BRITISH STANDARD

BS EN
13342:2000

Characterization of sludges — Determination of Kjeldahl nitrogen

The European Standard EN 13342:2000 has the status of a British Standard

ICS 13.030.20

National foreword

This British Standard is the official English language version of EN 13342:2000.

The UK participation in its preparation was entrusted to Technical Committee EH/5, Sludge characterization, which has the responsibility to:

— aid enquirers to understand the text;

— present to the responsible European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;

— monitor related international and European developments and promulgate them in the UK.

A list of organizations represented on this committee can be obtained on request to its secretary.

Further information

Users of this standard are informed that the UK submitted some substantial comments at the final voting stage of the draft EN for the following reasons.

1) In annex A, it is essential that the description of the four samples used in the inter-laboratory comparison is given. This can be achieved by the addition of a simple footnote. It is recommended that this topic is discussed at the TC308 meeting in Utrecht. A documented minimum requirement for inter-laboratory comparisons is needed.

2) The following note should be added to the scope: "The validation for this standard has only been carried out using materials as described in annex A. For other sludges, the user should validate the method using recovery and reproducibility tests".

3) The date that the laboratory inter-comparison was carried out should be also given.

4) The final phrase "and sludge products", in the first sentence of the scope should be removed as it is inappropriate.

5) In **5.1**, suggest replacing the first sentence, "The digestion fails to determine nitrogen in the form ....", with "The digestion may fail to fully recover nitrogen in the form of ....". Also suggest that a cross-reference to the UK Blue Book method be made. This has a useful introductory historical section (**A1**) on recoveries of "difficult" nitrogen species using the Kjeldahl method. [Kjeldahl Nitrogen in Waters 1987, HMSO 1988, ISBN 0 11 752129 9]

6) In annex A:

(i) CV_R, in column **6**, should be CV_r in all three language versions:

(ii) all of the English and German coefficients of variation of both reproducibility (CV_R) and repeatability (CV_r) are wrongly calculated. The values are wrong by up to a factor three, which is to high.

This British Standard, having been prepared under the direction of the Health and Environment Sector Committee, was published under the authority of the Standards Committee and comes into effect on 15 October 2000

ISBN 0 580 36290 6

Amendments issued since publication

Amd. No.	Date	Comments

7) In the section on Analytical Quality Control (AQC), it is recommended that an additional brief section be added on the use of adequate AQC as per CEN/TC223 methods: "The analysis described in this standard should be carried out within a Quality Control system utilizing Analytical Quality Control measures. Where perfomance data is absent for the sample type, at a minimum recovery and reproducibility data should be obtained".

Cross-references

The British Standards which implement international or European publications referred to in this document may be found in the BSI Standards Catalogue under the section entitled "International Standards Correspondence Index", or by using the "Find" facility of the BSI Standards Electronic Catalogue.

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EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

EN 13342

August 2000

ICS 13.030.20

English version

Characterization of sludges - Determination of Kjeldahl nitrogen

Caractérisation des boues - Détermination de l'azote Kjeldahl

Charakterisierung von Schlämmen - Bestimmung des Stickstoffs nach Kjeldahl

This European Standard was approved by CEN on 5 August 2000.

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This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Central Secretariat has the same status as the official versions.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

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Ref. No. EN 13342:2000 E

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Foreword

This European Standard has been prepared by Technical Committee CEN/TC 308, Characterization of sludges, the Secretariat of which is held by AFNOR.

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 February 2001, and conflicting national standards shall be withdrawn at the latest by February 2001.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

The annex A is informative.

Introduction

Because sludge may be applied to land as a nutrient or as a disposal route, there is a need to monitor nitrogen content and application rates.

1 Scope

This method describes a procedure for the determination of "Kjeldahl Nitrogen" in sludge and sludge products. The digestion is catalysed by selenium or copper, the temperature being raised by a high concentration of sodium sulphate.

Although wet samples are normally taken for analysis, it is recognized practice to report results on a dry mass basis (g/kg). Consequently, it is also necessary to determine the dry residue of the homogenized sample used for analysis (see EN 12880).

