# International Standard ISO 6333

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# Water quality — Determination of manganese — Formaldoxime spectrometric method

*Qualité de l'eau — Dosage du manganèse — Méthode spectrométrique à la formaldoxime*

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## Foreword

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# Water quality — Determination of manganese — Formaldoxime spectrometric method

## 0 Introduction

In water containing oxygen, most of the manganese will be present as undissolved forms, often associated with micro-organisms and as complexes with, for example, humic acid. If the water is free of oxygen or strongly acidic, all manganese will be present in dissolved forms.

## 1 Scope and field of application

This International Standard specifies a formaldoxime spectrometric method for the determination of total manganese (including dissolved, suspended and organically bound manganese) in surface and drinking water.

The method is applicable to the determination of manganese concentrations between 0,01 mg/l and 5 mg/l. Manganese concentrations above 5 mg/l may be determined after suitable dilution of the sample.

For known possible interferences, see clause 8.

NOTE — This method is not applicable to highly contaminated waters such as industrial waste water.

## 2 Principle

Addition of a formaldoxime solution to a test portion and spectrometric measurement of the orange-red complex at a wavelength of about 450 nm.

If suspended or organically bound manganese is present, pretreatment is required to convert manganese to forms capable of reacting with formaldoxime.

The manganese formaldoxime complex is stable between pH values of 9,5 and 10,5, and the intensity of the colour produced is proportional to the amount of manganese present. The relationship between concentration and absorbance is linear up to a concentration of 5 mg/l. Maximum absorbance occurs at about 450 nm (specific molar absorbance coefficient of $11 \times 10^3$ l/mol·cm).

## 3 Reagents

**WARNING — The reagents described in 3.4, 3.5.1 and 3.5.3 should be regarded as special hazards. Hazardous operations should be carried out in a fume cupboard. Care must be taken to avoid ingestion or inhalation of vapours and to protect the hands, eyes and face. Gloves and goggles must be worn and any suspected skin contamination washed off immediately. Inhalation of the vapours of formaldehyde and formaldoxime will result in severe irritation and oedema of the upper respiratory tract.**

During the analysis, use only reagents of recognized analytical grade, and only deionized water or water distilled from an all-glass apparatus with a manganese content that is as low as possible.

**3.1 Oxidizing reagent.**

Either potassium peroxodisulfate ($K_2S_2O_8$) or sodium peroxodisulfate ($Na_2S_2O_8$).

**3.2 Sodium sulfite** ($Na_2SO_3$), anhydrous.

**3.3 EDTA, tetrasodium salt,** solution, $c$(EDTA) = 0,24 mol/l.

Dissolve 90 g of disodium ethylenedinitrilotetraacetic acid ($Na_2$EDTA) dihydrate ($C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$) and 19 g of sodium hydroxide (NaOH) in water and dilute to 1 000 ml.

Alternatively, dissolve 109 g of tetrasodium ethylenedinitrilotetraacetic acid ($Na_4$EDTA) tetrahydrate ($C_{10}H_{12}N_2Na_4O_8 \cdot 4H_2O$) or 100 g of tetrasodium ethylenedinitrilotetraacetic acid dihydrate ($C_{10}H_{12}N_2Na_4O_8 \cdot 2H_2O$) in water and dilute to 1 000 ml.

**3.4 Formaldoxime** solution.

Dissolve 10 g of hydroxylammonium chloride ($NH_3OHCl$) in about 50 ml of water. Add 5 ml of 35 % ($m/m$) methanal (HCHO) (formaldehyde) solution ($\varrho$ = 1,08 g/ml) and dilute with water to 100 ml.

Keep the bottle in a dark and cool place. The solution has a shelf-life of at least 1 month.

**3.5 Hydroxylammonium chloride/ammonia** solution.

**3.5.1 Hydroxylammonium chloride** solution, $c$($NH_3OHCl$) = 6 mol/l.

Dissolve 42 g of hydroxylammonium chloride in water and dilute to 100 ml.

**3.5.2 Ammonia** solution, $c(NH_3)$ = 4,7 mol/l.

Dilute 70 ml of concentrated ammonia ($\varrho$ = 0,91 g/ml) with water to 200 ml.

**3.5.3 Preparation**

Mix equal volumes of the ammonia solution (3.5.2) and the hydroxylammonium chloride solution (3.5.1).

**3.6 Ammonium iron(II) sulfate hexahydrate** solution, $[(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O]$, 700 mg/l.

**3.6.1 Sulfuric acid,** $c(H_2SO_4) \approx 3$ mol/l.

Carefully add 170 ml of concentrated sulfuric acid ($\varrho$ = 1,84 g/ml) to 750 ml of water. Allow to cool and dilute to 1 000 ml.

