BS EN 939:2016

BSI Standards Publication

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

National foreword

This British Standard is the UK implementation of EN 939:2016. It supersedes BS EN 939:2009 which is withdrawn.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.

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English Version

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

Produits chimiques utilisés pour le traitement de l'eau destinée à la consommation humaine - Acide chlorhydrique

Produkte zur Aufbereitung von Wasser für den menschlichen Gebrauch - Salzsäure

This European Standard was approved by CEN on 18 March 2016.

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COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

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Contents

European foreword

This document (EN 939:2016) 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of an identical text or by endorsement, at the latest by November 2016, and conflicting national standards shall be withdrawn at the latest by November 2016.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

This document supersedes EN 939:2009.

Significant technical differences between this edition and EN 939:2009 are as follows:

a) deletion of reference to EU Directive 67/548/EEC of June 27, 1967 in order to take into account the latest Regulation in force (see [2]);

b) use of the changed classification and labelling (see [2]).

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 product covered by this European Standard:

a) this European Standard provides no information as to whether the product 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 this product remain in force.

NOTE Conformity with this European 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 hydrochloric acid used for treatment of water intended for human consumption. It describes the characteristics of hydrochloric acid and specifies the requirements and the corresponding test methods for hydrochloric acid. It gives information on its use in water treatment (see Annex A). It also determines the rules relating to safe handling and use of hydrochloric acid (see Annex B).

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

ISO 904, *Hydrochloric acid for industrial use — Determination of total acidity — Titrimetric method*

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

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

ISO 6685, *Chemical products for industrial use — General method for determination of iron content — 1,10-Phenanthroline spectrophotometric method*

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*

3 Description

3.1 Identification

3.1.1 Chemical name

Hydrochloric acid.

3.1.2 Synonym or common names

Muriatic acid, hydrogen chloride.

3.1.3 Relative molecular mass

36,46.

3.1.4 Empirical formula

HCl.

3.1.5 Chemical formula

HCl.

3.1.6 CAS Registry Number[1)]

7647-01-0.

3.1.7 EINECS reference[2)]

231-595-7.

3.2 Commercial forms

The product is supplied as aqueous solutions of hydrochloric acid with mass fraction of 25 % to 38 % (concentrated acid).

Dilutions of these solutions are also available.

3.3 Physical properties

3.3.1 Appearance

The solution is colourless to yellow and slightly fuming to strongly fuming, depending on concentration.

3.3.2 Density

The density is between 1,135 g/ml and 1,185 g/ml at 20 °C, depending on concentration.

3.3.3 Solubility

The product is miscible with water in any proportion.

3.3.4 Vapour pressure

The vapour pressure for HCl at mass fraction 30 % depending on temperature is given in Table 1.

Table 1 — Vapour pressure of hydrochloric acid solutions

Temperature °C	p_{total} kPa	p_{HCl} kPa	$p_{\mathrm{H_2O}}$ kPa
20	2,13	1,41	0,72
50	13,73	9,46	4,27

3.3.5 Boiling point at 100 kPa

The boiling point of HCl depending on concentration is given in Table 2.

Table 2 — Boiling point of hydrochloric acid solutions

Concentration Mass fraction in %	**Boiling point at 100 kPa** [a] °C
25	104
30	90
38	50,5
[a] 100 kPa = 1 bar.	

[1)] Chemical Abstracts Service Registry Number.

[2)] European Inventory of Existing Commercial Chemical Substances.

3.3.6 Melting or freezing point

The melting or freezing point of HCl depending on concentration is given in Table 3.

Table 3 — Melting or freezing point

Concentration Mass fraction in %	**Melting or freezing point** °C
38	– 27
25	– 75

3.3.7 Specific heat

3,14 kJ/(kg · K) at 18 °C for HCl at mass fraction 16,83 %.

3.3.8 Viscosity (dynamic)

The viscosity of a HCl at mass fraction 30 %, solution at 15 °C, is 1,9 mPa.s.

3.3.9 Critical temperature

Not applicable.

3.3.10 Critical pressure

Not applicable.

3.3.11 Physical hardness

Not applicable.

3.4 Chemical properties

The solution of hydrochloric acid is a strong mineral acid.

4 Purity criteria

4.1 General

This European Standard specifies the minimum purity requirements for hydrochloric 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 relevant authorities.

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, required dosage, contents of other impurities and additives used in the product not stated in this product standard.

Limits have been given for impurities and chemical 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 leads to significant quantities of impurities, by-products or additives being present, this shall be notified to the user.

4.2 Composition of commercial product

As concentrated acid the concentration of HCl solution shall be at least at mass fraction of 25 %.

More diluted solutions are commercially available; the concentration of hydrochloric acid shall be equal to or greater than the manufacturer specified value.

4.3 Impurities and main by-products

The product shall conform to the requirements specified in Table 4.

Table 4 — Impurities

Impurity		Limit mg/kg of HCl mass fraction 100 %
Iron (Fe)	max.	170
Halogenated organic compounds (as Cl)	max.	17

4.4 Chemical parameters

The product shall conform to the requirements specified in Table 5.

Table 5 — Chemical parameters

Parameter		Limit mg/kg of HCl mass fraction 100 %	
		Type 1	Type 2
Arsenic (As)	max.	3	10
Cadmium (Cd)	max.	1	5
Chromium (Cr)	max.	3	10
Mercury (Hg)	max.	0,5	3
Nickel (Ni)	max.	3	10
Lead (Pb)	max.	3	20
Antimony (Sb)	max.	1	10
Selenium (Se)	max.	5	10
NOTE Pesticides and polycyclic aromatic hydrocarbons are not relevant in HCl. Cyanide which does not exist in a very acidic media, such as hydrochloric acid, is not a relevant chemical parameter. For parametric values of hydrochloric acid on trace metal content in drinking water, see [1].			

