BS EN 15039:2014

BSI Standards Publication

Chemicals used for treatment of water intended for human consumption — Antiscalants for membranes — Polycarboxilic acids and salts

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National foreword

This British Standard is the UK implementation of EN 15039:2014. It supersedes BS EN 15039:2006 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee CII/59, Chemicals for drinking water treatment.

A list of organizations represented on this committee can be obtained on request to its secretary.

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

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Compliance with a British Standard cannot confer immunity from legal obligations.

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Chemicals used for treatment of water intended for human consumption - Antiscalants for membranes - Polycarboxilic acids and salts

Produits chimiques pour le traitement de l'eau destinée à la consommation humaine - Produits antitartre pour membranes - Acides polycarboxyliques et sels

Produkte zur Aufbereitung von Wasser für den menschlichen Gebrauch - Antiscalants für Membranen - Polycarbonsäuren und deren Salze

This European Standard was approved by CEN on 5 January 2014.

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

CEN-CENELEC Management Centre: Avenue Marnix 17, B-1000 Brussels

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Foreword

This document (EN 15039:2014) 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of an identical text or by endorsement, at the latest by September 2014 and conflicting national standards shall be withdrawn at the latest by September 2014.

This document supersedes EN 15039:2006.

Significant technical differences between this edition and EN 15039:2006 are as follows:

- replacement of warning and safety precautions notes by labelling according to REGULATION (EC) No 1272/2008.

According to the CEN-CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

Introduction

In respect of potential adverse effects on the quality of water intended for human consumption, caused by the products covered by this European Standard:

a) this European Standard provides no information as to whether the products may be used without restriction in any of the Member States of the EU or EFTA;

b) it should be noted that, while awaiting the adoption of verifiable European criteria, existing national regulations concerning the use and/or the characteristics of these products remain in force.

NOTE Conformity with this European Standard does not confer or imply acceptance or approval of the products in any of the Member States of the EU or EFTA. The use of the products covered by this European Standard is subject to regulation or control by National Authorities.

1 Scope

This European Standard is applicable to polycarboxylic acids and salts used as antiscalants for membranes for the treatment of water intended for human consumption. It describes the characteristics and specifies the requirements and the corresponding analytical methods for polycarboxylic acids and salts. It gives information on their use as antiscalants for membranes in water treatment.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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

EN ISO 5961, *Water quality - Determination of cadmium by atomic absorption spectrometry (ISO 5961)*

EN ISO 11885, *Water quality - Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES) (ISO 11885)*

EN ISO 11969, *Water quality - Determination of arsenic - Atomic absorption spectrometric method (hydride technique) (ISO 11969)*

EN ISO 12846*, Water quality - Determination of mercury - Method using atomic absorption spectrometry (AAS) with and without enrichment (ISO 12846)*

ISO 3165, *Sampling of chemical products for industrial use — Safety in sampling*

ISO 6206, *Chemical products for industrial use — Sampling — Vocabulary*

ISO 6703-1, *Water quality — Determination of cyanide — Part 1: Determination of total cyanide*

ISO 8213, *Chemical products for industrial use — Sampling techniques — Solid chemical products in the form of particles varying from powders to coarse lumps*

ISO 8288:1986, *Water quality — Determination of cobalt, nickel, copper, zinc, cadmium and lead — Flame atomic absorption spectrometric methods*

ISO 9174, *Water quality — Determination of chromium — Atomic absorption spectrometric methods*

ISO 9965, *Water quality — Determination of selenium — Atomic absorption spectrometric method (hydride technique)*

3 Description

3.1 Identification

3.1.1 Chemical name

Homopolymers:

a) polyacrylic acid;

b) polymethacrylic acid;

c) polymaleic acid;

d) polyaspartic acid.

These acids can also be used as sodium, potassium, and ammonium salts.

Copolymers of acrylic acid, methacrylic acid, maleic acid, vinylsulfonic acid, allyl sulfonic acid, methylallyl sulfonic acid, 2-acrylamido-2-methyl-1-propanesulfonic acid, vinyl phosphonic acid, 2-methoxyethylphosphonic acid, ethyleneoxide, α-olefines, acrylamide, benzene sulfonic acid, 4-[(2-methyl-2-propenyl)oxy]-, sodium salt, benzene sulfonic acid, 4-vinyl-, sodium salt and 1-propanesulfonic acid, 2-hydroxy-3-(2-propenyloxy)-, monosodium salt.

