BRITISH STANDARD

BS EN 15765:2009

Foodstuffs — Determination of trace elements — Determination of tin by inductively coupled plasma mass spectrometry (ICP-MS) after pressure digestion

ICS 67.050

National foreword

This British Standard is the UK implementation of EN 15765:2009.

The UK participation in its preparation was entrusted to Technical Committee AW/-/3, Food analysis - Horizontal methods.

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

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This British Standard was published under the authority of the Standards Policy and Strategy Committee on 31 January 2010

ISBN 978 0 580 61087 5

Amendments/corrigenda issued since publication

Date	Comments

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 15765

December 2009

ICS 67.050

English Version

Foodstuffs - Determination of trace elements - Determination of tin by inductively coupled plasma mass spectrometry (ICP-MS) after pressure digestion

Produits alimentaires - Dosage des éléments traces - Dosage de l'étain par spectrométrie de masse à plasma induit par haute fréquence (ICP-MS) après digestion sous pression

Lebensmittel - Bestimmung von Elementspuren - Bestimmung von Zinn mit Massenspektrometrie mit induktiv gekoppeltem Plasma (ICP-MS) nach Druckaufschluss

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Ref. No. EN 15765:2009: E

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Foreword

This document (EN 15765:2009) 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of an identical text or by endorsement, at the latest by June 2010, and conflicting national standards shall be withdrawn at the latest by June 2010.

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1 Scope

This European Standard specifies a method for the determination of tin in foodstuffs by inductively coupled plasma mass spectrometry (ICP-MS) after pressurized digestion. The collaborative study included carrot puree, tomato puree, pineapple, mixed fruit, white wine, peach powder, tomato powder, beans powder, powdered fruit yoghurt and fish powder foodstuffs having a mass fraction of tin ranging from 2,5 mg/kg to 259 mg/kg.

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 sample is mineralized through pressurized digestion with nitric acid and hydrochloric acid in accordance with EN 13805. The digestion solution obtained thereby is diluted and then atomised and ionised in an inductively coupled argon plasma. After extraction from the plasma by a system of sampler and skimmer cones the positive (charged) tin ions are separated according to their mass charge ratio in a mass spectrometer and quantified in a detector system.

4 Reagents

4.1 General

The concentration of tin in the reagents and water used shall be low enough not to affect the results of the determination. Solution shall be understood as an aqueous solution unless otherwise specified.

4.2 Nitric acid, mass fraction $w(HNO_3) \geq 65$ %, mass concentration $\rho(HNO_3) \approx 1{,}4$ g/ml.

4.3 Hydrochloric acid, $w(HCl) \geq 30$ %, density $\rho(HCl) \approx 1{,}15$ g/ml.

4.4 Stock solutions

4.4.1 Tin stock solution, mass concentration $\rho(Sn) = 1\,000$ mg/l.

4.4.2 Rhodium stock solution (internal standard), mass concentration $\rho(Rh) = 1\,000$ mg/l.

4.5 Standard solutions

4.5.1 Tin standard solution 1, mass concentration $\rho(Sn) = 50$ mg/l

Fill a 50 ml volumetric flask with 10 ml to 20 ml of water, add 2,5 ml of hydrochloric acid (4.3) and mix. Cool to ambient temperature, and add by means of a pipette exactly 2,5 ml of tin stock solution (4.4.1) and dilute to volume with water. This solution is stable for at least one week.

4.5.2 Tin standard solution 2, mass concentration ρ(Sn) = 1,0 mg/l

Fill a 50 ml volumetric flask with 10 ml to 20 ml of water, add 2,5 ml of hydrochloric acid (4.3) and mix. Cool to ambient temperature, and add by means of a pipette exactly 1,0 ml of tin standard solution 1 (4.5.1) and dilute to volume with water. This solution is stable for one week.

4.5.3 Rhodium standard solution, mass concentration ρ(Rh) = 10 mg/l

Fill a 50 ml volumetric flask with 10 ml to 20 ml of water, add 2,5 ml of hydrochloric acid (4.3) and mix. Cool to ambient temperature, and add by means of a pipette exactly 0,5 ml of rhodium stock solution (4.4.2) and dilute to volume with water. This solution is stable for at least four weeks.

