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Winter service equipment and products — De-icing agents -

Part 1: Sodium chloride — Requirements and test methods

National foreword

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

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

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Contents

Page

European foreword 4

Introduction 5

1 Scope 6

2 Normative references 6

3 Terms and definitions 7

4 Requirements for sodium chloride 7
4.1 Chemical Requirements 7
4.2 Moisture 7
4.3 Sieve analysis 8
4.4 General requirements 8
4.5 Marking and product description 9

5 Requirements for brine 10
5.1 Chemical Requirements 10
5.2 General requirements 10
5.3 Marking and product description 11

6 Sampling 12

7 Test methods 12
7.1 General 12
7.2 NaCl 12
7.2.1 General 12
7.2.2 Direct method 12
7.2.3 Indirect method 12
7.3 Sulfate 12
7.4 Moisture 12
7.5 Sieve analysis 13
7.6 Anti-caking agent 13
7.7 Heavy metals, etc 13
7.8 Hydrocarbons 13
7.9 TOC (total organic carbon) 13
7.10 pH 13
7.11 Water insoluble matter 13
7.12 Bulk density 13
7.13 Density 13

Annex A (normative) **Product descriptions** 14
A.1 Product description for sodium chloride 14
A.2 Product description for brine 17

Annex B (normative) **Sampling** 19
B.1 Solid sodium chloride 19
B.1.1 Package shipments 19
B.1.2 Bulk shipments 19
B.2 Brine 19
B.3 Labelling and distribution of samples 19
B.4 Sampling report 19

Annex C (normative) **Analytical methods** 21
C.1 Determination of sodium chloride (potentiometric method) 21
C.1.1 Scope and field of application 21
C.1.2 Principle 21
C.1.3 Reagents 21
C.1.4 Apparatus 22
C.1.5 Sampling and samples 22
C.1.6 Procedure 22
C.1.7 Expression of results 23
C.2 Determination of aluminium, arsenic, cadmium, calcium, chromium, cobalt, copper, lead, magnesium, nickel, sulfate, zinc (inductively coupled plasma optical emission spectrometry (ICP/OES)) 24
C.2.1 General 24
C.2.2 Principle 25
C.2.3 Reagents 25
C.2.4 Apparatus (informative) 25
C.2.5 Sampling and samples 26
C.2.6 Procedure 26
C.2.7 Expression of results 29
C.2.8 Remarks 32
C.3 Determination of total mercury (cold vapour atomic absorption spectrometry) 32
C.3.1 General 32
C.3.2 Principle 33
C.3.3 Reagents 33
C.3.4 Apparatus (informative) 34
C.3.5 Procedure 35
C.3.6 Expression of results 36
C.4 Determination of anti-caking agent (molecular absorption spectrometry) 38
C.4.1 General 38
C.4.2 Principle 39
C.4.3 Reagents 39
C.4.4 Apparatus 39
C.4.5 Sampling and samples 40
C.4.6 Procedure 40
C.4.7 Expression of results 41

Bibliography 43

European foreword

This document (EN 16811-1:2016) has been prepared by Technical Committee CEN/TC 337 “Road operation equipment and products”, 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 February 2017, and conflicting national standards shall be withdrawn at the latest by February 2017.

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.

EN 16811, *Winter service equipment and products — De-icing agents*, is currently composed with the following parts:

— *Part 1: Sodium chloride — Requirements and test methods*;

— *Part 2: Calcium chloride and Magnesium chloride — Requirements and test methods*;

— *Part 3: Other solid and liquid de-icing agents — Requirements and test methods* [CEN/TS].

According to the CEN-CENELEC Internal Regulations, the national standards organisations 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

De-icing agents are important for the winter maintenance of roads. They can prevent and, in addition to it, eliminate slippery conditions.

The standard describes the requirements for de-icing salt and their testing methods. The requirements are different for using, storage and type of distribution (spreading and spraying). These need different properties.

The aim of this standard is an easy description of the product specifications for tenders and other purchasing procedures.

1 Scope

This European Standard specifies the essential requirements of sodium chloride (salt) for spreading on roads for winter maintenance and includes tests of these requirements. The requirements are specified for salt in crystallized form and for salt in solution (brine), which is delivered to the customer.

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 932-1, *Tests for general properties of aggregates — Part 1: Methods for sampling*

EN 1235, *Solid fertilizers — Test sieving (ISO 8397:1988 modified)*

EN 1236, *Fertilizers — Determination of bulk density (loose) (ISO 3944:1992 modified)*

EN 1484, *Water analysis — Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC)*

EN 15144, *Winter maintenance equipment — Terminology — Terms for winter maintenance*

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

EN ISO 9377-2, *Water quality — Determination of hydrocarbon oil index — Part 2: Method using solvent extraction and gas chromatography (ISO 9377-2)*

EN ISO 10523, *Water quality — Determination of pH (ISO 10523)*

ISO 565, *Test sieves — Metal wire cloth, perforated metal plate and electroformed sheet — Nominal sizes of openings*

ISO 649-2, *Laboratory glassware — Density hydrometers for general purposes — Part 2: Test methods and use*

ISO 758, *Liquid chemical products for industrial use — Determination of density at 20 degrees C*

ISO 2479, *Sodium chloride for industrial use — Determination of matter insoluble in water or in acid and preparation of principal solutions for other determinations*

ISO 2480, *Sodium chloride for industrial use — Determination of sulphate content — Barium sulphate gravimetric method*

ISO 2482, *Sodium chloride for industrial use — Determination of calcium and magnesium contents — EDTA complexometric methods*

ISO 2483, *Sodium chloride for industrial use — Determination of the loss of mass at 110 degrees C*

ISO 2591-1, *Test sieving — Part 1: Methods using test sieves of woven wire cloth and perforated metal plate*

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

3 Terms and definitions

For the purposes of this document, the terms and definitions given in EN 15144 and the following apply.

3.1
sodium chloride
salt
NaCl,
substance which is produced as rock salt, as solar salt and as vacuum salt

Note 1 to entry: Rock salt is extracted by mechanical mining of natural salt beds. Solar salt is produced by solar evaporation of sea water or brine from salt deposits and by extraction from salt lakes. Solar salt from sea water is named as sea salt. Vacuum salt is prepared by the evaporation of water from brine. Used salt (waste salt) comes from secondary aluminium smelters, from fishery industry, from leather industry, etc. REACH [4] registered synthetic by-product salts derive from chemical reactions (e.g. from gas cleaning in waste incinerators).

3.2
brine
solution of sodium chloride in water

Note 1 to entry: Brine is available as natural brine from underground deposits and from solar salt/sea salt production, and as solution of rock salt, solar salt/sea salt or vacuum salt in water. Further sources are used salts and by-product salts.

4 Requirements for sodium chloride

4.1 Chemical Requirements

The sodium chloride shall conform to the requirements specified in Table 1:

Table 1 — Chemical requirements for sodium chloride

Parameter	**Limit** Weight %
NaCl	min. 90[a]
Sulfate	max. 3[a]
NOTE 1 NaCl is determined as total chloride content and expressed as NaCl (weight % in the dry product). NOTE 2 Sulfate is determined as water soluble sulfate and expressed as SO_4 (weight % in the dry product).	
[a] The NaCI and sulfate content of salt can be specified within these limits by the purchaser depending on his individual needs. It can also be specified within these limits at the national level (National Annexes to this European Standard).	

4.2 Moisture

The sodium chloride shall conform to the requirements specified in Table 2.

Table 2 — Moisture limits for sodium chloride

	Limit Weight %		
	Dry salt	Semi-dry salt	Wet salt
Moisture	max. 0,6	max. 2,0	max. 6,0
For storage in silos dry salt is recommended. For rock salt a minimum moisture content of 0,2 weight % is recommended (to avoid dust during stocking and salt usage).			
NOTE 1 For undried vacuum salt the limit is max. 3,5 weight %. NOTE 2 The moisture contents are expressed as H_2O in the delivered undried salts.			

4.3 Sieve analysis

The sodium chloride shall conform to the requirements specified in Table 3.

