SLOVENSKI STANDARD
SIST EN 1302:2000

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Kemikalije, ki se uporabljajo za pripravo pitne vode - Koagulanti na osnovi aluminija - Analitske metode

Chemicals used for treatment of water intended for human consumption - Aluminium-based coagulants - Analytical methods

Produkte zur Aufbereitung von Wasser für den menschlichen Gebrauch - Flockungsmittel auf Aluminiumbasis - Analytische Methoden

Produits chimiques utilisés pour le traitement de l'eau destinée a la consommation humaine - Coagulants a base d'aluminium - Méthodes d'analyse

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13.060.20	Pitna voda	Drinking water
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EUROPEAN STANDARD
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EN 1302

April 1999

ICS 71.100.80

English version

Chemicals used for treatment of water intended for human consumption - Aluminium-based coagulants - Analytical methods

Produits chimiques utilisés pour le traitement de l'eau destinée à la consommation humaine - Coagulants à base d'aluminium - Méthodes d'analyse

Produkte zur Aufbereitung von Wasser für den menschlichen Gebrauch - Flockungsmittel auf Aluminiumbasis - Analytische Methoden

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Central Secretariat: rue de Stassart, 36 B-1050 Brussels

Contents

Foreword

This European Standard has been prepared by Technical Committee CEN/TC 164 "Water supply", the secretariat of which is held by AFNOR.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by October 1999, and conflicting national standards shall be withdrawn at the latest by October 1999.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

1 Scope

This European standard is applicable to aluminium-based coagulants used for treatment of water intended for human consumption. It specifies analytical methods to be used for products described in EN 878, EN 881, EN 882, EN 883, prEN 885, prEN 886, prEN 887 and prEN 935.

2 Normative references

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies.

EN 878, *Chemicals used for treatment of water intended for human consumption - Aluminium sulfate*

EN 881, *Chemicals used for treatment of water intended for human consumption - Aluminium chloride, aluminium chloride hydroxide and aluminium chloride hydroxide sulfate (monomeric).*

EN 882, *Chemicals used for treatment of water intended for human consumption - Sodium aluminate.*

EN 883, *Chemicals used for treatment of water intended for human consumption - Polyaluminium chloride hydroxide and Polyaluminium chloride hydroxide sulfate.*

prEN 885, *Chemicals used for treatment of water intended for human consumption - Polyaluminium chloride hydroxide silicate.*

prEN 886, *Chemicals used for treatment of water intended for human consumption - Polyaluminium hydroxide silicate sulfate.*

prEN 887, *Chemicals used for treatment of water intended for human consumption - Aluminium-iron (III) sulfate.*

prEN 935, *Chemicals used for treatment of water intended for human consumption - Aluminium-iron (III) chloride and aluminium-iron (III) chloride hydroxide (monomeric).*

EN ISO 3696, *Water for analytical use - Specification and test methods (ISO 3696:1987).*

ISO 5666-1:1983, *Water quality - Determination of total mercury by flameless atomic absorption spectrometry - Part 1 : Method after digestion with permanganate-peroxodisulfate.*

ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results – Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method.*

ISO 6206:1979, *Chemical products for industrial use – Sampling – Vocabulary.*

ISO 6227:1982, *Chemical products for industrial use - General method for determination of chloride ions - Potentiometric method.*

ISO 6382:1981, *General method for determination of silicon content - Reduced molybdosilicate spectrophotometric method.*

3 Preparation of the test sample

3.1 Definitions

For the purposes of this European Standard, the following definitions apply :

3.1.1
laboratory sample
a sample as prepared for sending to the laboratory and intended for inspection or testing [ISO 6206:1979].

3.1.2
test sample
a sample prepared from the laboratory sample and from which test portions will be taken [ISO 6206:1979].

3.1.3
test portion
the quantity of material drawn from the test sample (or from the laboratory sample if both are the same) and on which the test or observation is actually carried out [ISO 6206:1979]

3.2 Procedure

From the laboratory sample, prepare the test sample by grinding the solid samples until particle size is below 2,5 mm and homogenizing, and homogenize the liquid samples.

4 Methods of analysis

The methods to be used for analysis of aluminium-based coagulants and the principles of each method are listed in table 1 and described in full in annex A for reference methods and in annex B for routine methods.

The methods which are applicable to only some of the products described in EN 878, EN 879, EN 881, EN 882, prEN 885, prEN 886, prEN 887 and prEN 935 are listed in table 2.