Polymers of polyetherdiamines and phosphorous acid.

The acid monomers can also be used as sodium, potassium, and ammonium salts.

3.1.2 Synonym or common names

Nil.

3.1.3 Relative molecular mass

< 100 000 g/mol.

3.1.4 Empirical formula

Nil.

3.1.5 Chemical formula

Homopolymers:

a) $(C_2H_3COOH)_n$;

b) $(C_3H_5COOH)_n$;

c) $(HOOCC_2H_2COOH)_n$;

d) $(C_4H_5NO_4)_n$.

Monomers for the copolymers: C_2H_3COOH, C_3H_5COOH, $HOOCC_2H_2COOH$, $C_2H_4O_3S$, $C_3H_6O_3S$, $C_4H_8O_3S$, $C_7H_{13}NO_4S$, $C_2H_5O_3P$, $C_3H_9O_4P$, C_3H_5NO, $C_{10}H_{12}O_4SNa$, $C_8H_8O_3SNa$, $C_6H_{12}O_5SNa$.

Polymer made from polyetherdiamines $H_2N\text{-}C(R)HCH_2\text{-}(OCH_2C(R)H)_a\text{-}(OCH_2C(R)H)_b\text{-}NH_2$, a = 2 to 12, b = 0 to 1 and R is hydrogen or methyl, and H_3O_3P.

3.1.6 CAS Registry Number[1)]

Homopolymers (acids):

a) 9003-01-4;

b) 25087-26-7;

1) Chemical Abstracts Service Registry Number.

c) 26099-09-2;

d) 25608-40-6.

Table 1 — Salts

	Na^+	K^+	NH_4^+
Acrylic acid	9003–04–7 (part. neutralized) 25549–84–2	25608–12–2	9003–03–6 (part. neutralized) 28214–57–6
Methacrylic acid	54193–36–1	29297–93–6	28805–15–4
Maleic acid	30915–61–8		

Copolymers:

Polyacrylic acid-acrylamide: 9003-06-9;

Acrylic acid-methacrylic acid: 25751-21-7;

Acrylic acid-itaconic acid: 258948-33-8;

Acrylic acid-maleic acid: 29132-58-9;

Acrylic acid-methacrylic acid-ethyleneoxide: 1246089-72-4;

Maleic acid-α-olefine: 39612-00-5;

Conversion of acrylic acid with hypophosphite: 129898-01-7;

Conversion of acrylic acid with bisulfite: 68479-09-4;

Conversion of acrylic acid with isopropanol: 113133-74-7.

Monomers:

Benzene sulfonic acid, 4-[(2-methyl-2-propenyl)oxy]-, sodium salt: 1208-67-9;

Benzene sulfonic acid, 4-ethenyl-, sodium salt: 2695-37-6;

1-Propanesulfonic acid, 2-hydroxy-3-(2-propenyloxy)-, monosodium salt: 52556-42-0.

3.1.7 EINECS reference[2)]

The EINECS-declarations for all mentioned polymers are: POLYMER (All used monomers are listed on the EINECS inventory).

2) European Inventory of Existing Commercial Chemical Substances.

3.2 Commercial forms

The polycarboxylic acids and polyacrylates are available as aqueous solutions and as in granular and powder form. All concentrations mentioned refer to the active matter and shall be calculated accordingly.

3.3 Physical properties

3.3.1 Appearance

The products in solution are a colourless to amber solution and in solid form are white to yellow particles.

3.3.2 Density

The density of solid in granular and powder form has typical values between 400 g/dm^3 to 1200 g/dm^3.

The density of solution is 1,00 g/ml to 1,40 g/ml for a product concentration from mass fraction 20 % to 50 % of active matter at 20 °C.

3.3.3 Solubility in water

Solid: it is soluble in all portions of pure water;

Liquid: it is miscible in all proportions of pure water.

3.3.4 Vapour pressure

Not applicable.

3.3.5 Boiling point at 100 kPa[3)]

Solid: not applicable;

Liquid: approximately 100 °C .

3.3.6 Solidification point

Solid: not applicable;

Liquid: within –25 °C and 0 °C (aqueous product solution).

3.3.7 Specific heat

Not known.

3.3.8 Viscosity (dynamic)

For the liquid the viscosity is equal from 1 mPa.s to 25 mPa.s for a product concentration of 50 g/l.

3.3.9 Critical temperature

Not applicable.

