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Water quality — Determination of aluminium — Spectrometric method using pyrocatechol violet

Qualité de l'eau — Dosage de l'aluminium — Méthode par spectrométrie à l'aide du violet de pyrocatéchol

Reference number
ISO 10566:1994(E)

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 Standard ISO 10566 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical, biochemical methods*.

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Introduction

Aluminium occurs in a variety of types of compounds in nature, and can be found in acid, neutral and alkaline solutions. It can also form colloidal polymeric solutions and gels, as well as flocculant precipitates, all based on aquated positive ions or hydroxylated aluminates.

In addition, it can form complexes with organic acids and with ions such as fluoride, chloride and sulfate, most but not all of which are soluble.

Aluminium can also form lattice compounds with oxygen (and hydroxyl species), silicon, and some metals. Although insoluble, some of these compounds, notably the clays, micas and zeolites, can be found as fine suspended particles in rivers. Although they contain aluminium, these insoluble lattice compounds are not usually considered as aluminium compounds in the context of the water cycle.

The method described in this International Standard is restricted to the determination of the aquated cations and other forms of aluminium readily converted to that cationic form by acidification. The pretreatment with nitric acids is identical to that described in other International Standards using spectrometric methods with an electrothermal atomization or inductively coupled plasma procedure (methods of preparation).

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1 Scope

1.1 Type of sample

The method is applicable to the analysis of potable waters, ground waters, and lightly polluted surface and sea waters.

1.2 Substance determined

The method determines filterable (dissolved) and acid-soluble aluminium.

1.3 Range

The method includes low range determination up to 100 µg/l Al with 50 mm cells and high range determination up to 500 µg/l Al with 10 mm cells. The effective range depends on the sensitivity of the spectrometer and can be extended upwards by taking smaller test portions.

1.4 Limit of detection

The limit of detection is 2 µg/l when cells of optical path length 50 mm and a 25 ml test portion are used.

1.5 Sensitivity

An aluminium concentration of 100 µg/l gives an absorbance of about 0,20 ± 0,05 optical absorption units, using a 25 ml test portion and cells of optical path length 10 mm.

1.6 Precision

If not specified, the precision of volumes and masses mentioned in this International Standard is ± 1 % of the value.

2 Normative reference

The following standard contains provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the edition indicated was 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 edition of the standard indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

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

3 Principle

For dissolved aluminium, the sample is filtered through membrane filters with 0,45 µm pore size and then acidified with nitric acid to obtain a pH of 1,2 to 1,5.

For acid-soluble aluminium, the untreated sample is acidified with nitric acid to obtain a pH of 1,2 to 1,5, kept for at least 1 h at room temperature to dissolve the aluminium and then filtered.

Aluminium is reacted with pyrocatechol violet at a pH of 5,9 ± 0,1 followed by spectrometric measurement of the resulting coloured complex at a wavelength of 580 nm (the blue colour is visible only at high aluminium concentrations).

NOTE 1 For other kinds of determination, e.g. digestions, the sample is pretreated accordingly, using nitric acid at a pH of 1,2 to 1,5 in the final sample.

4 Reagents

Use only reagents of recognized analytical grade. Ensure that the aluminium content is negligible compared with the smallest concentration to be determined in the samples.

All reagent solutions shall be free of suspended particles (dust) which can interfere with spectrometry. If necessary, filter through a membrane filter of pore size 0,45 µm.

Solutions shall be stored in closed plastics laboratory bottles at room temperature, preferably not exposed to bright light.

4.1 Nitric acid (HNO_3), ρ = 1,40 g/ml, 65 % (*V/V*).

4.2 Distilled or deionized water which is free from aluminium, i.e. aluminium content below 1 µg/l or below 1 % of the range of determination.

4.3 Acidified water

Add 4,0 ml of nitric acid (4.1) to 1 000 ml of water (4.2).

