

Water quality — Gas chromatographic determination of some selected chlorophenols in water

The European Standard EN 12673:1998 has the status of a British Standard

ICS 13.060.50

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National foreword

This British Standard is the English language version of EN 12673:1998.

The UK participation in its preparation was entrusted by Technical Committee EH/3, Water quality, to Subcommittee EH/3/2, Physical, chemical and biochemical methods, which has the responsibility to:

- aid enquirers to understand the text;
- present to the responsible international/European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;
- monitor related international and European developments and promulgate them in the UK.

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

BS EN 12673 is one of a series of standards on water quality, others of which have been, or will be, published as Sections of BS 6068. This standard has therefore been given the secondary identifier BS 6068-2.65. The various Sections of BS 6068 are comprised within Parts 1 to 7, which, together with Part 0, are listed below.

- Part 0 *Introduction*
- Part 1 *Glossary*
- Part 2 *Physical, chemical and biochemical methods*
- Part 3 *Radiological methods*
- Part 4 *Microbiological methods*
- Part 5 *Biological methods*
- Part 6 *Sampling*
- Part 7 *Precision and accuracy*

NOTE The tests described in this British Standard should only be carried out by suitably qualified persons with an appropriate level of chemical expertise. Standard chemical procedures should be followed throughout.

Cross-references

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

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Summary of pages

This document comprises a front cover, an inside front cover, the EN title page, pages 2 to 16, an inside back cover and a back cover.

Amendments issued since publication

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English version

Water quality — Gas chromatographic determination of some selected chlorophenols in water

Qualité de l'eau — Dosage par chromatographie en phase gazeuse de certains chlorophénols dans les eaux

Wasserbeschaffenheit — Gaschromatographische Bestimmung einiger ausgewählter Chlorphenole in Wasser

This European Standard was approved by CEN on 26 November 1998.

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CEN

European Committee for Standardization
Comité Européen de Normalisation
Europäisches Komitee für Normung

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Foreword

This European Standard has been prepared by Technical Committee CEN/TC 230, Water analysis, the Secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by June 1999, and conflicting national standards shall be withdrawn at the latest by June 1999.

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

Annexes designated “informative” are only given for information. In this standard annexes A to G are informative.

It is absolutely essential that tests conducted according to this standard are carried out by suitably qualified staff.

1 Scope

This European Standard describes the gas chromatographic determination of 19 chlorophenols (2-, 3-, and 4-chlorophenol, 2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-dichlorophenol, 2,3,4-, 2,3,5-, 2,3,6-, 2,4,5-, 2,4,6 and 3,4,5-trichlorophenol, 2,3,4,5-, 2,3,4,6-, and 2,3,5,6-tetrachlorophenol and pentachlorophenol) in drinking water, groundwater, rainwater, waste water, sea water and surface water.

This standard describes an acetylation followed by a liquid/liquid extraction and determination by gas chromatography and electron capture detection or mass selective detection. The method is validated for drinking water, surface water and waste water, but may be used for all above mentioned types of water.

With this method chlorophenols can be determined over a range of concentrations from 0,1 µg/l to 1 mg/l, depending on the quantity of sample used and the component sensitivity (level of chlorination) (see annex A).

In some cases complete separation of isomers cannot be achieved. Then the sum is reported.

This method may be applicable to other halogenated phenolic compounds, provided the method is validated for each case.

2 Normative references

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies.

ISO 5667-5:1991, *Water quality — Sampling — Part 5: Guidance on sampling of drinking water and water used for food and beverage processing*.

ISO 5667-6:1990, *Water quality — Sampling — Part 6: Guidance on sampling of rivers and streams*.

ISO 5667-8:1993, *Water quality — Sampling — Part 8: Guidance on sampling of wet deposition*.

ISO 5667-9:1992, *Water quality — Sampling — Part 9: Guidance on sampling from marine waters*.

ISO 5667-10:1992, *Water quality — Sampling — Part 10: Guidance on sampling from waste waters*.