3) 100 kPa = 1 bar.

3.3.10 Critical pressure

Not applicable.

3.3.11 Physical hardness

Not applicable.

3.4 Chemical properties

The polycarboxylic acids and solutions of polycarboxylic acid salts have acidic to alkaline reactions. The pH value of an aqueous solution of a mass fraction of 1 % is approximately between 2 to 11.

4 Purity criteria

4.1 General

This European Standard specifies the minimum purity requirements for polycarboxylic acids and salts used as antiscalants for the membranes in the treatment of water intended for human consumption. Limits are given for impurities commonly present in the products. Depending on the raw material and the manufacturing process other impurities may be present and, if so, this shall be notified to the user and when necessary to relevant authorities.

Users of these products should check the national regulations in order to clarify whether it is of appropriate purity for treatment of water intended for human consumption, taking into account raw water quality, required dosage, contents of other impurities and additives used in the products not stated in this product standard.

Limits have been given for impurities and chemicals parameters where these are likely to be present in significant quantities from the current production process and raw materials. If the production process or raw materials lead to significant quantities of impurities, by-products or additives being present, this shall be notified to the user.

4.2 Composition of commercial product

The product in solid form shall have a polymer content in mass fraction between 85 % to 100 %.

The product in aqueous solution shall conform to the following requirements on a dry mass basis :

— polymer content : mass fraction of (20 to 50) %.

If additional requirements are agreed between the customer and the manufacturer/supplier, the latter should provide the necessary test methods, if requested, so that the customer can carry out his own quality checks. A certificate of analysis should be provided by the manufacturer/supplier if requested.

4.3 Impurities and main by-products

The content of acrylic acid in polycarboxylic acids and salts shall not exceed 1 500 mg/kg of dry product.

4.4 Chemical parameters

Content of various metals depends on the origin of the raw materials, most of these elements are present only as traces.

The product shall conform to the requirements specified in Table 2.

Table 2 — Chemical parameters

Parameter		Limit mg/kg of dry product
Antimony (Sb)	max.	3
Arsenic (As)	max.	3
Cadmium (Cd)	max.	3
Chromium (Cr)	max.	10
Cyanide (CN^-)	max.	5
Lead (Pb)	max.	10
Mercury (Hg)	max.	1
Nickel (Ni)	max.	10
Selenium (Se)	max.	3
NOTE Pesticides and polycyclic aromatic hydrocarbons are not relevant in these products. For other parameters see [1].		

5 Test methods

5.1 Sampling

5.1.1 General

Observe the recommendations of ISO 3165 and take into account ISO 6206.

5.1.2 Solid

Prepare the laboratory sample(s) required by the relevant procedure described in ISO 8213.

5.1.3 Liquid

5.1.3.1 Sampling from drums and bottles

5.1.3.1.1 General

5.1.3.1.1.1 Mix the contents of each container to be sampled by shaking the container, by rolling it or by rocking it from side to side, taking care not to damage the container or spill any of the liquid.

5.1.3.1.1.2 If the design of the container is such (for example, a narrow-necked bottle) that it is impracticable to use a sampling implement, take a sample by pouring after the contents have been thoroughly mixed. Otherwise, proceed as described in 5.1.3.1.1.3.

5.1.3.1.1.3 Examine the surface of the liquid. If there are signs of surface contamination, take samples from the surface as described in 5.1.3.1.2; otherwise, take samples as described in 5.1.3.1.3.

5.1.3.1.2 Surface sampling

Take a sample using a suitable ladle. Lower the ladle into the liquid until the rim is just below the surface, so that the surface layer runs into it. Withdraw the ladle just before it fills completely and allow any liquid adhering to the ladle to drain off. If necessary, repeat this operation so that, when the other selected containers have been sampled in a similar manner, the total volume of sample required for subsequent analysis is obtained.

5.1.3.1.3 Bottom sampling

Take a sample using an open sampling tube, or a bottom-valve sampling tube, suited to the size of container and the viscosity of the liquid.

When using an open sampling tube, close it at the top and then lower the bottom end to the bottom of the container. Open the tube and move it rapidly so that the bottom of the tube traverses the bottom of the container before the tube is filled. Close the tube, withdraw it from the container and allow any liquid adhering to the outside of the tube to drain off.

When using a bottom-valve sampling tube, close the valve before lowering the tube into the container and then proceed in a similar manner to that when using an open sampling tube.

