DRAFT FOR DEVELOPMENT

DD 257-5:2003

Methods of analysis of wood preservatives and treated timber —

Part 5: Determination of carboxylic acid type in zinc and copper carboxylate preservative solutions by gas chromatography

ICS 71.040.50; 71.100.50

British Standards

Committees responsible for this Draft for Development

The preparation of this Draft for Development was entrusted by Technical Committee B/515, Wood preservatives, to Subcommittee B/515/2, Specifications and chemical testing of wood preservatives, upon which the following bodies were represented:

Association of Consulting Scientists

British Wood Preserving and Damp-proofing Association

Chemical Industries Association

Creosote Council

Department of Trade and Industry — represented by the Building Research Establishment

Timber Trade Federation

Co-opted members

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Contents

Foreword

This part of DD 257 has been prepared by Subcommittee B/515/2 under the direction of Technical Committee B/515.

DD 257 gives a variety of methods of analysis of wood preservatives and treated timber:

— DD 257-1 describes a titrimetric method and a colorimetric method for the determination of boron compounds as boric acid in preservative solutions (both aqueous solutions and solutions in hydrocarbon solvents) and in treated timber;

— DD 257-2 describes a polarographic method and a thin-layer chromatographic method for the determination of tributyltin, dibutyltin and monobutyltin compounds present in wood preservative solutions and in treated timber;

— DD 257-3 describes a high performance liquid chromatographic method and a gas chromatographic method for the separation and determination of the cis and trans isomers of permethrin in organic solvent-based solutions of wood preservatives;

— DD 257-4 describes a high performance liquid chromatographic method and a gas chromatographic method for the separation and determination of the cis and trans isomers of cypermethrin in organic solvent-based wood preservative solutions;

— DD 257-5 describes gas chromatographic methods for the qualitative identification of carboxylic acids in wood preservative solutions containing zinc and copper carboxylates.

WARNING. This part of DD 257 calls for the use of substances and/or procedures that may be injurious to health if adequate precautions are not taken. It refers only to technical suitability and does not absolve the user from legal obligations relating to health and safety at any stage.

Attention is drawn to the Health and Safety at Work etc. Act 1974 [1] and the Control of Substances Hazardous to Health Regulations 1994 (as amended) [2], and to the need for ensuring that the method of test specified in this standard is carried out with suitable precautions. See safety precautions mentioned in BS 5666-1:1987, Clause **3**.

It has been assumed in the preparation of this part of DD 257 that the execution of its provisions will be entrusted to appropriately qualified and experienced people, for whose use it has been produced.

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

This publication is not to be regarded as a British Standard.

It is being issued in the Draft for Development series of publications and is of a provisional nature because there is at present insufficient experience in the use of the test method. It should be applied on this provisional basis, so that information and experience of its practical application can be obtained.

A review of this Draft for Development will be carried out not later than 2 years after its publication. Notification of the start of the review period, with a request for the submission of comments from users of this Draft for Development, will be made in an announcement in the appropriate issue of *Update Standards*.

According to the replies received, the responsible BSI Committee will judge whether the Draft for Development can be converted into a British Standard or what other action should be taken.

Observations which it is felt should receive attention before the official call for comments will be welcomed.

These should be sent to the Secretary of BSI Technical Committee B/515 at British Standards House, 389 Chiswick High Road, London, W4 4AL.

Summary of pages

This document comprises a front cover, an inside front cover, pages i to iv, pages 1 to 9 and a back cover.

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Introduction

Two gas chromatographic options are described in this part of DD 257: one using a capillary column, the other a packed column. However, the capillary column is the preferred method as the resolution of the peaks is very much better than that obtained by the packed column. Both methods have been found suitable for the identification of carboxylic acids in the presence of tri-*n*-butyltin oxide, pentachlorophenol, 2-phenylphenol, γ-HCH, dieldrin, permethrin, cypermethrin and water repellent waxes and resins normally incorporated in organic solvent-based wood preservative formulations.

