BS EN 14664:2004

Chemicals used for treatment of water intended for human consumption — Iron(III) sulfate, solid

The European Standard EN 14664:2004 has the status of a British Standard

ICS 71.100.80

British Standards

National foreword

This British Standard is the official English language version of EN 14664:2004.

The UK participation in its preparation was entrusted to Technical Committee CII/59, Chemicals for drinking water treatment, which has the responsibility to:

- aid enquirers to understand the text;
- present to the responsible European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;
- monitor related international and European developments and promulgate them in the UK.

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

Cross-references

The British Standards which implement international or European publications referred to in this document may be found in the *BSI Catalogue* under the section entitled "International Standards Correspondence Index", or by using the "Search" facility of the *BSI Electronic Catalogue* or of British Standards Online.

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

Compliance with a British Standard does not of itself confer immunity from legal obligations.

Summary of pages

This document comprises a front cover, an inside front cover, the EN title page, pages 2 to 39 and a back cover.

The BSI copyright notice displayed in this document indicates when the document was last issued.

This British Standard was published under the authority of the Standards Policy and Strategy Committee on 24 November 2004

ISBN 0 580 44867 3

Amendments issued since publication

Amd. No.	Date	Comments

EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

EN 14664

November 2004

ICS 71.100.80

English version

Chemicals used for treatment of water intended for human consumption - Iron (III) sulfate, solid

Produits chimiques utilisés pour le traitment de l'eau destinée à la consommation humaine - Sulfate de fer (III) solide

Produkte zur Aufbereitung von Wasser für den meschlichen Gebrauch - Eisen(III)sulfat, fest

This European Standard was approved by CEN on 30 September 2004.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Central Secretariat has the same status as the official versions.

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

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

Management Centre: rue de Stassart, 36 B-1050 Brussels

Ref. No. EN 14664:2004: E

Contents

Foreword

This document (EN 14664:2004) 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 May 2005, and conflicting national standards shall be withdrawn at the latest by May 2005.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Slovakia, Slovenia, Spain, Sweden, Switzerland and 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 document:

a) This document 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 document does not confer or imply acceptance or approval of the product in any or the Member States of the EU or EFTA. The use of the product covered by this document is subject to regulation or control by National Authorities.

1 Scope

This standard is applicable to iron (III) sulfate solid used for treatment of water intended for human consumption. It describes the characteristics of iron (III) sulfate solid and specifies the requirements and the corresponding analytical methods for iron (III) sulfate solid (analytical methods are given in Annex C) and gives information on its use in water treatment. It also determines the rules relating to safe handling and use of iron (III) sulfate solid (see Annex B).

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

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

ISO 5790:1979, *Inorganic chemical products for industrial use – General method for the determination of chloride content - Mercurimetric method*

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

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

3 Description

3.1 Identification

3.1.1 Chemical name

Iron (III) sulfate solid.

3.1.2 Synonym or common names

Ferric sulfate solid.

3.1.3 Relative molecular mass

561,9.

3.1.4 Empirical formula

$Fe_2(SO_4)_3.\ x\ H_2O$ where x is approximately 5,5.

3.1.5 Chemical formula

$Fe_2(SO_4)_3.\ x\ H_2O$ where x is approximately 5,5.

3.1.6 CAS Registry Number [1]

10028-22-5.

3.1.7 EINECS reference [2]

233-072-9.

3.2 Commercial form

The iron (III) sulfate solid is available as free flowing granules or powder, with a particle size range from 0,1 mm to 10 mm and 0,055 mm to 0,060 mm respectively and the angle of repose is approximately 37.

3.3 Physical properties

3.3.1 Appearance

The iron (III) sulfate solid consists of greyish or yellowish granules.

3.3.2 Density

The bulk density is approximately equal to 1 300 kg/m^3 for granules and 1 000 kg/m^3 for powders at 20 °C.

3.3.3 Solubility (in water)

Iron (III) sulfate solid dissolves rapidly in water. The solubility is approximately 550 g/l, corresponding to approximately mass fraction 11 % of Fe at 20 °C. At concentrations lower than mass fraction of 0,3 % Fe, hydrolysis and formation of iron (III) hydroxide will occur.

3.3.4 Vapour pressure

Not known.

3.3.5 Boiling point at 100 kPa [3]

Not applicable.

3.3.6 Melting point

Iron (III) sulfate solid decomposes when heated.

3.3.7 Specific heat

Not known.

3.3.8 Viscosity (dynamic)

Not applicable.

---

1) Chemical Abstract Service Registry Number.

2) European Inventory of Existing Commercial Chemical Substances.

3) 100 kPa = 1 bar.

3.3.9 Critical temperature

Not applicable.

3.3.10 Critical pressure

Not applicable.

3.3.11 Physical hardness

The granule strength is higher than 50 N.

3.4 Chemical properties

Iron (III) sulfate solid is slightly hygroscopic at relative humidity higher than 50 %.

Iron (III) sulfate solutions are acidic.

4 Purity criteria

4.1 General

This document specifies the minimum purity requirements for iron (III) sulfate solid 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.

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, 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 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 shall contain not less than mass fraction of 64 % of $Fe_2(SO_4)_3$ or not less than a mass fraction of 18 % of Fe and shall be within ± 3 % of the manufacturer's declared values.

4.3 Impurities and main by-products

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

The concentration limits refer to Fe (III).

Table 1 – Impurities

Impurity		Limit Mass fraction in % of Fe (III) content		
		Grade 1	Grade 2	Grade 3
Manganese	max.	0,5	1	2
Iron(II) [a]	max.	3,5	3,5	3,5
H_2SO_4 free	max.	8	8	8
Insoluble matters[b]	max.	10	10	10

[a] Fe (II) has a lower coagulant efficiency compared to Fe (III).

Also hydrolysis of Fe (II) starts at pH value 8, and therefore Fe (II) can remain into the water at lower pH values

[b] An excess of insoluble matters indicates the presence of foreign matter. Iron is a component of the product will usually be removed in the treatment process.

4.4 Chemical parameters

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

The concentration limits are specified in milligrams per kilogram of Fe (III).

Table 2 – Chemical parameters

Parameter		Limit in mg/kg of Fe (III)		
		Type 1	Type 2	Type 3
Arsenic (As)	max.	1	20	50
Cadmium (Cd)	max.	1	25	50
Chromium (Cr)	max.	100	350	500
Mercury (Hg)	max.	2,5	5	10
Nickel (Ni)	max.	300	350	500
Lead (Pb)	max.	2,5	100	400
Antimony (Sb)	max.	10	20	60
Selenium (Se)	max.	5	20	60

NOTE Cyanide (CN^-) is usually not relevant because of the acidity of the product. Pesticides and polycyclic aromatic hydrocarbons are not relevant since the raw materials used in the manufacturing process are free of them.

For maximum impact of iron (III) sulfate on trace metal content in drinking water see A.2.

5 Test methods

5.1 Sampling

Observe the general recommendations in ISO 3165 and take into account ISO 6206. Prepare the laboratory sample required by the relevant procedure described in ISO 8213.

5.2 Analyses

5.2.1 Main product

Iron (III) sulfate is determined as Fe (III) contents in the test sample. Fe (III) content is determined as the difference between total iron content and Fe (II) content (see C.1).

5.2.2 Impurities

5.2.2.1 Manganese

The manganese content shall be determined by flame atomic absorption spectrometry (FAAS) (see C.2).

5.2.2.2 Iron (II) (Fe (II))

The Fe (II) content is expressed as $C_{(II)}$ (see C.1.2.5.3).

5.2.2.3 Insoluble matter

The mass fraction in % of the insoluble matter shall be determined in accordance with the method described in C.3.

5.2.2.4 Free acid

The free acid shall be determined in accordance with the method described in C.4.

5.2.3 Chemical parameters

5.2.3.1 Preparation of sample solution

5.2.3.1.1 General

Oxidation and wet digestion is used to bring the samples into a stable solution.

5.2.3.1.2 Principle

Oxidation with hydrogen peroxide (H_2O_2) followed by digestion with hydrochloric acid (HCl).