5.1.3.2 Sampling from tanks and tankers

From each access point, take samples as follows:

a) from the surface of the liquid, using a ladle as described in 5.1.3.1.2;

b) from the bottom of the tank or tanker, using a sampling tube as described in 5.1.3.1.3 or using a specially designed bottom-sampling apparatus;

c) from one or more positions, depending on the overall depth, between the bottom and the surface using a weighted sampling can.

5.2 Analyses

5.2.1 Polymer content (main product)

5.2.1.1 General

The concentration of polymer (polycarboxilic acid) shall be determined by potentiometric titration.

5.2.1.2 Principle

Determination of the amount of polycarboxilic acid by potentiometric titration where the total amount of carboxylic groups is measured, whether they are acidic or neutralized. Dilution of the polymer and the solution is brought back to a pH value below or equal to 0,9 with hydrochloric acid. Titration of this dilution by sodium hydroxide gives the total amount of carboxylic groups available. If the polymer is titrated directly by sodium hydroxide without prior addition of hydrochloric acid, only the un-neutralised carboxylic groups will be measured.

The titration is preferably realised with an automatic titrator that can detect pH jumps.

5.2.1.3 Reagents

5.2.1.3.1 General

All the reagents shall be of a recognised analytical grade.

5.2.1.3.2 Deionized water

The water shall have conductivity below 1 µS.

5.2.1.3.3 Sodium hydroxide standard volumetric solution, *c*(NaOH) = 1 mol/l.

When prepared, the exact concentration of the solution is determined by titration with potassium hydrogen phthalate.

5.2.1.3.4 Hydrochloric acid standard volumetric solution, *c*(HCl) = 1 mol/l.

When prepared, the exact concentration of the solution is determined by titration with the sodium hydroxide solution (5.2.1.3.3).

5.2.1.3.5 Buffer solutions

Standard buffer solutions at pH values of 4, 7 and 10 are used for the calibration of the pH electrode.

5.2.1.4 Apparatus

Ordinary laboratory apparatus and:

5.2.1.4.1 Automatic titrator capable of detecting potentiometric jumps

5.2.1.4.2 pH electrode for aqueous measurements

5.2.1.5 Procedure

5.2.1.5.1 Test solution

Weigh, to the nearest 0,001 g, approximately 1 g (*m*) of polymer as dry product (2 g of commercial polymer if its solids content is of 50 %) into a 100 ml flask.

Add between 10 ml and 50 ml of water (5.2.1.3.2) and mix.

5.2.1.5.2 Calibration

Since the titration will be done over a large range of pH values (1 to 12), the pH value of electrode shall be calibrated with a three points method using the buffer solutions at pH values 4, 7 and 10.

5.2.1.5.3 Determination

Immerse the pH electrode (5.2.1.4.2) connected to the titrator (5.2.1.4.1) into the test solution (5.2.1.5.1), stir and add the hydrochloric acid standard volumetric solution (5.2.1.3.4) (V_3) to reach a pH value of 0,9 or less.

Then titrate with the sodium hydroxide standard volumetric solution (5.2.1.3.3). The titrator shall be able to to adjust its increments as a function of the pH curve, i.e. by decreasing the increment size when reaching a potentiometric jump.

The titration is performed up to a pH value of 12.

Record the amount consumed at the equivalent (inflexion) points (volumes V_1 and V_2).

5.2.1.6 Expression of results

The content of polymer (total polycarboxilic acid), w_1, expressed as percentage mass fraction of the dry product is given by the Formula (1) :

$$w_1 = \frac{(V_2 - V_1) \times c_1}{1000} \times \frac{72}{m} \times 100 \qquad (1)$$

The content of polymer (polycarboxilic acid salts), w_2, expressed as percentage mass fraction of the dry product is given by the Formula (2):

$$w_2 = \frac{(V_3 \times c_2) - (V_1 \times c_1)}{(V_2 - V_1) \times c_1} \times 100 \quad (2)$$

where

m is the mass of the test portion in g;

c_1 is the concentration of the sodium hydroxide standard volumetric solution (5.2.1.3.3), in mol/l;

c_2 is the concentration of the hydrochloric acid standard volumetric solution (5.2.1.3.4), in mol/l;

V_1 is the volume of sodium hydroxide standard volumetric solution (5.2.1.3.3) at the first equivalent point, in ml;

V_2 is the volume of sodium hydroxide standard volumetric solution (5.2.1.3.3) at the second equivalent point, in ml;

V_3 is the volume of hydrochloric acid standard volumetric solution (5.2.1.3.4) added in 5.2.1.5.3, in ml.

