SLOVENSKI STANDARD
SIST ISO 11083:1996

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Kakovost vode - Določanje kroma (VI) - Spektrofotometrijska metoda z uporabo 1,5 -difenilkarbazida

Water quality -- Determination of chromium(VI) -- Spectrometric method using 1,5-diphenylcarbazide

Qualité de l'eau -- Dosage du chrome(VI) -- Méthode par spectrométrie d'absorption moléculaire avec la 1,5-diphénylcarbazide

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Water quality — Determination of chromium(VI) — Spectrometric method using 1,5-diphenylcarbazide

Qualité de l'eau — Dosage du chrome(VI) — Méthode par spectrométrie d'absorption moléculaire avec la 1,5-diphénylcarbazide

Reference number
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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 11083 was prepared by Technical Committee ISO/TC 147, *Water quality*, Sub-Committee SC 2, *Physical, chemical, biochemical methods*.

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Water quality — Determination of chromium(VI) — Spectrometric method using 1,5-diphenylcarbazide

1 Scope

This International Standard specifies a spectrometric method for determination of chromium(VI) in water. The method is applicable to the determination of dissolved chromium(VI) in waters in the concentration range of 0,05 mg/l to 3 mg/l. The application range may be extended by dilution of the sample.

2 Principle

After sample pretreatment (which aims at stabilizing the valency states of chromium(VI) and chromium(III), if present) chromium(VI) reacts with 1,5-diphenylcarbazide to form a red-violet chromium-1,5-diphenylcarbazone complex. The absorbance of this complex is then measured at a wavelength between 540 nm and 550 nm, the exact wavelength being given in the test report.

3 Reagents

Use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

Commercially available reagents with guaranteed concentrations may also be used.

3.1 Phosphate buffer solution, pH = 9,0 ± 0,2.

Dissolve 456 g of dipotassium hydrogen phosphate ($K_2HPO_4.3H_2O$) in 1 000 ml of water. Check the pH and adjust if necessary.

3.2 Sodium hydroxide solution.

Dissolve 20 g of sodium hydroxide (NaOH) in 100 ml of water.

3.3 Phosphoric acid solution A.

Dilute 10 ml of phosphoric acid (H_3PO_4, ρ = 1,71 g/ml) to 100 ml with water.

3.4 Phosphoric acid solution B.

Dilute 700 ml of phosphoric acid (H_3PO_4, ρ = 1,71 g/ml) to 1 000 ml with water.

3.5 Aluminium sulfate solution.

Dissolve 247 g of aluminium sulfate [$Al_2(SO_4)_3.18H_2O$] in 1 000 ml of water.

3.6 Sulfite solution.

Dissolve 11,8 g of sodium sulfite (Na_2SO_3) in water and dilute to 100 ml.

This solution is stable for about a week.

3.7 Sulfite test paper.

3.8 1,5-diphenylcarbazide solution.

Dissolve 1 g of 1,5-diphenylcarbazide ($C_{13}H_{14}N_4O$) in 100 ml of propanone (acetone), C_3H_6O, and acidify with one drop of glacial acetic acid.

Stored in a brown glass bottle in a refrigerator at 4 °C, this solution is stable for two weeks. Discard the solution if it becomes discoloured.

3.9 Sodium hypochlorite solution.

Dilute 70 ml of sodium hypochlorite solution (NaOCl, approximately 150 g of free Cl_2 per litre) with water to 1 000 ml.

Stored in a brown glass bottle in a refrigerator at 4 °C, this solution is stable for one week.

3.10 Potassium iodide starch test paper.

3.11 Chromium(VI) stock solution.

WARNING — Potassium chromate may be carcinogenic.

Dissolve 2,829 g of potassium dichromate ($K_2Cr_2O_7$) in water in a 1 000 ml volumetric flask and dilute to volume.

This solution is stable indefinitely.

1 ml of this solution contains 1 mg of Cr.

3.12 Chromium(VI) standard solution.

Transfer 5 ml of the chromium(VI) stock solution (3.11) to a 1 000 ml volumetric flask and dilute to volume with water.

Prepare this solution on the day of use.

1 ml of this solution contains 5 µg of Cr.

3.13 Sodium chloride, NaCl.

4 Apparatus

Ordinary laboratory apparatus and

4.1 Photometer or **spectrometer,** equipped with cells of optical path lengths between 10 mm and 50 mm.

4.2 Membrane filtration device, equipped with membrane filters with a pore size of 0,4 µm to 0,45 µm.

4.3 pH-measuring equipment.