Table 1 - Methods of analysis

Determination	Method	Principle
Aluminium	A.1 [a)]	EDTA complexometric titration with EDTA
Aluminium	A.2	Separation of iron, CDTA complexometric titration
Iron	A.3	Atomic absorption spectrometry (flame)
Iron	A.4	Potentiometric titration
Sodium	A.5	Atomic absorption spectrometry (flame)
Calcium	A.6	Atomic absorption spectrometry (flame)
Chloride	A.7	Potentiometric titration
Sulfate	A.8	Barium sulfate gravimetry
Silicate	A.9	Reduced molybdosilicate spectrophotometry
Free acidity	A.10	Acidimetric titration
Basicity	A.11	Acidimetric titration, oxalate method
Basicity	A.12	Acidimetric titration, KF method
Insoluble matter	A.13	Gravimetry
Arsenic	A.15	Inductively coupled plasma optical emission spectrometry (ICP/OES) (hydride)
Cadmium	A.14	Inductively coupled plasma optical emission spectrometry (ICP/OES)
Chromium	A.14	Inductively coupled plasma optical emission spectrometry (ICP/OES)
Mercury	A.16	Atomic absorption spectrometry (flameless)
Nickel	A.14	Inductive coupled plasma optical emission spectrometry (ICP/OES)
Lead	A.14	Inductive coupled plasma optical emission spectrometry (ICP/OES)
Antimony	A.15	Inductively coupled plasma optical emission spectrometry (ICP/OES) (hydride)
Selenium	A.15	Inductive coupled plasma optical emission spectrometry(ICP/OES) (hydride)

a) Only applicable for determination of aluminium in EN 881 for low iron grades or other grades.

Table 2 - Applicability methods of analysis

EN/prEN	878	881	882	883	885	886	887	935
Aluminium	A.1/A.2	A.2	A.1	A.2	A.2	A.2	A.2	A.2
Aluminium Fe/Al < 0,01 % (m/m)		A.1		A.1	A.1	A.1		A.1
Iron	A.3/A.4	A.3	A.3	A.3	A.3	A.3	A.4	A.4
Sodium					A5	A.5		
Calcium				A.6	A.6	A.6		
Chloride		A.7		A.7	A.7			A.7
Sulfate	A.8	A.8		A.8		A.8	A.8	
Silicate					A.9	A.9		
Free acidity	A.10	A.10					A.10	A.10
Basicity Oxalate method.	A.11	A.11	A.11	A.11			A.11	A.11
Basicity KF method.					A.12	A.12		

NOTE : The method given in B.2 should only be used for determination of basicity by calculation method in EN 883, prEN 885 and prEN 886.

5 Expression of results

5.1 Aluminium content

The aluminium content shall be expressed as Al. The following equation gives the aluminium content expressed as alumina (Al_2O_3) :

$$(Al_2O_3) = (Al) \times \frac{102}{54}$$

5.2 Repeatability

Each laboratory shall calculate the repeatability of the method under their laboratory conditions according to the procedure defined in ISO 5725-2.

Annexe A (normative)

Reference methods of analysis

A.1 Determination of aluminium (EDTA complexometric method)

A.1.1 General

This method is applicable for the determination of aluminium in aluminium-based coagulants used for treatment of water intended for human consumption,

- as the reference method for products described in EN 878 (iron free grade) and EN 882 ;
- as a routine method for products described in EN 878 (low iron grade), EN 881, EN 883, prEN 885, prEN 886 and prEN 935 containing no more than 10 g of Fe per kilogram of aluminium.

A.1.2 Principle

Dissolution in water, in the case of solid products, or dilution with water in the case of products in solution, of a test sample.

Complexation of aluminium, in a hot acidic medium with an excess of ethylenediaminetetraacetic acid (EDTA) solution. Titration of the excess EDTA with a standard volumetric solution of zinc in the presence of xylenol orange as indicator.

$Al^{3+} + EDTA^{4-} \rightarrow AlEDTA^{-}$

$Zn^{2+} + EDTA^{4-} \rightarrow ZnEDTA^{2-}$

A.1.3 Reagents

All reagents shall be of a recognized analytical grade and the water used shall conform to grade 3 in accordance with EN ISO 3696.

A.1.3.1 Sodium acetate solution, 80 g/l.

A.1.3.2 Sodium hydroxide solution, 100 g/l.

A.1.3.3 Hydrochloric acid :

Dilute one volume of hydrochloric acid (ρ = 1,19 g/ml) with one volume of water.

A.1.3.4 Hydrochloric acid, 36,5 g/l, c(HCl) = 1 mol/l.

