BRITISH STANDARD

BS EN 973:2009

Chemicals used for treatment of water intended for human consumption — Sodium chloride for regeneration of ion exchangers

ICS 13.060.20; 71.100.80

British Standards

National foreword

This British Standard is the UK implementation of EN 973:2009. It supersedes BS EN 973:2002 which is withdrawn.

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

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

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

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

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English Version

Chemicals used for treatment of water intended for human consumption - Sodium chloride for regeneration of ion exchangers

Produits chimiques utilisés pour le traitement de l'eau destinée à la consommation humaine - Chlorure de sodium pour la régénération des résines échangeuses d'ions

Produkte zur Aufbereitung von Wasser für den menschlichen Gebrauch - Natriumchlorid zum Regenerieren von Ionenaustauschern

This European Standard was approved by CEN on 23 July 2009.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
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Contents

Foreword

This document (EN 973:2009) has been prepared by Technical Committee CEN/TC 164 “Water supply”, the secretariat of which is held by AFNOR.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by February 2010, and conflicting national standards shall be withdrawn at the latest by February 2010.

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

This document supersedes EN 973:2002.

Differences between this edition and EN 973:2002 are editorial to harmonise the text with other standards in this series.

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Introduction

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

a) this standard provides no information as to whether the product may be used without restriction in any of 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 the standard does not confer or imply acceptance or approval of the product in any of the Member States of the EU or EFTA. The use of the product covered by this European Standard is subject to regulation or control by National Authorities.

1 Scope

This European Standard is applicable to sodium chloride intended for use only in water treatment apparatus, for the regeneration of ion exchangers, intended for water for human consumption. It describes the characteristics and specifies the requirements and the corresponding test methods for sodium chloride. It gives information on its use in water treatment.

2 Normative references

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

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

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 °C*

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

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

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

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

Sodium chloride.

3.1.2 Synonym or common name

Salt.

3.1.3 Relative molecular mass

58,45.

3.1.4 Empirical formula

NaCl.

3.1.5 Chemical formula

NaCl.

3.1.6 CAS Registry Number[1]

7647-14-5.

3.1.7 EINECS Reference[2]

231-598-3.

3.2 Commercial forms

The product is available as rock salt, sea salt or evaporated salt, and it is supplied as free-flowing crystals or their compacted forms.

3.3 Physical properties

3.3.1 Appearance

The product is white and crystalline.

3.3.2 Density

The density of the solid crystal is 2,16 g/cm^3 at 20 °C.

The bulk density depends on the particle size distribution.

3.3.3 Solubility (in water)

The solubility of the product depends on the temperature as given in Figure 1.

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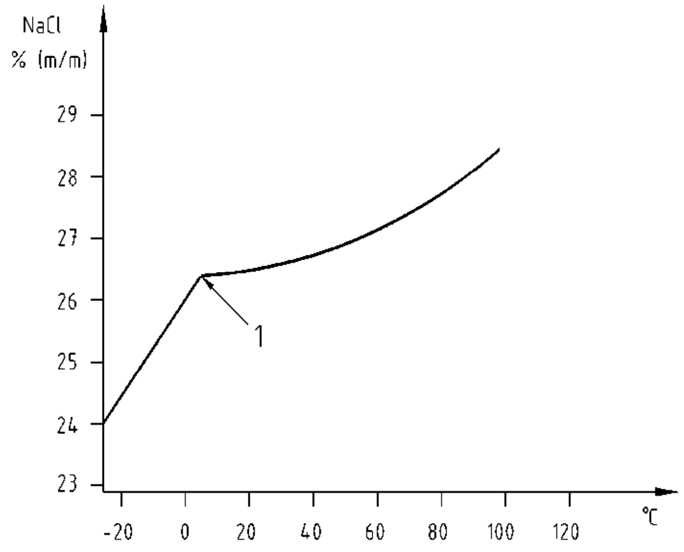
[1] Chemical Abstract Service Registry Number.

[2] European Inventory of Existing Commercial Chemical Substances.



Temperature °C	NaCl solution % (*m/m*)
- 10	25,0
0	26,34
10	26,35
20	26,43
30	26,56
40	26,71
50	26,89
60	27,09
70	27,30
80	27,53
90	27,80
100	28,12

Key

1 Transition point
NaCl → $NaCl.2H_2O$

Figure 1 - Solubility curve for sodium chloride in water

3.3.4 Vapour pressure

Not applicable.

3.3.5 Boiling point at 100 kPa[3]

Not applicable.

3.3.6 Melting point

802 °C.

3.3.7 Specific heat

Approximately 850 J/(kg·K) at 25 °C for the solid.

3.3.8 Viscosity (dynamic)

The viscosity of the saturated solution at 20 °C is approximately 1,9 mPa·s.

3.3.9 Critical temperature

Not applicable.

3.3.10 Critical pressure

Not applicable.

3.3.11 Physical hardness

The hardness of solid salt is given as 2 to 2,5 on the Mohs' scale of hardness.

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[3] 100 kPa = 1 bar.

3.4 Chemical properties

Sodium chloride is stable, non-volatile and aqueous solutions have good electrical conductivity.

Sodium chloride is decomposed by a number of acids. It reacts with sulfuric acid, phosphoric acid and strong oxidizing agents. The reactions are often complex and require heat for completion.

NOTE Under certain conditions a sodium chloride solution can cause corrosion of metallic surfaces.

4 Purity criteria

4.1 General

This European Standard specifies the minimum purity requirements for sodium chloride for regeneration of ion exchangers 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, contents of other impurities and additives used in the products not stated in the 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 content of sodium chloride in the dry product shall not be less than:

- grade A: mass fraction 99,4 % of dry NaCl;
- grade B: mass fraction 98,5 % of dry NaCl.

NOTE An anticaking agent, sodium or potassium hexacyanoferrate [4], is allowed up to a maximum level in the final product of 20 mg/kg, expressed as the anhydrous hexacyanoferrate ion $[Fe(CN)_6]^{-4}$ and for the determination see B.3.

4.3 Impurities and main by-products

The product shall conform to the requirements specified in Table 1 and Table 2.

Table 1 – Impurities

Impurity	**Limit** **Mass fraction % of NaCl content**		
Water-insoluble matter		Grade A	Grade B
	max.	0,05	0,35

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[4] E number 535 or 536 (see [2]).

Table 2 – Moisture content

Impurity	Limit % (*m/m*) of **NaCl** content		
Moisture content		Dry salt	Undried salt
	max	0,6	5

Potassium, calcium, magnesium and sulfate are natural impurities. Their contents are not relevant.

4.4 Chemical parameters

The product shall conform to the requirements specified in Table 3.

Table 3 – Chemical parameters

Parameter		Limits in mg/kg of commercial product
Arsenic (As)	max.	13
Cadmium (Cd)	max.	1,3
Chromium (Cr)	max.	13
Mercury (Hg)	max.	0,26
Nickel (Ni)	max.	13
Lead (Pb)	max.	13
Antimony (Sb)	max.	2,6
Selenium (Se)	max.	2,6
NOTE Other chemical parameters and indicator parameters as listed in EU Directive 98/83/EC (see [1]) are not relevant in sodium chloride.		

5 Test methods

5.1 Sampling

A test sample of about 500 g shall be taken for analysis, ensuring that it is representative of the whole batch, and taking account of ISO 3165 and also ISO 6206. Prepare the laboratory sample(s) required in accordance with ISO 8213.

NOTE It should be ensured that no trace of the impurities to be determined is introduced in the sample during the sampling operations.

5.2 Analyses

5.2.1 Main product

The percentage mass fraction of sodium chloride (NaCl) shall be determined by calculation, on the basis of the results of the determinations of sulfate (according to ISO 2480), halogens (according to ISO 6227), calcium and magnesium (according to ISO 2482), potassium (see B.4) and loss of mass on drying (according to ISO 2483). Convert sulfate to calcium sulfate and unused calcium to calcium chloride, unless sulfate in sample exceeds the amount necessary to combine with calcium, in which case convert calcium to calcium sulfate and unused sulfate to magnesium sulfate and the remaining sulfate to sodium sulfate. Convert unused magnesium to magnesium chloride. Convert potassium to potassium chloride. Convert unused halogens to sodium chloride. Report the sodium chloride contents on a dry matter basis, multiplying the percentage of sodium chloride by 100/(100 - P), where P is the percentage mass fraction of the loss of mass on drying (see 5.2.2.2).

5.2.2 Impurities

5.2.2.1 Water-insoluble matter

The content of water-insoluble matter shall be determined in accordance with ISO 2479.

5.2.2.2 Moisture content

The loss of mass at 110 °C shall be determined in accordance with ISO 2483.

5.2.3 Chemical parameters

5.2.3.1 Arsenic, cadmium, chromium, nickel, lead, antimony, selenium

The contents of chemical parameters, except for mercury, shall be determined by inductively coupled plasma optical emission spectrometry (ICP/OES) (see B.1).

NOTE Alternatively, the determination of contents of some chemical parameters can be carried out by atomic absorption spectrometry (AAS) and the analytical methods are given in Annex C and Annex D.

5.2.3.2 Mercury

The content of mercury shall be determined by cold vapour atomic absorption spectrometry (see B.2).

6 Labelling – Transportation - Storage

6.1 Means of delivery

Sodium chloride shall be delivered in bulk or in bags.

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 in accordance with the EU directives [5]

Sodium chloride is not subjected to labelling regulations.

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

6.3 Transportation regulations and labelling

Sodium chloride is not listed under a UN Number[6] . Sodium chloride is not classified as a dangerous product for road, rail, sea and air transportation.

6.4 Marking

Each container shall be marked with at least the following information:

- the name "sodium chloride, regeneration salt" or "sodium chloride, salt for water softening", "compacted dry salt" or "undried salt", trade name and grade;
- the net mass;

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[5] See [3].

[6] United Nations Number.

- the name and the address of the supplier and/or manufacturer;
- the statement "this product conforms to EN 973".

6.5 Storage

6.5.1 Long term stability

Sodium chloride is stable during long term storage, providing it is kept in a dry place.

6.5.2 Storage incompatibilities

Sodium chloride shall be stored in hygienic and safe conditions so as to avoid any risk of contamination.

The product shall not be allowed to come into contact with sulfuric acid, phosphoric acid and strong oxidizing agents.

Annex A
(informative)

General information on sodium chloride

A.1 Origin

a) Rock salt: salt produced by mining salt deposits of different geological formations derived from ancient seas.

b) Sea salt: salt produced by seawater evaporation via the action of sun and wind.

c) Evaporated salt: salt produced by evaporating water from a salt solution in a special evaporator leading to the recrystallization of the salt.