4.6 Calibration solutions

The following concentrations of the calibration solutions are examples and may be changed according to the sensitivity of measuring instrument and the concentration range to be investigated. Care shall be taken that calibration is carried out within the linear range of the detector system while paying attention to the varying frequency of isotopes. The quantity of internal standard added should be sufficient enough to obtain a stable and reproducible intensity. For calibration at least three calibration solutions of different concentration shall be used. The acid concentration should correspond to the one in the measuring solution.

The preparation of the following solutions is given as an example:

Calibration solutions with mass concentrations of 5 µg/l, 10 µg/l, 20 µg/l and 40 µg/l.

The calibration solutions are prepared from the tin standard solution 2 (4.5.2) according to following procedure:

Fill four 50 ml volumetric flasks with 10 ml to 20 ml of water, add 0,5 ml of nitric acid (4.2) and 0,1 ml of hydrochloric acid (4.3) and mix. Cool to ambient temperature, and pipette exactly the same amount of internal standard, e.g. 0,5 ml of rhodium standard solution (4.5.3), into each of the measuring flasks. Then, for the calibration solutions of mass concentrations of 5 µg/l, 10 µg/l, 20 µg/l and 40 µg/l, pipette exactly 0,25 ml, 0,50 ml, 1,0 ml and 2,0 ml of the standard solution 2 (4.5.2), respectively, into the four separate 50 ml volumetric flasks and make up to volume with water. These solutions shall be freshly prepared on each day of measurement.

The calibration solutions described here shall be understood as examples. The concentrations prepared shall be in the linear range of the ICP-MS detector system. Furthermore, the acid concentration of the calibration solutions shall be matched to the amounts of acid being present in the diluted digestion solution.

4.7 Blank solution (blank solution)

The blank solution contains water, nitric acid and hydrochloric acid in amounts that correspond to the concentrations in the measurement solution, for example 0,5 ml of nitric acid (4.2) and 0,1 ml of hydrochloric acid (4.3) in 50 ml as well as the same amount of internal standard (0,5 ml rhodium standard solution (4.5.3)) as used for the calibration solutions in 50 ml.

5 Apparatus and equipment

5.1 General

All apparatus and equipment that come into direct contact with the sample and solutions shall be pre-cleaned appropriately.

5.2 ICP-MS instrument with inductively coupled argon plasma as ionisation unit, sample feeding and nebulising system as well as an instrument controlling unit and an evaluation unit.

6 Procedure

6.1 Digestion of the sample

Mineralize the sample by pressurized digestion in accordance with EN 13805. For the quantification of tin, add 0,5 ml to 1 ml of hydrochloric acid (4.3) to the digestion vessel, which contains nitric acid (4.2) used for digestion, at an amount that corresponds to the amount of nitric acid. Do not add the hydrochloric acid until the spontaneous reaction with nitric acid has subsided. After addition of the hydrochloric acid close the digestion vessel immediately in order to avoid loss of active chlorine. Start pressurized digestion shortly thereafter. The digestion requirements are based on the specifications of the instrument manufacturer, the reactivity of the sample, the maximum pressure stability of the digestion vessel and the attainable temperature.

EXAMPLE 1 Precisely weigh 0,4 g to 0,5 g of dry sample (residual moisture of less than 20 %) into a 100 ml digestion vessel and add 5 ml of nitric acid (4.2). Carefully shake the digestion vessel to prevent clots from forming in the sample. After the spontaneous reaction has subsided, add 1 ml of hydrochloric acid (4.3) and close the digestion vessel as quickly as possible. For samples with a higher degree of moisture content, the weighed quantities can be increased.

The digestion solution that results from the pressurized digestion according to EN 13805 is made up to a defined volume, e.g. 20 ml, by water. This solution is diluted, using water, by a factor of 10 or higher for the subsequent determination of tin. It is important that the amount of internal standard is exactly the same, both in the measurement solutions and in the calibrations solutions.