A.1.3.5 Disodium ethylenediaminetetraacetate dihydrate (NaEDTA), standard volumetric solution, $c(C_{10}H_{14}N_2O_8Na_2.2H_2O)$ = 0,05 mol/l. Weigh to the nearest 0,000 1 g, 18,625 g of NaEDTA. Dissolve in water, transfer the solution quantitatively to a 1 000 ml volumetric flask. Dilute to volume with water and homogenize.

NOTE : Commercial standard volumetric solution could be used.

A.1.3.6 Zinc, standard volumetric solution, c(Zn) = 0,05 mol/l. Weigh to the nearest 0,000 1 g, 6,537 0 g(m)of pure zinc (minimum content 99,9 % (m/m)).

Dissolve in 60 ml of hydrochloric acid solution (A.1.3.3). During the reaction, cover the beaker with a watch-glass. At the end of the reaction, boil the solution for 10 min, then cool to room temperature. Dilute to about 500 ml with water and add sodium acetate solution (A.1.3.1) until a pH of 5,5 ± 0,1 is obtained. Transfer the solution quantitatively to a 2 000 ml volumetric flask. Dilute to volume with water and homogenize.

NOTE 1 : if the mass of zinc is not exactly that stated above, the zinc concentration is given by the equation :

$$c(\mathrm{Zn}) = \frac{m}{2 \times 65{,}37}$$

where :

m is the mass in grams of zinc weighed ;

65,37 is the relative molecular mass of zinc ;

c(Zn) is the concentration of zinc solution, in moles per litre, calculated to the fourth significant figure.

NOTE 2 : Commercial standard solution could be used.

A.1.3.7 Buffer solution, pH 5,5.

Weigh 50 g of sodium acetate trihydrate ($CH_3COONa.3H_2O$). Dissolve in 500 ml of water and add glacial acetic acid (CH_3COOH) until a pH of 5,5 ± 0,1 is obtained.

A.1.3.8 Xylenol orange.

Grind 1,0 g of xylenol orange with 99 g of potassium nitrate in a mortar until an homogeneous mass is obtained.

A.1.4 Apparatus

Ordinary laboratory apparatus and glassware, and optionally :

A.1.4.1 Automatic titrator and photometer with fibre optic probe.

A.1.4.2 Microwave equipment.

A.1.5 Procedure

A.1.5.1 Preparation of the test solution

Weigh, to the nearest 0,001 g, about 25 g of the test sample (m_0) into a 400 ml beaker.

Add approximately 150 ml of water at 80°C to 90°C. Stir until dissolved, using a glass stirrer.

Transfer quantitatively to a 500 ml volumetric flask. Dilute to volume with water and homogenize. Filter if necessary through a filter paper (particle retention size 2,5 µm) (test solution V_0).

Place V_1 ml of this solution (see table A.1) into a 200 ml volumetric flask. Dilute to volume with water and homogenize (diluted test solution V_2).

Table A.1 - Aliquot portion V_1 for Al determination (EDTA method)

Expected content Al g/kg	Volume V_1 ml
< 27	100
27 to 66	50
66 to 133	20
133 to 265	10

A.1.5.2 Blank test

Perform a blank test following the same procedure and using the same quantities of all the reagents as indicated in A.1.5.3. Record the volume used for the titration (V_5).

A.1.5.3 Determination

Transfer 100,0 ml of solution (A.1.5.1) (V_3) to a 250 ml beaker and adjust to pH 5 to 6 with hydrochloric acid solution (A.1.3.3) or sodium hydroxide solution (A.1.3.2). Add 5 ml of hydrochloric acid solution (A.1.3.4) and 50,0 ml of the standard volumetric solution of EDTA (A.1.3.5). Cover with a watch glass. Heat the solution at 80 °C to 90 °C for at least 20 min. Cool to room temperature. Rinse the watch glass with water into the beaker. Neutralize with sodium acetate solution (A.1.3.1). The pH value shall be between 7 to 7,5 and add 10 ml of the buffer solution (A.1.3.7).

Add 30 mg to 50 mg of xylenol orange mixture (A.1.3.8). Titrate with the standard volumetric zinc solution (A.1.3.6) until the indicator changes from yellow to definite red or determine the equivalence point using an automatic titrator. Record the volume (V_4) used.

If microwave equipment (A.1.4.2) is used, the volume V_1 and the volume of the aliquot portion (A.1.5.1) can be different from those indicated above. Transfer the test portion to a 250 ml conical flask and adjust to pH 5 to 6 with hydrochloric acid (A.1.3.3) or sodium hydroxide solution (A.1.3.2). Add 5 ml of hydrochloric acid solution (A.1.3.4) and the suitable volume of the standard volumetric solution of EDTA (A.1.3.5). Transfer to the microwave equipment. Operate the microwave equipment at a power setting to achieve a temperature at 80 °C to 90 °C for 15 min. Then cool to room temperature. Transfer quantitatively to a 250 ml beaker or to the automatic titration cell.