5.2.3.1.3 Reagents

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

5.2.3.1.3.2 Hydrochloric acid (HCl), solution, mass fraction 30 %.

5.2.3.1.3.3 Hydrogen peroxide (H_2O_2), solution, mass fraction 30 %.

5.2.3.1.4 Apparatus

5.2.3.1.4.1 Ordinary laboratory apparatus and glassware together with the following

5.2.3.1.4.2 Analytical balance.

5.2.3.1.4.3 Graduated cylinder, 50 ml.

5.2.3.1.4.4 Round flask with reflux condenser.

5.2.3.1.4.5 Hot plate.

5.2.3.1.4.6 Volumetric flask, 200 ml.

5.2.3.1.5 Procedure

Dissolve with 20 ml of water 20,0 g of the iron salt. Filter and wash the filter cake with hot water. Add to the mixed filtrate and wash water 5 ml hydrogen peroxide solution (5.2.3.1.3.3) to iron (**III**)-samples. After adding 50 ml hydrochloric acid (5.2.3.1.3.2) boil the solution for 15 min by using a reflux condenser (5.2.3.1.4.4). Cool down the solution, transfer to a 200 ml volumetric flask (5.2.3.1.4.6) and fill up to the mark with water. This is the sample solution.

5.2.3.2 Arsenic

The arsenic content shall be determined by hydride generation atomic absorption spectrometry (see C.5).

5.2.3.3 Cadmium

The cadmium content shall be determined by graphite furnace atomic absorption spectrometry (see C.7).

5.2.3.4 Chromium

The chromium content shall be determined by graphite furnace atomic absorption spectrometry (see C.7).

5.2.3.5 Mercury

The mercury content shall be determined by cold vapour atomic absorption spectrometry (see C.6).

5.2.3.6 Nickel

The nickel content shall be determined by graphite furnace atomic absorption spectrometry (see C.7).

5.2.3.7 Lead

The lead content shall be determined by graphite furnace atomic absorption spectrometry (see C.7).

5.2.3.8 Antimony

The antimony content shall be determined by hydride generation atomic absorption spectrometry (see C.5).

5.2.3.9 Selenium

The selenium content shall be determined by hydride generation atomic absorption spectrometry (see C.5).

6 Labelling - Transportation - Storage

6.1 Means of delivery

The product shall be delivered in suitable packages, paper of plastics bags, or by rubber-lined or plastics-lined bulk truck.

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 Risk and safety labelling according to the EU Directives [4]

The following labelling requirements shall apply to iron (III) sulfate solid at the date of the publication of this document.

- symbols and indications of danger :
  - X_i : Irritant;
  - Xn Harmful
- nature of special risks attributed to dangerous substances:
  - R 22: Harmful by ingestion;
  - R 36/37/38 : Irritating to eyes, respiratory system and skin;
- safety advice concerning dangerous substances:
  - S 26 : In case of contact with eyes, rinse immediately with plenty of water and seek medical advice;
  - S 28 : After contact with skin, wash immediately with plenty of water;
  - S 37/39 : Wear suitable gloves and eye/face protection.

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 1 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.

6.3 Transportation regulations and labelling

Iron (III) sulfate solid is not listed under a UN number [5].

Iron (III) sulfate solid is not classified as a dangerous product for road, rail, sea and air transportation.

6.4 Marking

The marking shall include the following information:

- name "iron(III) sulfate solid", trade name, grade and type;
- net mass;
- name and the address of the supplier and/or manufacturer;
- statement "this product conforms to EN 14664".

6.5 Storage

6.5.1 General

Iron (III) sulfate solid is not corrosive.

---

[4] See [2].

[5] United Nations Number.

6.5.2 Long term stability

Iron (III) sulfate solid is stable at relative humidity lower than 50 %.

6.5.3 Storage incompatibilities

- Avoid contact with water because iron (III) sulfate solution formed is acidic and corrosive.

Annex A
(informative)

General information on iron (III) sulfate solid

A.1 Origin

A.1.1 Raw materials

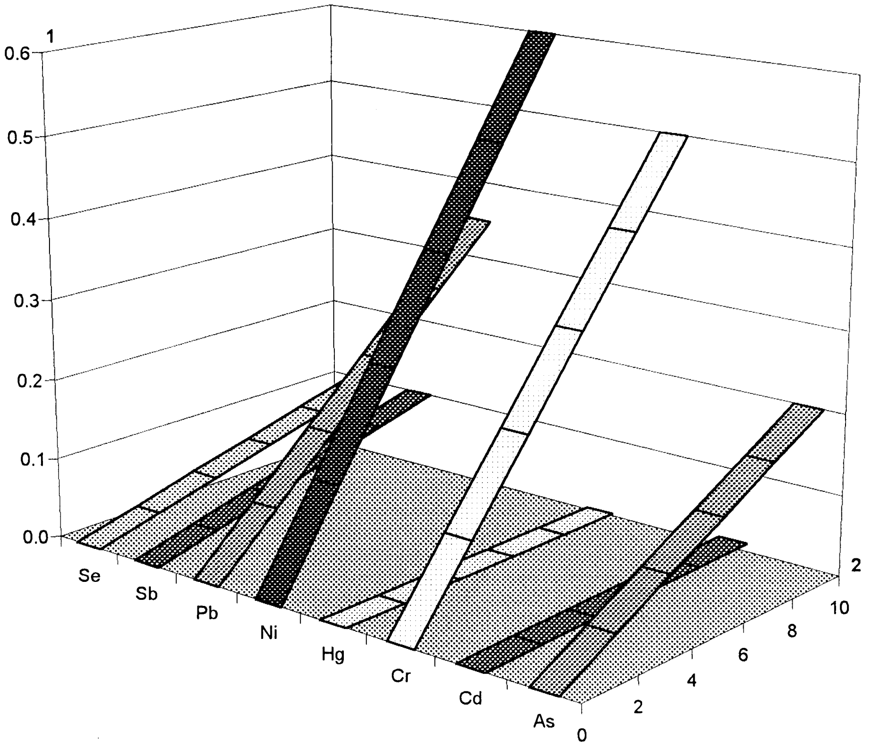
The product is manufactured from sulfuric acid, iron (II) sulfate and oxygen.

A.1.2 Manufacturing process

Iron (III) sulfate solid is produced by dissolving iron (II) sulfate in sulfuric acid with oxygen as oxidant at elevated temperature followed by granulation or as powder produced by atomized drier of liquid iron (III) sulfate.

A.2 Quality of commercial product

The three types of iron (III) sulfate solid specified in Table 2 reflect the quality of commercially available products. Figures A.1 to A.3 show the maximum concentrations of trace metals that would be added to the raw water by the addition of products corresponding to the purity levels specified in Table 2. It can be seen that the concentrations of metal added are well below the Parametric Values given in the EU Directive 98/83/EC (see [1]) at typical product doses. Furthermore, the figures overstate the concentration of metals that would be present in the treated water since a substantial proportion of the trace metals will be incorporated in the sludge. Users of this product should select an appropriate grade an Type to enable them to achieve treated water quality targets taking into account raw water characteristics, required dosage, process plant conditions and other relevant factors.

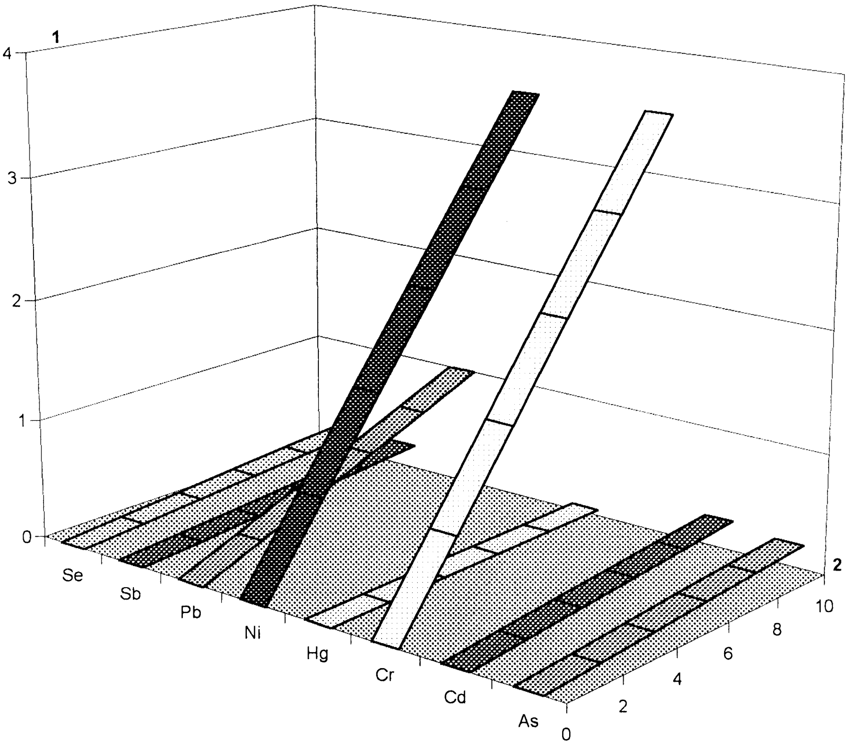


Element	Drinking water limit ug/l
As	10
Cd	5
Cr	50
Hg	1
Ni	20
Pb	10
Sb	5
Se	10

Key

1	Maximum addition to water µg/l metal
2	Product dosage mg/l Fe – Typical dose

Figure A.1 – Maximum impact of iron (III) sulfate solid, Type 1, on trace metal content of water



