolic sodium hydroxide (NaOH), 0,1 mol/l.

Dissolve 4 g NaOH pellets in ethanol (5.4) and dilute with the same ethanol to 1 000 ml.

5.8 Neutral methylene blue, solution.

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

Dissolve 0,350 g 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 8.2) measured against chloroform, shall not exceed 0,02 per 10 mm layer thickness at 650 nm. In the case of higher blank absorbances, other batches of methylene blue should be used and/or the methylene blue solution should be purified by extraction as follows.

Place the methylene blue solution in a suitably large separating funnel. For each 100 ml methylene blue solution, add 200 ml buffer solution (5.10) and 200 ml chloroform (5.3). 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 methylene blue solution. Repeat the extraction and rinse as before. Discard the chloroform extracts (collect for reuse after treatment).

5.9 Acid methylene blue, solution.

Dissolve 0,350 g methylene blue in 500 ml water and add 6,50 ml 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 8.2), measured against chloroform, shall not exceed 0,02 per 10 mm layer thickness at 650 nm. At higher blank absorbances, the methylene blue solution should be washed twice with chloroform for purification (see 5.8) or other batches of methylene blue should be used.

5.10 Buffer solution, pH 10.

5.10.1 Dissolve 24 g sodium hydrogencarbonate ($NaHCO_3$) and 27 g anhydrous sodium carbonate (Na_2CO_3) in water and dilute to 1 000 ml with water.

5.10.2 Alternatively, especially for water with high hardness, use the following buffer solution.

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

Dissolve 19 g disodium tetraborate decahydrate in 1 litre of water.

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

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

Dissolve 4 g sodium hydroxide pellets in 1 litre of water.

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

5.10.2.3 Alkaline borate solution.

Mix equal volumes of 0,05 mol/l sodium borate solution (5.10.2.1) and 0,1 mol/l sodium hydroxide solution (5.10.2.2).

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

5.11 Dodecyl benzene sulfonic acid methyl ester ($C_{19}H_{32}O_3S$), standard solution.

Weigh, preferably from a weighing pipette, 400 to 450 mg of dodecyl benzene sulfonic acid methyl ester to the nearest 0,1 mg into a round bottom flask, add 50 ml of ethanolic sodium hydroxide solution (5.7) and some bumping granules. Adjust the reflux condenser and boil for 1 h. After cooling, rinse the condenser and the ground glass joint with about 30 ml of ethanol (5.4) and add the rinsings to the contents of the flask. Neutralize the solution with sulfuric acid (5.6) against phenolphthalein (5.12) 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 dodecyl benzene sulfonic acid methyl ester is preferable as it is a guaranteed non-hygroscopic standard, the calibration graph (see 8.3) may alternatively be established with the aid of the 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 ($C_{20}H_{37}NaO_7S$).

5.12 Phenolphthalein, indicator solution.

Dissolve 1,0 g phenolphthalein in 50 ml ethanol (5.4) and add, while stirring continuously, 50 ml water. Filter off any precipitate that forms.

6 Apparatus

Ordinary laboratory equipment, and

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

6.2 Spectrometer with selectors for discontinuous variation, capable of measurement at 650 nm, equipped with 10 to 50 mm cells.

6.3 Gas-stripping apparatus (see the figure; the apparatus is commercially available).

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

NOTE — To make cleaning easier, the apparatus should preferably be equipped with a spherical connection under the stripping funnel. The steady should also be divisible.

NOTE ON PRELIMINARY CLEANING OF GLASSWARE

All glassware should be washed thoroughly with water and then with ethanolic 10 % (m/m) hydrochloric acid and subsequently rinsed with water.

7 Sampling and samples

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

Samples should not be withdrawn through a foam layer. Clean glass bottles, previously washed with methanol (5.5) should be used for sampling and storage. Cooling to 4 °C is recommended for preservation over short periods. The addition of a preservative should be considered 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 days while saturating with chloroform is suitable for periods up to 8 days. Test samples should normally be free of suspended matter which can be separated by centrifugation; however, it has to be appreciated that, as a result of such a separation, surfactant adsorbed on suspended matter will not be determined.

8 Procedure

8.1 Concentration and separation of the surfactant

For all types of water with known matrices and/or free of interferences, proceed according to 8.4. For determination of the total amount of surfactant in the presence of solids, proceed to 8.4, although quantitative recovery is not guaranteed due to sorption effects. For analysis of the amount of dissolved surfactant, use this concentration and separation procedure.

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

Place a measured quantity of the laboratory sample (the test sample), up to 1 000 ml, into the stripping apparatus (see 6.3).

Install the apparatus (6.3) in a well ventilated hood to carry off ethyl acetate vapour.

Separation is improved by the addition of sodium chloride. If the test sample volume exceeds 500 ml, add 100 g of sodium chloride (solid) and dissolve by passing nitrogen gas or air through it. If a smaller test sample volume is used, dissolve 100 g sodium chloride in 400 ml of water and add this solution to the test sample.

If necessary, add water up to the level of the upper stopcock. Add 100 ml ethyl acetate (5.2). Fill the wash bottle in the gas line (nitrogen or air) two-thirds full with ethyl acetate. Pass a gas stream of 20 to 50 l/h through the apparatus. The use of a variable area flowmeter[1] is recommended. The gas flow should be adjusted in such a way that the phases remain separate and no turbulence is produced at the interface. The significant mixing of the phases and consequent solution of ethyl acetate in the water is avoided. Stop the gas flow after 5 min.

