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Water quality — Determination of six complexing agents — Gas-chromatographic method

Qualité de l'eau — Dosage de six agents complexants — Méthode par chromatographie en phase gazeuse

Reference number
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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 3.

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 International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 16588 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

Annex A of this International Standard is for information only.

Introduction

It is essential that the test described in this International Standard be carried out by suitably qualified staff.

It should be investigated whether and to what extent particular problems will require the specification of additional conditions.

Water quality — Determination of six complexing agents — Gas-chromatographic method

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.

1 Scope

This International Standard specifies a method for the determination of the water-soluble organic complexing agents listed in Table 1 in the concentration range from 0,5 μg/l to 200 μg/l, if a sample volume between 50 ml and 100 ml is used. The concentration range may change if diluted solutions are analysed. The method is applicable to drinking, ground, surface and waste water.

Table 1 — Complexing agents determinable by this method

No.	Name	Composition	Molecular mass	CAS number[a]
1	EDTA — ethylenedinitrilotetraacetic acid	$C_{10}H_{16}O_8N_2$	292,25	60-00-4
2	NTA — nitrilotriacetic acid	$C_6H_9O_6N$	191,14	139-13-9
3	DTPA — diethylenetrinitrilopentaacetic acid	$C_{14}H_{23}O_{10}N_3$	393,35	67-43-6
4	MGDA — methylglycinediacetic acid	$C_7H_{11}O_6N$	205,17	29578-05-0
5	β-ADA — β-alaninediacetic acid	$C_7H_{11}O_6N$	205,17	6245-75-6
6	1,3-PDTA — 1,3-propylenedinitrilotetraacetic acid	$C_{11}H_{18}O_8N_2$	306,27	1939-36-2

[a] CAS: Chemical Abstracts System

In waste water analysis, it is recommended that a smaller sample volume, e.g. 5 ml or 10 ml, be used in order to reduce matrix effects.

The adsorption of the six complexing agents on solid materials is negligibly low.

Other complexing agents of similar composition may also be determined using this method, provided they behave similarly during sample pretreatment, derivatization and gas chromatography. This shall be checked in each individual case.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*

ISO 5667-1:1980, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes*

ISO 5667-2:1991, *Water quality — Sampling — Part 2: Guidance on sampling techniques*

3 Principle

A test sample is stabilized with formaldehyde and evaporated to dryness. Hydrochloric or formic acid is added and the sample again evaporated to dryness. The complexing agents are then esterified to the *n*-propyl, iso-propyl or *n*-butyl esters. Water is added and the esters are extracted with *n*-hexane, separated and identified by gas chromatography, and determined quantitatively with a nitrogen-sensitive detector or by mass spectrometry.

For the determination of EDTA, DTPA, and 1,3-PDTA, 1,2-propylenedinitrotetraacetic acid (1,2-PDTA) is used as an internal standard through the whole procedure. When a nitrogen-sensitive detector is used, heptadecane- and/or octadecanenitrile is used as a control standard in the gas-chromatographic step. 1-Chorotetradecane may be used as the control standard if detection by mass spectrometry is chosen.

Alternatively, ^{13}C-labelled standards may be used.

4 Interferences

In spite of their stability, complexes of these complexing agents with heavy metals are broken up and the complexing agents determined, except in the case of bismuth. With samples containing bismuth in concentrations $>$ 100 µg/l, losses can be expected.

In the case of high salt concentrations ($>$ 2 g/l of NaCl, corresponding to an electrical conductivity of about 400 mS/m), complete evaporation to dryness may be difficult. The complete removal of water is necessary, however, for the subsequent esterification. Therefore, samples have to be diluted or smaller sample volumes have to be taken. In the presence of calcium ions in concentrations exceeding 200 mg/l of Ca^{2+}, losses of EDTA will occur.

5 Reagents

All reagents shall be free from impurities which could interfere with the reactions. Throughout the procedure, use only deionized water (5.1).

5.1 Deionized water, grade 1 as specified in ISO 3696.

5.2 Gases for gas chromatography and mass spectrometry, as specified by the instrument manufacturers.

5.3 Nitrogen, of purity $\geqslant$ 99,996 %.

5.4 *n*-Propanol or **iso-propanol** or ***n*-butanol** for the preparation of esterification reagent (5.6).

5.5 Acetyl chloride.

5.6 Esterification reagent.

Cautiously mix by swirling in a 400 ml beaker 90 ml of *n*-propanol or iso-propanol or *n*-butanol (5.4) with 10 ml of acetyl chloride (5.5).

