International Standard 7875/2

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

Qualité de l'eau — Dosage des agents de surface — Partie 2: Dosage des agents de surface non ioniques à l'aide du réactif de Dragendorff

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Foreword

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

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 method for the determination of non-ionic surfactants in aqueous media using Dragendorff reagent.

2 Field of application

This part of ISO 7875 applies to the determination of low concentrations of bismuth active substances (BiAS), i.e. non-ionic surfactants of the alkylphenol-alkylene oxide and alcohol-alkylene oxide adduct types, as long as they can be stripped and precipitated with Dragendorff reagent (for example ethoxylates with about 5 to 30 ethylene oxide groups per molecule). The method is suitable for influents and effluents of sewage treatment plants and waste water. When investigating surface waters it may be necessary to handle large sample volumes (up to 5 000 ml).

The detection limit is 0,05 mg/l for a 1 litre sample and the optimum range of application is 250 to 800 µg.

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

Air stripping of surfactants from the sample and collection in ethyl acetate. Removal of ethyl acetate and precipitation of the non-ionic surfactants with Dragendorff reagent ($KBiI_4$ + $BaCl_2$ + acetic acid).

Isolation and dissolution of the precipitate, and potentiometric determination of the concentration of bismuth equivalent to the concentration of non-ionic surfactant with sodium pyrrolidin-1-yl dithiocarboxylate solution.

Alternative methods for the determination of the bismuth ion are, among others, atomic absorption and UV spectrometry (see the annex).

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 Sodium hydrogencarbonate ($NaHCO_3$).

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

CAUTION — Ethyl acetate is flammable and toxic.

5.4 Methanol (CH_3OH), freshly distilled, stored in a glass bottle.

5.5 Glacial acetic acid (CH_3COOH), ϱ = 1,05 g/ml.

Lower concentrations are not suitable.

5.6 Hydrochloric acid.

Add 1 ml HCl (ϱ = 1,12 g/ml) to 100 ml water.

1) At present at the stage of draft.

5.7 Methanolic hydrochloric acid.

Dilute 10 ml HCl (ϱ = 1,12 g/ml) with methanol (5.4) to 100 ml.

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

5.9 Ammonia, solution.

Add 10,0 ml ammonia solution, (ϱ = 0,91 g/ml) to 250 ml water.

5.10 Ammonium tartrate, solution.

Add 12,40 g tartaric acid ($C_4H_6O_6$) to 12,40 g ammonia solution (ϱ = 0,91 g/ml) and dilute to 1 000 ml with water.

5.11 Solution A.

Dissolve 1,70 g bismuth(III) oxynitrate monohydrate ($BiONO_3 \cdot H_2O$) in 20 ml glacial acetic acid (5.5) and dilute to 100 ml with water.

Dissolve 65,0 g potassium iodide (KI) in about 200 ml water.

Mix both solutions in a 1 000 ml one-mark volumetric flask, add 200 ml glacial acetic acid (5.5) and dilute to the mark with water.

The solution is stable for about 1 week when stored in the dark.

5.12 Solution B.

Dissolve 290,0 g barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$) in 1 000 ml water.

5.13 Precipitating agent.

Mix two parts by volume of solution A (5.11) with one part by volume of solution B (5.12).

The solution is stable for about 1 week if stored in a brown glass bottle.

5.14 Standard acetate buffer.

Dissolve 40,0 g sodium hydroxide (NaOH) in about 500 ml water. Add 120 ml glacial acetic acid (5.5). Mix thoroughly, cool, and dilute with water to 1 000 ml in a volumetric flask.

5.15 Sodium pyrrolidin-1-yl dithiocarboxylate, 0,5 mmol/l solution.

Dissolve 103,0 mg sodium pyrrolidin-1-yl dithiocarboxylate dihydrate ($C_5H_8NS_2Na \cdot 2H_2O$) in about 500 ml water. Add 10,0 ml amyl alcohol $C_5H_{11}OH$) and 0,50 g sodium hydrogencarbonate (5.2), dilute with water to 1 000 ml.

