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Water quality — Determination of chromium — Atomic absorption spectrometric methods

Qualité de l'eau — Dosage du chrome — Méthodes par spectrométrie d'absorption atomique

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Contents

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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 Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

International Standard ISO 9174 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical, biochemical methods.*

This second edition cancels and replaces the first edition (ISO 9174:1990), which has been technically revised.

Annexes A and B of this International Standard are for information only.

Introduction

Chromium occurs in water in the oxidation states III and VI. The two methods described in this International Standard determine chromium in both oxidation states, either as acid-soluble chromium or as water-soluble chromium, depending on the sample pretreatment. The method chosen depends on the concentration of chromium in the water to be examined.

Annex A provides information on pretreatment and digestion of chromium from sludges and sediments.

Water quality — Determination of chromium — Atomic absorption spectrometric methods

1 Scope

This International Standard specifies two methods for the determination of chromium in water by atomic absorption spectrometry. The two methods are covered in separate clauses as follows:

— Clause 3: Determination of chromium by flame atomic absorption spectrometry;

— Clause 4: Determination of chromium by electrothermal atomization atomic absorption spectrometry.

Clause 3 is applicable to the analysis of water and waste water when the concentration range is between 0,5 mg/l and 20 mg/l of chromium. When the concentration is below 0,5 mg/l, the determination can be carried out after carefully evaporating an acidified sample to small volume, taking care to avoid the formation of a precipitate.

NOTE The use of evaporation will increase the effect of interfering substances and therefore for concentrations below 0,1 mg/l the method in clause 4 is given.

Clause 4 is applicable to the analysis of water and waste water when the concentration range is between 5 µg/l and 100 µg/l of chromium by injecting a sample volume of 20 µl. It is applicable to the determination of higher concentrations by using a smaller sample volume.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

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

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

3 Determination of chromium by flame atomic absorption spectrometry

3.1 Principle

The method is based on the atomic absorption spectrometric measurement of the chromium content of the acidified sample in a nitrous oxide/acetylene flame. Measurement at a wavelength of 357,9 nm. Addition of lanthanum salt to reduce matrix interferences is necessary.

3.2 Reagents

All reagents shall be of recognized analytical grade. Use deionized water or water distilled from an all-glass apparatus. The water used for blank tests and for preparing reagents and standard solutions shall have a chromium content that is negligible compared with the smallest concentrations to be determined in the samples.

3.2.1 Hydrochloric acid, HCl, $\rho \approx$ 1,18 g/ml.

3.2.2 Nitric acid, HNO_3, $\rho \approx$ 1,42 g/ml.

3.2.3 Nitric acid, $c(HNO_3)$ = 1,5 mol/l.

Introduce about 500 ml of water into a 1 000 ml volumetric flask, add 100 ml of nitric acid (see 3.2.2) and dilute to the mark with water.

3.2.4 Hydrogen peroxide, H_2O_2, 30 % mass fraction solution.

3.2.5 Lanthanum chloride, ($LaCl_3$), solution with ρ (La) = 20 g/l.

Dissolve 23,5 g of lanthanum oxide La_2O_3 in 200 ml of hydrochloric acid (see 3.2.1), dilute to 1 000 ml with water and mix.

WARNING: Observe appropriate precautions. The reaction of La_2O_3 with hydrochloric acid is strongly exothermic.

3.2.6 Chromium solutions.

3.2.6.1 Chromium, stock solution, with ρ(Cr) = 1,000 g/l.

Dry a portion of potassium dichromate ($K_2Cr_2O_7$) at 105 °C ± 2 °C for about 2 h. Cool and dissolve 2,825 g ± 0,001 g of the dried potassium dichromate in water. Add 5 ml ± 1 ml of nitric acid (see 3.2.2) and dilute to 1 000 ml with water in a volumetric flask.

1 ml of this stock solution contains 1,00 mg of chromium.

Store this solution in either polyethene or borosilicate glass containers at room temperature. The solution is stable at room temperature for about year if it is stored in the dark and at a pH between 1 and 2.

NOTE Chromium stock solutions are commercially available.

3.2.6.2 Chromium, standard solution, with ρ(Cr) = 50 mg/l.

Introduce 50,00 ml ± 0,01 ml of the chromium stock solution (see 3.2.6.1) into a 1 000 ml volumetric flask. Add 1 ml of nitric acid (see 3.2.2), make up to the mark with water and mix.

This solution is stable for at least 1 month.

