

AS/NZS 1604.3:2021



Australian/New Zealand Standard™

Preservative-treated wood-based products

Part 3: Test methods



AS/NZS 1604.3:2021

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- Australian Forest Products Association
- Australian Timber Flooring Association
- Australian Timber Importers Federation
- Building Research Association of New Zealand
- Engineered Wood Products Association of Australasia
- Forest and Wood Products Australia
- Forestry Corporation of NSW
- Glued Laminated Timber Association of Australia
- Ministry of Business, Innovation and Employment (NZ)
- National Centre for Timber Durability and Design Life
- NATSPEC
- New Zealand Timber Industry Federation
- New Zealand Timber Preservation Council
- New Zealand Wood Processors Association
- Responsible Care New Zealand
- Scion
- Tasmanian Timber Promotion Board
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Australian/New Zealand Standard™

Preservative-treated wood-based products

Part 3: Test methods

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Preface

This Standard was prepared by the Joint Standards Australia/Standards New Zealand Committee TM-012, Timber Grading and Preservation, to supersede AS/NZS 1605.1:2018, *Methods for sampling and analysing timber preservatives and preservative-treated timber, Part 1: General requirements, sampling, and determination of sapwood and heartwood presence*, AS/NZS 1605.2:2018, *Methods for sampling and analysing timber preservatives and preservative-treated timber, Part 2: Determination of preservative penetration by spot tests*, AS/NZS 1605.3:2018, *Methods for sampling and analysing timber preservatives and preservative-treated timber, Part 3: Analysis methods for determination of preservative retention* and AS/NZS 1605.4:2018, *Methods for sampling and analysing timber preservatives and preservative-treated timber, Part 4: Analysis methods for determination of preservative solution concentration*.

The objective of this Standard is to provide prescriptive methods for testing and analysing preservatives and preservative-treated wood-based products for use by manufacturers (treaters) and associated parties.

This Standard is part of a series on preservative-treated wood-based products as follows:

AS/NZS 1604.1, *Preservative-treated wood-based products, Part 1: Products and treatment*

AS/NZS 1604.2, *Preservative-treated wood-based products, Part 2: Verification requirements*

AS/NZS 1604.3, *Preservative-treated wood-based products, Part 3: Test methods*

The revision of the series includes:

- (a) An improved performance-oriented approach.
- (b) Improved clarity and uniformity around the requirements for preservative penetration.
- (c) Better definition of the framework for treating, specifying and using conforming products.
- (d) A new system for verifying the key characteristics of conforming products.
- (e) Revised presentation and information content to ensure efficient application of each Part.
- (f) Some modifications and additions to the treatment specifications and test methods.
- (g) A reorganization of the test methods including removal of those no longer in common use.

The terms “normative” and “informative” are used in Standards to define the application of the appendices to which they apply. A “normative” appendix is an integral part of a Standard, whereas an “informative” appendix is for information and guidance only.

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NOTES

Australian/New Zealand Standard

Preservative-treated wood-based products

Part 3: Test methods

Section 1 Scope and general

1.1 Scope

This Standard specifies general requirements for testing and analysing preservatives and preservative-treated wood-based products. The types of test methods included are —

- (a) solution analysis ([Section 2](#));
- (b) penetration spot tests ([Section 3](#)); and
- (c) retention tests ([Section 4](#)).

NOTE 1 Methods for determining the presence of sapwood and heartwood in wood-based products are included in [Section 1](#) to facilitate the correct application and interpretation of the test methods.

NOTE 2 The test methods presented are those considered to be in current use at the time of publication of this Standard and are listed in approximate order of common usage in each case.

NOTE 3 Test methods included in previous versions of this Standard, but now not considered to be in common use, are not included but may, if necessary, be obtained from the previous standards. These methods are listed, for information purposes, in [Appendix A](#).

1.2 Application

This Standard is intended for use in conjunction with AS/NZS 1604.1 and AS/NZS 1604.2, NZS 3640 or the relevant standard to which the wood-based product is claimed to have been treated. AS/NZS 1604.1 specifies that preservative-treated wood-based products be verified in accordance with AS/NZS 1604.2 using the test methods in this Standard.

NOTE Test results should be achieved within the level of accuracy appropriate to the test procedure.

1.3 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document:

NOTE Documents referenced for informative purposes are listed in the Bibliography.

AS 2026, *Laboratory glassware—Density hydrometers*

AS 3529, *Solvents—Toluene*

AS/NZS 1604.1, *Preservative-treated wood-based products, Part 1: Products and treatments*

AS/NZS 1604.2, *Preservative-treated wood-based products, Part 2: Verification requirements*

AS/NZS 4491, *Timber—Glossary of terms in timber-related Standards*

NZS 3640, *Chemical preservation of round and sawn timber*

ISO 2719, *Determination of flash point — Pensky-Martens closed cup method*

ISO 5272, *Toluene for industrial use — Specifications*

BS 676, *Specification for flasks with graduated necks (phenols type)*

ASTM D370, *Standard practice for dehydration of oil-type preservatives*

ASTM E1, *Standard Specification for ASTM Liquid-in-Glass Thermometers*

ASTM D1193, *Standard Specification for Reagent Water*

1.4 Terms and definitions

For the purpose of this Standard, the definitions given in AS/NZS 4491, AS/NZS 1604.1, AS/NZS 1604.2 and those below apply. Where the definitions in this standard differ from those in AS/NZS 4491, those below apply.