The result shall be given with one decimal place.

5.2.1.7 Precision

5.2.1.7.1 Repeatability limit

The absolute difference between two independent single test results, obtained using the same method on identical test material in the same laboratory by the same operator using the same equipment within a short interval of time, will not exceed the repeatability limit, 0,5 %, in more than 5 % of cases.

5.2.1.7.2 Reproducibility limit

The absolute difference between two single test results, obtained using the same method on identical test material in different laboratories by different operators using different equipment, will not exceed the reproducibility limit, 0,5 %, in more than 5 % of cases.

5.2.2 Impurities

5.2.2.1 Acrylic acid

The acrylic acid content shall be determined in accordance with the method described in Annex B.

5.2.3 Chemical parameters

5.2.3.1 General

When preparing the products for analysis, it is important to ensure that the chemical parameters are effectively dissolved. The concentration of the solution should be sufficient to permit adequate sensitivity in analysis of the chemical parameters and appropriate steps should be taken to compensate for any matrix interference caused by the concentration of the products.

5.2.3.2 Determination of antimony (Sb), arsenic (As), cadmium (Cd), chromium (Cr), cyanide (CN^-), lead (Pb), mercury (Hg), nickel (Ni) and selenium (Se)

5.2.3.2.1 Principle

The elements antimony, arsenic, cadmium, chromium, lead, mercury, nickel and selenium are determined by atomic absorption spectrometry. Cyanide is determined by molecular absorption spectrometry.

5.2.3.2.2 Reagents

5.2.3.2.2.1 General

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

5.2.3.2.2.2 Hydrochloric acid, concentrated density ρ = 1,42 g/ml.

5.2.3.2.3 Procedure

5.2.3.2.3.1 Test portion

Weigh, to the nearest 0,001 g, 2,5 g (m) from the laboratory sample into a 100 ml one - mark volumetric flask.

5.2.3.2.3.2 Test solution

Add 20 ml of water and 2 ml of the hydrochloric acid (5.2.3.2.2.2), dissolve and make up to the mark with water and mix.

5.2.3.2.3.3 Determination

Determine the content of chemical parameters in the test solution (5.2.3.2.3.2) in accordance with the following methods :

Ni and Pb :	in accordance with ISO 8288:1986, method A;
Cd :	in accordance with EN ISO 5961;
CN^- :	in accordance with ISO 6703-1;
Cr	in accordance with ISO 9174;
As :	in accordance with EN ISO 11969;
Se :	in accordance with ISO 9965;
Sb :	in accordance with EN ISO 11885;
Hg :	in accordance with EN ISO 12846.

These methods provide an interim result (y) expressed in mg/l, which needs to be converted to give the final concentration according to the equation in 5.2.3.2.3.4.

5.2.3.2.3.4 Expression of results

From the interim result (y) determined (see 5.2.3.2.3.3), the content, w_3, of each element in the laboratory sample, expressed in mg/kg of dry antiscalant products is given by the following Formula (3).

$$w_3 = y \times \frac{V}{m} \qquad (3)$$

y is the interim result (5.2.3.2.3.3) ;

V is the volume, expressed in ml, of the test solution (5.2.3.2.3.2) (= 100 ml) ;

m is the mass, expressed in g, of the test portion.

6 Labelling - Transportation - Storage

6.1 Means of delivery

Polycarboxylic acids and salts in solution shall be delivered in bulk, containers, plastic drums or paper bags for dry products or big bags for products in granular or powder form.

In order that the purity of the products is not affected, the means of delivery shall not have been used previously for any different product or it shall have been specially cleaned and prepared before use.

6.2 Risk and safety labelling according to the EU legislation[4)]

The following labelling requirements shall apply to polycarboxylic acids and salts at the date of the publication of this standard:

Hazard pictogram

Signal word

Warning

– Classification - Hazard statements:

H302: Harmful if swallowed

Figure 1 GHS07

The legislation, [2] and its amendments for the purposes of its adaptation to technical and scientific progress, contains a list of substances classified by the EU. Substances not listed in this regulation should be classified on the basis of their intrinsic properties according to the criteria in the regulation by the person responsible for the marketing of the substance.