1 Scope

This part of DD 257 describes a method for the qualitative identification of carboxylic acids in wood preservative solutions containing zinc and copper carboxylates. It gives two gas chromatographic options: one using a capillary column and one using a packed column.

It is applicable primarily to the analysis of preservative formulations conforming to BS 5707.

2 Normative references

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

BS 245, *Specification for mineral solvents (white spirit and related hydrocarbon solvents) for paints and other purposes.*

BS 5666-1:1987, *Methods of analysis of wood preservatives and treated timber — Part 1: Guide to sampling and preparation of wood preservatives and treated timber for analysis.*

BS 5707, *Specification for preparations of wood preservatives in organic solvents.*

BS EN ISO 3696, *Water for analytical laboratory use — Specification and test methods.*

3 Terms and definitions

For the purposes of this part of DD 257, the following terms and definitions apply.

3.1
carboxylate
zinc and copper salts of those carboxylic acids that give rise to compounds soluble in appropriate hydrocarbon solvents, and that have been approved for use in the UK as wood preservatives

NOTE 1 BS 5707 defines the purity and composition of both zinc and copper carboxylate preparations used in the production of light organic solvent wood preservatives.

NOTE 2 Petroleum distillate or coal tar distillate or a mixture of these are deemed to be appropriate hydrocarbon solvents.

4 Method

4.1 Principle

The preservative solution is treated with hydrochloric acid to liberate the carboxylic acid component of the zinc or copper carboxylate. The liberated acid is separated from the hydrocarbon solvent by saponification and reacidification into chloroform, and subsequently analysed by gas-liquid chromatography. The gas chromatograph is fitted with a flame ionization detector (FID) and either a capillary or a packed column. The chromatogram obtained is compared with that of a known reference standard to establish the identity of the carboxylic acid. Retentions are measured relative to a known component (hexanoic acid) added to both reference and test solutions.

4.2 Reagents and materials

4.2.1 *General*

Except where otherwise specified, all reagents shall be of recognized analytical grade and water conforming to BS EN ISO 3696:1995, grade 3 shall be used throughout.

4.2.2 *Reagents*

4.2.2.1 *White spirit* conforming to BS 245.

4.2.2.2 *Hydrochloric acid solution*, c(HCl) = 5 mol/l approximately. Dilute 500 ml of hydrochloric acid, HCl, 425 g/l (ρ_{20} = 1.18 g/ml) to 1 l with water.

4.2.2.3 *Sodium hydroxide solution*, c(NaOH) = 5 mol/l approximately. Dissolve 200 g of sodium hydroxide, NaOH, in 1 l of water.

4.2.2.4 *Chloroform* ($CHCl_3$).

4.2.2.5 *Sodium sulfate* (Na_2SO_4), anhydrous powder.

4.2.2.6 *Hexanoic acid* [$CH_3(CH_2)_4COOH$], of purity not less than 99.5 %.

4.2.2.7 *Reference carboxylic acids*.

NOTE For information on suitable reference carboxylic acids, contact the Secretary of BSI Technical Committee B/515 at British Standards House, 389 Chiswick High Road, London, W4 4AL.

4.2.3 *Materials*

4.2.3.1 *Air* at not less than 150 kPa pressure.

4.2.3.2 *Hydrogen* at not less than 100 kPa pressure.

4.2.3.3 *Helium* at not less than 150 kPa pressure.

4.2.3.4 *Nitrogen* at not less than 620 kPa pressure.

4.3 Apparatus

4.3.1 *General*

4.3.1.1 *Gas chromatograph*, fitted with a flame ionization detector supplied with air (**4.2.3.1**) and hydrogen (**4.2.3.2**), and set up according to the manufacturer's instructions for either capillary or packed column use as detailed in **4.3.2** and **4.3.3** respectively.

4.3.2 *Capillary column option*

4.3.2.1 *Injection system*, consisting of a separately heated split/splitless injector in split mode fitted with a disposable glass liner, capable of being controlled within the nominal temperature range 265 °C to 275 °C.

4.3.2.2 *Injection volume of 0.4 µl* delivered from a suitable 1 µl injection syringe.

