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Water quality — Determination of aluminium — Atomic absorption spectrometric methods

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

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Foreword

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International Standard ISO 12020 was prepared by Technical Committee ISO/TC 147, *Water Quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

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

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Introduction

Aluminium may be present in water in ionic or complex form. It may be dissolved or finely dispersed. Even with the digestion described in 2.5.3, silicates and oxidic aluminium compounds may not in all cases be quantitatively covered by these methods. Clause 2 refers to the determination of aluminium by flame atomic absorption spectrometry (AAS); in clause 3 a graphite furnace AAS method is described.

Water quality – Determination of aluminium – Atomic absorption spectrometric methods

1 Scope

This International Standard describes two atomic absorption spectrometric (AAS) methods for the determination of aluminium in water.

1.1 Flame AAS

The flame AAS method (clause 2) is applicable for the determination of aluminium in water in mass concentrations from 5 mg/l to 100 mg/l. Higher concentrations may be determined after an appropriate dilution of the sample. Careful evaporation of the sample, acidified with nitric acid, may be used to extend the working range of the method to lower concentrations as long as no precipitation is observed.

NOTE – If the linear range of the instrument is sufficiently large, concentrations < 5 mg/l may be determined with this method; otherwise the determination needs to be carried out in the graphite furnace, as described in clause 3.

If the determination of the total content of aluminium is required, a digestion of the sample according to 2.5.3 is necessary. Silicates and aluminium oxide compounds may, however, not be quantitatively determined with this digestion procedure.

1.2 Graphite furnace

The graphite furnace AAS method (clause 3) is applicable for the determination of aluminium in waters and waste waters in mass concentrations from 10 µg/l to 100 µg/l applying a dosing volume of 20 µl. The working range can be shifted to higher concentrations either by dilution of the sample or by using a smaller sample volume.

2 Determination of aluminium by atomic absorption spectrometry in a nitrous oxide/acetylene flame

2.1 Interferences

The following ions can interfere with the flame AAS method, if the concentrations listed below are exceeded:

Sulfate	10 000 mg/l
Chloride	10 000 mg/l
Phosphate	10 000 mg/l
Sodium	10 000 mg/l
Potassium	10 000 mg/l
Magnesium	10 000 mg/l
Calcium	10 000 mg/l
Iron	10 000 mg/l
Nickel	10 000 mg/l
Cobalt	10 000 mg/l
Cadmium	3 000 mg/l
Lead	10 000 mg/l

Silicate	200 mg/l
Fluoroborate	2 000 mg/l
Titanium	1 000 mg/l
Fluoride	3 000 mg/l 1)

1) This concentration is applicable for strongly acidic samples or measuring solutions with pH < 1. In less acidic solutions precipitation may occur.

The total salt content of the measuring solution should not exceed 15 g/l, or its electrical conductivity should not be higher than 2 000 mS/m. For samples whose matrix influence is unknown, the conductivity should be investigated and compensated for, if possible, for example by dilution of the sample or by application of the method of standard additions.

2.2 Principle

Acid is added to the water sample which is then aspirated into a nitrous oxide/acetylene flame of an atomic absorption spectrometer. The absorbance is measured at a wavelength of 309,3 nm and the aluminium content calculated.

2.3 Reagents

2.3.1 General requirements

Use only reagents of at least recognized analytical grade quality and double-distilled water or water of equivalent purity. The aluminium content of the water or the reagents used shall be negligibly low, compared with the lowest concentration of aluminium to be determined.

2.3.2 Hydrochloric acid, $\rho_{HCl} = 1{,}16$ g/ml.

2.3.3 Nitric acid, $\rho_{HNO_3} = 1{,}40$ g/ml.

2.3.4 Hydrogen peroxide (dihydrogen dioxide), $w_{H_2O_2} = 30$ %.

2.3.5 Caesium chloride solution, $\rho_{Cs} = 20$ g/l.

Dissolve 25,3 g of CsCl in 100 ml of HCl (2.3.2) and make up to 1 000 ml with water (2.3.1).