6.3 Transportation regulations and labelling

The products are not listed under a UN number[5)]

6.4 Marking

The marking shall include the following information:

— the name “polycarboxylic acid” or “polycarboxylic acid salt”, trade name and grade;

— net mass;

— name and the address of the supplier and/or manufacturer;

— the statement “this product conforms to EN 15039”.

6.5 Storage

6.5.1 Material

Use plastics or stainless steel, avoid contact with other metals.

4) See [2]

5) United Nations Number.

6.5.2 Long term stability

Polycarboxylic acids and salts are stable for at least one year if stored at ambient temperatures.

Follow supplier's advice.

6.5.3 Storage incompatibilities

For polycarboxylic acids and salts stored in cool and dry location, the container shall be closed when not in use.

Annex A
(informative)

General information on polycarboxylic acids and salts

A.1 Origin

A.1.1 Raw materials

The monomers are produced according to different industrial processes.

A.1.2 Manufacturing process

An aqueous solution of the monomers is polymerized in a free radical polymerization. For acid products, the acid monomer is polymerized. Polycarboxylic acid salts can be produced either by neutralization of a polycarboxylic acid with the corresponding base or by neutralization of the monomer prior to the polymerization. Production is performed using substances to initiate and modulate the polymerization process (“starters, modulators").

A.2 Use

A.2.1 Function

Polycarboxylic acids and salts are used as antiscalant especially for reverse osmosis (RO) and nanofiltration membranes to prevent $CaCO_3$, $CaSO_4$, $BaSO_4$, $SrSO_4$, CaF_2 scale deposition and fouling by iron, aluminium, manganese and silicates. They will not pass the membranes and are rejected to the wastewater with the concentrate.

Disposal of wastewater should be done in accordance with all applicable local, national, and federal regulations.

In its concentrated form polycarboxylic acids are corrosive. Corrosion resistant dosing equipment should therefore be used.

A.2.2 Form in which it is used

Polycarboxylic acids and salts are mainly used as a solution and within the range of mass fraction of 20 % to 50 % active matter (free acid).

A.2.3 Treatment dose

The prime application for polycarboxylic acids and salts are for the inhibition of calcium carbonate fouling. A typical dosage range is from 0,1 mg/l to 20 mg/l in the make-up water.

A.2.4 Means of application

The product can be pumped directly from the containers as supplied or the product can be diluted with permeate water prior to dose into the RO feed water stream.

Dosage point : feed water prior to the high pressure pumps.

Dosage frequency : continuous using a suitably sized dosing pump.

Product dosage : neat as supplied or diluted with permeate water.

A.2.5 Secondary effects

The product has no secondary effects.

A.2.6 Removal of excess product

Not applicable.

A.2.7 Ecological review

Refer to Safety Data Sheet (SDS) data of the specified product and in particular the standard heading 12 “Ecological information” as defined in ISO 11014:2009, Clause 5 [3].

A.3 General rules relating to safety

A.3.1 Rules for safe handling and use

The supplier will provide current safety instructions.

A.3.2 Emergency procedures

A.3.2.1 First aid

In case of contact with eyes or skin, it is recommended to rinse immediately with plenty of water.

A.3.2.2 Spillage

It is recommended to remove mechanically as much as possible of the solid product, then to rinse the area with plenty of water.

A.3.2.3 Fire

No incompatibilities with fire extinguishing agents are known.

Annex B
(normative)

Analytical methods for polycarboxylic acids and salts

B.1 Determination of dry solid

B.1.1 Principle

The product is heat dried and the mass difference is determined gravimetrically.

B.1.2 Apparatus

Ordinary laboratory apparatus and glassware together with the following:

B.1.2.1 Analytical balance accurate to ± 0,1 mg.

B.1.2.2 Oven, capable of maintaining (110 ± 1) °C vented to fume cupboard.

B.1.2.3 Desiccator, containing dried silica gel.

B.1.2.4 Porcelain crucible, 57 mm diameter.

B.1.3 Procedure

Place a porcelain crucible (B.1.2.4) in an oven (B.1.2.2) at 110 °C for at least 10 min.

Remove the crucible from the oven, place in a desiccator (B.1.2.3) and allow to cool for at least 10 min.

Weigh the crucible to the nearest 0,1 mg.

Shake the sample in its container to ensure that it is homogeneous.

Add 1 g to 2 g test portion of the product sample to the crucible and weigh to the nearest 0,1 mg.

