

DIN 38414-17

German standard methods for the examination of water, waste water and sludge — Sludge and sediments (group S) — Part 17: Determination of the organically bound halogens amenable to extraction (EOX) (S 17);

Deutsche Einheitsverfahren zur Wasser-, Abwasser-, und Schlammuntersuchung — Schlamm und Sedimente (Gruppe S) — Teil 17: Bestimmung von extrahierbaren organisch gebundenen Halogenen (EOX) (S 17)

Méthodes normalisées allemandes pour l'analyse des eaux, des eaux résiduaires et des boues — Boues et sédiments (groupe S) — Partie 17: Dosage des composées organo-halogénés soumis à libération et extraction (EOX) (S 17)

Foreword

This standard has been prepared jointly with the "Wasserchemische Gesellschaft" (Water Chemical Society) — a study group within the "Gesellschaft Deutscher Chemiker" (German Chemists' Society) (see annex A).

Expert assistance or specialised Laboratories will be required to perform the analyses according to this Standard and applicable safety instructions have to be considered.

Depending on the objective of the analysis, a check shall be made in individual cases whether and to what extent additional boundary conditions will have to be specified.

DIN 38414 "German standard methods for the examination of water, waste water and sludge — Sludge and sediments (Group S)" consists of further parts. Annex A provides an overall view of the groups A to T of the "German standard methods".

Annex A is informative.

Amendments

Compared to DIN 38414-17:1989-11 following modifications have been introduced:

- a) Drying according DIN 38414-22;
- b) extraction time of at least 8 hours (approximately 100 extraction cycles);
- c) mineralization in oxygen stream at a minimum temperature of 950 °C, and
- d) deletion of determination of strippable organically bound halogens (purgeable organic halids, POX).

Warning — Users of this standard should be familiar with ordinary laboratory praxis. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and protection measures/practices and to ensure their conformity with national regulations.

Waste and sludge samples may contain hazardous and combustible substances. Further they may contain germs and tend to biological activity. Therefore, samples should be handled very carefully. Gases which can be produced by microbiological activity pressurise sample containers and might be combustible. Fragments of exploding bottles can be contaminated and pathogen aerosols can lead to infection risk.

1 Scope

This standard specifies a method for examination of sludge and sediments. The content of extractable organically bound halogens (extractable organic halids, EOX) is determined. The lower application limit is at 0,2 mg Cl per kg dry mass (matter).

Highly volatile and medium volatile organic halogen compounds are not fully determined.

2 Normative references

This 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 amendments to or revisions of any of these publications apply to this Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies.

DIN 12252, *Laboratory glassware — Interchangeable ground glass stoppers.*

DIN 12449, *Paper laboratory ware — extraction thimbles.*

DIN 12491, *Laboratory glassware — Vacuum desiccators.*

DIN 12591, *Laboratory glassware — Dimroth condensers with standard ground glass joints.*

DIN 12602, *Laboratory glassware — Soxhlet extractors with standard ground glass joints.*

DIN 12697, *Laboratory glassware — Graduated pipettes, short delivery time, waiting time 15 s, class AS.*

DIN 38409-8, *German standard methods for the examination of water, waste water and sludge — Summary indices of actions and substances (group H) — Part 8: Determination of extractable organically bonded halogens (EOX) (H 8).*

DIN 38409-22, *German standard methods for the examination of water, waste water and sludge — General methods of effects and substances (group H) — Part 22: Determination of dissolved adsorbable and organically bound halogens in salt loaded water (SPE-AOX) (H 22).*

DIN 38414-22, *German standard methods for the examination of water, waste water and sludge — Sludge and sediments (group S) — Teil 22: Determination of dry residue by freezing and preparation of the freeze dried mass of sludge (S 22).*

DIN EN 12880, *Characterisation of sludge — Determination of dry residue and water content; German Version of EN 12880:2000.*

DIN EN ISO 1042, *Laboratory glassware — One-mark volumetric flasks (ISO 1042:1998); German Version EN ISO 1042:1999.*

DIN EN ISO 4796-2, *Laboratory glassware — Bottles — Part 2: Conical neck bottles (ISO 4796-2:2000); German Version EN ISO 4796-2:2000.*