3.3 Apparatus

3.3.1 Atomic absorption spectrometer, equipped with a chromium hollow cathode lamp and a nitrous oxide/acetylene burner, and operated in accordance with the manufacturer's instructions. It is essential that the manufacturer's safety recommendations are strictly observed when using the nitrous oxide/acetylene flame.

3.3.2 Glassware.

Before use carefully soak all glassware for about 24 h in nitric acid (see 3.2.3), then rinse thoroughly with water.

If low concentrations are expected (for example in ground water), the glassware should be kept under nitric acid (see 3.2.3) until use.

Do not use glassware which has been cleaned with chromic acid.

3.3.3 Membrane filters, of nominal pore diameter 0,45 µm, washed thoroughly with nitric acid (see 3.2.3) and rinsed with water (see 3.2).

3.4 Sampling and preparation of test portions

3.4.1 General

Collect and preserve samples in accordance with ISO 5667-2 and ISO 5667-3. See also annex A.

Collect samples in high density polyethene or borosilicate glass containers which have been previously cleaned with nitric acid (see 3.2.3) and then rinsed with water (see 3.2).

3.4.2 Acid-soluble chromium

Treat the samples by addition of sufficient nitric acid (see 3.2.2), immediately after collection, to adjust the pH to between 1 and 2.

To 90 ml of the acidified sample, or another suitable aliquot in accordance with the expected concentration, add 1 ml of hydrogen peroxide (see 3.2.4) and 2 ml of nitric acid (see 3.2.2). Boil and evaporate to a volume of approximately 50 ml.

The sample shall not be reduced to dryness.

In the case of samples with low chromium concentrations, this digestion method should be carried out in an autoclave or a microwave oven.

It is important to follow the manufacturer's instructions.

Add 10 ml of nitric acid (see 3.2.2) to the evaporated solution. Transfer the solution to a 100 ml volumetric flask. Add 10 ml of lanthanum chloride solution (see 3.2.5) into the flask, dilute to the mark with water and mix.

3.4.3 Water-soluble chromium

Filter the sample through a membrane filter (see 3.3.3), as soon as possible after collection, and acidify the filtrate immediately with nitric acid (see 3.2.2) to give a pH between 1 and 2.

Add 10 ml of lanthanum chloride solution (see 3.2.5) to a 100 ml volumetric flask and make up to the mark with the acidified filtrate, or use another suitable aliquot in accordance with the expected concentration, and mix.

3.5 Procedure

3.5.1 Blank test

Carry out a blank test in parallel with the determination by the same procedure and using the same quantities of all the reagents as in the sampling and determination, but replacing the test portion by water.

3.5.2 Preparation of the calibration solutions

Before each set of determinations, prepare from the chromium standard solution (see 3.2.6.2) at least five calibration solutions covering the range of concentrations to be determined; for example:

pipette 1,0 ml, 2,5 ml, 5,0 ml, 10,0 ml and 20,0 ml of chromium standard solution (see 3.2.6.2) into a series of 100 ml volumetric flasks. Add to each flask depending on the pretreatment (see 3.4.2 and 3.4.3) 10 ml or 2 ml of nitric acid (see 3.2.2) respectively and 10 ml of lanthanum chloride solution (see 3.2.5), dilute to the mark with water and mix. These solutions correspond to chromium concentrations of 0,50 mg/l; 1,25 mg/l; 2,50 mg/l; 5,00 mg/l and 10,0 mg/l respectively. Proceed accordingly for other concentration ranges of interest.

3.5.3 Calibration

Set up the instrument in accordance with the manufacturer's instructions (at wavelength λ = 357,9 nm) using a nitrous oxide/acetylene flame.

Aspirate a calibration solution (see 3.5.2) and optimize the aspiration, the burner height and the flame conditions. Adjust the response of the instrument to zero absorbance with water.

In turn, aspirate the set of calibration solutions (see 3.5.2) and the blank solution (see 3.5.1). Plot a graph having the chromium concentrations of the calibration solutions, in milligrams per litre, as abscissa and the corresponding absorbance values as ordinate. Alternatively, data-processing facilities can be used to equate the concentration against the absorbance.

3.5.4 Test portion measurement

Aspirate the prepared test portion (see 3.4.2 or 3.4.3) into the flame and measure the absorbance for chromium. After each measurement aspirate water and readjust the zero, if necessary.

3.6 Expression of results

By reference to the calibration graph obtained (see 3.5.3) or data-processing facilities used, determine the concentration of chromium corresponding to the absorbances of the test portion (see 3.5.4) and of the blank solution (see 3.5.1).