4.4 Gas flow control.

5 Sampling and sample pretreatment

Perform these pretreatment steps immediately after sample collection. Analyse the samples as soon as possible after collection.

NOTE 1 If in doubt as to which procedure to use, take two samples and treat them according to either 5.1 and 7.1, or 5.2 and 7.2. If the results do not differ significantly, the procedures described in 5.1 and 7.1 may be used.

5.1 Samples in the absence of oxidizing or reducing substances

Collect a 1 000 ml sample in a glass bottle, add 10 ml of buffer solution (3.1) and mix. Measure the pH using the equipment (4.3); it shall be between 7,5 and 8,0.

If the pH is outside this range, adjust with sodium hydroxide solution (3.2) or phosphoric acid solution A (3.3), accordingly.

Add 1 ml of aluminium sulfate solution (3.5) and mix. Check the pH; it shall be between 7,0 and 7,2.

If the pH is outside this range, adjust with phosphoric acid solution A (3.3).

Allow the precipitate to settle for at least 2 h. Decant the supernatant and filter 200 ml through a membrane filter (4.2), discarding the first 50 ml of filtrate.

5.2 Samples in the presence of oxidizing or reducing substances

Collect a 1 000 ml sample in a glass bottle, add 10 ml of buffer solution (3.1) and mix. Measure the pH using the equipment (4.3); it shall be between 7,5 and 8,0.

If the pH is outside this range, adjust with sodium hydroxide solution (3.2) or phosphoric acid solution A (3.3), accordingly.

Add 1 ml of aluminium sulfate solution (3.5) and mix. Check the pH; it shall be between 7,0 and 7,2.

If the pH is outside this range, adjust with phosphoric acid solution A (3.3).

Add 1 ml of sulfite solution (3.6), checking for an excess of sulfite using sulfite test paper (3.7). If there is no excess of sulfite, add more sulfite solution until an excess is obtained.

Allow the precipitate to settle for at least 2 h. Decant the supernatant and filter 200 ml through a membrane filter (4.2), discarding the first 50 ml of filtrate.

6 Interferences

In the presence of lead, barium and silver ions (salts), chromates of low solubility may be formed and the chromium(VI) contained in them will not be determined.

Hexavalent molybdenum and mercury salts also form a yellow or blue colour respectively with the reagent, but the intensities are much lower than for chromium(VI). Iron(III) forms a yellow colour at concentrations above 1 mg/l and vanadium forms a yellow colour that fades.

Chromium(III) and other interfering metal ions are precipitated in a phosphate-buffered solution using aluminium sulfate as a precipitation aid and are removed by filtration.

Valency changes of chromium due to the presence of oxidizing or reducing substances can be avoided by using the following pretreatment steps.

Oxidizing substances are reduced by the addition of sulfite to the neutralized sample; chromium(VI) will not react under these conditions. Excess sulfite and other reducing substances are then oxidized with hypochlorite. Excess hypochlorite and any chloroamines formed are destroyed in the acid solution by the addition of sodium chloride and the chlorine formed is purged with air.

In spite of this pretreatment of the sample, slow reduction of chromium(VI) may occur in some waters. Leachate from landfills, raw domestic waste water and certain waste waters from chemical plants will show losses of chromium(VI) after several hours. It is therefore essential that these samples be analysed as soon as possible after collection.

Ammonia nitrogen does not interfere in concentrations below 500 mg/l, but amine compounds may be transformed by hypochlorite into chloroamines, which are not always decomposed by the addition of chloride. This interference is indicated by the appearance of a yellow or brownish colour on addition of 1,5-diphenylcarbazide.

Nitrite nitrogen interferes with the formation of the red violet chromium(VI)-1,5-diphenylcarbazone complex in concentrations exceeding 20 mg/l.

Vanadium in excess of 4 mg/l, and molybdenum and mercury each in excess of 200 mg/l may interfere.

7 Procedure

7.1 Procedure in the absence of oxidizing or reducing substances

Transfer 50 ml (volume V) of the filtrate (5.1) to a 100 ml volumetric flask. Add 2 ml of phosphoric acid solution B (3.4) and 2 ml of diphenylcarbazide solution (3.8) and dilute to 100 ml with water.

Measure the absorbance after 5 min to 15 min at a wavelength between 540 nm and 550 nm using water in the reference cell (absorbance A_s), and cells with an optical path length of 40 mm or 50 mm for concentrations below 0,5 mg/l, and of 10 mm for concentrations between 0,5 mg/l and 3 mg/l.