1.4.1

batch

quantity of preservative-treated wood-based products of the same product type produced by the same process over a specified period of time, or a supplied parcel or shipment of preservative-treated wood-based products

1.4.2

charge

quantity of timber actually processed in a timber preservation plant by one complete treatment process cycle

1.4.3

hazard class

number prefixed with the letter “H”, identifying the degree of hazard as specified in AS/NZS 1604.1, for which the wood-based product incorporating the brand has been treated (e.g. “H2”)

1.4.4

lot

quantity of timber produced under uniform conditions

1.4.5

may

indicates the existence of an option

1.4.6

mark

legible mark (or brand) applied to preservative-treated wood-based products, sufficiently permanent to convey the information specified in AS/NZS 1604.1 or the relevant standard

1.4.7

parcel

lot of preservative-treated wood-based products from one or more charges, production runs, or part thereof, of the same treatment type

1.4.8

penetration

depth to which a prescribed preservative has entered the wood-based product

1.4.9

penetration tracer

non-diffusible, chemical compound added to a treating solution and used as a penetration indicator chemical, the penetration of which correlates with the penetration of the active ingredient(s)

1.4.10

penetration zone

zone of the wood-based product that is required to be penetrated by the preservative

1.4.11**preservative**

chemical or a mixture of chemicals in a form suitable for application to a wood-based product in order to preserve it from attack by timber-destroying agents

Note 1 to entry: A description of preservatives is given in AS/NZS 1604.1.

1.4.12**preservative-treated wood-based products**

wood-based products containing preservatives, the characteristics of which are as described in AS/NZS 1604.1, including sawn and round timber, reconstituted wood-based products, plywood, laminated veneer lumber and glued laminated timber products

1.4.13**relevant standard**

standard to which the wood-based product is claimed to have been treated

1.4.14**retention**

quantity of preservative in the specified penetration zone of the wood-based product

1.4.15**shall**

indicates that a statement is mandatory

1.4.16**should**

indicates a recommendation

1.5 Report of test results**1.5.1 Analysis of preservative-treated wood-based products**

The following information shall be included on the analytical test certificate for preservative-treated timber:

(a) *Certificate heading:*

- (i) Reference to this series, i.e. the AS/NZS 1604 series.
- (ii) Name of the organization certifying the results obtained.
- (iii) Number of the certificate.
- (iv) Date on which the certificate was issued.
- (v) Source of the samples.
- (vi) Sapwood and heartwood amount if required.
- (vii) Date on which the samples were submitted for analysis.

(b) *Certificate body:*

- (i) Analysing organization's sample identification.
- (ii) Where available, identification mark of the organization providing the sample.
- (iii) Sample description, e.g. species, dimensions and profile.
- (iv) Hazard class to which the samples were treated.

- (v) Name of the preservative.
- (vi) Sapwood penetration result — pass or fail.
- (vii) Heartwood penetration result — pass or fail.
- (viii) Required retention of the preservative for the specified hazard class.
- (ix) Result of the retention analysis carried out.
- (x) Assessment (i.e. pass or fail) against the criteria specified in AS/NZS 1604.1 or the relevant standard.
- (xi) Any deviation from the test method.

NOTE Where the hazard class is unknown, Items (b)(iv), (b)(viii) and (b)(x) may be omitted.

(c) *Certificate footer:*

- (i) Postal address to which the certificate shall be sent.
- (ii) Name of the contact person and his or her address; phone and facsimile number of the work unit preparing the analytical certificate.
- (iii) Signature and position within the work unit of the person certifying the result.
- (iv) Comments that may apply to the work carried out.

1.5.2 Analysis of preservatives

The following information shall be included on the analytical test certificate for preservatives:

(a) *Certificate heading:*

- (i) Reference to this series, i.e. the AS/NZS 1604 series.
- (ii) Name of the organization certifying the results obtained.
- (iii) Number of the certificate.
- (iv) Date on which the certificate was issued.
- (v) Source of the samples.
- (vi) Name of the person or organization who took the samples.
- (vii) Date on which the samples were submitted for analysis.

(b) *Certificate body:*

- (i) Analysing organization's identifying mark.
- (ii) Supplier's identification mark.
- (iii) Type of analysis carried out.
- (iv) Analysis result.
- (v) Any appropriate comment.
- (vi) Any deviation from the test method.

(c) *Certificate footer:*

- (i) Postal address to which the certificate shall be sent.

- (ii) Contact details of the person certifying the result.
- (iii) Signature of the person certifying the result.
- (iv) Comments that may apply.

1.6 Other methods of analysis

The list of methods presented in this Standard is not exhaustive. Other methods may be used provided there is data demonstrating comparable accuracy.

1.7 Sampling preservative liquid — Requirements

The sampling of preservative liquid is required for the determination of conformance to a specified composition (refer to AS/NZS 1604.1:2021, Clause 1.6.2.2).

Sampling of preservative liquid shall be as specified in this clause for the purposes of AS/NZS 1604.1 or the relevant standard where AS/NZS 1604.1 does not apply.

Before sampling, the preservative liquid shall be thoroughly stirred, with heating as necessary to produce a homogeneous mixture.

All containers used for removing or transporting the liquid sample shall be thoroughly rinsed with the liquid to be tested, with rinsings being returned to the bulk storage tank from which the liquid came.

All lines used in the sampling process shall be thoroughly flushed before the test sample is removed. Flushings shall be returned to the bulk liquid storage tank.

A liquid sample of sufficient volume to ensure accuracy shall be taken.

1.8 Sampling preservative-treated wood-based products

For the purposes of verification using AS/NZS 1604.2, the sampling of preservative-treated wood-based products shall be in accordance with the requirements of that standard. Where AS/NZS 1604.2 does not apply, sampling shall be in accordance with the relevant standard.

1.9 Presence of sapwood and heartwood in some softwoods

1.9.1 Principle

The presence of sapwood is determined visually on the end-grain of a freshly prepared timber surface by the formation of a yellow colour under alkaline conditions.

1.9.2 Reagents

All reagents shall be of analytical reagent quality.

The water used for preparing the reagents shall be distilled.

The following reagents shall be used:

- (a) *Variamine blue RT salt (VBRT)* — Dissolve 0.2 g VBRT (N-phenyl-p-phenylenediamine, diazonium salt, CAS registry No. 4477-28-5) in 100 mL water.

NOTE This reagent is temperature sensitive and should be stored in a refrigerator.

- (b) *4 % ammonia solution* — Dilute 1 volume of ammonia ($d = 0.880$) with 5 volumes of water.
- (c) *2 % hydrochloric acid solution* — Dilute 20 mL 32 % hydrochloric acid with 1 000 mL water.