4.3.2.3 *Helium* (**4.2.3.3**) *carrier gas supply* at a pressure of 50 kPa to a nominal split ratio of 1:2.

4.3.2.4 *Programmed oven temperature*. Initial oven temperature of 150 °C maintained for 5 min following injection of sample, then heated at a rate of 20 °C/min to 260 °C and maintained at this temperature for 9.5 min. Allow 5 min equilibration between runs after the column oven has been cooled to 150 °C.

4.3.2.5 *Fused silica wall-coated open tubular column*, 10 m in length and 0.32 mm internal diameter with 0.4 µm film thickness silicone[1].

NOTE As a result of the natural variation in column performance with age, and the use of equivalent but not identical stationary phases, it can be necessary to make adjustments to the stated instrument conditions in order to obtain a suitable chromatogram.

4.3.3 *Packed column option*

4.3.3.1 *Injection system*, consisting of a separately heated injection block and fitted with a disposable glass liner, capable of being controlled within the nominal temperature range 270 °C to 280 °C.

4.3.3.2 *Injection volume of 1 µl*, delivered from a suitable 1 µl injection syringe.

4.3.3.3 *Nitrogen* (**4.2.3.4**) *carrier gas flow* of 40 ml/min at a pressure that is sufficient to maintain a constant flow rate throughout the temperature-programmed procedure (**4.3.3.4**).

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[1] OV351™ is a trade mark owned by Ohio Valley Specialty Chemical, 115 Industry Road, Marietta, Ohio 45750, USA, and is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by BSI of this product.

4.3.3.4 *Programmed oven temperature.* Initial oven temperature of 165 °C maintained for 20 min following injection of sample, then heated at a rate of 10 °C/min to 230 °C and maintained at this temperature for 20 min. Allow 5 min equilibration between runs after the column has been cooled to 165 °C.

4.3.3.5 *Glass column*, 2 m in length and 3 mm internal diameter, packed with 80 to 100 mesh (50 µm to 175 µm) support[2)].

NOTE As a result of the natural variation in column performance with age, and the use of equivalent but not identical stationary phases, it can be necessary to make adjustments to the stated instrument conditions in order to obtain a suitable chromatogram.

4.4 Procedure

4.4.1 *Preparation of the column*

When employing the capillary column method (**4.3.2**), condition the column by passing helium (**4.2.3.4**) through it for at least 16 h at a temperature of approximately 280 °C and with the column disconnected from the detector.

When employing the packed column method (**4.3.3**), condition the column by passing nitrogen (**4.2.3.4**) through it for at least 16 h at a temperature of approximately 250 °C and with the column disconnected from the detector.

4.4.2 *Extraction of carboxylic acids*

Weigh approximately 5 g of preservative solution into a tared 50 ml separating funnel.

NOTE 1 The mass of preservative solution may be adjusted to obtain a theoretical carboxylic acid content within the range of this procedure.

NOTE 2 This part of DD 257 is qualitative in nature. Where it is required to determine the copper content in accordance with BS 5666-4 or the zinc content in accordance with BS 5666-5, the mass of preservative solution taken should be weighed to the nearest 1 mg. However, if the copper or zinc content is not required then the mass of preservative solution taken can be weighed to the nearest 0.1 g.

Add 10 ml of white spirit (**4.2.2.1**) and mix well. Extract successively with three 20 ml portions of the hydrochloric acid solution (**4.2.2.2**). For each extraction, shake the funnel vigorously for 90 s, allow to settle, and run off the aqueous phase.

NOTE 3 Where the copper or zinc content is to be determined according to BS 5666-4 or BS 5666-5 respectively, the successive aqueous phase separations should be retained and made up to 500 ml in a one-mark volumetric flask to BS EN ISO 1042:2000, class A as the test solution.

Extract the retained organic phase with three 10 ml portions of the sodium hydroxide solution (**4.2.2.3**). For each extraction, shake the funnel for 90 s and allow to settle. Bulk the aqueous phase from each of the successive extractions into a 100 ml separating funnel. To this funnel add 40 ml of the hydrochloric acid solution (**4.2.2.2**), shake and allow to cool.

