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Water quality — Determination of iron — Spectrometric method using 1,10-phenanthroline

Qualité de l'eau — Dosage du fer — Méthode spectrométrique à la phénanthroline-1,10

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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 6332 was prepared by Technical Committee ISO/TC 147, *Water quality.*

This second edition cancels and replaces the first edition (ISO 6332 : 1982), of which it constitutes a technical revision.

Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

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Water quality — Determination of iron — Spectrometric method using 1,10-phenanthroline

1 Scope and field of application

This International Standard specifies a 1,10-phenanthroline spectrometric method for the determination of iron in water and waste water. Procedures are described for the determination of

a) total iron (sum of dissolved and undissolved iron) :

1) direct determination,

2) determination after decomposition;

b) total dissolved iron [sum of dissolved iron(II) and iron(III)];

c) determination of dissolved iron(II).

The methods are applicable to the determination of iron concentrations between 0,01 and 5 mg/l. Iron concentrations above 5 mg/l may be determined after suitable dilution of the sample.

For interferences see clause 10.

2 Reference

ISO 5667-1, *Water quality — Sampling — Part 1 : Guidance on the design of sampling programmes.*

3 Principle

Addition of 1,10-phenanthroline solution to a test portion and photometric measurement of the orange-red complex at a wavelength of about 510 nm.

If determining total iron or total soluble iron, hydroxylammonium chloride is added to reduce iron(III) to iron(II). If undissolved iron, iron oxides or iron complexes are present, pretreatment is necessary to bring such compounds into solution (see 7.1.2).

The iron(II)-1,10-phenanthroline complex is stable in the pH range from 2,5 to 9 and the intensity of the colour is proportional to the amount of iron(II) present. The relationship between concentration and absorbance is linear up to a concentration of 5,0 mg of iron per litre. Maximum absorbance occurs at about 510 nm [molar absorption coefficient 11×10^3 l/(mol·cm)].

4 Reagents

Use only reagents of recognized analytical grade.

The water used shall have as low an iron concentration as possible; a measurable iron concentration in the reagents is permissible provided that the lowest concentration to be determined is at least three times the standard deviation of the predetermined results of blank tests. Deionized water or water distilled from an all-glass apparatus has been found to be suitable.

4.1 Sulfuric acid, ϱ = 1,84 g/ml.

4.2 Sulfuric acid solution, $c(1/2\ H_2SO_4) \approx 4{,}5$ mol/l.

Add slowly and with vigorous stirring 1 volume of concentrated sulfuric acid (4.1) to 3 volumes of water while cooling.

4.3 Nitric acid, concentrated, ϱ = 1,40 g/ml.

4.4 Hydrochloric acid solution, ϱ = 1,12 g/ml, $c(HCl) \approx 7{,}7$ mol/l.

4.5 Acetate buffer.

Dissolve 40 g of ammonium acetate (CH_3COONH_4) and 50 ml of glacial acetic acid (CH_3COOH) (ϱ = 1,06 g/ml) in water and dilute to 100 ml with water.

4.6 Hydroxylammonium chloride, 100 g/l solution.

Dissolve 10 g of hydroxylammonium chloride ($NH_2OH{\cdot}HCl$) in water and dilute to 100 ml.

This solution is stable for at least 1 week.

4.7 1,10-phenanthroline solution.

Dissolve 0,5 g of 1,10-phenanthroline chloride (monohydrate) ($C_{12}H_9ClN_2{\cdot}H_2O$) in water and dilute to 100 ml.

Alternatively, dissolve 0,42 g of 1,10-phenanthroline monohydrate ($C_{12}H_8N_2{\cdot}H_2O$) in 100 ml of water containing 2 drops of hydrochloric acid (4.4).

This solution is stable for 1 week if stored in the dark.

4.8 Potassium peroxodisulfate, 40 g/l solution.

Dissolve 4 g of potassium peroxodisulfate ($K_2S_2O_8$) in water and dilute to 100 ml.

This solution is stable for several weeks if stored at room temperature in a dark glass bottle.

4.9 Iron, stock solution corresponding to 0,10 g of iron per litre.

Weigh 50,0 mg of iron wire (purity 99,99 %) into a 500 ml volumetric flask. Add 20 ml of water, 5 ml of the hydrochloric acid solution (4.4), and warm gently to dissolve. Cool, and make up to the mark with water.

1 ml of this stock solution contains 0,10 mg of iron.

This solution is stable for at least 1 month if stored in a resistant glass or plastics bottle.

Commercial iron stock solutions may be used.

4.10 Iron, standard solution I, corresponding to 20 mg of iron per litre.

Pipette 100 ml of iron stock solution (4.9) into a 500 ml one-mark volumetric flask and make up to the mark with water.

