SLOVENSKI STANDARD
SIST EN 12918:2000

01-december-2000

Kakovost vode - Določevanje parationa, parationmetila in drugih organofosfornih spojin v vodi z ekstrakcijo z diklorometanom in metodo plinske kromatografije

Water quality - Determination of parathion, parathion-methyl and some other organophosphorus compounds in water by dichloromethane extraction and gas chromatographic analysis

Wasserbeschaffenheit - Bestimmung von Parathion, Parathion-methyl und einigen anderen Organphosphor-Verbindungen in Wasser mittels Dichlormethan-Extraktion und gaschromatographischer Analyse

Qualité de l'eau - Dosage du parathion, méthyl-parathion et certains autres composés organophosphorés dans les eaux apres extraction au dichlorométhane et analyse par chromatographie en phase gazeuse

Ta slovenski standard je istoveten z: **EN 12918:1999**

ICS:

13.060.50	Preiskava vode na kemične snovi	Examination of water for chemical substances
71.040.50	Fizikalnokemijske analitske metode	Physicochemical methods of analysis

SIST EN 12918:2000 **en**

EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

EN 12918

August 1999

ICS 13.060.50

English version

Water quality - Determination of parathion, parathion-methyl and some other organophosphorus compounds in water by dichloromethane extraction and gas chromatographic analysis

Qualité de l'eau - Dosage du parathion, méthyl-parathion et certains autres composés organophosphorés dans les eaux après extraction au dichlorométhane et analyse par chromatographie en phase gazeuse

Wasserbeschaffenheit - Bestimmung von Parathion, Parathion-methyl und einigen anderen Organphosphor-Verbindungen in Wasser mittels Dichlormethan-Extraktion und gaschromatographischer Analyse

This European Standard was approved by CEN on 23 July 1999.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Central Secretariat has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and United Kingdom.

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 February 2000, and conflicting national standards shall be withdrawn at the latest by February 2000.

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, B, and C are informative.

1 Scope

This European Standard specifies the extraction processes and gas chromatographic (GC) methods for determining parathion, parathion-methyl and some other organophosphorus compounds in drinking waters, surface waters and waste waters. This standard can also be suitable for the determination of other organic compounds.

The range is dependent on the compound and the source of water and is typically up to 1 µg/l with a reporting limit of 0,01 µg/l for drinking waters involving a 1 000 to 1 extraction ratio.

Extraction efficiencies are normally less than 100 %. Bias will vary with the extraction efficiency of any particular compound, the type of water and the method used.

Annex A contains a table of organophosphorus compounds and their recoveries.

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 applies.

EN 1528-3:1996
Fatty food – Determination of pesticides and polychlorinated biphenyls (PCBs) – Part 3 : Clean-up methods

ENV ISO 13530
Water quality - Guide to analytical quality control for water analysis (ISO/TR 13530:1997)

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)

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

ISO 5667-6
Water quality – Sampling – Part 6: Guidance on sampling of rivers and streams

ISO 5667-8
Water quality – Sampling – Part 8: Guidance on the sampling of wet deposition

ISO 5667-9
Water quality – Sampling – Part 9: Guidance on sampling from marine waters

ISO 5667-10
Water quality – Sampling – Part 10: Guidance on sampling from waste waters

ISO 5667-11
Water quality – Sampling – Part 11: Guidance on sampling of groundwaters

3 Principle

The organophosphorus compounds are extracted by dichloromethane.

The dried extracts are concentrated by evaporation to a suitable volume before injection into a gas chromatograph for quantitative analysis.

4 Interferences

Surfactants, emulsifiers, chelating agents and solvents can affect the extraction stage.
Suspended particles in the water can also reduce the recovery.
Other liquid phases in the sample (e.g. mineral oil, hydrocarbons, emulsified fats and waxes) can affect sampling, extraction and enrichment stages. In those cases the analysis is restricted to the aqueous phase and the portion of the non-aqueous phase is reported separately.

5 Reagents

5.1 General

All reagents shall be of sufficient 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. Reagents shall be stored in glass containers.

All refrigerated solutions shall be brought to ambient temperature prior to use.