5.16 Copper(II) sulfate, stock solution.

Dissolve 1,249 g copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) in 50 ml sulfuric acid (5.8) and 200 ml water, and dilute with water to 1 000 ml.

Do not use broken or soft crystals.

5.17 Copper(II) sulfate, standard solution.

Dilute 50,0 ml of the copper stock solution (5.16) and 10 ml sulfuric acid (5.8) with water to 1 000 ml.

5.18 Bromocresol purple, solution.

Dissolve 0,10 g dye in 100 ml methanol (5.4).

5.19 Cation exchange resin, SO_3H^+ form (50 to 100 mesh = 0,15 to 0,30 mm), alcohol-resistant.

6 Apparatus

Ordinary laboratory equipment, and

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

The diameter of the sintered disc shall be of the same size 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.

6.2 Ion exchange column, of diameter 16 mm, and height 200 mm.

6.3 Recording potentiometer, with platinum/calomel or platinum/silver chloride electrodes, range 250 mV, with automatic burette, 20 to 25 ml capacity, or appropriate manual equipment.

NOTE ON PRELIMINARY CLEANING OF GLASSWARE

All glassware should be washed thoroughly with water and then with ethanolic 10 % (m/m) hydrochloric acid and subsequenty 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 (5.4) 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

Install the apparatus (6.1) in a well ventilated hood to carry off ethyl acetate vapour.

The laboratory samples should be centrifuged if considerable amounts of suspended matter — more than 0,3 g/l — are present.

Place a measured quantity of the laboratory sample (the test sample) containing between 200 and 1 000 µg non-ionic surfactant, into the stripping apparatus. Weigh out 100 g sodium chloride (5.1) and 5 g sodium hydrogencarbonate (5.2). If the test sample volume exceeds 500 ml, add these salts in solid form and dissolve by passing nitrogen gas or air through it. If a smaller test sample volume is used, dissolve the salts in 400 ml water and add in solution.

If necessary, add water up to the level of the upper stopcock. Add 100 ml ethyl acetate (5.3). 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 phases remain separate and no turbulence is produced at the interface. Thus significant mixing of the phases and 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 the first portion. Rinse the 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.

8.2 Blank test

With each series of samples, carry out a blank test in parallel with the determination, using 5 ml methanol (5.4) and 40 ml water instead of the test portion. The consumption of sodium pyrrolidin-1-yl dithiocarboxylate solution should be less than 1 ml; otherwise the reagents shall be checked for their content of heavy metals.

8.3 Precipitation and filtration

Dissolve the dry residue from 8.1 after the removal of any interferences (see clause 10) in 5 ml methanol (5.4), transfer to a beaker, add 40 ml water and 0,5 ml hydrochloric acid (5.6), stir with a magnetic stirrer, and add from a measuring cylinder 30 ml precipitating agent (5.13). The precipitate is formed during continuous stirring. Discontinue stirring after 10 min and wait for at least 5 min.

Place a sintered glass crucible (porosity 4, capacity 40 ml) into a suitable adapter attached to a 500 ml filter flask. A glass-fibre filter paper may also be inserted; this prolongs the life of the crucible. Wet the filter under suction with about 2 ml glacial acetic acid (5.5). Filter the precipitate through the crucible. (It is essential that rubber collars, if used, do not come into contact with any of the reagents.) The use of a polyethylene squirt bottle for the acetic acid is recommended. It is not necessary to transfer the precipitate quantitatively on to the filter because a solution of the precipitate (see 8.4) is transferred back to the same beaker prior to titration, thereby ensuring that any precipitate remaining in the beaker also becomes dissolved.

8.4 Dissolution of the precipitate

Place the crucible in a glass adapter on a 250 ml filter flask. Dissolve the precipitate by adding hot (at approximately 80 °C) ammonium tartrate solution (5.10) in three portions of 10 ml. Pour the contents of the filter flask into the beaker with an additional 20 ml of hot tartrate solution to dissolve any remaining precipitate. Carefully wash the crucible, adapter, and the filter flask with a further 20 ml of hot tartrate solution to dissolve any remaining precipitate. Carefully wash the crucible, adapter, and the filter flask with 100 to 150 ml water and add to the contents of the beaker.