Table 3 — Sieve analysis for sodium chloride

Weight % passing test sieve			
Grade EF (extra fine salt)	Grade F (fine salt)	Grade M (medium salt)	Grade C (coarse salt)
0,125 mm max. 5 0,8 mm 25 to 100 2,0 mm 100 (2 weight % production related tolerance with max. 3 mm grain size)	0,125 mm max. 5 0,8 mm 10 to 40 1,6 mm 30 to 80 3,15 mm 90 to 100 5,0 mm 100 (2 weight % production related tolerance with max. 8 mm grain size)	0,125 mm max. 7 0,8 mm 5 to 35 1,6 mm 10 to 60 3,15 mm 45 to 90 6,3 mm 100 (2 weight % production related tolerance with max. 8 mm grain size)	0,8 mm max. 35 3,15 mm 30 to 80 6,3 mm 75 to 95 10 mm 100 (2 weight % production related tolerance with max. 12 mm grain size)

4.4 General requirements

The sodium chloride shall arrive at purchaser’s delivery point in a free-flowing and usable condition and shall conform to the requirements specified in Table 4.

Table 4 — General requirements for sodium chloride

Parameter	Limit	Unit
Anti-caking agent (sodium-, potassium-, or calcium ferrocyanide)	min. 3 to max. 125 (expressed as $Fe(CN)_6$-anion)	mg/kg
pH of 10 weight % solution	between 5 and 10	
Al (Aluminium)	≤ 50	mg/kg
As (Arsenic)	≤ 2,5	mg/kg
Cd (Cadmium)	≤ 2	mg/kg
Co (Cobalt)	≤ 2	mg/kg
Cr (Chromium)	≤ 5	mg/kg
Cu (Copper)	≤ 5	mg/kg
Hg (Mercury)	≤ 0,5	mg/kg
Ni (Nickel)	≤ 5	mg/kg
Pb (Lead)	≤ 5	mg/kg
Zn (Zinc)	≤ 20	mg/kg
Hydrocarbons	≤ 100	mg/kg

NOTE 1 Other anti-caking agents are allowed if they have the same performance as the ferrocyanides.

NOTE 2 The limits for Al (Aluminium) and hydrocarbons are foreseen for by-product salts and waste salts. There is no need to determine these parameters in natural based salts (rock salt, solar salt, vacuum salt).

NOTE 3 The determination of heavy metals is performed in a solution with pH 4 (except mercury).

NOTE 4 The parameters stated as mg/kg of dry product.

For salt which is not of natural origin the supplier shall supply the content of total organic carbon (TOC) for the evaluation of the environmental impact.

4.5 Marking and product description

The sodium chloride shall be delivered in bulk lots, or in bags or other containers acceptable to the purchaser. The following information shall be marked on the salt packaging or on associated documents:

a) the name and address of the producer or supplier;

b) the words “Salt for winter maintenance”;

c) sieve analysis grade (extra fine, fine, medium or coarse salt);

d) moisture class (dry, semi-dry or wet salt);

e) the origin of salt (rock salt, solar salt/sea salt, vacuum salt, used salt or by-product salt);

f) the net weight;

g) the number of this European Standard.

In tendering processes the offers shall include a product description which is dated not longer than 12 months before the date of the offer. The supplier shall supply the bulk density (loose) for information purposes (see A.1).

All information shall be given in the languages of the countries of destination.

5 Requirements for brine

5.1 Chemical Requirements

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

Table 5 — Chemical requirements for brine

Parameter	**Limit** Weight %
NaCl	18 to 26
Sulfate	max. 0,6[a]
Water insoluble matter	max. 0,03[b]
The concentration of brine shall be specified by the purchaser. Typical concentrations vary from 18 weight % to 26 weight %.	
NOTE 1 NaCl is determined as total chloride content and expressed as NaCl. NOTE 2 Sulfate expressed as SO_4 and measured in a 10 weight % brine.	
[a] For sulfate a lower limit can be defined at the national level. [b] 10 l of brine shall pass a test sieve (size 0,5 mm) without water insoluble residues after washing with water on the sieve.	

5.2 General requirements

The brine shall conform to the requirements in Table 6.

Table 6 — General requirements for brine

Parameter	Limit	Unit
pH of 10 weight % solution	between 5 and 10	
Al (Aluminium)	≤ 50	mg/kg
As (Arsenic)	≤ 2,5	mg/kg
Cd (Cadmium)	≤ 2	mg/kg
Co (Cobalt)	≤ 2	mg/kg
Cr (Chromium)	≤ 5	mg/kg
Cu (Copper)	≤ 5	mg/kg
Hg (Mercury)	≤ 0,5	mg/kg
Ni (Nickel)	≤ 5	mg/kg
Pb (Lead)	≤ 5	mg/kg
Zinc (Zn)	≤ 20	mg/kg
Hydrocarbons	≤ 100	mg/kg

NOTE 1 The limits for Al (Aluminium) and hydrocarbons are foreseen for brine which is not of natural origin. There is no need to determine these parameters in brines which are based on natural salts (rock salt, solar salt, vacuum salt).

NOTE 2 The determination of heavy metals is performed in brine with pH 4 (except mercury).

NOTE 3 The parameters stated as mg/kg of dry product.

For brine which is derived from chemical reactions or made from used salts and by-products salts the supplier shall supply the content of total organic carbon (TOC) for the evaluation of the environmental impact.

5.3 Marking and product description

The brine shall be delivered in containers acceptable to the purchaser. The following information shall be marked on delivery documents:

a) the name and address of the producer or supplier;

b) the words “Brine for winter maintenance”;

c) the NaCl concentration (weight %);

d) the net weight;

e) the number of this European Standard.

In tendering processes the offers shall include a product description which is dated not longer than 12 months before the date of the offer. The supplier shall supply the density (20 °C) for information purposes (see A.2).

All information shall be given in the languages of the countries of destination.

6 Sampling

The sampling of solid and liquid forms of sodium chloride shall be according the procedures described in Annex B.

7 Test methods

7.1 General

The test for compliance with the requirements shall be in accordance with the following methods or in accordance with validated methods.

7.2 NaCl

7.2.1 General

The determination of the NaCl content in commercial salts can be carried out either by the direct method or by the indirect method:

7.2.2 Direct method

The NaCl shall be determined by potentiometric titration in accordance with the analytical method given in C.1. It is possible to carry out this determination without an automatic titrator.

7.2.3 Indirect method

This method allows the calculation of sodium chloride content on the basis of the results of the determination of sulfate (see 7.3), calcium and magnesium, water insoluble matter (see 7.11) und loss of mass on drying (see 7.4). Convert sulfate to calcium sulfate and unused sulfate first to magnesium sulfate and any remaining sulfate to sodium sulfate.

Calcium and magnesium shall be determined in accordance with the test method given in C.2. For salts with high concentrations of calcium and magnesium the contents of these elements shall be determined by complexometric titration with ethylendiaminetetraacetate (EDTA) solution in accordance with the test method in ISO 2482.

The percentage mass fraction of NaCl of commercial salt shall be determined by calculation:

$$\text{Percentage NaCl on a dry matter basis} = (100 - \text{percentage non-chloride impurities}) \times 100/100 - \text{percentage loss of mass on drying}$$

For rock salt and solar/sea salt pulverize the sample before dissolving; after dissolving filtrate the test solution.

For the determination of the NaCl content in used salts, by-product salts and brines the direct method shall be used.

7.3 Sulfate

The sulfate shall be determined in accordance with the test method in ISO 2480 (gravimetric method) or with the analytical method given in C.2. To catch the soluble sulfate completely it is necessary to dissolve the product sample with hot water.

7.4 Moisture

The loss of mass at 110 °C shall be determined in accordance with the test method in ISO 2483, modified as follows:

— with 100 g test sample (instead of 10 g as in ISO 2483);

— stir up the samples of wet salts in the course of drying delicately;

— stop the test with obtaining constant mass (delta of 10 mg on the weighing), normally a duration of 90 min is necessary.

7.5 Sieve analysis

The particle size distribution shall be determined by dry sieving in accordance with the test method in ISO 2591-1 (test sieves according ISO 565) or in accordance with the test method in EN 1235. The salt shall be dried (see 7.4) before sieving. For sieves with a diameter up to 200 mm use test portions with 100 g, for bigger sieves use test portions of 1 000 g.

7.6 Anti-caking agent

The content of anti-caking agent (ferrocyanide) shall be determined by molecular absorption spectrometry (see C.4).