5.2 Standard solutions of organophosphorus compounds

WARNING: SOME ORGANOPHOSPHORUS PESTICIDES ARE VERY TOXIC. EXERCISE EXTREME CAUTION WHEN PREPARING THE STOCK SOLUTIONS. AVOID SKIN CONTACT, INGESTION AND INHALATION.

5.2.1 Stock solutions

These shall be prepared by dissolving pure or certified materials in acetone (5.5). A suitable concentration is 50 mg/100 ml. Unless manufacturers' information or stability trials indicate otherwise, store the solutions at ≤ -18°C, protected from light. Confirm their concentration and identity prior to use.

NOTE : Septa can harden at these low temperatures with possible consequential losses.

5.2.2 Intermediate standards

Prepare these by suitable dilution of the stock solutions (5.2.1) with acetone (5.5). A suitable concentration is 10 mg/100 ml. Store the solutions at 4°C, protected from light. Confirm their concentrations and identity prior to use.

5.2.3 Working standards

Prepare a minimum of five different concentrations by suitable dilutions of the intermediate solutions (5.2.2) with the injection solvent. A suitable concentration range is from 1 µg/100 ml to 100 µg/100 ml.

NOTE 1: In order not to compromise the chromatography and detection, the concentration of the acetone should be ≤ 1% of the injection solvent.

Store the solutions at 4°C, protected from light. Unless manufacturers' information or stability trials indicate otherwise, their storage life is limited to one week. If possible, confirm their concentration and identity prior to use.

NOTE 2: At these lower concentrations degradation by light and adsorption on to glass become more apparent.

5.3 Gases

5.3.1 Nitrogen, N_2, interference free, for drying and evaporative concentration.

5.3.2 Gas chromatograph gases, including air, hydrogen, nitrogen and helium. They shall be of a purity as recommended by the gas chromatograph manufacturer.

5.4 Water, interference free.

5.5 Propan-2-one (Acetone), (C_3H_6O).

5.6 Hydrochloric acid, aqueous solution, c(HCl) = 0,1 mol/l.

5.7 Sodium hydroxide, aqueous solution, c(NaOH) = 0,1 mol/l.

5.8 Dichloromethane (CH_2Cl_2).

5.9 Methanol, (CH_3OH).

5.10 2,2,4-Trimethylpentane, (Iso-octane), C_8H_{18}.

5.11 Sodium sulfate, (Na_2SO_4), anhydrous, granular, neutral. Roast in a muffle furnace at (500 ± 20)°C for 4 hours ± 30 min. Allow to cool and store in a desiccator.

NOTE : Some batches of sodium sulfate have been found to be alkaline; in these circumstances, prior to roasting, washing with methanol containing 0.5 ml concentrated hydrochloric acid per litre and drying on a steam bath is recommended.

5.12 Anti-bumping granules, acetone and dichloromethane washed.

5.13 Sodium chloride (NaCl)- anhydrous, granular, neutral. Roast in a muffle furnace at (500 ± 20)°C for 4 hours ± 30 min. Allow to cool and store in a desiccator.

6 Apparatus

6.1 General

Glassware shall be clean, dry and grease-free.

NOTE : Rinsing with acetone before use assists in freeing glassware from possible contamination.

6.2 Sample bottles, all glass, or with polytetrafluoroethylene (PTFE) lined caps, nominal capacity 1 l to 5 l. A random bottle per batch of bottles shall be analysed to verify the absence of interfering contamination by running as a blank determination prior to use.

6.3 Volumetric flask, all glass.

6.4 Capillary gas chromatograph - equipped with an injector system which limits decomposition of the sample (on-column or programmable temperature vapouriser), a detector (flame photometric, nitrogen phosphorus, mass spectrometer, atomic emission detector) and a recorder system (integrator, computer etc.).

6.5 Capillary columns - at least two columns with stationary phases of different polarity. Annex C provides examples of gas chromatographic conditions and the corresponding gas chromatograms. If a mass spectrometer is used as a detector then one capillary column is normally sufficient.

6.6 Calibrated tubes - glass, at least 10 ml, 0,1 ml graduations, tapered, glass or PTFE stoppered.

6.7 Concentration equipment - Kuderna-Danish style evaporator or rotary evaporator or helical nitrogen flow evaporator. Nitrogen blow-down facility. Steam or water bath.