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 amendments 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 12880, *Characterization of sludges – Determination of dry residue and water content*.

EN 25663, *Water quality – Determination of Kjeldahl nitrogen – Method after mineralization with selenium* (ISO 5663:1984).

EN ISO 3696, *Water for analytical laboratory use – Specification and test methods* (ISO 3696:1987).

EN ISO 5667-13, *Water quality – Sampling – Part 13: Guidance on sampling of sludges from sewage and water-treatment works* (ISO 5667-13:1997).

ISO 5664, *Water quality – Determination of ammonium – Distillation and titration method*.

3 Terms and definitions

For the purposes of this European Standard, the following terms and definitions apply.

3.1
Kjeldahl nitrogen
nitrogen that is contributed by free ammonia, inorganic ammonia compounds and those types of organic nitrogen compounds that are converted to ammonium sulphate by the digestion process described (catalysed sulphuric acid digestion)

3.2
dry residue
the dry mass portion of the sludge obtained after the specified drying process. It is expressed in percent or in grams per kilogram (see EN 12880)

4 Principle

Rigorous acid digestion of the sample in the presence of selenium or copper converts most nitrogen compounds present to ammonium sulphate. Sodium sulphate is added to raise the digest to the appropriate temperature.

Distillation of the digest under alkaline conditions into excess dilute sulphuric acid (or excess boric acid) liberates the ammonia giving a solution of ammonium sulphate (or ammonium borate). This solution can then be analysed for ammonia using the appropriate method (see ISO 5664 and EN 25663).

5 Limitations and interferences

5.1 Limitations

The digestion fails to determine nitrogen in the form of azide, azine, azo-compounds, hydrazine, nitrate, nitrite, nitroso-compounds, oxime, semi-carbazone and nitrile.

5.2 Nitrate/Nitrite

The presence of nitrate or nitrite may cause erratic results, but not at the levels normally found in sludge.

6 Reagents

During the analysis, use water of purity grade 2 as specified in EN ISO 3696 and reagents of recognized analytical grade.

6.1 Sulphuric acid, H_2SO_4, ρ = 1,84 g/ml.

6.2 Digestion catalyst.

6.2.1 General

Previous experience has shown that equivalent results can be obtained using a less toxic copper catalyst (6.2.3) in place of the selenium catalyst (6.2.2). However, before employing this catalyst, the user should demonstrate that equivalent results can be obtained for the typical range of sludges analysed. If the results are to be used for legal purposes or to resolve trade disputes, then the selenium catalyst should be used. The selenium catalyst method should be regarded as the absolute reference method. For the vast majority of sludges, the copper catalyst should give fit for purpose results.

6.2.2 Selenium catalyst

Thoroughly mix (1 000 ± 20) g of anhydrous sodium sulphate with (50 ± 1) g of selenium powder or previously ground selenium pellets.

WARNING This mixture is toxic. Inhalation of any dust resulting from its preparation or use shall be avoided. All residues containing selenium shall be collected for selenium recovery or controlled disposal.

NOTE This catalyst is commercially available as tablets.

6.2.3 Copper catalyst (see 6.2.1)

Thoroughly mix (1 000 ± 20) g of anhydrous sodium sulphate with (100 ± 2) g of copper sulphate pentahydrate ($CuSO_4 \cdot 5H_2O$).

NOTE This catalyst is commercially available as tablets.

6.3 Sodium hydroxide solution

Cautiously add approximately 800 ml of water to (500 ± 20) g of sodium hydroxide pellets contained in a plastics beaker, with stirring and dissolve. It is strongly recommended that the outside of the beaker is cooled with running cold water whilst adding the 800 ml of water. When cooled, dilute with water to 1 000 ml in a stoppered measurement cylinder. Store in a polyethylene bottle.

6.4 Ammonia receiving reagents

6.4.1 General

A reagent for a colorimetric and a reagent for a titrimetric endpoint are given.