5 Test methods

5.1 Sampling

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

5.2 Analysis

5.2.1 Determination of hydrochloric acid content (main product)

The determination of total acidity is carried out by titration in accordance with ISO 904.

5.2.2 Impurities

5.2.2.1 Determination of iron content

5.2.2.1.1 Preparation of the test solution

In accordance with ISO 6685.

5.2.2.1.2 Procedure

In accordance with ISO 6685.

5.2.2.2 Determination of content of halogenated organic compounds

5.2.2.2.1 General

Halogenated organic compounds are determined as the extractable organic halogens (EOX). This method applies to hydrochloric acid solutions with a content of EOX, expressed as chloride, exceeding 20 μg/l.

5.2.2.2.2 Principle

EOX are extracted from hydrochloric acid in two stages using heptane. The extract is burned in an oxy-hydrogen flame. The mineralization products occurring in the condensate are determined on the basis of an argentometric reaction or an equivalent method.

5.2.2.2.3 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.

5.2.2.2.3.1 Sulfuric acid, (H_2SO_4), density (ρ) = 1,84 g/ml.

5.2.2.2.3.2 Hydrochloric acid (HCl) pure.

5.2.2.2.3.3 Sodium sulfate, (Na_2SO_4).

Heat for 1 h at 600 °C to remove organic halogen compounds.

5.2.2.2.3.4 Heptane.

5.2.2.2.3.5 Oxygen, (O_2).

5.2.2.2.3.6 Hydrogen, (H_2).

5.2.2.2.3.7 Pentachlorophenol, (C_6Cl_5OH).

5.2.2.2.3.8 Halogen stock solution, ρ(Cl) = 100 mg/l.

Weigh 15,0 mg of pentachlorophenol (5.2.2.2.3.7) into a 100 ml volumetric flask; make up to volume with heptane (5.2.2.2.3.4). This solution is stable for about one week.

5.2.2.2.3.9 Halogen standard solution, ρ(Cl) = 10 mg/l.

Pipette 10 ml of the halogen stock solution (5.2.2.2.3.8) into a 100 ml volumetric flask and make up to volume with heptane (5.2.2.2.3.4). This solution is stable for about one week.

5.2.2.2.3.10 Sodium chloride, (NaCl).

5.2.2.2.3.11 Chloride stock solution, ρ(Cl) = 100 mg/l.

Dissolve 0,165 g of sodium chloride (5.2.2.2.3.10) in water and make up to volume with water in a 1 000 ml volumetric flask.

5.2.2.2.3.12 Chloride standard solution, ρ(Cl) = 1 000 µg/l.

Pipette 10 ml of the chloride stock solution (5.2.2.2.3.11) into a 1 000 ml volumetric flask; make up to volume with water.

Prepare a fresh solution prior to using.

5.2.2.2.4 Apparatus

Ordinary laboratory apparatus and the following:

5.2.2.2.4.1 Dispenser with selectable volume capacity 50 ml.

5.2.2.2.4.2 Magnetic stirrer, for rotational speeds up to 1 100 min^{-1}.

5.2.2.2.4.3 Combustion apparatus.

5.2.2.2.4.4 Halide detection apparatus, e.g. coulometer, electrode, photometer.

5.2.2.2.5 Procedure

5.2.2.2.5.1 Test portion

Weigh, to the nearest 0,1 g, about 300 g (*m*) of hydrochloric acid from the laboratory sample.

5.2.2.2.5.2 Test solution

Transfer 20 g of sodium sulfate (5.2.2.2.3.3) and the test portion (5.2.2.2.5.1) to a 1 000 ml one mark volumetric flask. Immerse the volumetric flask in an ice bath, in order to prevent any increase in the temperature. Make up to the mark with water. Carry out a blank determination using pure hydrochloric acid (5.2.2.2.3.2) and follow the same analytical procedure as given in the method referred to.

5.2.2.2.5.3 Extraction

After introducing a magnetic stirring rod, add 25 ml of heptane (5.2.2.2.3.4) to the test solution (5.2.2.2.5.2), close the volumetric flask and stir the mixture for 10 min at a speed of about 1 100 min^{-1}.

After phase separation (about 10 min) pipette off the extract carefully and as completely as possible and transfer to a 50 ml volumetric flask.

Add to the test solution remaining in the volumetric flask 25 ml of heptane.

After closing the volumetric flask, stir the mixture again for 10 min under the same conditions. After phase separation, pipette off the second extract and combine it with the first in the volumetric flask.

Make up to volume the total extract with heptane.

Depending on the moisture content, add at least 4 g of sodium sulfate (5.2.2.2.3.3) to the volumetric flask; shake for about 2 min. Then let the salt settle.

A recovery of the extraction medium greater than 80 % shall be aimed at. If the recovery is lower, this shall be noted in the test report.

5.2.2.2.5.4 Combustion of the organic extract

Depending on the content of halogens, burn an aliquot part of the extract volume in conformity with the instructions of the manufacturer of the combustion apparatus (see 5.2.2.2.4.3).

a) Cleaning and preparation of the combustion apparatus:

   If the apparatus has stood idle for some considerable time, take out the burner and substitute for it a ground male tapered joint with tubing connector. Attach plastics tubing to the connector for washing out the apparatus. Using this tubing, wash out the apparatus with about 5 l of hot water. Insert the burner again, close the intake tap and allow combustion to continue for about 10 min. Measure chloride in the condensate and again allow combustion for about 10 min. Continue this procedure until the blank readings remain constant. Keep a record of the blank readings so that any changes can be ascertained;

b) Combustion:

   Take care that no sodium sulfate enters into the combustion space.

