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Water quality — Determination of the methylene blue active substances (MBAS) index — Method using continuous flow analysis (CFA)

Qualité de l'eau — Mesurage de l'indice des substances actives au bleu de méthylène (SABM) — Méthode par analyse en flux continu (CFA)

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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. 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.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 16265 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

Introduction

Methods using flow analysis automate wet chemical procedures and are particularly suitable for the processing of many analytes in water in large numbers of samples at a high analysis frequency (up to 100 samples per hour).

A differentiation is made between flow injection analysis (FIA) [1], [2] and continuous flow analysis (CFA) [3]. Both methods share the feature of an automatic dosage of the sample into a flow system (manifold) where the analytes in the sample react with the reagent solutions on their way through the manifold. The sample preparation may be integrated in the manifold. The reaction product is measured in a flow detector (e.g. a photometer). The detector produces a signal from which the concentration of the parameter is calculated.

The MBAS (methylene blue active substances) index is an analytical convention (a method-defined parameter) used for water quality control purposes. It measures surfactants and other substances that react with methylene blue under specified conditions.

The user should be aware that particular problems could require the specification of additional conditions.

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WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

IMPORTANT — It is absolutely essential that tests conducted in accordance with this International Standard be carried out by suitably trained staff.

Trichloromethane and methanol waste solutions should be disposed of properly.

1 Scope

This International Standard specifies a procedure for the determination of the methylene blue active substances (MBAS) index, in the ranges 0,05 mg/l to 0,5 mg/l and 0,5 mg/l to 5,0 mg/l, in various water samples (e.g. ground water, drinking water, surface water, waste water and leachates). Anionic surfactants are the most important substances showing methylene blue activity. This method is therefore useful for estimating the anionic surfactant content [including anionic surfactants with carboxylate groups (e.g. soaps)] of water. Other types of substance may also show methylene blue activity and contribute to the result. On a case-by-case basis, the range of the analysis may be changed and the method used for other concentration ranges provided they cover exactly one decade of concentration units.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the reference document (including any amendments) applies.

ISO 648, *Laboratory glassware — Single-volume pipettes*

ISO 1042, *Laboratory glassware — One-mark volumetric flasks*

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

3 Interferences

The following substances can interfere with the analysis:

— Cationic compounds able to form strong ion-pairs with the active substances in methylene blue.

— Humic acids in concentrations $>$ 20 mg/l.

— Chemicals with a high surface activity (e.g. non methylene blue active surfactants in concentrations $>$ 50 mg/l).

— Chemicals with a strong reductive potential for the oxidation of methylene blue (e.g. S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, OCl^-). These chemicals shall be removed (e.g. with H_2O_2) prior to analysis.

— High concentrations of inorganic anions (e.g. nitrate, chloride, bromide) may cause positive bias.

— Chemicals which react with any of the reagents used to form a coloured compound soluble in trichloromethane ($CHCl_3$) (excluded are methylene blue active substances).

Filtration of the sample before analysis is advisable for samples containing particles larger than 100 µm in size. Otherwise the particles in the sample may clog the transport tubes. If filtration is necessary, significant losses of anionic surfactants due to adsorbance effects are possible.

The absorbance due to the colour of the sample can be compensated for by a blank analysis which omits the methylene blue from the reagents. The responses of the sample with and without reagent addition are determined. The difference between the two responses is used in Equations (3) and (4).

Samples with an MBAS index concentration > 5 mg/l shall be diluted before analysis.

4 Principle

The sample is mixed, in a continuously flowing stream, with an alkaline methylene blue solution, forming coloured ion-pairs with certain types of organic substance (e.g. anionic surfactants) contained in the sample. The ion-pairs are extracted with trichloromethane. The organic phase is treated with an acidic methylene blue solution and its absorbance determined photometrically at a wavelength of 650 nm ± 10 nm.

The result is expressed in terms of sodium dodecyl sulfate concentration.

5 Reagents

Unless otherwise stated, use only reagents of recognized analytical grade.