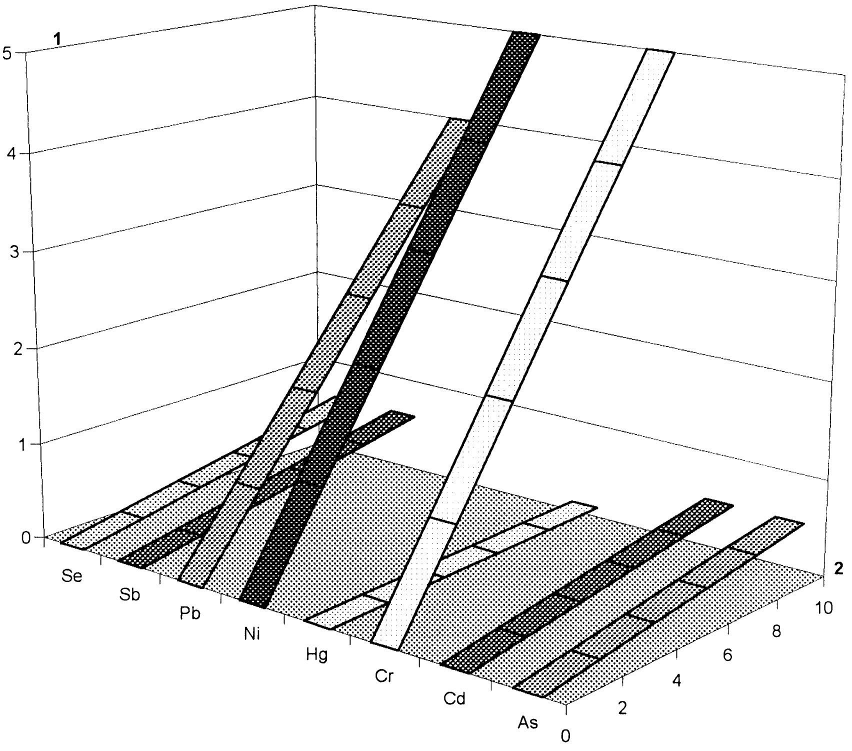
Element	Drinking water limit ug/l
As	10
Cd	5
Cr	50
Hg	1
Ni	20
Pb	10
Sb	5
Se	10

Key

1 Maximum addition to water µg/l metal

2 Product dosage mg/l Fe – Typical dose

Figure A.2 – Maximum impact of iron (III) sulfate solid, Type 2, on trace metal content of water



Element	Drinking water limit ug/l
As	10
Cd	5
Cr	50
Hg	1
Ni	20
Pb	10
Sb	5
Se	10

Key

1 Maximum addition to water µg/l metal

2 Product dosage mg/l Fe – Typical dose

Figure A.3 – Maximum impact of iron (III) sulfate solid, Type 3, on trace metal content of water

A.3 Use

A.3.1 Function

The product is used as primary coagulant.

A.3.2 Form in which it is used

The product in used as delivered or dissolved in water.

A.3.3 Treatment dose

The treatment dose is variable depending on raw water quality and corresponds to a treatment dose between 4 g/m^3 and 10 g/m^3 expressed as Fe.

A.3.4 Means of application

Product can be dosed continuously from a silo by a dry feeder into a solution tank for continuously overflowing into the raw water. To promote a rapid dispersion a high turbulence at the point of addition is desirable. Iron (III) sulfate solution is acidic and equipments in contact with the solution therefore should be made of corrosion resistant materials (stainless, plastics, rubber, lead etc).

A.3.5 Secondary effects

Increase of the sulfate content. Reduction of alkalinity and pH value.

A.3.6 Removal of excess product

The coagulation process includes the hydrolysis of the ferric ions to ferric hydroxide. This precipitate is removed by sedimentation, flotation and/or finally filtration.

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 skin, wash with plenty of water.

In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.

If swallowed, provided patient is conscious, wash out the mouth with water and mass fraction of 5 % sodium bicarbonate solution and give a demulcent such as milk. Seek medical advice immediately

B.2.2 Spillage

Small spillage: wash away with large quantities of water.

Large spillage: neutralize with lime or soda ash, then dispose of according to local regulations. Water can be used if washings can go to drain. Immediately inform police and local authorities if product has entered public drains or waterways.

B.2.3 Fire

Product is not combustible. However, in contact with metals, iron (III) sulfate can liberate the flammable gas hydrogen.

Annex C
(normative)

Analytical methods

C.1 Determination of iron (III) sulfate

C.1.1 Total iron

C.1.1.1 General

This method applies to products with iron contents greater than a mass fraction of 0,4 %.

C.1.1.2 Principle

Iron is reduced by tin (II) chloride and is subsequently titrated with potassium dichromate solution.

C.1.1.3 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.

C.1.1.3.1 Hydrochloric acid, HCl concentrated, density $\rho = 1{,}19$ g/ml.

C.1.1.3.2 Tin (II) chloride solution, $c(SnCl_2.2H_2O) = 0{,}5$ mol/l. Dissolve 22,6 g of $SnCl_2$ $.2H_2O$ with 20 ml of hydrochloric acid (C.1.1.3.1) and dilute with water to 200 ml. Keep this solution in the dark.

C.1.1.3.3 Mercury (II) chloride, saturated solution $c(HgCl_2) = 0{,}27$ mol/l.

C.1.1.3.4 Sulfuric acid, H_2SO_4 concentrated, density $\rho = 1{,}84$ g/ml.

C.1.1.3.5 Phosphoric acid, H_3PO_4 concentrated, density $\rho = 1{,}71$ g/ml.

C.1.1.3.6 Barium diphenylamine sulfonate solution, $c(Ba(C_6H_5\text{-}NH\text{-}C_6H_4SO_3)_2) = 8$ mmol/l.

C.1.1.3.7 Potassium dichromate solution, $c(K_2Cr_2O_7) = 0{,}0166$ mol/l.

C.1.1.4 Apparatus

Ordinary laboratory apparatus and glassware.

C.1.1.5 Procedure

C.1.1.5.1 Test solution

Weigh about, to the nearest 0,1 mg, 7 g of the laboratory sample and dissolve in 150 ml water. Remove insoluble matters by filtering. Wash the filter cake with hot water. Transfer filtrate and wash water to a 200 ml volumetric flask, dilute to the mark with water.

C.1.1.5.2 Determination

Pipette 10 ml of the test solution and transfer to a 500 ml conical flask.

Add some drops of hydrochloric acid (C.1.1.3.1) and heat until boiling while stirring.

Add drop by drop tin (II) chloride solution (C.1.1.3.2) until discoloration.

Reduction shall be achieved with great care. Two drops of tin (II) chloride (C.1.1.3.2) are necessary, more shall be avoided.

Cool the solution rapidly in cool water. Add 10 ml of mercury (II) chloride (C.1.1.3.3). Dilute to 200 ml and wait 3 min. A slight white cloud will appear regarding to mercury (II) chloride addition. If a precipitate appears, stop the titration and reduce another aliquot of the test solution. Add 10 ml of sulfuric acid (C.1.1.3.4) and 10 ml of phosphoric acid (C.1.1.3.5).

NOTE An alternative reduction method is given in Annex D.

Titrate the test solution with potassium dichromate (C.1.1.3.7) with a volumetric burette and add five drops of barium diphenylamine sulfonate (C.1.1.3.6) near the end-point.

End-point is achieved when a persistent purple colour appears. Record the volume (*V*) of potassium dichromate required for the complete titration.

SAFETY PRECAUTIONS — Collect the residual solutions obtained from titrations and treat them in accordance with Annex B of ISO 5790:1979, in order to prevent pollution of waste water.