ISO 5667-11:1993, *Water quality — Sampling — Part 11: Guidance on sampling from ground waters*.

3 Definitions

For the purpose of this European Standard the following definition applies.

3.1

chlorophenol

compound having an aromatic nucleus carrying one hydroxyl group and from one to five chlorine atoms

4 Principle

Chlorophenols present in the aqueous samples are derivatized with acetic anhydride to their corresponding acetates. The derivatives formed are extracted from the sample with hexane. The hexane fraction is analysed by gas chromatography with electron capture detection or mass selective detection. Depending on the sample type pretreatment involves acid-base partition prior to the derivatization step.

5 Interferences

Surfactants, emulsifiers, higher concentrations of polar solvents and other phenolic substances can affect the extractive derivatization step.

Suspended particles in the water can also interfere and reduce the recovery. A second liquid phase in the water (e.g. mineral oil compounds, highly volatile halogenated hydrocarbons, emulsified fats and waxes) disturbs sampling, sample preparation and the enrichment. In those cases the examination is restricted to the aqueous phase and the portion of the non-aqueous phase is reported separately.

6 Reagents

WARNING The use of this European Standard may involve hazardous materials, operations and equipment. This standard does not purport to address all the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

6.1 General requirements

All reagents shall be of such a purity that they do not give rise to significant interfering peaks in the gas chromatographic analysis of the extracts. This shall be verified for each batch of material by running procedural blanks with each batch of samples analyzed. Reagents shall be stored in all glass containers with glass stoppers or with polytetrafluoroethylene (PTFE) lined caps.

6.2 Gas chromatographic gases, including helium, argon/methane, nitrogen or hydrogen. They shall be of a purity as recommended by the gas chromatograph manufacturer.

6.3 Ethanol, C₂H₅OH.

6.4 n-Hexane, C₆H₁₄.

6.5 Potassium carbonate solution, c(K₂CO₃) = 1,0 mol/l.

6.6 Potassium carbonate solution, c(K₂CO₃) = 0,1 mol/l.

6.7 Acetic anhydride, C₄H₆O₃.

NOTE Impurities in the acetic anhydride may affect the recovery. In that case it is possible to purify acetic anhydride by distillation.

6.8 *Toluene*, C_7H_8 .

6.9 *Phosphoric acid*, $c(H_3PO_4) = 0,5 \text{ mol/l}$.

6.10 *Sodium sulfate*, Na_2SO_4 , anhydrous, neutral.

NOTE Some batches of sodium sulfate have been found to be alkaline. In these circumstances it is possible to wash with methanol containing 0,5 ml concentrated hydrochloric acid per litre and to dry on a steam bath before roasting in a muffle furnace (7.6) at $500^\circ\text{C} \pm 20^\circ\text{C}$ for $4 \text{ h} \pm 0,5 \text{ h}$.

6.11 *Sodium hydroxide*, $c(NaOH) = 0,1 \text{ mol/l}$.

6.12 *Sodium thiosulfate pentahydrate*, $(Na_2S_2O_3 \cdot 5H_2O)$, crystals or a 10 % (m/m) solution.

6.13 *2-chlorophenol*, C_6H_5OCl .

6.14 *3-chlorophenol*, C_6H_5OCl .

6.15 *4-chlorophenol*, C_6H_5OCl .

6.16 *2,3-dichlorophenol*, $C_6H_4OCl_2$.

6.17 *2,4-dichlorophenol*, $C_6H_4OCl_2$.

6.18 *2,5-dichlorophenol*, $C_6H_4OCl_2$.

6.19 *2,6-dichlorophenol*, $C_6H_4OCl_2$.

6.20 *3,4-dichlorophenol*, $C_6H_4OCl_2$.

6.21 *3,5-dichlorophenol*, $C_6H_4OCl_2$.

6.22 *2,3,4-trichlorophenol*, $C_6H_3OCl_3$.

6.23 *2,3,5-trichlorophenol*, $C_6H_3OCl_3$.

