

Chemicals used for treatment of water intended for human consumption — Sulfuric acid

ICS 71.100.80

National foreword

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

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Chemicals used for treatment of water intended for human consumption - Sulphuric acid

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Foreword

This document (EN 899:2009) 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of an identical text or by endorsement, at the latest by September 2009, and conflicting national standards shall be withdrawn at the latest by September 2009.

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This document supersedes EN 899:2003.

Differences between this edition and EN 899:2003 are editorial to harmonize the text with other standards in this series.

Annex A is informative; Annex B is normative.

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Introduction

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

- a) this standard provides no information as to whether the product may be used without restriction in any of 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 this product remain in force.

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

1 Scope

This European Standard is applicable to sulfuric acid used for treatment of water intended for human consumption. It describes the characteristics of sulfuric acid and specifies the requirements and the corresponding test methods for sulfuric acid. It gives information on its use in water treatment.

2 Normative references

The following referenced documents are indispensable for the application 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 1483, *Water quality – Determination of mercury – Method using atomic absorption spectrometry*

EN 26595, *Water quality - Determination of total arsenic – Silver diethyldithiocarbamate spectrophotometric method (ISO 6595:1982)*

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

EN ISO 11885, *Water quality – determination of 33 elements by inductively coupled plasma atomic emission spectroscopy (ISO 11885:1996)*

ISO 910, *Sulphuric acid and oleum for industrial use – Determination of total acidity, and calculation of free sulphur trioxide content of oleum – Titrimetric method*

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

ISO 3423, *Sulphuric acid and oleums for industrial use – Determination of sulphur dioxide content - Iodometric method*

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

ISO 6332, *Water quality – Determination of iron – Spectrometric method using 1,10-phenanthroline*

ISO 8288, *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

Sulfuric acid.

3.1.2 Synonym or common name

Oil of vitriol.

3.1.3 Relative molecular mass

98.

3.1.4 Empirical formula

H₂SO₄.

3.1.5 Chemical formula

H₂SO₄.

3.1.6 CAS Registry Number ¹⁾

7664-93-9.

3.1.7 EINECS reference ²⁾

231-639-5.

3.2 Commercial forms

Sulfuric acid is available as aqueous solutions.

NOTE For some water treatment applications, diluted acid can be used.

3.3 Physical properties

3.3.1 Appearance

The product is clear or slightly turbid, colourless liquid.

3.3.2 Density

1,84 g/ml for sulfuric acid concentration of mass fraction of 96 % at 20 °C.

1,71 g/ml for sulfuric acid concentration of mass fraction of 78 % at 20 °C.

1,18 g/ml for sulfuric acid concentration of mass fraction of 25 % at 20 °C.

3.3.3 Solubility in water

At all concentrations, the product is miscible with water.

1) Chemical Abstracts Service Registry Number.

2) European Inventory of Existing Commercial Chemical Substances.

3.3.4 Vapour pressure

Below 0,00001 kPa for sulfuric acid concentration of mass fraction of 96 % at 20 °C.

Below 0,1 kPa for sulfuric acid concentration of mass fraction of 78 % at 20 °C.

Below 1,9 kPa for sulfuric acid concentration of mass fraction of 25 % at 20 °C.

3.3.5 Boiling point at 100 kPa ³⁾

+ 310 °C for sulphuric acid concentration of mass fraction of 96 %.

Approximately + 200 °C for sulfuric acid concentration of mass fraction of 78 %.

+ 106,5 °C for sulfuric acid concentration of mass fraction of 25 %.

3.3.6 Melting point

+ 5 °C for sulfuric acid concentration of mass fraction of 98 %.

- 10 °C for sulfuric acid concentration of mass fraction of 96 %.

- 11 °C for sulfuric acid concentration of mass fraction of 78 %.

- 22 °C for sulfuric acid concentration of mass fraction of 25 %.

3.3.7 Specific heat

1,465 kJ/(kg.K) for sulfuric acid concentration of mass fraction of 96 % at 20 °C.

