SLOVENSKI STANDARD
SIST EN 15763:2010

01-marec-2010

Ģivila - Doloļ evanje elementov v sledovih - Doloļ evanje arzena, ģivega srebra in svinca z masno spektrometrijo z induktivno sklopljeno plazmo (ICP-MS) pod pritiskom

Foodstuffs - Determination of trace elements - Determination of arsenic, cadmium, mercury and lead in foodstuffs by inductively coupled plasma mass spectrometry (ICP-MS) after pressure digestion

Lebensmittel - Bestimmung von Elementspuren - Bestimmung von Arsen, Cadmium, Quecksilber und Blei in Lebensmitteln mit induktiv gekoppelter Plasma-Massenspektrometrie (ICP-MS) nach Druckaufschluss

Produits alimentaires - Dosage des éléments traces - Dosage de l'arsenic, du cadmium, du mercure et du plomb par spectrométrie d'émission avec plasma induit par haute fréquence et spectromètre de masse (ICP-MS) après digestion sous pression

Ta slovenski standard je istoveten z: **EN 15763:2009**

ICS:

67.050	Splošne preskusne in analizne metode za živilske proizvode	General methods of tests and analysis for food products

SIST EN 15763:2010 **en,fr,de**

EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

EN 15763

December 2009

ICS 67.050

English Version

Foodstuffs - Determination of trace elements - Determination of arsenic, cadmium, mercury and lead in foodstuffs by inductively coupled plasma mass spectrometry (ICP-MS) after pressure digestion

Produits alimentaires - Dosage des éléments traces - Dosage de l'arsenic, du cadmium, du mercure et du plomb par spectrométrie d'émission avec plasma induit par haute fréquence et spectromètre de masse (ICP-MS) après digestion sous pression

Lebensmittel - Bestimmung von Elementspuren - Bestimmung von Arsen, Cadmium, Quecksilber und Blei in Lebensmitteln mit induktiv gekoppelter Plasma-Massenspektrometrie (ICP-MS) nach Druckaufschluss

This European Standard was approved by CEN on 7 November 2009.

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

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

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

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

Management Centre: Avenue Marnix 17, B-1000 Brussels

Ref. No. EN 15763:2009: E

Contents

Foreword

This document (EN 15763:2009) has been prepared by Technical Committee CEN/TC 275 “Food analysis - Horizontal methods”, the secretariat of which is held by DIN.

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 June 2010, and conflicting national standards shall be withdrawn at the latest by June 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.

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

1 Scope

This European Standard specifies a method for the determination of arsenic, cadmium, mercury and lead in foodstuffs by inductively coupled plasma mass spectrometry (ICP-MS).

The collaborative study included foodstuffs such as carrots, fish homogenate, Mushrooms (CRM), graham flour, a simulated diet E (CRM), scampi, mussel and a Tort-2 CRM having an arsenic mass fraction ranging from 0,06 mg/kg to 21,5 mg/kg dry matter (d. m.), cadmium ranging from 0,03 mg/kg to 28,3 mg/kg d. m., mercury ranging from 0,04 mg/kg to 0,56 mg/kg d. m. and lead from 0,01 mg/kg to 2,4 mg/kg d. m.

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 13805*, Foodstuffs — Determination of trace elements — Pressure digestion*

3 Principle

The test solution, obtained by pressure digestion, is nebulised and the aerosol transferred to a high frequency inductively coupled argon plasma. The high temperature of the plasma is used to dry the aerosol and to atomise and ionise the elements. The ions are extracted from the plasma by a set of sampler and skimmer cones and transferred to a mass spectrometer where the ions are separated by their mass/charge ratio and determined by a pulse-count and/or analogue detector.

WARNING — The use of this method may involve hazardous materials, operations and equipment. This method does not purport to address all the safety problems associated with its use. It is the responsibility of the user of this method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

4 Reagents

4.1 General

The concentration of the trace elements in the reagents and water used shall be low enough not to affect the results of the determination. Using a multielemental method of high sensitivity like ICP-MS, the control of the blank levels of water and acid is very important. Generally ultrapure water and acid of high purity, e.g. cleaned by sub boil distillation, are recommended. Special facilities should be used in order to avoid contamination during the steps of preparation and measurements (e.g. use of laminar flow benches or comparable clean room facilities).

4.2 Nitric acid

Mass fraction not less than $w(HNO_3)$ = 65 %, with a density of approximately 1,4 g/ml.