1.9.3 Procedure

The procedure shall be as follows:

- (a) Spray VBRT solution on a freshly prepared cross-section of the material to be tested. Allow time for the reagent to be absorbed in the timber.
- (b) Once the VBRT is absorbed in the timber, over-spray the test surface with 4 % ammonia solution.
- (c) Observe colour changes.

Under the conditions of this test, sapwood turns yellow and heartwood turns red/magenta.

In the case of hoop pine, after application of VBRT and ammonia solution, allow enough time for colour development and follow by over-spraying with 2 % hydrochloric acid solution. Heartwood will turn blue-black.

1.10 Presence of sapwood and heartwood in some hardwoods

1.10.1 Principle

The presence of sapwood is determined visually on the end-grain of a freshly prepared timber surface by the formation of a red colour in the heartwood. The test relies on the difference in acidity between the sapwood and heartwood of some hardwoods.

1.10.2 Reagent — 0.1 % methyl orange

The reagent shall be of analytical reagent quality.

Dissolve 0.1 g (p-((p-(dimethylamino)phenyl)azo)benzenesulfonic, acid sodium salt, CAS registry No. 547-58-0) in 100 mL methanol.

1.10.3 Procedure

The procedure shall be as follows:

- (a) Spray the 0.1 % methyl orange solution on a freshly prepared cross-section of the material to be tested.
- (b) Observe colour changes.

Sapwood will remain yellow, and heartwood will develop a red colour.

Section 2 Solution analysis

2.1 Scope and general requirements

2.1.1 Scope of section

This section specifies analysis methods for the determination of preservative solution concentration. Analytical procedures for the determination of specific preservative components are given for oil-borne and waterborne preservatives. Calculations are provided for determining conformance to relevant standards, including AS/NZS 1604.1 and NZS 3640.

2.1.2 Preparation of preservative liquids and solutions for analysis

2.1.2.1 Oil-borne preservatives

A sample of preservative taken in accordance with [Clause 1.7](#) shall be heated to between 40 °C and 60 °C to allow foreign matter (bark, chips and similar) to be screened off. The screened sample shall be heated to 40 °C, thoroughly stirred and filtered through a Whatman No. 41 filter paper or equivalent filter before drawing off enough solution for the required analysis.

2.1.2.2 Waterborne preservatives

A sample of water-soluble or emulsion preservative taken in accordance with [Clause 1.7](#) shall be thoroughly stirred before filtering enough solution for the required analysis through a Whatman No. 41 filter paper or equivalent filter at ambient temperature.

If the preservative is a suspension or similar with non-dissolved particles, a sample taken in accordance with [Clause 1.7](#) shall be thoroughly stirred at ambient temperature immediately prior to enough solution being taken for the required analysis. Some coarse filtration may be required to remove foreign matter such as bark, chips or similar.

2.1.2.3 Creosote

A creosote sample taken in accordance with [Clause 1.7](#) shall be placed in a clean, dry, airtight container allowing about 5 % ullage. When sampling, the creosote shall be examined for the presence of separated undissolved matter, particularly water and crystalline solids, or sludge, the presence or absence of which shall be reported. If the creosote contains crystalline solids and has been sampled after heating and mixing, this shall be reported. Care shall be taken at all times to avoid the risk of contaminating the contents in any way.

The sample shall be thoroughly mixed immediately before any portion is withdrawn for testing. If there are any deposits (such as crystalline substances) present, the container shall be warmed on a water bath or by other suitable means enough to dissolve them, and portions for test shall then be taken from the warmed, mixed sample. A naked flame or other source of intense heat shall not be used to warm the sample.

2.1.2.4 Light organic solvent preservative (LOSP)

A sample of LOSP taken in accordance with [Clause 1.7](#) shall be thoroughly stirred before filtering enough solution for the required analysis through a Whatman No. 41 filter paper or equivalent filter at ambient temperature.

2.1.3 Related methods of analysis

The analytical methods given in this section are intended as reference methods for the determination of solution concentrations.

Alternative methods shall be compared with methods presented in this section before being routinely used, provided that they are of comparable accuracy.

2.2 Determination of copper, chromium and arsenic in CCA preservative solutions

2.2.1 Principle

Copper and arsenic are determined by atomic-absorption spectrophotometry. Hexavalent chromium is determined by back-titration of excess iron added as ferrous ammonium sulfate.

This method is applicable to CCA mix tank or working tank solutions.

2.2.2 Reagents

All reagents shall be of analytical reagent quality.

The water used for preparing the reagents shall be distilled.

The following reagents shall be used:

- (a) *BDS indicator* — Make a slurry of 0.2 g barium diphenylamine sulfonate in 1 mL to 2 mL water, gradually diluting to 100 mL, with stirring. Filter the solution into the reagent flask.
- (b) *Ferrous ammonium sulfate (FAS) solution* — Dissolve 140 g ferrous ammonium sulfate in 500 mL water before adding 25 mL concentrated sulfuric acid and final dilution to 1 000 mL.
Dilute this stock solution 10:1 volumetrically before use.
- (c) *Mixed acid solution* — Gradually add, with stirring, 500 mL concentrated sulfuric acid to 500 mL water. When cool, adjust the volume to 1 000 mL with water and add 500 mL orthophosphoric acid to complete the mixture.
- (d) *Standard potassium dichromate solution* — Dissolve exactly 10.000 g potassium dichromate in water and dilute volumetrically to 1 000 mL.
Dilute this stock solution volumetrically 10:1 before use (1 mL contains exactly 0.0010 g K₂Cr₂O₇ after dilution and is equivalent to 0.3535 mg Cr).
- (e) *Standard copper solution, 1 000 µg copper/mL* — Dissolve 7.8580 g copper sulfate pentahydrate in water and dilute to 2 000 mL in a volumetric flask.
- (f) *Standard arsenic solution, 1 000 µg As/mL* — Dissolve 2.6415 g arsenous trioxide (As₂O₃) in 50 mL of 20 % potassium hydroxide solution, and dilute to 2 000 mL with 1 % aqueous sulfuric acid.