(Draft Standard) DIN EN ISO 4797, *Laboratory glassware — Boiling flasks with conical ground joints (ISO/DIS 4797:2002); German Version prEN ISO 4797-2:2002.*

(Draft Standard) DIN EN ISO 9562, *Water quality — Determination of adsorbable organically bound halogens (AOX) (ISO/DIS 9562:2003); German Version prEN ISO 9562:2003.*

DIN ISO 3696, *Water for analytical and laboratory use — Specification and test methods; Identical with ISO 3696:1987.*

3 Terms and definitions

For the purposes of this Standard, the following term and definition applies.

3.1

organically bound halogens

total content of the halogens chlorine, bromine and iodine in the organic matter of sludge and sediments, which are determined under the conditions specified in this standard

NOTE They are expressed in mg chlorine per kg dry mass. EOX: extractable organically bound halogens.

4 Principle

The extractable organically bound halogens (EOX) are determined after freeze-drying by extraction with *n*-hexane and combustion in an oxygen stream. This results in the conversion of the organically bound halogens to hydrohalogens, the content by mass of which is determined.

5 Interference

To prevent losses of EOX no plastic containers shall be used for sampling.

To prevent contamination with halogenated hydrocarbons, the samples shall be examined only in enclosed parts of laboratories where no work carried out involves the handling of halogenated hydrocarbons or none of them is stored.

For the same reason, extracts should be mineralized immediately after their preparation. Storage in refrigerators may lead to contamination by cooling agents (coolants).

6 Designation

The designation of the method for determination of extractable organically bound halogens (EOX) (S 17) is:

Method DIN 38414-S 17

7 Reagents

7.1 General

Use only reagents of analytical grade and water of grade 1 according to DIN ISO 3696.

The extractants and desiccants specified in 7.2, 7.3 and 7.11 and the gases (7.4 and 7.5) shall be checked for their purity to ensure that the content of organically bound halogens is negligible compared with the lowest EOX content to be determined.

7.2 *n*-Hexane, C₆H₁₄, alternatively ***n*-pentane**, C₅H₁₂, or ***n*-heptane**, C₇H₁₆ (see 7.1)

7.3 Sodium sulphate, Na₂SO₄ (see 7.1)

7.4 Nitrogen, N₂, alternatively **argon**, Ar (see 7.1)

7.5 Oxygen, O₂ (see 7.1)

7.6 Decachlorobiphenyl (PCB-209), C₁₂Cl₁₀

7.7 Decachlorobiphenyl standard solution, ρ(Cl) = 10 mg/l

Weigh 14,4 mg of decachlorobiphenyl (7.6) into a 1 000 ml volumetric flask; make up to the mark with *n*-hexane, *n*-pentane or *n*-heptane (7.2)

7.8 p-Chlorophenol, C_6H_5ClO

7.9 Chlorophenol stock solution, $\rho(Cl) = 100 \text{ mg/l}$

Weigh 36,3 mg of chlorophenol (7.8) into a 1 000 ml volumetric flask; make up to the mark with *n*-hexane, *n*-pentane or *n*-heptane (7.2).

This solution can be stored for one month.

Note Alternatively to p-chlorophenol certified standard solutions with known content of EOX may be used. A suitable example for this are aldrin standards.

7.10 Chlorophenol standard solution, $\rho(Cl) = 10 \text{ mg/l}$.

Pipette 10 ml of the chlorophenol stock solution (7.9) into a 100 ml volumetric flask and make up to the mark with *n*-hexane, *n*-pentane or *n*-heptane (7.2).

This solution can be stored for about one week.

7.11 Hydrochloric acid, $c(HCl) = 0,01 \text{ mol/l}$.

7.12 Sulphuric acid, $\rho(H_2SO_4) = 1,84 \text{ g/ml}$ (see 7.1).

8 Apparatus

8.1 Wide neck (mouth), flat bottom flask (brown), nominal capacity of 500 ml or 1 000 ml, e.g. laboratory bottle ISO 4796-2—500 WS with stopper according DIN 12252.