4.3 Element stock solutions

Commercially available single or multielemental standards with a mass concentration of $\rho = 1\,000$ mg/l of As, Au, Cd, Hg, Lu, Rh and Pb are recommended. Such standards are available in suitable concentrations from different suppliers. Stock solutions in diluted nitric acid are preferred.

4.4 Diluted mercury stock solution, ρ(Hg) = 10 mg/l

Pipette 1 ml of Hg stock solution of ρ(Hg) = 1 000 mg/l (4.3) and 1 ml of nitric acid (4.2) in a 100 ml volumetric flask and dilute with water to mark.

4.5 Diluted multi-element stock solution

The concentration levels of the elements in the diluted multi-element stock solution may be chosen in the relation to the type of samples analysed.

EXAMPLE ρ(As) = 20 mg/l, ρ(Cd), ρ(Pb) = 10 mg/l. Pipette 2 ml of As, 1 ml of Cd and Pb, respectively of each stock solution into a 100 ml volumetric flask , add 1 ml of nitric acid (4.2), dilute with water to the mark and transfer the solution into a suitable vessel.

4.6 Multi-element calibration solution

According to the example given under 4.5, the multi-element calibration solution contains: $\rho = 100$ µg/l As, $\rho = 50$ µg/l Cd, Hg, Pb. Pipette 0,5 ml diluted mercury stock solution (4.4) and 0,5 ml of the diluted multi-element stock solution (4.5) to a 100 ml volumetric flask, add 1 ml nitric acid (4.2), dilute with water to the mark and transfer the solution into a suitable vessel (PFA or quartz is recommended).

4.7 Internal standard solution

The internal standard solution contains Rhodium and Lutetium with a mass concentration of $\rho = 1\,000$ mg/l. Gold is used to stabilise mercury in the solution and reduce memory effects. The internal standard/s should cover the mass range used for determination of the elements. Their concentrations in the test solutions should be negligible.

4.8 Diluted internal standard solution

The concentration of the diluted internal standard solution should be high enough to give sufficient signal intensity. For an internal standard solution of ρ(Au, Rh, Lu) = 5 mg/l, pipette 0,5 ml of Au, Rh and Lu internal standard solution (4.7) each into a 100 ml flask, add 1 ml of nitric acid (4.2), dilute to volume with water and transfer the solution into a suitable vessel.

4.9 Optimising solution

The optimising solution is used for check and optimising procedures during set up of the ICP-MS. It is used for mass calibration purposes and for adjustment of maximum sensitivity at low rates of oxides and doubly charged ions. The optimising solution should contain elements that cover the whole mass range giving a high rate of oxides and doubly charged ions. The solutions recommended by the manufacturer of the ICP-MS instrument may be used. A solution containing e.g. Y, Rh, Ce and Pb is suitable for those purposes. The concentration of these elements should be chosen in order to achieve a count rate of 10 000 to 100 000.

4.10 Blank solution

The blank solution contains water and the same amount of acid used in the calibration solution.

5 Apparatus and equipment

5.1 General

Stability of test and diluted stock solutions are greatly influenced by the material of which the storage vessel is made. For the determination of elements in trace or ultra trace concentrations vessels made of quartz or fluoropolymers (polytetrafluoroethylene – PTFE, perfluoroalkoxy – PFA) are highly recommended. Glass or polyvinylchloride (PVC) should not be used. Vessels made of other materials may be used as long as they do not affect the results. The vessels should be carefully cleaned and rinsed.

5.2 Inductively Coupled Plasma – Mass Spectrometer (ICP-MS)

Mass spectrometer with inductively coupled argon plasma operating in a mass range from 5 amu to 240 amu. Using routine settings the mass spectrometer shall be capable to resolve 1 amu peak width at 5 % peak height or better (resolution 300) and have a sensitivity to achieve the detection limits listed in Table 2. Mass spectrometers with additional reaction or collision cells may be used to reduce the influence of polyatomic ions. Sectorfield mass spectrometers that allow the separation of the polyatomic ions by the use of high resolution settings may also be used.

The ICP-MS, having a nebulising system with a low pulsion peristaltic pump, should be equipped with a mass flow controller for the nebuliser gas.

5.3 Argon

Purity of at least 99,99 %.