6.8 Separating funnel - glass, nominal 1 l to 5 l capacity, with grease free glass or PTFE taps.

6.9 Drying columns - glass tubes capable of drying the extracts with sodium sulfate (5.11) (for example a tube approximately 130 mm long by 5 mm to 6 mm internal diameter fitted with a reservoir at the top and a jet at the bottom. The jet shall be loosely plugged with acetone-washed cotton wool or glass wool and the tube shall be half filled with sodium sulfate).

6.10 Muffle furnace, set to (500 ± 20)°C.

6.11 Shaking machine

7 Sampling and preservation of samples

Some organophosphorus compounds can degrade rapidly in an aqueous environment, therefore unless experimental stability trials indicate otherwise, extract the sample within one day of sampling. If extraction is delayed beyond one day, the extent of the delay shall be noted in the test report.

Refer to EN 25667 parts 1 and 2, and ISO 5667 parts 5,6,8,9,10 and 11 for relevant guidance on sampling.

Fill the bottle to the brim with the water sample and stopper.

On sample collection, ensure no extraneous interfering substances contaminate the water sample, and no losses of the determinands occur. This is especially important if plastics are used with the sampling apparatus. If necessary, it shall be proved by control tests that no losses by adsorption occur. Glass and stainless steel devices shall be preferred.

Measure the pH. If necessary (see NOTE), using hydrochloric acid (5.6) or sodium hydroxide (5.7), adjust the pH immediately after collection in order to be in the range pH 3,5 to 4,5. If the pH is not checked and controlled at the time of sampling, this fact shall be stated in the test report. Note the volume of acid / base added.

NOTE : Under alkaline conditions some of the organophosphorus compounds will be hydrolysed. This has been determined for dimethoate.

The neck and stopper of the bottle shall be protected from contamination by covering with aluminium foil.

During transport keep the sample in the dark, avoiding contamination. If storage is necessary, keep the sample at 4°C, in the dark, avoiding contamination.

8 Procedure

8.1 General

Varying recoveries and reproducibilities can be obtained with different water types. The yields of the procedure shall be checked and the number of extraction steps required to get satisfactory yields, ≥ 60 % (see clause 8.6 determination of recovery), shall be determined by the laboratory. A minimum of two extraction stages shall be done.

NOTE : The volume of water extracted is dependent on the desired limit of detection required. Typically a sample volume of 1 litre and a final extract volume of 1 ml is used. The water type, sensitivity of the detector and the final volume of the extract will influence the limit of the detection.

8.2 Extraction

Homogenise the sample by shaking the bottle.

Pour a measured volume, typically 1 l, of the water sample into a separating funnel.

NOTE 1: If dimethoate is to be analysed then, because of its solubility, increasing the ionic strength of the sample by the addition of sodium chloride (5.13) can increase its recovery.

Typically for a sample volume of 1 l add (50 ± 5) ml of dichloromethane (5.8).

Stopper and shake vigorously for 2 min.

NOTE 2: A mechanical shaker can be used but the shaking period should be extended to a minimum of 10 min.

Allow the phases to separate.

Run off and collect the dichloromethane extract.

Repeat the extraction and separation step.

NOTE 3: Washing the sample bottle with dichloromethane and combining the washings with the extracts can increase the recovery of any compounds adsorbed on the glass walls. Recovery errors can occur if only a portion of the water sample has been extracted.

If previous tests indicate yields < 60 % or strong emulsions are encountered, repeat the extraction and separation step a third time.

Pass the combined dichloromethane extracts through a drying column, previously washed with dichloromethane, into an evaporator vessel.

Wash the drying column with (10 ± 1) ml of dichloromethane into the evaporator vessel.

NOTE 4: Alternatively the dichloromethane extract can be placed in a freezer for one hour to freeze out the water. The dichloromethane can then be removed from the ice crystals and passed through a drying column quarter filled with sodium sulfate. This minimises the use of sodium sulfate.

If a Kuderna-Danish style evaporator is used, add two anti-bumping granules to the evaporator vessel. Concentrate the extract to (5 ± 2) ml on a steam bath.

