

Australian/New Zealand Standard™

**Methods for sampling and analysing
timber preservatives and preservative-
treated timber**

**Part 4: Analysis methods for
determination of preservative solution
concentration**



AS/NZS 1605.4:2018

This Joint Australian/New Zealand Standard was prepared by Joint Technical Committee TM-012, Timber Grading and Preservation. It was approved on behalf of the Council of Standards Australia on 22 December 2017 and by the New Zealand Standards Approval Board on 5 March 2018.
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Australian and New Zealand Timber Preservative Manufacturers Association
Australian Forest Products Association
Australian Pesticides and Veterinary Medicines Authority
Australian Timber Flooring Association
Australian Timber Importers Federation
Building Research Association of New Zealand
Department of Agriculture, Fisheries and Forestry, Qld
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Australian/New Zealand Standard™

Methods for sampling and analysing timber preservatives and preservative- treated timber

Part 4: Analysis methods for determination of preservative solution concentration

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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 1605.4:2006.

The objective of this Standard is to set out methods for sampling and analysing preservative solution concentrations.

This Standard is part of a series of Standards that cover the sampling and analysing of timber preservatives and preservative-treated timber, as follows:

AS/NZS

- | | |
|--------|---|
| 1605 | Methods for sampling and analysing timber preservatives and preservative-treated timber |
| 1605.1 | Part 1: General requirements, sampling, and determination of sapwood and heartwood presence |
| 1605.2 | Part 2: Determination of preservative penetration by spot tests |
| 1605.3 | Part 3: Analysis methods for determination of preservative retention |
| 1605.4 | Part 4: Analysis methods for determination of preservative solution concentration (this Standard) |

This Standard is intended to be read in conjunction with the AS/NZS 1604 series, NZS 3640 or the relevant Standard to which timber is claimed to have been treated, and AS/NZS 1605.1. The preservatives incorporated in the AS/NZS 1604 series are required to be accompanied by analytical methods for their determination, which are incorporated in the AS/NZS 1605 series.

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STANDARDS AUSTRALIA/STANDARDS NEW ZEALAND

Australian/New Zealand Standard**Methods for sampling and analysing timber preservatives and preservative-treated timber****Part 4: Analysis methods for determination of preservative solution concentration**

SECTION 1 SCOPE AND GENERAL

1.1 SCOPE

This Standard 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 compliance with relevant standards, including the AS/NZS 1604 series and NZS 3640.

1.2 APPLICATION

This Standard should be read in conjunction with—

- (a) the AS/NZS 1604 series, NZS 3640 or the relevant Standard to which timber is claimed to have been treated; and
- (b) AS/NZS 1605.1.

Methods for sampling and analysing timber preservatives and preservative-treated timber are categorized into the following parts of the AS/NZS 1605 series, according to the general nature of the tests:

- (i) Sampling preservative liquids and preservative-treated timber Part 1.
- (ii) Determination of presence of sapwood and heartwood Part 1.
- (iii) Determination of preservative penetration by spot tests Part 2.
- (iv) Analysis of preservative retention Part 3.
- (v) Analysis of preservative solution concentration Part 4.

1.3 REFERENCED DOCUMENTS

The following documents are referred to in this Standard:

AS	
2026	Laboratory glassware—Density hydrometers
2163	Laboratory glassware—Measuring cylinders
3529	Solvents—Toluene
5604	Timber—Natural durability ratings
NZS	
3640	Chemical preservation of round and sawn timber

AS/NZS

- 1148 Timber—Nomenclature—Australian, New Zealand and imported species
- 1604 Specification for preservative treatment (all parts)
- 1605 Methods for sampling and analysing timber preservatives and preservative-treated timber
- 1605.1 Part 1: General requirements, sampling, and determination of sapwood and heartwood presence
- 4491 Timber—Glossary of terms in timber-related Standards

ASTM

- D370 Standard practice for dehydration of oil-type preservatives
- E1 Standard specification for ASTM liquid-in-glass thermometers

BS

- 676 Specification for flasks with graduated necks (phenols type)

ISO

- 2719 Determination of flash point—Pensky-Martens closed cup method
- 5272 Toluene for industrial use—Specifications

1.4 DEFINITIONS

Refer to AS/NZS 1605.1 for applicable definitions.