6 Procedure

6.1 Sample pretreatment

Food samples are treated by a pressure digestion method according to EN 13805. The digested solution is diluted by water to a known volume (test solution). The concentration of nitric acid used in the calibration solutions should be similar to the final concentrations of nitric acid in the test solution. If hydrogen peroxide was added for the digestion, the calibration solutions need no addition of hydrogen peroxide.

6.2 ICP-MS

6.2.1 General

The correlation between the concentration of the element and the count rate measured is linear over some orders of magnitude. Therefore linear calibration functions can be used. The concentration range of the linearity should be checked regularly for each element. ICP-MS instruments with dual-detector capabilities, having an extended linear range, additionally need a regular check of the cross calibration factor of the two detectors.

6.2.2 ICP-MS settings

Table 1 — Example of instrument settings for ICP-MS

Parameter	Setting
RF-Power (W)	1 500
Carrier gas flow (l/min)	1,2
Plasma gas flow (l/min)	15
Auxiliary gas flow (l/min)	1,0
Spray chamber	Water cooled double pass
Spray chamber temperature (°C)	2
Lens voltage	4,5
Mass resolution	0,8
Integration time points/ms	3
Points per peak	3
Replicates	3

The instrument parameters described in the manufacturer's operating manual should be used. Generally, a plasma power of 1 100 W to 1 500 W should be chosen. By use of shorter or longer integration times on the isotope, the sensitivity may be influenced in some extend. Generally, three repeated measurements of each solution should be done. An example of instrument settings is given in Table 1.

6.2.3 Set up procedures for the ICP-MS

Before starting routine measurements the following set up procedure should be run: The ICP-MS should warm up in full running mode for a minimum 20 min to 30 min. Mass resolution, mass calibration, sensitivity and stability of the system are checked by the use of a suitable optimising solution (4.9). With an optimising solution the ICP-MS is adjusted daily to achieve maximum ion signals and both low oxide rates (e.g. < 2 %) and low rates of doubly charged ions (e.g. < 2 %). If a collision or reaction cell instrument is used, the flow rate of the cell gas(es) should be optimised, in order to ensure sufficient reduction of polyatomic interferences. If a high resolution mass spectrometer is used, mass calibration and sensitivity shall be checked for every range of resolution used. Check the sample feed and washout times with respect to the length of the tubing. If large differences in concentration of the test solutions are expected, the sample feed and washout times should be prolonged.

6.3 Interferences

6.3.1 General

Different types of interferences can influence the results obtained by ICP-MS measurements. Non-spectral interferences are caused by e.g. viscosity and the amount of matrix of the test solution. High amounts of salt can lead to deposition effects especially in the cone system. Generally the amount of salt in the test solution should not exceed 0,2 % (mass fraction). By the use of internal standards some of the non-spectral interference effects can be corrected for. Memory effects in the sample delivery system can influence the results of samples analysed after measurement of high concentrations. Especially high concentrations of Hg need prolonged washout times and control runs of blank solutions. In ICP-MS measurements spectral interferences (6.3.2, 6.3.3) are of high significance; most important ones are listed in Table 2. The detection limits vary from instrument to instrument and are influenced by the mass resolution of the instrument and e.g. matrix, working conditions and laboratory environment. The instrument used for ICP-MS determination should be capable to achieve the instrumental detection limits listed in Table 2 on the basis of pure standard solutions and the instrument settings used for routine measurement. The calculation of the detection limit is based on 3 × standard deviation of the mean level in the blank solution.

Table 2 — Recommended isotopes, instrumental detection limits and potential interferences

Element	Isotope	Instrumental detection limit µg/l	Interferences by isobaric or doubly charged ions	Possible interferences by polyatomic ions depending on mass resolution	
				300	10 000
As	75	0,5		$ArCl^+$, KAr^+, $CaCl^+$, KS^+, CaS^+, CoO^+, $CoNH^+$, NiN^+, $NiNH^+$	
Au	197	Internal Standard		TaO^+, $HfOH^+$, WOH^+	
Cd	111	0,5		MoO^+, $MoOH^+$, $AsAr^+$, $SeCl^+$, SeS^+, BrS^+, $ZnAr^+$	MoO^+, $MoOH^+$
	112[a]				
	114	0,2	Sn^+	MoO^+, $MoOH^+$, $SeCl^+$, SeS^+, $SeAr^+$, $BrCl^+$, BrS^+	MoO^+, $MoOH^+$
Hg	199[a]				
	200	1		HgH^+, WO^+, WOH^+	HgH^+
	201[a]				
	202	0,2		HgH^+, WO^+	HgH^+
Lu	175	Internal Standard		$BaCl^+$, $BaAr^+$, $CeCl^+$, $LaAr^+$	
Pb	206	0,3		$RhRh^+$	
	207	0,3		PbH^+, IrO^+	PbH^+
	208	0,2		PbH^+, HgC^+, PtO^+	PbH^+
Rh	103	Internal Standard		Pb^{2++}, $CuAr^+$, SrO^+, $SrOH^+$, $SrNH^+$, $KrOH^+$, $ZnCl^+$	SrO^+