Calculate the concentration of chromium of the sample using the equation:

$$\rho = \frac{(A_s - A_{so}) \cdot V_w}{V_p \cdot b}$$

where:

ρ is the chromium concentration of the sample, in milligrams per litre;

A_s is the absorbance of the test portion;

A_{so} is the absorbance of the blank;

V_p is the volume of the acidified sample in accordance with 3.4.2 or 3.4.3, in millilitres;

b is the sensitivity (slope of the calibration graph), in litres per milligram;

V_w is the volume of the test portion in accordance with 3.4.2 or 3.4.3, in millilitres.

Precision data for this method are given in Table B.1.

3.7 Interferences

The following ions have been tested and shown not to cause interference below the concentration given in Table 1.

This information was taken from practical tests carried out in a working group in 1984.

Table 1 — Interfering ions

Ion	Concentration mg/l	Ion	Concentration mg/l
Sulfate	10 000	Iron	500
Chloride	12 000	Nickel	100
Sodium	9 000	Copper	100
Potassium	9 000	Cobalt	100
Magnesium	2 000	Aluminium	100
Calcium	2 000	Zinc	100

The total dry residue of the sample shall not exceed 15 g/l and the conductivity should be lower than 2000 mS/m.

NOTE It is possible to determine the effect of possible interferences by analysing samples spiked with chromium and various concentrations of the potential interfering substance using the method of standard additions.

3.8 Test report

The test report shall contain at least the following information:

a) a reference to this International Standard;

b) a reference to the procedure used;

c) complete identification of the sample;

d) the results of the analysis (see 3.6);

e) any other information relevant to the procedure.

4 Determination of chromium by electrothermal atomization atomic absorption spectrometry

4.1 Principle

Chromium is determined directly in acidified samples by electrothermal atomization atomic absorption spectrometry. The sample is introduced into an electrically heated graphite tube and the absorbance is measured at a wavelength of 357,9 nm. If necessary, the standard additions technique is employed.

4.2 Reagents

All reagents shall be of recognized analytical grade. Use deionized water or water distilled from an all-glass apparatus. The water used for blank tests and for preparing reagents and standard solutions shall have a chromium content that is negligible compared with the smallest concentrations to be determined in the samples.

4.2.1 Chromium standard solution, with $\rho(\mathrm{Cr}) = 0{,}5$ mg/l.

Add 10,00 ml ± 0,01 ml of the chromium standard solution (see 3.2.6.2) to a 1 000 ml volumetric flask. Add 10 ml of nitric acid (see 3.2.2) and dilute to the mark with water.

This solution is stable for at least 1 month.

4.3 Apparatus

4.3.1 Atomic absorption spectrometer, equipped with an electrothermal atomizer, chromium hollow cathode lamp and a suitable device for correction of non-specific absorbants.

4.3.2 Atomizer tubes.

The atomizer tubes will vary according to the instrument used but shall be pyrolytically coated and preconditioned before use in accordance with the manufacturer's instructions.

NOTE It is permissible to use a L'vov platform.

4.3.3 Automatic sample injector (autosampler) or microsyringe, of appropriate volume.

For high precision, an automatic sample injector is necessary.

4.4 Sampling and preparation of test portions

Follow the procedures described in 3.4 but omit the lanthanum chloride solution.

Because of the very low levels of chromium being determined, take particular care to avoid any contamination at all stages of sampling and analysis.

4.5 Procedure

4.5.1 Blank test

Carry out a blank test in parallel with the determination by the same procedure and using the same quantities of all the reagents as in the sampling and determination, but replacing the test portion by water.

4.5.2 Preparation of calibration solutions

Before each set of determinations, prepare from the chromium standard solution (see 4.2.1) at least five calibration solutions covering the range of concentrations to be determined.

Prepare the blank solution (see 4.5.1) and use it for zero setting.

The range of linearity of the calibration graph will depend on the type of instrumentation used, therefore check the range of linearity of the graph before use. If the calibration graph departs significantly from linearity, use as the highest calibration standard the one with the highest concentration in the linear portion of the calibration curve, and then adjust accordingly the concentration range of the method.

For example, to cover the range between 5 µg/l and 25 µg/l of chromium, add 1,0 ml, 2,0 ml, 3,0 ml, 4,0 ml and 5,0 ml of chromium standard solution (see 4.2.1) into a series of 100 ml volumetric flasks, add in accordance with the procedure (see 3.4.2 and 3.4.3) 10 ml or 2 ml respectively of nitric acid (see 3.2.2) to each flask.