A.2 Use

A.2.1 Function

Regeneration of the resin in ion exchange apparatus is performed with a solution of sodium chloride.

A.2.2 Form in which the product is used

It is used in the form of a saturated solution that is diluted before being applied to the resin.

A.2.3 Consumption of salt for regeneration of resins

The consumption is variable and depends on the mineral content of water, the type of resin and the performance of the apparatus.

A.2.4 Means of application

An appropriate dosage device such as a metering pump controls the sodium chloride consumption.

A.2.5 Secondary effects in ion exchange apparatus

None.

A.2.6 Removal of excess product

Not applicable.

A.3 Rules for safe handling and use

No particular precaution is necessary.

A.4 Emergency procedures

A.4.1 First aid

Not applicable.

A.4.2 Spillage

The product should be collected, then the area should be rinsed with plenty of water.

A.4.3 Fire

Sodium chloride is not combustible.

Annex B
(normative)

Analytical methods

B.1 Determination of antimony, arsenic, cadmium, chromium, lead, nickel and selenium (inductively coupled plasma optical emission spectrometry (ICP/OES))

B.1.1 General

The range covered for each element is given in the Table B.1.

Table B.1 - Concentration range

Element	Concentration range, in mg/kg of commercial product
As	1,0 to 50
Cd	0,15 to 50
Cr	0,1 to 50
Ni	0,25 to 50
Pb	2,5 to 50
Sb	2,0 to 50
Se	1,0 to 50

NOTE Different types of ICP/OES instruments can have different performance levels. The performance depends also on the quality of the reagents. This means that the mentioned values should be considered as indicative values.

The limits quoted in Table B.1 are based on the equation $\mathrm{LOQ}\left(\text{limit of quantification}\right)=10\times s_\mathrm{r}$ where s_r is the repeatability standard deviation of test samples having concentrations near the expected LOQ.

B.1.2 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, cobalt, etc. can improve the quality of the results especially using a simultaneous spectrometer. Every mention of this optional reagent (here scandium) is stated in brackets.

B.1.3 Reagents

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

Store all prepared solutions in polyethylene or polytetrafluorethylene (PTFE) flasks to prevent contamination.

B.1.3.1 **Nitric acid** solution $\rho \approx$ 1,40 g/ml, mass fraction 65 %.

B.1.3.2 **Hydrochloric acid** solution $\rho \approx$ 1,19 g/ml, mass fraction 37 %.

B.1.3.3 **Sodium chloride** solution, *c*(NaCl) = 250 g/l.

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

NOTE The contents of the particular elements in the high purity sodium chloride reagent should be less than one tenth of the lower limits quoted in Table B.1.

B.1.3.4 Scandium (reference element) solution, c(Sc) = 50 mg/l.

Transfer 50 ml of a scandium stock solution c(Sc) = 1 000 mg/l and 10 ml nitric acid (B.1.3.1) to a 1 000 ml volumetric flask. Make up to the mark with water and mix.

B.1.3.5 As, Cd, Cr, Ni, Pb, Sb or Se element, stock solution, *c*(element) = 1 000 mg/l commercial solution.

B.1.3.6 Argon, the pressure shall not less than 700 kPa and the argon used can be compress or liquefied gas.

B.1.4 Apparatus

Ordinary laboratory apparatus and glassware together with the following:

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

B.1.4.1 Inductively coupled plasma optical emission spectrometer ICP/OES fitted with nebulizer for high salt concentration. This instrument can be simultaneous and/or sequential. Typical parameters and operating conditions for the spectrometer are given in Table B.2.

Table B.2 - Typical parameters and operating conditions of the spectrometer

Parameter	Unit	Specifications
Type		monochromator or/and polychromator
Argon humidifier (water)		Yes
Argon (B.1.3.6) flows:		
— plasma	l/min	12 to 15
— auxiliary	l/min	≈ 1,5
— nebulizer	l/min	≈ 0,7
Sample flow	ml/min	≈ 1,5
RF power	W	1 000 to 1 250
Integration time:	s	
— simultaneous measurement		10
— sequential measurement		3

B.1.5 Procedure

B.1.5.1 Test portion

Weigh, to the nearest 0,1 g, about 10 g of the laboratory sample (*m*).

B.1.5.2 Test solution

Transfer the test portion (B.1.5.1) and water to a 100 ml volumetric flask and stir to dissolve. Add 1 ml nitric acid (B.1.3.), [*5 ml of scandium solution (B.1.3.4)*], make up to the mark with water and mix.

B.1.5.3 Calibration and verification solutions

Transfer 40 ml of sodium chloride solution (B.1.3.3), 1 ml of nitric acid (B.1.3.1), [*5 ml of scandium solution* (*B.1.3.4*)] and the volumes of mono-element solution (B.1.3.5) given in the Table B.3 to a series of 100 ml one-mark volumetric flasks. Make up to the mark with water and mix.

Table B.3 - Calibration solutions for the different elements

Calibration solution N°	Mono-element solution ml	Corresponding concentration (As, Cd, Cr, Ni, Pb, Sb, Se) mg/l
1 [a]	0	0
2 [b]	0,250	2,50
3	0,500	5,00
4 [c]	0,500	5,00

[a] Blank calibration solution.

[b] Linearity verification solution.

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

B.1.5.4 Determination

B.1.5.4.1 Preparation of the apparatus

Set all instrument parameters of the optical emission spectrometer (B.1.4.1) in accordance with the operating manual of the instrument's manufacturer.

Prepare the analytical procedure including the lines shown in the Table B.4, with background correction, concentrations of calibration solutions 1 and 3 described in B.1.5.3 (and applying the reference technique).

Table B.4 - Wavelength per element

Element	**Wavelength** nm	
	line	**background**
As	189,082	to be determined with each instrument
	193,759	
Cd	214,438	
	228,802	
Cr	267,716	
Ni	221,647	
Pb	168,220	
Sb	217,581	
Se	196,026	
Sc (internal standard)	424,683 or 361,384	

B.1.5.4.2 Spectrometric measurements

Repeat the measurements for at least five integration periods.

Rinse with the blank calibration solution (solution 1) after each solution.

Calibrate the instrument with the calibration solutions 1 and 3 (B.1.5.3).

Control and check the linearity of the calibration curve by measurement of the following calibration solutions (B.1.5.3) considered as unknown solutions:

- solution 3;
- solution 1;
- solution 1;
- solution 2;
- solution 4;
- solution 3.

Continue the measurements in the following order:

- solution 3;
- solution 1;
- solution 1;
- test solution (B.1.5.2);
- solution 3;
- solution 1 (B.1.5.3);
- solution 1 (B.1.5.3).

B.1.6 Expression of results

B.1.6.1 Evaluation

If necessary, correct for drift the results obtained with the test solution and control solutions 2 and 4:

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

NOTE 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.

B.1.6.2 Calculation

The element content of the sample, $c(\mathrm{element})$ in milligrams per kilogram of sodium chloride is given by the following equation:

$$c(element) = \frac{100}{m} \times c \qquad (1)$$

where

m is the mass in grams of the test portion (B.1.5.1);

c is the corrected concentration of element, in milligrams per litre, in the test solution (B.1.5.2).

B.1.6.3 Repeatability and reproducibility

Analyses, carried out on some samples (enriched or not) by several laboratories, have given the following statistical results, each laboratory having furnished results obtained by the same operator performing three analyses per sample:

Table B.5 – Repeatability and reproducibility

Element	*c*(element)		s_r	s_R
As	0,84		0,11	0,18
	2,04		0,08	0,17
	8,16		0,21	0,58
Cd	0,02		0,01	0,02
	0,40		0,02	0,02
	8,00		0,11	0,20
Cr	0,00		0,01	0,03
	0,39		0,01	0,03
	7,96		0,08	0,26
Pb	0,80		0,16	0,24
	1,92		0,26	0,29
	7,76		0,26	0,51
Ni	- 0,04		0,03	0,13
	0,37		0,02	0,11
	8,04		0,06	0,25
Sb	0,76		0,17	0,21
	2,20		0,23	0,84
	7,92		0,34	1,33
Se	0,76		0,09	0,11
	1,96		0,11	0,11
	7,88		0,27	0,37

where

$c(element)$ is the element content (mean value), in milligrams per kilogram of sodium chloride;

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

s_R is the reproducibility standard deviation, in mg of element/kg.

B.2 Determination of total mercury (cold vapour atomic absorption spectrometry)

B.2.1 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.

B.2.2 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.

B.2.3 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.

B.2.3.1 **Sodium chloride** with a mercury content less than 20 µg/kg.

B.2.3.2 **Hydrochloric acid**, $c(\mathrm{HCl}) \approx 6$ mol/l (azeotropic mixture).

Purify this solution as follows.

Add 500 ml of water and 5 ml of sulfuric acid density $\rho \approx 1{,}84$ g/ml, mass fraction 96 % solution to 500 ml of hydrochloric acid density $\rho \approx 1{,}19$ g/ml, mass fraction 37 % solution. Distill the azeotropic mixture.

B.2.3.3 **Sodium chlorate** ($NaClO_3$), approximately 100 g/l solution.

B.2.3.4 **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 $\rho \approx 1{,}40$ g/ml, mass fraction 65 % solution and mix.

B.2.3.5 **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 $\rho \approx 1{,}19$ 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.

B.2.3.6 **Hydroxylamine hydrochloride** ($NH_2OH.HCl$), approximately 100 g/l solution.

B.2.3.7 **Mercury, stock standard solution (I)**, $c_{(\mathrm{Hg})}$ = 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 (B.2.3.2) and add 50 ml of potassium dichromate solution (B.2.3.4). 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.

B.2.3.8 **Mercury, standard solution (II),** $c_{(\mathrm{Hg})}$ = 1 mg/l.

Prepare this solution just before use by successive dilutions of the stock standard solution (I) (B.2.3.7). Add 50 ml of potassium dichromate solution (B.2.3.4) for preparing 1 000 ml of final solution.

B.2.3.9 **Air or nitrogen**

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

NOTE Any mercury present should be removed by a charcoal filter.

B.2.4 Apparatus

Ordinary laboratory apparatus and glassware.

NOTE 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 $c(HNO_3) \approx 7$ 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.

B.2.4.1 Apparatus allowing the determination of mercury

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

B.2.4.1.1 Atomic absorption spectrometer

B.2.4.1.2 Mercury hollow cathode lamp

B.2.4.1.3 Low-pressure mercury vapour lamp

B.2.4.1.4 Measuring cell, minimum path length 10 cm with windows transparent to radiation of 253,7 nm.

B.2.4.1.5 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 $\rho \approx 1{,}19$ g/ml, mass fraction 37 % solution.