2.2.3 Procedure

2.2.3.1 Instrument settings and operation

The instrument settings and operating conditions for the determination of copper and arsenic shall be as specified in the instrument user's manual. Copper shall be determined in a fuel-lean air acetylene flame at 324.8 nm or 3.28 µm, and arsenic in a nitrous oxide/acetylene flame at 193.7 nm, with background correction for non-atomic absorption.

2.2.3.2 Preparation of calibration solutions

The calibration solutions shall be prepared as follows:

- (a) Transfer aliquot portions of 2, 4, 8 and 16 mL of the standard [as defined in [Clauses 2.2.2\(e\)](#) and [2.2.2\(f\)](#)] copper and arsenic solutions to a series of 200 mL one-marked volumetric flasks.

- (b) Add 2 mL of concentrated sulfuric acid to each, cool, dilute to the mark with water, and mix.

NOTE A 1 mL aliquot of the solutions so constituted contains 10, 20, 40 and 80 µg, respectively, of copper and of arsenic.

2.2.3.3 Analysis of preservative solutions

The procedures shall be as follows:

- (a) *Hexavalent chromium:*
- (i) Filter the solution through a Whatman No. 542 paper or equivalent.
 - (ii) Transfer a 1 mL aliquot of the filtered solution to a 500 mL conical flask, add 100 mL water, 10 mL mixed acid, and 1 mL BDS indicator.
 - (iii) Add 20 mL aliquot of FAS working solution to the flask, until excess iron is indicated by the green colour.
 - (iv) Back-titrate the excess with standard potassium dichromate solution, until a permanent purple is obtained.
 - (v) Obtain a blank titre by repeating the procedure, using the same volume of FAS solution, with reagents only in the flask.
- (b) *Copper and arsenic:*
- (i) Filter the solution through a Whatman No. 542 paper or equivalent.
 - (ii) Transfer a suitable aliquot of the filtered solution to a one-marked volumetric flask from [Table 2.2.3.3](#).
 - (iii) Add to the aliquot 100 mL water and either 2 mL or 5 mL sulfuric acid, so that the diluted solution contains 1 % acid. Mix well, allow to cool, and dilute to the mark.
 - (iv) Maintaining suitable operating conditions, aspirate a blank containing 1 % sulfuric acid, followed by the range of calibration solutions and the test solution(s).
 - (v) Check the calibration solutions after the last test solution has been run.
 - (vi) Plot calibration curves of copper and arsenic (in µg/mL) against absorbance.
 - (vii) Determine the contents of copper and arsenic in the test solutions from the calibration curves.

Table 2.2.3.3 — Suitable aliquot of filtered solution

Option	A	B	C
Total CCA salt in solution, %	< 3	3 to 10	> 10
Aliquot volume taken, mL	2.00	1.00	1.00
Total dilution volume, mL	200	200	500

2.2.4 Calculations of the percentage of metals

2.2.4.1 Hexavalent chromium

The percentage by volume of hexavalent chromium (Cr) shall be calculated from the following equation:

$$\text{Percent Cr (VI)} = 0.0354 \times (B - T) \quad 2.2.4.1$$

where

B = blank titre [see [Clause 2.2.3.3\(a\)](#)]

T = test solution titre [see [Clause 2.3.3\(a\)](#)]

2.2.4.2 Copper or arsenic

The percentage by volume of copper or arsenic shall be calculated from any one the following equations:

(a) Option A:

$$\text{Percent metal} = \frac{X}{100} \quad 2.2.4.2(1)$$

(b) Option B:

$$\text{Percent metal} = \frac{X}{50} \quad 2.2.4.2(2)$$

(c) Option C:

$$\text{Percent metal} = \frac{X}{20} \quad 2.2.4.2(3)$$

where

X = concentration of the appropriate metal, in micrograms per millilitre ($\mu\text{g/mL}$), of the test solution (see [Clause 2.2.3.2](#)).

2.3 Determination of boron in preservative solution

2.3.1 Principle

After dry-ashing the solution sample in lime-eschka mixture, boron is determined titrimetrically using mannitol.

2.3.2 Reagents

All reagents shall be of analytical reagent quality.

The water used for preparing the reagents shall be distilled.

The following reagents shall be used:

- (a) *Lime eschka* — Mix 250 g anhydrous sodium carbonate and 750 g anhydrous powdered calcium oxide.
- (b) *Mannitol solution* — Dissolve 15 g mannitol in 100 mL water. Prepare freshly before use because of biodegradation.

- (c) *Phenolphthalein indicator* — Dissolve 0.25 g phenolphthalein in 50 mL ethanol, then add 50 mL water. Adjust pH by adding dilute sodium hydroxide solution until the faint pink colouration persists.
- (d) *Methyl red indicator* — Filtered, saturated solution of methyl red in ethanol.
- (e) *Standard sodium hydroxide solution, 0.05 M* — Dissolve 2 g sodium hydroxide in 1 000 mL water, and standardize as follows:
 - (i) Accurately weigh three 0.1 g portions of potassium hydrogen phthalate (KHP) and dissolve in 25 mL water. After adding 0.5 mL phenolphthalein indicator, titrate with the sodium hydroxide solution.
 - (ii) The molarity (M) shall be calculated from the following equation:

$$M = \frac{(\text{Weight of KHP}) \times 1000}{(\text{Titre}) \times 204.22} \quad 2.3.2$$

2.3.3 Procedure

The procedure shall be as follows:

- (a) Weigh 1 g lime eschka into a numbered porcelain crucible.
- (b) Accurately pipette 2 mL of sample into the centre of the lime eschka in the crucible and then cover with an additional 1 g lime eschka.
- (c) Ash at 550 °C for 1 h and allow to cool.
- (d) Transfer the ash to a beaker and rinse out the crucible with small portions of dilute (10 %) hydrochloric acid and water using a policeman, then transfer the washings to the beaker.
- (e) Carefully add 10 mL concentrated hydrochloric acid to the beaker, covering with a watch-glass to prevent spattering.

NOTE More acid may be required if the solid contents are not completely dissolved.