2.3.6 Aluminium stock solution, $\rho_{Al} = 1\,000$ mg/l.

Dissolve 1,000 g of aluminium, minimum purity 99,9 % or band, in a graduated flask, nominal capacity 1 000 ml, in approximately 15 ml of hydrochloric acid (2.3.2) and make up to volume with water (2.3.1).

Alternatively, prepare the solution with a commercially available aluminium standard which contains (1,000 ± 0,002) g Al.

2.3.7 Aluminium standard solution, $\rho_{Al} = 100$ mg/l.

Pipette 100 ml of the aluminium stock solution (2.3.6) into a 1 000-ml graduated flask, add 10 ml of nitric acid (2.3.3), and make up to volume with water (2.3.1).

2.3.8 Aluminium calibration solutions.

In accordance with the aluminium concentration expected in the sample, prepare at least five calibration solutions from the aluminium standard solution (2.3.7). For the working range of 5 mg/l to 50 mg/l, proceed, for example, as follows.

a) Pipette, into a series of 100-ml graduated flasks, 5 ml, 10 ml, 20 ml, 30 ml and 50 ml of the aluminium standard solution (2.3.7);

b) add 2 ml of caesium chloride solution (2.3.5);

c) acidify each of these solutions with 1 ml of nitric acid (2.3.3);

d) make up to volume with water and mix.

The calibration solutions contain 5 mg/l, 10 mg/l, 20 mg/l, 30 mg/l or 50 mg/l of aluminium, respectively. Prepare the calibration solutions on the day of use.

NOTE – It is advantageous to use additional calibration solutions in the main part of the working range.

2.3.9 Blank solution.

Pipette 1 ml of nitric acid (2.3.3) into a 100-ml graduated flask, and make up to volume with water.

If the sample is to be digested or evaporated to a smaller volume, the blank solution shall be submitted to the same pretreatment (2.5.3).

2.3.10 Zeroing solution.

Use water (2.3.1) as zeroing solution. The blank solution (2.3.9) may also be used to zero the instrument, provided the aluminium content of the blank solution is negligibly low.

The zeroing solutions shall not be stored in bottles made of polyolefins (see 2.5.1).

2.4 Apparatus

2.4.1 Atomic absorption spectrometer, with background correction and radiation source for the determination of aluminium.

2.4.2 Gas supply with nitrous oxide and acetylene; the residual pressure of the acetylene tanks shall never fall below 500 kPa. The nitrous oxide/acetylene supply should be designed to allow high supply quantities.

2.4.3 Graduated flasks, nominal capacities 10 ml, 100 ml and 1 000 ml.

2.4.4 One-mark pipettes, nominal capacities 5 ml, 10 ml, 20 ml, 30 ml and 50 ml.

2.4.5 Microlitre pipette or diluter.

2.4.6 Silica glass beaker, nominal capacity 250 ml.

2.4.7 Heating appliance, e.g. electric heating plate.

2.4.8 Membrane filtration device, with membrane filters of pore size 0,45 μm.

2.5 Sampling and sample preparation

2.5.1 General requirements

Clean the glassware immediately before use with warm dilute nitric acid, $c(HNO_3) \approx 0{,}2$ mol/l, and thoroughly rinse with water (2.3.1).

Check incoming batches of pipette tips and one-way vessels for possible aluminium contamination.

Collect the samples in bottles made of an appropriate plastics material. Bottles made of polyolefins shall not be used because they may contain traces of aluminium.

Clean the sample containers as specified for glassware.

2.5.2 Pretreatment for the determination of dissolved aluminium

a) Filter the water sample as soon as possible after sample collection (2.5.1) through a membrane filter, pore size 0,45 µm.

b) Acidify the filtrate with 1 ml of nitric acid (2.3.3) per 1 000 ml of water sample for stabilization.

c) The resulting pH shall be < 2, otherwise add more acid.