B.2.5 Procedure

B.2.5.1 Test portion

Weigh, to the nearest 0,1 g, about 10 g (m_1) of the laboratory sample.

B.2.5.2 Test solution

Transfer the test portion (B.2.5.1) to a 100 ml conical flask and add 30 ml of water.

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

B.2.5.3 Blank test solution

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

B.2.5.4 Calibration solutions

To take into account the influence of sodium chloride on mercury evolution, take a quantity of sodium chloride equal to the test portion (B.2.5.1) for the preparation of calibration solutions.

Transfer 10 g of sodium chloride (B.2.3.1), 30 ml of water and the volumes of mercury standard solution (II) (B.2.3.8) given in Table B.6 to a series of 100 ml conical flasks.

Table B.6 - 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.		

B.2.5.5 Determination

B.2.5.5.1 Mineralization

Proceed as follows with the conical flasks prepared in B.2.5.2, B.2.5.3 and B.2.5.4.

Add some glass beads, 4 ml of hydrochloric acid (B.2.3.2) and 3 ml of sodium chlorate solution (B.2.3.3). 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.

B.2.5.5.2 Preparation of the apparatus

Equip the spectrometer (B.2.4.1.1) with the mercury lamp (B.2.4.1.2 or B.2.4.1.3). 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.

B.2.5.5.3 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 B.2.5.5.1 in the following way.

- Transfer 10,0 ml of solution (B.2.5.5.1) and 3,0 ml of hydroxylamine hydrochloride solution (B.2.3.6) to the reaction vessel (B.2.4.1.5).
- Fill to the mark (60 ml) with water, add 2 ml of tin (II) chloride solution (B.2.3.5) and place the flask (B.2.4.1.5) immediately into the apparatus system (B.2.4.1).
- 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 (B.2.3.4) to oxidize any traces of tin (II) and rinse thoroughly with water.

NOTE 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.

B.2.5.5.4 Calibration curve

Subtract the absorbance of the zero calibration solution from that of each other calibration solution (B.2.5.4) 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.

B.2.6 Expression of results

B.2.6.1 Calculation

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

$$c(Hg) = \frac{1000}{m_1}(m_3 - m_2) \tag{2}$$

where

m_1 is the mass, in grams, of the test portion (B.2.5.1);

m_2 is the mass of mercury (Hg), in micrograms, corresponding to the absorbance obtained in B.2.5.5.3 for the blank test solution;

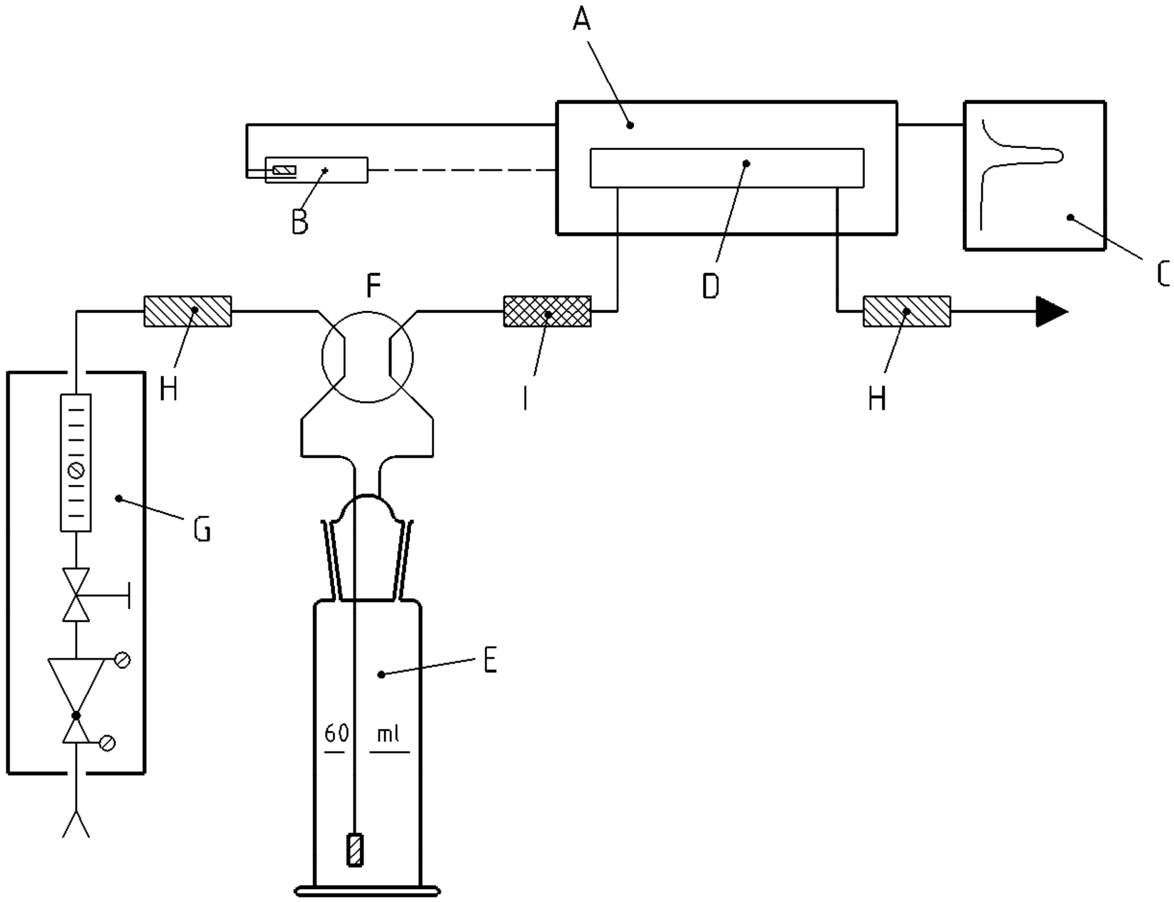
m_3 is the mass of mercury (Hg), in micrograms, corresponding to the absorbance obtained in B.2.5.5.3 for the test solution.

B.2.6.2 Repeatability and reproducibility

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 B.7 - Repeatability and reproducibility

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



Key

A Atomic absorption spectrometer or mercury vapour meter
B Mercury hollow cathode lamp or low-pressure mercury vapour lamp
C Recorder or maximum deflection indicator
D Measuring cell
E Reaction vessel with sintered glass inlet or pointed immersion tube
F Four-way stopcock
G Flow control system (e.g. pressure regulator, needle valve and flow meter)
H Absorption tube with charcoal
I Absorption tube with drying agent

Figure B.1 - Determination of mercury by atomic absorption spectrometry - Typical apparatus

B.3 Determination of water-soluble hexacyanoferrate (II) (molecular absorption spectrometry)

B.3.1 General

This method is applicable to products with an hexacyanoferrate (II) content, expressed as [$K_4Fe(CN)_6$] of:

— 2,5 mg/kg to 40 mg/kg when using the direct method;

— 0,25 mg/kg to 4 mg/kg when using the filtration method.

B.3.2 Principle

Ferrocyanide [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 $Fe_4[Fe(CN)_6]_3$ Prussian Blue.

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

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

B.3.3 Reagents

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

B.3.3.1 **Sodium chloride**, hexacyanoferrate-free.

B.3.3.2 **Sulfuric acid solution**, $c(H_2SO_4) \approx 0,5$ mol/l.

B.3.3.3 **Potassium hydroxide solution,** $c(KOH) \approx 0,05$ mol/l.

B.3.3.4 **Fe(II) - Fe(III) solution**

Add 200 g of ammonium iron (II) sulfate $[(NH_4)_2SO_4.\ FeSO_4.\ 6H_2O]$ and 25 g of ammonium iron (III) sulfate $[(NH_4)_2SO_4.\ Fe_2(SO_4)_{3.}\ 24H_2O]$ into a 1 000 ml volumetric flask. Dissolve with water, add 100 ml of sulfuric acid solution (B.3.3.2), dilute to the mark and mix.

Filter the solution and store in a dark bottle.

B.3.3.5 **Potassium hexacyanoferrate (II), stock standard solution (I)**, $c(K_4[Fe(CN)_6].\ 3H_2O) = 1,000$ g/l.

Transfer 1,000 g of potassium hexacyanoferrate (II) $K_4[Fe(CN)_6].\ 3H_2O$ to a 1 000 ml volumetric flask. Dissolve with water, add 5 ml of potassium hydroxide solution (B.3.3.3), dilute to the mark and mix.

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

B.3.3.6 **Potassium hexacyanoferrate (II), standard solution (II),** $c(K_4[Fe(CN)_6].\ 3H_2O) = 50,0$ mg/l.

Transfer 50,0 ml of the stock solution (I) (B.3.3.5) and 5 ml of potassium hydroxide solution (B.3.3.3) to a 1 000 ml volumetric flask. Dilute to the mark and mix.

Prepare this solution just before use.

B.3.4 Apparatus

Ordinary laboratory apparatus and glassware together with the following.

B.3.4.1 **Spectrometer,** or

B.3.4.2 **Photocolorimeter**, fitted with a filter ensuring maximum transmission between 690 nm and 710 nm.

NOTE The type of apparatus used (spectrometer or photocolorimeter), the path length and the wavelength (or type of filter) should be specified.

B.3.4.3 **Membrane filter** about 50 mm diameter, 0,3 µm maximum porosity.

B.3.5 Procedure

B.3.5.1 Test portion

Weigh, to the nearest 0,1 g, about 100 g (*m*) of the laboratory sample.

B.3.5.2 Test solution

Transfer the test portion (B.3.5.1) and water to a 500 ml volumetric flask. Dilute to the mark and mix.

B.3.5.3 Blank test solution

Prepare a solution containing 100 g of sodium chloride (B.3.3.1) per litre.

B.3.5.4 Calibration

B.3.5.4.1 Calibration solutions

Transfer 10,0 g of sodium chloride (B.3.3.1) and the volumes of standard solution (II) (B.3.3.6) given in the Table B.8 to a series of 100 ml one-mark volumetric flasks. Dilute to about 50 ml with water and add 10 ml of potassium hydroxide solution (B.3.3.3).

Table B.8 - Calibration solutions

Calibration solution N°	**Standard solution (II)** (B.3.3.6) ml	**Corresponding mass of** $K_4[Fe(CN)_6]. 3H_2O$ µg
1 [a]	0	0
2	2	100
3	5	250
4	10	500
5	15	750

[a] Zero calibration solution.

B.3.5.4.2 Colour development

Add in each flask, mixing after each addition, 5 ml of sulfuric acid solution (B.3.3.2) and 5 ml of Fe(II) - Fe(III) solution (B.3.3.4). Dilute to the mark, mix and allow to stand for 15 min.