1.5 PREPARATION OF PRESERVATIVE LIQUIDS AND SOLUTIONS FOR ANALYSIS

1.5.1 Oil-borne preservatives

A sample of preservative taken in accordance with AS/NZS 1605.1 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 before drawing off sufficient for the required analysis.

1.5.2 Waterborne preservatives

A sample of preservative taken in accordance with AS/NZS 1605.1 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.

1.5.3 Creosote

A creosote sample taken in accordance with AS/NZS 1605.1 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 just sufficiently 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.

1.6 RELATED METHODS OF ANALYSIS

The analytical methods given in this Standard are intended as referee methods for the determination of timber preservative retentions. Alternative methods should be compared with methods presented in this Standard before being routinely used, provided that they are of comparable accuracy, e.g. CCA treated timber may be analysed by AAS, XRF, or ICP methods, and boron treated timber by alternative water extracted titration method.

SECTION 2 DETERMINATION OF COPPER, HEXAVALENT CHROMIUM AND ARSENIC IN CCA PRESERVATIVE SOLUTIONS

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 sulphate.

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

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 sulphonate in 1 mL to 2 mL water, gradually diluting to 100 mL, with stirring. Filter the solution into the reagent flask.
- (b) *Ferrous ammonium sulphate (FAS) solution* Dissolve 140 g ferrous ammonium sulphate in 500 mL water before adding 25 mL concentrated sulphuric acid and final dilution to 1000 mL.

Dilute this stock solution 10:1 volumetrically before use.

- (c) *Mixed acid solution* Gradually add, with stirring, 500 mL concentrated sulphuric acid to 500 mL water. When cool adjust the volume to 1000 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 1000 mL.
Dilute this stock solution volumetrically 10:1 before use (1 mL contains exactly 0.0010 g $K_2Cr_2O_7$ after dilution and is equivalent to 0.3535 mg Cr).
- (e) *Standard copper solution, 1000 μ g copper/mL* Dissolve 7.8580 g copper sulphate pentahydrate in water and dilute to 2000 mL in a volumetric flask.
- (f) *Standard arsenic solution, 1000 μ g As/mL* Dissolve 2.6415 g arsenous trioxide (As_2O_3) in 50 mL of 20% potassium hydroxide solution, and dilute to 2000 mL with 1% aqueous sulphuric acid.

2.3 PROCEDURE

2.3.1 Instrument settings and operation

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

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 solutions [Clauses 2.2(e) and 2.2(f)] to a series of 200 mL one-marked volumetric flasks.

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

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

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 2.3.3.
 - (iii) Add to the aliquot 100 mL water and either 2 mL or 5 mL sulphuric 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% sulphuric 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 2.3.3
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

2.4 CALCULATIONS OF THE PERCENTAGE OF METALS

2.4.1 Hexavalent chromium

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

$$\text{Percent Cr (VI)} = 0.0354 \times (B - T) \quad \dots 2.4.1$$

where

B = the blank titre [Clause 2.3.3(a)]

T = the test solution titre [Clause 2.3.3(a)]

2.4.2 Copper or arsenic

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

(a) Option A: Percent metal = $\frac{X}{100}$... 2.4.2(1)

(b) Option B: Percent metal = $\frac{X}{50}$... 2.4.2(2)

(c) Option C: Percent metal = $\frac{X}{20}$... 2.4.2(3)

where X is the concentration of the appropriate metal in $\mu\text{g/mL}$ of the test solution (Clause 2.3.2).

SECTION 3 DETERMINATION OF BORON IN PRESERVATIVE SOLUTION

3.1 PRINCIPLE

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

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 1000 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) is given by the following equation:

$$M = \frac{(\text{Weight of KHP}) \times 1000}{(\text{Titre}) \times 204.22} \quad \dots 3.2$$

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. (The precipitate is transferred to the volumetric flask.)
- (i) Filter a portion of the solution through a Whatman No. 542 filter paper.
- (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, the acid aliquot shall be refluxed to eliminate carbon dioxide, and the solution shall be cooled.
- (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.

3.4 CALCULATIONS

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

$$\text{Percent boron} = 1.162 \times (T - B) \times (C) \times (M) \quad \dots 3.4$$

where

T and B = titre and blank volumes of M standard sodium hydroxide solution
[Clause 3.2(e)(ii)]

C = 1.1, the correction factor

M = molarity [see Clause 3.2(e)(ii)]

SECTION 4 DETERMINATION OF FLUORIDE IN PRESERVATIVE SOLUTION BY ION- SELECTIVE ELECTRODE

4.1 PRINCIPLE

Fluoride is determined by dilution of the preservative solution with distilled water and determination by ion-selective electrode.