EXAMPLE 2 For preparation of the measurement solution directly in the vessel used for measurement, pipette exactly 1,0 ml digestion solution and 0,5 ml rhodium standard solution (4.5.3) into the measurement vessel and make up with water to 10 ml. This solution should be measured on the day of preparation.

6.2 Inductively coupled plasma mass spectrometry

6.2.1 ICP-MS operating conditions

Set the instrument according to the manufacturer's specifications and ignite the plasma. Following sufficient warming up and stabilization of the instrument, optimise the settings.

6.2.2 Determination by ICP-MS

Once the instrument is optimised start the measurements. For evaluation tin isotopes of the masses 117 and 118 shall be used. The internal standard rhodium is analysed for the mass 103. Correction with internal standard is implemented by the method settings of the instrument software.

Measure the blank solution (4.7) and calibration solutions (4.6) and use the counting rate (counts/s) and concentrations to generate a calibration curve. Determine the linear range of the calibration function.

The measurement solution is aspirated and measured. Use the calibration curve to convert the determined counting rate into concentration units.

6.3 Quality control

For quality control, analyse a reference material with reliably known content of tin in parallel to each series of measurements. Include all procedural steps starting at the digestion. This also applies to each series of digestions including all procedural steps to prepare and measure blank solutions.

7 Evaluations

7.1 Calculation of the tin content in foodstuffs

Calculate the tin content, w, in milligrams per kilogram of sample or ϕ, in milligrams per litre of sample according to Equation (1):

$$w \text{ or } \phi = \frac{a \times V \times 1\,000 \times F}{E \times 1\,000 \times 1\,000} \quad (1)$$

where

a is the mass concentration of tin of the measurement solution, in micrograms per litre (µg/l);

V is the volume of the digestion solution diluted to volume, in millilitres (ml);

E is the initial sample mass, in grams (g), or the initial sample volume, in millilitres (ml);

F is the dilution factor (≥ 10).

7.2 Limit of quantification

The ICP-MS instrument should be able to quantify 1 µg/l tin in the diluted digestion solution. When using ICP-MS, the limit of quantification in the digestion solution prepared according to EN 13805 is mainly affected by the matrix content.

Regarding the foodstuff, the limit of quantification depends on the amount of sample used for digestion, on the final volume of digestion solution and on the minimum dilution applied (in this case 10). For trace elements the limit of quantification is conventionally defined as 6σ, where σ is the standard deviation of the field blank signal. Table 1 lists relevant examples.

Table 1 — Examples of quantification limits in the sample

Weighed quantity of sample g	**Final volume** ml	**Dilution**	**Mass fraction of tin** mg/kg
0,5	20	1:10	0,4
2,0	20	1:10	0,1

8 Precision

8.1 General

Details of an inter-laboratory test are summarised in Annex A. The values derived from this inter-laboratory test may not be applicable to concentration ranges and matrices other than those given in Annex A.

8.2 Repeatability

The absolute difference between two independent single test results obtained with the same test method on identical test material in the same laboratory by the same operator using the same apparatus within a short time interval will exceed the repeatability limit r given in Table 2 in not more than 5 % of the cases.

8.3 Reproducibility

The absolute difference between two single test results obtained with the same test method on identical test material in different laboratories by different operators using different equipment will exceed the reproducibility

limit R given in Table 2 in not more than 5 % of the cases.

Table 2 — Mean value, repeatability and reproducibility for ICP-MS

Sample	$\bar{x}$ mg/kg	r mg/kg	R mg/kg
Carrot puree	227	17,6	44,2
Tomato puree	165	13,1	28,4
Pineapple	259	22,9	37,6
Mixed fruit	71,9	5,2	11,5
White wine	2,49	0,18	0,44
Peach powder	84,8	5,94	13,4
Tomato powder	143	12,7	26,7
Bean powder	249	15,1	46,9
Fruit yoghurt, powdered	52,1	3,2	9,9
Fish powder	41,8	5,6	9,4

9 Test report

The test report shall specify at least the following:

a) all information necessary for the complete identification of the sample;

b) the test method used, with reference to this European Standard;

c) the results obtained and the units in which they are specified;

d) the date of sampling and sampling procedure (if known);

e) the date when the analysis was finished;

f) whether the requirement of the repeatability limit has been fulfilled;

g) all operating details not specified in this European Standard or regarded as optional, together with details of any incidents occurred when performing the method which might have influenced the test result(s).