   Adjust the intake rate so that the flame burns free of soot.

   Use a volumetric flask of suitable volume, e.g. 50 ml, as receiver.

   Dilute the condensate obtained to the volume with water.

5.2.2.2.5.5 Determination of halides in the combustion condensate

Determine the halides in the total volume, in an aliquot part, if necessary in the concentrate or in the condensate.

To improve the limit of determination, the volume of the test solution, the volume of the extract and the volume of the condensate may be chosen freely as a function of the content of halogenated organic compounds: this shall be taken into account in the expression of results.

The ratio of the test solution volume to the volume of the extraction medium shall in any case be 20:1. For the same reason, the aqueous solution of the mineralization products also may be evaporated in quartz vessels.

5.2.2.2.5.6 Checking the mineralization

For checking the functional efficiency of the whole apparatus and the detection method, carry out the treatment described in 5.2.2.2.5.4 to 5.2.2.2.5.5 twice using 10 ml of the halogen standard solution each time. The recovery in terms of organically bonded chlorine shall be not less than 90 % for both portions of standard solution.

5.2.2.2.5.7 Blank test

For determining the blank reading in each series, add 50 ml of heptane or 25 ml of heptane and 25 ml of the further extraction medium to the same mass of sodium sulfate as in the measurement procedure, mineralize corresponding aliquots analogously and detect.

The blank chloride readings shall both be greater than 60 μg per 50 ml of extraction medium.

Carry out three blank determinations; use the mean of these blank determinations to correct the test solution reading.

5.2.2.2.5.8 Calibration curve

To suit the expected content of extractable organic halogens, prepare 10 portions of calibration solution using aqueous sodium chloride solutions such their concentrations in equidistant step cover the envisaged measuring range. For example, for the range from 20 μg/l to 200 μg/l of extractable organic halogens (as chloride) proceed as follows.

Pipette into 10 100 ml volumetric flasks, between 2 ml and 20 ml of the chloride standard solution (5.2.2.2.3.12). Fill up the flasks to the mark with water. Determine the mass concentration of chloride in all 10 samples.

The calibration solutions so obtained shall have the following chloride concentrations: 20 μg/l, 40 μg/l, 60 μg/l, 80 μg/l, 100 μg/l, 120 μg/l, 140 μg/l, 160 μg/l, 180 μg/l and 200 μg/l.

On the abscissa of a graph plot the mass concentrations of chloride in the calibration solutions. The mass concentration of chloride ρ(Cl) in micrograms per litre in the calibration solution concerned is given by the following formula:

$$\rho(\mathrm{Cl}) = \frac{V_\mathrm{s} \times \rho_\mathrm{s}}{V} \tag{1}$$

where

V_s is the volume in millilitres of the chloride standard solution used;

V is the maximum volume in millilitres of the calibration solution (here V = 1 000 ml);

ρ_s is the mass concentration in micrograms per litre of chloride in the chloride standard solution used.

On the ordinate plot the corresponding measurement readings. For the series of readings so obtained, determine the regression line (calibration line). The slope of this line gives the sensitivity *b*. The slope and the ordinate intercept of the line shall be checked from time to time for any significant deviation, particularly when a new batch of one of the reagents needed is brought into use. There shall be no significant deviation between calculated blank readings (ordinate intercept of the calibration line) and measured blank readings.

For the part of the curve associated with the halide detected the value applying for the calibration is ρ(EOX) = 0,015 mg/l to 0,020 mg/l.

5.2.2.2.5.9 Determination

Use a method based on argentometric reaction or an equivalent method.

5.2.2.2.6 Expression of results

The mass concentration of extractable organic halogens c(EOX) expressed as chloride in micrograms per litre in the test solution is given by the following formula:

$$\rho(\mathrm{EOX}) = \frac{V_1 \times V_3 \times (\rho_1 - \rho_0)}{V_2 \times V_4 \times b} \tag{2}$$

where

V_1 is the total volume in millilitres of the organic extract, (here V_1 = 50 ml);

V_2 is the part of volume in millilitres of the extract used for combustion;

V_3 is the volume in millilitres of the aqueous solution of the combustion products;

V_4 is the part of volume in millilitres of the aqueous solution of the combustion products used for the halide determination;

ρ_1 is the halide reading in micrograms per litre of the test solution;

ρ_0 is the calculated blank value in micrograms per litre of the calibration line;

b is the sensitivity (as specified in 5.2.2.2.5.8).

The concentration of halogenated organic compounds (EOX) expressed in milligrams per kilogram of HCl mass fraction 100 % is given by the following formula:

$$_{(\mathrm{EOX})} = \frac{\rho_{(\mathrm{EOX})}}{m} \times \frac{100}{c_{(\mathrm{HCl})}} \tag{3}$$

where

m is the mass in grams of hydrochloric acid test portion (see 5.2.2.2.5.1);

$c_{(\mathrm{HCl})}$ is the hydrochloric acid content in percentage by mass (5.2.1).

5.2.3 Chemical parameters

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

5.2.3.1.1 Principle

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

5.2.3.1.2 Reagents

All reagents shall be of a recognized analytical grade and the water used shall conform to the grade 2 specified in EN ISO 3696.

5.2.3.1.2.1 Nitric acid, concentrated, density ρ = 1,42 g/ml.

5.2.3.1.3 Procedure

5.2.3.1.3.1 Test portion

Weigh, to the nearest 0,001 g, 20 g (m_1) from the laboratory sample into a glass beaker.

