SLOVENSKI STANDARD
SIST EN 12673:2000

01-januar-2000

Kakovost vode ï Določ evanje izbranih klorofenolov v vodi s plinsko kromatografijo

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

Wasserbeschaffenheit - Gaschromatographische Bestimmung einiger ausgewählter Chlorphenole in Wasser

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

Ta slovenski standard je istoveten z: **EN 12673:1998**

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13.060.50	Preiskava vode na kemiț ne snovi	Examination of water for chemical substances

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English version

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

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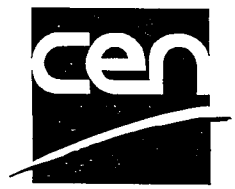

EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Central Secretariat: rue de Stassart, 36 B-1050 Brussels

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of an identical text or by endorsement, at the latest by June 1999, and conflicting national standards shall be withdrawn at the latest by June 1999.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 reference 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: a 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, C_2H_5OH

6.4 n-Hexane, C_6H_{14}

6.5 Potassium carbonate solution, $c(K_2CO_3)$ = 1,0 mol/l

6.6 Potassium carbonate solution, $c(K_2CO_3)$ = 0,1 mol/l

6.7 Acetic anhydride, $C_4H_6O_3$

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 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 °C ± 20 °C for 4 h ± 0,5 h.

6.11 Sodium hydroxide, c(NaOH) = 0,1 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 µg/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 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 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 µm or equivalent.

7.6 Muffle furnace - set to 500 °C ± 20 °C

7.7 Apparatus for liquid/liquid (L/L) extraction

7.7.1 Separating funnels - 500 ml and 250 ml with grease free glass or PTFE taps.

7.7.2 Shaking machine

8 Sampling

For sampling the following ISO methods are applicable:

drinking water:	ISO 5667-5
surface water:	ISO 5667-6
rainwater:	ISO 5667-8
sea water:	ISO 5667-9
waste water:	ISO 5667-10
groundwater:	ISO 5667-11.

The bottles shall be filled to the brim with the water sample and stoppered.

On sample collection, take care that no interfering substances enter the water sample, and no losses of the determinands occur. This is especially important in the use of any plastic tubing used within the sampling apparatus. If necessary, it shall be proved by control tests that no losses by adsorption occur. Glass and stainless steel devices are preferable.

Some chlorophenols may degrade in an aqueous environment, therefore unless experimental stability trials indicate otherwise, extract samples within two days of sampling. If extraction is extended beyond two days this shall be noted in the test report.

If the interval between sampling and extraction exceeds one day, keep the samples at 4 °C in the dark.

If free halogens are suspected add, at the time of sampling, some crystals of $Na_2S_2O_3.5H_2O$ or 0,1 ml of a 10 %(*m/m*) $Na_2S_2O_3$ solution (6.12) per 125 ml of sample.

Otherwise, do not add any preservation agent.

9 Procedure

9.1 Sample pretreatment

In this section two procedures are given:

– a method including acid-base partition which may be applied for dirty samples or when enrichment of the sample is required (9.1.1);

– a procedure employing direct acetylation suitable for relatively clean samples (9.1.2).

It is permissible for sample volumes to be increased if required. The volumes of all other reagents (except the internal standard) shall be adjusted accordingly. Moreover, as the calibration is based on the total procedure, the volumes used for the preparation of calibration solutions shall also be adjusted accordingly.

Apply one of the following procedures:

9.1.1 Clean up/enrichment procedure

Adjust the pH of the sample to pH = 4 by addition of phosphoric acid (6.9). Pour 200 ml of the sample into a 500 ml separating funnel (7.7.1). Add 200 µl of internal standard (6.32.1). Extract successively with 40 ml, 40 ml and 20 ml of toluene (6.8). Shake for 10 minutes each time using the shaking machine (7.7.2).

NOTE: If an emulsion forms during the extraction process, the emulsion can be broken by e.g. violent shaking, deep freezing, ultrasonification or separating out by means of the addition of salts.

Shake the collected toluene extract with a 3 × 20 ml 0,1 mol/l potassium carbonate solution (6.6), for 3 minutes each time, in a 250 ml separating funnel. Collect the water layers and proceed with 9.2.2.

9.1.2 Pretreatment if no clean up/enrichment procedure is followed

Take a sample of 50 ml or an aliquot diluted with distilled water to a volume of 50 ml. Neutralize acidic samples with sodium hydroxide (6.11) to a pH value of about 7 and alkaline samples with phosphoric acid (6.9) to a pH of about 10.
Add 200 µl of internal standard (6.32.1).

9.2 Acetylation procedure

9.2.1 Acetylation of the working standards

Treat each of the working standards (6.32.4) as follows.

Transfer with a pipette into a 100 ml open flask (7.3) :

– 50 ml of distilled water

– 2,00 ml of the working standard (6.32.4)

– 200 µl of the internal standard (6.32.1)

The following steps shall be carried out in the exact times given and without interruption.