7.7 Heavy metals, etc

The contents of heavy metals, etc., except for mercury, shall be determined by inductively coupled plasma optical emission spectrometry (ICP-OES) (see C.2).

NOTE Alternatively, the determination of contents of heavy metals, etc. can be carried out by atomic absorption spectrometry (AAS), in accordance with EN ISO 15586.

The content of mercury shall be determined by cold vapour atomic absorption spectrometry (see C.3).

7.8 Hydrocarbons

The content of hydrocarbons shall be determined in accordance with the test method in EN ISO 9377-2 (modified: procedure for test samples).

7.9 TOC (total organic carbon)

The content of total organic carbon shall be determined on the basis of the test method in EN 1484 (modified: the presence of chloride requires an appropriate pre-treatment).

7.10 pH

The pH of salt and brine shall be determined in accordance with the test method in EN ISO 10523 (modified: determination in 10 weight % salt solution; brine samples are diluted to a concentration of 10 weight %.).

7.11 Water insoluble matter

The matter insoluble in water shall be determined in accordance with the test method in ISO 2479. To dissolve the soluble components completely it is necessary to use hot water. With brine, start with filtration of the undiluted test sample (min. 350 ml).

7.12 Bulk density

The bulk density of loose salt shall be determined in accordance with the test method in EN 1236. On the basis of the same method the bulk density of salts which contain more than 20 weight % of particles exceeding 5 mm in diameter shall be determined.

7.13 Density

The density of brine at 20 °C shall be determined in accordance with the test method in ISO 758 or in accordance with the test method in ISO 649-2.

Annex A
(normative)

Product descriptions

A.1 Product description for sodium chloride

Product

Trade name ……

Natural origin ☐

Other origin

Synthetic by-product salt
(salt from chemical reactions) ☐ REACH registration no.: ……………………

Used salt (waste salt) ☐

Supplier

……

……

Product specification (results of supplier tests; requirements in brackets)

- **NaCl:** …………………………….. Weight % (min. 90)
- **Sulphate:** ……………………… Weight % (max. 3)
- **Moisture:** …………………………Weight % (dry salt max. 0,6, semi-dry salt max. 2,0,
  wet salt max. 6,0/max. 3,5 % for undried vacuum salt)
- **Anti-caking agent**

  Chemical substance: …………………………………………………………………….

  CAS no.: ………………………………………………………………………………….

  Content: ………………………………..mg/kg (min. 3 to max. 125, expressed as $Fe(CN)_6$-anion)
- **pH:** ……………………………………..(5 – 10, in 10 weight % solution)

- **Sieve analysis**
  Weight % passing test sieve:

Grade EF (extra fine salt)	Grade F (fine salt)
0,125 mm ………………… (max. 5)	0,125 mm ………………… (max. 5)
0,8 mm ………………… (25 to 100)	0,8 mm ………………… (10 to 40)
2,0 mm ………………….. (100*)	1,6 mm ………………… (30 to 80)
	3,15 mm ………………… (90 to 100)
	5,0 mm ………………… (100**)

Grade M (medium salt)	Grade C (coarse salt)
0,125 mm ………………… (max. 7)	0,8 mm ………………… (max. 35)
0,8 mm ………………… (5 to 35)	3,15 mm ………………… (30 to 80)
1,6 mm ………………… (10 to 60)	6,3 mm …………………… (75 to 95)
3,15 mm ………………… (45 to 90)	10 mm …………………… (100***)
6,3 mm ……………….. (100**)	

* 2 weight % production related tolerance with max. 3 mm grain size

** 2 weight % production related tolerance with max. 8 mm grain size

*** 2 weight % production related tolerance with max. 12 mm grain size

- **Heavy metals, hydrocarbons, etc.:**

Al (Aluminium)*	………………………..	mg/kg (≤ 50)
As (Arsenic)	………………………..	mg/kg (≤ 2,5)
Cd (Cadmium)	………………………..	mg/kg (≤ 2)
Co (Cobalt)	………………………..	mg/kg (≤ 2)
Cr (Chromium)	………………………..	mg/kg (≤ 5)
Cu (Copper)	………………………..	mg/kg (≤ 5)
Hg (Mercury)	………………………..	mg/kg (≤ 0,5)
Ni (Nickel)	………………………..	mg/kg (≤ 5)
Pb (Lead)	………………………..	mg/kg (≤ 5)
Zn (Zinc)	………………………..	mg/kg (≤ 20)
Hydrocarbons*	………………………..	mg/kg (≤ 100)
TOC*	………………………..	mg/kg

*data necessary if the salt is not of natural origin

- **Bulk density (loose): ………………………………** kg/m^3

Other information (added colours, etc.):

………

………

………

………

Date, signature and stamp of supplier

A.2 Product description for brine

Product

Trade name ………..

Natural origin ☐

Other origin

- Brine derived from chemical reactions or from synthetic by-product salts ☐

  REACH registration no.: ……………………………………..

- Brine from used salt ☐

Supplier

………

………

Product specification (results of supplier tests; requirements in brackets)

- **NaCl: ……………………………………………** Weight % (18 to 26)
- **Sulphate: ……………………………………** Weight % (max. 0,6, in 10 weight % solution)
- **Water insoluble matter: ……………………** Weight % (max. 0,03)
- **pH: …………………………………………….** (5 – 10, in 10 weight % solution)

- **Heavy metals, hydrocarbons, etc.:**

Al (Aluminium)** ………………….. mg/kg* (≤ 50)
As (Arsenic) ………………… mg/kg* (≤ 2.5)
Cd (Cadmium) ………………… mg/kg* (≤ 2)
Co (Cobalt) ………………… mg/kg* (≤ 2)
Cr (Chromium) ………………….. mg/kg* (≤ 5)
Cu (Copper) ………………….. mg/kg* (≤ 5)
Hg (Mercury) ………………….. mg/kg* (≤ 0,5)
Ni (Nickel) …………………... mg/kg* (≤ 5)
Pb (Lead) ………………….. mg/kg* (≤ 5)
Zn (Zinc) …………………... mg/kg* (≤ 20)

Hydrocarbons** ………………….. mg/kg* (≤ 100)
TOC** ………………….. mg/kg*

*Calculated as dry matter
**Data necessary if the brine is derived from chemical reactions or made from used salts and by-products salts.

- **Density (20 °C): ………………………………………………. kg/dm^3**

Other information:

Brine with a concentration above 23 weight % must be diluted to ≤ 23 weight % at the user site after delivery.
……

……

……

……
Date, signature and stamp of supplier

Annex B
(normative)

Sampling

B.1 Solid sodium chloride

B.1.1 Package shipments

Select not less than three containers at random from the shipment. For bags, take 1,0 kg samples by means of a sampling tube or other method that will ensure a sample that is representative of the material in the bag. Penetrate with the sampling tube or other method at least 300 mm into the bag.

B.1.2 Bulk shipments

For solid sodium chlorides in bulk lots the sampling shall be in accordance with the methods described in EN 932-1.

Select samples from at least three locations in the shipment. Scrape aside the top layer to a depth of approximately 300 mm. Use a sampling tube or another method according EN 932-1 to obtain a sample extending from the cleared surface to a maximum depth. Each sample shall contain at least 1,0 kg of material.

Thoroughly mix the individual samples to form a representative composite sample of material and store in a sealed glass or suitable plastic container.

B.2 Brine

Obtain a sample of at least 500 ml from the bulk shipping container or storage tank or during discharge. Recirculate the brine in the tank until it is homogenous, then take one or more samples by means of an appropriate sampling device.

If more than one sample is taken, immediately and thoroughly mix the individual samples to form a representative composite sample of material and store in a sealed glass or suitable plastic container.

B.3 Labelling and distribution of samples

The container with the samples shall have labels as follows:

- trade name of the product;
- address of the point of sampling;
- date of the sampling;
- number of the sampling report.

The sample shall be sent to the test laboratory. If more than one sample is taken, the other samples are for tests by the supplier and used as retain samples.

B.4 Sampling report

The sampling report should include the following information:

- purchasing organization;
- trade name of product;
- active ingredient (sodium chloride/brine);
- name and address of supplier;
- date of delivery (delivery note);
- quantity of the delivered product;
- date of sampling;
- point of sampling;
- responsible organization for sampling;
- persons present during sampling;
- short description of sampling procedure;
- number of samples;
- weight of sample;
- addressee of the samples;
- requested tests;
- other comments;
- signature of persons present during sampling.