8.5 Standardization of the sodium pyrrolidin-1-yl dithiocarboxylate solution

The concentration of the sodium pyrrolidin-1-yl dithiocarboxylate solution (5.15) shall be checked prior to each use, or, in case of routine analyses, once a day. For this purpose, titrate a mixture of 10,0 ml copper sulfate standard solution (5.17), 100 ml water and 10,0 ml standard acetate buffer (5.14).

The factor t of the sodium pyrrolidin-1-yl dithiocarboxylate solution is given by the equation

$$t = \frac{V_1}{V_2}$$

where

V_1 is the volume, in millilitres, of standard solution (here 10 ml);

V_2 is the consumption, in millilitres, of sodium pyrrolidin-1-yl dithiocarboxylate solution.

8.6 Titration

Stir the solution with a magnetic stirrer, add a few drops of bromocresol purple (5.18) and ammonia solution (5.9) until the colour turns violet (the solution may be slightly acidic due to the rinsing with acetic acid).

Add 10 ml standard acetate buffer (5.14), immerse the electrodes and titrate with sodium pyrrolidin-1-yl dithiocarboxylate solution (5.15) with the burette tip immersed in the solution.

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

Titrate beyond significant potential drop. Adjust the titration speed to 2 ml/min and the paper advance to about 4 cm/ml.

The end-point is the intersection of the tangents to the two branches of the potential curve. Sometimes the inflection in the potential curves may be flattened, this can be eliminated by carefully cleaning the platinum electrode (polishing with emery paper).

9 Expression of results

9.1 Calculation

As every non-ionic surfactant has its own conversion factor depending upon the length of the ethylene oxide chain, calculations usually refer to a standard substance. For this purpose a nonyl phenol with 10 ethylene oxide units (NP 10) is suitable. An empirical factor of 54 was determined for this substance. That means 1 ml of the sodium pyrrolidin-1-yl dithiocarboxylate solution (5.15) is equivalent to 54 µg of NP 10.

The non-ionic surfactant mass concentration, ϱ_X, expressed in milligrams per litre, of the sample, expressed as NP 10, is given by the equation

$$\varrho_X = \frac{(V_3 - V_4)\, t\, f}{V_0}$$

where

V_0 is the sample volume, in millilitres;

V_3 is the consumption, in millilitres, of sodium pyrrolidin-1-yl dithiocarboxylate solution by the sample;

V_4 is the consumption, in millilitres, of sodium pyrrolidin-1-yl dithiocarboxylate solution by the blank;

t is the factor of the sodium pyrrolidin-1-yl dithiocarboxylate solution (see 8.5);

f is the calculation factor (54 mg/l).

9.2 Reproducibility

In the concentration range from about 0,5 to 1,0 mg/l, the relative standard deviation, s, was calculated to be $s = \pm 10\,\%$.

10 Interferences

Anionic surfactants up to a tenfold excess do not interfere. Cationic surfactants are determined as well and shall, if necessary, be separated by cation exchange. Although sublation excludes polyethylene glycols and the majority of non-surface active substances which might otherwise interfere, there is little detailed information concerning interfering substances and their effect. Total recovery may not be obtained in samples having very high contents of suspended solids (see 8.1).

Cationic surfactants react with the precipitating agent (5.13) and simulate a non-ionic surfactant content. If present, cationic surfactants shall be removed by the following procedure.

Evaporate the ethyl acetate from the extract and dissolve the residue in about 20 ml methanol (5.4). Pass through an ion exchange column (6.2) filled with 10 ml of cation exchange resin (5.19). Adjust the flow rate to a series of fast drops. Wash the column with about 50 to 60 ml methanol and evaporate the combined methanol solutions on a water-bath. If higher ethoxylated surfactants are expected (more than 25 ethylene oxide groups per molecule), use a mixture of four parts by volume of methanol and one part by volume of methylene chloride instead of pure methanol.

