SLOVENSKI STANDARD
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Analiza živil - Določevanje Ag, As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Se, Tl, U in Zn v živilih z masno spektrometrijo z induktivno sklopljeno plazmo (ICP-MS) po razklopu pod tlakom

Analysis of Foodstuffs - Determination of Ag, As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Se, Tl, U and Zn in foodstuffs by inductively coupled plasma mass spectrometry (ICP-MS) after pressure digestion

Lebensmittel - Bestimmung von Elementen und ihren Verbindungen - Bestimmung von Ag, As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Se, Tl, U und Zn mit ICP-MS nach Druckaufschluss

Analyse des produits alimentaires - Dosage des éléments Ag, As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Se, Tl, U et Zn dans les produits alimentaires par spectrométrie de masse avec plasma à couplage inductif (ICP-MS) après digestion sous pression

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

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European foreword

This document (prEN 17851:2022) has been prepared by Technical Committee CEN/TC 275 “Food analysis – Horizontal methods”, the secretariat of which is held by DIN.

This document is currently submitted to the CEN Enquiry.

1 Scope

This document specifies a method for the determination of Ag, As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Se, Tl, U and Zn in foodstuffs by ICP-MS after pressure digestion.

The following foodstuffs were analysed for the elements listed in Table 1 in an interlaboratory study: Banana (deep-frozen), Cocoa powder, Wheat noodle powder, Currant nectar (deep-frozen), Milk powder, Oyster (dried), Celery (dried), Dogfish liver (dried), Liver (deep-frozen), Kale (dried).

Table 1 — Range[a]

Element	Mass fraction mg/kg	
	Lower range	Upper range
Arsenic	0,02	36,6
Lead	0,004	0,58
Cadmium	0,006	15,2
Chromium	0,06	5,71
Cobalt	0,03	7,49
Copper	0,71	74,0
Manganese	0,31	73,5
Molybdenum	0,05	1,88
Nickel	0,11	11,0
Selenium	0,06	8,70
Silver	0,011	1,98
Thallium	0,008	0,12
Uranium	0,003	0,26
Zinc	1,8	1 582

[a] Table 1 lists the ranges analysed in the interlaboratory study, indicating for each element the lowest and highest content found in the ten analysed food matrices (see Annex B, Table B.1 to Table B.14). The lower limit of the method's range varies depending on the food matrix and the food's water content. It is a laboratory-specific value and is defined by the laboratory for each element when calculating the limit of quantification (see 9.2).

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 13804, *Foodstuffs — Determination of elements and their chemical species — General considerations and specific requirements*

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

EN 15765, *Foodstuffs — Determination of trace elements — Determination of tin by inductively coupled plasma mass spectrometry (ICP-MS) after pressure digestion*

EN 17264, *Foodstuffs — Determination of elements and their chemical species - Determination of aluminium by inductively coupled plasma mass spectrometry (ICP-MS)*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— IEC Electropedia: available at https://www.electropedia.org/

— ISO Online browsing platform: available at https://www.iso.org/obp

4 Principle

The sample is digested using the pressure digestion process described in EN 13805, in the case of foodstuffs with a low water content, after adding water. In the digestion solution, the elements silver, arsenic, cadmium, cobalt, chromium, copper, manganese, molybdenum, nickel, lead, selenium, thallium, uranium and zinc are quantified by ICP-MS. For this purpose, the digestion solution is nebulized and the aerosol is transferred to an inductively coupled argon plasma where the elements are ionized. The ions are transferred via sampling cones into a mass spectrometer, where they are separated according to mass-to-charge ratio and detected by pulse and/or analogue detector.

The respective content of the elements mentioned in Clause 1 is understood as the total content measured using this described method. It is expressed in mg/kg or mg/l, depending on the sample type.

EN 17264 and EN 15765 shall be referred to for the determination of aluminium and tin in foodstuffs.

5 Reagents

The chemicals, gases and water used shall be free enough from the elements to be determined to not affect the results. Unless otherwise specified, "solutions" are understood to be aqueous solutions.

5.1 Nitric acid, ω = at least 65 %, density = approximately 1,4 g/ml.

5.2 Stock solutions

A commercially available multi-element stock solution, for example with ρ = 10 mg/l, can be used for silver, cadmium, cobalt, chromium, copper, manganese, molybdenum, nickel, lead, thallium, uranium and for example with ρ = 100 mg/l for arsenic, selenium and zinc.