4.4 Mixed reagent

Add 1,0 ml of nitric acid (4.1) to approximately 70 ml of water (4.2) in a 200 ml plastics laboratory beaker (5.3). To this solution, add 25,0 g of magnesium sulfate heptahydrate [$MgSO_4 \cdot 7H_2O$], 5,0 g of ascorbic acid ($C_6H_8O_6$), 0,25 g of 1,10-phenanthroline monohydrate [$C_{12}H_8N_2 \cdot H_2O$] and 5,0 ml of aluminium standard solution (4.8). Transfer to a 100 ml one-mark volumetric flask and make up to the mark with water.

This solution is stable for one month.

NOTE 2 Accurate addition of the aluminium standard solution is essential in order to allow a linear calibration at low concentrations.

4.5 Pyrocatechol violet solution

Carefully dissolve 0,050 g of pyrocatechol violet [($C_{19}H_{14}O_7S$) 3,3′, 4′-trihydroxyfuchsine-2″-sulfonic acid] in approximately 20 ml of water. Transfer to a 100 ml one-mark volumetric flask and make up to the mark with water (4.2).

This solution is stable for one month.

NOTE 3 As pyrocatechol violet is a dye which may vary with brand and batch, applicability should be checked with every new batch. As a guideline, a standard solution of 100 µg/l Al should produce spectral absorption of about 0,20 cm^{-1} ± 0,05 cm^{-1} using this method.

4.6 Hexamine buffer solution

Dissolve 210 g hexamethylene-tetramine ($C_6H_{12}N_4$) in approximately 200 ml of water (4.2). Transfer the solution to a 500 ml one-mark volumetric flask and make up to the mark with water.

This solution is stable for at least 2 months.

NOTE 4 This solution is close to saturation. It should be kept above 15 °C to prevent crystallization. Some brands of hexamine contain dust particles, in which case the buffer should be filtered after preparation.

4.7 Aluminium stock solution, 1 000 mg/l.

Weigh 100 mg of aluminium foil to a precision of ± 0,5 mg. Dissolve the aluminium in a 100 ml one-mark volumetric flask, using 1 ml of nitric acid (4.1) and a few millilitres of water (4.2). When dissolution is complete, make up to the mark with water.

NOTE 5 Commercially available aluminium standard solutions may be used.

The solution is stable at room temperature, unless no loss from evaporation occurs.

4.8 Aluminium standard solution, 10 mg/l.

Pipette 1,00 ml of aluminium stock solution (4.7) into a 100 ml one-mark volumetric flask and make up to the mark with acidified water (4.3).

4.9 Sodium hydrogen carbonate, 2,0 mol/l solution.

Dissolve 85 g of sodium hydrogen carbonate ($NaHCO_3$) in about 400 ml of water. Transfer the solution to a 500 ml one-mark volumetric flask and make up to the mark with water (4.2).

NOTE 6 This reagent is used to raise the pH of the sample when it is below 1,2 (e.g. from digestion). Sodium hydroxide (NaOH) is not recommended because even analytical grades may contain aluminium, while sodium hydrogen carbonate is extremely low in aluminium, particularly the pharmaceutical grades.

5 Apparatus

Ordinary laboratory equipment and

5.1 Spectrometer, capable of operating at a wavelength of 580 nm and equipped with cells of optical path length 10 mm and 50 mm. Other cell path lengths may be used with appropriate calibration ranges.

NOTE 7 The sensitivity and precision of this method also depends on the performance of the spectrometer.

5.2 Filtration device, fitted with membrane filters with an average pore size of 0,45 µm.

5.3 Plastics laboratory beakers, e.g. of capacity 100 ml, 200 ml or 500 ml.

5.4 One-mark volumetric plastics flasks, e.g. of capacity 100 ml, 200 ml or 500 ml.

5.5 Capped sample bottles, e.g. of capacity 100 ml or 500 ml, made of plastics laboratory ware.

Soak new plastics laboratory ware in 10 % (*V/V*) nitric acid [nitric acid (4.1) diluted 1:10 with water (4.2)], rinse and store overnight in acidified water (4.3). Check suitability by running test samples with stored water; the aluminium content should be below 2 µg/l. Reserve the plastics ware and optical cells, if possible, solely for aluminium determinations. Remove all residual aluminium from previous determinations by cleaning all plastics ware and optical cells by filling with, or soaking in, acidified water (4.3) overnight. Do not use detergent or chromic acid.