8.2 Milling device, e.g. ball mill.

8.3 Volumetric flasks, nominal capacity of 10 ml, 25 ml, 50 ml, 100 ml and 1 000 ml, e.g. volumetric flask ISO 1042—A50—C.

8.4 Measuring pipettes, nominal capacity of 2 ml and 10 ml, e.g. pipette DIN 12697—MPAS 2—002.

8.5 Oven (drying cabinet).

8.6 Deep freezer, capable of cooling down to at least $-35 \text{ }^\circ\text{C}$, performance according to DIN 38414.

8.7 Freeze dryer, capability $\leq 37 \text{ Pa}$ according to DIN 38414-22.

8.8 Flat trays, made of aluminium or stainless steel, e.g. 20 cm diameter, rim height approximately 2,5 cm.

8.9 Flat sieves, made of stainless steel, 0,2 mm mesh size.

8.10 Desiccator, e.g. desiccator DIN 12491-200.

8.11 Extraction apparatus, e.g. consisting of:

- round bottom(ed) flask, nominal capacity of 100 ml, e.g. round-bottom flask according to ISO 4797;
- Soxhlet extractor, 30 ml nominal capacity, e.g. extractor DIN 12602—30;
- Dimroth condenser, e.g. condenser DIN 12591—D 250—29;

- heating bath.

8.12 Extraction thimbles, e.g. according to DIN 12449.

8.13 Combustion apparatus according to ISO 9562.

8.14 Halide detection apparatus, e.g. microcoulometer.

8.15 Rotary (film) evaporator with constant vacuum control.

9 Procedure

9.1 Sampling

- Before use, clean the flasks and remove any solvent under a hood, then place them upside down in a ventilated oven and bake them at 150 °C for not less than 1 h.

- Pour the sludge and sediment samples into brown wide neck, flat bottom flasks with solid ground glass stoppers.

- Process the samples immediately.

If this is not possible, samples shall be stored in the dark at 4 °C until the analysis is carried out.

9.2 Sample preparation

With a separate sample portion determine the dry residue according to DIN EN 12880 before performing the examination.

9.2.1 Drying

According to DIN 38414-22:

- Deep freeze the sample, which has been homogenised, e.g. by stirring, at a temperature of at least -35 °C and then freeze-dry until constant mass.

- Grind the dry sample to a particle size ≤ 2 mm using a suitable milling device.

9.2.2 Extraction

- Extract a defined mass, e.g. 20 g, of the sample dried according to 9.2.1 with 75 ml *n*-hexane (7.2) for at least 8 h (approximately 100 extraction cycles) in a Soxhlet extractor. Before extraction determine the residual water content of the dried sample according to DIN EN 12880 and take it into account when expressing the result.

- For residual water contents of >2 % perform chemical drying by triturating with anhydrous sodium sulphate (7.3).

- Reduce the extract to approximately 10 ml in a rotary evaporator, transfer it into a measuring flask and make up to the mark with *n*-hexane.

9.2.3 Extraction for determination of blank value

- Subject 75 ml *n*-hexane (7.2) to the procedure according to 9.2.2.

9.3 Determination of EOX content

The method involves the combustion of the organic solution, determining of halides in the combustion condensate and checking the mineralization:

- To avoid blockades of the injection syringe and to ensure mineralization free of interference dilute the extracts of heavily matrix effected samples before combustion using *n*-hexane (7.2).
- For this combust by controlled injection an aliquot of extract (e.g. 200 µl) in the combustion apparatus (8.13) in an oxygen stream.
- To check for reproducibility of mineralization carry out duplicate determinations.

For this purpose EOX values shall not differ from each other by more then 10 %.

For the whole duration of analysis the temperature in the combustion chamber shall be at least at 950 °C while all other parameters and injection conditions are chosen according to the manufacturer's instructions.

- Connect the gas supply line to the combustion tube and the combustion tube to the absorber.

Warning — Avoid back flow of sulphuric acid into the combustion tube. This may occur in case of temperature or pressure drop.

- Set gas flow (rate) to 150 ml/min.
- By controlled injection combust an aliquot of extract (e.g. 200 µl) in the combustion apparatus (8.13) in an oxygen stream.

Warning — Pay attention to advises of the manufacturers of equipment.