Add 5 ml of the 1 mol/l potassium carbonate solution (6.5) and subsequently 1 ml of the acetic anhydride (6.7) and stir vigorously for 5 min to allow the release of carbon dioxide.

NOTE 1: This procedure can also be carried out using a separating funnel or a microseparator (see Annex C).

Allow to stand for 10 min and then add 5,0 ml of n-hexane (6.4). Close the flask with the stopper and stir for 5 min. Allow the two phases to separate. Transfer as large a portion as possible of the hexane phase to a vial. Dry the hexane phase with anhydrous sodium sulfate (6.10) or by freezing. Store at 4 °C.

These acetylated solutions are the calibration solutions. Calculate the content of each substance (µg/ml) in each of the calibration solutions.

NOTE 2: The efficiency of the derivatization step may be checked with a selection of chlorophenolacetates. Generally these compounds are not suitable for calibration purposes because sufficiently pure chlorophenolacetates are not always available.

9.2.2 Acetylation of the sample

Transfer the collected aqueous phases or an aliquot of 9.1.1 or the (neutralized) sample of 9.1.2 into a 100 ml open flask (7.3) and add 5 ml of the 1 mol/l potassium carbonate solution (6.5).

Carry out the following steps in the exact times given and without interruption.

NOTE 1: This procedure can also be carried out using a separating funnel or a microseparator (see Annex C).

Add 1 ml of acetic anhydride (6.7). Stir vigorously for 5 min to allow the release of carbon dioxide. Allow to stand at room temperature for 10 min and add 5,0 ml of n-hexane (6.4). Close the flask with the stopper and stir for 5 min. Allow the phases to separate. Remove the water layer and dry the hexane phase with anhydrous sodium sulfate (6.10) or by freezing.

NOTE 2: If an emulsion forms during the extraction process, the emulsion can be broken by e.g. violent shaking, deep freezing, ultrasonification or separating out by means of the addition of salts. In case of emulsification recoveries should be checked.

9.3 Calibration

9.3.1 Gas chromatograph calibration

Set up the gas chromatographic instrument, equipped with the columns (7.5), according to the manufacturer's instructions. Optimise gas flows. Ensure it is in a stable condition. Guidance on the initial gas chromatographic conditions is given in Annex D.

Calibrate by direct injection of the acetylated working standards (9.2.1) and in addition run a blank. Measure the gas chromatographic signals for each substance against concentration. This gives information on retention times and relative responses of the determinands and the linear working range of the gas chromatograph and detector.

NOTE 1: Chromatograms of standards should be checked for retention time and peak resolution changes, and losses caused by decomposition within the injection liner.

NOTE 2: Separation can be considered as satisfactory if the height measured from the base line of the trough between the two adjacent peaks is no more than 20 % of the height of the highest peak; the peaks in this instance need to be of comparable height.
Separation between 2,3,4,5-tetrachlorophenol acetate and 2,3,4,6-tetrachlorophenol acetate can be critical. The resolution should at least be 0,5. Generally the acetates of 2,4- and 2,5-dichlorophenol are not separated.

9.3.2 Calibration of the procedure

For explanation of the subscripts used see Table 1.

Table 1: Explanation of the subscripts

Subscript	Meaning
i	Identity of the substance
e	Calibration
s	Internal standard

Determine the calibration function by regression analysis using the ratios y_{ie}/y_{se} and ρ_{ie}/ρ_{se}.
Establish the linear regression function using the pairs of ratios y_{ie}/y_{se} and ρ_{ie}/ρ_{se} of the measured series in the following equation.

$$\frac{y_{ie}}{y_{se}} = m_i \frac{\rho_{ie}}{\rho_{se}} + b_i \quad (1)$$

Where:

y_{ie}	is the measured value of the determinand i as e.g. peak height or peak area;
y_{se}	is the measured value of the internal standard s as e.g. peak height or peak area;
ρ_{ie}	is the mass concentration of the determinand i in the calibration solution in micrograms per litre;
ρ_{se}	is the mass concentration of the internal standard s in the calibration solution in micrograms per litre;
m_i	is the slope of the calibration function, also called the response factor;
b_i	is the intercept of the calibration function with the ordinate as e.g. peak height or peak area.

9.4 Measurement

Prepare gas chromatograms of the extracts obtained in 9.2.2 by injecting a defined volume, typically 1 µl to 5 µl (but the same volume as in 9.3.1), into the gas chromatograph.
This procedure shall be performed by analysing the samples on the two capillary columns of a differing polarity (7.5).

The following measurement conditions shall be observed in the detection of substances using a mass spectrometer.
Ionization procedure: electron ionization, electron energy at least 45 eV
Mass range during registration of the spectra: 46 to 280 absolute mass units (u), at least 10 u above the highest molecular mass of the substances in question.
If there is interference e.g. due to CO_2, the spectra registration can be begun at 46 u.
Cycle time: < 2 sec - at least 5 spectra should be registered for each substance peak.
If, with increased sensitivity only selected ions are detected register the base peak with 2 additional ions (as they appear in the spectra) with the same cycle time as above.