If a loss of more than 20 % (V/V) of the organic phase has occurred due to solution in the water phase, discard the test sample.

Run off the organic phase completely into a separating funnel. Any water in the separating funnel — it should only be a few millilitres — is returned to the stripping apparatus.

Filter the ethyl acetate solution through a dry qualitative filter paper into a flask (250 ml). Add a further 100 ml ethyl acetate to the stripping apparatus and again pass nitrogen or air for 5 min. Separate the organic layer as given above, using the same separating funnel, filter, and add it to first portion. Rinse filter and funnel with 25 ml ethyl acetate. Remove all the ethyl acetate solution on a water-bath under a hood. To speed up the process, direct a gentle air stream over the surface of the solution.

Dissolve the residue in about 5 ml of methanol (5.5) and 50 ml of water. Transfer the solution quantitatively to a 100 ml one-mark volumetric flask and dilute to the mark with water.

8.2 Blank test

With each series of samples, carry out a blank test in parallel with the determination, using the zero member of the set of calibration solutions (see 8.3).

1) The commonly used term "Rotameter" is a trade name.

The interpolated absorbance, A_1, is subtracted from the absorbance, A_0, of the sample. Under the given conditions the absorbance, A_1, of the blank test should not exceed 0,02 per 10 mm layer, otherwise the equipment and the reagent shall be checked carefully for any contamination.

8.3 Calibration

From the stock surfactant solution (5.11), prepare a working standard by transferring 25 ml (use a pipette) to a 500 ml one-mark volumetric flask, dilute to the mark with water and mix.

The MBAS mass concentration, ϱ_X, expressed in micrograms per millilitre, of this standard solution is given by the equation

$$\varrho_X = \frac{m f_1}{V}$$

where

m is the mass, in milligrams, of the MBAS (as ester) used for preparation of the standard solution according to 5.11;

f_1 is a conversion factor from ester to MBAS, here $f_1 = 1{,}023\ 3$;

V is a volume correction factor, here $V = 20{,}000$ ml.

Place 0,0 (the zero member); 1,0; 2,0; 4,0; 6,0 and 8,0 ml of the working standard in a series of separating funnels (250 ml capacity), dilute with water to 100 ml and continue as described in 8.4.

Measure the absorbance of each of the set of calibration solutions, including the zero member, at a wavelength of 650 nm in 10 and 50 mm cells. Prepare a calibration graph by plotting the absorbance against the mass, in micrograms, of standard surfactant for 10 and 50 mm cells. Subtract the interpolated intersection with the ordinate from each of the absorbance values.

Calibration is recommended 1 to 2 times a month or whenever new batches of chemicals are used.

If the calibration is done with one of the alternative surfactants (see the note to 5.11), the conversion factors shown in the table shall be used.

Table

Surfactant	Conversion factor, f_1
Dodecyl benzene sulfonic acid, sodium salt	1,000
Dodecane-1-sulfonic acid, sodium salt	0,781 6
Dodecane-1-sulfuric acid, sodium salt	0,827 6
Dioctyl sulfosuccinic acid, sodium salt	1,276 0

8.4 Determination

Transfer a measured volume of the test sample, if necessary treated according to 8.1, into a separating funnel. This test portion should contain between 20 and 200 µg MBAS. In the lower MBAS range, a test portion of up to 100 ml may be used; if the volume of the test portion is less than 100 ml, dilute with water to 100 ml. Add 5,0 ml neutral methylene blue solution (5.8), 10 ml buffer solution (5.10) [not necessary if a pre-extracted methylene blue solution (5.8) is used], and 15 ml chloroform (5.3). Shake evenly and gently at about twice a second for 1 min, preferably in a horizontal plane. Allow the layers to separate as completely as possible and swirl the funnel to dislodge droplets from the sides of the funnel.

Allow to settle for 2 min then run as much as possible of the chloroform layer into a second separating funnel, containing 110 ml water and 5,0 ml acidic methylene blue solution (5.9). Shake uniformly but not too vigorously for 1 min as previously. Filter the chloroform layer through a cotton or glass wool filter wetted with chloroform (5.3) into a 50 ml volumetric flask. (On cotton-wool some absorption of surfactants may take place, on glass wool water may not be absorbed completely.)

Repeat the extraction of the alkaline and acid solutions using a 10 ml portion of chloroform (5.3) for the extraction. Separate the chloroform layer and filter it, through the same filter, into the volumetric flask. Repeat the extraction using a further 10 ml portion of chloroform and filter that into the 50 ml volumetric flask. Dilute to the mark with chloroform (5.3) and mix.

For each batch of samples, carry out the complete extraction for a blank determination on 100 ml of water and on one of the calibration solutions (see 8.3).

Before each determination, shake the contents of the volumetric flask, rinse the cell three times and then fill the cell.

Measure the absorbances for samples, calibration solutions and the blank test with a spectrometer at 650 nm in 10 to 50 mm cells against chloroform. Comparison measurements on standards should have been made in the same size of cells. Wash out the cells with chloroform after each reading.

NOTES

1 Check the cell error frequently by measuring the absorbance difference when chloroform is used in both cells and correct for any error. If this error increases, clean the cell by immersion in nitric acid, rinse with water, and dry with acetone and chloroform. Mark one cell and reserve for the reference chloroform.

2 If the absorbance of the test solution of the sample when read in 10 mm cells is less than 0,1, repeat readings of calibration solutions, blank test and sample in 40 or 50 mm cells.

3 If the calibration solutions run with the sample batch differ significantly from the calibration graph value, repeat the procedure with all samples and a full set of calibration solutions.