B.3.5.4.3 Spectrometric measurements

Adjust the apparatus to zero absorbance against water.

Carry out the spectrometric measurements using a spectrometer (B.3.4.1) set up at the maximum of absorbance (wavelength around 700 nm) or a photocolorimeter (B.3.4.2) fitted with the appropriate filter in cells of 4 cm to 5 cm optical path length.

B.3.5.4.4 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.

B.3.5.5 Determination

B.3.5.5.1 Direct method

Transfer 50,0 ml of the blank test solution (B.3.5.2) or of the blank test solution (B.3.5.3) to a 100 ml one-mark volumetric flask and continue as described in B.3.5.4.2.

B.3.5.5.2 Filtration method

Transfer the 500 ml of test solution (B.3.5.2) or of the blank test solution (B.3.5.3) to a 600 ml beaker.

Add, mixing after each addition, 10 ml of sulfuric acid solution (B.3.3.2) and 25 ml of Fe(II)- Fe(III) solution (B.3.3.4). Allow to stand for 15 min.

Filter under vacuum through a membrane filter (B.3.4.3) and wash twice with 15 ml of water (pH < 7).

Transfer the filter into a beaker containing 10 ml of the potassium hydroxide solution (B.3.3.3) and dissolve the precipitate.

Transfer the solution to a 100 ml one-mark volumetric flask, add 10,0 g of sodium chloride (B.3.3.1), dilute to 60 ml, mix and continue as described in B.3.5.4.2.

B.3.5.5.3 Spectrometric measurements

Carry out the spectrometric measurements of the two solutions obtained in B.3.5.5.1 or B.3.5.5.2 according to the instructions given in B.3.5.4.3.

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

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

B.3.6 Expression of results

The hexacyanoferrate (II) content, in milligrams per kilogram of sodium chloride, is given by the following equations:

— Expressed as $\mathrm{Fe(CN)_6} = 0{,}502 \dfrac{500(m_1 - m_0)}{m \times V}$ (3)

— Expressed as $\mathrm{K_4[Fe(CN)_6].\ 3H_2O} = \dfrac{500(m_1 - m_0)}{m \times V}$ (4)

— Expressed as $\mathrm{Na_4[Fe(CN)_6].\ 10H_2O} = 1{,}146 \dfrac{500(m_1 - m_0)}{m \times V}$ (5)

where

m is the mass, in grams, of the test portion (B.3.5.1);

m_1 is the mass, in micrograms, of hexacyanoferrate (II) expressed as $\mathrm{K_4[Fe(CN)_6].3H_2O}$), found in the final solution obtained in B.3.5.5.1 or B.3.5.5.2 with the test solution;

m_0 is the mass, in micrograms, of hexacyanoferrate (II) expressed as $\mathrm{K_4[Fe(CN)_6].3H_2O}$, found in the final solution obtained in B.3.5.5.1 or B.3.5.5.2 with the blank test solution;

V is the volume, in millilitres, of test solution used in B.3.5.5.1 or B.3.5.5.2.

B.4 Determination of potassium (Flame atomic absorption spectrometric method)

B.4.1 General

The method is applicable to products of potassium content (K) equal to or greater than 2 mg/kg.

B.4.2 Principle

Dissolution of the sample in water or in acid and, if necessary, filtration of insoluble matters. Addition of cesium chloride as ionisation buffer, atomization of the test solution in an acetylene-air flame and measurement of the absorbance at a wavelength of 766,5 nm or 769,9 nm.

B.4.3 Reagents

Unless otherwise stated, all reagents shall be of recognized analytical grade and the water used shall conform to grade 3 in accordance with EN ISO 3696.

B.4.3.1 **Cesium chloride** (CsCl), 6,3 g/l solution.

B.4.3.2 **Potassium, stock standard solution (I),** $c(\mathrm{K}) = 1\,000$ mg/l, commercial standard solution or to be prepared as follows: weigh, to the nearest 0,1 mg, 1 907 mg of potassium chloride previously dried for at least 1 h at 400 °C and then cooled in a desiccator. Dissolve with water, transfer to a 1 000 ml one-mark volumetric flask, make up to the mark and mix.

B.4.3.3 **Potassium, standard solution (II),** $c(\mathrm{K}) = 10$ mg/l.

Transfer 10,0 ml of potassium stock standard solution (I) (B.4.3.2) to a 1 000 ml one-mark volumetric flask, make up to volume and mix.

B.4.4 Apparatus

Ordinary laboratory apparatus and glassware together with the following.

NOTE All new glassware used for this determination should be washed as follows and carefully rinsed with water after each operation:

- with a brush and detergent if the walls are greasy;
- with diluted nitric acid $c(\mathrm{HNO_3}) \approx 7$ mol/l.

B.4.4.1 **Atomic absorption spectrometer,** fitted with an acetylene-air burner.

B.4.4.2 **Potassium hollow cathode lamp**

B.4.5 Procedure

B.4.5.1 Test portion

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

B.4.5.2 Test solution

Prepare 1 000 ml of a solution A (water solution) or of a solution B (acid solution) with the test portion (B.4.5.1) as described in ISO 2479.

Transfer 1,00 ml of solution A or B and 20 ml of cesium solution (B.4.3.1) to a 100 ml volumetric flask. Make up to volume and mix.

NOTE If the estimated level of potassium is less than 50 mg/kg, the test solution with 5 ml of solution A or B should be prepared. The formula for calculation (B.4.6.1) should be modified accordingly.

If the estimated level of potassium is higher than 2 000 mg/kg proceed as follows:

- either dilute the solution A or B (see B.4.5.2) and take an aliquot of this solution; or
- measure the solutions at the wavelength of 769,9 nm. In this case, use the solutions 1, 4, 5, 6, 7 and 8 (B.4.5.4) as calibration solutions.

The formula for calculation (B.4.6.1) should be modified accordingly.

B.4.5.3 Blank test solution

Dilute to 1 000 ml the same quantities of all the reagents used for the preparation of solution B (see B.4.5.2).

Transfer 1,00 ml of this solution and 20 ml of cesium solution (B.4.3.1) to a 100 ml volumetric flask. Make up to volume and mix.

NOTE When sodium chloride is dissolved in water and not in acid in accordance with ISO 2479 (usual case), the zero calibration solution (see B.4.5.4) can replace the blank test solution (B.4.5.3).

B.4.5.4 Calibration solutions

Transfer 20 ml of cesium solution (B.4.3.1) and the volumes of potassium standard solution (II) (B.4.3.3) as shown in the Table B.9 to a series of eight 100 ml one-mark volumetric flasks. Make up to volume and mix.

Table B.9- Calibration solutions

Calibration solution N°	Potassium, standard solution (II) ml	Potassium concentration mg/l
1 [a]	0	0
2	0,5	0,05
3	2,0	0,20
4	5,0	0,50
5	10,0	1,00
6	15,0	1,50
7	20,0	2,00
8 [b]	50,0	5,00

[a] Zero calibration solution.

[b] Prepare this solution only in measurements are to be performed at 769,9 nm.

B.4.5.5 Determination

B.4.5.5.1 Preparation of the apparatus

Equip the spectrometer (B.4.4.1) with the potassium hollow cathode lamp (B.4.4.2).

Set the lamp current, the slit and the pressure of acetylene and air according to the instruction manual of the instrument. Adjust the wavelength at the maximum of emission of the lamp at about 766,5 nm or 769,9 nm.

B.4.5.5.2 Spectrometric measurements

Aspirate water after measurement.

Aspirate the solutions into the acetylene-air flame and determine the absorbance of each one in the following order:

- the calibration solutions (B.4.5.4);

- the blank test solution (B.4.5.3);
- the test solution (B.4.5.2);
- the calibration solutions (B.4.5.4).

B.4.5.6 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 concentrations of potassium (K), in milligrams per litre, on the abscissa and the corresponding corrected absorbances on the ordinate.

B.4.6 Expression of results

B.4.6.1 Calculation

The potassium content of the sample $c(K)$, in milligrams per kilogram of sodium chloride, is given by the following equation:

$$c(K) = \frac{10^5}{m} \cdot (C_1 - C_0) \tag{6}$$

where:

m is the mass, in grams, of the test portion (B.4.5.1);

C_1 is the concentration of potassium, in milligrams per litre, of the test solution (B.4.5.2);

C_0 is the concentration of potassium, in milligrams per litre, of the blank test solution (B.4.5.3).

B.4.6.2 Repeatability and reproducibility

Analyses, carried out 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 B.10 - Repeatability and reproducibility

Number of laboratories	15
Results, K, mg/kg Mean	 562
Standard deviation for: — repeatability (s_r) — reproducibility (s_R)	 8 53

Annex C
(informative)

Determination of cadmium, chromium, nickel and lead (flame atomic absorption spectrometry

C.1 Determination of cadmium

C.1.1 General

The method applies to products of cadmium content (Cd) equal to or greater than 0,05 mg/kg.

NOTE The limits 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;
- high purity reagents.

C.1.2 Principle

Dissolution of the test sample in nitric acid for the total mineralization of cadmium.

Complexation of the metal by ammonium pyrrolidine dithiocarbamate, extraction of metal carbamates into chloroform and back-extraction into nitric acid.

Nebulization of the nitric extract into an acetylene-air flame and measurement of the absorbance at a wavelength of 228,8 nm.

Determination of the cadmium content using the standard addition method.

C.1.3 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.1.3.1 **Nitric acid**, density $\rho \approx$ 1,40 g/ml, mass fraction 65 % solution.

C.1.3.2 **Chloroform**, density $\rho \approx$ 1,48 g/ml.

C.1.3.3 **Ammonium pyrrolidine dithiocarbamate (APDC)**, 20 g/l solution.

Prepare this solution just before use.

NOTE Solid APDC can decompose with loss of ammonium group. The decomposition product results in a scum on the surface of the aqueous solution which can readily be separated by filtration.

C.1.3.4 **Buffer solution**

Dissolve 113 g of diammonium hydrogen citrate ($(NH_4)_2\ HC_6H_5O_7$) in about 500 ml of water and transfer this solution to a 1 000 ml separating funnel.

Purify this solution as follows:

Shake with 50 ml of APDC solution (C.1.3.3) and extract three times respectively with 50 ml, 25 ml and 25 ml of chloroform (C.1.3.2).

Back-extract the combined three organic extracts first into only 5 ml of nitric acid (C.1.3.1) and then after addition of 45 ml of water.

Repeat the extraction procedure until, aspirating the nitric extracts into the acetylene-air flame, the absorbance measured at 228,8 nm is lower than 10 times the absorbance of 20 ml chloroform extracted in 1 ml of nitric acid and 9 ml of water.