Examples for injection conditions:

EXAMPLE 1

- Inject into a injection chamber which is purged with nitrogen (7.4) and heated to about 500 °C over a platinum gauze as catalyst (e.g. 2 min injection time).
- Then increase the injection chamber temperature from 500 °C to at least 950 °C (e.g. 5 min heating time) and replace the nitrogen used for purging in order to ensure complete mineralization.

EXAMPLE 2

- Inject into an injection module with multistage expansion chambers, heated to 500 °C and purged with a mixture of oxygen (7.5) and argon (7.4).
- Then let the gases pass a coil-shaped high temperature zone (1 300 °C) and allow them to mineralize at excess of oxygen.

During coulometric determination combustion gases pass an absorber loaded with concentrated sulphuric acid and subsequently are introduced into the microcoulometer.

- Modify the test of the combustion apparatus accordingly.
- For testing the combustion apparatus analyse six standard solutions of each (7.7 and 7.10) with known chlorine concentration (*mlm*).

A recovery (rate) of 95 % to 105 % should be reached. A check of a measuring point in the central region of working range is sufficient for the regular test of the whole system.

If necessary, completeness of recovery may be checked by doping, e.g. with PCB 209, a sludge or sediment sample free of EOX.

NOTE Equivalent mineralization methods, such as the determination according to DIN 38409-8, are permitted.

9.4 Test of measuring apparatus for determination of halide concentration

- Carry out the test of the measuring apparatus for the determination of halide concentration according to DIN 38409-22 as follows:

In case of microcoulometric determination the measuring device should be tested every working day within the relevant working range by using at least one test solution.

- Inject directly a volume (between 50 μl to 80 μl) of hydrochloric acid (7.11) into the titration cell.
- Measure the charge quantity transformed in this test.

Coulometry assumes a 100 % electrical (current) efficiency. Test quantity a is obtained using equation (1):

$$a = Q/Q_t \quad (1)$$

where

a is the test quantity;

Q is the transformed charge quantity measured for the hydrochloric acid sample, in Coulomb (C);

Q_t is the theoretical charge quantity for the hydrochloric acid sample, in Coulomb (C).

The theoretical charge quantity Q_t is calculated using equation (2):

$$Q_t = V \cdot c_{\text{Cl}} \cdot F \quad (2)$$

where

Q_t see equation (1);

V is the volume of the hydrochloric acid sample, in litre (l);

c_{Cl} is the chlorine concentration of the hydrochloric acid sample, in mole per litre (mol/l);

F is the Faraday's constant, $F = 96\,487\text{ C/mol}$.

If the test quantity lies in the range between 0,97 and 1,03, measuring equipment is suitable for analysis.

9.5 Plotting the reference graph required for evaluation

- Plot the reference (calibration) graph as described in DIN 38409-8.

10 Evaluation

The content of mass of the extractable organic bound halogens, related to dry mass, is calculated using equation (3):

$$\varpi = \frac{(N_1 - N_0) \cdot V_{E1}}{m_T \cdot F_T \cdot V_{E2}} \quad (3)$$

where

ϖ is the content (*m/m*) of EOX in the sample, expressed as chlorine, in milligram per kilogram (mg/kg);

N_1 is the measured value for the combustion products of the sample extract (9.3), in microgram (μg);

N_0 is the measured value for the combustion products of the blank (value) extract (9.3), in microgram (μg);

V_{E1} is the total volume of the extract (9.2.2), in millilitre (ml);

V_{E2} is the aliquot (volume) of extract used for combustion, in millilitre (ml);

m_T is the dry mass of the used sludge or sediment sample, in gram (g);

F_T is the dry mass content according to DIN EN 12880.

11 Expression of results

Analytical results obtained by application of this standard incorporate an uncertainty, which has to be considered when interpreting the results. For the determination of the measuring uncertainty procedures have been developed, which allow for estimation of this uncertainty from quality management measures (range or average-value control cards) as well as for validation and acceptance trials. Measuring uncertainty is preferably expressed as extended measuring uncertainty. For this purpose the determined combined standard measuring uncertainty, expressed as standard deviation or coefficient of variation, is multiplied by an extension factor of 2. This corresponds to a confidence level of approximately 95 %.