9.5 Quality control experiment

For the quality control of the analytical procedure take the following steps:
Determine the substance specific blanks by running the background gas chromatograms of the respective total method as applied to a sample of interference free water (i.e. pretreatment, extraction, purification, gas chromatography).

If blank values are unusually high (more than 10 % of the lowest measured values) every step in the procedure shall be checked in order to find the reason for these high blanks.
If samples concentrations are close to the limit of determination, however, blank values higher than 10 % of the lowest measured value have to be tolerated.
When the blank value significantly differs from the intercept of the calibration curve the cause shall be determined.

The minimum validity of the calibration shall be checked with every batch of samples. Inject two standard extracts, one at approx. 20 % and the other at approx. 80 % of the selected linear working range. Repeat the injections once.

Compare the means of the two concentrations with the calibration curve. If the values are within the confidence interval of the corresponding values used in the procedure, it is permissible to use them as a calibration curve. If not, check the entire procedure and establish a complete new calibration curve.

10 Expression of results

10.1 Interpretation and quantification

10.1.1 GC-ECD

The following steps shall be done for each column separately.

By means of the absolute retention times, identify the peaks of the internal standards. For the remaining relevant peaks of the gas chromatograms, determine the relative retention time as compared with both internal standards. Consider that a compound has been shown if the relative retention time differs by less than 0,2 % from the relative retention time obtained as in 9.3.1.

The chlorophenols are quantified by using an internal standard added to the sample. Errors can occur when an interfering compound co-elutes with the internal standard in the chromatogram of the extract. For this reason at least two internal standards are used to determine whether interfering compounds are present or absent.
This presence or absence of interfering compounds can be determined from the measured responses of the internal standards. When no interfering compounds are present in the extract, the ratio between the responses of the internal standard is equal to that of the ratio in the working standard. The quotient of these ratios is called the relative response ratio, *RRR*.
When no interfering compounds are present in the extract the value of *RRR* is in principle 1,00. In this standard it is assumed that no interfering compounds are present in the extract when $RRR = 1{,}00 \pm 0{,}10$.

When the value of *RRR* deviates from 1,00 ± 0,10 the response of one of the internal standards is influenced by an interfering compound present in the extract. In that case the chlorophenols are quantified by using the undisturbed internal standard.

10.1.2 GC-MS

Identify the peaks by means of retention times as described in 10.1.1. Information on characteristic ions is given in Annex F.

When the full scan mode is used correct the spectra by background substraction. Identify the compounds by matching the spectra from the sample with the spectra of the reference substances taking into account the limits given in the following clauses. Produce all spectra under the same instrumental conditions. The individual reference spectra shall be created by each individual laboratory on the same GC-MS system used for the samples. The reference spectra may be stored in a spectra library or derived from the corresponding calibration.

In the case of acquiring selected ions (SIM mode), at least three characteristic ions shall be used. (see Annex F). The signal-to-noise ratio of the least intensive ion should be at least 3 (S/N>3). The ratio of the three masses in a spectra shall be evaluated from the mass peak height scanned at the peak maximum applying identical measurement conditions with sample and reference substance. The ratio of abundance of the two less intensive ions to the base peak shall not deviate by more than 10 % between these acquisitions.

Structural isomers producing similar mass spectra can only be identified clearly if their GC retention times are sufficiently different. Acceptable resolution is achieved if the height of the valley between two peaks is less than 25 % of the average height of the two peaks. Otherwise, structural isomers are identified as isomeric pairs.

In general, all ions present above 10 % relative abundance in the mass spectra of the standard should be present in the mass spectra of the sample component. The abundance between different ions (intensity ratio) shall agree within 20 % (absolute) between the sample and reference spectra. At least three most important ions (see Annex F) should be used for this test.

10.1.3 Calculation

Calculate the mass concentration of the substance using equation (2) (following the solution of equation (1)).

$$\rho_i = \frac{\frac{y_i}{y_s} - b_i}{f \times m_i} \times \rho_s \qquad (2)$$

Where:

y_i is the measured value of the determinand i as e.g. peak height or peak area;
y_s is the measured value of the internal standard in the sample as e.g. peak height or peak area;
ρ_s is the mass concentration of the internal standard in the sample e.g. in micrograms per litre;
ρ_i is the mass concentration of substance i, e.g. in micrograms per litre;
m_i is the slope of the calibration function;
b_i is the intercept of the calibration function with the ordinate as e.g. peak height or peak area.
f concentration factor, 4 for the procedure with clean-up/enrichment (9.1.1); 1 for direct procedure (9.1.2)

Using mass spectrometry take for y_i or y_s respectively the peak height or peak area of the most intensive (fragment-) mass (base peak) from the corresponding substance's spectrum.