- (f) Wash down the watch-glass and beaker sides with distilled water and add 1 mL phenolphthalein indicator.
- (g) Turn the solution just alkaline with cool, freshly prepared 15 % sodium hydroxide solution. Stir vigorously and add drop-wise to achieve the pink-grey precipitate colour required.
- (h) Quantitatively transfer the contents of the beaker to a 100 mL volumetric flask and make up to the mark when cool.
- (i) Filter a portion of the solution through a Whatman No. 542 filter paper or equivalent.
- (j) Pipette 25 mL of the filtrate into a 250 mL Erlenmeyer flask, dilute to 50 mL with water, and add 1 mL phenolphthalein indicator.
- (k) Add dilute hydrochloric acid drop-wise until phenolphthalein turns colourless.
- (l) Add 0.5 mL methyl red indicator.

NOTE The solution should turn yellow.

- (m) Add dilute hydrochloric acid drop-wise until methyl red turns red. If the solution stands for 4 h or more, reflux the acid aliquot to eliminate carbon dioxide, and cool the solution.
- (n) Add the standard sodium hydroxide solution drop-wise until the red colour is just discharged, leaving the solution straw yellow.

- (o) Add 10 mL 15 % freshly prepared mannitol solution.

NOTE The solution should again turn to the red colour of methyl red.

- (p) Titrate the solution with the standard sodium hydroxide. During the course of titration, the colour will change from red to the yellow of methyl red, and then to the pink of phenolphthalein. The end-point is the first permanent appearance of this pink colour.
- (q) Run a blank determination in conjunction with the above procedure using distilled water in the initial stages.
- (r) Obtain the titre for this blank determination in exactly the same way as for the sample determination.

2.3.4 Calculation

The percentage by mass of boron in the preservative solution shall be calculated from the following equation:

$$\text{Percent boron} = 1.162 \times (T - B) \times (C) \times (M) \quad 2.3.4$$

where

T and B = titre and blank volumes of M standard sodium hydroxide solution [see [Clause 2.3.2\(e\)\(ii\)](#)]

C = correction factor

= 1.1

M = molarity [see [Clause 2.3.2\(e\)\(ii\)](#)]

2.4 Determination of quaternary ammonium compounds in solutions

2.4.1 General

This method is applicable to the determination of didecyldimethylammonium chloride (DDAC) and benzalkonium chloride (BAC) in solutions by titration using sodium tetraphenylboron (STPB) as titrant and 2',7'-dichlorofluorescein as a colour indicator. For concentrates, a suitable dilution shall be prepared before analysis. In the case of alkaline solutions, the solution shall be neutralized first.

2.4.2 Reagents

All reagents shall be of analytical reagent quality.

The water used for preparing the reagents shall be distilled water.

The following reagents shall be used:

- (a) *Sodium tetraphenylboron (0.0025 M)* — Dissolve 0.865 g sodium tetraphenylboron in distilled water and dilute to 1 L in a volumetric flask.
- (b) *2',7'-dichlorofluorescein (0.1 %)* — Dissolve 0.1 g 2',7'-dichlorofluorescein in 100 mL isopropyl alcohol.
- (c) *Hyamine 1622 (0.004 M)* — Dry hyamine 1622 (Diisobutyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride) to constant weight in an oven at 105 °C. Weigh 1.75 g to 1.85 g (to nearest 0.1 g) and dissolve in distilled water. Dilute to 1 000 mL in a volumetric flask.

- (d) *Phosphoric acid (20 %)* — Add 20 mL concentrated phosphoric acid to 80 mL water.

2.4.3 Standardization of sodium tetraphenylboron solution

The standardization of sodium tetraphenylboron solution shall be as follows:

- (a) Pipette 10 mL hyamine 1622 solution into a 125 mL flask.
- (b) Add 25 mL distilled water and 7 drops of 2',7'-dichlorofluorescein indicator solution.
- (c) Slowly titrate with sodium tetraphenylboron solution until a lemon-green colour end-point.

NOTE It is common for a precipitate to form just prior to the end-point.

2.4.4 Analysis procedure

The analysis procedure shall be as follows:

- (a) Weigh 1 g to 2 g (or 0.30 g of 5 %) of treatment solution into a 250 mL conical flask. Record weight (*W*).
- (b) Add 25 mL distilled water.
- (c) Neutralize the solution by drop-wise addition of 20 % phosphoric acid to pH approximately 7, as indicated by the disappearance of the deep blue colour and formation of a very light blue precipitate.

NOTE The pH should be checked with pH paper to ensure that the solution has been neutralized and to prevent the addition of excess acid.

- (d) Add 14 drops of 2',7'-dichlorofluorescein indicator solution.
- (e) Titrate with sodium tetraphenylboron solution until a green/lemon end-point.
- (f) Record the sodium tetraphenylboron used.

2.4.5 Calculations

The following shall be calculated:

- (a) *Hyamine concentrations:*

$$M(\text{hyamine}) = \frac{m_{(H)}}{448.1} \quad 2.4.5(1)$$

where

$$\begin{aligned} m_{(H)} &= \text{mass of hyamine, in grams} \\ 448.1 &= \text{molecular weight of hyamine, in g/mol} \end{aligned}$$

- (b) *Sodium tetraphenylboron (STPB) concentration:*

$$M(\text{STPB}) = \frac{M(\text{hyamine}) \times v_{(H)}}{v_{(\text{STPB})}} \quad 2.4.5(2)$$

where

$v_{(H)}$ = volume of hyamine, in millilitres

$v_{(STPB)}$ = volume of added STPB, in millilitres

(c) % Quat in solution:

$$\% \text{ Quat} = \frac{v_{(STPB)} \times M(STPB) \times MW}{10 \times W} \quad 2.4.5(3)$$

where

$v_{(STPB)}$ = volume of added STPB, in millilitres

MW = 362.1 g/mol for DDAC

= 354 g/mol for BAC

W = weight of sample taken [see [Clause 2.4.4\(a\)](#)]

2.5 Determination of copper in copper-based preservative solutions

2.5.1 Principle

Copper is determined using a fuel-lean air/acetylene flame at 327.4 nm.

2.5.2 Reagents

All reagents shall be of analytical reagent quality.

The water used for preparing the reagents shall be distilled.

