
Kakovost vode - Določanje anionskih površinsko aktivnih snovi z metilen modrim MBAS (ISO 7875-1:1984, modificiran)

Water quality - Determination of anionic surfactants by measurement of the methylene blue index MBAS (ISO 7875-1:1984 modified)

Wasserbeschaffenheit - Bestimmung von anionischen oberflächenaktiven Stoffen durch Messung des Methylenblau Index MBAS (ISO 7875-1:1984 modifiziert)

Qualité de l'eau - Dosage des agents de surface anioniques par mesurage de l'indice au bleu de méthylène SABM (ISO 7875-1:1984 modifiée)

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ICS:

13.060.50	Preiskava vode na kemične snovi	Examination of water for chemical substances
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English version

**Water quality - Determination of anionic
surfactants by measurement of the methylene
blue index MBAS (ISO 7875-1:1984 modified)**

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Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

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CEN

European Committee for Standardization
Comité Européen de Normalisation
Europäisches Komitee für Normung

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Foreword

The text of the International Standard ISO 7875-1:1984 "Water quality - Determination of surfactants - Part 1: Determination of anionic surfactants by the methylene blue spectrometric method" prepared by ISO/TC 147 "Water quality" together with common modifications prepared by the Technical Committee CEN/TC 230 "Water analysis" was submitted to the formal vote and approved by CEN as a European Standard.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by April 1994, and conflicting national standards shall be withdrawn at the latest by April 1994.

The standard was approved and in accordance with the CEN/CENELEC Internal Regulations, the following countries are bound to implement this European Standard: Austria, Belgium, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland, United Kingdom.

Endorsement notice

The text of the International Standard ISO 7875-1:1984 was approved by CEN as a European Standard with agreed common modifications as given below.

- 1) The title was changed and specified in order to clarify that the determination deals with the sum parameter MBAS-index (Methylene blue active substances index).
- 2) The clauses "Scope" and "Field of application" are unified under one number and the wording was adjusted in order to meet with the title.
- 3) In clause 5.2 (in ISO: 6.2) the optical path length of the cells is given as 10 and 50 mm (in ISO: 10 to 50 mm).
- 4) In clause 7.1 (in ISO: 8.1) the wording is adjusted in order to meet with the title.
- 5) In clause 7.2 as well as in clause 7.3 (in ISO: 8.2) the indices for A_0 and A_1 were corrected.
- 6) In clause 7.3 (in ISO: 8.3) the wording of the calibration was adjusted in order to meet with the title.
- 7) In clause 8.1 (in ISO: 9.1) the given anionic surfactant mass concentration was changed into the MBAX-index. Furthermore the indices of A_0 and A_1 were corrected.

0 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 method.

1 Field of application

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

The method is applicable to drinking water, surface water as well as waste water, e.g. for the determination of the primary degradation of surfactants being under investigation in test systems containing natural or synthetic waste water. This applies for both laboratory scaled 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 to a considerable extent also natural anionic surface active substances.

The range of this method is applicable to concentrations of 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.

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2 Normative references

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendment to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies.

EN 25667-2:1993 Water quality - Sampling - Part 2: Guidance on sampling techniques

ISO 5667-3:1985 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, 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).

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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 ($\text{C}_4\text{H}_8\text{O}_2$), 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 desirable to replace it by another solvent. Research work is going on.

4.4 Ethanol ($\text{C}_2\text{H}_5\text{OH}$), 95 % (V/V).

4.5 Methanol (CH_3OH), freshly distilled. In order to avoid high results in blank tests (8.2) store in a glass bottle.

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

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

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

4.8 Neutral methylene blue, 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 0,02 per 10 mm layer thickness at 650 nm. In the case of higher blank absorbances, 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 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 methylene blue solution. Repeat the extraction and rinse as before. Discard the chloroform extracts; collect for reuse after treatment.

4.9 Acid methylene blue, solution.

Dissolve 0,350 g of methylene blue in 500 ml of water and add 6,50 ml of sulfuric acid, $\rho = 1,84$ 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 layer thickness at 650 nm. In the case of higher blank absorbances, either wash twice the methylene blue solution with chloroform for purification (see 4.8) or use other batches of methylene blue.

4.10 Buffer solution, pH 10.

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

4.10.2 Alternatively, especially for water with high hardness, the following buffer solution may be used.

4.10.2.1 Disodium tetraborate, ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), 0,05 mol/l, solution.

Dissolve 19 g of disodium tetraborate decahydrate in 1000 ml of water.

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

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

Dissolve 4 g of 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.

4.10.2.3 Alkaline borate solution.

Mix equal volumes of sodium 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 polyethylene stoppered glass bottle.

4.11 Dodecyl benzene sulfonic acid methyl ester (tetra-propylene type) ($C_{19}H_{32}O_3S$), stock standard solution.

Weigh, preferably from a weighing pipette, 400 mg 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 (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 phenolphthalein (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 dodecyl benzene sulfonic acid methyl ester is preferable as it is a guaranteed non-hygroscopic standard, the calibration graph (see 7.3) 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 ($C_{20}H_{37}NaO_7S$).

4.12 Phenolphthalein, indicator solution.

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

5 Apparatus

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Ordinary laboratory equipment, and

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 cells of optical path length with 10 to 50 mm cells.

5.3 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 fixing member should also be divisible.

NOTE ON PRELIMINARY CLEANING OF GLASSWARE:

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

6 Sampling and samples

Instructions for sampling are given in EN 25667-2 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 days while saturating with chloroform is suitable for periods up to 8 days.

NOTE: 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.

7 Procedure

7.1 Concentration and separation of the surfactant

For all types of 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, proceed to 7.4 as well, 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.

Non-surfactant methylene blue active substances can cause errors in the methylene blue determination. In surface water and other types of water with unknown composition, or known to contain interfering compounds, separate the surfactants by stripping (solvent sublimation) (3.5.3). 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 laboratory sample, up to 1000 ml, into the stripping apparatus (see 5.3).

Install the apparatus (5.3) 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 of sodium chloride in 400 ml of water and add this solution to the sample.

If necessary, add water to bring the sample surface up to the level of the upper stopcock. Add 100 ml of ethyl acetate (4.2). 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. Use of a variable area flow-meter is recommended. Adjust the gas flow 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.