This solution is commercially available ($H_2SO_4$, $\varrho$ = 1,19 g/ml).

**3.6.2 Preparation**

Dissolve 700 mg of ammonium iron(II) sulfate hexahydrate in water, add 1 ml of sulfuric acid (3.6.1) and dilute to 1 000 ml.

**3.7 Sodium hydroxide** solution, $c(NaOH)$ = 4 mol/l.

Dissolve 160 g of sodium hydroxide in water and dilute to 1 000 ml.

**3.8 Manganese,** standard solution, corresponding to 100 mg of Mn per litre.

Dissolve 308 mg of manganese sulfate monohydrate ($MnSO_4 \cdot H_2O$) in water in a 1 000 ml one-mark volumetric flask. Add 10 ml of sulfuric acid (3.6.1), make up to the mark with water and mix.

1 ml of this standard solution contains 0,1 mg of Mn.

Commercially available standard solutions can also be used.

## 4 Apparatus

Usual laboratory equipment and

**4.1 Spectrometer,** with selectors for continuous variation (prism or grating type) or discontinuous variation (narrow band pass optical filter) capable of measuring absorbance at approximately 450 nm, equipped with cells of optical path lengths up to 100 mm (for manganese concentrations of less than 0,3 mg/l) and 10 mm (for manganese concentrations above 0,3 mg/l).

**4.2 Glass bottles,** of capacity 100 ml, provided with ground glass stoppers and metal clamps or with screw-caps of non-coloured plastic, suitable for autoclaving.

**4.3 Autoclave** or **pressure cooker,** capable of maintaining a temperature of 120 °C and a pressure of 200 kPa.

NOTE ON PREPARATION OF GLASSWARE, ETC.

All glassware and sampling containers shall be washed with approximately 1 mol/l hydrochloric acid (HCl) and rinsed with water before use.

## 5 Sampling and samples

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

Collect the sample in a polyethylene, polyvinyl chloride or glass container and acidify the sample with sulfuric acid (3.6.1) until the pH is approximately, but not less than, 1. This acidification minimizes adsorption of manganese on the walls of the container and also assists in the dissolution of colloidal and particulate forms of manganese.

## 6 Procedure

### 6.1 Test portion

Take as the test portion 50 ml, or an accurately measured aliquot diluted to 50 ml, of the acidified test sample containing less than 0,25 mg of manganese (5 mg/l).

### 6.2 Preparation of test solution

If organically bound or suspended manganese is present, add 225 ± 25 mg of oxidizing reagent (3.1) to the test portion (6.1). The oxidation can be performed in one of two ways:

a) autoclave the mixture for 30 min in a bottle (4.2); cool and add approximately 0,5 g of sodium sulfite (3.2) to reduce oxidizing substances;

b) boil the mixture in a 100 ml conical flask or beaker for about 40 min; cool and transfer the mixture to a 50 ml one-mark volumetric flask, make up to the mark with water and add approximately 0,5 g of sodium sulfite (3.2) to reduce oxidizing substances.

Autoclaving is preferable in the case of samples containing humic acids.

If the procedure is not to be continued immediately, the pretreated sample may be kept overnight.

NOTE — Any turbidity and colour is destroyed during the pretreatment. If experience has shown that this pretreatment stage is not required, for example in most cases for drinking water, it may be omitted.

### 6.3 Blank test

Carry out a blank test in parallel with the determination, replacing the test portion by 50 ml of water. If the absorbance of the blank test differs significantly from the extrapolated absorbance of the zero member (6.4.4), the reasons for this difference shall be investigated.

### 6.4 Calibration

#### 6.4.1 Preparation of the set of calibration solutions

*Range A:* 0 to 0,5 mg/l manganese

Dilute 5 ± 0,05 ml of standard manganese solution (3.8) to 1 000 ml with water in a 1 000 ml one-mark volumetric flask. To a series of five 50 ml one-mark volumetric flasks add 0, 10, 20, 30 and 40 ml of this diluted manganese solution and dilute to the mark with water. This gives calibration standard solutions of 0; 0,1; 0,2; 0,3 and 0,4 mg/l of manganese.

*Range B:* 0 to 5 mg/l manganese

Dilute 50 ± 0,5 ml of standard manganese solution (3.8) to 1 000 ml with water in a 1 000 ml one-mark volumetric flask. To a series of five 50 ml one-mark volumetric flasks add 0, 10, 20, 30 and 40 ml of this diluted manganese solution and dilute to the mark with water. This gives calibration standard solutions of 0, 1, 2, 3 and 4 mg/l manganese.

#### 6.4.2 Colour development

Add 1 ml of ammonium iron(II) sulfate solution (3.6) and 2 ml of EDTA solution (3.3) to each of the solutions. After mixing, add 1 ml of the formaldoxime solution (3.4) and immediately add 2 ml of sodium hydroxide solution (3.7).