Annex C
(normative)

Analytical methods

C.1 Determination of sodium chloride (potentiometric method)

C.1.1 Scope and field of application

The present analytical standard describes a potentiometric method for the determination of chloride in sodium chloride. It is an application of the ISO 6227 standard to sodium chloride.

C.1.2 Principle

Chloride is determined by potentiometric titration with a standard silver nitrate solution using an automatic titrator.

NOTE Polyvinyl alcohol is added to the solution to be analysed to avoid occlusions of chloride in the silver chloride precipitate.

C.1.3 Reagents

Unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

C.1.3.1 **Nitric acid,** c(HNO_3) approximately 1,4 mol/l.

Dilute 100 ml of concentrated nitric acid, ρ approximately 1,40 g/ml, 65 % (m/m), to 1 000 ml with water.

C.1.3.2 **Sodium chloride solution,** β(NaCl) = 10,00 g/l.

Dissolve 10,00 g of sodium chloride (>99,9 %), weighed to the nearest 1 mg, and previously dried at 250 °C for 1 h, in water. Make up to 1 000 ml in a volumetric flask and mix. This solution is usable for one month.

C.1.3.3 **Polyvinyl alcohol (PVA) solution,** β(PVA) approximately 2 g/l.

Dissolve 2 g of water soluble PVA in 1 l of water and heat to 60 °C – 70 °C for better solubility.

C.1.3.4 **Silver nitrate solution,** c(AgNO3) = 0,100 mol/l, standard volumetric solution.

This solution is standardized as described hereafter: Transfer 10,00 ml of the sodium chloride solution (C.1.3.2) and 2 ml of nitric acid (C.1.3.1) and 5 ml of PVA solution (C.1.3.3) into the titration vessel. Dilute to about 50 ml with water. Titrate the chloride with the silver nitrate solution (C.1.3.4) as described in C.1.6.3.2. The concentration of the silver nitrate solution, c($AgNO_3$), expressed in mol/l is given by the formula:

$$\omega(\mathrm{AgNO_3}) = \frac{m}{58,443} \times \frac{10}{V}$$

where

m is the exact mass of sodium chloride, in g, used for the preparation of the solution (C.1.3.2);

V is the volume of silver nitrate solution, in ml, used for the titration.

Carry out three determinations and calculate the mean value of $c(AgNO_3)$.

C.1.4 Apparatus

Usual laboratory equipment and:

C.1.4.1 Automatic titrator fitted with:

- silver electrode and double junction reference electrode ($Ag/AgCl/KCl/KNO_3$); the KNO_3 solution in the outlet compartment shall be renewed each month;
- 20 ml burette;
- 150 ml titration vessel.

This instrument should be able to operate under the conditions shown in the next table:

Table C.1 — Conditions for titration

Titration parameters	Values
Mode	Potentiometric detection with dynamic equivalence point titration
Increment near the equivalence point (EP)	25 µl
Signal drift after addition of titrant	15 mV/min
Maximum waiting time after addition of titrant	40 sec
Stirring	yes

C.1.4.2 Magnetic stirrer and stirring bars.

C.1.5 Sampling and samples

A test sample of about 500 g should be taken for analysis, ensuring that it is representative of the whole batch.

C.1.6 Procedure

C.1.6.1 Test portion

Weigh, to the nearest 1 mg, about 10 g of the solid test sample. For brine the test portion is 30 g.

C.1.6.2 Test solution

Transfer the test portion (C.1.6.1) into a 100 ml volumetric flask and dissolve in water. Dilute to the mark with water and mix.

C.1.6.3 Determination

C.1.6.3.1 Apparatus setting

Set all instrumental parameters of the titrator in accordance with the operating manual of the instrument's manufacturer including the parameters cited in (C.1.4.1).

C.1.6.3.2 Measurement

With the pipette used for the calibration of the silver nitrate solution (C.1.3.4), transfer 1,00 ml of the test solution (C.1.6.2) into the titration vessel. Add 2 ml of nitric acid (C.1.3.1), 5 ml of PVA solution (C.1.3.3) and dilute to about 50 ml with water. Titrate with the silver nitrate solution (C.1.3.4).

C.1.7 Expression of results

C.1.7.1 Method of calculation

The chloride content of the sample, $\omega_{(Cl)}$, is given by the formula and rounded to one decimal place:

$$\omega_{(Cl)} = V \times c_{(AgNO3)} \frac{1\,000}{10 \times m} \times 35,453$$

where

$\omega_{(Cl)}$	is the chloride content, in grams per kilogram of sample,
m	is the mass, in grams, of the test portion (C.1.6.1),
$c_{(AgNO3)}$	is the concentration of the silver nitrate solution (C.1.3.4) in mol/l,
V	is the volume of the silver nitrate solution used for the titration of the test solution (C.1.6.2).

The sodium chloride content of the sample $\omega_{(NaCl)}$ is given by the formula and rounded to one decimal place:

$$\omega_{(NaCl)} = \omega_{(Cl)} \times \frac{58,443}{35,453}$$

where

$\omega_{(NaCl)}$	is the sodium chloride content, in grams per kilogram of sample.

C.1.7.2 Repeatability and reproducibility (informative)

Analyses, carried out on four samples by 14 laboratories, have given the following statistical results, each laboratory having furnished results obtained by the same operator performing three analyses per sample:

Table C.2 — Repeatability and reproducibility

	Vacuum salt 1	**Vacuum salt 2**	**Sea salt**	**Rock salt**
Number of laboratories retained after eliminating outliers	14	14	13	14
Results, g NaCl/kg salt Mean	999,9	998,5	999,2	992,1
Standard deviation for:				
– repeatability (sr)	1,2	1,3	1,1	2,1
– reproducibility (sR)	1,5	2,1	1,6	4,9
Repeatability limit (r)	3,4	3,8	3,1	6,0
Reproducibility limit (R)	4,3	6,0	4,6	14,0

C.2 Determination of aluminium, arsenic, cadmium, calcium, chromium, cobalt, copper, lead, magnesium, nickel, sulfate, zinc (inductively coupled plasma optical emission spectrometry (ICP/OES))

C.2.1 General

This analytical standard describes an inductively coupled plasma optical emission spectrometry method for the determination of elements soluble in diluted acid, in salt. The limit of detection (LOD) for each element, determined in an inter-laboratory study is given in Table C.3.

Table C.3 — Limit of detection (LOD)

Element	**LOD** µg/kg of salt
Aluminium (Al)	15
Arsenic (As)	60
Calcium (Ca)	not relevant
Cadmium (Cd)	4
Cobalt (Co)	15
Chromium (Cr)	7,5
Copper (Cu)	10
Magnesium (Mg)	not relevant
Nickel (Ni)	15
Lead (Pb)	60
Sulfur (S)	100
Zink (Zn)	10

The limit of detection (LOD) – the lowest concentration of the element which can be detected with a coefficient of variation of 30 % - is calculated based on the repeatability standard deviation S_r of each element near the estimated LOD.

C.2.2 Principle

Dissolution of the sample with nitric acid (0,1 mol/l) and direct nebulization of the acid solution into an inductively coupled argon plasma formed by a high frequency. Measurement of the radiation at specific wavelengths using background correction.

NOTE The use of reference element (internal standard) as scandium, yttrium or cobalt can improve the quality of the results especially using a simultaneous spectrometer. Every mention of this optional reagent (here scandium) is stated in italics and in brackets.

C.2.3 Reagents

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

C.2.3.1 Nitric acid, ρ approximately 1,40 g/ml, mass fraction 65 % (m/m).

C.2.3.2 Sodium chloride solution, c(NaCl) = 250 g/l.

Dissolve 250 g of very pure NaCl (see NOTE) in water and transfer to a 1 000 ml volumetric flask. Make up to the mark with water and mix.

NOTE A very pure salt is a salt with elemental impurities at least 10 times lower than the respective limits of detection given in Table C.3.

C.2.3.3 Scandium (reference element) solution, β(Sc) = 50 mg/l.

