SLOVENSKI STANDARD
oSIST prEN 1302:2023

01-julij-2023

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 à la consommation humaine - Coagulants à base d'aluminium - Méthodes d'analyse

Ta slovenski standard je istoveten z: **prEN 1302**

ICS:

13.060.20	Pitna voda	Drinking water
71.100.80	Kemikalije za čiščenje vode	Chemicals for purification of water

oSIST prEN 1302:2023 **en,fr,de**

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

DRAFT
prEN 1302

May 2023

ICS 71.100.80

Will supersede EN 1302:1999

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

This draft European Standard is submitted to CEN members for enquiry. It has been drawn up by the Technical Committee CEN/TC 164.

If this draft becomes a European Standard, CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration.

This draft European Standard was established by CEN in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the CEN-CENELEC Management Centre has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Republic of North Macedonia, Romania, Serbia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Türkiye and United Kingdom.

Recipients of this draft are invited to submit, with their comments, notification of any relevant patent rights of which they are aware and to provide supporting documentation.

Warning : This document is not a European Standard. It is distributed for review and comments. It is subject to change without notice and shall not be referred to as a European Standard.

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

CEN-CENELEC Management Centre: Rue de la Science 23, B-1040 Brussels

Ref. No. prEN 1302:2023 E

Contents

Page

European foreword 3
1 Scope 4
2 Normative references 4
3 Terms and definitions 4
4 Methods of analysis 5
5 Sampling 7
6 Expression of results 8
6.1 Aluminium content 8
6.2 Iron 8
6.3 Sodium, calcium, chloride, sulfate and silicate 8
6.4 Free acid 8
6.5 Basicity 8
6.6 Insoluble matters 8
6.7 Chemical parameters 8
6.8 Repeatability 8
Annex A (normative) Analysis of aluminium content 9
Annex B (normative) Analysis of chemical parameters and impurities 15
Annex C (informative) Routine methods 37
Bibliography 56

European foreword

This document (prEN 1302:2023) has been prepared by Technical Committee CEN/TC 164 “Water supply”, the secretariat of which is held by AFNOR.

This document is currently submitted to the CEN Enquiry.

This document will supersede EN 1302:1999.

In comparison with the previous edition, the following technical modifications have been made:

— Replacement of the withdrawn aluminium product standards EN 881 and EN 883 by EN 17034.

— Replacement of the withdrawn mercury analysing standard ISO 5666-1:1983 by ISO 12846:2012.

— Removal of the withdrawn standard ISO 6382:1981. As there was no replacement, the analysing method for silicon content based on this standard was removed.

— Removal of routine methods used for determinate arsenic. Method: Silver diethyldithiocarbamate spectrophotometric method based on standard ISO 6595:1982 as this standard has been withdrawn without replacement.

— Removal of routine methods used for determinate iron. Method: 1,10-Phenanthroline spectrophotometric method based on standard ISO 6685:1982 as this standard has been withdrawn without replacement.

— Removal of a method for determination of iron (total and Fe^{2+}) (volumetric method) as EN 5790 has been removed as the standard has been withdrawn without replacement. Furthermore, the method uses potassium dichromate and there are other options for iron determination.

— Update of the clause titles to correspond the CEN Standard form.

— Update of Table 1 and 2 to correspond the analytical methods available in the standard.

1 Scope

This document 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 882, EN 885, EN 886, EN 887, EN 935 and EN 17034.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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

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

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

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

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

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

EN 17034, *Chemicals used for treatment of water intended for human consumption - Aluminium chloride anhydrous, aluminium chloride basic, dialuminium chloride pentahydroxide and aluminium chloride hydroxide sulfate*

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

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

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp/

— IEC Electropedia: available at https://www.electropedia.org/

3.1
laboratory sample
sample as prepared for sending to the laboratory and intended for inspection or testing

[SOURCE: ISO 6206:1979]

3.2
test sample
sample prepared from the laboratory sample and from which test portions will be taken

[SOURCE: ISO 6206:1979]

3.3
test portion
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

[SOURCE: ISO 6206:1979]

4 Methods of analysis

The methods of analysis are used to analyse the product quality. Table 1 lists the methods which shall be used for analysis of aluminium-based coagulants composition as commercial product and the principles of each method. The reference methods which shall be used are described in full in Annexes A and B. Other methods can be used for quality control.

