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Durability of wood and wood-based products — Quantitative determination of quaternary ammonium compounds in wood

ICS 79.080

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TECHNICAL REPORT

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English Version

Durability of wood and wood-based products - Quantitative determination of quaternary ammonium compounds in wood

Durabilité du bois et des matériaux dérivés du bois - Détermination quantitative des composés ammonium quaternaire dans le bois

Dauerhaftigkeit von Holz und Holzprodukten - Quantitative Bestimmung von quartären Ammoniumverbindungen in Holz

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Foreword

This Technical Report (CEN/TR 15314:2006) has been prepared by Technical Committee CEN/TC 38 “Durability of wood and wood-based products”, the secretariat of which is held by AFNOR.

Introduction

At present, no standardised method for the analysis of quaternary ammonium compounds (QAC) in wood is recognised in Europe. Only a few national standards are available world wide, e.g. ASTM D5584-94, AWPA A 16-93 or AWPA A 18-04.

This CEN Technical Report has been issued in order to facilitate the analysis of QAC-treated wood.

1 Scope

This CEN Technical Report specifies a laboratory method of determining the content of quaternary ammonium compounds in commercially QAC-treated wood. The method described has a measurement range up to QAC contents of 1 500 mg/kg of dry matter.

NOTE 1 This method may need some modifications with some wood species such as hardwoods.

NOTE 2 It is applicable to QAC with a molar mass ranging between 200 g/mol and 500 g/mol.

NOTE 3 The method has a quantification limit corresponding to 250 mg of QAC per kilogram of wood expressed as dry matter.

2 Normative references

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

EN 322, *Wood-based panel — Determination of moisture content*

EN ISO 1042, *Laboratory glassware — One-mark volumetric flasks (ISO 1042:1998)*

EN ISO 2871-2:1994, *Surface active agents — Detergents — Determination of cationic-active matter content — Part 2: Cationic active matter of low molecular mass (between 200 and 500) (ISO 2871-2:1990)*

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

EN ISO 4788, *Laboratory glassware —Graduated measuring cylinders (ISO 4788:2005)*

ISO 385-1, *Laboratory glassware — Burettes — Part 1: General requirements*

ISO 648, *Laboratory glassware —One-mark pipettes*

ISO 835-2, *Laboratory glassware — Graduated pipettes — Part 2: Pipettes for which no waiting time is specified*

3 Safety precautions

Persons using this method shall be familiar with normal analytical laboratory procedures and practice.

This method does not purport to address all the safety problems, if any, associated with its use.

It is the responsibility of the user to establish health and safety practices and to ensure compliance with any.

European or national regulatory conditions (also see Annex B for environmental, health and safety precautions) shall be taken into account.

4 Principle

The quaternary ammonium compound is extracted from the wood material using a mixture of methanol and hydrochloric acid in an ultrasonic bath.

The quaternary ammonium compound (cationic substance) is quantified by titration with an anionic surface active agent standard solution (sodium dodecyl sulfate) containing a mixture of a cationic and an anionic dye. The titration is performed in a 2-phase system consisting of water and trichloromethane according to EN ISO 2871-2. Cationic substances and the anionic dye (disulphine blue VN 150) constitute a salt which is soluble in trichloromethane and results in a blue colour.

The anionic dye in the salt is replaced gradually by the anionic surface active agent during the titration process leading to a discoloration of the organic phase at equivalence point. At the same time the disulphine blue moves into the water.

NOTE 1 Cationic surface active agents as well as other disulphine blue active substances will also react with the titrant and be determined as QAC.

NOTE 2 In order to determine the mass of QAC its molar mass is required.

5 Reagents

During the analysis, unless, otherwise specified, use only reagents of recognised analytical grade that have been checked in advance as to not interfere with the analytical results, and water complying with grade 3 as defined in EN ISO 3696.

5.1 Trichloromethane (CAS 67-66-3) ($CHCl_3$).

5.2 Methanol (CH_3OH).

NOTE Other solvents may be used instead of methanol as some extraction difficulties can occur with some wood species (e.g. hardwoods). It is recommended to cross check the extraction efficiency of any other solvent or solvent mixture with that of methanol / hydrochloric acid used.

