SLOVENSKI STANDARD
SIST EN 14207:2003

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Kakovost vode ï Doloļ evanje epiklorohidrina

Water quality - Determination of epichlorohydrin

Wasserbeschaffenheit - Bestimmung von Epichlorhydrin

Qualité de l'eau - Dosage de l'épichlorhydrine

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Water quality - Determination of epichlorohydrin

Qualité de l'eau - Dosage de l'épichlorhydrine

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Foreword

This document EN 14207:2003 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of an identical text or by endorsement, at the latest by October 2003, and conflicting national standards shall be withdrawn at the latest by October 2003.

Annexes A, B and C are informative.

WARNING — Persons using this standard should be familiar with normal laboratory practice. This standard does not propose to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

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, Hungary, Iceland, Ireland, Italy, Luxembourg, Malta, Netherlands, Norway, Portugal, Slovakia, Spain, Sweden, Switzerland and the United Kingdom.

Introduction

It is highly recommended that the test described in this standard be carried out by suitably qualified staff.

It should be investigated whether and to what extent particular problems will require the specification of additional marginal conditions.

1 Scope

This European Standard specifies a method for the determination of epichlorohydrin in drinking water and water used for drinking water processing. According to the given procedure, the limit of determination in routine analysis is about 0,5 µg/l [1)]. The limit of determination can be lowered to monitor 0,1 µg/l.

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 (including amendments).

EN 25667-1, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes (ISO 5667-1:1980).*

EN 25667-2, *Water quality — Sampling — Part 2: Guidance on sampling techniques (ISO 5667-2:1991).*

1) This value was checked in an interlaboratory trial.

EN ISO 5667-3, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of samples (ISO 5667-3:1994).*

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

ISO 8466-1, *Water quality - Calibration and evaluation of analytical methods and estimation of performance characteristics - Part 1: Statistical evaluation of the linear calibration function.*

3 Principle

Solid phase extraction of epichlorohydrin from the drinking water sample followed by gas chromatography using a mass spectrometer (MS) as detector. Alternatively, an electron capture detector (ECD) can be used.

4 Interferences / Losses

4.1 Interferences during sampling

In order to avoid interferences, withdraw the sample according to clause 7, taking into account the information given in EN 25667-1, EN 25667-2 and EN ISO 5667-3.

In order to avoid losses due to the easy decomposition of epichlorohydrin, avoid unnecessary storage and analyse the sample as soon as possible after sampling. If storage is unavoidable, store between 2 °C and 5 °C until sample pretreatment.

4.2 Interferences during enrichment

The commercially available adsorbance materials are often of varying quality. Considerable batch-to-batch differences in quality and selectivity of these materials are possible. Perform calibration and analysis with one and the same batch of material. Make sure to avoid any losses when removing the residual water in the adsorbance material (8.1.2).

4.3 Interferences in the gas chromatography and mass spectrometry

Set the operational conditions in accordance with the manufacturer’s instructions. Check these settings at regular intervals.

General interferences, caused by the injection system can be eliminated with the help of special laboratory experience and the instruments manuals.

The stability of the analytical system should be checked (for example by application of a measuring standard).

5 Reagents

Use reagents of the reagent grade “for residual analysis” or equivalent as far as available. Impurities in the reagents and in the water contributing to the blank shall be negligibly low. Check the blank regularly, especially prior to the use of a new batch.

5.1 Water

Use double-distilled water or water of comparable purity.

5.2 Operating gases for the gas chromatography / mass spectrometry / ECD, according to the manufacturer's instructions. The operating gases shall be of high purity.

5.3 Nitrogen, high purity, minimum 99,996 % (v/v), for removal of water in the sorbent packing after sample extraction.

5.4 Solvents

5.4.1 Diisopropyl ether, $C_6H_{14}O$.

5.4.2 Methanol, CH_3OH, as conditioning agent.

5.5 Reducing agents, e.g. sodium thiosulfate ($Na_2S_2O_3$).

5.6 Epichlorohydrin stock solution

Weigh 50 mg of epichlorohydrin (C_3H_5ClO) into a 100-ml volumetric flask containing diisopropyl ether (5.4.1) up to the neck and fill to mark with diisopropyl ether (5.4.1). Store the solution in a refrigerator between 2 °C and 5 °C. The shelf-life of the solution is limited (about 6 months). Check the concentration prior to analysis in order to make sure that no significant differences arise.