5.6 pH-metre.

5.7 Microlitre pipettes, with disposable tips.

6 Sampling and samples

See ISO 5667-3.

Collect samples in polyethylene bottles. Clean the sample bottles and filtration device according to the procedure described in clause 5.

6.1 Filtrable aluminium

Immediately after sampling, filter the sample through a membrane filter (5.2). Acidify the filtrate by adding 0,30 ml of nitric acid (4.1) per 100 ml of sample.

6.2 Acid-soluble aluminium

Add 0,30 ml of nitric acid (4.1) per 100 ml of sample. The pH shall be 1,2 to 1,5, if not, add more acid. Store for at least 1 h at room temperature and filter the sample through a membrane filter (5.2).

For special purposes other pretreatment procedures may be used (see clause 7).

NOTE 8 Failure of proper acidification of the sample leads to incorrect results because the pH during reaction and measurement is not buffered to the correct value. If the pH of the sample solution is too low, it may be increased by addition of the sodium hydrogen carbonate solution (4.9).

7 Interferences

The most important interference with microdeterminations of aluminium is the release of aluminium from the surface of the vessels used for sampling and handling. In particular, aluminium is easily leached from most items of glassware. Thus, glassware shall not be used for aluminium determinations in the range below 50 µg/l Al. It is strongly recommended to use only plastics laboratory ware pretreated as described in clause 5.

Fluoride ions form stable complexes with aluminium, thus preventing the formation of the aluminium-pyrocatechol violet complex. The resulting negative bias interferes especially at low aluminium concentrations. This effect is almost totally eliminated by the addition of magnesium ions (see 4.4) which form relatively strong complexes with fluoride.

Iron forms a coloured complex with pyrocatechol violet. Interference effects caused by iron are minimized by reduction to the ferrous state followed by complexing with 1,10-phenanthroline. This iron complex gives rise to a very small absorbance at 580 nm. 1,0 mg/l of iron is equivalent to 0,05 µg/l of aluminium.

Coloured compounds, inorganic as well as organic, that give an absorbance at 580 nm generally interfere with this determination, when absorbance exceeds 0,050 cm^{-1}. An oxidative digestion can destroy the coloured species and allow proper determination.

Humic substances and other organic compounds with complexing properties can interfere. Interference is evident when addition of aluminium to the sample gives a smaller increase in absorbance than expected for that additional amount. This kind of interference is eliminated by digestion with H_2O_2 and HNO_3.

8 Procedure

Depending on the cell path length and sensitivity of the spectrometer, the procedure comprises two ranges:

a low level range up to 100 µg/l Al with 50 mm cells;

a high level range up to 500 µg/l Al with 10 mm cells.

8.1 Test portions

Take a test portion volume of 25 ml from samples 6.1 or 6.2. In order to accommodate higher aluminium concentrations, use smaller test portions and adjust the volume to 25 ml by the addition of acidified water (4.3) and note the dilution factor f (see clause 9).

8.2 Calibration solutions

8.2.1 Preparation of high range calibration solutions (e.g. 500 µg/l Al with 10 mm cells)

Pipette 0 ml (blank), 1,00 ml, 2,00 ml, 3,00 ml, 4,00 ml and 5,00 ml respectively of the aluminium standard solution (4.8) into a series of 100 ml one-mark volumetric flasks (5.4). Make up to the mark with acidified water (4.3). These solutions contain 0 µg/l (blank), 100 µg/l, 200 µg/l, 300 µg/l, 400 µg/l and 500 µg/l Al respectively.

8.2.2 Preparation of low range calibration solutions (e.g. 50 µg/l Al with 50 mm cells)

Pipette, for example, 0 ml (blank), 100 µl, 200 µl, 300 µl, 400 µl and 500 µl respectively of the standard solution (4.8) into a series of 100 ml one-mark volumetric flasks (5.4). Make up to the mark with acidified water (4.3). These solutions contain 0 µg/l (blank), 10 µg/l, 20 µg/l, 30 µg/l, 40 µg/l and 50 µg/l Al respectively.