NOTE : If an automatic titrator (A.1.4.1) is used, the volume of the aliquot portion (A.1.5.1) and the volumes of the reagents can be different from those indicated above. They should be such that the required precision is achieved.

A.1.6 Expression of results

The aluminium content, X_1 expressed in grams of aluminium per kilogram of product (Al g/kg) is given by the equation :

$$X_1 = 0{,}026\,98 \times (V_5 - V_4) \times c \times \frac{V_2}{V_3} \times \frac{V_0}{V_1} \times \frac{1\,000}{m_0}$$

where :

m_0 is the mass, in grams, of the test sample ;

V_0 is the volume, in millilitres, of the test solution ;

V_1 is the volume, in millilitres, of test solution diluted to V_2 ;

V_2 is the volume, in millilitres, of the diluted test solution ;

V_3 is the volume, in millilitres, of the aliquot for the determination ;

V_4 is the volume, in millilitres, of the standard volumetric solution of zinc used for the titration of the sample test ;

V_5 is the volume, in millilitres, of the standard volumetric solution of zinc used for the titration of the blank test ;

c is the actual concentration, in moles per litre, of the standard volumetric solution of zinc ;

0,02698 is the mass of Al, in grams, corresponding to 1 ml of standard volumetric solution of zinc, c(Zn) = 1 mol/l.

With $V_0 = 500$ ml, $V_2 = 200$ ml, $V_3 = 100$ ml :

$$X_1 = 26\,980 \times \frac{(V_5 - V_4) \times c}{V_1 m_0}$$

A.2 Determination of aluminium (CDTA complexometric method after separation of iron)

A.2.1 General

This method is applicable for the determination of aluminium in aluminium-based coagulants used for treatment of water intended for human consumption, as the reference method for products described in EN 878 (low iron grade or other grades), EN 881, EN 883, prEN 885, prEN 886, prEN 887 and prEN 935.

A.2.2 Principle

Dissolution in water, in the case of solid products, or dilution with water, in the case of products in solution, of a test sample.

Separation of iron by precipitation with a solution of sodium hydroxide and filtration of the precipitate.

Complexation of aluminium, in a hot acidic medium with an excess of 1,2 -cyclohexylenedinitrilo tetraacetic acid monohydrate (CDTA) solution. Titration of the excess CDTA with a standard volumetric solution of zinc in the presence of xylenol orange as indicator.

$Al^{3+} + CDTA^{4-} \rightarrow AlCDTA^{-}$

$Zn^{2+} + CDTA^{4-} \rightarrow ZnCDTA^{2-}$

A.2.3 Reagents

All reagents shall be of a recognized analytical grade and the water used shall conform to grade 3 in accordance with EN ISO 3696.

A.2.3.1 Sodium acetate solution, 80 g/l.

A.2.3.2 Sodium hydroxide solution, 100 g/l.

A.2.3.3 Hydrochloric acid

Dilute one volume of hydrochloric acid ($\rho = 1{,}19$ g/ml) with one volume of water.

A.2.3.4 Hydrochloric acid, 36,5 g/l, c(HCl) = 1 mol/l.

A.2.3.5 Trans-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid monohydrate (CDTA),(1,2-cyclohexylenedinitrilotetraacetic acid monohydrate) standard volumetric solution $c(C_{14}H_{22}N_2O_8.H_2O) = 0,05$ mol/l.

Weigh, to the nearest 0,000 1 g, 18,255 g of this product. Dissolve in 80 ml of the sodium hydroxide solution (A.2.3.2), transfer the solution quantitatively to a 1 000 ml volumetric flask. Dilute to volume with water and homogenize.

A.2.3.6 Zinc, standard volumetric solution, $c(Zn) = 0,05$ mol/l.

Weigh to the nearest 0,000 1 g, 6,537 0 g(m) of pure zinc (minimum content 99,9 % (m/m)). Dissolve in 60 ml of hydrochloric acid solution (A.2.3.3). During the reaction, cover the beaker with a watch-glass. At the end of the reaction, boil the solution for 10 min, then cool to room temperature. Dilute to about 500 ml with water and add sodium acetate solution (A.2.3.1) until a pH of 5,5 ± 0,1 is obtained. Transfer the solution quantitatively to a 2 000 ml volumetric flask. Dilute to volume with water and homogenize.