5.7 Internal standard stock solution

The internal standard shall not be present in the sample itself.

5.7.1 $^{13}C_3$-epichlorohydrin stock solution for GC-MS

This solution may be purchased as certified solution (e.g. at a concentration of 100 µg/ml in nonane) or prepared from pure standard material according to 5.6. Never add more than 100 µl of a diluted internal standard stock solution in diisopropyl ether (5.4.1) to 100 ml of the water sample, a greater volume may result in poor recovery.

NOTE The peak area of the internal standard should be equivalent to that of 1 µg/l of the analyte. For example, if the concentration of the stock solution is 100 µg/ml of $^{13}C_3$-epichlorohydrin in nonane, 100 µl, dissolved in 1 ml diisopropyl ether (5.4.1) is required to produce a 10 µg/ml spiking solution from which a volume of 10 µl can be injected directly into 100 ml of water (5.1).

5.7.2 Ethyl 2-chloropropionate ($C_5H_9ClO_2$) stock solution for GC-ECD (see 5.6)

5.8 Epichlorohydrin spiking solutions

Using stock standard solution (5.6), prepare spiking solutions by appropriate dilution in a 100-ml volumetric flask containing diisopropyl ether (5.4.1). Prepare the spiking solutions at concentrations such that the aqueous calibration solutions (5.9) will cover the working range of the analytical system. Store spiking solutions in a refrigerator between 2 °C and 5 °C. Let the solutions adjust to room temperature before preparing calibration solutions. The storage time shall not exceed one month.

5.9 Epichlorohydrin calibration solutions for the multipoint calibration

Prepare aqueous calibration solutions from the spiking solutions (5.8) by injection of an appropriate volume (e.g. 10 µl) of the spiking solution directly into 100 ml of water (5.1). However, do not use more than 100 µl of a spiking solution to produce the calibration solutions. Mix the aqueous calibration solutions thoroughly by inverting the flask several times. Prepare five different concentration levels. Prepare calibration solutions fresh daily.

Table 1 gives an example for a dilution scheme.

Table 1 — Dilution scheme

Millilitre of 5.6 added to 100 ml 5.4.1	Analyte concentration in the spiking solution in milligram per millilitre	Concentration (in microgram per litre) in the calibration solution (10 µl of the spiking solution added to 100 ml water)
0,2	0,001	0,1
0,6	0,003	0,3
1,0	0,005	0,5
1,4	0,007	0,7
1,8	0,009	0,9

If the desired measuring range differs from that of Table 1, different solution ratios should be taken.

5.10 Solid phase material

Solid phase material on styrene-divinylbenzene copolymer basis is normally used, e.g. commercially available cartridges or adequately glass columns filled with a minimum packing of 200 mg of the sorbent (see annex A). A recovery of ≥ 80 % of the analyte is required.

6 Apparatus

6.1 General requirements

Equipment or parts of it which may come into contact with the water sample or the extract should be free from interfering compounds.

6.2 Sample bottles, preferably brown glass, 500 ml, with glass stoppers or PTFE-lined (PTFE = polytetrafluoro-ethene) screw caps.

6.3 Solid phase extraction cartridges, see 5.10.

6.4 Vacuum or pressure assembly, for the extraction step.

6.5 Volumetric flasks with inert stopper.

6.6 Vials, suitable for automatic or manual injection, preferably brown glass, with PTFE-lined septa.

6.7 Capillary gas chromatograph, equipped with a mass spectrometer as detector or an ECD. Preferably use an autosampler for sample injection. For operational aspects of the instruments the manufacturer's instructions should be followed.

6.8 Capillary injector, for split-splitless, cold on-column or programmed temperature vaporizing (PTV) injection.

6.9 Capillary columns for gas chromatography, examples see annex B.

6.10 Injection syringes, nominal capacity 5 µl or 10 µl.

7 Sampling

Collect samples according to EN 25667-1, EN 25667-2, EN ISO 5667-3, and ISO 5667-5.