Wash the acidified extract with three 5 ml portions of chloroform (**4.2.2.4**). Bulk the chloroform extracts and evaporate gently on a water bath to approximately 3 ml. Filter through anhydrous sodium sulfate (**4.2.2.5**) into a 5 ml one-mark volumetric flask, add 0.1 g of the hexanoic acid (**4.2.2.6**) and make up to the mark with chloroform (**4.2.2.4**).

NOTE 4 Filtration through 0.5 g of anhydrous sodium sulfate (**4.2.2.5**) contained in a 9 cm diameter filter paper[3)] has been found to be suitable.

4.4.3 *Preparation of reference solutions*

Into a 25 ml one-mark volumetric flask, weigh approximately 2.5 g of the pure carboxylic acid or carboxylic acid mixture (**4.2.2.7**) to be used as the reference solution. Add 0.5 g of the hexanoic acid (**4.2.2.6**) and make up to the mark with chloroform (**4.2.2.4**).

[2)] Chromosorb G® is a registered trade mark owned by Restek Corporation, 110 Benner Circle, Bellefont, Pennsylvania 16823, USA, and when either acid washed (AW) or treated with dimethyldicholorosilane (DMCS), carrying 3 % of free fatty acid phase (FFAP), is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by BSI of this product.

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4.4.4 *Measurement*

With the gas chromatograph (**4.3.1.1**) in operation under the conditions specified (**4.3.2** or **4.3.3**), inject successively the reference solution and test solution into the gas chromatograph, adjusting the instrument sensitivity as required to obtain a satisfactory chromatogram. If necessary, increase the instrument sensitivity to give adequate characterization of peaks from naphthenic acids after approximately 5 min for the capillary column (**4.3.2**) or after approximately 14 min for the packed column (**4.3.3**).

4.5 Interpretation of results

Conduct an initial evaluation of chromatographic data by visual comparison of the chromatogram for the reference and test solutions to identify similar peak groupings.

NOTE 1 Under the conditions specified in **4.3.2** the retention time of hexanoic acid (**4.2.2.6**) is about 1.3 min. Typical chromatograms for synthetic carboxylic and naphthenic acid mixtures are given in Figure 1 and Figure 2 respectively.

NOTE 2 Under the conditions specified in **4.3.3** the retention time of hexanoic acid (**4.2.2.6**) is about 4.5 min. Typical chromatograms for synthetic carboxylic and naphthenic acid mixtures are given in Figure 3 and Figure 4 respectively.

For each of the major peaks in the reference and test solution gas-liquid chromatograms, calculate the relative retention of the component compared to hexanoic acid (**4.2.2.6**) according to the following:

$$\frac{R_x}{R_s}$$

where

R_s is the retention time, in minutes (min), of hexanoic acid;

R_x is the retention time, in minutes (min), of an individual acid component peak in the chromatogram.

The relative retentions of the major components from the test solution shall be within ±2 % of their value in the reference chromatogram.

NOTE 3 For synthetic carboxylic acids relative retentions for the major peaks in the range 1.0 to 3.0 would be expected. For naphthenic acids, relative retentions of the range 1.0 to 10.0 with a characteristic grouping of peaks in the range 3.5 to 10.0 are to be expected.

NOTE 4 For synthetic carboxylic acids it is necessary that further points of similarity be established between the test solution chromatogram and the reference chromatogram so that, for instance, carboxylates that are not approved are not identified wrongly simply because the chromatogram is broadly similar to a reference chromatogram.