3.3.8 Viscosity (dynamic)

22 mPa.s for sulfuric acid concentration of mass fraction of 96 % at 20 °C.

16,7 mPa.s for sulfuric acid concentration of mass fraction of 78 % at 20 °C.

3.3.9 Critical temperature

Not applicable.

3.3.10 Critical pressure

Not applicable.

3.3.11 Physical hardness

Not applicable.

3) 100 kPa = 1 bar.

3.4 Chemical properties

Concentrated sulfuric acid reacts violently:

- with bases or with water (exothermic reaction);
- with reducing agents due to oxidizing properties;
- with combustible materials due to oxidizing and dehydrating properties.

The concentrated acid is a strong oxidizing agent and can cause ignition in contact with organic materials.

Sulfuric acid (of sulfuric acid content less than a mass fraction of 70 % attacks most common metals, e.g. iron, zinc, liberating the flammable gas hydrogen.

WARNING — Mixing with water produces a marked temperature rise. Therefore ALWAYS ADD THE ACID TO THE WATER (NEVER THE REVERSE), slowly and agitating continuously.

4 Purity criteria

4.1 General

This European Standard specifies the minimum purity requirements for sulfuric acid used for the treatment of water intended for human consumption. Limits are given for impurities commonly present in the product. 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 the relevant authorities.

NOTE Users of this product 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, contents of other impurities and additives used in the products not stated in the 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 usual commercial concentrations of sulfuric acid available have a mass fraction of 96 % or 98 %.

Other concentrations of sulfuric acid between a mass fraction of 25 % and 80 % are also available.

If sold as concentrated acid, the mass fraction of sulfuric acid shall be in the range of 92 % to 98 %.

The concentration of sulfuric acid shall be within a mass fraction of ± 1 % of the manufacturer's declared value.

4.3 Chemical parameters and indicator parameters

The product shall conform to the requirements specified in Table 1.

Table 1 — Chemical parameters and indicator parameters

Parameter		Limit of H ₂ SO ₄ mg/kg
Sulfur dioxide (SO ₂)	max.	100
Iron (Fe)	max.	100
Arsenic (As)	max.	0,4
Cadmium (Cd)	max.	0,1
Chromium (Cr)	max.	4
Mercury (Hg)	max.	0,1
Nickel (Ni)	max.	4
Lead (Pb)	max.	4
Antimony (Sb)	max.	1
Selenium (Se)	max.	1
NOTE For chemical parameter values of trace metals in drinking water, see [1].		

5 Test methods

5.1 Sampling

5.1.1 General

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

NOTE The sampling is carried out at the premises of the manufacturer of the concentrated sulfuric acid unless the customer has adequate facilities to carry out this operation safely at his own premises.

5.1.2 Sampling from drums and bottles

5.1.2.1 General

5.1.2.1.1 Mix the contents of the 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.

5.1.2.1.2 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 5.1.2.1.3.

5.1.2.1.3 Examine the surface of the liquid. If there are signs of surface contamination, take samples from the surface as described in 5.1.2.2. Otherwise, take samples as described in 5.1.2.3.

5.1.2.2 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 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.

5.1.2.3 Procedure using a sampling tube

Use a tube made of polytetrafluoroethylene (PTFE), approximately 1 500 mm long, with 14,5 mm inside diameter and 1,25 mm wall thickness tapering to an inside diameter of approximately 5 mm at one end. Fit a rubber tube approximately 200 mm long which can be closed by means of a pinch clip, to the other end. When taking the samples, insert the sampling tube as far as possible into the acid to be tested with the clip released. Do this slowly so that the levels of liquid in the sampling tube and in the acid container are the same.

Close the clip, withdraw the sampling tube from the acid, allow any liquid adhering to the outside of the tube to drain off, and by releasing the clip discharge the contents of the sampling tube into a glass bottle of 1 000 ml nominal capacity provided with a ground glass stopper. Stopper the bottle immediately after filling with each charge of the sampling tube. After shaking thoroughly, fill from the collective sample three glass bottles, each with a volume of approximately 250 ml and provided with a ground glass stopper. Stopper, seal and label the bottles. One of these samples is to be tested by the consignee; the other two shall be kept in case subsequent complaint requires further testing to be carried out.