C.1.1.5.3 Expression of results

The total iron content, C_{tot} expressed in mass fraction in %, is given by the following equation:

$$C_{tot} = \frac{V \times 11,16}{m}$$

where

V is the volume, in millilitres, of potassium dichromate required for the titration;

m is the mass, in grams, of the sample used for the test solution.

C.1.2 Determination of iron(II) (Fe(II))

C.1.2.1 General

This method applies to products with iron contents greater than a mass fraction of 0,4 %.

C.1.2.2 Principle

Iron is directly titrated with potassium dichromate solution.

C.1.2.3 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.

C.1.2.3.1 Sulfuric acid, H_2SO_4 concentrated, density $\rho = 1,84$ g/ml.

C.1.2.3.2 Phosphoric acid, H_3PO_4 concentrated, density $\rho = 1,71$ g/ml.

C.1.2.3.3 Barium diphenylamine sulfonate solution, $c(\mathrm{Ba(C_6H_5\text{-}NH\text{-}C_6H_4SO_3)_2}) = 8$ mmol/l.

C.1.2.3.4 Potassium dichromate solution, $c(\mathrm{K_2Cr_2O_7}) = 0{,}0166$ mol/l.

C.1.2.4 Apparatus

Ordinary laboratory apparatus and glassware.

C.1.2.5 Procedure

C.1.2.5.1 Test solution

In a 500 ml conical flask, pour 200 ml of water, add 10 ml of sulfuric acid (C.1.2.3.1) and 10 ml of phosphoric acid (C.1.2.3.2). Cool with water.

Pipette 100 ml from the volumetric flask in C.1.1.5.1 and transfer to the conical flask containing the acid solution.

C.1.2.5.2 Determination

Titrate the test solution with potassium dichromate (C.1.2.3.4) with a volumetric burette and add five drops of barium diphenylamine sulfonate (C.1.2.3.3) near the end-point.

End-point is achieved when a persistent purple colour appears, record the volume (V) of potassium dichromate required for the complete titration.

C.1.2.5.3 Expression of results

The iron(II) content, $C_{\mathrm{(II)}}$ expressed in mass fraction in %, is given by the following equation :

$$C_{\mathrm{(II)}} = \frac{V \times 1{,}113}{m}$$

where

V is the volume, in millilitres, of potassium dichromate required for the titration;

m is the mass, in grams, of the sample used for the test solution.

C.1.3 Determination of iron (III) (Fe (III))

The iron (III) content, $C_{\mathrm{(III)}}$ expressed in mass fraction in %, is given by the following equation:

$$C_{\mathrm{(III)}} = C_{tot} - C_{\mathrm{(II)}}$$

where

C_{tot} is the total iron content (C.1.1.5.3), expressed as mass fraction;

$C_{\mathrm{(II)}}$ is the iron (II) content (C.1.2.5.3), expressed as mass fraction.

C.2 Determination of manganese

C.2.1 General

This method is applicable to iron salts or iron solutions with manganese content greater than mass fraction of 0,05 %.

C.2.2 Principle

Iron salts are diluted in water. Manganese is determined in this diluted solution by direct injection of the solution into the flame of an atomic absorption spectrometer. Manganese is converted to the atomic state by thermal dissociation. The absorption of the atoms is measured in the light path of the FAAS at a wavelength specific to the element. The concentrations are calculated by means of a calibration curve.

C.2.3 Reagents

All reagents shall be a recognized analytical grade, water shall conform to the Grade 3 specified in EN ISO 3696 and ultra pure grade acid shall be used.

C.2.3.1 Hydrochloric acid (HCl), solution of mass fraction 30 %.

C.2.3.2 Manganese, standard stock solution, c_0 (Mn) = 1 g/l.

C.2.3.3 Manganese, intermediate standard solution, c_1 (Mn) = 100 mg/l : Pipette 10 ml of standard stock solution (C.2.3.2) into a 100 ml volumetric flask (C.2.4.1), add 3 ml of hydrochloric acid (C.2.3.1) and dilute to the mark with water.

C.2.3.4 Manganese, standard solution, c_2 (Mn) = 0,5 mg/l : Pipette 0,5 ml of intermediate standard solution (C.2.3.3) into a 100 ml volumetric flask (C.2.4.1) and dilute to the mark with water .

C.2.3.5 Manganese, standard solution, c_3 (Mn) = 1 mg/l : Pipette 1 ml of intermediate standard solution (C.2.3.3) into a 100 ml volumetric flask (C.2.4.1) and dilute to the mark with water .

C.2.3.6 Manganese, standard solution, c_4 (Mn) = 2 mg/l : Pipette 2 ml of intermediate standard solution (C.2.3.3) into a 100 ml volumetric flask (C.2.4.1) and dilute to the mark with water .

C.2.3.7 Manganese, standard solution, c_5 (Mn) = 3 mg/l : Pipette 3 ml of intermediate standard solution (C.2.3.3) into a 100 ml volumetric flask (C.2.4.1) and dilute to the mark with water .

C.2.3.8 Blank solution : Pipette 3 ml of hydrochloric acid (C.2.3.1) into a 200 ml volumetric flask (C.2.4.1) and dilute to the mark with water .

C.2.4 Apparatus

Ordinary laboratory apparatus and glassware together with the following

C.2.4.1 Volumetric flasks, 100 ml and 200 ml.

C.2.4.2 Analytical balance with an accuracy of 0,1 mg.

C.2.4.3 Flame atomic absorption spectrometer.

C.2.4.4 Electrode-less discharge or hollow cathode lamp for the determination of manganese.

C.2.5 Procedure

C.2.5.1 Test solution

See C.1.1.5.1.

C.2.5.2 Spectrometer settings

The operating parameters of the flame atomic absorption spectrometer are adjusted in accordance with the operating manual issued by the manufacturer.

The spectrometer is operated at the wavelength specific for manganese: 279,5 nm. The flame composition is the following: Air: 13,5 l/min - Acetylene: 2,0 l/min.

C.2.5.3 Determination

C.2.5.3.1 Test solution

Pipette 5 ml of the test solution (C.2.5.1) into a 100 ml volumetric flask (C.2.4.1), add 3 ml of hydrochloric acid (C.2.3.1) and dilute to the mark with water.

C.2.5.3.2 Measurement

Inject the test solution (C.2.5.3.1) directly into the flame by aspiration through the nebulizer, setting the spectrometer as described in C.2.5.2. Repeat the injection three times, record the absorbance and calculate the mean.

C.2.5.4 Calibration function

To provide the calibration function, measure the absorbance of the four standard solutions (C.2.3.7, C.2.3.6, C.2.3.5 and C.2.3.4) and the absorbance of the blank solution (C.2.3.8) respectively in the same way as the sample solutions (see C.2.5.3.2). Calculate a calibration function with the absorbance means, expressed in absorbance unit, of each solutions on vertical axis and the concentrations, expressed in milligrams per litre, on the horizontal axis.

C.2.5.5 Expression of results

The manganese concentration (C_{Mn}) in the test solution is calculated with the calibration function (C.2.5.4).

The manganese concentration of the iron salts or iron solutions (C_s) expressed in milligrams per kilogram of iron product is calculated as follows:

$$C_s = \frac{C_{Mn} \times 100 \times 200}{5 \times m} = C_{Mn} \times \frac{4000}{m}$$

where

C_{Mn} is the manganese concentration in the test solution in milligrams per litre;

m is the mass, in grams, of the sample used for the test solution.

C.3 Determination of insoluble matter

C.3.1 General

This method is applicable to the determination of insoluble matter in iron based coagulants.

The measuring range of insoluble matters is between a mass fraction of 0,002 % and 10 % .

C.3.2 Principle

The sample is dissolved with hydrochloric acid, in order to maintain the pH value below 2, and filtered through a dried 0,22 μm pore size membrane filter. The filter is washed with diluted hydrochloric acid and dried at 105 °C. The mass of material retained by the filter is determined.

C.3.3 Reagents

C.3.3.1 Water conforming to Grade 3 specified in EN ISO3696.

C.3.3.2 Hydrochloric acid solution, $c(\mathrm{HCl})$ = 0,2 mol/l.

C.3.3.3 Hydrochloric acid solution. Dissolve 5,0 ml hydrochloric acid (C.3.3.2) with 100 ml water (C.3.3.1). The pH of the solution shall be less than 2.

C.3.4 Apparatus

Ordinary laboratory apparatus and glassware together with the following

C.3.4.1 Membrane filter pore size 0,22 μm.

C.3.4.2 Desiccator with dry silica gel.