Annex A
(informative)

Results of the inter-laboratory test

The precision of the method was established in 2006 by the Working group "Balanced diets - trace element analysis" established by the Federal Office of Consumer Protection and Food Safety (BVL) for the execution of § 64 of the German Food and Feed Code (LFGB) and by the Working Group "Inorganic Constituents" of the Food Chemistry Society of the German Chemists Society and has been verified in an inter-laboratory test evaluated in accordance with ISO 5725-1 [3] and ISO 5725-2 [4]. The results are given in Tables A.1 and A.2.

Number of samples "1" means that the results are based on a double determination of one sample. The results under number of samples "2" are based on one result of a blind duplicate sample.

Table A.1 — Statistical results of the inter-laboratory tests for fresh samples

Sample	**Carrot puree**	**Tomato puree**	**Pine-apple**	**Mixed fruit**	**White wine**
Parameter	Fresh samples				
Number of samples	1	1	1	1	1
Number of laboratories	14	15	14	15	15
Number of laboratories after elimination of outliers	14	15	14	15	13
Number of outliers	0	0	0	0	2
Number of results accepted	28	30	28	30	26
Mean value $\bar{x}$ (mg/kg)	227	165	259	71,9	2,49
Repeatability limit r (mg/kg)	17,6	13,1	22,9	5,2	0,18
Repeatability standard deviation s_r (mg/kg)	6,2	4,6	8,1	1,8	0,06
Horwitz value r	4,7	4,9	4,6	5,5	9,2
Horrat r index	0,59	0,57	0,68	0,46	0,27
Reproducibility limit R (mg/kg)	44,2	28,4	37,6	11,5	0,44
Reproducibility standard deviation S_R (mg/kg)	15,6	10,0	13,3	4,1	0,15
Horwitz value R	7,1	7,4	6,9	8,4	13,9
Horrat R index	0,97	0,82	0,74	0,67	0,45

Table A.2 — Statistical results of the inter-laboratory tests for lyophilised samples

Sample	Peach powder	Tomato powder	Bean powder	Fruit yoghurt, powdered	Fish powder
Parameter	Lyophilised samples				
Number of samples	2	1	2	2	1
Number of laboratories	15	15	15	15	15
Number of laboratories after elimination of outliers	14	15	15	12	14
Number of outliers	1	0	0	3	1
Number of results accepted	28	30	30	24	28
Mean value $\bar{x}$ (mg/kg)	84,8	143	249	52,1	41,8
Repeatability limit r (mg/kg)	5,9	12,7	15,1	3,2	5,6
Repeatability standard deviation s_r (mg/kg)	2,1	4,5	5,3	1,1	2,0
Horwitz value r	5,4	5,0	4,6	5,8	6,0
Horrat r index	0,46	0,63	0,47	0,38	0,79
Reproducibility limit R (mg/kg)	13,4	26,7	46,9	9,9	9,4
Reproducibility standard deviation S_R (mg/kg)	4,7	9,4	16,6	3,5	3,3
Horwitz value R	8,2	7,6	7,0	8,8	9,1
Horrat R index	0,68	0,87	0,95	0,76	0,87

Table A.3 — Trueness results

Sample	Mean value mg/kg	Reproducibility standard deviation S_R mg/kg	Assigned value mg/kg	Confidence interval (95 %) mg/kg	Z-Score
Carrot puree	227	16	222	32	0,3
Tomato puree	165	10	162	24	0,2
Mixed fruit	71,9	4,1	69,5	19	0,3
White wine	2,49	0,15	2,38	0,25	0,9
Bean powder	249	17	249	24	0,0

Bibliography

[1] Montaser, A.: Inductively Coupled Mass Spectrometry, 1998, Wiley-VCH.

[2] Thomas, R.; Practical Guide to ICP-MS, 2004, Marcel Dekker.

[3] ISO 5725-1, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions*

[4] ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

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