5.2.3.1.3.2 Test solution

Evaporate until a wet residue is obtained, cool, add 1 ml of nitric acid (5.2.3.1.2.1), dilute with a few millilitres of water, transfer quantitatively to a 100 ml volumetric flask, make up to the volume with water and mix.

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

5.2.3.1.3.3 Determination

Determine the content of elements in the test solution (5.2.3.1.3.2) in accordance with the following methods:

1) Cd, Ni and Pb: in accordance with ISO 8288, Method A;

2) Cr: in accordance with ISO 9174;

3) As, Se and Sb: in accordance with the method given in Annex C.

These methods will give an interim result (y) expressed in milligrams per litre which needs to be converted to give the final concentration according to Formula (4) in 5.2.3.1.3.4.

5.2.3.1.3.4 Expression of results

From the interim result (y) determined (see 5.2.3.1.3.3), the content, C_1, of each element in the laboratory sample, expressed in milligrams per kilogram of hydrochloric acid, mass fraction 100 %, is given by the following formula:

$$C_1 = y \times \frac{V_3}{m_1} \times \frac{100}{C_{(\mathrm{HCl})}} \tag{4}$$

where

y is the interim result (5.2.3.1.3.3);

V_3 is the volume, expressed in millilitres, of the test solution (5.2.3.1.3.2) (here V = 100 ml);

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

$C_{(\mathrm{HCl})}$ is the hydrochloric acid content in mass fraction in % (5.2.1).

5.2.3.2 Determination of mercury content (Hg)

5.2.3.2.1 Principle

The element mercury is determined by flameless atomic absorption spectrometry in accordance with EN ISO 12846.

5.2.3.2.2 Reagents

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

5.2.3.2.2.1 Potassium permanganate solution, $\rho(\mathrm{KMnO_4})$ = 50 g/l.

5.2.3.2.2.2 Sulfuric acid, concentrated, density ρ = 1,84 g/ml.

5.2.3.2.2.3 Hydroxylammonium chloride solution, $\rho(\mathrm{NH_2OH.HCl})$ = 100 g/l.

5.2.3.2.2.4 Potassium dichromate solution, $\rho(\mathrm{K_2Cr_2O_7})$ = 4 g/l in a volume fraction of 50 % nitric acid solution.

5.2.3.2.3 Procedure

5.2.3.2.3.1 Test portion

Weigh, to the nearest 0,01 g, 10 g (m_2) from the laboratory sample, into a glass beaker.

5.2.3.2.3.2 Test solution

Quantitatively transfer the test portion to a gas washing flask, capacity 250 ml, with the gas inlet equipped with a porous glass frit. Dilute the contents of the gas washing flask with water to obtain a total volume of 100 ml. Transfer to a volumetric flask (solution A).

Pipette, accurately 10 ml of the hydrochloric acid (solution A). Transfer to a 250 ml conical flask and add 60 ml of water, 20 ml of a potassium permanganate solution (5.2.3.2.2.1) and five 1 ml portions of sulfuric acid (5.2.3.2.2.2). Heat and keep boiling for 10 min. Allow to cool. Just dissolve the precipitate (MnO_2) with hydroxylammonium chloride (5.2.3.2.2.3), add 5 ml of the potassium dichromate solution (5.2.3.2.2.4) and transfer to a 100 ml (V_T) volumetric flask. Dilute to the mark with water and mix.

5.2.3.2.3.3 Determination

Proceed as described in EN ISO 12846.

5.2.3.2.4 Expression of results

The interim result for mercury content (y) expressed in milligrams per litre is given by the following formula:

$$y = y_A \times \frac{V_T}{10} \tag{5}$$

where

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

V_T is the volume in millilitres of the test solution;

The content of mercury, C_2, in milligrams per kilogram of hydrochloric acid, mass fraction 100 %, is given by the following formula:

$$C_2 = y \times \frac{10}{m_2} \times \frac{100}{c_{(HCl)}} \tag{6}$$

where

m_2 is the mass expressed in grams, of the test portion;

$C_{(HCl)}$ is the available chlorine content in mass fraction in % (5.2.1).

6 Labelling – Transportation – Storage

6.1 Means of delivery

The product shall be delivered in vessels used solely for that purpose of capacity appropriate to the application (varying from 25 kg carboys to 25 t bulk containers).

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.

6.2 Labelling according to the EU legislation[3)]

The following labelling requirements (see Table 6) shall apply to hydrochloric acid at the date of publication of this standard.

[3)] See [2].

Table 6 — Labelling requirements

Solutions of hydrochloric acid concentration	
$C \geq 25\ \%$	H314, H335
$10\ \% \leq C < 25\ \%$	H315, H319, H335
$C < 10\ \%$	-

Hazard pictogram

Figure 1 — GHS05

Figure 2 — GHS07

- — Signal word: **Danger**
- — Hazard statements:

H314: Cause severe skin burns and eye damage

H315: Causes skin irritation

H319: Causes serious eye irritation

H335: May cause respiratory irritation

Precautionary statements ('P statements') should be provided by the company being responsible for the marketing of the substance. They should be indicated on the packaging label and in the extended safety data sheet (eSDS) of the substance.

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

Hydrochloric acid is listed as UN Number [4] 1789.

RID [5] /ADR [6]: class 8, classification code C1,packing group II.

IMDG [7]: class 8, packing group II.

IATA [8]: class 8, packing group II.

6.4 Marking

The marking shall include the following:

- name “hydrochloric acid”, trade name, grade and type;
- net mass;
- name and the address of supplier and/or manufacturer;
- statement “this product conforms to EN 939”.