Table 2 lists the methods which shall be used for analysis of main by-products and chemical parameters. These are applicable to all aluminium based coagulants (EN 878, EN 882, EN 885, EN 886, EN 887, EN 935 and EN 17034). The relevant limit value for each coagulant is available in the product standard.

Table 1 — Methods of analysis of the composition of commercial product

Determination	Reference method	Informative method	EN 878	EN 882	EN 885	EN 886	EN 887	EN 935	EN 17034	Principle	Annex
Aluminium[a]	x		x		x	x	x	x	x	EDTA complexometric titration	A.1
Aluminium		x	x[b]		x	x	x	x	x	CDTA complexometric titration	Annex A
Aluminium	x			x						Gluconate	A.2
Iron	x		x	x	x	x	x	x	x	ICP-OES	B.8
Iron		x	x	x	x	x	x	x	x	FAAS	A.1
Iron		x	x	x	x	x	x	x	x	ICP-MS [c]	
Sodium	x		x		x	x	x	x	x	ICP-OES	B.8
Sodium		x			x	x				AAS	A.1
Sodium		x		x						Gluconate	A.2
Calcium		x			x	x			x	AAS	A.1
Calsium	x				x	x			x	ICP-OES	B.8
Chloride	x				x			x	x	Potentiometric titration	B.1
Sulfate	x		x			x	x		x	Barium sulfate gravimetry	B.2
Free acid			x				x	x	x	Acidimetric titration	B.4
Basicity	x		x	x			x	x	x	Acidimetric titration, oxalate method	B.5
Basicity					x	x				Acidimetric titration, KF method	B.6
Basicity		x								Calculation method	C.7

Key
AAS: Atomic Absorption Spectrometry
AFS: Atomic Fluorescence Spectrometry
ICP-OES: Inductively Coupled Plasma Optical Emission Spectrometry
ICP-MS: Inductively Coupled Plasma Mass Spectrometry

[a] Only applicable for determination of aluminium if iron content is lower than 1,6 g Fe per kilogram of aluminium.

[b] The reference method when iron content is higher than 1,6 g Fe per kilogram of aluminium.

[c] This document does not give a description for this method of analysis.

Table 2 — Applicability methods of analysis to main by-products and chemical parameters

Determination	Reference method	Routine method	Principle
Insoluble matter	B.7		Gravimetry
Arsenic	B.8		ICP-OES
		C.3	ICP-MS
		x	AAS
Cadmium	B.8		ICP-OES
		C.3	ICP-MS
		x	AAS
Chromium	B.8		ICP-OES
		x	ICP-MS
		x	AAS
Mercury	B.10		AAS (cold vapour)
		B.9	AFS
Nickel	B.8		ICP-OES
		x	ICP-MS
		x	AAS
Lead	B.8		ICP-OES
		C.3	ICP-MS
		x	AAS
Antimony	B.8		ICP-OES
		C.3	ICP-MS
		x	AAS
Selenium	B.8		ICP-OES
		C.3	ICP-MS
		x	AAS
Key AAS: Atomic Absorption Spectrometry AFS: Atomic Fluorescence Spectrometry ICP-OES: Inductively Coupled Plasma Optical Emission Spectrometry ICP-MS: Inductively Coupled Plasma Mass Spectrometry			

5 Sampling

Sampling methods are mentioned in the product standards (EN 878, EN 882, EN 885, EN 886, EN 887, EN 935 and EN 17034). Choose the relevant sampling method.

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

6 Expression of results

6.1 Aluminium content

The aluminium content shall be expressed as aluminium mass fraction in % or as Al in grams per kg of product.

6.2 Iron

The iron content shall be expressed as iron mass fraction in % or ar Fe in grams per kg of product depending on analytical method.

6.3 Sodium, calcium, chloride, sulfate and silicate

The sodium, calcium, chloride or sulfate content shall be expressed as grams of substance per kilogram of product or as mass fraction in % depending on analytical method.

6.4 Free acid

Free acid shall be expressed as in grams of sulfuric acid per kilogram of product (H_2SO_4 g/kg) or in grams of hydrochloric acid per kilogram of product (HCl g/kg).

6.5 Basicity

The basicity shall be expressed in grams of hydroxide per kilogram of product (OH^- g/kg) or as the relative basicity expressed in moles of OH^- per moles of Al (OH/Al) or as in % (OH/AL *100/3).