Transfer 50 ml of a scandium stock solution β(Sc) = 1 000 mg/l and 10 ml nitric acid (C.2.3.2) to a 1 000 ml volumetric flask. Make up to the mark with water and mix.

C.2.3.4 Element stock solution, *β(each element)* = 1 000 mg/l certified commercial solutions.

The stock solution shall be certified not only for the element itself but also for the other analyte elements (impurities).

C.2.3.5 Argon, pressure not less than 7 bar.

The argon used can be compressed or liquefied gas (informative).

C.2.4 Apparatus (informative)

Usual laboratory equipment and ICP/OES.

C.2.4.1 Inductively coupled plasma optical emission spectrometer fitted with a nebulizer and torch for high salt concentrations and with an argon humidifier filled with water.

This instrument may measure simultaneously and/or sequential. The specifications and operating conditions used with most spectrometers are given in Table C.4.

Table C.4 — Typical operating conditions for most ICP spectrometers[1]

Parameter	Specification
Argon flows (l/min) – plasma – auxiliary – nebulizer	 12 – 15 approximately 1,5 approximately 0,7
Sample flow (ml/min)	approximately 1,5
RF power (W)	1 000 – 1 250
Integration time (sec) – simultaneous – sequential	 approximately 10 approximately 3

C.2.5 Sampling and samples

A test sample of about 500 g should be taken for analysis, ensuring that it is representative of the whole batch.

C.2.6 Procedure

C.2.6.1 Test portion

Weigh, to the nearest 0,1 g, about 10 g of the solid test sample. For brine the test portion is 30 g.

For samples with high sulfate concentrations take less test portion or dilute the test solution (C.2.6.2).

C.2.6.2 Test sample solution

Transfer the test portion (C.2.6.1) and 20 ml water with pH 4 (use diluted nitric acid for pH adjustment) to a 100 ml volumetric flask and stir to dissolve. Filter under vacuum through a membrane filter (0,45 µm maximum porosity). Add 1 ml nitric acid (C.2.3.1), [5 ml of scandium solution (C.2.3.3)], make up to the mark with water and mix.

C.2.6.3 Calibration and verification solutions (informative)

Calibration solution No. 1 is the blank calibration solution and contains 1 ml of nitric acid (C.2.3.1). Transfer 40 ml of sodium chloride solution (C.2.3.2), 1 ml of nitric acid (C.2.3.1), [5 ml of scandium solution (C.2.3.3)] and the volumes of each stock solution (C.2.3.4) to obtain the concentrations indicated in Table C.5, into a series of further three 100 ml volumetric flasks to obtain the calibration solutions No. 2 – 4. Make up to the mark with water and mix.

---

1) Check for use with high salinity solutions.

Table C.5 — Calibration solutions

Calibration solution No.	**Concentration of NaCl (see C.2.8)** g/l	**Concentration of elements** mg/l
1[a]	0	0
2[b]	100	2,5[d]
3	100	5,0[e]
4[c]	100	5,0[e]

[a] Blank calibration solution.

[b] Linearity verification solution.

[c] Control calibration solution prepared with different pipettes, flasks and if possible with different stock solutions.

[d] Except for SO_4: 50 mg/l.

[e] Except for SO4: 100 mg/l.

C.2.6.4 Determination

C.2.6.4.1 Settings of the apparatus (informative)

Set all instrument parameters of the optical emission spectrometer (C.2.4.1) in accordance with the operating manual of the instrument's manufacturer.

Prepare the analytical procedure including the lines shown in Table C.6 (or lines with similar sensitivity and free from interferences), with background correction and concentrations of calibration solutions 1 and 3 described in C.2.6.3 (and applying the reference technique).

Table C.6 — Typical wavelength per element

Element	Wavelength (nm)
Aluminium (Al)	167,081 396,152
Arsenic (As)	189,042 193,696
Calcium (Ca)	317,933 393,366
Cadmium (Cd)	214.,438 228,802
Cobalt (Co)	228,616
Chromium (Cr)	267,716
Copper (Cu)	324,754
Magnesium (Mg)	279,553 280,270
Nickel (Ni)	221,647 231,604
Lead (Pb)	168,220 220,353
Sulfur (S)	182,034 180,731
Zink (Zn)	231,856
Scandium (Sc) *(reference element)*	424,683 361,384

Other lines with similar sensitivity and free from interferences may be used.

C.2.6.4.2 Spectrometric measurements

Repeat the measurements for at least five integration periods.

If necessary, rinse with the blank calibration solution (solution 1) after each solution.

Calibrate the instrument with the calibration solutions 1 and 3 (C.2.6.3).

Control and check the linearity of the calibration curve by measurement of the following calibration solutions (C.2.6.3) considered as unknown solutions:

- — solution 3;
- — solution 1;
- — solution 1;
- — solution 2;

- solution 4;
- solution 3.

If the calibration function does not appear to be a linear one, the corresponding calibration range should be decreased.

Continue the measurements in the following order:

- solution 3 (C.2.6.3);
- solution 1 (C.2.6.3);
- solution 1 (C.2.6.3);
- test sample solution (C.2.6.2);
- solution 3 (C.2.6.3);
- solution 1 (C.2.6.3);
- solution 1 (C.2.6.3).

Five to 10 test sample solutions may be analysed consecutively, provided the stability of the measurements is sufficient.

C.2.7 Expression of results

C.2.7.1 Evaluation

If necessary, correct the results obtained with the test sample solution for drift:

- for baseline drift by interpolating in time between both second measurements (the first may be cross-contaminated) of the blank calibration solution (solution 1);
- for sensitivity drift by interpolating in time between the corrected measurements for baseline drift of the solution 3.

C.2.7.2 Calculation

The element content of the sample, $\omega_{(element)}$ in micrograms per kilogram of salt is given by the following formula:

$$\omega_{(element)} = \frac{100}{m} \times \beta(element) \times 1\,000$$

where

m is the mass in grams of the test portion (C.2.6.1);

β is the corrected concentration of element, in milligrams per litre, in the test sample solution (C.2.6.2).

The sulfate concentration in the sample is calculated from the concentration of the element sulfur.

Report the result as given in Table C.7.

Table C.7 — Report of results

Element concentration µg/kg of salt	
< LOD	as < LOD
LOD – 10	to the nearest 0,1 µg/kg of salt
10 – 100	to the nearest 1 µg/kg of salt
> 100	to the nearest 10 µg/kg of salt

C.2.7.3 Repeatability and reproducibility (informative)

Analyses, carried out on five samples, containing the elements in different concentrations, by 16 laboratories, gave the following statistical results, each laboratory performed three replicates under repeatability conditions:

Table C.8 — Repeatability and reproducibility

Sample	Ω	S_r	S_R	r	R
Aluminium					
1	0,02	0,034	0,034	0,10	0,10
2	0,44	0,050	0,060	0,14	0,17
3	8,32	0,145	0,482	0,41	1,36
4	2,16	0,056	0,169	0,16	0,48
5	16,12	0,473	1,174	1,34	3,32
Arsenic					
1	0,08	0,124	0,216	0,35	0,61
2	0,84	0,106	0,181	0,30	0,51
3	2,04	0,079	0,166	0,22	0,47
4	20,76	0,312	1,120	0,88	3,17
5	8,16	0,210	0,577	0,59	1,63
Cadmium					
1	0,02	0,009	0,021	0,02	0,06
2	0,40	0,018	0,023	0,05	0,05
3	8,00	0,107	0,196	0,30	0,55
4	2,08	0,030	0,106	0,08	0,30
5	15,48	0,318	0,822	0,90	2,33
Calcium					
1	0,03	0,001	0,004	0,004	0,01
2	0,68	0,006	0,030	0,02	0,08