6.5 Storage

6.5.1 Containers

The product shall be stored in tightly-closed containers made of rubber-lined steel, polyvinyl chloride, polyethylene, polypropylene, glass, stoneware or polytetrafluorethylene, or glass-reinforced plastics providing the resin is not attacked by hydrochloric acid in a cool, well ventilated place.

6.5.2 Long term stability

The product is stable in appropriate storage.

6.5.3 Storage incompatibilities

The product and its vapour shall not be allowed to come into contact with metals, with which it reacts, in most cases, to produce hydrogen gas which forms explosive mixtures with air. Also, the product shall not be allowed to come into contact with bases, alkalis, sulfites and any oxychlorine compounds.

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4) United Nations Number.

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

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

7) International Maritime transport of Dangerous Goods.

8) International Air Transport Association.

Annex A
(informative)

General information on hydrochloric acid

A.1 Origin

A.1.1 Raw materials

Hydrochloric acid is manufactured from the following:

1) chlorine and hydrogen;
2) chlorine and organic compounds;
3) alkali chloride and sulfuric acid;
4) chlorinated residues.

A.1.2 Manufacturing process

It is produced from:

1) chlorine and hydrogen by combustion ;
2) organic reactions of organic compounds with chlorine;
3) chlorides and acids;
4) incineration of chlorinated residues.

A.2 Use

A.2.1 Function

Its functions in water treatment are the lowering of pH, the generation of chlorine dioxide for oxidation and disinfection and as regenerant for ion exchange resins.

A.2.2 Form in which it is used

It is used in aqueous solution, as delivered or diluted with water.

A.2.3 Treatment dose

The treatment dose depends on the applications.

A.2.4 Mean of application

It is applied using a metering-pump.

A.2.5 Secondary effects

The secondary effect is an increase in the chloride content.

A.2.6 Removal of excess product

The excess product can be removed by neutralization with alkali.

A.3 Routine analyses

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

As:	in accordance with ISO 17378-2 (see [3]);
Se:	in accordance with ISO/TS 17379-2 (AAS) (see [4]).

Annex B
(normative)

General rules relating to safety

B.1 Rules for safe handling and use

The supplier shall provide current safety instructions.

B.2 Emergency procedures

B.2.1 First aid

In case of contact with the skin, remove victim form source of contamination. Promptly flush contaminated skin with water. Promptly remove clothing if soaked through and flush skin with water. Seek medical advice immediately.

In case of contact with the eyes, promptly wash with lots of water while lifting eye lids. Seek medical advice immediately. Continue to rinse.

In case if inhalation, move the exposed person to fresh air at once. Perform artificial respiration if breathing has stopped. Keep affected person warm and at rest. Seek medical advice immediately.

In case of ingestion, never make an unconscious person vomit or drink fluids. Even if conscious do not include vomiting. Seek medical advice immediately. Let victim drink lots of water to dilute chemical.

The effects can be delayed and the affected person should be kept under observation.

B.2.2 Spillage

Take the following actions with any spillages:

a) wear respiratory equipment and protective clothing;

b) stop any leak if this can be done without any danger. Avoid any contact with the spilt material;

c) neutralize the spilt materials with sodium carbonate or sodium hydrogen carbonate non-combustible or other non-combustible basic chemicals;

d) flush the area with water and then collect it in suitable containers;

e) inform the appropriate authorities if a major spillage occurs.

B.2.3 Fire

Extinguishing media: use extinguisher to suit cause of fire. Hydrochloric acid is non-flammable, but can develop corrosive fumes if heated. Hydrochloric acid reacts with many metals generating hydrogen which forms explosive mixtures with air.

Annex C
(normative)

Determination of arsenic, antimony and selenium (atomic absorption spectrometry hydride technique)

C.1 Safety precautions

SAFETY PRECAUTIONS — Arsenic, antimony and selenium and their hydrides are toxic. Handle with care.

C.2 General principle

Arsenious acid, antimonic acid and selenious acid, the As(III), Sb(III) and Se(IV) oxidation states of arsenic, antimony and selenium, respectively, are instantaneously converted by sodium borohydride reagent in acid solution to their volatile hydrides. The hydrides are purged continuously by argon or nitrogen into an appropriate atomizer of an atomic absorption spectrometer and converted to the gas-phase atoms. The sodium borohydride reducing agent, by rapid generation of the elemental hydrides in an appropriate reaction cell, minimizes dilution of the hydrides by the carrier gas and provides rapid, sensitive determinations of arsenic, antimony and selenium.

The sample is digested to solubilize particulate As, Sb and Se. The digested solutions are treated separately for determination of As, Sb and Se to convert them to As(III), Sb(III) and Se(IV) oxidation states respectively.

C.3 Interferences

Interferences are minimized because the As, Sb and Se hydrides are removed from the solution containing most potential interfering substances. Slight response variations occur when acid matrices are varied. Control these variations by treating standards and samples in the same manner. Low concentrations of noble metals (approximately 100 μg/l of Ag, Au, Pt, Pd, etc.) concentrations of Cu, Ni and Pb at or greater than 1 mg/l, and concentrations between 0,1 mg/l and 1 mg/l of hydride-forming elements (Bi, Sn and Te) can suppress the response of As, Sb and Se hydrides due to the formation of mixed metal – As-Sb or -Se compounds. The presence of As, Sb and Se in each other's matrices can cause similar suppression. Reduced nitrogen oxides resulting from HNO_3 digestion and nitrite also can suppress instrumental response for all elements. Large concentrations of iodide interfere with the Se determination by reducing Se to its elemental form. Do not use any glassware for determining Se that has been used with iodide reduction of As(V).

C.4 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.

C.4.1 Sodium tetrahydroborate (sodium borohydride).