5.1.3 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 5.1.2.2;
- b) from the bottom of the tank or tanker, using a sampling tube as described in 5.1.2.3 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 Sulfuric acid (main product)

Determine the total acidity of sulfuric acid, conventionally expressed as H_2SO_4 , in accordance with ISO 910.

5.2.2 Chemical parameters and indicator parameters

5.2.2.1 Content of sulfur dioxide

Determine the sulfur dioxide content of sulfuric acid in accordance with ISO 3423.

5.2.2.2 Determination of antimony (Sb), arsenic (As), cadmium (Cd), chromium (Cr), iron (Fe), lead (Pb), nickel (Ni), and selenium (Se)

5.2.2.2.1 Principle

The elements antimony, cadmium, chromium, lead, nickel, mercury and selenium are determined by atomic absorption spectrometry. Arsenic and iron are determined by molecular absorption spectrometry.

5.2.2.2.2 Reagents

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

Nitric acid, concentrated density $\rho = 1,42$ g/ml.

5.2.2.2.3 Procedure

5.2.2.2.3.1 Test portion

Weigh, to the nearest 0,001 g, 20 g (*m*) from the laboratory sample into a platinum dish.

5.2.2.2.3.2 Test solution

Evaporate until a wet residue is obtained, cool, add 1 ml of nitric acid (5.2.2.2.2); dilute with a few millilitres of water, transfer quantitatively to a 100 ml one-mark volumetric flask, dilute to volume with water and mix.

Carry out the evaporation carefully and not to dryness in order to avoid possible losses of arsenic and selenium.

5.2.2.2.3.3 Determination

Determine the content of metals in the test solution (5.2.2.2.3.2) in accordance with the following methods:

- **Fe** : in accordance with ISO 6332;
- **Cd, Ni and Pb** : in accordance with ISO 8288, Method C;
- **Cr** : in accordance with ISO 9174;
- **As** : in accordance with EN 26595;
- **Se** : in accordance with ISO 9965;
- **Sb** : in accordance with EN ISO 11885.

These methods will provide an interim result (*y*) expressed in milligrams per litre which is corrected to give the final concentration according to 5.2.2.2.3.4.

5.2.2.2.3.4 Expression of results

From the interim results (*y*) determined (see 5.2.2.2.3.3), the content, (*C*₂), of each chemical parameter in the laboratory sample, expressed in milligrams per kilogram of a mass fraction of 100 % sulfuric acid is given by the following equation:

$$C_2 = y \times \frac{V \times 100}{m \times C_1} \quad (1)$$

where

- y* is the interim result (5.2.2.2.3.3);
- V* is the volume, expressed in millilitres, of the test solution (5.2.2.2.3.2) (= 100 ml);
- m* is the mass, expressed in grams, of the test portion;
- C*₁ is the concentration, expressed in mass fraction % of sulfuric acid (see 5.2.1).

5.2.2.3 Determination of mercury content (Hg)

5.2.2.3.1 Principle

The element mercury is determined by flameless atomic absorption spectrometry in accordance with EN 1483.

5.2.2.3.2 Reagents

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

5.2.2.3.2.1 Potassium permanganate solution, $c(\text{KMnO}_4) = 50 \text{ g/l}$.

5.2.2.3.2.2 Sulfuric acid, concentrated, $\rho = 1,84 \text{ g/ml}$.

5.2.2.3.2.3 Hydroxylammonium chloride solution, $c(\text{NH}_2\text{OH}\cdot\text{HCl}) = 100 \text{ g/l}$.

5.2.2.3.2.4 Potassium dichromate solution, $c(\text{K}_2\text{Cr}_2\text{O}_7) = 4 \text{ g/l}$ in 50 % by volume nitric acid solution.

5.2.2.3.3 Procedure

5.2.2.3.3.1 Test portion

Pipette to the nearest 0,001 g, 10 g (m_1) of the laboratory sample and transfer drop by drop to a beaker containing approximately 70 ml of water, taking care to avoid sputtering.

