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Water quality — Determination of total chromium — Atomic absorption spectrometric methods

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



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Foreword

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Introduction

Chromium may occur in water in the oxydation states III and VI. The two methods described determine total chromium in both oxidation states, either as acid soluble chromium or as soluble chromium, depending on the sample pre-treatment. The method chosen depends on the concentration of chromium in the water to be examined.

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Water quality — Determination of total chromium — Atomic absorption spectrometric methods

Section 1: General

1.1 Scope

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

Section 2: Method A — Determination of total chromium by flame atomic absorption spectrometry.

Section 3: Method B — Determination of total chromium by electrothermal atomization atomic absorption spectrometry.

Method A 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 bulk, taking care to avoid the formation of a precipitate.

IMPORTANT — The use of evaporation will increase the effect of interfering substances and therefore for concentrations below 0,1 mg/l method B is given.

For interferences see clause 2.7.

Method B 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 µg/l. It is applicable to the determination of higher concentrations by using a smaller sample volume.

For interferences see clause 3.7.

1.2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 5667-2:1982, *Water quality — Sampling — Part 2: Guidance on sampling techniques*.

ISO 5667-3:1985, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of samples*.

Section 2: Methode A — Determination of total chromium by flame atomic absorption spectrometry

2.1 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 to reduce matrix interferences.

2.2 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 determinations 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.

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

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

2.2.3 Nitric acid, $c(\text{HNO}_3) = 1,5$ mol/l.

Add 100 ml of nitric acid (2.2.2) to 600 ml of water and dilute to 1 000 ml.

2.2.4 Hydrogen peroxide, 30 % (m/m) solution.

2.2.5 Lanthanum chloride, (LaCl_3), solution containing 20 g of La per litre.

Dissolve 23,5 g of lanthanum oxide (La_2O_3), in 200 ml of the hydrochloric acid (2.2.1), dilute to 1 000 ml with water and mix.

CAUTION — Appropriate precautions must be observed when preparing this solution because the reaction of La_2O_3 with HCl is strongly exothermic.

2.2.6 Chromium solutions

2.2.6.1 Chromium, stock solution containing 1,000 g of Cr per litre.

Dry a portion of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) at $105^\circ\text{C} \pm 2^\circ\text{C}$ for 2 h. Cool and dissolve $2,825 \text{ g} \pm 0,001 \text{ g}$ of the dried potassium dichromate in water, add 5 ml of nitric acid (2.2.2) and dilute to 1 000 ml with water in a one-mark volumetric flask.

1 ml of this standard solution contains 1,00 mg of Cr.

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

NOTE 1 Chromium stock solutions are commercially available.

2.2.6.2 Chromium, standard solution containing 50 μg of Cr per millilitre.

Pipette 50 ml of the chromium stock solution (2.2.6.1) into a 1 000 ml one-mark volumetric flask. Add 1 ml of nitric acid (2.2.2), make up to the mark with water and mix.

Store this solution in either polyethylene or borosilicate glass containers at room temperature. The solution is stable at room temperature for 1 month if it is stored in the dark.

2.3 Apparatus

Usual laboratory apparatus and

2.3.1 Atomic absorption spectrometer, equipped with a chromium hollow cathode lamp and a nitrous oxide/acetylene burner, and operated according to the manufacturer's instructions.

CAUTION — It is essential that the manufacturer's safety recommendations are strictly observed when using the nitrous oxide/acetylene flame.

2.3.2 Glassware.

Before use carefully soak all glassware for 24 h in the nitric acid (2.2.3) then rinse thoroughly with water.

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

2.3.3 Membrane filters, of nominal pore diameter $0,45 \mu\text{m}$, washed thoroughly with nitric acid (2.2.3) and rinsed with water (see clause 2.2).

2.4 Sampling and preparation of test portions

2.4.1 Collect samples in polyethylene or borosilicate glass containers which have been previously cleaned with nitric acid (2.2.3) and then rinsed with water.

2.4.2 Acid-soluble chromium

2.4.2.1 Treat the samples by addition of sufficient nitric acid (2.2.2), immediately after collection, to adjust the pH value to between 1 and 2.

2.4.2.2 To 90 ml of the acidified sample, or another suitable aliquot according to the expected concentration, add 1 ml of hydrogen peroxide (2.2.4) and 1 ml of nitric acid (2.2.2). Boil and evaporate to a volume of approximately 50 ml.

IMPORTANT — It is essential that the sample is not reduced to dryness.

2.4.2.3 Add 10 ml of the nitric acid (2.2.3) to the evaporated solution. Transfer the solution to a 100 ml one-mark volumetric flask. Pipette 10 ml of the lanthanum chloride solution (2.2.5) into the flask, dilute to the mark with water (see clause 2.2) and mix.

2.4.3 Soluble chromium

2.4.3.1 Filter the sample through a membrane filter (2.3.3), as soon as possible after collection, and acidify the filtrate immediately with nitric acid (2.2.2) to give a pH between 1 and 2.

2.4.3.2 Pipette 10 ml of the lanthanum chloride solution (2.2.5) into a 100 ml one-mark volumetric flask and make up to the mark with the acidified filtrate (2.4.3.1), or other suitable aliquot according to the expected concentration, and mix.

2.5 Procedure

2.5.1 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 sample by water (see clause 2.2).

2.5.2 Preparation of the calibration solutions

Before each batch of determinations, prepare from the chromium standard solution (2.2.6.2) at least five calibration solutions covering the range of concentrations to be determined as follows: pipette 1,00 ml, 2,50 ml, 5,00 ml, 10,00 ml and 20,00 ml of chromium standard solution (2.2.6.2) into a series of 100 ml one-mark volumetric flasks. Add to each flask 2 ml of nitric acid (2.2.2) and 10 ml of lanthanum solution (2.2.5), dilute to the mark with water and mix. These solutions correspond to chromium concentrations

of 0,5 mg/l, 1 mg/l, 2,5 mg/l, 5 mg/l and 10 mg/l respectively.