Degas reagents if air bubbles appear spontaneously. Unless otherwise specified, degas by passing helium gas at 20 l/h through the reagent for 15 min. Add detergent after degassing. Avoid using reagents showing any turbidity, filtering them if necessary.

5.1 Water, complying with grade 1 as defined in ISO 3696.

5.2 Sodium hydroxide, NaOH.

5.3 Sodium tetraborate decahydrate, $Na_2B_4O_7 \cdot 10H_2O$.

5.4 Sodium dihydrogen phosphate monohydrate, $NaH_2PO_4 \cdot H_2O$.

5.5 Potassium dihydrogen phosphate monohydrate, $KH_2PO_4 \cdot H_2O$.

5.6 Sulfuric acid, H_2SO_4, $\rho(H_2SO_4) = 1{,}84$ g/ml.

5.7 Hydrochloric acid, HCl, $\rho(HCl) = 1{,}18$ g/ml.

5.8 Methylene blue, $C_{16}H_{18}N_3SCl \cdot 2H_2O$.

5.9 Methanol, CH_3OH.

5.10 Ethanol, C_2H_5OH, $w(C_2H_5OH) \approx 96$ %.

5.11 Trichloromethane, $CHCl_3$.

Trichloromethane is stable for 3 months if stored in a dark place.

Before use, degas the trichloromethane for 30 min by purging with a stream of He or by using an ultrasonic bath.

5.12 Sodium dodecyl sulfate (sodium lauryl sulfate), $CH_3(CH_2)_{11}OSO_3Na$.

5.13 Petroleum ether.

5.14 Poly(ethylene glycol) dodecyl ether, $HO(CH_2CH_2O)_nC_{12}H_{25}$, aqueous solution, $w = 30$ %.

5.15 Alkaline borate solution.

Dissolve 15,83 g of sodium tetraborate decahydrate (5.3) and 3,3 g of sodium hydroxide (5.2) in approximately 800 ml of water (5.1) and make up to 1 000 ml with water (5.1) in a volumetric flask (6.2.1).

This solution is stable for one week if stored at room temperature.

5.16 Stock methylene blue solution.

Dissolve 0,35 g of methylene blue in 500 ml of ethanol (5.10) and make up to 1 000 ml with water (5.1) in a volumetric flask (6.2.1).

This solution is stable for 6 months if stored at room temperature.

5.17 Alkaline methylene blue solution.

Add 100 ml of stock methylene blue solution (5.16) to 50 ml of alkaline borate solution (5.15) and mix. Wash this mixture three times with 20 ml of trichloromethane (5.11) until the organic layer is no longer blue, removing the organic layer each time. Extract the aqueous solution thus obtained with 25 ml of petroleum ether (5.13) to remove the trichloromethane remaining in the solution. Filter through a paper filter (pore width 0,45 µm) and make up to 500 ml with water (5.1) in a volumetric flask (6.2.1).

Prepare this solution freshly before use.

5.18 Acidified methylene blue solution.

Add 6,8 ml of sulfuric acid (5.6) to 42,5 ml of stock methylene blue solution (5.16). Dissolve in this mixture 50 g of sodium dihydrogen phosphate monohydrate (5.4). Make up to a volume of 1 000 ml with water (5.1) in a volumetric flask (6.2.1).

This solution is stable for one week if stored at room temperature.

5.19 Trichloromethane extraction solution ($CHCl_3$ in Figure A.1).

Add 1 ml of poly(ethene glycol) dodecyl ether (5.14) to 1 000 ml of trichloromethane (5.11) and mix.

This solution is stable for one week if stored at room temperature.

5.20 Rinsing solution for the sampler.

Dissolve 1,1 g of potassium dihydrogen phosphate monohydrate (5.5) in approximately 800 ml of water (5.1) and make up to 1 000 ml with water (5.1) in a volumetric flask (6.2.1).

This solution is stable for one week if stored at room temperature.

5.21 Methanol solution.

To 800 ml of methanol (5.9) add 100 ml of hydrochloric acid (5.7) and make up to 1 000 ml with methanol (5.9).

This solution is stable for 6 months if stored at room temperature.