Transfer the purified solution into a 1 000 ml one-mark volumetric flask and add 100 ml of ammonia solution ($\rho \approx 0{,}9$ g/ml). Dilute to the mark with water and mix.

C.1.3.5 Cadmium, stock standard solution (I), $c(\text{Cd}) = 1\ 000$ mg/l, commercial solution or to be prepared as follows:

Dissolve 1,000 g of cadmium (metal mass fraction 99,99 %) in 10 ml of nitric acid (C.1.3.1).

Transfer quantitatively to a 1 000 ml one-mark volumetric flask. Make up to volume with water and mix.

C.1.3.6 Cadmium, standard solution (II), $c(\text{Cd}) = 5$ mg/l.

Transfer 5,0 ml of cadmium stock standard solution (C.1.3.5) and 1 ml of nitric acid (C.1.3.1) to a 1 000 ml one-mark volumetric flask. Make up to volume with water and mix.

C.1.4 Apparatus

Ordinary laboratory apparatus and glassware together with the following:

NOTE All new glassware used for this determination should be washed as follows and thoroughly rinsed with water after each operation:

- with a brush and detergent if the walls are greasy,
- with diluted nitric acid $c(\text{HNO}_3) \approx 7$ mol/l.

C.1.4.1 Atomic absorption spectrometer, fitted with an acetylene-air burner.

NOTE In order to reduce the interferences of non-specific absorption, the use of background correction devices is recommended.

C.1.4.2 Cadmium hollow cathode lamp

C.1.5 Procedure

C.1.5.1 Test portion

Weigh, to the nearest 1 g, about 250 g of the laboratory sample (*m*).

C.1.5.2 Test solution

Transfer the test portion (C.1.5.1), 850 ml of water, 10,0 ml of nitric acid (C.1.3.1) to a 2 000 ml beaker. Stir to dissolve.

Add some glass beads, heat and keep boiling for 30 min. Take care that the total volume never becomes less than 800 ml and add some water in case.

Allow to cool and transfer quantitatively to a 1 000 ml one-mark volumetric flask. Dilute to the mark with water and mix.

NOTE In the special case of sodium chloride containing acid insoluble matter, the details of any operations not included in this standard, or regarded as optional, together with any incidents likely to have had an influence upon the results, should be reported in the test report.

C.1.5.3 Blank test solution

Solution containing 10,0 ml of nitric acid (C.1.3.1) per litre.

C.1.5.4 Calibration solutions (for the blank test solution)

Transfer 0,5 ml of nitric acid (C.1.3.1) and the volumes of cadmium standard solution (II) (C.1.3.6) indicated in the Table C.1 into a series of four 50 ml volumetric flasks. Make up to volume with water and mix.

Table C.1 – Calibration solutions

Calibration solution N°	Cadmium standard solution (II) ml	Corresponding mass of cadmium µg
1 [a]	0	0
2	0,5	2,5
3	1,0	5,0
4	2,0	10,0

[a] Zero calibration solution.

C.1.5.5 Calibration solution (for the test solution)

Transfer 200 ml of test solution (C.1.5.2) and the volumes of cadmium standard solution (II) (C.1.3.6) indicated in Table C.1 into a series of four 500 ml separating funnels.

The solution No. 1 is the non-spiked test solution.

C.1.5.6 Determination

C.1.5.6.1 Complexation and extractions

Transfer 200 ml of blank test solution (C.1.5.3) to a 500 ml separating funnel.

Proceed as follows with this separating funnel and the four other ones prepared (C.1.5.5).

Complexation:

- Add 20,0 ml of buffer solution (C.1.3.4), 5,0 ml of APDC solution (C.1.3.3) and shake for 30 s.

Extractions:

- add 10,0 ml of chloroform (C.1.3.2) and shake vigorously for 1 min;
- allow the organic layer drain into a previously dried 100 ml separating funnel containing 1,0 ml of nitric acid (C.1.3.1) after the phase of separation;
- repeat this extraction procedure twice, using 5 ml of chloroform each time;
- combine the three organic extracts in the 100 ml separating funnel.

Back-extraction:

- shake vigorously the 100 ml separating funnel for 30 s;
- add 9,0 ml of water and shake again vigorously for 1 min;

- discard the lower organic layer when the layers have separated and collect the upper aqueous layer into a dry tube.

C.1.5.6.2 Preparation of the apparatus

Equip the spectrometer (C.1.4.1) with the cadmium hollow cathode lamp (C.1.4.2).

Set the lamp current, the slit and the pressure of acetylene and air according to the instruction manual of the instrument. Adjust the wavelength at the maximum of absorbance at about 228,8 nm.

C.1.5.6.3 Spectrometric measurements

Aspirate water after each measurement.

Aspirate the solutions into the acetylene-air flame and determine the absorbance of each one in the following order:

- the four solutions prepared in (C.1.5.4);
- the nitric acid obtained in C.1.5.6.1 for the blank test solution (C.1.5.3);
- the four nitric extracts obtained in C.1.5.6.1 for the solutions prepared in C.1.5.5.

C.1.5.7 Calibration curves

C.1.5.7.1 For the blank test solution

Subtract the absorbance of the zero calibration solution from that of each other calibration solution (C.1.5.4) and plot a graph with the masses of cadmium (Cd), in micrograms, on the abscissa and the corresponding corrected absorbances on the ordinate.

C.1.5.7.2 For the test solution

Subtract the absorbance of the nitric extract obtained for the solution No. 1 (non spiked test solution of C.1.5.5) from that of each extract obtained for the solutions No. 2, 3 and 4 (spiked test solutions of C.1.5.5) and plot a graph with the masses of cadmium (Cd), in micrograms, used to prepare these calibration solutions, on the abscissa and the corresponding corrected absorbances on the ordinate.

C.1.6 Expression of results

C.1.6.1 Calculation

The cadmium content of the sample, $c(\mathrm{Cd})$ in milligrams per kilogram of sodium chloride, is given by the following equation:

$$c(Cd) = 5\,\frac{m_2 - m_1}{m} \tag{7}$$

where

m is the mass, in grams, of the test portion (C.1.5.1);

m_1 is the mass of cadmium, in micrograms, read on the calibration curve (C.1.5.7.1) corresponding to the absorbance obtained for the extract of blank test solution (C.1.5.3);

m_2 is the mass of cadmium, in micrograms, read on the calibration curve (C.1.5.7.2) corresponding to the absorbance obtained for the extract of the solution No. 1 prepared in (C.1.5.5).

C.1.6.2 Repeatability and reproducibility

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.2 – Repeatability and reproducibility

	Rock salt	**Evaporated salt**	**Sea salt**
Number of laboratories	14	15	15
Results, Cd mg/kg Mean	< *LOQ* [a]	< *LOQ* [a]	< *LOQ* [a]
Standard deviation for: — repeatability (s_r)	0,0026	0,0054	0,0022
— reproducibility (s_R)	0,0119	0,0104	0,0102

[a] *LOQ* = Limit of quantification.

C.2 Determination of chromium

C.2.1 General

The method applies to products of chromium content (Cr) greater than 0,01 mg/kg.

C.2.2 Principle

The chromium(III) ions in the test sample are extracted at pH 7 as an oxinate with methyl isobutyl ketone. The extract is nebulized in a nitrous oxide-acetylene flame. The absorbance is measured at a wavelength of 357,9 nm. Chromium (VI), if present, is previously reduced to chromium(III) with sodium dithionite.

C.2.3 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.2.3.1 **Hydrochloric acid,** *c*(HCl) = 12 mol/l.

C.2.3.2 **Acetic acid,** $c(CH_3COOH)$ = 17 mol/l.

C.2.3.3 **Sodium hydroxide solution,** *c*(NaOH) = 4 mol/l.

C.2.3.4 **8 – Hydroxyquinoline (oxine)** solution mass fraction 5 % in ethanol.

C.2.3.5 **4 – Methyl – 2 – pentan-one (methyl isobutyl ketone)**

C.2.3.6 **Acetylene**

C.2.3.7 **Dinitrogen oxide (nitrous oxide) (N_2O)**

C.2.3.8 **Sodium dithionite ($Na_2S_2O_4$)**

C.2.3.9 **Chromium,** standard solution at 0,1 µg/l.

Dissolve, by heating, 100 mg of metallic chromium in 10 ml of hydrochloric acid (C.2.3.1). Make up to 1 000 ml one-mark volumetric flask with water and mix.

NOTE Commercially available standard solutions can also be used if the pH of the solution is < 2. For the preparation of the standard solution, a metal salt can also be used.

C.2.4 Apparatus

Ordinary laboratory apparatus and glassware together with the following:

C.2.4.1 **Atomic absorption spectrometer**, with burner head, suitable for a nitrous oxide-acetylene flame.

C.2.4.2 **Chromium hollow cathode lamp**

C.2.4.3 **Gas cylinders or gas tubes** with pressure regulators (for acetylene (C.2.3.6) nitrous oxide (C.2.3.7)).

C.2.4.4 **pH-meter**, with glass and reference electrodes.

C.2.4.5 **Extraction flasks**, 500 ml type Karamian (see Figure C.1).

C.2.5 Procedure

C.2.5.1 Test portion

Weigh, to the nearest 0,1 g, about 100 g (m) maximum of the laboratory sample.

C.2.5.2 Test solution

Transfer the test portion (C.2.5.1) to an extraction flask (C.2.4.5).

Dissolve in water and dilute to 400 ml. Acidify the solution, if necessary with the hydrochloric acid (C.2.3.1) to pH < 2 determined with the pH-meter (C.2.4.4).

Add 5 mg of sodium dithionite (C.2.3.8), 1 ml of the acetic acid solution (C.2.3.2) and 1 ml of the oxine solution (C.2.3.4) successively. Neutralize the solution with the sodium hydroxide solution (C.2.3.3) to pH 7,0 ± 0,1 determined with the pH-meter (C.2.4.4).

Add about 10 ml of methyl isobutyl ketone (C.2.3.5). As the solubility of methyl isobutyl ketone in water depends on the electrolyte concentration of the solution, add as much methyl isobutyl ketone as is needed in order to obtain a separate phase of 10 ml.

Shake for 1 min and allow the layers to separate.

C.2.5.3 Blank test solution

At the same time as the determination (C.2.5.5), carry out a blank test using the same quantities of all the reagents used for the preparation of the test solution but omitting the test portion. Adjust the volume of the solution to the same as that of the test solution.

C.2.5.4 Calibration solutions

Transfer to three extraction flasks (C.2.4.5) the same mass (m) of the test portion as taken in C.2.5.2.

Add 5 µg, 10 µg and 25 µg of chromium respectively from chromium standard solution (C.2.3.9). Dissolve in water and dilute to 400 ml.