[a] The isotopes can be used to check isotope ratios as a quality control.

6.3.2 Isobaric interferences

Isobaric interferences, e.g. 114 Cd and 114 Sn, can be corrected by the use of correction formulae (example in Table 3). The correction factor is based on the natural abundances of the isotopes:

EXAMPLE Calculation of the correction factor for the interference of 114 Sn on the determination of 114 Cd using 118 Sn (0,65 = % abundance of 114 Sn; 24,22 = % abundance of 118 Sn), see Equation (1):

$$\frac{0{,}65 \times 114\,Sn}{24{,}22 \times 118\,Sn} = 0{,}026\ 84 \tag{1}$$

Usually interference correction formulas are included in the software of the ICP-MS instrument.

Table 3 — Equations for correction of some isobaric interference

Isotope	Recommended correction
75 As	- 3,127 × (77 Se + 0,322 × 78 Se) Alternatively: - 3,127 × (77 Se – 0,826 × 82 Se)
114 Cd	- 0,026 83 × 118 Sn

6.3.3 Polyatomic interferences

These interferences are caused by the plasma gas, reagents and matrix present in the plasma. Examples are listed in Table 2. The amount of this type of interferences is strongly influenced by the plasma settings of the instrument (e.g. oxide ratio) and the type and amount of matrix present. Corrections may be carried out by mathematical factors or by measurement of the influence effect of the interfering element. Most of the polyatomic interferences can be resolved by the use of a sector field ICP mass spectrometer with a mass resolution of up to 10 000.

6.4 Calibration solutions

For calibration of the instrument a set of at least three different concentrations are used. The concentration range should be chosen with respect to the concentrations expected and with respect to the linear dynamic range. It is important that the concentration of nitric acid in the sample solutions and the calibration solutions are approximately the same.

The following description can be seen as an example:

Calibration solution 1: ρ(As) = 1 µg/l, ρ(Cd, Hg, Pb) = 0,5 µg/l
Pipette 0,5 ml of the diluted multi-element calibration solution (4.6) to a 50 ml volumetric flask, add 1 ml of nitric acid (4.2) and dilute with water to the mark.

Calibration solution 2: ρ(As) = 5 µg/l, ρ(Cd, Hg, Pb) = 2,5 µg/l
Pipette 2,5 ml of the diluted multi-element calibration solution (4.6) to a 50 ml volumetric flask, add 1 ml of nitric acid (4.2) and dilute with water to the mark.

Calibration solution 3: ρ(As) =20 µg/l, ρ(Cd, Hg, Pb) = 10 µg/l
Pipette 10 ml of the diluted multi-element calibration solution (4.6) to a 50 ml volumetric flask, add 1 ml of nitric acid (4.2) and dilute with water to the mark.

These calibration solutions should be prepared freshly before use.

6.5 Preparation of calibration solutions and test solutions for ICP-MS measurement

Every solution to be measured in the ICP-MS during routine runs should contain an internal standard. The concentration of the internal standard(s) shall be equal in all of the solutions. For the determination of mercury, gold shall be added, in order to stabilise the mercury. The test sample obtained by pressure digestion (according to EN 13805) should be analysed after dilution.

EXAMPLE Pipette 10 ml of zero member or calibration solution to a sample vessel, add 0,1 ml of diluted internal standard solution (4.8) and mix. Pipette 2 ml of test sample to a sample vessel, add 8 ml of water and 0,1 ml of diluted internal standard solution (4.8) and mix. Every solution contains approximately 10 µg/l of the internal standard Rh.

The internal standard solution may also be added on-line by a different channel on the peristaltic pump used for the analyses. Adjust the concentration of the internal standard solution and the pump flow rate in order to achieve a mass concentration of the internal standard of approximately ρ = 50 µg/l.