If a rotary evaporator is used, place the extract in a tapered flask with an ampoule extension. Place a Kuderna-Danish style evaporation flask between the evaporating vessel and the rotary evaporator. Concentrate the extract to (5 ± 2) ml at a constant vacuum relative to atmosphere pressure of greater than 340 mbar.

NOTE 5: A water bath not exceeding 40°C can be used to aid evaporation.

If a helical nitrogen flow apparatus is used, follow the manufacturer's instructions to concentrate the extract to (5 ± 2) ml .

When the concentration is finished, carefully rinse the walls of the evaporator vessel with a small volume of dichloromethane.

Add 1 ml of 2,2,4-trimethylpentane (5.10) to the extract and further concentrate the extract to between 0,5 to 0,9 ml using a gentle stream of dry nitrogen in a fume cupboard with the tube placed in a warm water bath (not exceeding 40°C).

Make up to (1,0 ± 0,05) ml with 2,2,4-trimethylpentane.

NOTE 6: Extracts need to be stored at 4°C, protected from light, if they are not analysed immediately.

NOTE 7: If a mass spectrometer is used as a detector, then the solvent exchange from dichloromethane to 2,2,4-trimethylpentane can be omitted.

8.3 Cleanup

The extraction procedure can also extract substances that can interfere with the measurement of the analytes. For these extracts use the gel permeation chromatography (GPC) clean-up procedure described as method G in EN 1528-3:1996. Cleanup procedures, as they can cause losses of the more polar organophosphorus compounds, are recommended only when necessary.

8.4 Blank determination

Consult the following document for advice on analytical quality control:

ENV 13530 Guide to analytical quality control for water analysis

Determine the substance specific blanks by running the background gas chromatogram of an extract from a sample of water (5.4) submitted to the total method (e.g. pretreatment, extraction, concentration, purification, gas chromatography).

The gas chromatogram obtained is checked for overlaps of interfering peaks occurring at the retention times of the determinands. If there is interference, the cleanup procedure and / or change of chromatographic columns is necessary. A change in the temperature programme of the gas chromatograph can aid separation.

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 and to minimise their effects.

If sample concentrations are close to the limit of determination, however, blank values higher than 10% of the lowest measured value have to be tolerated.

Only subtract the blank value if the between batch standard deviation of the blank value does not significantly exceed the standard deviation of the calibration function.

8.5 Calibration

8.5.1 General

There are three possible calibration methods that are allowable:

a) calibration of the gas chromatographic step, using external standards (8.5.2)

b) calibration of the total procedure (extraction, concentration, cleanup and chromatography), using external standards (8.5.3)

c) calibration of the total procedure (extraction, concentration, cleanup and chromatography), using internal standards (8.5.4)

The recovery data can be determined by a combination of the data produced in 8.5.2 and 8.5.3.

8.5.2 Gas chromatograph calibration

Set up the gas chromatographic instrument, equipped with a column, according to the manufacturer's instructions. Optimise gas flows. Ensure it is in a stable condition.

Condition the chromatographic system by injection of a working standard solution (5.2.3).

Calibrate by direct injection of solvent diluted standard solutions. Use appropriate working standard solutions (5.2.3), at least 5 different concentrations plus a blank.

Inject these working standard solutions into the gas chromatograph.

Keep the same gas chromatographic conditions throughout the process. Keep the same solvent compositions for the working standard dilutions (5.2.3) and the extracts.

Evaluate 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: Chromatograms of standards should be checked for retention time, peak resolution changes, and losses caused by decomposition within the chromatographic system. Any change in the solvent composition can affect the chromatography and / or detector response. To minimise interpretation, it is recommended that the chromatographic column(s) is reserved solely for this analysis.

Table 1 indicates the different subscripts used in the text.

Table 1: Subscripts and their meaning

Subscript	Meaning
i	Identity of the substance
s	Identity of internal standard
e	Calibration value
g	Overall extraction value
j	Consecutive number for pairs of values

Plot the values y_{iej} (peak areas, peak heights or integration units) for each substance i on the ordinate and the associated mass concentration ρ_{iej} on the abscissa.

