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

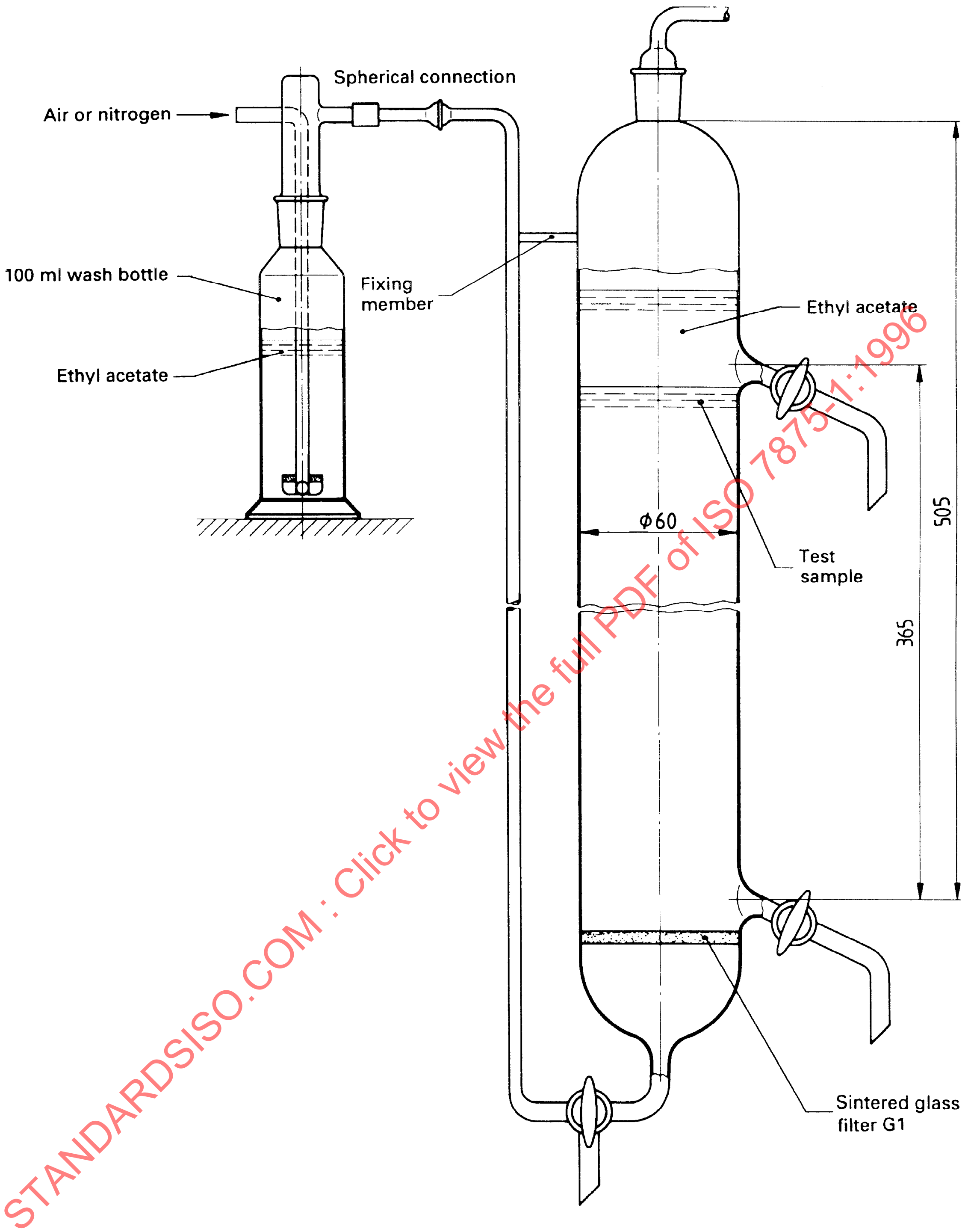

Figure 1 — Gas-stripping apparatus (see note to 5.3)

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.

Separation is improved by the addition of sodium chloride. If the test sample volume exceeds 500 ml, add 100 g of solid sodium chloride 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 test sample.

If necessary, add water to bring the sample surface up to the level of the upper stopcock (see figure 1). 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 l/h to 50 l/h through the gas-stripping apparatus. Use of a flowmeter with variable area 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.

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. Return any water in the separating funnel (there should only be a few millilitres) to the gas-stripping apparatus.

Filter the ethyl acetate solution through a dry qualitative gas-filter paper into a 250 ml flask. Add a further 100 ml of ethyl acetate to the gas-stripping apparatus and again pass nitrogen or air through it for 5 min. Separate the organic layer as described above, using the same separating funnel, filter, and add it to the first portion. Rinse the filter paper and funnel with 25 ml of 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 (4.5) and 50 ml of water. Transfer the solution quantitatively to a 100 ml one-mark volumetric flask and dilute to the mark with water.