Where no obvious visual difference exists between the test solution and reference acids, identify components A to F or A to D by reference to the typical chromatograms shown in Figure 1 or Figure 3 as appropriate. Determine the peak area (or height) of each component and then calculate the following ratio:

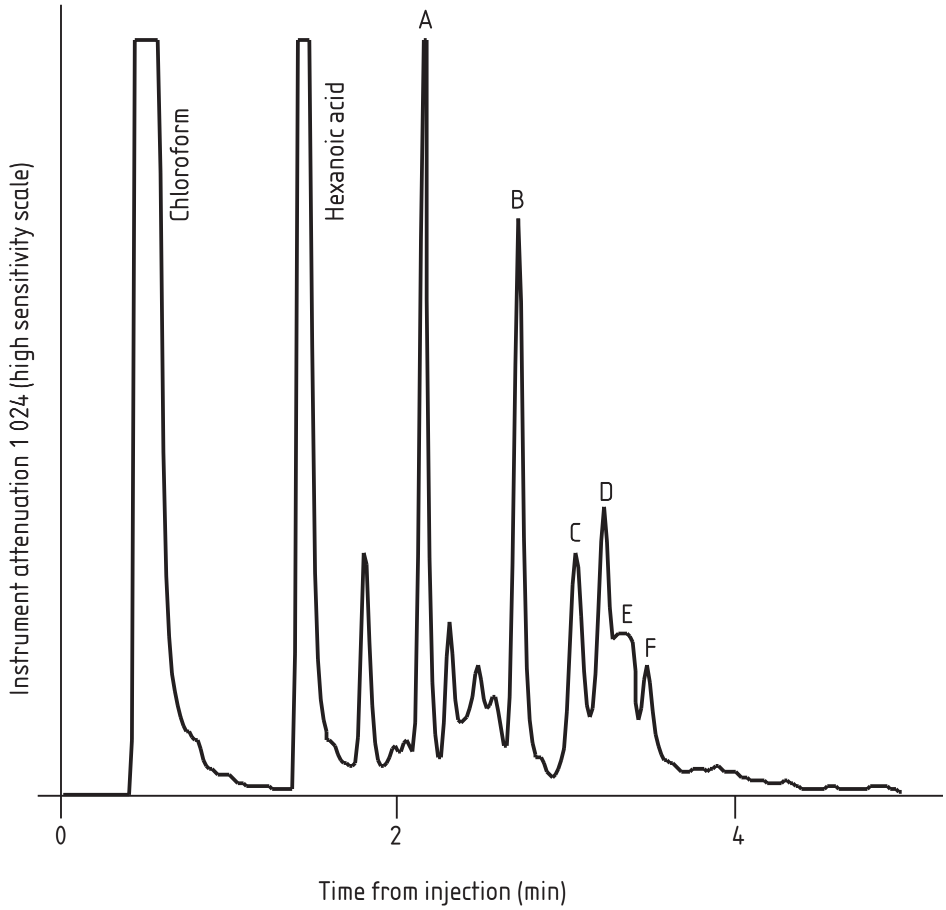
$$k = \frac{A}{S}$$

where

A is the area or height of component A;

S is the sum of the areas or heights of components B to F or B to D as appropriate.

The calculated value of k shall lie within the range 0.4 to 0.7 for a typical synthetic carboxylic acid mixture.



Key

A to F carboxylic acid peaks used in the calculations in **4.5**

Figure 1 — Typical chromatogram for a synthetic carboxylic acid mixture analysed under the conditions specified in 4.3.2