Prepare the solution on the day of use.

4.11 Iron, standard solution II, corresponding to 1 mg of iron per litre.

Pipette 5 ml of the standard solution I into a 500 ml one-mark volumetric flask and make up to the mark with water.

Prepare the solution on the day of use.

5 Apparatus

All glassware, including sample containers, shall be washed with hydrochloric acid (4.4) and rinsed with water before use.

Usual laboratory equipment, and

5.1 Spectrometer, prism or grating type, suitable for making measurements at 510 nm.

5.2 Photometric cells, with an optical path length of at least 10 mm and appropriate to the expected absorbance of the test solution.

NOTE — Cells of longer optical path length are preferable for determining iron concentrations less than 1,0 mg/l.

5.3 Membrane filter, average pore size 0,45 µm.

5.4 Oxygen flask (Winkler flask), capacity 100 ml.

6 Sampling and preparation of test samples

WARNING — Take appropriate safety precausions when acidifying samples, owing to the possibility of release of toxic gases.

6.1 Sample

Take the sample in accordance with ISO 5667-1 and any specific recommendations for the type of water under examination. Appropriate containers such as polyethylene shall be used.

6.2 Total iron

Acidify the sample immediately after collection to pH 1. In general, 1 ml of concentrated sulfuric acid (4.1) is sufficient for 100 ml of sample. If necessary, adjust the pH by addition of dilute sulfuric acid (4.2) and take into account any dilution in the final calculations.

6.3 Total soluble iron

Filter the sample (6.1) immediately after sampling.

Acidify the filtrate to pH 1 [approximately 1 ml of sulfuric acid (4.1) per 100 ml of sample].

6.4 Iron(II)

Place 1 ml of sulfuric acid (4.1) in an oxygen flask (5.4). Fill completely with the water sample. Avoid unnecessary contact with air.

7 Procedure

7.1 Total iron

7.1.1 Direct determination

Take, as the test portion, 50,0 ml of the acidified test sample (6.2).

If undissolved iron, iron oxides or iron complexes are present transfer the test portion (7.1) to a 100 ml boiling flask and carry out the following pretreatment.

7.1.1.1 Oxidation

Add 5 ml of potassium peroxodisulfate solution (4.8) and gently boil for about 40 min, ensuring that the volume does not fall below about 20 ml. Then cool and transfer to a one-mark volumetric flask of capacity 50 ml and make up to the mark with water.

NOTE — Alternatively, the mixture may be autoclaved in a 100 ml closed bottle for 30 min, then cooled and diluted to 100 ml. This dilution should be taken into account in calculating the result by multiplying by a factor of 2.

If the solution is turbid after oxidation and before dilution, filter it immediately through the membrane filter (5.3) into the

volumetric flask. Rinse the filter with a small amount of water, adding the washings to the filtrate, and make up to the mark with water.

7.1.1.2 Reduction to iron(II)

Transfer the solution to a 100 ml flask, add 1 ml of hydroxylammonium chloride (4.6) and mix thoroughly. Add 2 ml of acetate buffer solution (4.5) and bring to a pH of 3,5 to 5,5; preferably 4,5.

NOTE — The reduction of iron(III) to iron(II) proceeds most effectively at pH 1. The buffer solution should therefore be added last.

7.1.1.3 Formation of the absorbing compound

Add 2 ml of 1,10-phenanthroline solution (4.7) to the solution from 7.1.1.2 and place in the dark for 15 min.

7.1.1.4 Photometric measurement

Measure the absorbance of the solution from 7.1.1.3 using the spectrometer (5.1) at 510 nm with water in the reference cell.

7.1.2 Total iron after decomposition

Place 50,0 ml of the acidified test sample (6.2) in a 100 ml beaker, add 5 ml of nitric acid (4.3) and 10 ml of hydrochloric acid (4.4) and bring the mixture to 70 — 80 °C until complete solution is achieved. After about 30 min, add 2 ml of sulfuric acid (4.1) and evaporate the solution to the appearance of white sulfur trioxide fumes. Avoid boiling dry. Cool to room temperature and add 20 ml of water, transfer to a 50 ml one-mark volumetric flask and make up to the mark with water.

Continue as described in 7.1.1.2 to 7.1.1.4.

7.2 Determination of dissolved iron

Take, as the test portion, 50,0 ml of the sample (6.3) and transfer it to a 100 ml flask.

Proceed as specified in 7.1.1.2 to 7.1.1.4.

7.3 Determination of iron(II)

Take, as the test portion, 50,0 ml of the sample (6.4) and transfer it to a 100 ml flask.

Proceed as specified in 7.1.1.2 without addition of the hydroxylammonium chloride.

Proceed as specified in 7.1.1.3 and 7.1.1.4.