Dissolve 8 g $NaBH_4$ in 200 ml of NaOH, c(NaOH) = 0,1 mol/l. Prepare fresh daily.

C.4.2 Sodium iodide, prereductant solution.

Dissolve 50 g Nal in 500 ml water. Prepare fresh daily.

C.4.3 Sulfuric acid, solution $c(H_2SO_4) = 9$ mol/l.

C.4.4 Sulfuric acid, solution $c(H_2SO_4) = 1,25$ mol/l.

Cautiously add 35 ml sulfuric acid, density (ρ) = 1,84 g/ml to about 400 ml water, allow to cool, and adjust volume to 500 ml.

C.4.5 Nitric acid, density (ρ) = 1,42 g/ml.

C.4.6 Perchloric acid, density (ρ) = 1,66 g/ml.

C.4.7 Hydrochloric acid, density (ρ) = 1,16 g/ml.

C.4.8 Argon (or nitrogen), commercial grade.

C.4.9 Hydrogen, commercial grade.

C.4.10 Arsenic(III) solutions:

a) stock As(III) solution: Dissolve 1,320 g arsenic trioxide, As_2O_3, in water containing 4 g of NaOH. Transfer quantitatively to 1 000 ml one-mark volumetric flask and make up to the mark with water and mix; 1,00 ml contains 1,00 mg As(III);

b) intermediate As(III) solution: Dilute into 1 000 ml one-mark volumetric flask 10 ml stock As(III) solution to the mark with water containing 5 ml hydrochloric acid (C.4.7) and mix ; 1,00 ml contains 10,0 μg As(III);

c) standard As(III) solution: Dilute into 1 000 ml one-mark volumetric flask 10 ml intermediate As(III) solution to the mark with water containing the same concentration of acid used for sample preservation (2 ml to 5 ml nitric acid (C.4.5)) and mix; 1,00 ml contains 0,100 μg As(III). Prepare diluted solutions daily.

C.4.11 Arsenic(V) solutions:

a) stock As(V) solution: Dissolve 1,534 g arsenic pentoxide, As_2O_5, in water containing 4 g NaOH. Transfer quantitatively to 1 000 ml one-mark volumetric flask and make up to the mark with water and mix; 1,00 ml contains 1,00 mg As(V);

b) intermediate As(V) solution: Prepare as for As(III) above ; 1,00 ml contains 10,0 μg As(V);

c) standard As(V) solution: Prepare as for As(III) above ; 1,00 ml contains 0,100 μg As(V).

C.4.12 Selenium(IV) solutions:

a) stock Se(IV) solution: Dissolve 2,190 g sodium selenite, Na_2SeO_3 in water containing 10 ml hydrochloric acid (C.4.7) and transfer quantitatively to 1 000 ml one-mark volumetric flask and make up to the mark with water and mix; 1,00 ml contains 1,00 mg Se(IV);

b) intermediate Se(IV) solution: Dilute into 1 000 ml one-mark volumetric flask 10 ml stock Se (IV) solution to the mark with water containing 10 ml hydrochloric acid (C.4.7) and mix; 1,00 ml contains 10,0 μg Se(IV);

c) standard Se(IV) solution: Dilute into 1 000 ml one-mark volumetric flask 10 ml intermediate Se(IV) solution to the mark with water containing the same concentration of acid used for sample preservation (2 ml to 5 ml nitric acid (C.4.5)) and mix. Prepare solution daily when checking the equivalent of instrument response for Se(IV) and Se(VI) ; 1,00 ml contains 0,100 μg Se(IV).

C.4.13 Selenium(VI) solutions:

a) stock Se(VI) solution: Dissolve 2,393 g sodium selenate Na_2SeO_4 in water containing 10 ml nitric acid (C.4.5). Transfer quantitatively to 1 000 ml one-mark volumetric flask and make up to the mark with water and mix; 1,00 ml contains 1,00 mg Se(VI);

b) intermediate Se(VI) solution: Prepare as for Se(IV) above; 1,00 ml contains 10,0 μg Se(VI);

c) standard Se(VI) solution: Prepare as for Se(IV) above; 1,00 ml contains 0,100 μg Se(VI).

C.4.14 Antimony solutions:

a) stock Sb solution: Dry 2 g of potassium antimonyl tartrate hemihydrate (antimony potassium tartrate) ($C_4H_4O_7SbK.0,5\ H_2O$) at 100 °C for 1 h. Dissolve 1,669 g in water transfer quantitatively to 1 000 ml one-mark volumetric flask and make up to the mark with water and mix; 1,00 ml contains 1,00 mg Sb;

b) intermediate Sb solution: Dilute into 1 000 ml one-mark volumetric flask 10 ml stock Sb solution to the mark with water containing 10 ml hydrochloric acid (C.4.7) and mix; 1,00 ml contains 10,0 μg Sb;

c) standard Sb solution: Dilute into 1 000 ml one-mark volumetric flask 10 ml intermediate Sb solution to the mark with water containing the same concentration of acid used for sample preservation (2 ml to 5 ml nitric acid (C.4.5)) and mix; 1,00 ml contains 0,100 μg Sb. Prepare diluted solutions daily.

C.5 Apparatus

Ordinary laboratory apparatus (such as spectrometers computer with updated software) **and glassware,** together with the following:

C.5.1 Atomic absorption spectrometer, equipped with gas flow meters for argon (or nitrogen) and hydrogen, As,Sb and Se electrodeless discharge lamps with, background correction at measurement wavelengths and appropriate strip-chart recorder.

NOTE Certain atomic absorption atomizers and hydride reaction cells are available commercially for use with the sodium borohydride reagent.

C.5.2 Atomizer.