C.3.4.3 Oven**.**

C.3.5 Procedure

Dry a 0,22 μm pore size membrane filter (C.3.4.1) in an oven (C.3.4.3) for 30 min at 105 °C. Transfer the membrane filter to a desiccator with dry silica gel (C.3.4.2) and let it cool to room temperature. Determine the mass of the dried filter on a balance weighing to an accuracy of 0,001 g.

Dissolve about 30 g of the sample with 100 ml diluted hydrochloric acid (C.3.3.3). Filter the diluted sample through the weighed dried filter. Wash the filter with three 50 ml portions of diluted hydrochloric acid (C.3.3.3).

Dry the filter for 2 h at 105 °C. Cool the filter in a desiccators. Weigh the filter.

C.3.6 Calculation

The insoluble matter (l_m) as mass fraction in % is given by the following equation:

$$l_m = \frac{\left(m_2 - m_1\right) \times 100}{m_0}$$

where

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

m_1 is the mass, in grams, of the dry filter ;

m_2 is the mass, in grams, of the dry filter cake with filter.

C.3.7 Precision

Under the repeatability conditions the coefficient of variation is 18 % with 10 measurements.

C.4 Determination of free acid

C.4.1 General

This method is applicable to the determination of acidity in iron based coagulants.

The measuring range shall be between a mass fraction of 0,05 % and 10 %.

The limit of determination is a mass fraction of 0,1 %.

C.4.2 Principle

Dissolution in water. Addition of an excess of sulfuric acid in order to depolymerize the sample.

The depolymerisation is accelerated by heating.

Fluoride ions are added in excess. These form a strong complex with iron (III) ions, and thereby remove their acidic properties.

The number of hydrogen ions is determined by titration with sodium hydroxide to pH 9,0 or using phenolphthalein as an indicator.

C.4.3 Interferences

Aluminium and silica interfere with fluoride.

Silicon containing sample gives wrong results.

C.4.4 Reagents

C.4.4.1 Water conforming to Grade 3 specified in EN ISO3696.

C.4.4.2 Sodium hydroxide solution, $c(\text{NaOH}) = 0{,}2$ mol/l.

C.4.4.3 Sulfuric acid solution, $c(H_2SO_4) = 0{,}1$ mol/l.

C.4.4.4 Potassium fluoride, KF.2 H_2O.

C.4.4.5 Potassium fluoride solution, 200 g/l. Dissolve 310 g KF (C.4.4.4) with 1 000 ml water, adjust pH to 9,0.

C.4.4.6 Phenolphthalein solution, 0,5 g in 100 ml ethanol.

C.4.5 Apparatus

Ordinary laboratory apparatus and glassware together with the following

C.4.5.1 Ion meter.

C.4.6 Procedure

Pipette a 20 ml of the test solution (C.1.1.5.1) in the 200 ml volumetric flask into a 250 ml beaker. Add 25 ml of sulfuric acid (C.4.4.3) and cover with a watch-glass. Boil the sample for 5 min.

Cool to room temperature. Rinse the watch-glass with water into the beaker. Add 20 ml of KF solution (C.4.4.5) and three drops to five drops of phenolphthalein solution (C.4.4.6).

Titrate the solution with sodium hydroxide (C.4.4.2) to the appearance of a faint permanent pink colour or to pH 9,0 with ion meter (C.4.5.1).

C.4.7 Calculation

The free acid (C_a) expressed as a mass fraction of sulfuric acid in % is given by the following equation:

$$C_a = \frac{V_2C_2 - V_1C_1 \times 500 \times 98{,}3}{m_o \times 20 \times 1000 \times 2} \text{ x } 100$$

where

m_o is the mass, in grams, of the test portion;

V_1 is the volume, in millilitres, of the sodium hydroxide solution used (C.4.4.2);

C_1 is the actual concentration, expressed in moles of NaOH per litre, of this solution;

V_2 is the volume, in millilitres, of the sulfuric acid solution (C.4.4.3);

C_2 is the actual concentration, expressed in moles of H_2SO_4 per litre, of this solution.

C.5 Determination of arsenic, antimony and selenium by hydride generation atomic absorption spectrometry (AAS)

C.5.1 General

This method is suitable for the determination of low concentrations of arsenic, antimony and selenium in iron salts.

The suitable concentration ranges of this method are:

- As : 0,1 mg/kg to 0,5 mg/kg ;
- Sb : 0,1 mg/kg to 0,5 mg/kg ;
- Se : 0,1 mg/kg to 0,5 mg/kg.

For higher concentrations the sample solution shall be diluted.

C.5.2 Principle

Arsenic (As), antimony (Sb) and selenium (Se) are reduced to the elemental hydrides AsH_3, SbH_3 and SeH_4 by sodium tetrahydroborate. The gaseous hydrides are conveyed with argon gas to a heated quartz cuvette and thermally decomposed. The absorption of the atoms is measured in the light path of an atomic absorption spectrometer at a wavelength specific to the element. The concentrations are calculated by means of calibration curves.

C.5.3 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.

C.5.3.1 Hydrochloric acid (HCl) solution, mass fraction 30 %

C.5.3.2 L-ascorbic acid solution, 100 g/l.

C.5.3.3 Oxalic acid solution, 100 g/l.

C.5.3.4 Potassium iodide solution, 100 g/l.

C.5.3.5 Sulfuric acid solution, $c(H_2SO_4)$ = 1 mol/l.

C.5.3.6 Sodium tetrahydroborate solution, mass fraction 5 % of $NaBH_4$ in NaOH solution of mass fraction 1 %

C.5.3.7 Element stock solutions, c_0 (As, Sb, Se) = 1 g/l.

C.5.3.8 Standard element solutions, c_1 (As, Sb, Se) = 10 mg/l, to be prepared by dilution of C.5.3.7.

C.5.3.9 Standard element solutions, c_2 (As, Sb, Se) = 0,1 mg/l, to be prepared by dilution of C.5.3.8.

C.5.3.10 Element reference solutions, prepared by pipetting 1 ml, 2 ml, 4 ml, 8 ml and 10 ml of each of the standard element solutions (C.5.3.9) into a series of 100 ml volumetric flasks (C.5.4.3), adding 30 ml oxalic acid (C.5.3.3), 10 ml potassium iodide (C.5.3.4), 5 ml ascorbic acid (C.5.3.2) and 5 ml hydrochloric acid (C.5.3.1) for As and Sb. Then fill the volumetric flasks up to the mark with water. The concentrations of the reference solutions will be 1 µg/l, 2 µg/l, 4 µg/l, 8 µg/l and 10 µg/l.

C.5.3.11 Sample blank solution.

C.5.4 Apparatus

Ordinary laboratory apparatus and glassware together with the following

C.5.4.1 Pipettes, 5 ml, 10 ml and 20 ml.

C.5.4.2 Graduated cylinder, 50 ml.

C.5.4.3 Volumetric flasks, 100 ml.

C.5.4.4 Atomic absorption spectrometer.

C.5.4.5 Electrode-less discharge lamps for the determination of As, Sb and Se.

C.5.4.6 Hydride system consisting of a heatable quartz cuvette, a reaction unit and a control unit

C.5.4.7 Argon gas supply.

C.5.5 Procedure

C.5.5.1 Spectrometer settings

The atomic absorption spectrometer (C.5.4.5) and the hydride generator unit (C.5.4.4) are adjusted in accordance with the operating manual issued by the manufacturer. The spectrometer is operating at the wavelength for each element:

- As : 193,7 nm ;
- Sb : 217,6 nm ;
- Se : 196,0 nm.

The quartz cuvette is heated to 900 °C.

C.5.5.2 Measurement of arsenic and antimony

Take 20 ml of the sample solution (5.2.3.1.5) with a pipette (C.5.4.1) and transfer to a 100 ml volumetric flask (C.5.4.3). Add with a graduated cylinder (C.5.4.2) 30 ml oxalic acid (C.5.3.3), 10 ml potassium iodide (C.5.3.4), 5 ml ascorbic acid (C.5.3.2) and 5 ml hydrochloric acid (C.5.3.1), then make up to the mark with water. The prepared solution shall be allowed to stand for 3 h to ensure complete reaction. Then transfer 5 ml of the solution with a pipette (C.5.4.1) to the reduction vessel, add 10 ml sulfuric acid (C.5.3.5) and start the hydride control unit. The solution is reduced with $NaBH_4$ and immediately AsH_3 and SbH_3 are transferred with the argon gas (C.5.4.7) to the 900 °C heated quartz cuvette. Measure the absorption of arsenic with an arsenic specific lamp (C.5.4.5) at wavelength 193,7 nm. Measure the absorption of antimony with an antimony specific lamp (C.5.4.5) at wavelength 217,6 nm.