Avoid contact with air as far as possible.

7.4 Blank test

Prepare a blank test solution using exactly the same procedure as for the test sample, but replacing the 50 ml of the test portion with 50 ml of water.

7.5 Calibration

7.5.1 Preparation of reference solutions

Prepare a series of iron reference solutions to cover a range of concentrations appropriate to the expected iron concentration of the test sample by transferring appropriate accurately known volumes of the iron standard solutions (4.10) and (4.11) to a series of one-mark volumetric flasks each of capacity 50 ml. Add 0,5 ml of dilute sulfuric acid (4.2) to each flask and make up to the mark with water.

Treat a series of iron reference solutions in a similar fashion to the test solutions, according to the appropriate procedure for each form of iron to be determined (see 7.1 to 7.3).

7.5.2 Plotting the calibration graphs

For each series of calibration solutions prepare a calibration graph by plotting the iron concentration of the test solution in milligrams per litre as abscissae against the corresponding measured absorbance as ordinates.

A separate calibration curve is required for each form of iron, for each photometric instrument and for each optical path length of cell.

7.5.3 Frequency of calibration

Check the calibration periodically and especially for each new batch of reagents.

8 Expression of results

8.1 Calculation

The iron concentration, ϱ, expressed in milligrams per litre, of the sample is given by the formula

$$f(A_1 - A_0)$$

where

f is the slope of the appropriate calibration graph (7.5.2);

A_1 is the absorbance of the test solution (7.1.1.4);

A_0 is the absorbance of the blank test solution (7.4).

NOTE — The volume of sulfuric acid added to the sample should be taken into consideration in the calculation.

8.2 Reporting the results

Report the results, by indicating the form of iron determined :

a) to the nearest 0,001 mg/l for iron concentrations from 0,010 up 0,100 mg/l;

b) to the nearest 0,01 mg/l for iron concentrations greater than 0,100 mg/l up to 10 mg/l;

c) to the nearest 0,1 mg/l for iron concentrations greater than 10 mg/l.

9 Precision

See the table.

Table — Statistical data on the repeatability of the method

Iron concentration mg/l	Laboratory	Path length[1] mm	Mean value of 30 results mg/l	Standard deviation mg/l
0,010	1	100	0,010	0,002
	2	—	0,010	0
	3	50	0,010	0,001
	4	10	0,010	0,011
	5	—	0,010	0,000
0,040	5	—	0,041	0,002
0,050	1	100	0,046	0,005
	2	—	0,048	0,004
	3	—	0,045	0,004 6
	4	10	0,048	0,011
0,100	1	50	0,104	0,015
	2	—	0,102	0,004
	3	—	0,096	0,006
	4	10	0,101	0,014
	5	—	0,099	0,006
0,500	1	50	0,48	0,025
	2	—	0,500	0,012
	3	—	0,494	0,005
	4	10	0,498	0,016
1,000	1	10	0,97	0,05
	2	—	1,003	0,008
	3	—	1,009	0,006
	4	10	1,004	0,019
	5	—	1,018	0,004
2,000	1	10	2,05	0,07
	3	—	2,016	0,008
	4	10	1,994	0,017
4,000	1	10	4,02	0,08
	3	—	3,989	0,013
	4	10	3,968	0,033
	5	—	4,003	0,019
5,000	1	10	5,01	0,07
	5	—	5,032	0,015

1) Where no path length is indicated, the path length was not specified by the laboratory.

10 Interferences

Determinations of iron concentrations using 1,10-phenanthroline are relatively free from interferences in comparison with other methods using other reagents. The following should be noted.

Copper, cobalt, chromium and zinc interfere if present in concentrations ten times that of the iron concentration. Nickel interferes if present in concentrations exceeding 2 mg/l. These interferences are avoided by adjusting the pH to between 3,5 and 5.5.

Bismuth, silver and mercury interfere in concentrations exceeding 1 mg/l. Cadmium interferes in concentrations exceeding 50 mg/l.

Cyanides interfere with the determination but are usually removed by acidification of the sample except in the case of some complex cyanides where the decomposition step given in 7.1.2 is recommended.

WARNING — Acidification of samples containing cyanide or sulfide ions must be carried out with care owing to the formation of highly toxic vapours.

The acidification of the sample also converts pyrophosphates and polyphosphates to orthophosphates which do not interfere at PO_4^{3-} concentrations up to ten times that of the iron concentration. If higher concentrations are present, decomposition as described in 7.1.2 is recommended.

11 Test report

The test report shall include the following information :

a) an identification of the sample;

b) the reference of the method used;

c) the results and the method of expression used;

d) the method of elimination of interferences;

e) any unusual features noted during the determination;

f) any operations not specified in this International Standard, or regarded as optional.