6.24 *2,3,6-trichlorophenol*, $C_6H_3OCl_3$.

6.25 *2,4,5-trichlorophenol*, $C_6H_3OCl_3$.

6.26 *2,4,6-trichlorophenol*, $C_6H_3OCl_3$.

6.27 *3,4,5-trichlorophenol*, $C_6H_3OCl_3$.

6.28 *2,3,4,5-tetrachlorophenol*, $C_6H_2OCl_4$.

6.29 *2,3,4,6-tetrachlorophenol*, $C_6H_2OCl_4$.

6.30 *2,3,5,6-tetrachlorophenol*, $C_6H_2OCl_4$.

6.31 *Pentachlorophenol*, C_6Cl_5OH .

6.32 Standard solutions of chlorophenols

6.32.1 Internal standard solutions

Prepare solutions of at least two internal standards in ethanol (see 6.3).

For electron capture detection the following internal standard can be used:

- 2,4-dibromophenol, $C_6H_4OBr_2$;
- 2,6-dibromophenol, $C_6H_4OBr_2$;
- 2,3,6-trichlorophenol (see 6.24), $C_6H_3OCl_3$;
- 2,4,6-tribromophenol, $C_6H_3OBr_3$.

For mass selective detection similar labelled compounds can be used.

NOTE The two internal standards are used as a control for the analytical procedure. The choice of the two internal standards should reflect the anticipated occurrence of the chlorophenols in the sample (e.g. if dichlorophenols are expected 2,4-dibromophenol and 2,6-dibromophenol should be used).

Prepare a mixed standard of two component solutions in such a concentration that if a small volume is added to a sample, the amount of the internal standards gives peak heights on the chromatogram in the upper part of the linear working range.

Typically a concentration of $10 \mu\text{g/ml}$ can be used. Confirm their concentration prior to use.

6.32.2 Stock solutions

Prepare stock solutions of the chlorophenols by weighing each compound (6.13 to 6.31) and dissolving it in ethanol (6.3). Typical concentrations of the stock solutions are given in annex B. Alternatively, commercially available standard solutions can be used. Confirm the concentrations.

NOTE 1 Confirmation may be accomplished by spectrometric methods (e.g. UV spectrometry) or comparison with a standard of known concentration or from another source.

NOTE 2 Stock solutions are stable for at least half a year when stored in the dark at 4°C . At a temperature of -18°C they are stable for at least one year.

6.32.3 Intermediate standards

Prepare this mixed standard solution by dilution of the stock solutions (6.32.2). Suitable concentrations are given in annex B. The intermediate standards should be prepared freshly every month.

6.32.4 Working standards

Prepare a minimum of five different concentrations by suitable dilutions of the intermediate solution (6.32.3) with ethanol (6.3). Suitable concentrations are given in annex B. The working standards may be used for 5 days.

7 Apparatus

7.1 General requirements

Standard laboratory glassware cleaned to eliminate all interferences.

NOTE Heating to a temperature above 150°C before use assists in freeing glassware from possible contaminations. This procedure should not be used for volumetric bottles. Also an alkaline washing procedure can be used.

7.2 Sample bottles, all glass, with glass stoppers or with PTFE lined caps. A random bottle per batch shall be checked for interfering contamination by running a blank determination prior to use (see 9.5).

7.3 Flasks with ground stopper, glass, 100 ml.

7.4 Capillary gas chromatograph, equipped with an injector system which minimizes decomposition of the sample (e.g. on-column or glass-lined injector), an electron capture detector or mass selective detector and a recorder system (integrator, computer etc.).

7.5 Capillary columns, fused silica; for electron capture detection at least two with stationary phases of different polarity; for mass spectrometric detection one column suffices.

Typical: length 30 m, internal diameter $< 0,4 \text{ mm}$, coated with chemically bonded methyl silicones or phenyl (5 %) methyl silicones (apolar) or cyanopropylene (14 %) methylsilicones (polar) and with a film thickness of $0,25 \mu\text{m}$ or equivalent.