C.5.5.3 Measurement of selenium

Transfer 20 ml of the sample solution (5.2.3.1.5) with a pipette (C.5.4.1) to a 100 ml volumetric flask. Add 30 ml oxalic acid (C.5.3.3) and 5 ml hydrochloric acid (C.5.3.1), then make up to the mark with water. Transfer 5 ml of the solution with a pipette to the reduction vessel, add 10 ml sulfuric acid (C.5.3.5) and start the hydride control unit. The solution is reduced with $NaBH_4$ and immediately SeH_4 is transferred with the argon gas (C.5.4.7) to the 900 °C heated quartz cuvette. Measure the absorption of selenium with a selenium specific lamp (C.5.4.5) at wavelength 196,0 nm.

C.5.5.4 Calculation and expression of results

The As, Sb and Se concentrations C_e in the sample solution expressed in micrograms per litre are read out from the calibration function or regression function:

$$C_\mathrm{e} = \frac{A_\mathrm{e} - A_B}{S}$$

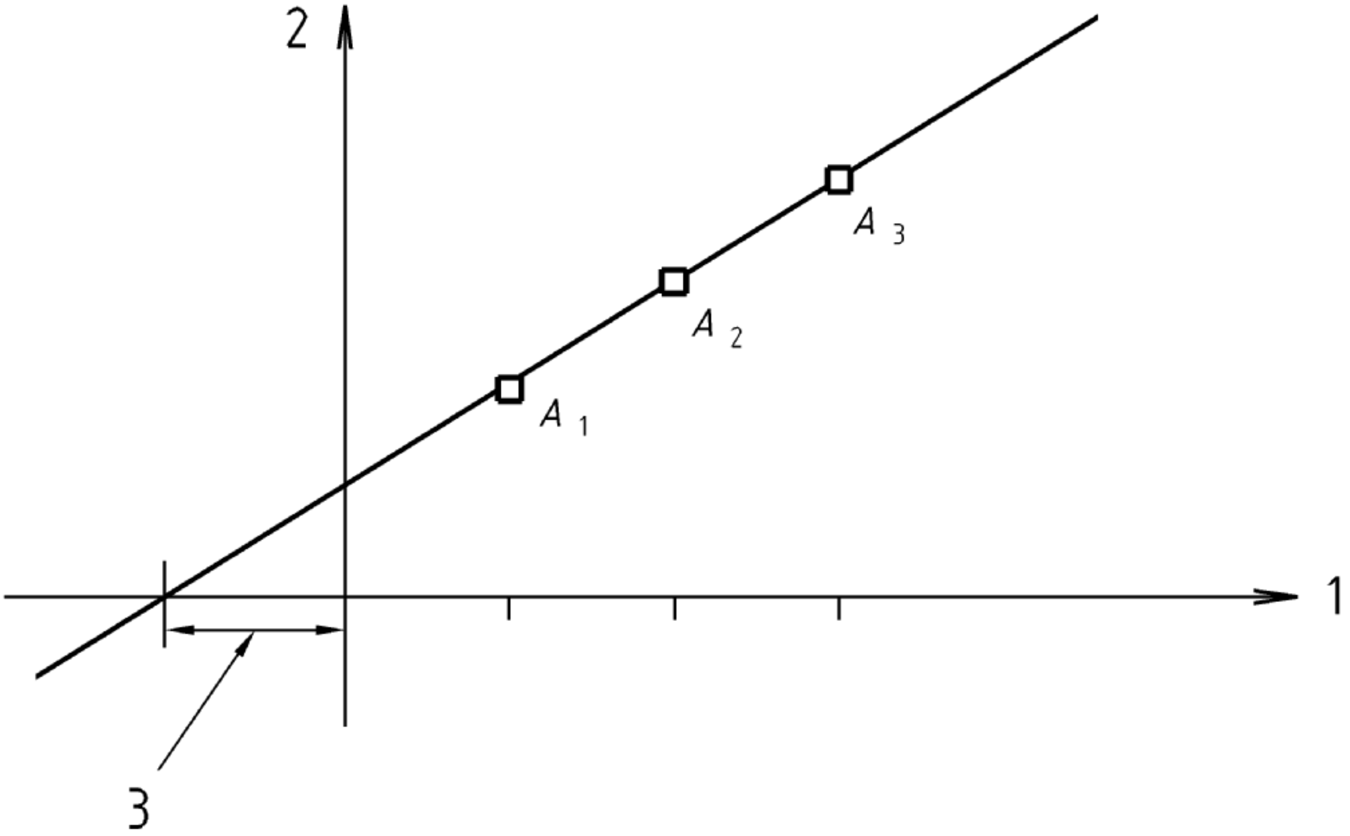
where

A_e is the absorbance of the sample solution;

A_B is the absorbance of the blank solution;

S is the slope of the calibration line in litres per microgram.

The calculation by the standard addition method can be carried as shown in Figure C.1:



Key

1	Concentration of added standard in micrograms per litre
2	Absorbance A
3	Concentration in the sample solution in micrograms per litre
A1, A2, A3,	Spiking

Figure C.1 – Example for the calculation of metal concentration in the sample solution by standard addition method

The concentration in the sample solution is the intersection of the extrapolated calibration curve of the spiked concentration versus absorbance and the horizontal axis on the left side.

The As, Sb and Se concentration (C_S) of the iron salts in milligrams per kilogram iron product are calculated using the following equation:

$$C_s = \frac{C_e \times 100 \times 200}{20 \times 1000 \times 20} = \frac{C_e}{20}$$

where

C_e is the element concentration in micrograms per litre in the sample solution.

NOTE The following equation gives the relation between the concentration C_f in milligrams per kilogram of Fe (III) and the concentration C_s in milligrams per kilogram of product: $C_f = C_s \times 100 / C_{(III)}$

C.6 Determination of mercury by cold vapour atomic absorption spectrometry (AAS)

C.6.1 General

This method is suitable for the determination of mercury in iron salts.

The suitable concentration range of this method is:

- Hg : 0,01 mg/kg to 0,1 mg/kg

For higher concentrations the sample solution shall be diluted.

C.6.2 Principle

Divalent mercury in the sample solution (5.2.3.1.5) is reduced to the element by tin (II) chloride or sodium tetrahydroborate solutions. Mercury is stripped from this solution in an inert gas stream and converted to the amalgam on a gold/platinum gauze for the purpose of enrichment. Mercury is released again by rapidly heating the absorber and conveyed to a quartz cuvette. The absorption of the mercury atoms is measured in a light path of an atomic absorption spectrometer at a wavelength specific to mercury (253,7 nm). The concentration is calculated by means of a calibration curve.

C.6.3 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.

C.6.3.1 Hydrochloric acid (HCl) solution, mass fraction 30 %.

C.6.3.2 Sulfuric acid solution, $c(H_2SO_4)$ = 1 mol/l.

C.6.3.3 Tin (II) chloride solution, mass fraction 10 % $SnCl_2$ in HCl solution of mass fraction of 5 %.

C.6.3.4 Stabilizing solution (0,5 g $KMnO_4$ in 100 ml of water).

C.6.3.5 Mercury stock solution, c_0 (Hg) = 1 g/l.

C.6.3.6 Standard mercury solution, c_1 (Hg) = 10 mg/l to be prepared by dilution of C.6.3.5.

C.6.3.7 Standard mercury solution, c_2 (Hg) = 0,1 mg/l, to be prepared by dilution of C.6.3.6.

C.6.3.8 Mercury reference solution, to be prepared by pipetting 1 ml, 2 ml, 4 ml, 8 ml and 10 ml of the standard solution (C.6.3.7) into a series of 100 ml volumetric flasks (C.6.4.2), adding 1 ml of stabilizing solution (C.6.3.4), 5 ml of hydrochloric acid (C.6.3.1), and making up to the mark with water. The reference solutions contain 1 µg/l, 2 µg/l, 4 µg/l, 8 µg/l and 10 µg/l mercury.

C.6.3.9 Sample blank solution.

C.6.4 Apparatus

Ordinary laboratory apparatus and glassware together with the following

C.6.4.1 Pipettes, 1 ml, 5 ml and 10 ml.

C.6.4.2 Volumetric flasks, 100 ml.

C.6.4.3 Atomic absorption spectrometer.