Regenerate the cation exchange resin prior to each use with methanolic hydrochloric acid (5.7). Rinse the column with methanol until no reaction takes place on the addition of methyl red. Store the cation exchange resin under methanol.

11 Test report

The test report shall include the following information:

a) an identification of the sample;

b) the reference of the method used;

c) the results and the method of expression used;

d) any unusual features noted during the determination;

e) any operations not specified in this part of ISO 7875 or regarded as optional.

Dimensions in millimetres

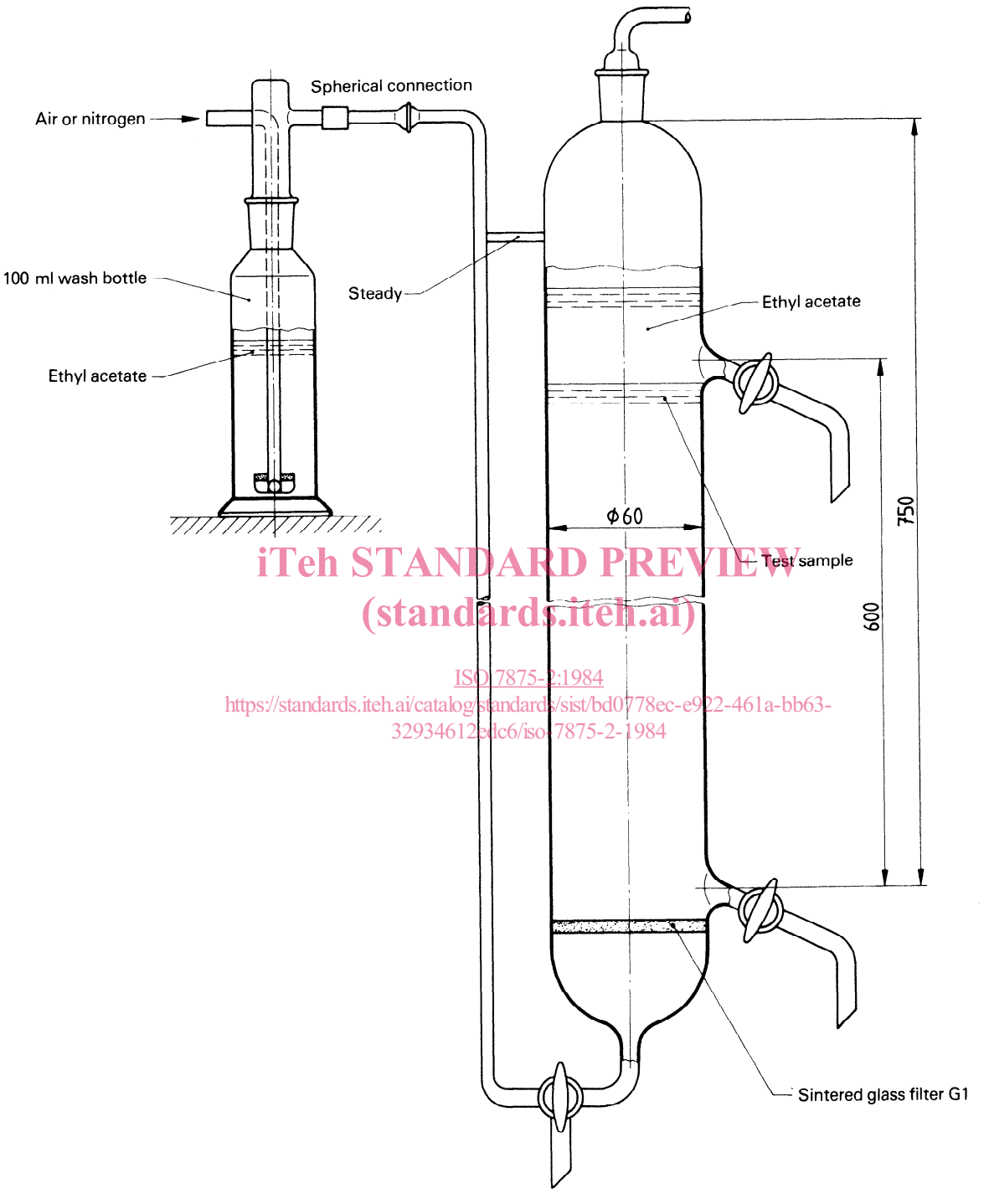

Figure — Gas-stripping apparatus
(See the note to 6.1)