8.3 Colour development

Pipette each 25 ml of acidified sample (see 8.1) or calibration solutions (8.2) into 100 ml plastics beakers (5.3).

Add to each sample, with mixing after each addition, in the following order:

1,0 ml of mixed reagent (4.4);

1,0 ml of pyrocatechol violet solution (4.5); and

5,0 ml of hexamine buffer solution (4.6).

Allow to react for at least 15 min, and carry out the spectrometric measurement within 60 min after the start of reaction.

The reaction pH of the solutions shall be in the range 5,9 ± 0,1. If it is not, check for errors in preparation.

8.4 Spectrometric measurement

Using the spectrometer (5.1) set up according to the manufacturer's instructions, measure the absorbance of each solution at a wavelength of 580 nm against acidified water (4.3) as a reference.

Use cells of an optical path length that is appropriate for the selected range and sensitivity.

Measure the blank and standard solutions with cells of the same size.

Read the absorbance A_s of each standard of sample.

8.5 Plotting the calibration graph

Plot a calibration graph with the mass concentrations of aluminium ρ_{Al} on the abscissa and the corresponding absorbance A_s of the standards on the ordinate.

The slope of the calibration curve is a measure of the sensitivity of the method, in litres per milligram. The intersection with the ordinate is the absorbance of the sample (calculated blank) without the addition of aluminium in the standard solution.

The blank and the slope shall be checked from time to time, in accordance with good analytical quality control practice, especially when new batches of reagents are used.

8.6 Determination

From the appropriate sample [(6.1) or (6.2)] pipette the test portion (8.1) into a 100 ml beaker. If necessary, dilute the sample with acidified water (4.3) such that the mass concentration of aluminium lies within the calibration range, and record the dilution factor f. Proceed according to 8.3 and 8.4. Choose a cell of appropriate path length. Take absorbance reading A_s from the spectrometer.

NOTE 9 The reaction pH normally lies within 5,9 ± 0,1. If not, check that the pH of the sample is in the range of 1,2 and 1,5. Adjust the sample pH to this range using sodium hydrogen carbonate solution (4.9) or nitric acid (4.1). Make sure that the result is corrected for dilution by adjusting the pH.

9 Calculation and expression of results

Taking the appropriate calibration graph for 10 mm or 50 mm optical path length, calculate the mass concentration of aluminium according to the following equation:

$$\rho_{Al} = \frac{(A_s - A_{so}) \times f}{b}$$

where

ρ_{Al} is the mass concentration, in micrograms per litre, of aluminium in the sample;

A_s is the absorbance of the water sample;

A_{so} is the calculated absorbance of the blank, according to 8.2;

f is the dilution factor;

b is the slope of the calibration curve, in litres per microgram, according to 8.2.

Round the values of ρ_{Al} to the nearest 5 % of calibration range, i.e.

2 µg/l in the range below 50 µg/l;

5 µg/l in the range between 50 µg/l and 200 µg/l; and

10 µg/l in the range between 500 µg/l and 200 µg/l.

10 Precision data

The following results were obtained with this method in a German round robin test in 1993.

11 Test report

The test report shall include the following information:

a) a reference to this International Standard;

b) precise identification of the sample;

c) information on sample pretreatment (e.g. dissolved aluminium, acid-soluble aluminium etc.);

d) the result expressed in micrograms of aluminium per litre (if necessary including information on the range of determination and precision data);

e) any other information which may have affected the results.

Type of sample	**Blank** µg/l	**Water** µg/l	**Synthetic** µg/l	**Synthetic** µg/l	**Water** µg/l
True value	0		35	150	
General average	1,0	8,2	31,3	141	1 050
Reproducibility standard deviation	0,8	1,6	2,7	9,7	30,4
Repeatability standard deviation	0,4	0,8	0,7	2,2	10,0
Number of determinations	36	36	36	36	36
Number of laboratories	9	9	9	9	9