4.2 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) *Sodium hydroxide concentrate, 60%* Dissolve 600 g sodium hydroxide in 1000 mL water. Cool and store in polyethylene.
- (b) *SSA-EDTA buffer* Dissolve 204 g sulphosalicylic acid (SSA) and 74 g disodium dehydrate EDTA in 700 mL water and adjust the pH to 9.5 with concentrated (s.g.:0.880) ammonia solution before dilution to 1000 mL. This buffer is 0.8M SSA and 0.2M EDTA.
- (c) *Fluoride standard, 1000 µg/mL* Dissolve 2.210 g sodium fluoride in water and dilute to 1000 mL. Store in polyethylene.

4.3 PROCEDURE

4.3.1 Instrument operation

Several different types of ion-selective meters are available, and each has different operating characteristics. The operating manual shall be followed.

Particular attention shall be given to measuring electrode slope and setting the meter to the current slope value, and solutions shall be gently stirred during electrode equilibration.

4.3.2 Preparation of calibration solutions

The calibration solutions shall be prepared as follows:

- (a) Transfer a 200 mL aliquot of the 1000 µg/mL fluoride standard [Clause 4.2(c)] to a 1000 mL one-marked volumetric flask, dilute to the mark, and mix well.
- (b) Transfer aliquot of 1 and 10 mL of this 200 µg/mL standard solution to 200 mL one-marked volumetric flasks.
- (c) Transfer a 20 mL aliquot of the original 1000 µg/mL fluoride standard [Clause 4.2(c)] to a third 200 mL one-marked volumetric flask.
- (d) To each of the three volumetric flasks, add 10 mL of sodium hydroxide concentrate [Clause 4.2(a)] and 100 mL of SSA-EDTA buffer [Clause 4.2(b)] and dilute to the mark and mix well. These calibration solutions contain 1, 10 and 100 µg fluoride/mL, respectively. They shall be stored in polyethylene containers.

4.3.3 Analysis of treatment solution

The treatment solution shall be analysed as follows:

- (a) Transfer 2 mL of preservative solution to a 1000 mL volumetric flask and dilute to the mark with water.
- (b) Filter the solution (or allow the solids to settle first) and pipette 25 mL into a small beaker, together with 25 mL SSA-EDTA buffer.
- (c) Using suitable operating procedures for the electrode/meter combination, use calibration solutions (Clause 4.3.2) and set up the instrument calibration at 1, 10 and 100 µg/mL fluoride, ensuring that sufficient equilibration time is allowed, especially at 1 µg/mL.
- (d) Read the fluoride content of the solutions on the calibrated instrument, together with a reagent blank solution.

If the fluoride content of the solution is expected to be below 0.2% sodium fluoride, the dilution to 1000 mL of the preservative solution should be reduced to 500 mL, and an appropriate factor introduced into the calculations.

4.4 CALCULATIONS

The percentage by mass of fluoride (NaF) in the preservative solution shall be expressed in terms of equivalent sodium fluoride, and calculated from the following equation:

$$\text{Percent NaF} = 0.02210 X \quad \dots 4.4$$

where

X = the fluoride concentration of the test solution, in µg/mL

SECTION 5 DETERMINATION OF PENTACHLOROPHENOL (PCP) IN PRESERVATIVE SOLUTIONS

5.1 PRINCIPLE

Pentachlorophenol is analysed by dilution of the organic solvent with methanol and analysis by HPLC.

5.2 REAGENTS

All reagents shall be of chromatographic solvent purity. The water used for the preparation of the reagents shall be distilled.

The following reagents shall be used:

- (a) *Methanol.*
- (b) *Acetonitrile:water:acetic acid 75:25:0.1* Add 1.0 mL of glacial acetic acid to a mixture of 750 mL acetonitrile and 250 mL freshly glass-distilled water. Degas before use.
- (c) *Acetonitrile:water:acetic acid 100:0:0.1* Add 1.0 mL of acetic acid to 1000 mL of acetonitrile. Degas before use.
- (d) *Pentachlorophenol* Purified for use as a standard.
- (e) *Standard solutions*

NOTE: Working standards should contain 0.002% and 0.020% mass/volume pure pentachlorophenol in methanol.