C.6.4.4 Electrode-less discharge lamp for the determination of mercury.

C.6.4.5 Reduction system consisting of a reaction unit with tin (II) chloride, a quartz cuvette and a control unit.

C.6.4.6 Argon gas supply.

C.6.4.7 Attachment for the amalgam technique.

C.6.5 Procedure

C.6.5.1 Spectrometer settings

The atomic absorption spectrometer (C.6.4.3) and the reduction unit (C.6.4.5) are adjusted in accordance with the operating manual issued by the manufacturer. The spectrometer is operated at the wavelength 253,7 nm specific for mercury. The quartz cuvette is heated to 200 °C.

C.6.5.2 Measurement of mercury

Transfer 5 ml of the sample solution (5.2.3.1.5) with a pipette (C.6.4.1) to the reduction vessel (C.6.4.5). Add 10 ml sulfuric acid (C.6.3.2) and 1 ml stabilizing solution (C.6.3.4). The reaction with tin(II) chloride is started from the control unit and the mercury vapour is enriched at the gold / platinum gauze (C.6.4.7). After rapidly heating the absorber, mercury is transferred with the argon gas (C.6.4.6) to the 200 °C heated quartz cuvette. Measure and record the absorption of mercury with a mercury specific lamp (C.6.4.4) at wavelength 253,7 nm.

C.6.5.3 Calibration curve

To provide the calibration curve measure the blank solution and at least five reference solutions (C.6.3.8) in the same way as the sample solution, so that 5 ml of the reference solutions are also pipetted in the reduction vessel. The further procedure is the same as in C.6.5.2. The standard addition method is also possible to avoid matrix effects.

C.6.5.4 Calculation

The mercury concentration (C_{Hg}) in the sample solution is read out from the calibration curve and the calculation is the same as in C.5.5.4.

The mercury concentration (C_s) of the iron salts in milligrams per kilogram of iron product is calculated using the following equation:

$$C_s = \frac{C_{Hg} \times 200}{1000 \times 20} = \frac{C_{Hg}}{100}$$

where

C_{Hg} is the mercury concentration in micrograms per litre in the same sample solution.

NOTE The following equation gives the relation between the concentration C_f in milligrams per kilogram of Fe (III) and the concentration C_s in milligrams per kilogram of product: $C_f = C_s \times 100 / C_{(III)}$

C.7 Determination of cadmium, chromium, nickel and lead by graphite furnace atomic absorption spectrometry (AAS)

C.7.1 General

This method is suitable for the determination of low concentrations of cadmium, chromium, nickel and lead in iron salts.

The suitable concentration ranges of this method are:

- Cd : 0,1 mg/kg to 1,0 mg/kg;
- Cr : 1,0 mg/kg to 10 mg/kg;
- Ni : 1,0 mg/kg to 10 mg/kg;
- Pb : 1,0 mg/kg to 10 mg/kg.

NOTE For higher concentrations the sample solution should be diluted or inductively coupled plasma optical emission spectrometry (ICP/OES) and flame atomic absorption spectrometry (FAAS) can be used.

C.7.2 Principle

Cadmium, chromium, nickel and lead are converted to the atomic state by thermal dissociation in an electrically-heated graphite tube of an atomic absorption spectrometer. As the temperature is raised in steps, the stages of drying, thermal decomposition of the matrix and thermal cleavage into free atoms are passed through in that order. The absorption of the atoms is measured in the light path of the atomic absorption spectrometer at a wavelength specific to the element. Interferences due to background absorption resulting from high salt concentrations can be suppressed with a background correction system such as the Zeeman effect. The concentrations are calculated by means of calibration curves.

C.7.3 Reagents

Only reagents of a recognized analytical grade, water conform to the Grade 3 specified in EN ISO 3696 and high-purity grade hydrochloric acid shall be used.

C.7.3.1 Hydrochloric acid (HCl) solution, mass fraction 30 %.

C.7.3.2 Element stock solutions, c_0 (Cd, Cr, Ni, Pb) = 1 g/l.

C.7.3.3 Standard element solutions, c_1 (Cd, Cr, Ni, Pb) = 10 mg/l, to be prepared by dilution of C.7.3.2.

C.7.3.4 Standard element solutions, c_2 (Cr, Ni, Pb) = 1 mg/l and c_3 (Cd) = 0,1 mg/l, to be prepared by dilution of C.7.3.3.

C.7.3.5 Element reference solutions, to be prepared by pipetting 1ml, 2 ml, 4 ml, 8 ml and 10 ml of each of the standard solutions (C.7.3.4) into a series of 100 ml volumetric flasks (C.7.4.2), adding 3 ml hydrochloric acid (C.7.3.1) and filling up to the mark with water. The chromium, nickel and lead concentration of the reference solutions will be 10 µg/l, 20 µg/l, 40 µg/l, 80 µg/l and 100 µg/l. The cadmium concentration of the reference solutions will be 1 µg/l, 2 µg/l , 4 µg/l, 8 µg/l and 10 µg/l.

C.7.3.6 Sample blank solution.

C.7.4 Apparatus

Ordinary laboratory apparatus and glassware together with the following:

C.7.4.1 Pipettes, 1 ml, 5 ml and 10 ml.

C.7.4.2 Volumetric flasks, 100 ml.

C.7.4.3 Atomic absorption spectrometer equipped with graphite furnace and temperature controller.

C.7.4.4 Electrode-less discharge or hollow cathode lamps for the determination of cadmium, chromium, nickel and lead.

C.7.4.5 Background compensator (e.g. Zeeman).

C.7.4.6 Auto-sampler, capable of being adjusted to pipetting volumes from 5 µl to 20 µl.

C.7.5 Procedure

C.7.5.1 Spectrometer settings

Adjust in accordance with the operating manual issued by the manufacturer the operating parameters of the graphite furnace atomic absorption spectrometer (C.7.4.3). The spectrometer is operated at the wavelength specific for each element:

- Cd : 228,8 nm
- Cr : 357,9 nm
- Ni : 232,0 nm
- Pb : 283,3 nm

A suitable background correction (see C.7.4.5) is highly recommended. Optimized heat programs are used for each atomization of Cd, Cr, Ni and Pb, an example is given in C.7.5.2.

C.7.5.2 Measurement of cadmium, chromium, nickel and lead

Transfer 10 ml of the sample solution (5.2.3.1.5) with a pipette (C.7.4.1) to a 100 ml volumetric flask (C.7.4.2), add 1 ml of hydrochloric acid (C.7.3.1), and make up with water. Inject 10 µl of this sample solution in the graphite tube by means of an auto-sampler (C.7.4.6). Then start the heat programme (e.g. see Table C.1).

Table C.1 Heat programme of the spectrometer

Cd, Pb	Ramp, in s	Hold, in s	Temperature in °C
Preheating	5	10	90
Drying	20	10	130
Ashing	30	10	850
Atomisation	0	3	1 800
Cleaning	1	4	2 650
Cr, Ni			
Preheating	5	10	90
Drying	20	10	130
Ashing	30	10	1 400
Atomisation	0	4	2 500
Cleaning	1	4	2 650

Carry out the measurements with gas-stop mode during the atomization phase. Use the L'vov platform for cadmium, nickel and lead. Wall atomization is preferred for chromium. Measure the absorption using the specific lamp (C.7.4.4) of the atomized elements cadmium, chromium, nickel and lead at the specific wavelength given in C.7.5.1.

C.7.5.3 Calibration function

To provide the calibration curve measure the blank solution and at least five reference solutions (C.7.3.5), in the same way as the sample solutions, so that 10 µl of the reference solutions are also injected in the graphite tube. The further procedure is the same as in C.7.5.2, the standard addition method is strongly recommended to avoid matrix effects.

C.7.5.4 Calculation

The cadmium, chromium, nickel and lead concentration in the sample solution are read out from the calibration curve and the calculation is the same as in C.5.5.4.

The cadmium, chromium, nickel and lead concentrations (C_s) for the iron salts in milligrams per kilogram of iron product are calculated using the following equation:

$$C_s = \frac{C_e \times 100 \times 200}{10 \times 1000 \times 20} = \frac{C_e}{10}$$

where

C_e is the element concentration in the sample solution in micrograms per litre.

NOTE 1 The following equation gives the relation between the concentration C_f in milligrams per kilogram of Fe (III) and the concentration C_s in milligrams per kilogram of product: $C_f = C_s$ x 100/ $C_{(III)}$

NOTE 2 An alternative method for determination of cadmium, chromium, nickel and lead with the ICP optical emission spectrometry is described in Annex E.