5.2.2.3.3.2 Test solution

Quantitatively transfer the test portion to a 100 ml (V_1) volumetric flask. Dilute with water to the mark and mix.

5.2.2.3.3.3 Determination

Proceed as described in EN 1483.

5.2.2.3.3.4 Expression of results

The interim result for mercury content (y_1), expressed in milligrams per litre, is given by the following equation:

$$y_1 = y_A \times V_1 \quad (2)$$

where

y_A is the result obtained in 5.2.2.3.3.3, for the concentration of mercury in the test solution, expressed in milligrams per litre;

V_1 is the volume, in millilitres, of the test solution;

The mercury content, C_3 , in milligrams per kilogram of a mass fraction of 100 % sulfuric acid is given by the following equation:

$$C_3 = y_1 \times \frac{V_1}{m_1} \times \frac{100}{C_1} \quad (3)$$

where

y_1 is the previously determined interim result for mercury content;

V_1 is the volume, in millilitres, of the test solution (see 5.2.2.3.3.2);

m_1 is the mass, expressed in grams, of the test portion (5.2.2.3.3.1);

C_1 is the concentration expressed in mass fraction % of sulfuric acid (see 5.2.1).

6 Labelling - Transportation - Storage

6.1 Means of delivery

In order that the purity of the product 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.

Sulfuric acid shall be delivered in containers made of, or lined with, one of the materials given in Table 2, depending on the temperature and concentration of the acid.

Table 2 — Materials for containers

Material	Acid concentration % (m/m) H ₂ SO ₄	Maximum working temperature °C
Rubber (lining)	up to 50	40
Polypropylene (lining) Polyethylene (lining)	up to 98	50
Polytetrafluoroethylene (PTFE) (lining)	all concentrations	175
Mild steel	between 75 and 100	45
Acid-resistant high-alloy steel (Ni, Cr, Mo) Stainless steel equivalent to 316 L (Belgium), Z2 CND 17.12 and Z2 CND 17.13 (France), 1.4404 and 1.4435 (Germany), 2348 and 2353 (Sweden), 316 S 13 (UK).	greater than 90	30
Carbon steel : A516, A573, A662, A131 Gr.B Carbon steel with phenolic lining	70 to 100	40
Carbon steel : A516, A573, A662, A131 Gr.B	up to 65	40

6.2 Risk and safety labelling according to the EU Directives ⁴⁾

The following labelling requirements apply to sulfuric acid at the date of the publication of this standard.

NOTE Annex I of the Directive 67/548/EEC on Classification, packaging and labelling of dangerous substances and its amendments and adaptations in the European Union contains a list of substances classified by the EU. Substances not in this Annex I should be classified on the basis of their intrinsic properties according to the criteria in the Directive by the person responsible for the marketing of the substance.

4) See [2].

For sulfuric acid of mass concentration greater than a mass fraction of 15 %:

- Symbols and indications of danger:
 - C : corrosive.
- Nature of special risks attributed to dangerous substances:
 - R 35: causes severe burns.
- Safety advice concerning dangerous chemical substances:
 - S 1/2: keep locked up and out of the reach of children;
 - S 26: in case of contact with eyes, rinse immediately with plenty of water and seek medical advice;
 - S 30: never add water to this product;
 - S 45: in case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).

For sulfuric acid of mass concentrations between a mass fraction of 5 % and 15 % H₂SO₄:

- Symbols and indications of danger:
 - Xi : irritating.
- Nature of special risks attributed to dangerous substances:
 - R 36/38: irritating to eyes and skin.
- Safety advice concerning dangerous chemical substances:
 - S 1/2: keep locked up and out of the reach of children;
 - S 26: in case of contact with eyes, rinse immediately with plenty of water and seek medical advice;
 - S 30: never add water to this product;
 - S 45: in case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).

6.3 Transportation regulations and labelling

Sulfuric acid of mass concentration greater than a mass fraction of 51 % is listed as UN number ⁵⁾ 1830.