Establish the linear regression function using the pairs of values y_{iej} and ρ_{iej} of the measured series in the following equation :

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

Where :

y_{ie} is the measured value of substance i obtained from the calibration, dependent on ρ_{ie}; units depend on the evaluation, e.g. area values;

ρ_{ie} is the mass concentration of substance i, e.g. in nanogram per microlitre;

m_i is the slope of the calibration function of substance i, its units depend on the evaluation, e.g. area value times microlitre per nanogram;

b_i is the ordinate intercept of the calibration line, units depend upon evaluation, e.g. area value.

8.5.3 Calibration of overall procedure using external standards

To calibrate the entire procedure, prepare aqueous solutions of the compounds to be determined by diluting the intermediate standard solution (5.2.2) with the required amount of water (5.4). The volume of water shall be the same as that used for samples. The volumes used shall be such that not more than 1ml of solvent is added to 1 l of water, in order that the partitioning coefficients of the substances are not seriously affected.

The calibration process shall consist of a minimum of five aqueous solutions of different concentrations plus a blank. Prepare a blank by adding a similar amount of solvent (5.5) to the same volume of water as used to prepare the aqueous standards.

Extract these aqueous solutions and concentrate the extracts. If cleanup is to be employed then process the extracts in the same way.

Inject these extracts into the gas chromatograph.

Keep the same gas chromatographic conditions throughout the process. Keep the same solvent compositions for the working standard dilutions (5.2.3) and the extracts.

Evaluate the gas chromatographic signals for each substance against concentration.

Plot the values y_{iegj} (peak areas, peak heights or integration units) for each substance i on the ordinate and the associated mass concentration ρ_{iegj} on the abscissa.

Establish the linear regression function using the pairs of values y_{iegj} and ρ_{iegj} of the measured series in the following equation :

$$y_{ieg} = m_{ig} \cdot \rho_{ieg} + b_{ig} \quad (2)$$

Where:

y_{ieg} is the measured value of substance i obtained from the calibration, dependent on ρ_{ieg}, unit depends on the evaluation, e.g. area values;

ρ_{ieg} is the mass concentration of substance i, e.g. in micrograms per litre;

m_{ig} is the slope of the calibration function of substance i, unit depends on the evaluation, e.g. area values times litre per microgram;

b_{ig} is the ordinate intercept of the calibration line, unit depends on the evaluation, e.g. area values.

8.5.4 Determination of the total method using an internal standard

This method compensates for injection errors and matrix effects. This is true as long as the recovery of the internal standard is very similar to the analyte. The internal standard shall have similar physical and chemical properties (extraction behaviour, retention time, detector response) to those of the compounds analysed. Neither this substance, nor a substance with the same retention time, shall be a constituent of the sample. Isotopically labelled compounds, e.g. deuterium or carbon-13 can be used if a mass spectrometer is the detector and the substances have non-interfering spectra.

The choice of internal standard depends on the analytical problem e.g. the sample matrix. The suitability shall be checked prior to use. It is possible to use more than one internal standard.

Prepare aqueous solutions of the compounds to be determined by diluting the intermediate standard solution (5.2.2) with the required amount of water (5.4). Add a known concentration of the internal standard to all samples prior to analysis. The concentration should be as similar as possible to the concentration of interest of the substances being analysed. The volume of water should be the same as that used for samples. The volumes used shall be such that not more than 1 ml of solvent is added to 1 l of water, in order that the partitioning coefficients of the substances are not seriously affected.

The calibration process shall consist of a minimum of five aqueous solutions of different concentrations plus a blank. Prepare a blank by adding a similar amount of solvent (5.5) to the same volume of water as used to prepare the aqueous standards.

Extract these aqueous solutions and concentrate the extracts. If cleanup is to be employed then process the extracts in the same way.

Inject these extracts into the gas chromatograph.

Keep the same gas chromatographic conditions throughout the process. Keep the same solvent compositions for the working standard dilutions and the extracts.

Evaluate the gas chromatographic signals for each substance against that of the internal standard.

Plot the ratio of the values y_{iegj}/y_{segj} (peak areas, peak heights or integration units) for each substance i on the ordinate and the associated ratio of mass concentration ρ_{iegj}/ρ_{segj} on the abscissa.
Establish the linear regression function using the pairs of ratioed values y_{iegj}/y_{segj} and ρ_{iegj}/ρ_{segj} of the measured series in the following equation :