Annex

Bismuth determination

A.1 Atomic absorption spectrometric method

Prepare the precipitate as described in 8.3 and dissolve it in an appropriate volume of hot ammonium tartrate solution as in 8.4 or in nitric acid as follows.

Add 2 ml of nitric acid (ϱ = 1,420 g/ml) to the washed precipitate, imparting a swirling motion to the crucible but do not apply a vacuum. Add 2 to 3 ml water with swirling and apply a vacuum. Repeat the process twice to dissolve and remove all the precipitate. Rinse the crucible and adapter with water to ensure complete transfer into the Buchner flask. Transfer the solution in the Buchner flask to a 100 ml one-mark volumetric flask and make up to the mark with water.

Prepare a standard volumetric solution of bismuth by accurately weighing out 0,500 ± 0,005 g of pure bismuth powder and dissolving in a few drops of nitric acid (ϱ = 1,420 g/ml) and, finally diluting with water to 500 ml in a volumetric flask. Prepare a set of calibration solutions from this solution to contain 1; 2; 3; 4; and 5 mg/l of bismuth.

Ensure that each calibration solution contains approximately the same amount of nitric acid or ammonium tartrate (whichever has been used to dissolve the precipitate) as the solution of the sample above.

Set up the atomic absorption spectrometer and operate it in accordance with the manufacturer's instructions. Measure absorbances of the samples and the calibration solutions. Hence calculate the concentration of bismuth in the sample solutions and thus the concentration of non-ionic surfactant in the original samples.

A.2 Ultraviolet spectrometric method

Prepare the precipitate as described in 8.3. Heat 50 ± 1 ml of ammonium tartrate solution contained in a 150 ml conical flask to about 80 °C on a hotplate. Place the crucible in a suitably sized filter flask, fitted with an adapter and dissolve the precipitate in 15 to 20 ml of the hot ammonium tartrate solution. Use a further 15 ml of the tartrate solution to rinse the sides of the beaker (used in 8.3) to dissolve any remaining precipitate. Filter the contents of the beaker through the crucible and wash the crucible with the remainder of the tartrate solution, followed by 10 ml of water. Transfer the contents of the filter flask to the beaker, washing out the flask with two portions (10 ml and 5 ml) of water; add the washings to the beaker. Add 4 ml of 0,02 mol/l ethylenediaminetetraacetic acid (EDTA) solution to the contents of the beaker, mix and transfer to a 100 ml volumetric flask. Wash the beaker with water and use the washings to make up the solution in the flask to 100 ml (see note 1).

Set up the UV spectrometer in accordance with the manufacturer's instructions. Using a 20 mm cell, read the absorbance of the solution in the volumetric flask against a water reference at a wavelength of 263,5 nm. Prepare calibration solutions containing 0; 200; 400; 600; and 1 000 µg of a standard non-ionic surfactant by dissolving portions in 5 ml of methanol and 40 ml of water, and prepare the precipitates as in 8.3. Dissolve the precipitates as above and read the absorbances using the 20 mm cells, as in the case of the sample. Plot a calibration graph of absorbances at 263,5 nm against the concentrations of the standard non-ionic surfactant. Calculate the mass of non-ionic surfactant in the test sample by reference to the standard calibration graph (see note 2).

NOTES

1 Since the absorbance of the bismuth-EDTA complex at 263,5 nm is constant over the pH range 2 to 9, no pH control in the colorimetric estimation is required; the pH of the final solutions is generally in the range 4 to 5.

2 Both the tartrate ion and EDTA absorb slightly at 263,5 nm and contribute to the absorbance reading for the reagent blank — typical blanks are 0,03 to 0,04 absorbance.