5.3 Dimidiumbromide (CAS 518-67-2) ($C_{20}H_{18}BrN_3$).

5.4 Disulphine blue VN 150 (CAS 129-17-9) ($C_{27}H_{31}N_2S_2O_6Na$).

5.5 Sodium dodecyl sulfate for analysis of surface active agents (CAS 151-21-3) ($C_{12}H_{25}SO_4Na$).

5.6 Hydrochloric acid solution, c(HCl) = 1 mol/l.

Dilute 9 ml of concentrated hydrochloric acid (ρ_{20} = 1,18 g/ml) to 100 ml with water.

NOTE Test ampoules containing a definite amount may be used for the preparation of the hydrochloric acid solution instead of concentrated hydrochloric acid.

5.7 Ethanol, (C_2H_5OH) aqueous solution volume fraction 10 %.

Add 30 ml of ethanol to 270 ml of water and mix well.

5.8 Sulfuric acid, solution $c(H_2SO_4)$= 2,5 mol/l.

Cautiously add, with stirring and cooling, 14 ml of concentrated sulfuric acid (ρ_{20} = 1,84 g/ml) to about 80 ml of water and dilute to 100 ml with water.

NOTE Test ampoules containing a definite amount may be used for the preparation of the sulfuric acid solution instead of concentrated sulfuric acid.

6 Apparatus

Ordinary laboratory apparatus and the following.

NOTE Glassware should be thoroughly cleaned prior to use by means of ethanol.

6.1 Analytical balance, accurate to 0,1 mg.

6.2 Ultra-sonic bath.

6.3 Volumetric glassware, of class A quality in accordance with ISO 385-1 for the burettes, ISO 835-2 and ISO 648 for the pipettes, EN ISO 4788 for the measuring cylinders and EN ISO 1042 for the volumetric flasks. The burette shall be 10 ml graduated in 0,02 ml.

6.4 Conical flasks with glass stopper, 100 ml capacity.

6.5 Polytetrafluoroethylene (PTFE) filter, porosity 0,45 µm (e.g. combined with a syringe).

6.6 Variable dispenser (5ml to 30ml).

7 Preparation of the test sample

Collect at least 20 g of the sample material taken according to e.g. EN 212. This sample material is preferably ground under mild conditions to a powder with a particle size of less than 0,5 mm diameter.

Homogenise the ground material to obtain a representative sample, and store it in a brown glass bottle with screw caps with a polytetrafluoroethylene (PTFE) insert. This is the test sample.

8 Procedure

8.1 General

It is recommended to carry out at least two parallel analyses. If the results differ by more than 10 % an additional analysis shall be made.

8.2 Standard solutions

8.2.1 Sodium dodecyl sulfate solution

Dissolve 1,442 g sodium dodecyl sulfate (5.5) in water into a 1 000 ml volumetric flask (6.3) resulting in a concentration of 0,005 mol/l.

NOTE The purity of the sodium dodecyl sulfate may be determined by the method given in 4.2.1 of EN ISO 2871-2:1994.

8.2.2 Indicator solution

Weigh (500 ± 5) mg dimidiumbromide (5.3) into a 100 ml beaker and dissolve it in 30 ml hot aqueous ethanol (5.7). Then weigh (250 ± 5) mg disulphine blue VN 150 (5.4) into a 100 ml beaker and dissolve it in 30 ml hot aqueous ethanol (5.7). After cooling, transfer both solutions quantitatively into a 250 ml volumetric flask and make up to the mark with aqueous ethanol. Transfer 20 ml of this solution into a 500 ml volumetric flask which already contains approximately 200 ml water. Finally add 20 ml of 2,5 mol/l sulfuric acid (5.8) and make up to the mark with water.

NOTE The indicator solution should be stored in the dark.

8.3 Determination of the QAC content in treated timber

8.3.1 Extraction

From the prepared timber sample (Clause 7), remove a small portion of this sample (0,5 ± 0,05) g and determine its moisture content according to EN 322; record the value obtained.