Thoroughly mix the solutions and allow to stand for 5 to 10 min, then add, whilst mixing, 3 ml of hydroxylammonium chloride/ammonia solution (3.5) and leave to stand for at least 1 h.

#### 6.4.3 Spectrometric measurements

Between 1 and 4 h after colour development, measure the absorbances of the solutions using the spectrometer at a wavelength of 450 nm against water as reference. For calibration solutions in range A (0 to 0,5 mg/l manganese) use cells of 100 mm optical path length, and for range B (0 to 5 mg/l manganese) use cells of 10 mm optical path length.

#### 6.4.4 Plotting the calibration graph

For each set of calibration solutions, prepare a calibration graph by plotting the manganese concentration, expressed in milligrams per litre, of the solution as abscissa against the corresponding absorbance as ordinate. It is essential that a linear calibration graph be achieved. The calibration factor, $f$, is the reciprocal of the slope of the calibration graph.

The intercept of the calibration graph on the ordinate gives the extrapolated absorbance of the zero member of the set of calibration solutions.

The calibration factor can also be calculated by regression analysis.

#### 6.4.5 Frequency of calibration

Each graph shall be checked periodically, and especially when new reagents are used, to ensure repeatability.

### 6.5 Determination

#### 6.5.1 Colour development

Proceed in accordance with 6.4.2, but using the test solution (6.2) instead of the calibration solutions.

If the test solution has been pretreated (see 6.2), increase the amount of sodium hydroxide solution (3.7) from 2 to 2,5 ml.

#### 6.5.2 Spectrometric measurements

See 6.4.3.

## 7 Expression of results

### 7.1 Calculation

The manganese concentration, $\varrho_{Mn}$, expressed in milligrams per litre, is given by the formula:

$$\varrho_{Mn} = f(A_1 - A_0)g$$

where

$f$ is the calibration factor appropriate to the particular calibration graph chosen and derived as stated in 6.4.4, expressed in milligrams per litre;

$A_1$ is the absorbance of the test solution (6.5.2);

$A_0$ is the extrapolated absorbance of the zero member (6.4.4);

$g$ is a factor given by the formula:

$$g = \frac{V_1}{V_2}$$

$V_1$ being the maximum volume, in millilitres, of the test portion (here 50 ml);

$V_2$ being the volume, in millilitres, of the test portion if an aliquot was taken.

NOTE — The volume of acid added (clause 5) to the sample shall be taken into consideration in the calculation.

Report the results

a) to the nearest 0,01 mg/l for manganese concentrations from 0,01 to 1 mg/l;

b) to the nearest 0,1 mg/l for manganese concentrations greater than 1 mg/l.

### 7.2 Precision

See the table.

## 8 Interferences

**8.1** Iron(II) ions form a violet complex with formaldoxime which interferes with manganese determination. The addition of EDTA (3.3) and hydroxylammonium chloride/ammonia (3.5)

reduces the interference; however, it has been shown that the best method of overcoming this effect is to add a constant known amount of iron(II) as ammonium iron(II) sulfate to each calibration solution, blank test and test solution.

**8.2** The presence of 1 mg of cobalt (Co) per litre gives a response equivalent to 40 µg of manganese per litre.

**8.3** If calcium is present, orthophosphate concentrations above 2 mg of phosphorus (P) per litre cause low results.

**8.4** The presence of calcium and magnesium in combined concentrations above 300 mg/l causes high results.

**8.5** If turbidity is present after formation of the coloured complex, centrifuge the solution before measurement of the absorbance (6.4.3).

## 9 Test report

The test report shall include the following information:

a) a reference to this International Standard;

b) an identification of the sample;

c) the reference of the method used;

d) the results and the method used to eliminate any interferences;

e) any unusual features noted during the determination;

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

**Table — Reproducibility of the method**
(Data derived from an interlaboratory trial carried out in 1982)

| Manganese concentration (mg/l) | Laboratory | Number of results | Mean value (mg/l) | Standard deviation (mg/l) |
|---|---|---|---|---|
| 0,050 | B | 30 | 0,049 | 0,003 5 |
| 0,100 | A | 30 | 0,12 | 0,025 |
| 0,100 | B | 30 | 0,099 | 0,002 1 |
| 0,500 | B | 30 | 0,497 | 0,008 5 |
| 1,000 | A | 30 | 1,01 | 0,04 |
| 1,000 | B | 30 | 1,001 | 0,009 1 |
| 2,000 | A | 30 | 1,99 | 0,035 |
| 2,000 | B | 30 | 2,055 | 0,011 1 |
| 4,000 | A | 30 | 4,02 | 0,047 |
| 4,000 | B | 30 | 4,198 | 0,133 3 |

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