Dilute to the mark with the water and mix.

These solutions contain 5,0 µg/l; 10,0 µg/l; 15,0 µg/l; 20,0 µg/l and 25,0 µg/l of chromium respectively. Prepare these solutions immediately before use.

4.5.3 Calibration and determination

4.5.3.1 Direct measurement

Set up the instrument in accordance with the manufacturer's instructions.

Introduce into the atomizer tube (see 4.3.2) a volume of calibration solution (see 4.5.2) sufficient to obtain a satisfactory response on the instrument being used (see note 1), for example 20 µl. Optimize the setting of the instrument.

Using an autosampler or syringe (see 4.3.3) inject the blank solution (see 4.5.1) and calibration solutions (see 4.5.2).

Measure the instrument's response by using the peak area (or alternatively the peak height) and construct a calibration graph as described in 3.5.3.

Introduce the test portion (see 3.4.2 or 3.4.3) and measure the response by determination of the peak area (or peak height).

Carry out each determination in duplicate.

NOTE 1 An appropriate test portion volume should be in the range 5 µl to 30 µl depending on the instrument used, and the same volume for all test portions, calibration solutions and blanks should be used.

NOTE 2 A number of matrix modifiers have been suggested for this determination. Most manufacturers recommend suitable modifiers for their equipment.

4.5.3.2 Procedure using the method of standard additions

When matrix interferences are suspected, this procedure should be used.

For example, introduce 5 ml of the pretreated test portion (see 3.4.2 or 3.4.3) into each of four 10 ml volumetric flasks. To each flask add 0,5 ml of nitric acid (see 3.2.2). Pipette respectively into this series of flasks 0 ml; 0,10 ml; 0,30 ml and 0,60 ml of chromium standard solution (see 4.2.1). Make each flask up to the mark with water and mix.

Measure the absorbance of each solution following the procedure used in 4.5.3.1.

4.6 Expression of results

4.6.1 If direct measurement is used (see 4.5.3.1), determine the concentration of chromium from the calibration graph corresponding to the peak area (or peak height) of the sample and of the blank as described in 3.6.

4.6.2 If the method of standard additions (see 4.5.3.2) is used, construct a graph with the absorbance values plotted on the ordinate and the chromium concentrations plotted on the abscissa. Calculate the chromium concentration of the test portions from the value of the negative intercept on the abscissa, taking into account the blank value and any dilution of the sample during pretreatment. Alternatively, data processing facilities can be used for this purpose.

4.6.3 Precision data for this method are given in Table B.2.

4.7 Interferences

Determine the effect of possible interfering substances by the analysis of samples to which chromium and various concentrations of the potential interfering substances have been added (see 3.7).

4.8 Test report

The test report shall contain at least the following information:

a) a reference to this International Standard;

b) a reference to the procedure used;

c) complete identification of the sample;

d) the results of the analysis (see 4.6);

e) any other information relevant to the procedure.

Annex A
(informative)

Pretreatment and digestion of sludge and sediment samples

A.1 Pretreatment of sludge and sediment samples

After sampling, the sludge and sediment samples are stored in the original bottles (see 3.4.1) in a refrigerator, or frozen until further treatment.

If the determination is to be carried out on a dry residue, the sample is preferably freeze dried, or alternatively dried at 105 °C ± 2 °C for about 24 h. The dried sample is homogenized.

NOTE Dried sludges and sediments may be hygroscopic, and should therefore be dried again prior to analysis if stored for a very long time.

A.2 Digestion

As an alternative to the digestion described in 3.4.2, the following method can be used:

Transfer a precisely weighed amount of the samples to the digestion flask (a colourless bottle made of heat-resistant glass or an equivalent glass quality), volume about 100 ml. The bottle and the screw cap shall withstand at least a pressure of 200 kPa (120 °C). The largest permissible amount of sample is 1 g of dried material, or the equivalent amount of wet sample. Add 20 ml of nitric acid (see 3.2.2). Close the digestion flask tightly, and heat to 120 °C (200 kPa) for 30 min, following the directions given for the autoclave (alternatively, a microwave oven may be used). Cool to room temperature, transfer the solution quantitatively to a 100 ml volumetric flask, and dilute to the mark with water. After the undissolved material has settled, the determination is performed on the clear liquid phase.