Place the crucible in oven at 110 °C for 2 h.

After this time, transfer the crucible directly from the oven to the desiccator and allow to cool for at least 10 min.

Weigh the crucible containing the dry residue to the nearest 0,1 mg.

B.1.4 Expression of results

The dry solids content, w_4, expressed as a percentage mass fraction of the product, is given by the Formula (B.1):

$$w_4 = \frac{(m_3 - m_1)}{(m_2 - m_1)} \times 100 \qquad \text{(B.1)}$$

where

m_1 is the mass, in g, of the crucible ;

m_2 is the mass, in g, of the crucible and wet sample ;

m_3 is the mass, in g, of the crucible and dried sample.

The result shall be expressed to two decimal places.

B.1.5 Precision

The absolute difference between two single test results, obtained under repeatability conditions (see NOTE), shall not be greater than the repeatability limit, *r*, in more than 1 in 20 cases as calculated from the following equation :

$$r = 0,05\ z$$

where

z is the mean of the two results, expressed in percentage mass fraction.

NOTE Repeatability conditions are where mutually independent test results are obtained with the same method on identical test material in the same laboratory by the same operator using the same equipment within short intervals of time.

B.2 Determination of acrylic acid [6)]

B.2.1 Principle

Acrylic acid monomer is extracted from the sample into water. The solution is analysed by high-performance liquid chromatography (HPLC) using ultraviolet detection. Identification is made by comparison with an external standard and concentration determined by peak area measurement and ratio.

B.2.2 Reagents

B.2.2.1 General

Unless otherwise specified, all reagents shall be of recognised analytical grade.

6) The analytical method described can be modified when the method is validated and a proof is given that it adequately allows to check compliance with the limits for acrylic acid.

B.2.2.2 Ultrapure water (>18 MΩ/cm)

B.2.2.3 Acrylic acid monomer (min. mass fraction 99 %)

B.2.2.4 Sulfuric acid, mass fraction 96 %, density ρ = 1,84 g/ml

B.2.2.5 Phosphoric acid, mass fraction 88 %, density ρ = 1,75 g/ml

B.2.2.6 Helium gas, high purity

B.2.2.7 Eluent

Dissolve 26,04 g of sulfuric acid (B.2.2.4) with 250 ml of water (B.2.2.2). Mix 3,33 ml of this diluted sulfuric acid with 1 000 ml of water. Degas by use of an ultrasonic bath or by passing helium through the solution.

B.2.2.8 Acrylic acid stock solution (200 mg/l)

Weigh, to the nearest 0,001 g, 20 mg of acrylic acid (B.2.2.3.) and dissolve with water into a 200 ml one-mark volumetric flask. Make up to the mark with water (B.2.2.2) and mix.

B.2.3 Apparatus

Ordinary laboratory apparatus and glassware together with the following:

B.2.3.1 For extraction

B.2.3.1.1 Balance, with an accuracy of 0,1 mg

B.2.3.1.2 Laboratory stirrer

B.2.3.1.3 Measuring cylinders

B.2.3.1.4 Syringes, 2 ml capacity

B.2.3.1.5 Disposable syringe filters, 25 mm diameter, fitted with cellulose/mixture ester-membrane, pore size 0,45 µm.

B.2.3.2 For analyses

B.2.3.2.1 High-performance liquid chromatograph fitted with a constant flow solvent delivery system, a HPLC pump, a sample injection valve, a variable wavelength ultraviolet spectrometric detector, a computer/integrator with software (PC with HP ChemStation). Use a column of 300 mm length and 7,8 mm internal diameter with packaging for example (Knauer Eurokat-H 10 µm).[7)]

B.2.3.2.2 Volumetric flasks

B.2.3.2.3 Microlitre syringe

B.2.4 Procedure

B.2.4.1 Preparation of test solution

Weigh, to the nearest 0,001 g, 0,5 g of the sample in a 100 ml volumetric flask. Dissolve the test sample with 50 ml of ultrapure water (B.2.2.2) and acidify with two droplets of phosphoric acid (B.2.2.5). Make up to the mark with

7) Knauer Eurokat-H 10 µm is the trade name of a product supplied by Knauer. This information is given for the convenience of users of this document and does not constitute an endorsement by CEN of the product named. Equivalent products may be used if they can be shown to lead to the same results.

water and mix. Take 2 ml of the well mixed test solution with a syringe and filter through a syringe filter (B.2.3.1.5). The filtrate is ready for the HPLC analysis. The procedure assumes that the detector response is a linear function of concentration but linearity shall first be established by the operator by means of a calibration graph.