Depending on the expected QAC content, transfer 5 g to 10 g of the test sample (7) to a flask of known mass (m_1) and reweigh the flask and contents (m_2). Calculate the mass of the test sample ($m_3 = m_2 – m_1$) and add, to the nearest 0,5 ml, 7,0 times m_3 ml of methanol and, to the nearest 0,05 ml, 0,1 times m_3 ml of the hydrochloric acid (5.6).

NOTE 1 A 100 ml flask is suitable for test samples of 10 g.

Place the hydrochloric acidic suspension in an ultrasonic bath (6.2) and agitate it for 1 h. Allow the warm suspension to cool at room temperature, weigh and add methanol to give a total extract mass of 7,50 times m_3 (total mass of flask and contents is m_1 + 8,5 times m_3), to the nearest 0,1 g; record the total mass as m_4. Stopper the flask, swirl the contents vigorously and store to clear over night (at least 12 h). Remove a part of the clear solution and filter by means of a 0,45 µm PTFE-filter (6.5). Use 10 g to 30 g of the filtered solution for the quantitative determination of QAC depending on the expected concentration.

NOTE 2 Since a complete extraction is essential for a successful analysis, treated timber with a known QAC content should be analysed in parallel.

8.3.2 Sample analysis

Depending on the expected QAC concentration transfer up to 30 g of the methanolic extract into a tared conical flask (6.4) and weigh to determine the mass of extract taken (m_5). Add 20 ml water, swirl to mix and then add 15 ml trichloromethane (5.1) and 10 ml of indicator solution (8.2.2) by graduated cylinder.

Carry out the titration using the 0,005 mol/l sodium dodecyl sulfate solution (8.2.1) drop wise. Shake intensively after each drop and wait until the layers have separated again.

NOTE The aqueous layer is a light green colour near the equivalence point whereas the organic phase seems to be red-violet.

When the equivalence point is reached the addition of further sodium dodecyl sulfate results in a red-violet colour of the organic phase.

9 Calculation and expression of results

The QAC content, *w,* in moles per kilogram of the test sample is calculated using the following equation (1):

$$w = \frac{V \times c \times (m_4 - m_2)}{m_3 \times m_5} \qquad (1)$$

where

V is the volume, in millilitres, of the sodium dodecyl sulfate solution (8.2.1) used for titration;

C is the concentration of the sodium dodecyl sulfate solution (8.2.1) in moles per litre;

m_4 is the total mass of flask and contents in grams;

m_2 is the mass of flask and test sample in grams;

m_3 is the amount of test sample in grams;

m_5 is the amount of extract used for the titration, in grams.

The QAC content, w_t, in grams per kilogram of oven dry treated timber is calculated using the following equation (2):

$$w_t = \frac{w \times M \times (100 + m_c)}{100} \qquad (2)$$

where

w is the QAC content of the test sample in moles per kilogram (from equation (1));

M is the molar mass of the quaternary ammonium compound in grams per mole (see Annex C);

m_c is the percentage moisture content of the test sample (8.3.1).

The QAC content of the test sample is given in grams per kilogram of dry matter as the mean of independent determinations together with its measurement uncertainty.

10 Quality assurance

When establishing this method in the laboratory it is recommended that a reference material (RM) with a known QAC content is used for verification.

11 Precision

This method was validated in a laboratory inter-comparison with seven participating laboratories for three test samples at different levels of QAC content (see Annex A).

12 Test report

The test report shall contain the following information:

a) reference to this CEN Technical Report, i.e. CEN/TR 15314;

b) date of sampling;

c) sampling procedure followed, e.g. EN 212;

d) date of testing.

Annex A
(informative)

Ring test results

The summary of the results of the ring test with up to seven participating laboratories on three test samples with different levels of QAC is given in Table A.1[1]:

Table A.1 — Compilation of ring test results and statistics

Sample	QAC content (theoretical)	Mean value (measured)	σ_n [a]	σ_{n-1} [b]	Recovery rate (%)		
					mean	min.	max.
milled wood	1 000 mg/kg	975 mg/kg	41,117	44,413	97,5	92,9	103,1
milled wood	220 mg/kg	205,5 mg/kg	24,274	28,029	93,4	76,4	106,2
solid blocks	(3,35 ± 0,15) kg/m³	3,64 kg/m³	0,205 8	0,22	107,8	94,8	115,5

[a] σ_n is the sample standard deviation.