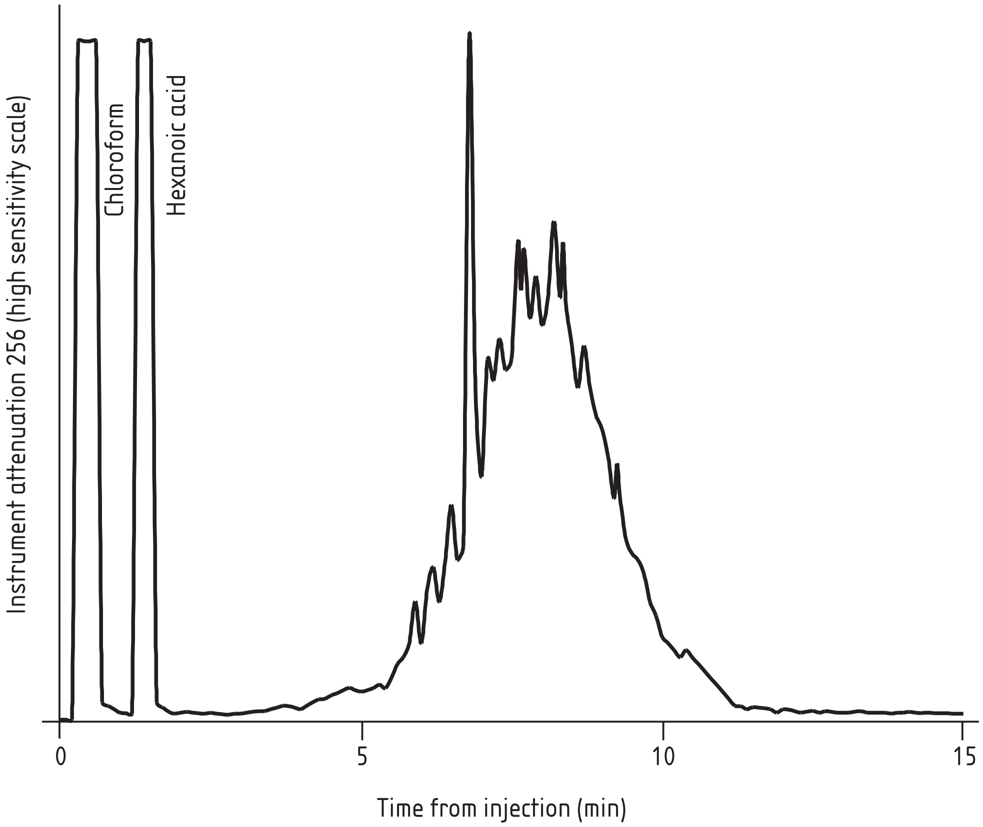
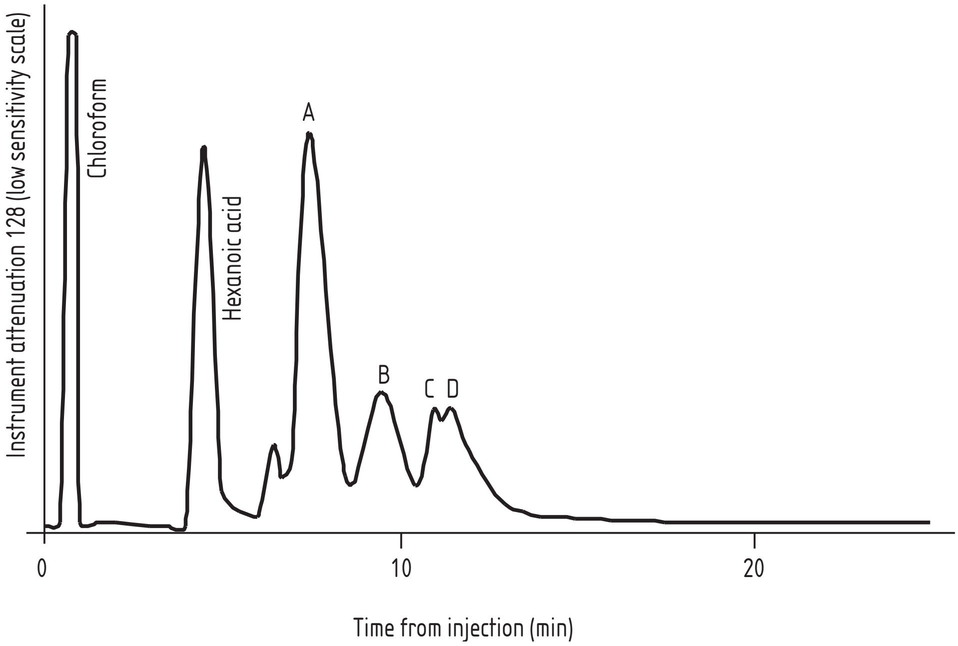


Figure 2 — Typical chromatogram for a naphthenic acid mixture analysed under the conditions specified in 4.3.2



Key

A to D carboxylic acid peaks used in the calculations in **4.5**

Figure 3 — Typical chromatogram for a synthetic carboxylic acid mixture analysed under the conditions specified in 4.3.3