Annex D
(informative)

Reduction of Fe (III) on a silver column

D.1 General

This method is an alternative reduction method to use instead of the method described in C.1.1.5.2.

D.2 Principle

The Fe (III) is reduced to Fe (II) by means of silver powder.

D.3 Reagents

D.3.1 Silver nitrate

D.3.2 Nitric acid solution, mass fraction 60 %.

D.3.3 Sulfuric acid, solution $c(H_2SO_4) = 3$ mol/l

D.3.4 Hydrochloric acid solution, $c(HCl) = 1$ mol/l

D.3.5 Sheet of copper metal.

D.3.6 Sodium hydrogen carbonate ($NaHCO_3$), saturated solution

D.3.7 Water conforming to Grade 3 specified in EN ISO3696.

D.4 Apparatus

Ordinary laboratory apparatus and glassware together with the following:

D.4.1 Cylindrical glass tube with a stopcock at the bottom, about 20 mm inside diameter and 20 cm length

D.4.2 Beaker, 800 ml

D.4.3 Glass wool.

D.5 Procedure

D.5.1 Preparation of the silver powder

Dissolve into a 800 ml beaker (D.4.2) 200 g silver nitrate (D.3.1) with 600 ml distilled water (D.3.7) and add a few drops of nitric acid (D.3.2). Put a sheet of copper metal (D.3.5) in this solution in order to precipitate metallic silver. The silver powder is separated from the sheet of copper and the solution. Then heat the silver powder in sulfuric acid (D.3.3) for 10 min, filter, wash with hot water and store in hydrochloric acid (D.3.4).

D.5.2 Reduction of Fe (III)

Fill the cylindrical tube (D.4.1) with some glass wool (D.4.3) at the bottom and then with the silver powder. Introduce 10 ml of the diluted test solution of Fe (III) into the silver column and discharge dropwise from the bottom to a conical flask which contains 5 ml saturated sodium hydrogen carbonate solution (D.3.6). Add 100 ml of hydrochloric acid (D.3.4) to the silver column. Then titrate the reduced iron solution with potassium dichromate as given in C.1.1.5.2.

Annex E
(informative)

Determination of cadmium, chromium, nickel and lead (inductively coupled plasma optical emission spectrometry (ICP/OES))

E.1 General

This method is suitable for the determination of cadmium, chromium, nickel and lead in iron salts.

The suitable concentration ranges of this method are:

- Cd : 1 mg/kg to 50 mg/kg ;
- Cr : 1 mg/kg to 50 mg/kg ;
- Ni : 1 mg/kg to 50 mg/kg ;
- Pb : 1 mg/kg to 50 mg/kg.

For higher concentrations the sample solution shall be diluted.

E.2 Principle

The basis of this method is the measurement of atomic emission by an optical spectroscope technique. Sample solutions are nebulized and the aerosol, that is produced with argon gas, is transported to the plasma torch where excitation occurs. Characteristic atomic line emission spectra are produced by an inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes. The concentrations are calculated by means of calibration curves.

E.3 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.

E.3.1 Hydrochloric acid (HCl), solution mass fraction 30 %.

E.3.2 Element stock solutions, c_0 (Cd, Cr, Ni, Pb) = 1 g/l.

E.3.3 Multi-element standard solution, to be prepared by pipetting 10 ml of each of the element stock solutions (E.3.2) to one 1 000 ml volumetric flask, adding 10 ml hydrochloric acid (E.3.1) and filling up to the mark with water. The concentration c_1 of the multi-element standard solution will be Cd: 10 mg/l, Cr: 10 mg/l, Ni: 10 mg/l and Pb: 10 mg/l.

E.3.4 Multi-element reference solutions, to be prepared by pipetting 1 ml, 5 ml, 10 ml, 20 ml and 50 ml of the multi-element standard solution (E.3.3) into a series of 100 ml volumetric flasks, adding 25 ml hydrochloric acid (E.3.1) and filling up with water. The Cd, Cr, Ni and Pb concentrations of the multi-element reference solutions will be 0,1 mg/l, 0,5 mg/l, 1 mg/l, 2 mg/l and 5 mg/l.

E.3.5 Sample blank solution.

E.4 Apparatus

Ordinary laboratory apparatus and glassware together with the following:

E.4.1 ICP optical emission spectrometer.

E.4.2 Argon gas supply.

E.5 Procedure

E.5.1 Spectrometer settings

Adjust the operating parameters of the ICP optical emission spectrometer in accordance with the operating manual issued by the manufacturer. Sensitivity, instrumental detection limit, precision, linear dynamic range and interference effects shall be investigated and established for each individual analyte line on that particular instrument. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions used satisfy the analytical requirements and to maintain quality control data confirming instrument performance and analytical results.

A background correction procedure is highly recommended. The analytical lines at wavelength:

- Cd : 228,80 nm
- Cr : 357,87 nm
- Ni : 231,60 nm
- Pb : 220,35 nm

are suitable for the determination of these elements in an iron matrix.

E.5.2 Calibration, measurement and calculation of the elements cadmium, chromium, nickel and lead

An analytical programme is designed to calibrate and measure cadmium, chromium, nickel and lead in the iron salt solution. To provide the calibration curves measure the blank solution (E.3.5) and the five multi-element reference solutions (E.3.4). Subtract the emission intensities from the blank solution from the reference solutions. These corrected emission intensities versus the concentrations are the calibration functions which are calculated by means of regression analysis.

Spray the sample solution (5.2.3.1.5) with argon gas (E.4.2) in a well adjusted and calibrated ICP-optical emission spectrometer (E.4.1). Run the analytical programme and record the results.

The cadmium, chromium, nickel and lead concentrations (C_s) of the iron salts in milligrams per kilogram iron product are calculated using the following equation:

$$C_s = C_e \times 10$$

where

C_e is the element concentration in milligrams per litre in the sample solution.

NOTE The following equation gives the relation between the concentration C_f in milligrams per kilogram of Fe (III) and the concentration C_s in milligrams per kilogram of product: $C_f = C_s \times 100/ C_{(III)}$

Bibliography

[1] 98/83/EC: *Council Directive of 3rd 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*

BSI — British Standards Institution

BSI is the independent national body responsible for preparing British Standards. It presents the UK view on standards in Europe and at the international level. It is incorporated by Royal Charter.

Revisions

British Standards are updated by amendment or revision. Users of British Standards should make sure that they possess the latest amendments or editions.

It is the constant aim of BSI to improve the quality of our products and services. We would be grateful if anyone finding an inaccuracy or ambiguity while using this British Standard would inform the Secretary of the technical committee responsible, the identity of which can be found on the inside front cover.
Tel: +44 (0)20 8996 9000. Fax: +44 (0)20 8996 7400.

BSI offers members an individual updating service called PLUS which ensures that subscribers automatically receive the latest editions of standards.

Buying standards

Orders for all BSI, international and foreign standards publications should be addressed to Customer Services. Tel: +44 (0)20 8996 9001.
Fax: +44 (0)20 8996 7001. Email: orders@bsi-global.com. Standards are also available from the BSI website at http://www.bsi-global.com.

In response to orders for international standards, it is BSI policy to supply the BSI implementation of those that have been published as British Standards, unless otherwise requested.

Information on standards

BSI provides a wide range of information on national, European and international standards through its Library and its Technical Help to Exporters Service. Various BSI electronic information services are also available which give details on all its products and services. Contact the Information Centre.
Tel: +44 (0)20 8996 7111. Fax: +44 (0)20 8996 7048. Email: info@bsi-global.com.

Subscribing members of BSI are kept up to date with standards developments and receive substantial discounts on the purchase price of standards. For details of these and other benefits contact Membership Administration.
Tel: +44 (0)20 8996 7002. Fax: +44 (0)20 8996 7001.
Email: membership@bsi-global.com.

Information regarding online access to British Standards via British Standards Online can be found at http://www.bsi-global.com/bsonline.

Further information about BSI is available on the BSI website at http://www.bsi-global.com.

Copyright

This does not preclude the free use, in the course of implementing the standard, of necessary details such as symbols, and size, type or grade designations. If these details are to be used for any other purpose than implementation then the prior written permission of BSI must be obtained.

Details and advice can be obtained from the Copyright & Licensing Manager.
Tel: +44 (0)20 8996 7070. Fax: +44 (0)20 8996 7553.
Email: copyright@bsi-global.com.

BSI
389 Chiswick High Road
London
W4 4AL