Acidify the solution, if necessary, with hydrochloric acid (C.2.3.1) to pH < 2 determined with the pH-meter (C.2.4.4).

Carry out the extraction as specified in C.2.5.2.

C.2.5.5 Determination

C.2.5.5.1 Preparation of the apparatus

Equip the spectrometer (C.2.4.1) with the chromium hollow cathode lamp (C.2.4.2). Set the lamp current, the monochromator slit, the spectral bandwidth and the flow of nitrous oxide (C.2.3.7) and acetylene (C.2.3.6) according to the instruction manual of the instrument. Adjust the wavelength at the maximum of absorbance at about 357,9 nm.

C.2.5.5.2 Spectrometric measurements

Nebulize the organic layers in the nitrous oxide – acetylene flame and determine respectively the absorbance of the calibration solutions (C.2.5.4) and the test solution (C.2.5.2) against methyl isobutyl ketone (C.2.3.5) saturated with water.

Supply the organic layer into the flame until a constant scale reading is obtained (about 10 s).

If the function between absorbance and concentration is not linear, the apparatus has to be checked again. The measurement shall be repeated.

NOTE The absorbances of the calibration solutions, determined before and after the measurement of the test solution, should not deviate more than 3 % to 4 % relatively. If they do, the measurement should be repeated. At serial analysis, a calibration solution should be measured after three test solutions.

C.2.5.5.3 Blank determination

Carry out a blank determination with all reagents used (absorbance A_o).

C.2.6 Expression of results

C.2.6.1 Calibration factor

The calibration factor (f) is given by the equation:

$$f = \frac{m_i}{(A_c - A_s)} \tag{8}$$

where

m_i is the mass of chromium, in micrograms, added to the calibration solution;

A_c is the absorbance of the calibration solution;

A_s is the absorbance of the test solution.

Use for further calculation the average of the calibration factors, and only use the calibration factors for the concentration range, where the relation between concentration and absorbance is a linear one.

C.2.6.2 Calculation

The chromium content of the sample $c(Cr)$, in milligrams per kilogram of sodium chloride, is given by the following equation:

$$c(Cr) = \frac{(A_s - A_o) \times f}{m} \tag{9}$$

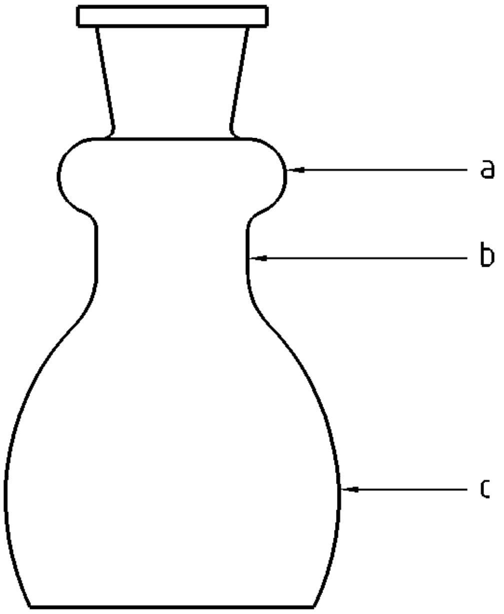
where

A_s is the absorbance of the test solution;

A_o is the absorbance of the blank test solution;

f is the calibration factor;

m is the mass, in grams, of the test portion (C.2.5.1).



Key

a Mixing space 190 ml
b Extraction solvent 10 ml
c Sample solution 500 ml

Figure C.1 – Extraction flask type Karamian

C.3 Determination of nickel

C.3.1 General

The method applies to products of nickel content (Ni) greater than 0,01 mg/kg.

C.3.2 Principle

The nickel in the test sample is extracted at pH 6 as an oxinate with methyl isobutyl ketone. The extract is nebulized in a nitrous oxide-acetylene flame. The absorbance is measured at a wavelength of 232,0 nm.

C.3.3 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.3.3.1 **Hydrochloric acid**, $c(\mathrm{HCl}) = 12$ mol/l.

C.3.3.2 **Acetic acid**, $c(\mathrm{CH_3COOH}) = 17$ mol/l.

C.3.3.3 **Sodium hydroxide solution,** $c(\mathrm{NaOH}) = 4$ mol/l.

C.3.3.4 **8 – Hydroxyquinoline (Oxine)** solution mass fraction 5 % in ethanol.

C.3.3.5 **4 – Methyl – 2 – pentan-one (Methyl isobutyl ketone)**

C.3.3.6 **Acetylene**

C.3.3.7 **Dinitrogen oxide (Nitrous oxide) (N_2O)**

C.3.3.8 **Nickel,** standard solution at 0,1 µg/l.

Dissolve, by heating, 100 mg of nickel in 10 ml of mixture (1 + 3) of nitric acid solution c(HNO_3) = 14 mol/l and hydrochloric acid solution (C.3.3.1). Make up to 1 000 ml one-mark volumetric flask with water and mix.

NOTE Commercially available standard solutions can also be used if the pH of the solution is < 2. For the preparation of the standard solution a metal salt can also be used.

C.3.4 Apparatus

Ordinary laboratory apparatus and glassware together with the following:

C.3.4.1 **Atomic absorption spectrometer**, with burner head, suitable for a nitrous oxide-acetylene flame.

C.3.4.2 **Nickel hollow cathode lamp**

C.3.4.3 **Gas cylinders or gas tubes** with pressure regulators (for acetylene (C.3.3.6) nitrous oxide (C.3.3.7).

C.3.4.4 **pH-meter**, with glass and reference electrodes.

C.3.4.5 **Extraction flasks**, 500 ml type Karamian (see Figure C.1).

C.3.5 Procedure

C.3.5.1 Test portion

Weigh, to the nearest 0,1 g, about 100 g maximum of the laboratory sample (*m*).

C.3.5.2 Test solution

Transfer the test portion (C.3.5.1) to an extraction flask (C.3.4.5).

Dissolve in water and dilute to 400 ml. Acidify the solution, if necessary with the hydrochloric acid (C.3.3.1) to pH < 2 determined with the pH-meter (C.3.4.4).

Add 1 ml of the acetic acid solution (C.3.3.2) and 1 ml of the oxine solution (C.3.3.4) successively. Neutralize the solution with the sodium hydroxide solution (C.3.3.3) to pH 6,0 ± 0,1 determined with the pH-meter (C.3.4.4).

Add about 10 ml of methyl isobutyl ketone (C.3.3.5). As the solubility of methyl isobutyl ketone in water depends on the electrolyte concentration of the solution, add as much methyl isobutyl ketone as is needed in order to obtain a separate phase of 10 ml.

Shake for 1 min and allow the layers to separate.

C.3.5.3 Blank test solution

At the same time as the determination (C.3.5.5), carry out a blank test using the same quantities of all the reagents used for the preparation of the test solution but omitting the test portion. Adjust the volume of the solution to the same as that of the test solution.

C.3.5.4 Calibration solutions

Transfer to three extraction flasks (C.3.4.5) the same mass (*m*) of the test portion as taken in C.3.5.2.

Add 10 µg, 50 µg and 100 µg of nickel respectively from the nickel standard solution (C.3.3.8). Dissolve in water and dilute to 400 ml.

Acidify the solution, if necessary, with hydrochloric acid (C.3.3.1) to pH < 2 determined with the pH-meter (C.3.4.4).

Carry out the extraction as specified in C.3.5.2.

C.3.5.5 Determination

C.3.5.5.1 Preparation of the apparatus

Equip the spectrometer (C.3.4.1) with the nickel hollow cathode lamp (C.3.4.2). Set the lamp current, the monochromator slit, the spectral bandwidth and the flow of nitrous oxide (C.3.3.7) and acetylene (C.3.3.6) according to the instruction manual of the instrument. Adjust the wavelength at the maximum of absorbance at about 232,0 nm.

C.3.5.5.2 Spectrometric measurements

Nebulize the organic layers in the nitrous oxide – acetylene flame and determine respectively the absorbance of the calibration solutions (C.3.5.4) and the test solution (C.3.5.2) against methyl isobutyl ketone (C.3.3.5) saturated with water.

Supply the organic layer into the flame until a constant scale reading is obtained (about 10 s).

If the function between absorbance and concentration is not linear, the apparatus has to be checked again. The measurement shall be repeated.

NOTE The absorbances of the calibration samples, determined before and after the measurement of the test solution, should not deviate more than 3 % to 4 % relatively. If they do, the measurement should be repeated.

At serial analysis, a calibration solution should be measured after three test solutions.

C.3.5.5.3 Blank determination

Carry out a blank determination with all reagents used (absorbance A_o).

C.3.6 Expression of results

C.3.6.1 Calibration factor

The calibration factor (f) is given by the equation:

$$f = \frac{m_i}{(A_c - A_s)} \tag{10}$$

where

m_i is the mass of nickel, in micrograms, added to the calibration solution;

A_c is the absorbance of the calibration solution;

A_s is the absorbance of the test solution.

Use for further calculation the average of the calibration factors, and only use the calibration factors for the concentration range, where the relation between concentration and absorbance is a linear one.

C.3.6.2 Calculation

The nickel content of the sample $c(Ni)$ in milligrams per kilogram of sodium chloride is given by the following equation:

$$c(Ni) = \frac{(A_s - A_o) \times f}{m_8} \tag{11}$$

where

A_s is the absorbance of the test solution;

A_o is the absorbance of the blank test solution;

f is the calibration factor;

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

C.4 Determination of lead

C.4.1 General

The method applies to products of lead content (Pb) equal to or greater than 0,5 mg/kg.

NOTE The limits 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;
- high purity reagents.

C.4.2 Principle

Dissolution of the test sample in nitric acid for the total mineralization of lead.

Complexation of the metal by ammonium pyrrolidine dithiocarbamate, extraction of metal carbamates into chloroform and back-extraction into nitric acid.

Nebulization of the nitric extract into an acetylene-air flam and measurement of the absorbance at a wavelength of 283,3 nm.

Determination of the lead content using the standard addition method.

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 **Nitric acid**, density $\rho \approx$ 1,40 g/ml, mass fraction 65 % solution.

C.4.3.2 **Chloroform**, density $\rho \approx$ 1,48 g/ml.

C.4.3.3 **Ammonium pyrrolidine dithiocarbamate** (APDC), 20 g/l solution.

Prepare this solution just before use.

NOTE Solid APDC can decompose with loss of ammonium group. The decomposition product results in a scum on the surface of the aqueous solution which can readily be separated by filtration.

C.4.3.4 **Buffer solution**

Dissolve 113 g of diammonium hydrogen citrate [$(NH_4)_2$ $HC_6H_5O_7$)] in about 500 ml of water and transfer this solution to a 1 000 ml separating funnel.