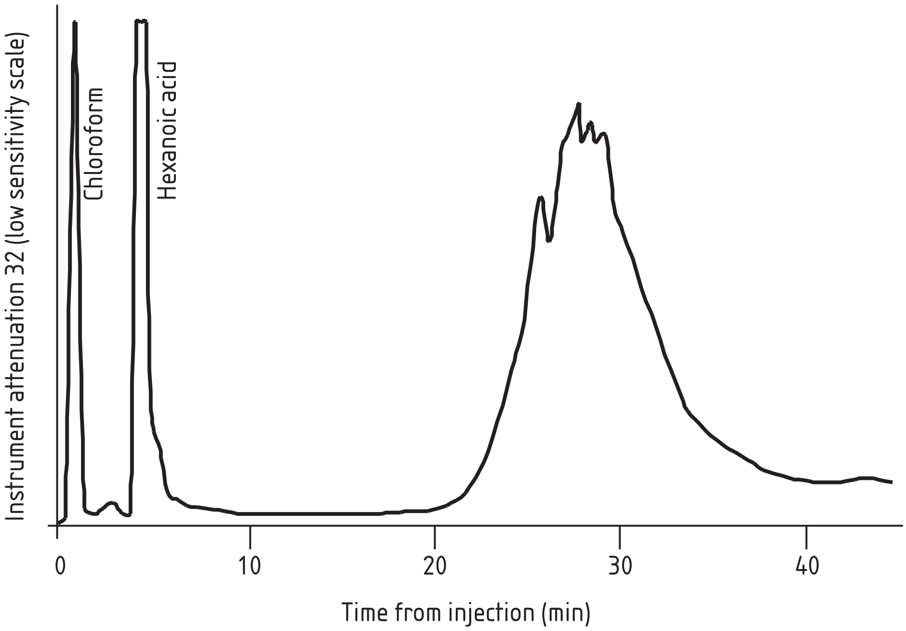


Figure 4 — Typical chromatogram for a naphthenic acid mixture analysed under the conditions specified in 4.3.3

5 Test report

The test report shall include at least the following information:

a) number and date of this part of DD 257, i.e. DD 257-5:2003;

b) type of column used;

c) full identification of the sample and details of the preparation of this sample for analysis;

d) results of the analysis;

e) any special conditions relating to the test, or departures from the test method;

f) any unusual features noted during the analysis;

g) name of the organization responsible for the report and the date of issue;

h) name and signature of the person responsible for the test.

Bibliography

Standards publications

BS 5666-4:1979, *Methods of analysis of wood preservatives and treated timber — Part 4: Quantitative analysis of preservatives and treated timber containing copper naphthenate.*

BS 5666-5:1986, *Methods of analysis of wood preservatives and treated timber — Part 5: Determination of zinc naphthenate in preservative solutions and treated timber.*

DD 257-1:2003, *Methods of analysis of wood preservatives and treated timber — Part 1: Quantitative analysis of wood preservative solutions and treated timber containing boron compounds — Determination of total boron.*

DD 257-2:2003, *Methods of analysis of wood preservatives and treated timber — Part 2: Quantitative analysis of wood preservative solutions and treated timber containing n-butyltin compounds — Determination of tributyltin, dibutyltin and monobutyltin.*

DD 257-3:2003, *Methods of analysis of wood preservatives and treated timber — Part 3: Quantitative analysis of permethrin in solutions of wood preservatives in organic solvents.*

DD 257-4:2003, *Methods of analysis of wood preservatives and treated timber — Part 4: Quantitative analysis of cypermethrin in solutions of wood preservatives in organic solvents.*

BS EN ISO 1042:2000, *Laboratory glassware — One-mark volumetric flasks.*

Other publications

[1] GREAT BRITAIN. The Health and Safety at Work, etc. Act 1974. London: The Stationery Office.

[2] GREAT BRITAIN. The Control of Substances Hazardous to Health Regulations 1994 (as amended). London: The Stationery Office.

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