6.4.2 **Sulphuric acid,** solution $c(H_2SO_4)$ = 0,05 mol/l (colorimetric endpoint)

Add (2,8 ± 0,1) ml of sulphuric acid (6,1) to 800 ml water (6.5) and dilute with water to (1 000 ± 5) ml.

6.4.3 Boric acid solution, H_3BO_3 40g/l (titrimetric endpoint)

Add (40 ± 1) g of boric acid to 800 ml water and dissolve. Add 6 ml pH 4,5 indicator solution and dilute to (1 000 ± 5) ml with water. One drop of 0,1 mol/l sodium hydroxide should be sufficient to change the colour of 20 ml of this reagent from purple to green. If not discard and prepare freshly.

NOTE This solution is commercially available.

7 Apparatus

7.1 Digestion vessels

The digestion vessel shall be suitable for the mass or volume of the test portion used. For example:

Kjeldahl destillation flasks, 300 ml nominal capacity;

or

Glass digestion tubes, 250 ml capacity for use with a temperature controlled heating block.

7.2 Heating device

Kjeldahl flasks can be heated singly or more usually, in a rack carrying several vessels, by use of either a Bunsen burner or electric heating mantle. It is important, however, that the glass surface above the digestion mixture receives no direct heating.

Heating blocks capable of maintaining a temperature sufficient to reflux the digestion mixture are commercially available. These hold typically up to 24 digestion tubes allowing for high laboratory throughput.

7.3 Distillation apparatus

The digestion vessel should be suitable for direct attachment to glass apparatus incorporating an anti-splash distillation head, a vertical water condenser and a delivery tube, the outlet of which is submerged in the absorbent solution.

Commercial automatic Kjeldahl steam distillation apparatus is suitable for this determination.

7.4 Boiling aids

Anti-bumping granules or glass beads.

8 Sample pretreatment

Drying of sludge will tend to deplete free ammonia and, depending on the pH, ammonium salts. For this reason, a test portion of a wet homogenized sample shall be used (see EN ISO 5667-13).

9 Procedure

9.1 Transfer a known mass of homogenized, wet sludge (equivalent to 0,25 g to 0,5 g of dry mass) to a digestion vessel (7.1).

A blank shall be run by substituting 5 ml of water instead of the wet sludge with each batch of samples.

NOTE For paste-like sludges, nitrogen-free paper can be used for sample transfer to the digestion vessel (7.1).

9.2 Add (5,0 ± 0,1) g of catalyst mixture (6.2) (or equivalent commercial tablets) and 2 or 3 anti-bumping aids (7.4).

9.3 Cautiously add (10 ± 0,5) ml of sulphuric acid (6.1), gently swirling the vessel.

9.4 Heat the vessel slowly in an extracted area (e.g. fume cupboard) to drive off the water present and while any foaming subsides.

9.5 Heat the vessel more strongly to maintain a brisk boiling. The sulphuric acid should reflux up to about half way along the neck of the vessel. White fumes of sulphur trioxide should be visible above the liquid.

NOTE If commercial digestion equipment is used, the manufacturer's instructions should be followed.

9.6 The contents of the vessel should eventually become clear or straw coloured. Continue the digestion for at least a further 60 min.

9.7 Allow the digest to cool and cautiously add (40 ± 5) ml of water whilst gently swirling the vessel in order to avoid crystallization of the digest.

9.8 If the digestion vessel (7.1) is suitable for direct attachment to the distillation apparatus, make up to approximately two thirds of its volume with water. If not, transfer the digest quantitatively to a Kjeldahl distillation flask adapted to the distillation (7.3) and make up to approximately two thirds of its volume with water (6.5).

9.9 Assemble the distillation apparatus adding 50 ml of 0,05 mol/l sulphuric acid (6.4.2) or 50 ml of boric acid (6.4.3) to the receiver flask, and ensure that the delivery tube is below the acid surface.

9.10 Cautiously add (30 ± 2) ml of sodium hydroxide solution (6.3) down the side of the distillation flask leading to two distinct layers. Assemble the apparatus and swirl the flask carefully to mix the contents without losing any liberated ammonia.