6.6 Insoluble matters

Insoluble matters shall be expressed in mass fraction in % or in grams per kilogram of product.

6.7 Chemical parameters

The chemical parameters mentioned in Table 2 shall be expressed as milligrams of element per kilogram of product.

6.8 Repeatability

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

Annex A
(normative)

Analysis of aluminium content

A.1 Determination of aluminium (EDTA complexometric method)

A.1.1 General

This method shall be used for the determination of aluminium in aluminium-based coagulants used for treatment of water intended for human consumption:

— as the reference method for products with iron content lower than 1,6 g of Fe per kilogram of aluminium e.g. described in EN 878 (iron free grade), EN 882 and applicable for the other standards if Fe content is low;

— as a routine method for products described in EN 878 (low iron grade), EN 885, EN 886, EN 935 and EN 17034 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- –> AlEDTA -

$Zn2+$ + EDTA $^{4-}$ –> 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 (p = 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 a 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.

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 and sodium in sodium aluminate

A.2.1 General

This method shall be used for determination of Na and Al in sodium aluminate.

If the carbonate content is high the calculated sodium content shall be corrected (A.2.2.2).

The measuring range of this method is 2-30 % Na and 2 %–30 % Al.

A.2.2 Principle

A.2.2.1 General

The composition of sodium aluminate solutions can be written:

$NaAl(OH)_4$ + a NaOH (excess) + b Na_2CO_3.

Sodium and aluminium are determined by titration methods:

A.2.2.2 Determination of sodium

Gluconate is added and after that the solution is titrated to pH 9,0 with hydrochloric acid. When the gluconate is added the following reaction takes place:

$$NaAl(OH)_4 + n\ Gl \rightarrow Al(OH)_3Gl_n + NaOH$$

When the pH is lowered to 9,0 the carbonate is mainly transformed to hydrogen carbonate:

$$Na_2CO_3 + H_2O \rightarrow NaHCO_3 + NaOH$$

The total amount of acid used in the titration thus is:

1 + a + b mole HCl/mole Al = 1 + a + 2b mole Na/mole Al

A.2.2.3 Determination of aluminium

Potassium fluoride is added to the titrated solution from a):

$$Al(OH)_3Gln + 6\ KF \rightarrow K_3AlF_6 + 3\ OH^- + 3\ K^+ + n\ Gl$$

An excess of hydrochloric acid is added and back titration to the pH 9,0 is carried out with sodium hydroxide. Three moles of acid consumed are thus equivalent to one mole of Al.

A.2.3 Reagents

All reagents shall be of a recognized analytical grade and the water used shall conform to grade 1 in accordance with EN ISO 3696.

A.2.3.1 Hydrochloric acid, HCl, 0,2 mol/l, ampoule.

A.2.3.2 Sodium hydroxide, NaOH, 0,2 mol/l, ampoule.

A.2.3.3 Sodium gluconate, $C_5H_6(OH)_5COONa$.

A.2.3.4 Sodium gluconate solution, 200 g/l.

Dissolve 40 g sodium gluconate (A.2.3.3) in 200 ml water. Adjust the solution to pH 9,0. Add 5 drops of phenolphthalein solution (A.2.3.7). Store the solution in a plastic bottle.

A.2.3.5 Potassium fluoride, KF, pa.

A.2.3.6 Potassium fluoride (KF) solution, 3,5 mol/l.

Dissolve 200 g KF (A.2.3.5) in water up to 1000 ml and adjust pH to 8,9. Fluoride ions react with glass, therefore store this solution in a plastic bottle.

A.2.3.7 Phenolphthalein solution, 0,5 g in 100 ml ethanol.

A.2.4 Apparatus

A.2.4.1 pH meter

A.2.4.2 Balance

Balance capable of weighing accurately 1 mg.

A.2.5 Procedure

A.2.5.1 Sample solution

Weigh 0,5xx to 0,6xx grams homogenized liquid sample or 0,25x to 0,3xx grams solid sample in a 250 ml beaker. Add about 50 ml water and stir. This is the sample solution.

A.2.5.2 Determination

Analysis of the Na content

Add 15 ml of sodium gluconate solution (A.2.3.4) and 3 to 5 drops of the phenolphthalein solution (A.2.3.7) to the sample solution (A.2.5.1).