Use for sampling carefully cleaned, preferably brown glass bottles, 500 ml . Fill the bottles completely with the water to be examined. Treat and analyse the samples as soon as possible after sampling. If storage is unavoidable, store the sample in a refrigerator between 2 °C and 5 °C prior to analysis.

Samples which are known or suspected to contain free chlorine or another oxidizing disinfectant shall be preserved with a reducing reagent. Add approximately 100 mg/l sodium thiosulfate (5.5) or another reducing reagent to the sample bottle prior to collecting the sample. After filling, seal the bottle and shake manually until reagent is dissolved.

8 Procedure

8.1 Solid phase extraction

8.1.1 Conditioning of the solid phase material

The following procedure is described for commercially available 3-ml and 6-ml cartridges (sorbent mass 200 mg).

Rinse the cartridge with 5 ml of diisopropyl ether (5.4.1). Let the cartridge drain after rinsing. Subsequently, rinse the cartridge with 5 ml of methanol (5.4.2), letting the cartridge drain after rinsing. The sorbent bed should not be allowed to run dry between this step and the next conditioning step. If the bed falls dry, repeat rinsing with methanol. Pass 5 ml of water (5.1) through the cartridge, and make sure that the sorbent packing in the cartridge does not run dry. Retain the water in the cartridge (water level just above the packing) to keep the sorbent activated.

8.1.2 Sample extraction

Start the extraction immediately after conditioning. Make sure that no air bubbles are trapped in the sorbent bed when changing from conditioning to extraction. Maintain the sorbent material in the cartridge immersed in water at all times.

Fill a 100-ml volumetric flask to the mark with sample. Add an internal standard (5.7) and mix thoroughly. Let this sample run through the column, conditioned as given in 8.1.1, with a flow rate of 1 ml/min to 3 ml/min, make sure that the flow rate remains constant. A sample volume of 100 ml shall not be exceeded in order to prevent breakthrough of epichlorohydrin.

After extraction remove the main portion of the residual water in the sorbent packing by passing nitrogen with a flow rate of 1 l/min to 2 l/min through the cartridge for 5 min. In order to avoid losses of epichlorohydrin, make sure that the residual mass of water in the sorbent packing is about 250 mg to 350 mg.

NOTE The colour of the moist adsorbant is brown, the dry material is light orange. The end of the removal of water from the cartridge may usually be recognized by brightening of the sorbent surface at the top edge of the sorbent packing in the cartridge.

8.1.3 Elution

Add 2 ml of diisopropyl ether (5.4.1) to the cartridge, allow to equilibrate for e.g. 10 min and elute the cartridge. Collect the eluate in a small flask or vial.

NOTE The small amounts of remaining water in the sorbent packing will form a separate phase in the eluate.

8.2 Gas chromatography

Capillary columns with dimethylpolysiloxane-based stationary phases (see annex B) are suitable.

Use a mass spectrometer for detection. Alternatively, an electron capture detector (ECD) can be used.

For chromatograms see annex C.

8.3 Blank monitoring

At least one blank measurement should be performed prior to analysing real samples in order to assess contamination from reagents, apparatus, and other sources. Analyse a 100-ml portion of water (5.1) with exactly the same procedure as an actual sample. If the blank produces any peak within the retention time window of epichlorohydrin, identify and eliminate the source of contamination.

8.4 Identification of epichlorohydrin

Identify the sample component by matching both retention times and spectra of sample component and epichlorohydrin standard.

The target compound is identified if:

— the sample component retention time in the total ion current or selected ion current chromatogram matches the retention time of epichlorohydrin within ± 0,08 min (4,8 s) in the chromatogram of the latest calibration standard, measured under identical conditions;

and if

— all ions present above 10 % relative abundance in the mass spectrum of epichlorohydrin are present in the mass spectrum of the sample component (after background subtraction) and agree within absolute ± 20 %. For example, if an ion has a relative abundance of 30 % in the standard spectrum, its abundance in the sample component spectrum should be in the range of 10 % to 50 %.

or if

— the relative intensities of the two selected diagnostic masses m/z 49 and m/z 51 of the sample component (after background subtraction) in the selected ion current chromatogram fall within ± 13 % of the relative intensities of these masses in a reference mass spectrum obtained from a epichlorohydrin standard analysed in the GC/MS system under identical conditions.