Purify this solution as follows:

Shake with 50 ml of APDC solution (C.4.3.3) and extract three times respectively with 50 ml, 25 ml and 25 ml of chloroform (C.4.3.2).

Back-extract the combined three organic extracts first into only 5 ml of nitric acid (C.4.3.1) and then after addition of 45 ml of water.

Repeat the extraction procedure until, aspirating the nitric extracts into the acetylene-air flame, the absorbance measured at 283,3 nm is lower than 10 times the absorbance of 20 ml chloroform extracted in 1 ml of nitric acid and 9 ml of water.

Transfer the purified solution into a 1 000 ml one-mark volumetric flask and add 100 ml of ammonia solution ($\rho \approx 0,9$ g/ml). Dilute to the mark with water and mix.

C.4.3.5 Lead, stock standard solution (I), $c_{(Pb)}$ = 1 000 mg/l, commercial solution or to be prepared as follows:

Dissolve in water 1,598 g of lead nitrate [$Pb\ (NO_3)_2$].

Transfer quantitatively to a 1 000 ml one-mark volumetric flask. Make up to volume with water and mix.

C.4.3.6 Lead, standard solution (II), $c_{(Pb)}$ = 10 mg/l.

Transfer 10,0 ml of lead stock standard solution (C.4.3.5) and 1 ml of nitric acid (C.4.3.1) to a 1 000 ml one-mark volumetric flask. Make up to volume with water and mix.

C.4.4 Apparatus

Ordinary laboratory apparatus and glassware together with the following:

NOTE All new glassware used for this determination should be washed as follows and thoroughly rinsed with water after each operation:

- with a brush and detergent if the walls are greasy,
- with diluted nitric acid $c(HNO_3) \approx 7$ mol/l.

C.4.4.1 Atomic absorption spectrometer, fitted with an acetylene-air burner.

NOTE In order to reduce the interferences of non-specific absorption, the use of background correction devices is recommended.

C.4.4.2 Lead hollow cathode lamp

C.4.5 Procedure

C.4.5.1 Test portion

Weigh, to the nearest 1 g, about 500 g of the laboratory sample (*m*).

C.4.5.2 Test solution

Transfer the test portion (C.4.5.1), 850 ml of water, 10,0 ml of nitric acid (C.4.3.1) to a 2 000 ml beaker. Stir to dissolve.

Add some glass beads, heat and keep boiling for 30 min. Take care that the total volume never becomes less than 800 ml and add some water in case.

Allow to cool and transfer quantitatively to a 1 000 ml one-mark volumetric flask. Dilute to the mark with water and mix.

NOTE In the special case of sodium chloride containing acid insoluble matter, the details of any operations not included in this standard, or regarded as optional, together with any incidents likely to have had an influence upon the results, should be reported in the test report.

C.4.5.3 Blank test solution

Solution containing 10,0 ml of nitric acid (C.4.3.1) per litre.

C.4.5.4 Calibration solutions (for the blank test solution)

Transfer 0,5 ml of nitric acid (C.4.3.1) and the volumes of lead standard solution (II) (C.4.3.6) indicated in the Table C.3 into a series of four 50 ml volumetric flasks. Make up to volume with water and mix.

Table C.3 – Calibration solutions

Calibration solution N°	Lead standard solution (II) ml	Corresponding mass of lead µg
1[a]	0	0
2	2,5	25
3	5,0	50
4	10,0	100

[a] Zero calibration solution.

C.4.5.5 Calibration solution (for the test solution)

Transfer 200 ml of test solution (C.4.5.2) and the volumes of lead standard solution (II) (C.4.3.6) indicated in Table C.3 into a series of four 500 ml separating funnels.

The solution No. 1 is the non-spiked test solution.

C.4.5.6 Determination

C.4.5.6.1 Complexation and extractions

Transfer 200 ml of blank test solution (C.4.5.3) into a 500 ml separating funnel.

Proceed as follows with this separating funnel and the four other ones prepared (C.4.5.5).

Complexation:

— add 20,0 ml of buffer solution (C.4.3.4), 5,0 ml of APDC solution (C.4.3.3) and shake for 30 s.

Extractions:

— add 10,0 ml of chloroform (C.4.3.2) and shake vigorously for 1 min;

— allow the organic layer drain into a previously dried 100 ml separating funnel containing 1,0 ml of nitric acid (C.4.3.1) after the phase of separation;

— repeat this extraction procedure twice, using 5 ml of chloroform each time;

— combine the three organic extracts in the 100 ml separating funnel.

Back-extraction:

— shake vigorously the 100 ml separating funnel for 30 s;

— add 9,0 ml of water and shake again vigorously for 1 min;

- discard the lower organic layer when the layers have separated and collect the upper aqueous layer into a dry tube.

C.4.5.6.2 Preparation of the apparatus

Equip the spectrometer (C.4.4.1) with the lead hollow cathode lamp (C.4.4.2).

Set the lamp current, the slit and the pressure of acetylene and air according to the instruction manual of the instrument. Adjust the wavelength at the maximum of absorbance at about 283,3 nm.

C.4.5.6.3 Spectrometric measurements

Aspirate water after each measurement.

Aspirate the solutions into the acetylene-air flame and determine the absorbance of each one in the following order:

- the four solutions prepared in (C.4.5.4);
- the nitric acid obtained in C.4.5.6.1 for the blank test solution (C.4.5.3);
- the four nitric extracts obtained in C.4.5.6.1 for the solutions prepared in C.4.5.5.

C.4.5.7 Calibration curves

C.4.5.7.1 For the blank test solution

Subtract the absorbance of the zero calibration solution from that of each other calibration solution (C.4.5.4) and plot a graph with the masses of lead (Pb), in micrograms, on the abscissa and the corresponding corrected absorbances on the ordinate.

C.4.5.7.2 For the test solution

Subtract the absorbance of the nitric extract obtained for the solution No. 1 (non spiked test solution of C.4.5.5) from that of each extract obtained for the solutions No. 2, 3 and 4 (spiked test solutions of C.4.5.5) and plot a graph with the masses of lead (Pb), in micrograms, used to prepare these calibration solutions, on the abscissa and the corresponding corrected absorbances on the ordinate.

C.4.6 Expression of results

C.4.6.1 Calculation

The lead content of the sample, $c(Pb)$ in milligrams per kilogram of sodium chloride, is given by the following equation:

$$c(Pb) = 5\frac{(m_2 - m_1)}{m} \tag{12}$$

where

m is the mass, in grams, of the test portion (C.4.5.1);

m_1 is the mass of lead, in micrograms, read on the calibration curve (C.4.5.7.1) corresponding to the absorbance obtained for the extract of blank test solution (C.4.5.3).

m_2 is the mass of lead, in micrograms, read on the calibration curve (C.4.5.7.2) corresponding to the absorbance obtained for the extract of the solution No. 1 prepared in (C.4.5.5).

C.4.6.2 Repeatability and reproducibility

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.4 – Repeatability and reproducibility

	Rock salt	**Evaporated salt**	**Sea salt**
Number of laboratories	15	14	15
Results, Pb mg/kg Mean	< LOQ[a]	< LOQ	< LOQ
Standard deviation for :			
— repeatability (s_r)	0,0566	0,0483	0,1254
— reproducibility (s_R)	0,1299	0,1566	0,4141

[a] LOQ = Limit of quantification.

Annex D
(informative)

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

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

D.1 General principle

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

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

D.2 Interferences

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

D.3 Reagents

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

D.3.1 **Sodium tetrahydroborate** (sodium borohydride)

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

D.3.2 **Sodium iodide**, prereductant solution

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

D.3.3 **Sulfuric acid**, solution $c(H_2SO_4) = 9$ mol/l.

D.3.4 **Sulfuric acid**, solution $c(H_2SO_4) = 1,25$ mol/l.

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

D.3.5 Nitric acid, density ρ = 1,42 g/ml.

D.3.6 Perchloric acid, density ρ = 1,66 g/ml.

D.3.7 Hydrochloric acid, density ρ = 1,16 g/ml.

D.3.8 Argon (or nitrogen), commercial grade.

D.3.9 Hydrogen, commercial grade.

D.3.10 Arsenic (III) solutions:

- stock As(III) solution: dissolve 1,320 g arsenic trioxide, As_2O_3, in water containing 4 g NaOH. Dilute to 1 000 ml; 1,00 ml = 1,00 mg As(III).
- intermediate As(III) solution: dilute 10 ml stock As (III) solution to 1 000 ml with water containing 5 ml hydrochloric acid (D.3.7); 1,00 ml =10,0 µg As(III).
- standard As(III) solution: dilute 10 ml intermediate As(III) solution to 1 000 ml with water containing the same concentration of acid used for sample preservation (2 ml to 5 ml nitric acid (D.3.5)); 1,00 ml = 0,100 µg As(III). Prepare diluted solutions daily.

D.3.11 Arsenic(V) solutions:

- stock As(V) solution; dissolve 1,534 g arsenic pentoxide, As_2O_5, in water containing 4 g NaOH. Dilute to 1 000 ml; 1,00 ml = 1,00 mg As(V).
- intermediate As(V) solution: prepare as for As(III) above; 1,00 ml = 10,0 µg As(V).
- standard As(V) solution: prepare as for As(III) above; 1,00 ml = 0,100 µg As(V).

D.3.12 Selenium(IV) solutions:

- stock Se(IV) solution: dissolve 2,190 g sodium selenite, Na_2SeO_3 in water containing 10 ml hydrochloric acid (D.3.7) and dilute to 1 000 ml; 1,00 ml = 1,00 mg Se(IV).
- intermediate Se(IV) solution: dilute 10 ml stock Se (IV) solution to 1 000 ml with water containing 10 ml hydrochloric acid (D.3.7); 1,00 ml = 10,0 µg Se(IV).
- standard Se(IV) solution: dilute 10 ml intermediate Se(IV) solution to 1 000 ml with water containing the same concentration of acid used for sample preservation (2 ml to 5 ml nitric acid (D.3.5)). Prepare solution daily when checking the equivalent of instrument response for Se(IV) and Se(VI); 1,00 ml = 0,100 µg Se(IV).

D.3.13 Selenium(VI) solutions:

- stock Se(VI) solution: dissolve 2,393 g sodium selenate Na_2SeO_4 in water containing 10 ml nitric acid (D.3.5). Dilute to 1 000 ml; 1,00 ml = 1,00 mg Se(VI).
- intermediate Se(VI) solution: prepare as for Se(IV) above ; 1,00 ml = 10,0 µg Se(VI).
- standard Se(VI) solution: prepare as for Se(IV) above; 1,00 ml = 0,100 µg Se(VI).