The following reagents shall be used:

- (a) *Sulfuric acid, concentrated.*
- (b) *Standard solution* — Dissolve 0.9825 g copper sulfate pentahydrate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, in 500 mL water in a volumetric flask.

2.5.3 Procedure

2.5.3.1 Instrument settings and operation

Copper shall be determined using a fuel-lean air/acetylene flame at 327.4 nm.

All other settings and conditions shall be as specified in the appropriate instrument user's manual.

2.5.3.2 Preparation of calibration solutions

The calibration solutions shall be prepared as follows:

- (a) Pipette 2, 4, 8, and 16 mL of the standard solution [see [Clause 2.5.2\(b\)](#)] into a series of 200 mL one-marked volumetric flasks.
- (b) Add 2 mL of the sulfuric acid [see [Clause 2.5.2\(a\)](#)].
- (c) Allow the solution to cool, then dilute to the mark with water. The resulting solutions have concentrations of 5, 10, 20, and 40 mg/L copper.

NOTE It may be necessary to adjust the number of calibration solutions and the range of concentrations covered to suit the sensitivity of the instrument used.

2.5.3.3 Analysis of preservative solution

The procedure for analysing the preservative solution shall be as follows:

- (a) Rinse a Pasteur pipette with the sample solution a couple of times and then use it to transfer ≈ 2 g of the solution to a tared 500 mL volumetric flask. Let the mass of solution be W_1 and record this weight to three decimal places.
- (b) Add 50 mL of water to the flask. Add 5 mL of concentrated sulfuric acid to the flask.
- (c) Allow the solution to cool, then make it up to the mark. This shall be the test solution.
- (d) Using the operating conditions suitable for the instrument, aspirate a suitable range of calibration solutions and then the test solution(s).
- (e) Check the calibration solutions after the last test solution has been run.
- (f) Plot calibration curve of copper (in milligrams per litre) against absorbance.
- (g) Determine the contents of copper in the test solutions by comparing the absorbance readings with the calibration curve.

NOTE If a number of samples are to be analysed it may be advisable to check the instrument stability by bracketing samples with appropriate standard solutions.

2.5.4 Calculation

The concentration of copper (Cu) in the solution shall be calculated from the following equation:

$$\text{Cu} (\% \text{ m/m}) = \frac{20X}{m} \quad 2.5.4$$

where

- X = concentration of copper in the test solution, in milligrams per litre
 m = mass of sample solution that was taken, in grams

2.6 Determination of bifenthrin in water-based solutions by gas chromatography (GC)

2.6.1 Principle

Water-based preservative solutions containing bifenthrin are diluted with acetone and the concentration of bifenthrin is determined by gas chromatography (GC).

2.6.2 Reagents

All reagents shall be of analytical reagent quality.

The water used for preparing the reagents shall be distilled water.

The following reagents shall be used:

- (a) *Bifenthrin* — Reference material 99.5 % assay.
- (b) *Squalene* — Sigma Cat. No. S3626 (98 % to 100 %).
- (c) *Acetone*.

2.6.3 Procedures

2.6.3.1 Instrument settings and operating conditions

The instrument settings and operating conditions shall be in accordance with [Table 2.6.3.1](#).

Table 2.6.3.1 — Gas chromatography conditions

Gas chromatography	Fitted with a FID (flame ionization detector) Syringe filter fitted with PTFE 13 mm filter from Micro Filtration Systems Cat. No. 13JP050AN
Column	SE-54 (30 m × 0.32 mm × 0.25 µm) Altech, Econo-Cap 5, Cat No. 19646
Oven temperature	210 °C for 4 min, 5 °C/min for 6 min to 240 °C
Detector	FID (flame ionization detector)
Injector	270 °C
Flow rate	25 mL/min
Pressure	100 kPa (145 psi)
Column flow rate after split	10.8 mL/min
Velocity	120
Split rate	10
Detector range	0

2.6.3.2 Solution preparation

The solution shall be prepared as follows:

(a) *Reference solution:*

- (i) *Bifenthrin solution* — Accurately weigh approximately 0.2 g bifenthrin into a dry 100 mL volumetric flask. Dissolve in approximately 20 mL acetone and dilute to volume with acetone. Shake well.
- (ii) *Internal standard (IS)* — Accurately weigh approximately 0.15 g squalene into a dry 100 mL volumetric flask. Dissolve in approximately 20 mL acetone and dilute to volume with acetone. Shake well.
- (iii) *Standard solution* — Pipette 2 mL bifenthrin solution and 2 mL internal standard into a 25 mL volumetric flask. Dilute to the mark with acetone and mix well. Inject 2 µL onto the gas chromatography column.

(b) *Sample preparation:*

The sample shall be prepared as follows:

- (i) Pipette 2 mL of sample into a 25 mL volumetric flask.
- (ii) Pipette 2 mL internal standard solution into the same volumetric flask and dilute to volume with acetone.
- (iii) Mix well.
- (iv) Filter the sample solution, through a PTFE filter using the syringe system, into a glass vial.
- (v) Inject 2 µL into the gas chromatography.

2.6.4 Calculations

The concentration of bifenthrin shall be calculated from the following equations:

$$\text{RF (relative factor)} = \frac{\text{Weight of bifenthrin} \times \text{Purity} \times \text{Area IS peak}}{\text{Weight IS} \times 100 \times \text{Area standard peak}} \quad 2.6.4(1)$$

$$\text{Bifenthrin (\% m/v)} = \frac{\text{Weight IS} \times \text{RF} \times \text{Area sample peak}}{\text{Volume of sample} \times \text{Area IS} \times 10} \quad 2.6.4(2)$$

2.7 Determination of propiconazole, tebuconazole and permethrin in preservative solutions

2.7.1 Principle

The samples are dissolved in isopropanol, sonicated and diluted to known volume. The stock solution is then diluted with mobile phase, then analysed for propiconazole, tebuconazole and permethrin using high-performance liquid chromatography (HPLC) with UV detection at a wavelength of 230 nm. Quantitation is by external standards prepared analogously to samples, covering the expected concentration range.

2.7.2 Reagents

All reagents shall be of analytical reagent quality.

The water used for preparing the reagents shall be distilled water.