NOTE The spectrum of epichlorohydrin exhibits two isotopic patterns at m/z 49/51 $(CH_2Cl)^+$ and 62/64 $(M - CH_2O)^+$, corresponding to the isotopic forms ^{35}Cl and ^{37}Cl in a relative abundance ratio of about 3:1. When using $^{13}C_3$-labelled epichlorohydrin as internal standard, the isotopic pattern m/z 62/64 of the target compound is interfered by the isotopic pattern m/z 64/66 of the internal standard (see spectra in the annex). Therefore, only the ions of the pair at m/z 49/51 are suitable diagnostic ions for identification. Due to the lack of thermodynamic stability of epichlorohydrin, a molecular ion will not be formed. The basic peak ion at m/z 57 is not specific, as many other compounds (n-alkanes, substances with n-alkane ligands) will also form a fragment ion of m/z 57. Therefore, these substances will lead to background interferences even in low concentrations.

If an ECD is used for identification, for positive findings a determination on two capillary columns of different polarity should be considered in order to reduce the risk of false positive results by overlapping peaks. The retention times on both columns should match with those of the standard.

9 Calibration

9.1 General requirements

Make sure to achieve a linear dependence of signal to concentration.

Determine the linear working range using at least five measuring points of different concentration (see ISO 8466-1).

The calibration function is valid only for the measured concentration range. Additionally, the calibration function depends on the condition of the gas chromatograph and shall be checked regularly. For routine analysis, a check of the calibration function by measurement of two points is sufficient.

9.2 Calibration using an internal standard

If an internal standard is used, the determination of the concentration is independent from possible errors made during injection. Apart from this, errors caused by sample losses during distinct steps of sample pretreatment or the difficult adjustment to a (low) sample volume may be avoided. Additionally, the determination of the concentration is independent from matrix effects in the sample, provided the recovery of the target compound and the internal standard are about the same. The internal standard shall not be present in the sample itself.

Prepare aqueous calibration solutions at a minimum of five concentration levels according to 5.9. To each calibration solution add a known amount of the internal standard (5.7). The lowest calibration solution should represent an analyte concentration near, but above, its limit of determination. The remaining calibration solutions should cover the analyte concentration expected in the water sample.

Pretreat and analyse the calibration solutions according to the procedure described in clause 8. Use the same solvent composition and internal standard concentration for the calibration solutions and the extract.

The subscripts used in the following are defined in Table 2.

Plot the rational values y_{ieg} / y_{leg} (peak areas, peak heights or integration units) for the substance *i* (*i* = epichlorohydrin) on the ordinate and the associated rational mass concentration ρ_{ieg} / ρ_{leg} on the abscissa. Establish the linear regression function for epichlorohydrin using the pairs y_{ieg} / y_{leg} and ρ_{ieg} / ρ_{leg} of the measured series in equation 1.

Table 2 — Definition of subscripts

Subscript	Meaning
i	Identity of the substance *i*
e	In the calibration step
g	Overall procedure
l	Internal standard

$$\frac{y_{ieg}}{y_{leg}} = m_{ilg} \cdot \frac{\rho_{ieg}}{\rho_{leg}} + b_{ilg} \qquad (1)$$

where

i is epichlorohydrin;

y_{ieg} is the measured response of epichlorohydrin obtained from the calibration as a function of ρ_{ieg} ; the unit depends on the evaluation, for example area value;

y_{leg} is the measured response of the internal standard *l* obtained from the calibration, dependent on ρ_{leg} ; the unit depends on the evaluation, for example area value;

ρ_{ieg} is the mass concentration of epichlorohydrin in the calibration solution, in micrograms per litre, µg/l;

ρ_{leg} is the mass concentration of the internal standard *l*, in micrograms per litre, µg/l;

m_{ilg} is the slope of the calibration curve from y_{ieg} / y_{leg} as a function of the mass concentration ratio ρ_{ieg} / ρ_{leg}, often called the response factor;