2.5.3 Calibration

Set up the instrument according to the manufacturer's instructions ($\lambda = 357,9 \text{ nm}$) using a nitrous oxide/acetylene flame.

Aspirate a calibration solution (2.5.2) and optimize the aspiration, the burner height and flame conditions. Adjust the response of the instrument to zero absorbance with water.

Aspirate the set of calibration solutions (2.5.2) and, as a zero member, the blank solution (2.5.1). Plot a graph having the chromium concentrations of the calibration solutions in milligrams per litre as abscissa and the corresponding absorbance values as ordinate.

2.5.4 Test portion measurement

Aspirate the prepared test portion (2.4.2 or 2.4.3) into the flame and measure the absorbance for chromium. After each measurement aspirate water (see clause 2.2) and re-adjust the zero if necessary.

2.6 Expression of results

2.6.1 By reference to the calibration graph obtained (see 2.5.3) determine the concentration of chromium corresponding to the absorbances of the test portion (2.5.4) and of the blank (see 2.5.1).

Calculate the concentration of chromium, expressed in milligrams per litre, of the sample using the formula

$$\rho(\text{Cr})_1 - \rho(\text{Cr})_0 \times \frac{100}{V}$$

where

$\rho(\text{Cr})_0$ is the chromium concentration, in milligrams per litre, corresponding to the absorbance of the blank;

$\rho(\text{Cr})_1$ is the chromium concentration, in milligrams per litre, corresponding to the absorbance of the test portion;

V is the volume, in millilitres, of the acidified sample taken for the analysis.

2.6.2 Precision

An inter-laboratory test carried out in January 1985 yielded the following data:

Type of sample	<i>l</i>	<i>n</i>	<i>x_s</i>	$\bar{x}$	<i>y</i>	σ_r	VC _r	σ_R	VC _R
Standard solution	11	43	15,0	14,64	97,5	0,084	0,6	0,798	5,5
Water with added concentration	14	56	2,0	2,06	103,0	0,053	2,6	0,218	10,6

where

- l* is the number of laboratories;
- n* is the number of samples (without outliers);
- x_s* is the concentration of samples, in milligrams per litre;
- $\bar{x}$ is the overall mean, in milligrams per litre;
- y* is the recovery rate, expressed as a percentage;
- σ_r is the repeatability standard deviation, in milligrams per litre;
- VC_r is the repeatability variation coefficient, expressed as a percentage;
- σ_R is the reproducibility standard deviation, in milligrams per litre;
- VC_R is the reproducibility variation coefficient, expressed as a percentage.

2.7 Interferences

The following ions have been tested and shown not to cause interference below the indicated concentrations.

Table 1

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 water sample shall not exceed 15 g/l and the conductivity should be lower than 20 mS/cm.

NOTE 2 The effect of possible interferences may be determined by analysing samples spiked with chromium and various concentrations of the potential interfering substance using the method of standard additions.

2.8 Test report

The test report shall contain the following information:

- a) a reference to this International Standard;
- b) a reference to the method used;
- c) complete identification of the sample;
- d) any other information relevant to the procedure.

Section 3: Method B — Determination of total chromium by electrothermal atomization atomic absorption spectrometry

3.1 Principle

Chromium is determined directly in acidified samples by electrothermal atomization atomic absorption spectrometry. The sample is injected 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.

3.2 Reagents

3.2.1 See clause 2.2.

3.2.2 **Chromium**, standard solution containing 0,5 µg of Cr per millilitre.

Pipette 10 ml of the chromium standard solution (2.2.6.2) into a 1 000 ml one-mark volumetric flask. Add 10 ml of nitric acid (2.2.2) and dilute to the mark with water.

Store in a polyethylene bottle at room temperature. This solution is stable for at least one month.

3.3 Apparatus

Usual laboratory apparatus and

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

3.3.2 **Atomizer tubes**.

These will vary according to the instrument used but shall be pyrolytically coated and pre-conditioned before use according to the manufacturer's instructions.

NOTE 3 It is permissible to use a L'vov platform.

3.3.3 **Automatic sample injector or micro-syringe**, of appropriate volume.

For good precision an automatic sample injector is required.

3.4 Sampling and preparation of test portions

Follow the procedures described in clause 2.4 but omit the lanthanum solution.

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

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 batch of determinations, prepare from the chromium standard solution (3.2.2) at least five calibration solutions covering the range of concentrations to be determined. Use as zero member the blank solution (see 3.5.1). The linearity of the calibration graph will depend on the type of instrumentation used, therefore check the 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 on 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 Cr, pipette 1 ml, 2 ml, 3 ml, 4 ml and 5 ml of chromium standard solution (3.2.2) into a 100 ml one-mark volumetric flask, add 1 ml of nitric acid (2.2.2) to each flask. Dilute to the mark with the water and mix. These solutions contain 5 µg/l, 10 µg/l, 15 µg/l, 20 µg/l and 25 µg/l of Cr respectively. Prepare these solutions immediately before use.

3.5.3 Calibration and determination

Set up the instrument according to the manufacturer's instructions.

3.5.3.1 Direct measurement

Inject into the atomizer tube (3.3.2) a volume of calibration solution ((3.5.2) sufficient to obtain a satisfactory response on the instrument being used (see note 1).

Using an autosampler or syringe (3.3.3) inject the blank solution (see 3.5.1) and calibration solutions (3.5.2). Measure the instrument's response by using