3	1,00	0,013	0,047	0,04	0,13
4	2,68	0,028	0,121	0,08	0,34
5	8,36	0,130	0,434	0,37	1,230
Cobalt					
1	0,00	0,021	0,032	0,06	0,09
2	0,40	0,024	0,031	0,07	0,09
3	7,96	0,155	0,268	0,44	0,76
4	2,00	0,034	0,062	0,10	0,18
5	15,60	0,320	0,920	0,90	2,60
Chromium					
1	0,00	0,010	0,028	0,03	0,08
2	0,39	0,014	0,033	0,04	0,09
3	7,96	0,080	0,258	0,23	0,73
4	2,00	0,031	0,074	0,09	0,21
5	15,44	0,378	0,971	1,07	2,75
Copper					
1	0,00	0,012	0,024	0,04	0,07
2	0,38	0,011	0,022	0,03	0,06
3	7,80	0,086	0,388	0,24	1,10
4	1,92	0,030	0,104	0,08	0,30
5	14,96	0,239	0,970	0,68	2,74
Magnesium					
1	0,06	0,120	0,200	0,04	0,06
2	3,72	0,316	0,155	0,09	0,44
3	4,00	0,568	0,176	0,16	0,50
4	5,84	0,056	0,350	0,16	0,99
5	11,48	0,364	0,740	1,03	2,09
Nickel					
1	−0,04	0,026	0,132	0,08	0,38
2	0,37	0,022	0,108	0,06	0,30
3	8,04	0,058	0,251	0,16	0,71
4	2,00	0,039	0,146	0,11	0,41
5	15,64	0,296	0,628	0,84	1,78
Lead[a]					
1	0,004	0,05	0,082	0,14	0,23

2	0,92	0,064	0,204	0,18	0,57
3	1,89	0,064	0,207	0,18	0,58
Zinc					
1	0,02	0,018	0,021	0,05	0,06
2	0,40	0,034	0,052	0,10	0,15
3	8,08	0,092	0,330	0,26	0,93
4	2,04	0,038	0,098	0,11	0,28
5	15,56	0,407	0,814	1,15	2,30
Sulfate[a]					
1	46	0,818	1,55	2,29	4,33
2	439	5,964	11,2	16,7	31,4
3	940	8,893	15,6	24,9	43,7

where:

ω is the element content (mean value), in mg of element/kg salt;

S_r is the repeatability standard deviation, in mg of element/kg salt;

S_R is the reproducibility standard deviation, in mg of element/kg salt;

r is the repeatability limit;

R is the reproducibility limit.

[a] Inter-laboratory study conducted with 13 laboratories participating.

NOTE Grey shaded values are below LOQ approximately 3 times LOD. The dimension in Table C.8 is mg element/kg of salt.

C.2.8 Remarks

All vessels (glassware, polyethylene-, polypropylene- and PTFE-flasks) should be washed successively with hydrochloric acid, c(HCl) approximately 6 mol/l and water.

Use the highest concentration of NaCl acceptable to the spectrometer and correct the calibration- and verification-solutions accordingly.

C.3 Determination of total mercury (cold vapour atomic absorption spectrometry)

C.3.1 General

The method applies to products of mercury content (Hg) equal to or greater than 20 µg/kg.

NOTE The lower limit of quantification, as stated here, can only be achieved if the procedure is carried out under optimum conditions:

- skilled operators experienced with this method;
- clean glassware, only used for such determination;

- optimum apparatus settings;
- very low mercury level of the ambient air;
- high purity reagents.

C.3.2 Principle

Dissolution of the sample with a mixture of water, sodium chlorate and hydrochloric acid.

Oxidation with the nascent chlorine, converting all forms of mercury to ionic mercury (II).

Reduction of the excess of oxidant by hydroxylamine hydrochloride and of mercury (II) to atomic mercury by tin (II) chloride.

Entrainment of the mercury in a stream of gas and measurement of the absorbance at a wavelength of 253,7 nm.

C.3.3 Reagents

All reagents shall be of recognized analytical grade having the lowest possible mercury content and the water used shall conform to grade 3 in accordance with EN ISO 3696.

Store all reagents in glass bottles.

C.3.3.1 **Sodium chloride** with a mercury content less than 20 µg/kg.

C.3.3.2 **Hydrochloric acid,** c(HCl) approximately 6 mol/l (azeotropic mixture):

Purify this solution as follows.

Add 500 ml of water and 5 ml of sulfuric acid density ρ approximately 1,84 g/ml, mass fraction 96 % solution to 500 ml of hydrochloric acid density ρ approximately 1,19 g/ml, mass fraction 37 % solution. Distill the azeotropic mixture.

C.3.3.3 **Sodium chlorate ($NaClO_3$),** approximately 100 g/l solution.

C.3.3.4 **Potassium dichromate ($K_2Cr_2O_7$),** approximately 4 g/l solution:

Dissolve 4 g of potassium dichromate with 500 ml of water. Add 500 ml of nitric acid ρ approximately 1,40 g/ml, mass fraction 65 % solution and mix.

C.3.3.5 **Tin(II) chloride ($SnCl_2.2H_2O$),** approximately 100 g/l solution:

Dissolve 25 g of tin (II) chloride dihydrate with 50 ml of warm hydrochloric acid ρ approximately 1,19 g/ml, mass fraction 37 % solution. Allow to cool and add 1 g to 2 g of metallic tin. Dilute to 250 ml with water and mix. Prepare this solution just before use and slowly pass nitrogen through during 30 min to remove the mercury.

Ensure that oxidation of solid tin (II) chloride by air is prevented.

C.3.3.6 **Hydroxylamine hydrochloride ($NH_2OH.HCl$),** approximately 100 g/l solution.

C.3.3.7 **Mercury, stock standard solution (I),** c(Hg) = 1 000 mg/l, commercial standard solution or to be prepared as follows:

- dissolve 1,354 g of mercury (II) chloride ($HgCl_2$) with 50 ml of hydrochloric acid solution (C.3.3.2) and add 50 ml of potassium dichromate solution (C.3.3.4). Transfer to a 1 000 ml volumetric flask, dilute to the mark with water and mix;

— store this solution in a cool, dark place and renew after two months.

C.3.3.8 Mercury, standard solution (II), c(Hg) = 1 mg/l.

Prepare this solution just before use by successive dilutions of the stock standard solution (I) (C.3.3.7). Add 50 ml of potassium dichromate solution (C.3.3.4) for preparing 1 000 ml of final solution.

C.3.3.9 Air or nitrogen.

Use a gas containing no mercury or other components capable to provide absorbing radiations at a wavelength of 253,7 nm.

Any mercury present should be removed by a charcoal filter.

C.3.4 Apparatus (informative)

Ordinary laboratory apparatus and glassware.

All new glassware used for this determination, including flasks used for reagents or samples should be washed as follows and thoroughly rinsed with water after each operation:

— with a brush and detergent if the walls are greasy;

— with dilute nitric acid c(HNO_3) approximately 7 mol/l.

The glassware should be checked by carrying out several blank tests until satisfactory results are obtained before using it for actual determinations. Thereafter such glassware should be used for mercury determination only.

C.3.4.1 Apparatus allowing the determination of mercury.

An example of suitable apparatus is shown in Figure C.1. This applies to an open-circuit measuring system and comprises principally the following:

C.3.4.1.1 Atomic absorption spectrometer.

C.3.4.1.2 Mercury hollow cathode lamp.

C.3.4.1.3 Low-pressure mercury vapour lamp.

C.3.4.1.4 Measuring cell, minimum path length 10 cm with windows transparent to radiation of 253,7 nm.

C.3.4.1.5 Reaction vessel:

Use, for example, a 100 ml gas washing bottle with sintered glass inlet or pointed immersion tube and 60 ml mark.

Fill the bottle with water when not in use.

If different bottles are used, check that the results are identical.

Traces of tin (IV) oxide which can have settled onto the walls shall be removed by hydrochloric acid ρ approximately 1,19 g/ml, mass fraction 37 % solution.

C.3.5 Procedure

C.3.5.1 Test portion

Weigh, to the nearest 0,1 g, about 10 g (m_1) of the laboratory sample. For brine the test portion is 30 g.

C.3.5.2 Test solution

Transfer the test portion (C.3.5.1) to a 100 ml conical flask and add 30 ml of water.

The test solutions should not be prepared in accordance with ISO 2479 because mercury losses can occur in those solutions.

C.3.5.3 Blank test solution

Transfer 30 ml of water to a 100 ml conical flask.

C.3.5.4 Calibration solutions (informative)

To take into account the influence of sodium chloride on mercury evolution, take a quantity of sodium chloride equal to the test portion (C.3.5.1) for the preparation of calibration solutions.

Transfer 10 g of sodium chloride (C.3.3.1), 30 ml of water and the volumes of mercury standard solution (II) (C.3.3.7) given in Table C.9 to a series of 100 ml conical flasks.