2.5.3 Pretreatment for the digestion procedure

a) Immediately after sample collection, add 1 ml of nitric acid (2.3.3) per 1 000 ml of sample.

b) The resulting pH shall be < 2, otherwise add more acid.

c) In a silica glass beaker add 1 ml of nitric acid (2.3.3) and 1 ml of hydrogen peroxide (2.3.4) to 100 ml of the homogenized sample and evaporate to a moist residue. To prevent losses, do not evaporate the water sample to complete dryness.

d) Take up the moist residue with 1 ml of nitric acid (2.3.3) and a small quantity of water (2.3.1), and make up to 100 ml. Treat the blanks in the same way.

2.5.4 Preparation of the measuring solution

a) Place 20 ml of the water sample, pretreated as described in 2.5.2 or 2.5.3, in a 25-ml graduated flask. Add 2 ml of caesium chloride solution (2.3.5), mix well and make up to volume with water (2.3.1).

b) Treat the blank solution and the calibration solutions in exactly the same way.

2.6 Procedure

a) Prior to the measurement, set the operating parameters of the atomic absorption spectrometer in accordance with the manufacturer's operating manual.

b) Zero the instrument by aspirating the zeroing solution (2.3.10) into the flame.

c) Calibrate by aspirating, in ascending order of concentration, the calibration solutions prepared as described in 2.3.8.

d) Re-set the instrument zero by aspirating the zeroing solution (2.3.10) after each calibration solution.

e) Measure the blank solution, prepared as described in 2.3.9 and then the measuring solutions, prepared as described in 2.5.4.

f) After each series of samples, but after at most 10 to 20 measurements, check the calibration function with the blank solution and a midrange calibration solution.

If the aluminium content of the measuring solution exceeds the range of validity of the calibration curve, dilute the measuring solution accordingly.

2.7 Calculation of results

Establish the calibration function from the measured data obtained from the calibration solutions.

Calculate the mass concentration of aluminium ρ_{Al}, in milligrams per litre of the water sample, using the following equation:

$$\rho_{\mathrm{Al}} = \frac{(A_{\mathrm{s}} - A_{\mathrm{s0}})V_{\mathrm{m}}}{b \cdot V_{\mathrm{p}}}$$

where

A_s is the absorbance of the measuring solution;

A_{s0} is the absorbance of the blank solution;

b is the slope, in litres per milligram, of the calibration function, estimated by regression;

V_p is the volume, in millilitres, of the water sample used for the preparation of the measuring solution;

V_m is the volume, in millilitres, of the measuring solution.

Any other dilutions in addition to those given here shall be taken into account.

2.8 Expression of results

Values shall be reported to the nearest 1 mg/l, with two significant figures at most.

EXAMPLES

Aluminium (Al) 7 mg/l

Aluminium (Al) 32 mg/l

3 Determination of aluminium by atomic absorption spectrometry in a graphite furnace

3.1 Interferences

The following ions will not interfere with the graphite furnace determination as long as the threshold mass concentrations specified are not exceeded:

a) threshold value of 100 mg/l for iron, copper, nickel, cobalt, cadmium, lead, tetrafluoroborate and silicate;

b) threshold value of 1 000 mg/l for sodium, potassium, calcium, chloride, sulfate, phosphate and acetate.

Fluoride will lead to signal depression even at low concentrations. This can be compensated up to a mass concentration of 50 µg/l of fluoride by an additional injection of 10 µl of sulfuric acid, $\rho = 1{,}07$ g/ml, into the graphite tube immediately after injection of the sample.

Because of the ubiquity of aluminium, low-level measurements are prone to contamination.

For the analysis of samples with unknown matrix composition, the method of standard addition (3.6.3) should be used. Bias due to nonspecific absorption can be compensated to a large extent by application of background compensation.

3.2 Principle

The measuring solutions are injected into the graphite tube of a graphite furnace aligned in the light path of the atomic absorption spectrometer. The absorbances, or the time-integrated absorbances, are measured at a wavelength of 309,3 nm.

3.3 Reagents

Concerning purity, see 2.3.1.

3.3.1 Hydrochloric acid, $\rho_{HCl} = 1{,}16$ g/ml.

3.3.2 Nitric acid, $\rho_{HNO_3} = 1{,}40$ g/ml.

3.3.3 Hydrogen peroxide (dihydrogen dioxide) $w_{H_2O_2} = 30$ %.

3.3.4 Matrix modifier solution.

Dissolve 500 mg of anhydrous magnesium nitrate with water (2.3.1) in a 100-ml graduated flask, and make up to volume with water.