If the concentration is higher than 3 mg/l, repeat the determination, using a smaller aliquot of the filtrate (volume V).

For the blank value, carry out a blank test in parallel with the determination using water in place of the sample (absorbance A_b).

NOTE 2 This blank does not take into account the chromium content of the precipitation reagents, which has been found to be negligible.

If the measured blank disagrees significantly with the blank from the calibration function (7.3), check the latter.

If the filtrate is coloured or turbid, take another aliquot and treat it as described in this subclause, omitting the 1,5-diphenylcarbazide solution. Use the absorbance measured as a colour correction (absorbance A_t).

7.2 Procedure in the presence of oxidizing or reducing substances

Transfer 50 ml (volume V) of the filtrate (5.2) to a 100 ml volumetric flask. Add 1 ml of sodium hypochlorite solution (3.9), after checking for 1 min for excess chlorine using the potassium iodide starch test paper (3.10).

If there is no excess chlorine, add more sodium hypochlorite solution (3.9) until an excess is obtained.

Add 2 ml of phosphoric acid solution B (3.4), dissolve 10 g of sodium chloride (3.13) in the sample, and pass air through the sample with a flow rate of approximately 40 l/h for 40 min. Perform this procedure in a fume chamber.

Add 2 ml of 1,5-diphenylcarbazide solution (3.8) and dilute to 100 ml with water.

Measure the absorbance after 5 min to 15 min at a wavelength between 540 nm and 550 nm using

water in the reference cell (absorbance A_s) and cells with an optical path length of 40 mm or 50 mm for concentrations below 0,5 mg/l, and of 10 mm for concentrations between 0,5 mg/l and 3 mg/l.

If the concentration is higher than 3 mg/l, repeat the determination, using a smaller aliquot of the filtrate (volume V).

For the blank value, repeat the procedure, using water in place of the filtrate (absorbance A_b).

NOTE 3 This blank does not take into account the chromium content of the precipitation reagents, which has been found to be negligible.

If the measured blank disagrees significantly with the blank from the calibration function (7.3), check the latter.

If the filtrate is coloured or turbid, take another aliquot and treat it as described in this subclause, omitting the 1,5-diphenylcarbazide solution. Use the absorbance measured as colour correction (absorbance A_t).

7.3 Calibration

Pipette, for example, 0 ml; 0,5 ml; 1,0 ml; 2,0 ml; 3,0 ml; 4,0 ml and 5,0 ml of chromium(VI) standard solution (3.12) into a series of 100 ml volumetric flasks. Dilute each to approximately 40 ml with water, add 2 ml of phosphoric acid solution B (3.4) and 2 ml of 1,5-diphenylcarbazide solution (3.8) and dilute to 100 ml with water.

These calibration solutions have concentrations of 0 mg/l; 0,025 mg/l; 0,05 mg/l; 0,10 mg/l; 0,15 mg/l; 0,20 mg/l and 0,25 mg/l of chromium(VI) respectively.

Measure the absorbance after 5 min to 15 min at a wavelength between 540 nm and 550 nm (absorbance A_c) in cells with an optical path length of 40 mm or 50 mm using water in the reference cell. The wavelength used shall be the same for the calibration and the measurement.

Plot the mass concentration of chromium(VI) against the absorbance values to establish the calibration graph. Alternatively, calculate the calibration graph by regression analysis.

The slope of the calibration graph is a measure of the sensitivity of the method. The ordinate intercept is the blank. Check both the slope of the graph and the blank regularly, especially when new batches of reagents are used.

For calibration of other concentration ranges, proceed in the same way using different calibration solutions.

For the high concentration range, use cells with an optical path length of 10 mm.

Establish separate calibration functions for cells with different optical path lengths.

8 Expression of results

8.1 Calculation

Calculate the mass concentration of chromium(VI), $\rho_{(CrVI)}$, in milligrams per litre, using the equation

$$\rho_{(CrVI)} = \frac{f\,(A_s - A_b)}{b}$$

or

$$\rho_{(CrVI)} = \frac{f\,(A_s - A_t - A_b)}{b}$$

(if a correction has been made for coloured and turbid solutions)

where

A_s is the absorbance of the sample;

A_b is the absorbance of the blank;

A_t is the absorbance of the correction solution;

f is the dilution factor (for V = 50 ml it is 2; if other aliquots are taken it is $100/V$);

b is the sensitivity (slope of the calibration graph).

Report the results to the nearest tenth of a milligram, if they exceed 10 mg/l, and to the nearest hundredth of a milligram, if they are below 10 mg/l.