Table C.9 — Calibration solutions for mercury

Calibration solution N°	**Mercury standard solution (II)** ml	**Corresponding mass of mercury** µg
1[a]	0	0
2	0,5	0,5
3	1,0	1,0
4	1,5	1,5
5	2,0	2,0
6	3,0	3,0

[a] Zero calibration solution.

C.3.5.5 Determination

C.3.5.5.1 Mineralization

Proceed as follows with the conical flasks prepared in C.3.5.2, C.3.5.3 and C.3.5.4.

Add some glass beads, 4 ml of hydrochloric acid (C.3.3.2) and 3 ml of sodium chlorate solution (C.3.3.3). Heat and keep boiling for 5 min.

Allow to cool and transfer quantitatively to a 100 ml volumetric flask. Dilute to the mark with water and mix.

C.3.5.5.2 Preparation of the apparatus

Equip the spectrometer (C.3.4.1.1) with the mercury lamp (C.3.4.1.2 or C.3.4.1.3). Set the lamp current, the slit and the flow of air or nitrogen according to the instruction manual of the instrument. Adjust the wavelength at the maximum of emission at about 253,7 nm.

C.3.5.5.3 Spectrometric measurements

A maximum signal is obtained only under optimum conditions. For instance, the gas flow and the waiting time between tin (II) chloride addition and start of stripping have great influence on the peak height. A typical waiting time will be in the order of 5 min. Therefore, those parameters shall be established experimentally for any individual apparatus and matrix.

The maximum absorbance also depends very strongly upon the temperature of the solution during aeration (A = 3 % per degree Celsius at room temperature). Therefore, all solutions shall be at the same temperature.

Test and blank solutions shall be analysed at the same time and with the same reagents.

Proceed with the solutions prepared in C.3.5.5.1 in the following way:

- Transfer 10,0 ml of solution (C.3.5.5.1) and 3,0 ml of hydroxylamine hydrochloride solution (C.3.3.6) to the reaction vessel (C.3.4.1.5).
- Fill to the mark (60 ml) with water, add 2 ml of tin (II) chloride solution (C.3.3.5) and place the flask (C.3.4.1.5) immediately into the apparatus system (C.3.4.1).
- Swirl to mix and allow to stand for a few minutes.
- Pass air or nitrogen through the reaction vessel and determine the maximum of absorbance. Stop the gas flow and remove the reaction vessel.
- Wash the vessel with potassium dichromate solution (C.3.3.4) to oxidize any traces of tin (II) and rinse thoroughly with water.

Samples of unknown composition should be tested for the presence of matrix effects, caused by present components other than sodium chloride, by the analyte addition technique.

C.3.5.5.4 Calibration curve

Subtract the absorbance of the zero calibration solution from that of each other calibration solution (C.3.5.4) and plot a graph with the masses of mercury (Hg), in micrograms, used to prepare the calibration solutions on the abscissa and the corresponding corrected absorbances on the ordinate.

C.3.6 Expression of results

C.3.6.1 Calculation

The mercury content of the sample, *c(Hg),* in micrograms per kilogram of sodium chloride, is given by the following formula:

$$c_{(Hg)} = \frac{1000}{m_1}\left(m_3 - m_2\right)$$

where

m_1 is the mass, in grams, of the test portion (C.3.5.1);

m_2 is the mass of mercury (Hg), in micrograms, corresponding to the absorbance obtained in

C.3.5.5.3 for the blank test solution;

m_3 is the mass of mercury (Hg), in micrograms, corresponding to the absorbance obtained in C.3.5.5.3 for the test solution.

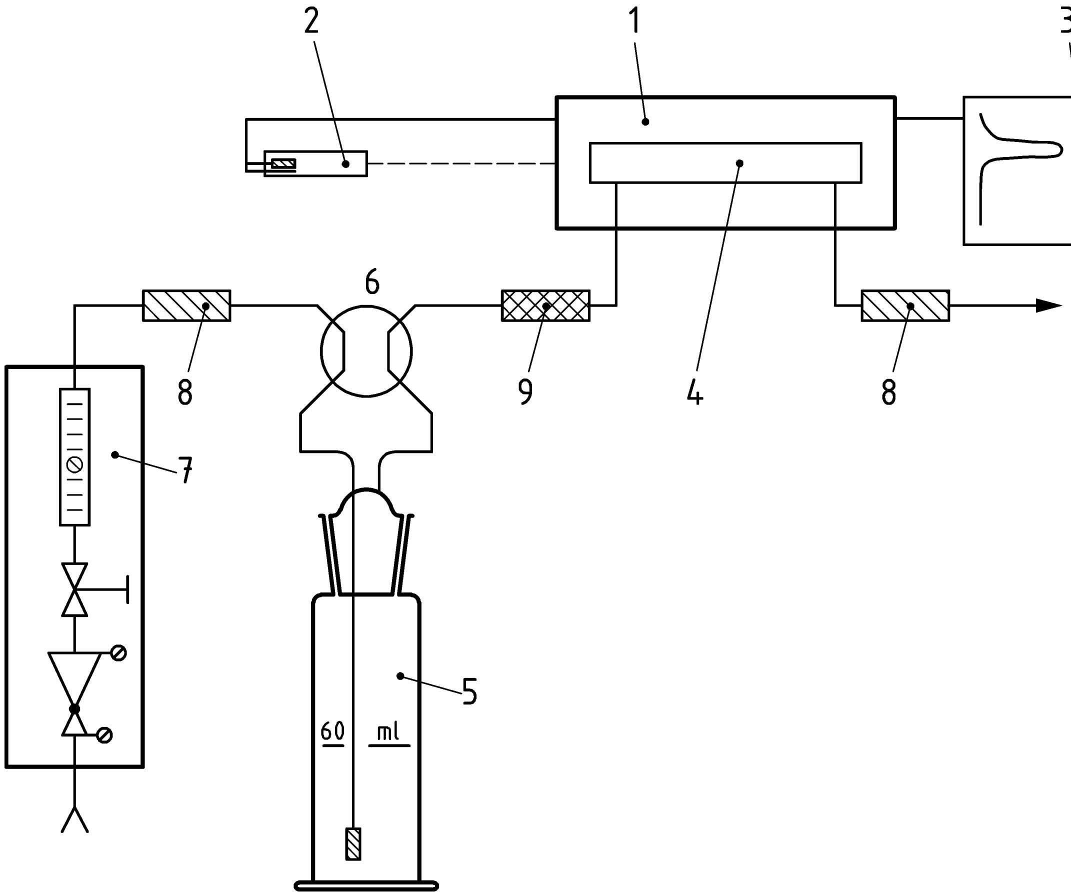
C.3.6.2 Repeatability and reproducibility (informative)

Analyses, carried out on three samples by several laboratories, have given the following statistical results, each laboratory having furnished results obtained by the same operator performing two analyses per sample:

Table C.10 — Repeatability and reproducibility

	Rock salt	**Vacuum salt**	**Sea salt**
Number of laboratories	14	12	12
Results, Hg in µg/kg salt Mean	< *LOQ*[a]	< *LOQ*[a]	< *LOQ*[a]
Standard deviation for - repeatability (s_r) - reproducibility (s_R)	3,98 24,10	2,78 11,42	3,12 15,98

[a] *LOQ* = Limit of quantification.



Key

1	atomic absorption spectrometer or mercury vapour meter
2	mercury hollow cathode lamp or low-pressure mercury vapour lamp
3	recorder or maximum deflection indicator
4	measuring cell
5	reaction vessel with sintered glass inlet or pointed immersion tube
6	four-way stopcock
7	flow control system (e.g. pressure regulator, needle valve and flow meter)
8	absorption tube with charcoal
9	absorption tube with drying agent

Figure C.1 — Determination of mercury by atomic absorption spectrometry – Typical apparatus

C.4 Determination of anti-caking agent (molecular absorption spectrometry)

C.4.1 General

This method is applicable to products with an ferrocyanide content, expressed as $Fe(CN)_6$:

— > 2,5 mg per kilogram of salt when using the direct method;

— > 0,25 mg per kilogram of salt when using the filtration method.

For products with higher ferrocyanide contents take less sample than described in C.4.6.1 or dilute the test solution (C.4.6.2).