[b] σ_{n-1} is the population standard deviation.

[1] Further details are given in the following paper: MELCHER, E.; BORNKESSEL, C.; GUNSCHERA, J.; HAMBERG, R.; HÄRTNER, H.; MARX, H.-N.; SCHOKNECHT, U.; WITTENZELLNER, J.: The quantitative determination of quaternary ammonium compounds in treated timber – Results of an extended round robin test. Stockholm: International Research Group on Wood Preservation (IRG), 2002, 11p., Document N° IRG/WP/02-20240.

Annex B
(informative)

Environmental, health and safety precautions within chemical/biological laboratory

When preparing this CEN Technical Report, consideration was given to the minimisation of environmental impacts caused by the use of the methods of analysis.

It is the users' responsibility to use safe and proper techniques in handling materials in the methods of analysis specified in this CEN Technical Report.

The following list is not exhaustive but users of this CEN Technical Report may use it as a guide to the use of safe and proper techniques. They should:

— investigate if European Directives, transposed European legislation and national laws, regulations and administrative provisions apply;

— consult manufacturers/suppliers for specific details such as material safety data sheets and other recommendations;

— use safety equipment and wear protective clothing, usually goggles and coats, appropriate for the test product and the test chemicals, in all laboratory areas, to ensure the safety of the operator;

— be careful about flammable materials and substances that are toxic and/ or human carcinogens and generally take care during transportation, decanting, diluting and dealing with spillages;

— use a fume cupboard during preparation of organic solvent solutions;

— store, handle and dispose of chemicals in a safe and environmentally satisfactory manner: including chemicals for laboratory test, test specimens, unused solvents and reagents that have to be disposed of.

Annex C
(informative)

Determination of the molar mass of the QAC

C.1 General

If the QAC used to treat the timber is available its molar mass can simply be determined by making up a solution of known concentration and titrating it against the sodium dodecyl sulfate standard solution.

C.2 Procedure

Weigh, to the nearest 1 mg, 1,000 g of QAC (active ingredient) (m_0) and transfer it quantitatively to a 1 000 ml one-mark graduated flask and make up to the mark with water. By pipette, transfer 5,00 ml to a conical flask, add 20 ml water, swirl to mix and then add 15 ml trichloromethane (5.1) and 10 ml of indicator solution (8.2.2) by graduated cylinder.

Carry out the titration using the 0,005 mol/l sodium dodecyl sulfate solution (8.2.1). Shake vigorously after each addition and wait until the layers have separated again.

Note 1 For molar masses of 200 g/mol to 500 g/mol, the titre will be between 5 ml and 2 ml.

Note 2 The aqueous layer is a light green colour near the equivalence point whereas the organic phase changes from blue to greyish pink at the equivalence point. The addition of further sodium dodecyl sulfate results in a red-violet colour of the organic phase.

The molar mass, M, of the QAC is calculated using the following equation (C.1):

$$M = \frac{m_0 \times 5}{V \times c} \qquad \text{(C.1)}$$

where

m_0 is the mass of the test portion of QAC;

V is the volume, in millilitres, of the sodium dodecyl sulfate solution (8.2.1) used for titration;

c is the concentration of the sodium dodecyl sulfate solution (8.2.1) in moles per litre.

Bibliography

[1] ASTM D5584-94, Standard Test Methods for Chemical Analysis of Ammoniacal Copper Quat, Type B (ACQ-B) (for dodecyldimethylammoniumchloride)

[2] AWPA Standard A 18-04: Standard for Determination of Quaternary Ammonium Compounds in Wood by 2-phase Titration

[3] AWPA Standard A 16-93: Standard for HPLC Method for Didecyldimethylammonium Chloride Determination in Treated Wood

[4] EN 212, *Wood preservatives — General guidance on sampling and preparation for analysis of wood preservatives and treated timber*

NOTE For further information, technical data or references: www.dgfh.de/index2.html under “Publikationen” and there “Veröffentlichungen zum Download”

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