3.3.5 Sulfuric acid, $\rho_{H_2SO_4} = 1{,}07$ g/ml.

3.3.6 Aluminium stock solution I, $\rho_{Al} = 1\,000$ mg/l.

a) Dissolve 1,000 g of aluminium band in a graduated flask, nominal capacity 1 000 ml, in about 15 ml hydrochloric acid (3.3.1) and make up to volume with water (2.3.1).

Alternatively, prepare the solution with a commercially available aluminium standard which contains (1,000 ± 0,002) g Al.

b) Store the solution in a plastics bottle. Bottles made of polyolefins shall not be used (see 2.5.1).

3.3.7 Aluminium stock solution II, $\rho_{Al} = 100$ mg/l.

a) Pipette 10 ml of aluminium stock solution I (3.3.6) into a 100-ml graduated flask, add 1 ml of nitric acid (3.3.2) and make up to volume with water (2.3.1).

b) Store the solution in a plastics bottle. Bottles made of polyolefins shall not be used (see 2.5.1).

3.3.8 Aluminium standard solution, $\rho_{Al} = 1\,000$ µg/l.

a) Pipette 10 ml of the aluminium stock solution II (3.3.7) into a 1 000-ml graduated flask, add 1 ml of nitric acid (3.3.2) and make up to volume with water (2.3.1).

b) Store the solution in a plastics bottle. Bottles made of polyolefins shall not be used (see 2.5.1).

3.3.9 Aluminium calibration solutions.

In accordance with the aluminium concentration expected in the sample, prepare at least five calibration solutions from the aluminium standard solution (3.3.8). For the working range of 10 µg/l to 100 µg/l proceed, for example, as follows:

a) Pipette into 100 ml graduated flasks 1 ml, 2 ml, 3 ml, 4 ml, 6 ml and 10 ml of the aluminium standard solution (3.3.8). Add to each of these solutions 1 ml of nitric acid (3.3.2).

b) Make up to volume with water (2.3.1) and mix.

The calibration solutions contain 10 µg/l, 20 µg/l, 30 µg/l, 40 µg/l, 60 µg/l or 100 µg/l of aluminium, respectively.

Prepare the calibration solutions immediately before use. If necessary, prepare additional calibration solutions for the main part of the working range.

3.3.10 Blank solution.

Pipette 1 ml of nitric acid (3.3.2) into a 100-ml graduated flask, and make up to volume with water (2.3.1).

If the sample is digested, the blank solution shall be submitted to the same pretreatment.

3.3.11 Zeroing solution.

Use water (2.3.1) as the zeroing solution.

The blank solution (3.3.10) may also be used to zero the instrument, provided the aluminium content of the blank solution is negligibly low.

3.4 Apparatus

3.4.1 Atomic absorption spectrometer, with background compensation and radiation source for the determination of aluminium.

3.4.2 Graphite furnace, with control unit.

NOTE – The use of pyrolytically-coated graphite tubes and application of the platform technique is advantageous.

3.4.3 Argon gas supply.

3.4.4 One-mark pipettes, nominal capacity 1 ml, 2 ml, 5 ml and 10 ml, or **diluter.**

3.4.5 Further apparatus, see 2.4.

3.5 Sampling and sample preparation

Proceed as described in 2.5.2 and 2.5.3.

3.6 Procedure

3.6.1 General requirements

Prior to the measurement, set the operating parameters of the atomic absorption spectrometer in accordance with the manufacturer's operating manual.

Zero the instrument with the zeroing solution (3.3.11).

Bottles made of polyolefins shall not be used (see 2.5.1).