C.4.2 Principle

Ferrocyanides [hexacyanoferrate (II)] and iron (II) form in acid solution, the iron (II) hexacyanoferrate (II) complex which, in presence of iron (III) oxidizes immediately to iron (III) hexacyanoferrate $Fe4[Fe(CN)_6]_3$ Prussian Blue.

The absorbance of this insoluble complex is measured at a wavelength of around 700 nm.

The Prussian Blue can be filtered on a membrane filter. After re-dissolution with potassium hydroxide, the Prussian Blue is reformed in a greatly reduced volume.

C.4.3 Reagents

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

C.4.3.1 Sodium chloride, ferrocyanide-free.

C.4.3.2 Sulphuric acid, c(H_2SO_4) approximately 0,5 mol/l.

C.4.3.3 Potassium hydroxide solution, c(KOH) approximately 0,05 mol/l.

C.4.3.4 Fe(II) - Fe(III) solution:

Add 200 g of ammonium iron (II) sulfate, $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$, and 25 g of ammonium iron (III) sulfate, $(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$, into a 1000 ml volumetric flask. Dissolve with water, add 100 ml of sulphuric acid solution (C.4.3.2), dilute to the mark and mix.

Filter the solution and store in a dark bottle.

C.4.3.5 Potassium hexacyanoferrate (II) stock solution I, c($K_4[Fe(CN)_6] \cdot 3H_20$) = 1,000 g/l.

Transfer 1 000 g of potassium hexacyanoferrate (II), $K_4[Fe(CN)_6] \cdot 3H_2O$ into a 1 000 ml volumetric flask. Dissolve in water, add 5 ml of potassium hydroxide solution (C.4.3.3), dilute to the mark and mix.

Store in a dark bottle for a maximum of one month.

C.4.3.6 Potassium hexacyanoferrate (II) stock solution II, c($K_4[Fe(CN)_6] \cdot 3H_20$) = 50,0 mg/l.

Transfer 50,0 ml of the stock solution (I) (C.4.3.5) and 5 ml of potassium hydroxide solution (C.4.3.3) into a 1 000 ml volumetric flask. Dilute to the mark and mix.

Prepare this solution just before use.

C.4.4 Apparatus

Ordinary laboratory apparatus and glassware together with the following.

C.4.4.1 Spectrophotometer, or

C.4.4.2 Photocolourimeter, fitted with a filter ensuring maximum transmission between 690 nm and 710 nm.

The type of apparatus used (spectrophotometer or photocolourimeter), the path length and the wavelength (or type of filter) should be specified.

C.4.4.3 Membrane filter about 50 mm diameter, 0,3 µm maximum porosity

The porosity of filters should be adapted to the purity of salt. For example, salt with a purity of less than 97 weight % NaCl is filtered through membranes with a porosity of 2 µm – 3 µm.

C.4.5 Sampling and samples

A test sample of 500 g should be taken for analysis, ensuring it is representative of the whole batch.

C.4.6 Procedure

C.4.6.1 Test portion

Weigh, to the nearest 0,1 g, 100 g (m) of the test sample.

C.4.6.2 Test solution

Transfer the test portion (C.4.6.1) and water into a 500 ml volumetric flask. Dilute to the mark and mix.

C.4.6.3 Blank test solution

Prepare a solution containing 100 g of sodium chloride (C.4.3.1) per 500 ml.

C.4.6.4 Calibration

C.4.6.4.1 Calibration solutions (informative)

Transfer 10 g of sodium chloride (C.4.3.1) and the volumes of stock solution II (C.4.3.6) indicated in the next table into a series of five 100 ml volumetric flasks. Dilute to about 50 ml with water and add 10 ml of potassium hydroxide solution (C.4.3.3).

Table C.11 — Calibration solutions

Calibration solution N°	**Standard solution (II)** (C.4.3.6) ml	**Corresponding mass of** $K_4Fe(CN)_6 \cdot 3H_2O$ µg
1[a]	0	0
2	2	100
3	5	250
4	10	500
5	15	750

[a] Zero calibration solution

C.4.6.4.2 Colour development

Add in each flask, mixing after each addition, 5 ml of sulfuric acid (C.4.3.2) and 5 ml of Fe(II) - Fe(III) solution (C.4.3.4). Dilute to the mark, mix and allow standing for 15 min.

C.4.6.4.3 Photometric measurements

Adjust the apparatus to zero absorbance against water.

Carry out the photometric measurements using a spectrophotometer (C.4.4.1) set up at the maximum of absorption (wavelength around 700 nm) or a photocolourimeter (C.4.4.2) fitted with the appropriate filter in cells of 4 cm to 5 cm optical path length or by using circulation cells with optical course of 2 cm.

C.4.6.4.4 Calibration curve

Subtract the absorbance of the zero calibration solution from that of each of the other calibration solutions and plot a graph showing the quantities of potassium ferrocyanide, in micrograms, on the abscissa and the corresponding absorbances on the ordinate.

C.4.6.5 Determination

C.4.6.5.1 Direct method

Transfer 50,0 ml of the test solution (C.4.6.2) or of the blank test solution (C.4.6.3) into a 100 ml volumetric flask. Add 10 ml of potassium hydroxide solution (C.4.3.3). Stir for 1 min and continue as described in (C.4.6.4.2).

C.4.6.5.2 Filtration method

Transfer the 500 ml of test solution (C.4.6.2) or of the blank test solution (C.4.6.3) into a 600 ml beaker.

Add, mixing after each addition, 10 ml of sulfuric acid (C.4.3.2) and 25 ml of Fe(II) - Fe(III) solution (C.4.3.4). Allow to stand for 15 min.

Filter under vacuum through a membrane filter (C.4.4.3) and wash twice with 15 ml of water (pH < 7).

Transfer the filter into a beaker containing 10 ml of the potassium hydroxide solution (C.4.3.3) and dissolve the precipitate.

Transfer the solution into a 100 ml volumetric flask, add 10,0 g of sodium chloride (C.4.3.1), dilute to 60 ml, mix and continue as described in C.4.6.4.2.

C.4.6.5.3 Photometric measurements

Carry out the photometric measurements of the two solutions obtained in C.4.6.5.1 or C.4.6.5.2 according to the instructions given in C.4.6.4.3.

NOTE 1 Hexacyanoferrate (II) is determined simultaneously with hexacyanoferrate (III).

NOTE 2 The intensity of the colour is dependent on the concentration of alkali metal present in the solution.

C.4.7 Expression of results

C.4.7.1 Evaluation

The ferrocyanide content, expressed as [$Fe(CN)_6$], in mg/kg of salt, is given by the following formula:

$$\mathrm{Fe(CN)_6} = 0{,}502 \times \frac{500 \times (m_1 - m_0)}{m \times V}$$

where

m is the mass in grams, of the test portion (C.4.6.1),

m_1 is the mass in micrograms, of hexacyanoferrate (II) expressed as [$K_4Fe(CN)_6 \cdot 3H_2O$], found in the final solution C.4.6.5.1 or C.4.6.5.2 with the test solution,

m_0 is the mass in micrograms, of hexacyanoferrate (II) expressed as [$K_4Fe(CN)_6 \cdot 3H_2O$], found in the final solution C.4.6.5.1 or C.4.6.5.2 with the blank test solution,

V is the volume, in millilitres, of test solution used in C.4.6.5.1 or C.4.6.5.2.

C.4.7.2 Repeatability and reproducibility (informative)

Analyses, carried out on one sample by several laboratories, have given the following statistical results, each laboratory having furnished results obtained by the same operator performing two analyses per sample:

Table C.12 — Repeatability and reproducibility

Number of laboratories	11
Results, mg $K_4Fe(CN)_6 \cdot 3H_2O$ per kilogram of salt Mean	3,1
Standard deviation for: - repeatability (s_r) - reproducibility (s_R)	 0,08 0,54

Bibliography

[1] EN 15597-1, *Winter maintenance equipment — Spreading machines (gritting machines) — Part 1: General requirements and definitions for spreading machines*

[2] CEN/TS 15597-2, *Winter maintenance equipment — Spreading machines (gritting machines) — Part 2: Requirements for distribution and its test*

[3] EN ISO 15586, *Water quality — Determination of trace elements using atomic absorption spectrometry with graphite furnace (ISO 15586)*

[4] REACH: Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC

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