B.2.4.2 Chromatographic conditions

Detection limit : 0,017 mg/kg

Quantification limit : 0,054 mg/kg

Lowest concentration: 0,019 mg/kg of acrylic acid

Highest concentration: 12,59 mg/kg of acrylic acid.

In accordance with these chromatographic conditions Table B.1 gives the data obtained.

Table B.1 — Values of peak areas in relation to acrylic acid content

Concentration mg/kg	Peak area
0,019	7,619
0,044	15,291
0,052	17,882
0,080	26,404
0,086	27,564
0,112	36,056
0,133	43,260
0,248	76,922
0,499	153,117
1,17	370,807
2,51	800,973
5,02	1602,093
7,65	2430,687
10,19	3258,458
12,59	4028,242

B.2.4.3 Calibration

Dilute the stock solution (B.2.2.8) with different amounts of water (B.2.2.2), so that the resulting solutions have concentrations between 0,00 mg/kg and 5,0 mg/kg of acrylic acid.

B.2.4.4 Determination

Analyse the filtrate of the test solution, the calibration solution and the blank solution (calibration 0).

B.2.5 Expression of results

The residual acrylic acid monomer content, w_5, expressed in mg/kg of the dry antiscalant product is given by the Formula (B.2)

$$w_5 = \frac{(A_T - A_B) \times c \times V}{(A_S - A_B) \times m} \quad \text{(B.2)}$$

where

A_T is the peak area of the test solution;

A_B is the peak area of the blank solution;

A_S is the peak area of the calibration solution;

c is the concentration of the calibration solution, in mg/l;

m is the mass, in g, of the test sample;

V is the volume of solution, in ml.

B.2.6 Precision

The absolute difference between two single test results, obtained under repeatability conditions (see NOTE), shall not be greater than the repeatability limit, *r*, in more than 1 in 20 cases as calculated from the following equation :

$$r = 0,05\ z$$

where

z is the mean of the two results, expressed in percentage mass fraction.

NOTE Repeatability conditions are where mutually independent test results are obtained with the same method on identical test material in the same laboratory by the same operator using the same equipment within short intervals of time.

B.3 Assessment of product quality

If additional requirements are agreed between the customer and the manufacturer/supplier, the latter shall provide the necessary test methods, if requested, so that the customer can carry out his own quality checks. A certificate of analysis shall be provided by the manufacturer/supplier, if requested.

NOTE A number of physical/chemical measurements can be used by manufacturers to ensure the consistent quality of products delivered to customers. For example, solution viscosity is commonly measured, this being done under strictly controlled conditions. The viscosity value obtained provides a reliable indication of relative molecular mass when comparing batches of a particular product, but has no significance in absolute terms, since it is highly dependent on the composition of the product, the solution preparation procedure, the measuring device and test conditions used. Other tests which can be carried out include determination of ionic charge and infrared spectroscopic analysis, depending on the product and manufacturer/supplier.

Annex C
(informative)

Environmental, health and safety precautions within chemical laboratory

When preparing the analytical methods for application of this document, consideration was given to the minimisation of environmental impacts caused by the use of the methods of analysis.

It is the users' responsibility to use safe and proper techniques in handling materials in the methods of analysis specified in this document.

The following list is not exhaustive but users of the analytical methods referred in this document may use it as a guide to the use of safe and proper techniques. They should:

— investigate if European Directives, transposed European legislation and national laws, regulations and administrative provisions apply;

— consult manufacturers/ suppliers for specific details such as material safety data sheets and other recommendations;

— use safety equipment and wear protective clothing, usually goggles and coats, appropriate for the test product and the test chemicals, in all laboratory areas, to ensure the safety of the operator;

— be careful about flammable materials and substances that are toxic and/ or human carcinogens and generally take care during transportation, decanting, diluting and dealing with spillages;

— use a fume cupboard during preparation of organic solvent solutions;

— store, handle and dispose of chemicals in a safe and environmentally satisfactory manner: including chemicals for laboratory test, test specimens, unused solvents and reagents.

Bibliography

[1] 98/83/EC, Council Directive of 3 November 1998 on the quality of water intended for human consumption

[2] Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006 (REACH)

[3] ISO 11014:2009, *Safety data sheet for chemical products – Content and order of sections*

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