NOTE 1 : if the mass of zinc is not exactly that stated above, the zinc concentration is given by the equation :

$$c(Zn) = \frac{m}{2 \times 65,37}$$

where :

m is the mass in grams of zinc weighed ;

65,37 is the relative molecular mass of zinc ;

$c(Zn)$ is the concentration of zinc solution, in moles per litre, calculated to the fourth significant figure.

NOTE 2 : Commercial standard solution could be used.

A.2.3.7 Buffer solution, pH 5,5.

Weigh 50 g of sodium acetate trihydrate ($CH_3COONa.3H_2O$). Dissolve in 500 ml of water and add glacial acetic acid (CH_3COOH) until a pH of 5,5 ± 0,1 is obtained.

A.2.3.8 Xylenol orange.

Grind 1,0 g of xylenol orange with 99 g of potassium nitrate in a mortar until an homogeneous mass is obtained.

A.2.4 Apparatus

Ordinary laboratory apparatus and glassware, and optionally :

A.2.4.1 Automatic titrator and photometer with fibre optic probe.

A.2.4.2 Microwave equipment.

A.2.5 Procedure

A.2.5.1 Preparation of the test solution

Weigh, to the nearest 0,001 g, about 25 g of the test sample (m_0) into a 400 ml beaker.

Add approximately 150 ml of water at 80°C to 90°C. Stir until dissolved, using a glass stirrer.

Transfer quantitatively to a 500 ml volumetric flask. Dilute to volume with water and homogenize. Filter if necessary through a filter paper (particle retention size 2,5 µm) (test solution V_0).

Place V_1 ml of this solution (see table A.2) into a beaker.

Table A.2 - Aliquot portion V_1 for Al determination (CDTA method)

Expected content Al g/kg	Volume V_1 ml
< 27	100
27 to 66	50
66 to 133	20
133 to 265	10

Add while stirring 40 ml of sodium hydroxide solution (A.2.3.2). Boil for 10 min. Cool to room temperature and transfer the solution quantitatively to a 200 ml volumetric flask. Dilute to volume with water and homogenize. Filter the solution on a dry filter paper for rapid filtration. Wash the filter with three 5 ml portions of water. Collect the wash waters together with filtrate in a clean and dry 200 ml volumetric flask. Dilute to volume with water and homogenize (diluted test solution V_2).

A.2.5.2 Blank test

Perform a blank test following the same procedure and using the same quantities of all the reagents as indicated in A.2.5.3. Record the volume (V_5) used for the titration.

A.2.5.3 Determination

Transfer 100,0 ml of solution (A.2.5.1) (V_3) to a 250 ml beaker and add hydrochloric acid solution (A.2.3.3) so that the pH reaches about 1. Then add a suitable volume of the standard volumetric solution of CDTA (A.2.3.5). Cover with a watch glass. Heat the solution at 80 °C to 90 °C for 1 h. Cool to room temperature. Rinse the watch glass with water into the beaker. Neutralize with sodium acetate solution (A.2.3.1). The pH value shall be between 7 to 7,5, and add 10 ml of the buffer solution (A.2.3.7).

Add 30 mg to 50 mg of xylenol orange mixture (A.2.3.8). Titrate with the standard volumetric zinc solution (A.2.3.6) until the indicator changes from yellow to definite red or determine the equivalence point using an automatic titrator. Record the volume (V_4) used.

If microwave equipment (A.2.4.2) is used, the volume V_1 and the volume of the aliquot portion (A.2.5.1) can be different from those indicated above. Transfer the aliquot portion into a 250 ml conical flask and add hydrochloric acid solution (A.2.3.3) so that the pH reaches about 1. Then add a suitable volume of the standard volumetric solution of CDTA (A.2.3.5). Transfer to the microwave equipment. Operate the microwave equipment at a power setting to achieve a temperature at 80 °C to 90 °C for 15 min. Then cool to room temperature. Transfer quantitatively to a 250 ml beaker or to the automatic titration cell.

NOTE : If an automatic titrator (A.2.4.1) is used, the volume of the aliquot portion (A.2.5.1) and the volumes of the reagents can be different from those indicated above. They should be such that the required precision is achieved.

A.2.6 Expression of results

The aluminium content, X_2, expressed in grams of aluminium per kilogram of product (Al g/kg) is given by the equation :

$$X_2 = 0{,}026\,98 \times (V_5 - V_4) \times c \times \frac{V_2}{V_3} \times \frac{V_0}{V_1} \times \frac{1\,000}{m_0}$$

where :

m_0 is the mass, in grams, of the test sample ;