Use one of the following atomizers:

1) boling-type burner[9] head for argon (or nitrogen)-air entrained-hydrogen flame;

2) cylindrical quartz cell, 10 cm to 20 cm long, electrically heated by external Ni-Cr wire from 800 °C to 900 °C;

3) cylindrical quartz cell with internal fuel rich hydrogen-oxygen (air) flame.

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[9] Boling is the name of the inventor of this type of burner for rapid combustion of the hydrides.

The transparency of quartz cells deteriorates over several months of use. The transparency can be restored by treatment with 40 % hydrofluoric acid (HF).

SAFETY PRECAUTIONS — Be careful in handling HF which is toxic and corrosive and avoid prolonged contact of quartz with HF.

C.5.3 Reaction cell for producing As, Sb or Se hydrides.

An example of reaction cell for producing As, Sb or Se hydrides is given in Figure C.1.

NOTE A commercially available system is acceptable if it utilizes liquid sodium borohydride reagents; accepts samples digested in accordance with C.6.3, accepts between 4 mol/l to 6 mol/l (HCl); and is efficiently and precisely stirred by the purging gas and/or a magnetic stirrer.

Irrespective of the hydride reaction cell-atomizer system selected, it shall meet the following quality-control considerations:

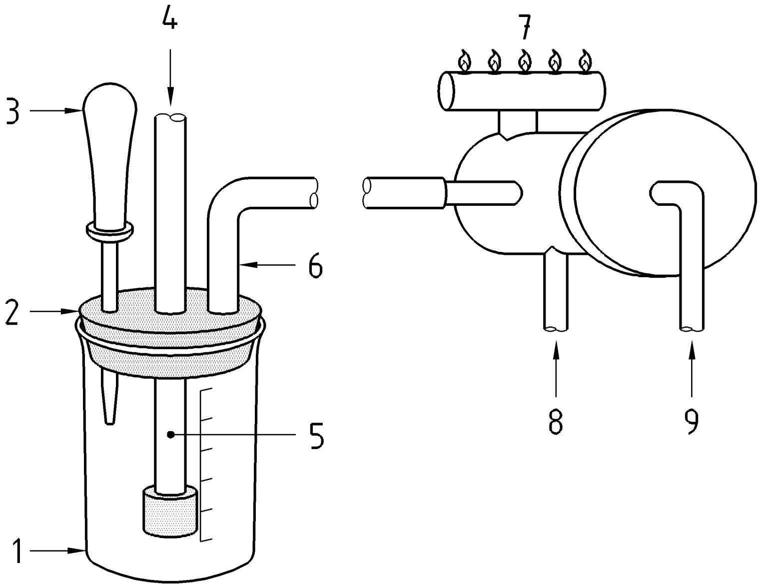
a) it shall provide a precise and reproducible calibration curve between 0 μg/l and 20 μg/l As, Sb or Se and a detection limit between 0,1 μg/l and 0,5 μg/l As, Sb or Se;

b) when carried through the entire procedure, oxidation state couples (As(III) - As(V) or Se(IV) - Se(VI)) shall cause equal instrument response; and

c) sample digestion shall yield 90 % or greater recovery of added As(III), As(V), Se(VI), Se(IV) or Sb.

C.5.4 Dropper and syringe capable of delivering 0,5 ml to 3,0 ml sodium borohydride reagent.

Exact and reproducible addition is required so that production of hydrogen gas does not vary significantly between determinations.



Key

1	beaker 250 ml
2	rubber stopper
3	dropper
4	auxiliary nitrogen
5	gas dispersion tube
6	outlet tube
7	burner
8	hydrogen
9	nitrogen

Figure C.1 — Reaction cell for producing As, Sb or Se hydrides

C.6 Procedure

C.6.1 Preparation of the apparatus

Connect inlet of reaction cell with auxiliary purging gas controlled by flow meter. If a drying cell between the reaction cell and atomizer is necessary, use only anhydrous $CaCl_2$ and not $CaSO_4$ because it can retain SeH_2. Before using the hydride generation/analysis system, optimize operating parameters. Aspirate aqueous solutions of As, Sb and Se directly into the flame to facilitate atomizer alignment. Align quartz atomizers for maximum absorbance. Establish purging gas flow, concentration and rate of addition of sodium borohydride reagent, solution volume, and stirring rate for optimum instrument response for the chemical species to be analyzed. If a quartz atomizer is used, optimize cell temperature. If sodium borohydride reagent is added too quickly, rapid evolution of hydrogen will unbalance the system. If the volume of solution being purged is too large, the absorption signal will be decreased. Recommended wavelengths are 193,7 nm 196,0 nm and 217,6 nm for As, Se and Sb, respectively.

C.6.2 Preparation of calibration solutions

Transfer 0,00 ml; 1,00 ml; 2,00 ml; 5,00 ml; 10,00 ml; 15,00 ml and 20,00 ml of standard solutions of As(III), Se(IV) or Sb to 100 ml volumetric flasks and make up to volume with water containing the same acid concentration used for sample preservation (commonly 2 ml to 5 ml nitric acid (C.4.5)).This yields calibrations solutions of 0 μg/l, 1 μg/l, 2 μg/l, 5 μg/l, 10 μg/l, 15 μg/l and 20 μg/l As, Se or Sb. Prepare fresh daily.