CAUTION — Considerable heat is evolved.

The mixture is stable for at least 1 month if stored at room temperature.

5.7 Reference compounds.

5.7.1 Nitrilotriacetic acid (NTA), $C_6H_9O_6N$, of purity $\geqslant$ 99 %.

5.7.2 Ethylenedinitrilotetraacetic acid (EDTA), $C_{10}H_{16}O_8N_2$, of purity $\geqslant$ 99 %.

5.7.3 Diethylenetrinitrilopentaacetic acid (DTPA), $C_{14}H_{23}O_{10}N_3$, of purity $\geqslant$ 99 %.

5.7.4 Methylglycinediacetic acid (MGDA), $C_7H_{11}O_6N$.

5.7.5 β-Alaninediacetic acid (β-ADA), $C_7H_{11}O_6N$.

5.7.6 1,3-Propylenedinitrilotetraacetic acid (1,3-PDTA), $C_{11}H_{18}O_8N_2$, of purity $\geqslant$ 99 %.

5.7.7 ^{13}C-labelled reference compounds as listed in 5.7.1 to 5.7.6 (optional).

5.8 Control standards and internal standard.

5.8.1 Octadecanenitrile, $C_{18}H_{35}N$, of purity $>$ 98 %.

5.8.2 Heptadecanenitrile, $C_{17}H_{33}N$, of purity $>$ 98 %.

5.8.3 1-Chlorotetradecane, $C_{14}H_{29}Cl$, of purity $>$ 98 %.

5.8.4 1,2-Propylenedinitrilotetraacetic acid (1,2-PDTA), $C_{11}H_{18}O_8N_2$, of purity $>$ 98 %.

5.9 Formaldehyde, 37 % by volume aqueous solution.

5.10 *n*-Hexane.

5.11 Sodium sulfate, anhydrous.

5.12 Sodium hydroxide solution, $c(\mathrm{NaOH}) = 1$ mol/l.

5.13 Hydrochloric acid, $c(\mathrm{HCl}) = 5$ mol/l.

5.14 Hydrochloric acid, $c(\mathrm{HCl}) = 1$ mol/l.

5.15 Formic acid, 50 % by volume aqueous solution.

5.16 Stock solutions for calibration purposes, 1 g/l.

Prepare 1 g/l stock solutions as follows. Weigh 100 mg of each of the complexing agents 5.7.1 to 5.7.6 and 5.8.4 into 100 ml volumetric flasks, dissolve in 2 ml of sodium hydroxide solution (5.12) and make up to the mark with water (5.1).

Stored in a refrigerator in brown glass bottles, the stock solutions are stable for at least 3 months.

5.17 Intermediate stock solutions, 1 mg/l and 10 mg/l.

Prior to each series of analyses, prepare intermediate stock solutions of 10 mg/l and 1 mg/l by diluting the 1 g/l stock solutions (5.16) with water (5.1).

5.18 Nitrile control standard, 0,5 mg/l solution in hexane.

Dissolve 100 mg of octadecanenitrile (5.8.1) and/or heptadecanenitrile (5.8.2) in 100 ml of *n*-hexane (5.10).

Store the solution in a refrigerator at 4 °C.

The solution is stable for at least 3 months.

Before use, dilute this solution to 0,5 mg/l.

5.19 1-Chlorotetradecane control standard, 0,5 mg/l solution in hexane.

Dissolve 100 mg of 1-chlorotetradecane (5.8.3) in 100 ml of *n*-hexane (5.10).

Store the solution in a refrigerator at 4 °C.

The solution is stable for at least 3 months.

Before use, dilute this solution to 0,5 mg/l.

6 Apparatus

6.1 Glassware, to be used only for the determination of complexing agents.

The use of detergents may lead to contamination. If contamination occurs, rinse the glassware with sodium hydroxide (5.12).

6.2 Ultrasonic bath.

6.3 Heating device, preferably a drying oven, suitable for evaporating water samples to dryness.

6.4 Equipment for passing an adjustable flow of nitrogen over the surface of the water samples during evaporation in the heating device (6.3).

6.5 Rotary evaporator.

6.6 Heating block, suitable for esterifying samples in sample vials (6.8) at (90 ± 3) °C.

During esterification, insert the sample vials into the heating block to about half of their volume (use metal rings to hold them in place).