D.3.14 Antimony solutions:

- stock Sb solution: dry 2 g of potassium antimonyl tartrate hemihydrate (antimony potassium tartrate) ($C_4H_4O_7$ Sb K. 0,5 H_2O) at 100°C for 1 h. Dissolve 1,669 g in water. Dilute to 1 000 ml and mix, 1,00 ml = 1,00 mg Sb.
- intermediate Sb solution: dilute 10 ml stock Sb solution to 1 000 ml with water containing 10 ml hydrochloric acid (D.3.7); 1,00 m = 10,0 µg Sb.

- standard Sb solution: dilute 10 ml intermediate Sb solution to 1 000 ml with water containing the same concentration of acid used for sample preservation (2 ml to 5 ml nitric acid (D.3.5); 1,00 ml = 0,100 µg Sb. Prepare diluted solutions daily.

D.4 Apparatus

Ordinary laboratory apparatus and glassware, together with the following.

D.4.1 Atomic absorption spectrometer, equipped with gas flow meters for argon (or nitrogen) and hydrogen, As,Sb and Se electrodless discharge lamps with background correction at measurement wavelengths and appropriate strip-chart recorder.

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

D.4.2 Atomizer

Use one of the following:

- Boling-type burner[7] head for argon (or nitrogen)-air entrained-hydrogen flame;
- cylindrical quartz cell, 10 cm to 20 cm long, electrically heated by external Ni-Cr wire to 800 °C to 900 °C;
- cylindrical quartz cell with internal fuel rich hydrogen-oxygen (air) flame.

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

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

D.4.3 Reaction cell for producing As, Sb or Se hydrides.

An example of reaction cell is given in Figure D.1.

NOTE A commercially available system is acceptable if it utilizes liquid sodium borohydride reagents; accepts samples digested in accordance with D.5.3, accepts between 4 mol/l to 6 mol/l (HCl); and is efficiently and precisely stirred by the purging gas and/or a magnetic stirrer.

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

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

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

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

D.4.4 Dropper and syringe, capable of delivering 0,5 ml to 3,0 ml sodium borohydride reagent. Exact and reproducible addition is required so that production of hydrogen gas does not vary significantly between determinations.

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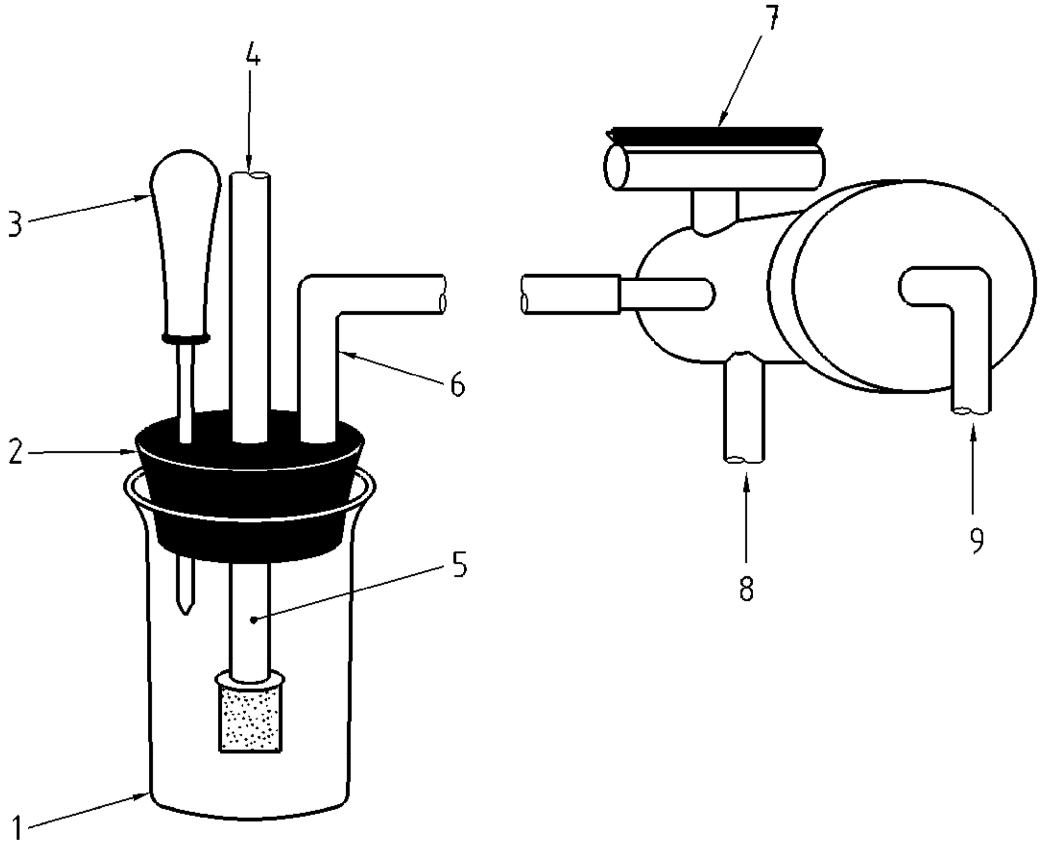
[7] Boling is the name of the inventor of this type of burner for rapid combustion of the hydrides.



Key

1	Beaker 250ml
2	Rubber stopper
3	Dropper
4	Auxiliary nitrogen
5	Gas dispersion tube
6	Outlet tube
7	Burner
8	Hydrogen
9	Nitrogen

Figure D.1 - Reaction cell for producing As, Sb or Se hydrides

D.5 Procedure

D.5.1 Preparation of the apparatus

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

D.5.2 Preparation of calibration solutions

Transfer 0,00 ml; 1,00 ml; 2,00 ml; 5,00 ml; 10,00 ml; 15,00 ml and 20,00 ml standard solutions of As(III), Se(IV) or Sb to 100 ml volumetric flasks and make up to volume with water containing the same acid concentration used for sample preservation (commonly 2 ml to 5 ml nitric acid (D.3.5)).This yields calibrations solutions of 0 µg/l, 1 µg/l, 2 µg/l, 5 µg/l, 10 µg/l, 15 µg/l and 20 µg/l As, Se or Sb. Prepare fresh samples daily.

D.5.3 Preparation of test solutions and standard solutions

Add 50 ml of the sample or As(III), Se(VI) or Sb standard solution to 250 ml beaker. Alternatively, prepare standard solutions by adding aliquots of solutions containing 5 µg As, Se or Sb directly to the beaker and dilute to 50 ml in this beaker, thus achieving a concentration of 100 µg/l of the respective solutions. Add 7 ml sulfuric acid $c(H_2SO_4) = 9$ mol/l (D.3.3) and 5 ml nitric acid (D.3.5). Add a small boiling chip or glass beads if necessary. Evaporate to SO_3 fumes. Maintain oxidizing conditions at all times by adding small amounts of nitric acid, to prevent solution from darkening.

Maintain an excess of nitric acid until all organic matter is destroyed. Complete digestion usually is indicated by a light-coloured solution. Cool slightly, add 25 ml water and 1 ml of perchloric acid (D.3.6) and again evaporate to SO_3 fumes to expel oxides of nitrogen.

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

D.5.4 Determination of arsenic with sodium borohydride

To 50 ml of the digested standard solution or the test solution in a 250 ml beaker (see Figure D.1) add 5 ml hydrochloric acid (D.3.7) and mix. Add 5 ml sodium iodide prereductant solution (D.3.2), mix and wait at least 30 min.

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

Attach one beaker at a time to the rubber stopper containing the gas dispersion tube for the purging gas, the sodium borohydride reagent inlet, and the outlet to the atomizer. Turn on strip-chart recorder and wait until the base line is established by the purging gas and all air is expelled from the reaction cell. Add 0,5 ml sodium borohydride reagent (D.3.1). After the instrument absorbance has reached a maximum and returned to the base line, remove beaker, rinse dispersion tube with water, and proceed to the next test solution or standard solution. Periodically compare standard As(III) and As(V) curves for response consistency. Check for presence of chemical interferences that suppress instrument response for arsine by treating a digested sample with 10 µg/l As(III) or As(V) as appropriate. Average recoveries shall be not less than 90 %.

D.5.5 Determination of selenium with sodium borohydride

To 30 ml of the digested standard solution or the test solution, or to 30 ml of the undigested standard, or the sample in a 250 ml beaker, add 15 ml hydrochloric acid (D.3.7) and mix. Heat for a predetermined period at 90 °C to 100 °C. Alternatively, autoclave at 121 °C in capped containers for 60 min, or heat for a predetermined time in open test tubes using a 90 °C to 100 °C hot water bath or an aluminium block digester. Check effectiveness of the selected heating by demonstrating equal instrument responses for calibration curves prepared either from standard Se(IV) or from Se(VI) solutions. Effective heat exposure for converting Se(VI) to Se(IV), with no loss of Se(IV), ranges between 5 min to 60 min when open beakers or test tubes are used. Do not digest standard Se(IV) and Se(VI) solutions used for this check of equivalency.

After prereduction of Se(VI) and Se(IV) attach beakers, one at a time, to the purge apparatus. For each, turn on the strip-chart recorder and wait until the base line is established. Add 0,50 ml sodium borohydride reagent (D.3.1). After the instrument absorbance has reached a maximum and returned to the base line, remove beaker, rinse dispersion tube with water and proceed to the next test solution or standard. Check for presence of chemical interferences that suppress selenium hydride instrument response by treating a digested sample with 10 µg/l Se(IV). Average recoveries shall be not less than 90 %.

D.5.6 Determination of antimony with sodium borohydride

To 30 ml of the digested standard solution or the test solution, or to 30 ml undigested standard, or the sample in a 250 ml beaker, add 15 ml hydrochloric acid (D.3.7) and mix. Heat for a predetermined period (between 5 min and 60 min) at 90 °C to 100 °C. After prereduction of Sb attach beakers, one at a time, to the purge apparatus. For each, turn on the strip-chart recorder and wait until the base line is established. Add 0,50 ml sodium borohydride reagent (D.3.1). After the instrument absorbance has reached a maximum and returned to the base line, remove beaker, rinse dispersion tube with water and proceed to the next test solution or standard. Check for presence of chemical interferences that suppress antimony hydride instrument response by treating a digested sample with 10 µg/l Sb. Average recoveries shall be not less than 90 %.

D.6 Calculation

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

Bibliography

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

[2] 95/2/EEC, *European Parliament and Council Directive of 20th February 1995 on food additives other than colours and sweeteners and its amendments.*

[3] 67/548/EEC; *Council Directive of 27th June 1967 on the approximation of the laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances and its amendments and adaptations*.

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