C.6.3 Preparation of test solutions and standard solutions

Add 50 ml of the sample or As(III), Se(VI) or Sb standard solution to 250 ml beaker. Alternatively, prepare standard solutions by adding aliquots of solutions containing 5 μg As, Se or Sb directly to the beaker and dilute to 50 ml in this beaker, thus achieving a concentration of 100 µg/l of the respective solutions. Add 7 ml sulfuric acid $c(H_2SO_4) = 9$ mol/l (C.4.3) and 5 ml nitric acid (C.4.5). Add a small boiling chip or glass beads if necessary. Evaporate to SO_3 fumes. Maintain oxidizing conditions at all times by adding small amounts of nitric acid, to prevent solution from darkening.

Maintain an excess of nitric acid until all organic matter is destroyed. Complete digestion usually is indicated by a light-coloured solution. Cool slightly, add 25 ml water and 1 ml of perchloric acid (C.4.6) and again evaporate to SO_3 fumes to expel oxides of nitrogen.

Monitor effectiveness of digestion procedure used by adding 5 ml of a standard arsenic solution, 5 ml of a standard selenium solution or 5 ml of a standard antimony solution to 50 ml of the sample and measuring recovery. Average recoveries shall be greater than 90 %. Alternatively, use 100 ml micro-Kjeldahl flasks for the digestion of total recoverable arsenic, selenium or antimony, thereby improving digestion effectiveness. After final evaporation of SO_3 fumes, dilute to 50 ml for arsenic measurements or 30 ml for selenium and antimony measurements.

C.6.4 Determination of arsenic with sodium borohydride

To 50 ml of the digested standard solution or test solution in a 250 ml beaker (see Figure C.1) add 5 ml hydrochloric acid (C.4.7) and mix. Add 5 ml sodium iodide prereductant solution (C.4.2), mix and wait at least 30 min.

NOTE The sodium iodide has not been found necessary for certain hydride reaction cell designs if a 20 % to 30 % loss in instrument sensitivity is not important and variables of solution acid conditions, temperatures, and volumes for production of As(V) and arsine can be controlled strictly. This can require an automated delivery system.

Attach one beaker at a first time to the rubber stopper containing the gas dispersion tube for the purging gas, the sodium borohydride reagent inlet, and the outlet to the atomizer. Turn on strip-chart recorder and wait until the base line is established by the purging gas and all air is expelled from the reaction cell. Add 0,5 ml sodium borohydride reagent (C.4.1). After the instrument absorbance has reached a maximum and returned to the base line, remove beaker, rinse dispersion tube with water, and proceed to the next test solution or standard solution. Periodically compare standard As(III) and As(V) curves for response consistency. Check for presence of chemical interferences that suppress instrument response for arsine by treating a digested sample with 10 μg/l As(III) or As(V) as appropriate. Average recoveries shall be not less than 90 %.

C.6.5 Determination of selenium with sodium borohydride

To 30 ml of the digested standard solution or test solution, or to 30 ml of the undigested standard, or the sample in a 250 ml beaker, add 15 ml hydrochloric acid (C.4.7) and mix. Heat for a predetermined period at temperature between 90 °C to 100 °C. Alternatively autoclave at 121 °C in capped containers for 60 min, or heat for a predetermined time in open test tubes using a 90 °C to 100 °C hot water bath or an aluminium block digester. Check effectiveness of the selected heating by demonstrating equal instrument responses for calibration curves prepared either from standard Se(IV) or from Se(VI) solutions. Effective heat exposure for converting Se(VI)to Se(IV), with no loss of Se(IV), ranges between 5 min to 60 min when open beakers or test tubes are used. Do not digest standard Se(IV) and Se(Vl) solutions used for this check of equivalency. After prereduction of Se(VI) and Se(IV) attach beakers, one at a time, to the purge apparatus. For each, turn on the strip-chart recorder and wait until the base line is established. Add 0,50 ml sodium borohydride reagent (C.4.1). After the instrument absorbance has reached a maximum and returned to the base line, remove beaker, rinse dispersion tube with water and proceed to the next test solution or standard solution. Check for presence of chemical interferences that suppress selenium hydride instrument response by treating a digested sample with 10 μg/l Se(IV). Average recoveries shall be not less than 90 %.

C.6.6 Determination of antimony with sodium borohydride

To 30 ml of the digested standard solution or the test solution, or to 30 ml of the undigested standard solution, or the test solution in a 250 ml beaker, add 15 ml hydrochloric acid (C.4.7) and mix. Heat for a predetermined period (between 5 min and 60 min) at a temperature between 90 °C to 100 °C. After prereduction of Sb attach beakers, one at a time, to the purge apparatus. For each, turn on the strip-chart recorder and wait until the base line is established. Add 0,50 ml sodium borohydride reagent (C.4.1). After the instrument absorbance has reached a maximum and returned to the base line, remove beaker, rinse dispersion tube with water and proceed to the next test solution or standard solution. Check for presence of chemical interferences that suppress antimony hydride instrument response by treating a digested sample with 10 μg/l Sb. Average recoveries shall be not less than 90 %.

C.7 Calculation

Determine the calibration curve by plotting peak heights of standard solutions versus concentration. Measure peak heights of samples and read concentrations from the calibration curve. If sample was diluted (or concentrated) before sample digestion, apply an appropriate factor.

The absolute difference between two single test results, obtained under repeatability conditions, shall not be greater than the repeatability value, r, as calculated from the following formula:

$$r = 0{,}001\, z$$

where

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

NOTE Repeatability conditions are conditions 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.

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[1] 98/83/EC, Council Directive of 3rd November 1998 relating to the Quality of Water intended for Human Consumption

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[3] ISO 17378-2, *Water quality — Determination of arsenic and antimony — Part 2: Method using hydride generation atomic absorption spectrometry (HG-AAS)*

[4] ISO/TS 17379-2, *Water quality — Determination of selenium — Part 2: Method using hydride generation atomic absorption spectrometry (HG-AAS)*

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