3.6.2 Calibrating and measuring with the standard calibration procedure

The application of the standard calibration procedure shall be allowed only if matrix interferences as described in 3.1 can be ruled out. Otherwise, the method of standard additions according to 3.6.3 shall be used.

a) Prior to each measurement, inject 10 µl of the matrix modifier solution (3.3.4) into the graphite tube.

b) Measure, following the instrument manufacturer's instructions, the absorbances or the time-integrated absorbances of the calibration solutions (3.3.9), of the blank solution (3.3.10) and of the measuring solutions (2.5.2) or (2.5.3), respectively.

c) In the presence of more than 0,05 µg/l of fluoride, additionally inject 10 µl of sulfuric acid (3.3.5) into the graphite tube.

d) Measure the absorbance of each solution at least twice.

3.6.3 Calibrating and measuring with the method of standard addition

NOTE – With this technique, matrix interferences can be compensated for in many cases, provided no additive errors occur and the aluminium contents of the measuring solution and of the spiked sample solutions are within the linear part of the working range.

a) Place into each of four 10 ml graduated flasks, 0,1 l of nitric acid (3.3.2) and 5 ml of sample solution (2.5).

For an aluminium content > 100 µg/l in the spiked sample solutions, use a smaller volume. Take this into account on calculation.

b) Make the first flask up to volume with water (2.3.1).

c) Into the remaining three flasks pipette 0,1 ml, 0,2 ml and 0,3 ml of the aluminium standard solution (3.3.8) and make up to volume with water (2.3.1).

NOTE – The addition of 0,1 ml of aluminium standard solution (3.3.8) corresponds to 20 µg/l Al, related to the sample and blank volume of 5 ml. The dilution by making up to 10 ml does not enter into the calculation.

d) Prepare the blank solution (3.3.10) in the same way.

e) Prior to each measurement, additionally inject 10 µl of the matrix modifier solution (3.3.4) into the graphite tube.

f) Measure the absorbances, or the time-integrated absorbances, respectively, as described in 3.6.2.

3.7 Calculation of results

3.7.1 Direct measurement

The calculation is carried out in accordance with 2.7, but the mass concentration here is expressed in micrograms aluminium per litre of water sample.

3.7.2 Standard addition

In a graph with concentration as the abscissa and signal obtained as the ordinate, enter the values measured for the measuring solutions and the values measured for the measuring solutions spiked with ascending aluminium mass concentrations. The regression line drawn through these points will intersect the abscissa on its negative side. This point of intersection is the mass concentration of aluminium in the measuring solution. From this value, the mass concentration of aluminium in the blank solution, measured in the same way, is subtracted. The difference is the mass concentration of aluminium in the water sample.

NOTE – The evaluation can also be performed using regression calculation.

3.8 Expression of results

Values shall be reported to the nearest 1 µg/l, with 2 significant figures at most.

EXAMPLE

Aluminium (Al) 48 µg/l

4 Precision

Details of an interlaboratory test on the precision of the method are summarized in annex A. The values derived from this interlaboratory test may not be applicable to concentration ranges and matrices other than those given.

5 Test report

The test report shall contain the following information:

a) a reference to the method used;

b) identification of the water sample;

c) sample pretreatment, if applicable;

d) results, expressed according to 2.8 or 3.8;

e) any deviation from the method specified, and all circumstances which may have influenced the result.

Annex A
(informative)

Results of an interlaboratory trial

An interlaboratory trial, carried out in autumn 1993 in Germany, resulted in the values given in table A.1.

Table A.1 — Precision data

Sample	L	N	**Outliers**	$\bar{x}$	s_R	CV_R
AA	15	42	0	9,78	0,159	1,6
AB	15	42	7	47,29	2,03	1,0
BA	6	13	–	11,3	0,935 1	8,3
BB	6	13	–	51,5	4,152 0	8,1

L	number of laboratories;
N	number of values;
$\bar{x}$	total mean, in µg/l;
s_R	reproducibility standard deviation, in µg/l;
CV_R	reproducibility variation coefficient, in %;
AA	drinking water, flame technique;
AB	river water, flame technique;
BA	river water, graphite furnace technique;
BB	industrial waste water, graphite furnace technique.

Annex B
(informative)
Bibliography

[1] ISO 5667-1:1980, *Water quality – Sampling – Part 1: Guidance on the design of sampling programmes.*

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

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

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