All samples shall be sonicated.

All reagents shall be nanograde, HPLC, analytical reference grade, or equivalent.

2.7.3 Procedures

2.7.3.1 HPLC equipment and conditions

The HPLC equipment and conditions shall be as follows:

- (a) Use a suitable HPLC pump, auto-sampler and detector, with an appropriate data system.
- (b) Carry out analysis with the following:
 - (i) An octadecyl silane (C18) silica column (150 mm × 4.6 mm × 5 mm).
 - (ii) 20 µL injection volume, UV/VIS detector at 230 nm.
 - (iii) Mobile phase of 65 % v/v acetonitrile/water.
- (c) Vary the flow rate of the HPLC pump according to [Table 2.7.3.1](#), with a total run time of approximately 28 min.

NOTE A Hewlett Packard HP1100 or equivalent system with quaternary pump and diode array detector and using a Phenomenex Luna C18 or equivalent column have proved suitable.

Table 2.7.3.1 — Flow rate of HPLC pump

Time min	Flow rate m/L/min
0 to 8	1.0
8.5 to 27.5	2.5
27.9	1.0

2.7.3.2 Sample preparation

The sample shall be prepared as follows:

- Prepare a stock standard solution of propiconazole, tebuconazole and permethrin in isopropanol.
- Prepare a working solution by diluting in mobile phase to give concentrations over the range of 10 mg/L to 120 mg/L for each analyte.
- Dissolve the samples in isopropanol, then dilute in mobile phase to give expected concentrations in the standard ranges for propiconazole, tebuconazole and permethrin.

2.7.4 Calculation

The peak area for each of propiconazole, tebuconazole and permethrin shall be calculated for the standard and the response function for peak area versus concentration shall be determined and used to calculate the concentrations in samples.

2.7.5 Suitability and specificity

Propiconazole, tebuconazole and permethrin are well separated, and any direct interfering peaks observed at their respective retention times from other constituents of the products have been evaluated, and contributed less than 1 % error to the integration process.

2.8 Determination of imidacloprid in preservative solutions**2.8.1 Principle**

Samples are diluted in methanol to a known volume and the concentration of imidacloprid is determined by reverse-phase high-performance liquid chromatography (HPLC).

2.8.2 Reagents

All reagents shall be of analytical reagent quality.

The water used for preparing the reagents shall be distilled water.

The following reagents shall be used:

- Mobile phase A* — Type 2 water conforming to ASTM D1193, adjusted to pH 3 with phosphoric acid.
- Mobile phase B* — Methanol for HPLC.
- Imidacloprid* — Imidacloprid (99.9 %).
- Stock imidacloprid standard* — Weigh to the nearest 0.1 mg approximately 0.010 g imidacloprid (see Item (c) above), dissolve in methanol and make up to 100 mL with methanol in a volumetric flask.

- (e) *Stock internal standard* — Weigh approximately 0.030 g etofenprox, dissolve in methanol and make up to 100 mL with methanol in a volumetric flask.

2.8.3 Procedures

2.8.3.1 Sample preparation

The sample shall be prepared as follows:

- (a) If necessary, screen or filter (e.g. using Whatman No. 41 or equivalent) the preservative sample to remove extraneous solids.
- (b) Dilute the preservative by accurately pipetting the required volume of imidacloprid-containing preservative solution into a 50 mL volumetric flask.
- (c) Into the same flask, pipette 5 mL stock internal standard. Make up to volume with methanol and mix well.
- (d) Filter a portion of the sample dilution into an HPLC sample vial using a syringe filter (0.2 mm, regenerated cellulose).

2.8.3.2 Preparation of working standard solution

A working standard solution shall be prepared as follows:

- (a) Accurately pipette 5 mL stock imidacloprid standard into a 50 mL volumetric flask.
- (b) Accurately pipette 5 mL stock internal standard into the same volumetric flask. Make up to volume with methanol and mix well.
- (c) Filter (0.2 mm regenerated cellulose) a portion of the working standard solution into an HPLC sample vial.

2.8.3.3 Chromatography

HPLC analysis shall be performed according to the conditions specified in [Table 2.8.3.3](#).

Table 2.8.3.3 — HPLC conditions

Column		Luna C18 (5 µm, 100 Å) 250 mm × 4.6 mm (Phenomenex 00G-4252-E0) C18 Security guard column (Phenomenex AJO-4287)									
Column temperature		40 °C									
Injection volume		25 µL									
Flow rate		1 mL/min									
Solvent program	Time, min	0	8	16	18	26	32	42	50	65	
	% B, v/v	5	25	50	50	75	100	100	5	5	
Detection		270 nm									
Retention times	Imidacloprid	17 min approx.									
	Etofenprox	38 min approx.									

2.8.4 Calculations

2.8.4.1 Relative response factor

The relative response factor (*RRF*) shall be calculated from the average of three injections of the working standard solution from the following equation:

$$RRF = \frac{W_S \times A_{IS}}{A_S} \quad 2.8.4.1$$

where

W_S = weight of imidacloprid standard corrected for percent purity, in grams, in the working standard solution

A_{IS} = area of internal standard peak

A_S = area of imidacloprid peak

2.8.4.2 Percentage mass per volume (m/v) of imidacloprid

The percentage mass/volume (m/v) of imidacloprid in the preservative solution shall be calculated from the following equation:

$$\text{Imidacloprid (\% m/v)} = \frac{A_S \times RRF \times 100}{A_{IS} \times V} \quad 2.8.4.2$$

where

V = volume of preservative, in millilitres

2.9 Determination of triadimefon and cyproconazole in aqueous solutions

2.9.1 Principle

The sample is dissolved in acetone and the triadimefon and cyproconazole content is determined by gas chromatography (GC) using flame ionization detection (FID). Quantification is done using an internal standard.

NOTE Suitable for aqueous solutions prepared from formulations containing from 250 g/L triadimefon and 25 g/L cyproconazole to 600 g/L triadimefon and 60 g/L cyproconazole.

2.9.2 Reagents

The following reagents shall be used:

- (a) *Acetone* — AR grade.
- (b) *Internal standard* — Dibutyl phthalate (technical grade is satisfactory).
- (c) *Standard* — Certified standards of triadimefon and cyproconazole of known purity (90 % min).