7.2 Blank test

With each series of test samples, carry out a blank test in parallel with the determination, using the zero member of the set of calibration solutions (see 7.3).

Subtract the interpolated absorbance, A_0, from the absorbance, A_1 of the test sample. Under the given conditions the absorbance, A_0, of the blank test shall not exceed 0,02 per 10 mm optical path length, otherwise the equipment and the reagent shall be checked carefully for any contamination.

7.3 Calibration

From the stock standard solution (4.11), prepare a working standard solution by transferring 25 ml with a pipette to a 500 ml one-mark volumetric flask, dilute to the mark with water and mix.

The mass concentration of MBAS, ρ_x, in milligrams per millilitre, of this working standard solution is given by the equation

$$\rho_x = \frac{mf_1}{V}$$

where

m is the mass, in milligrams, of the MBAS (as ester) used for preparation of the stock standard solution according to 4.11;

f_1 is a conversion factor from ester to MBAS, sodium salt of dodecylbenzene sulfonate, here f_1 = 1,023 5 (see table 1);

V is a volume correction factor, in millilitres, here V = 20 000 ml.

Place 0,0 ml (the zero member); 1,0 ml; 2,0 ml; 4,0 ml; 6.0 ml and 8.0 ml of the working standard in a series of separating funnels of capacity 250 ml, dilute with water to 100 ml and continue as described in 7.4.

Measure the absorbance of each of the set of the calibration solutions, including the zero member, at a wavelength of 650 nm in cells of optical path lengths 10 mm to 50 mm. Prepare a calibration graph by plotting the absorbance against the mass, in micrograms, of surfactant contained in the calibration solution and subtract the interpolated absorbances (intersection with the ordinate) of the blank from the absorbances, A_1, of each calibration solution (8.1).

Calibrate once or twice a month or whenever new batches of chemicals are used.

If the calibration is carried out with one of the alternative surfactants (see 4.11), use the conversion factors f_1 shown in table 1.

Table 1

Surfactant	Conversion factor, f_1
Dodecylbenzene sulfonic acid, sodium salt	1,000 0
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

7.4 Determination

Transfer a measured volume of the test sample, if necessary treated according to 7.1, into a separating funnel. This test portion should contain between 20 µg and 200 µg of 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 of neutral methylene blue solution (4.8), 10 ml of buffer solution (4.10) (not necessary if a pre-extracted methylene blue solution is used), and 15 ml of chloroform (4.3). Shake evenly and gently 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 of water and 5,0 ml of acidic methylene blue solution (4.9). Shake uniformly but not too vigorously for 1 min as previously described. Filter the chloroform layer through a cotton or glass wool filter wetted with chloroform (4.3) 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 (4.3) 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 and mix.

For each batch of test samples, carry out the complete extraction for a blank determination on 100 ml of water and on one of the calibration solutions (see 7.3).

Before each determination, shake the contents of the volumetric flask, rinse the optical cell of the spectrometer (5.2) three times with the solution in this flask, and then fill the cell.

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

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.

If the absorbance of the test solution of the sample when measured in cells of optical path length 10 mm is less than 0,1, repeat readings of calibration solutions, blank test and test sample in 40 mm and 50 mm cells.

If the standard 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.

8 Expression of results

8.1 Calculation

Calculate the MBAS index as mass concentration, ρ_y, expressed in micrograms per millilitre, calculated as the sodium salt of dodecyl benzene sulfonic acid using the equation

$$\rho_y = \frac{f_2 (A_1 - A_0)}{V_0}$$

where

- A_1 is the absorbance of the test sample;
- A_0 is the absorbance of the blank;
- f_2 is a calibration factor representing the mass, in micrograms, of MBAS (calculated as the sodium salt of dodecyl benzene sulfonic acid) which under the given conditions yields an absorbance of 1,000 (evaluated from the calibration graph);
- V_0 is the volume, in millilitres, of the test portion taken for analysis according to 7.4. If the sample was diluted, this shall be accounted for (see 7.1). If the sample was sublated, V_0 represents the 100 ml obtained according to 7.1

Alternatively, determine the MBAS mass concentration from the calibration graph (see 7.3). The mass concentration is calculated from the mass of MBAS in the test portion, taken from the calibration graph, and its volume.

8.2 Precision

The precision, P, of the method can be expressed as

$$P = 0{,}107\ \rho_y + 0{,}008$$

where ρ_y is the mass concentration, expressed in micrograms per millilitre, of MBAS.

At 0,1 µg/ml, the relative standard deviation, s, was calculated to be $s = \pm 19$ %

9 Interferences

MBAS values which are falsely low can be obtained in the presence of cationic substances such as quaternary ammonium compounds and proteins which form compounds with anionic surfactants. For example, if the sample contains anionic as well as cationic surfactants, these may form stable complexes which will not react with methylene blue.