5.3 PROCEDURE

5.3.1 Instrument settings and operation

A Waters 450 HPLC shall be used with a 481 UV detector set at 220 nm and a *ubondapak* C-18 steel column at 0.30 AUFS. The liquid shall flow at 2.5 mL/min beginning with 75:25:0.1 acetonitrile:water:acetic acid for 2 min after injection then step to 100:0:0.1 for 2 min followed by a return to 75:25:0.1 for 4 min.

5.3.2 Sample preparation

The samples shall be prepared as follows:

- (a) Dilute solution to be tested such that the level of pentachlorophenol lies between the two standards using methanol solvent.
- (b) Filter the final dilution through a 0.5 µm PTFE filter in a 13 mm Swinnex filter holder. Inject 25 µL for samples and standards.

5.4 CALCULATIONS

The percent mass/volume of pentachlorophenol (PCP) in the preservative solutions shall be calculated from the following equation:

$$\text{PCP (\% m/v)} = m \times D \quad \dots 5.4$$

where

m = percent pentachlorophenol in final solution (mass/volume)

D = dilution factor

SECTION 6 DETERMINATION OF ORGANOCHLORINE INSECTICIDES IN PRESERVATIVE TREATMENT SOLUTIONS

6.1 PRINCIPLE

Organochlorines are quantitatively extracted from water/emulsions using toluene. The extracts are then diluted to the appropriate range and analysed by gas chromatography (GC) using electron capture detection. This method is applicable to all solutions containing these preservatives.

6.2 REAGENT—STANDARD SOLUTION

The reagent used is standard solution, 100 µg aldrin/mL or 100 ppm. The reagent shall be of analytical reagent quality. The water used for the preparation of the reagent shall be distilled water.

The reagent shall be prepared as follows:

- (a) Weigh sufficient aldrin of known purity to obtain 50 mg aldrin exactly. Repeat the procedure using known purity heptachlor, chlordane, and chlordane dieldrin mixture.
- (b) Dissolve in toluene and dilute to 500 mL in a one-marked volumetric flask.
- (c) Store the standard stock solution in a well-sealed screw-top bottle to prevent evaporation.
- (d) Prepare working standards by adding 10 mL stock to a 100 mL volumetric flask and making up to the mark with toluene (1.0 ppm). Prepare the 0.1 ppm and 0.01 ppm standards by serial dilution of the 1.0 ppm working standard.

6.3 PROCEDURE

6.3.1 Instrument settings and operation

The instrument used shall be a Varian 3700 gas chromatography with a SGE 25AQ3/HT5 0.1 column and ECD detector. The column shall be maintained at 100°C for 1 min after injection then ramped at 25°C per minute to 200°C and held for 6 min. One micro-litre of sample shall be injected through a Varian 8000 auto-injection system.

6.3.2 Sample preparation

The procedure for sample preparation shall be as follows:

- (a) Pipette 1.00 mL freshly shaken solution into a 125 mL separating funnel with 50 mL distilled water and 25 mL hexane.
- (b) Rock the separating funnel gently for 3 min then allow the two layers to separate. (With some emulsions this may be difficult and better separation can be achieved by allowing as much of the aqueous layer as possible to settle out, draining off, adding saturated aqueous sodium sulphate, rocking a few seconds and allowing the separation to take place.)
- (c) Drain out the aqueous layer to a 100 mL beaker. Pour the hexane layer into a 100 mL volumetric flask. Add 25 mL fresh hexane, pour the aqueous layer back in and repeat the extraction. Repeat the separation and recover the aqueous layer.

- (d) Repeat the extraction once more (a total of three extractions).
- (e) Make up to the mark with hexane. Add anhydrous sodium sulphate to remove any water.
- (f) Dilute this solution 1:1000 with toluene. Place sample in 2 mL GC vials for analysis.

6.4 CALCULATIONS

The percent mass/volume of organochlorine in original solution shall be calculated from the following equation:

$$\text{organochlorine in original solution (\% m/v)} = \frac{p \times 10\,000}{1\,000\,000} \quad \dots 6.4$$

where

- p = ppm of each organochlorine in the final solution
- 1 000 000 = dilution factor (1/100 × 1/1000)
- divisor 10 000 = 10 000 ppm in 1%
- = conversion to percent mass/volume