RID ⁶⁾ /ADR ⁷⁾: Class 8, C1.

IMDG ⁸⁾: Class 8, packing group II.

IATA ⁹⁾: Class 8, packing group II.

5) United Nations Number.

6) Regulations concerning International carriage of Dangerous goods by rail.

7) European Agreement concerning the international carriage of Dangerous goods by Road.

8) International Maritime transport of Dangerous Goods.

9) International Air Transport Association.

6.4 Marking

The marking shall include the following information:

- the name "sulfuric acid", trade name and concentration;
- the net mass;
- the name and the address of the supplier and/or manufacturer;
- the statement "this product conforms to EN 899".

6.5 Storage

NOTE There is a risk of concentrated sulfuric acid freezing at temperatures below 10 °C.

6.5.1 Long term stability

The product is stable if the container is made of suitable material (see Table 2) and tightly closed.

6.5.2 Storage incompatibilities

The product shall not be allowed to come into contact with moisture, alkalis, metal powders, sulfides, sulfites, nitrates, chlorates, chlorites, hypochlorites or organic materials.

Annex A (informative)

General information on sulfuric acid

A.1 Origin

A.1.1 Raw materials

Sulfuric acid is manufactured from sulfur dioxide gas, which is produced, for example, by burning elemental sulfur or roasting of metal sulfide ores.

A.1.2 Manufacturing process

Sulfuric acid is produced by the catalytic oxidation of sulfur dioxide (SO₂) to sulfur trioxide (SO₃), absorption of sulfur trioxide in sulfuric acid and dilution with water to the required grade.

A.2 Use

A.2.1 Function

In the treatment of water for use as drinking water, sulfuric acid is used to adjust the pH value. Diluted sulfuric acid is used to regenerate ion exchangers.

Sulfuric acid can also be used in the treatment of water for swimming baths and industrial water.

A.2.2 Form in which it is used

Concentrated sulfuric acid is diluted to about a mass fraction of 5 % to 10 % before being added to the water to be treated (see B.1).

A.2.3 Treatment dose

The treatment dose depends on the quality of the raw water to be treated, e.g. pH value, sulfate content and on the function of the treatment.

A.2.4 Means of application

The treatment dose is usually applied using a metering pump.

A.2.5 Secondary effects

Corrosion of equipment and piping can occur, if sulfuric acid is added in excess.

Increase of the sulfate concentration: the maximum level of sulfate in drinking water should never exceed 250 mg/l.

A.2.6 Removal of excess product

The excess product is removed by neutralization.

Annex B (normative)

General rules relating to safety

B.1 Rules for safe handling and use

The supplier shall provide current safety instructions.

The place where sulfuric acid is stored or handled shall be made of acid-proof material inside a bunded area, to catch any spillage.

SAFETY PRECAUTIONS Mixing with water produces a marked temperature rise. Therefore **the acid shall always be added to the water (never the reverse)**, slowly and agitating continuously.

B.2 Emergency procedures

B.2.1 First aid

Immediately take off all contaminated clothing.

In case of contact with skin, wash immediately with plenty of water.

In case of contact with eyes: even if small amounts of sulfuric acid enter the eyes, immediately rinse with water for at least 15 min, with the eyelids held open. Immediately consult a doctor.

B.2.2 Spillage

Dilute small spillages with plenty of water, neutralize with lime or sodium carbonate. Small quantities shall be rinsed off with plenty of water.

Never use flammable material to absorb acid spills.

Large spillage: the acid shall be contained (see B.1), pumped to an appropriate container or tank. Seek expert assistance.

B.2.3 Fire

Sulfuric acid is not combustible.

Extinguishing media: no restriction in fire situations, however, concentrated sulfuric acid reacts violently with water (see 3.4).

Bibliography

- [1] 98/83/EC: *Council Directive of 3 November 1998 on the quality of water intended for human consumption*
- [2] 67/548/EEC: *Council Directive of 27th June 1967 on the approximation of the laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances and its amendments and adaptations*

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