NOTE This step may not be necessary for commercial automatic distillation apparatus; the manufacturer's instructions should be followed.

9.11 Heat the flask so that distillation proceeds at about 10 ml/min.

NOTE For commercial systems, the manufacturer's instructions should be followed.

9.12 Collect about 120 ml of distillate then lower the receiver so that the delivery tube is above the acid surface, and collect a further 30 ml of distillate.

NOTE For commercial systems, the manufacturer's instructions should be followed.

9.13 Stop the distillation and wash the delivery tube into the receiving flask with about 5 ml of water.

9.14 If necessary, dilute the distillate to a known volume with water and mix well.

NOTE For the titrimetric endpoint, the whole distillate can be titrated with acid. See clause 10.

9.15 Use the solution from 9.14 to determine the ammonia-nitrogen content of the made-up distillate in accordance with ISO 5664 or EN 25663.

NOTE Tryptophan ($C_{11}H_{12}N_2O_2$) or glycine ($C_2H_5NO_2$) can be used for checking the method efficiency. Ammonium sulphate (NH_4SO_4) can be used for checking the distillation efficiency. These three substances should be dried at 105 °C for at least two hours prior to use.

10 Expression of results

10.1 Calculation

10.1.1 Colorimetric determination

The Kjeldahl nitrogen content (N) is expressed in grams per kilogram dry mass and is given by equation (1):

$$N = \frac{(C - B) \times V}{m \times 10 \times W_{DR}} \quad (1)$$

where

C is the ammonia-nitrogen content of the made-up distillate, in milligrams per litre (9.15);

B is the result for the blank determination (9.1) of the made-up distillate, in milligrams per litre;

m is the wet mass of sample taken for digest, in grams;

V is the final volume of distillate, in millilitres;

W_{DR} is the dry residue of the sludge determined in accordance with EN 12880, in percent.

10.1.2 Titrimetric determination

The Kjeldahl nitrogen content (N) is expressed in grams per kilogram dry mass and is given for titration of the whole distillate by equation (2):

$$N = \frac{(V_1 - V_2) \times c \times 14{,}01}{m \times W_{DR}} \times 100 \quad (2)$$

where

c is the concentration of hydrochlorid acid in moles per litre;

V_1 is the titration volume, in millilitres;

V_2 is the titration volume of the blank sample, in millilitre;

m is the wet mass of sample taken for digest in grams;

W_{DR} is the dry residue content of the sludge determined in accordance with EN 12880, in percent;

14,01 is the atomic mass of nitrogen.

10.2 Precision data

See annex A.

11 Test report

The test report shall contain the following information:

a) reference to this European Standard;

b) all information necessary for complete identification of the sludge sample;

c) details of sample pre-treatment, if carried out;

d) results of the determination according to clause 10;

e) any detail not specified in this European Standard and any other factor which may have affected the results.

Annex A
(informative)

Performance data of interlaboratory comparison

The below data were determined within the frame of a joint interlaboratory comparison for the parameters "loss on ignition of dry mass" (EN 12879), "dry residue and water content" (EN 12880) and pH-value (EN 12176) and for this standard "Kjeldahl nitrogen".

Table A.1 — Precision data for Kjeldahl nitrogen

Sample	l	n	NAP %	$\overline{X}$ g/kg m_{dr}	σ_R g/kg m_{dr}	VC_R %	σ_r g/kg m_{dr}	VC_r %
1	4	17	0	28,48	2,15	16,84	2,13	12,65
2	4	15	0	21,87	3,22	16,30	3,5	21,47
3	4	15	0	27,52	1,07	9,81	0,7	7,13
4	4	15	0	16,28	0,718	13,58	0,65	4,79

l is the number of laboratories;

n is the number of values;

NAP is the percentage of outliers;

$\overline{X}$ is the overall mean;

σ_R is the standard deviation of reproducibility;

VC_R is the coefficient of variation of reproducibility;

σ_r is the standard deviation of repeatability;

VC_r is the coefficient of variation repeatability;

m_{dr} is the dry mass.

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