For the estimation of measuring uncertainty in the present standard the reproducibility coefficients of variation CV_R are used and multiplied with 2 (see table "characteristics of method"). The extended measuring uncertainty U of the method derived from it can only serve for orientation and cannot replace the estimation of the inherent measuring uncertainty from laboratory-internal data.

NOTE The measuring uncertainty depends on concentration and matrix and has its highest values in the lower application range.

The values of EOX concentration of the sample examined, expressed as chlorine, are rounded as follows but not expressed with more than 2 significant digits:

Example ϖ : 0,2 mg/kg to 10 mg/kg rounded to 0,1 mg/kg;
10 mg/kg to 100 mg/kg rounded to 1 mg/kg;
>100 mg/kg rounded to 10 mg/kg

12 Test report

The analytical report shall refer to this standard and include the following information:

- a) identification of the sample analysed;
- b) EOX concentration in accordance with clause 11 and dry residue according to DIN EN 12880;
- c) any circumstances that might have affected the results.

13 Characteristics of method

The characteristics of method will be introduced after performance of the interlaboratory trial.

Annex A (informative)

Explanatory notes

This standard incorporates the following German standard method jointly prepared by the Normenausschuss Wasserwesen (NAW, Water Practice Standards Committee) of DIN and the Wasserchemische Gesellschaft (Society of Water Chemistry) — a study group within the Gesellschaft Deutscher Chemiker:

"Determination of extractable organically bound halogens (EOX) (S 17)"

Standard methods published as DIN Standards are obtainable from Beuth Verlag GmbH, either individually or grouped in volumes. Furthermore, the standard methods included in the loose-leaf publication entitled "Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung" are published by Beuth Verlag GmbH in cooperation with Wiley-VCH Verlag.

All standard methods relevant for the Abwasserverordnung (AbwV, German Waste water regulation) — included in the new regulation regarding to § 7a of the Wasserhaushaltsgesetz (WHG, German Water Management Act) about "Anforderungen an das Einleiten von Abwasser in Gewässer und zur Anpassung des Abwasserabgabengesetzes" (requirements for the discharge (introduction) waste water into (natural) waters and the adaptation of the waste water tax law) — are published together with the AbwV and the WHG and all further applicable regulations for waste water management as loose-leaf publication "Analyseverfahren in der Abwasserverordnung — Rechtsvorschriften und Normen" accompanied by supplementary volume 1 (DIN Standards), supplementary volume 2 (DIN EN and DIN EN ISO Standards and supplementary volume 3 (DIN, DIN EN and DIN EN ISO Standards).

Standard methods or draft standards bearing the group title 'German standard methods for the examination of water, waste water and sludge' are classified under the following categories (main titles):

General information (group A) (DIN 38402)

Sensoric methods (group B) (DIN 38403)

Physical and physicochemical parameters (group C) (DIN 38404)

Anions (group D) (DIN 38405)

Cations (group E) (DIN 38406)

Substance group analysis (group F) (DIN 38407)

Gaseous constituents (group G) (DIN 38408)

Parameters characterizing effects and substances (group H) (DIN 38409)

Biological-ecological methods of analysis (group M) (DIN 38410)

Microbiological methods (group K) (DIN 38411)

Bio-assays (group L) (DIN 38412)

Individual constituents (group P) (DIN 38413)

Sludge and sediments (group S) (DIN 38414)

Suborganismic test methods (group T)(DIN 38415)

Next to the test methods standardized in the standard series DIN 38402 to DIN 38415 exist several European and International Standards as DIN EN and DIN EN ISO and DIN ISO standards, which are part of the "German standard methods".

Information on Parts of these series of standards that have already been published can be obtained from the offices of the Normenausschuss Wasserwesen (NAW) in the DIN Deutsches Institut für Normung e.V., telephone (030) 26 01-24 48, or from Beuth Verlag GmbH, D-10772 Berlin (residence: Burggrafenstr. 6, 10787 Berlin).

Bibliography

DIN 38414-18, *German standard methods for the examination of water, waste water and sludge; sludge and sediments (group S) — Determination of adsorbed organically bound halogens (AOX) (S 18).*