2.9.3 Procedures

2.9.3.1 Sample preparation

Duplicate samples shall be prepared as follows:

- (a) Weigh, accurately to ± 0.1 mg, enough sample to contain about 20 mg of triadimefon into a 50 mL bottle.
- (b) Add by pipette 5 mL of IS with a volumetric pipette.
- (c) Make up to shoulder of bottle with acetone.
- (d) Place in an ultrasonic bath for 10 min.
- (e) Allow solution to cool to 20 °C.
- (f) Filter sample through a 0.2 μ m syringe filter into a vial.

2.9.3.2 Preparation of working standard solution

A working standard solution shall be prepared as follows:

- (a) *Internal standard (IS):*
 - (i) Weigh 0.3 g of dibutyl phthalate, accurately to 0.1 mg, into a 100 mL volumetric flask.
 - (ii) Make up to mark with acetone and dissolve with ultrasonication.
- (b) *Standards:*
 - (i) Weigh, accurately to ± 0.1 mg, 15–25 mg of triadimefon into a 50 mL glass bottle.
 - (ii) Weigh, accurately to ± 0.1 mg, 15–25 mg of cyproconazole into the same bottle.
 - (iii) Add 5 mL of IS with a volumetric pipette.
 - (iv) Make up to the shoulder of the bottle with acetone and dissolve with ultrasonication.
 - (v) Filter standard through a 0.2 μ m syringe filter into a vial.
- (c) *Quantification:*

A 1 μ L aliquot of each solution is injected into the gas chromatograph with FID detection.

2.9.3.3 Gas chromatography using flame ionization detection

The instrument operating conditions shall be as follows:

- (a) *Temperature program:*

	Initial temperature	Hold time	Rate	Final temperature
	150 °C	1 min	15 °C	280 °C
	280 °C	5 min		
(i)	Flow/pressure mode			P.
(ii)	Injection temperature			2 800 °C.
(iii)	Detector temperature			2 800 °C.



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- (iv) Initial carrier gas velocity 27 cm/s.
- (v) Split ratio 1:20.
- (vi) Injection volume 1 µL.
- (vii) Run time 15 min.
- (b) *Order of elution:*
 - (i) Dibutyl phthalate.
 - (ii) Triadimefon.
 - (iii) Cyproconazole

2.9.4 Calculations

One of the following equations shall be used:

- (a) If the sample and standard have the same weight of IS:

$$RRF = \frac{Ana\ Wt \times IS\ Std}{Ana\ Std} \quad 2.9.4(1)$$

$$\% Ana = \frac{RRF \times Ana\ Sam \times 100}{Sam\ Wt \times IS\ Sam} \quad 2.9.4(2)$$

$$g/L\ Ana = \% Ana \times SG \times 10 \quad 2.9.4(3)$$

where

<i>RRF</i>	=	relative response factor
<i>IS Std</i>	=	area of IS peak in standard chromatogram
<i>IS Sam</i>	=	area of IS peak in sample chromatogram
<i>Ana Std</i>	=	area of analyte peak in standard chromatogram
<i>Ana Sam</i>	=	area of analyte peak in sample chromatogram
<i>Ana Wt</i>	=	weight of analyte in standard, in grams
<i>Sam Wt</i>	=	weight of analyte in sample in grams
<i>% Ana</i>	=	analyte concentration, weight per weight percent
<i>g/L Ana</i>	=	analyte concentration, in grams per litre
<i>SG</i>	=	specific gravity, in grams per millilitre

- (b) If the sample and standard have differing weights of IS:

$$IS\ Wt = \frac{IS\ Conc. (g/L) \times IS\ Vol. (mL)}{1000} \quad 2.9.4(4)$$

OR

$$IS\ Wt = \frac{IS\ Conc. (w/v\ \%) \times IS\ Vol. (mL)}{100} \quad 2.9.4(5)$$

$$RRF = \frac{Ana\ Wt \times IS\ Std}{Ana\ Std \times IS\ Wt\ Std} \quad 2.9.4(6)$$

$$\% Ana = \frac{RRF \times Ana\ Sam \times IS\ Wt\ Sam \times 100}{Sam\ Wt \times IS\ Sam} \quad 2.9.4(7)$$

$$g/L\ analyte = \% Ana \times SG \times 10 \quad 2.9.4(8)$$

where

<i>IS Wt Sam</i>	=	weight of internal standard in sample, in grams
<i>IS Wt Std</i>	=	weight of internal standard in standard, in grams
<i>IS Conc. Std</i>	=	concentration of IS in standard, weight per volume percent or grams per litre
<i>IS Conc. Sam</i>	=	concentration of IS in sample, weight per volume percent or grams per litre

2.10 Determination of copper in copper naphthenate solution

2.10.1 Principle

This method is based on the oxidation of iodide ions to iodine by cupric ions followed by titration of the iodine by thiosulfate. Many other oxidizing agents will interfere, such as nitric acid, dichromate, peroxides, permanganate, iron, arsenic, antimony, chlorate and hypochlorite. Steps need to be taken to overcome these interferences.

2.10.2 Reagents

The following reagents shall be used:

- (a) *Concentrated aqueous ammonium hydroxide.*
- (b) *0.025 N sodium thiosulfate.*
- (c) *Stabilized starch indicator solution.*

NOTE This solution slowly decomposes and a fresh solution should be purchased if a dark blue colour is not produced with a drop of tincture of iodine in 100 mL of water upon addition of a drop of starch indicator.

- (d) *Concentrated nitric acid.*

NOTE All nitric acid needs to be boiled off before iodide is added.

- (e) *Concentrated sulfuric acid.*
- (f) *20 % potassium iodide solution* — Dissolve 20 g of potassium iodide in 80 mL of water.

NOTE The water should turn white or pale yellow. If it is a deep yellow, discard the solution.

- (g) *Concentrated phosphoric acid.*
- (h) *20 % potassium or sodium thiocyanate solution* — Dissolve 20 g NaCNS or KCNS in 80 mL of water.