6.7 Pipettes, 0,1 ml to 10 ml, or dispensers.

6.8 Disposable vials with PTFE-lined septa (PTFE = polytetrafluoroethylene), 3 ml and 12 ml.

6.9 pH meter, accuracy ± 0,1.

6.10 Beakers, 400 ml.

6.11 Gas chromatograph with mass-spectrometric detector.

6.12 Gas chromatograph with nitrogen-sensitive (NPD) detector.

6.13 Capillary column for gas chromatography, made of fused silica, length e.g. 20 m to 30 m, inner diameter e.g. 0,25 mm to 0,33 mm, stationary phase e.g. 100 % dimethyl polysiloxane or 95 % dimethyl polysiloxane plus 5 % diphenyl polysiloxane, film thickness 0,1 μm to 0,3 μm (see annex A).

6.14 Microlitre syringes, of suitable sizes.

6.15 Volumetric flasks, 50 ml and 100 ml.

6.16 Measuring cylinders, 50 ml and 100 ml.

6.17 Conductivity-measuring device.

6.18 Microseparator, e.g. as described in reference [7] (see the Bibliography).

7 Sampling and sample stabilization

Take samples in accordance with ISO 5667-1 and ISO 5667-2.

Place samples in glass or plastics bottles. For cleaning of the bottles, see 6.1. In order to avoid losses of some of the complexing agents by biological degradation, add, immediately after sampling, formaldehyde solution (5.9) in the ratio 1:100.

Store the stabilized samples at 4 °C in the dark. Do not keep for longer than one month.

8 Procedure

8.1 Sample pretreatment

Withdraw test samples directly from the settled sample. Alternatively, the sample may be centrifuged.

Measure the dissolved organic carbon (DOC) and conductivity of the sample.

The adsorption of the six complexing agents on settled solids may be neglected. However, if the method is applied to other complexing agents, this shall be checked for each individual compound.

If the DOC is $<$ 20 mg/l, add 1,2-PDTA (or ^{13}C-labelled compounds) as the internal standard (see 9.2) in about the same concentration as the complexing agents to be determined.

Evaporate 50 ml to 100 ml of the sample to dryness, preferably in a drying oven (6.3). Dissolve the residue in 10 ml of hydrochloric acid (5.14) or formic acid (5.15) and transfer quantitatively to a 12 ml vial (6.8). Evaporate the acidified sample to dryness in a heating block (6.6) or rotary evaporator (6.5) at (90 ± 3) °C under a continuous stream of nitrogen.

In the case of samples with a DOC concentration $\geq$ 20 mg/l, use a smaller sample volume, so that the DOC does not exceed 2 mg (absolute). In addition, if the salt concentration is high, modify the procedure accordingly (see clause 4). Smaller sample volumes may be transferred directly to the 12 ml sample vial and treated with hydrochloric acid.

Strongly alkaline waste waters may possibly require the addition of more hydrochloric acid.

8.2 Esterification of the sample

Add 2 ml of the esterification reagent (5.6) to the dry residue from 8.1. Close the vial and transfer it to the heating block (6.6). Insert it to half of its volume and leave it in the heating block at (90 ± 3) °C for at least 30 min for butyl esters or at least 3 h for propyl esters.

Butyl esters are more easily extracted. Especially in the case of the determination of DTPA, however, they may lead to problems during gas chromatography due to their higher boiling points.

Let the vial cool down to room temperature, open it and add 1 ml of a 0,5 mg/l solution of nitrile control standard (5.18) (when using a nitrogen-sensitive detector) or 1-chlorotetradecane control standard (5.19) (when using a mass-spectrometric detector) in hexane and shake vigorously. Transfer the contents to a 50 ml volumetric flask and add 1 ml of sodium hydroxide solution (5.12). Rinse the vial several times with water, add the water to the flask and make up to the mark with water. Shake vigorously for 1 min. Immediately after phase separation, withdraw as much of the organic layer as possible using a pipette or a microseparator (6.18) and transfer to a 3 ml vial (6.8). Add 0,5 g of sodium sulfate (5.11), shake for 5 min to 10 min and transfer the dried extract to another 3 ml vial (6.8). The extract may be stored in a refrigerator for a maximum of 2 weeks. In the case of low concentrations (1 µg/l to 10 µg/l), reduce the volume to about one-tenth using nitrogen.

8.3 Gas-chromatographic determination

In order to avoid discrimination effects during sample injection, it is preferable to use a cold-vapour system or cold on-column injection.