Alternatively, commercially available single-element stock solutions, for example with ρ = 1 000 mg/l, can be used.

When using single-element stock solutions, attention shall be paid that they are suitable for ICP-MS, i.e. are of sufficiently high purity, to generate no additional contamination with other elements to be determined. If mixing the single-element stock solutions, attention shall also be paid to chemical compatibility.

NOTE Depending on the manufacturer, stock solutions with 10 000 mg/l can also be used if they are available in higher purities or have a better metrological traceability.

5.3 Multi-element standard solution

The dilutions of the stock solutions are depending on the concentration of the elements in the stock solutions and the concentration of the elements in the calibration solutions.

The multi-element stock solution (5.2) is used to prepare a multi-element standard solution, e.g. with ρ = 0,1 mg/l or ρ = 1,0 mg/l per element respectively. To prepare this standard solution, e.g. approximately 10 ml water and 2 ml nitric acid (5.1) are filled into a 50-ml volumetric flask and mixed. After cooling down to room temperature, exactly 0,5 ml multi-element stock solution (5.2) is added using a pipette and filled up with water.

The multi-element standard solution is stable for at least 1 month. The multi-element standard solution containing silver shall be stored protected from light.

Alternatively, the multi-element standard solution can also be prepared from single-element stock solutions by performing additional intermediate dilutions.

5.4 Stock solutions of internal standard, e.g ρ = 1 000 mg/l

When selecting internal standards, attention shall be paid that they cover the mass range of the analytes and have an ionization energy similar to that of the trace elements to be corrected. Attention shall also be paid that the concentration of the internal standards in the sample to be analysed is negligible and that they are not interfered by sample constituents.

For example, rhodium, indium and lutetium have proved suitable as internal standards.

Alternatively, other elements may also be used as internal standards (see Table 2 and Annex A).

Scandium (Sc) is not suitable as internal standard due to interferences of Ca and Si molecular ions.

Internal standards with a mass below 100 m/z should not be used, because matrix constituents may produce various interferences on the masses of such internal standards.

5.5 Standard solution of internal standard, e.g. ρ = 10 mg/l

To prepare this solution, approximately 10 ml water and 2 ml nitric acid (5.1) are filled into a 50-ml volumetric flask and mixed. After cooling down to room temperature, exactly 0,5 ml stock solution of internal standard (5.4) is added using a pipette and filled up with water. This standard solution is stable for at least three months.

5.6 Multi-element calibration solutions and Zero-point solution

5.6.1 General

The concentrations of the calibration solutions indicated below are exemplary and can be adapted depending on the instrument sensitivity and the concentration range to be covered. Make sure that the calibration is carried out within the linear range of the detector system. For calibration, at least 3 calibration solutions of different concentrations should be prepared. Make sure that the acid concentration of the calibration solutions corresponds to the test solution.

The calibration solutions are prepared from the multi-element standard solution (5.3) by adding internal standard (5.5) according to the following scheme:

To prepare these solutions, 10 ml to 20 ml water and 2 ml nitric acid (5.1) are filled into each 100 ml volumetric flask and mixed. After cooling down to room temperature, the multi-element standard solution (5.3) and 0,1 ml internal standard (5.5) are added one after the other using a pipette and then filled up to the mark with water. The calibration solutions shall be freshly prepared each working day.

NOTE The acid concentration of the calibration solutions in the example is adapted to a digestion with 4 ml nitric acid (5.1), a final volume of 20 ml and a dilution factor of 10 (in case of a dilution with water).

The internal standard solution can also be pumped via a separate channel of the tubing pump, mixed with the calibration solution using a Y-piece and then nebulized. When using this type of addition, the internal standard is not added to the calibration solution and shall be diluted accordingly. When using this

approach, attention shall be paid that the solutions are sufficiently mixed before they are nebulized and that the pump rate of both channels is constant.

5.6.2 Calibration solution 1

It is prepared from the multi-element standard solution (5.3), for example as follows:

Pipette 0,5 ml multi-element standard solution (5.3) into the 100 ml volumetric flask prepared according to 5.6 with water and nitric acid and follow the procedure described in 5.6.

ρ (silver, cadmium, cobalt, chromium, copper, manganese, molybdenum, nickel, lead, thallium and uranium) = 0,5 µg /l, ρ (arsenic, selenium and zinc) = 5 µg/l and internal standard ρ = 10 µg /l.

5.6.3 Calibration solution 2

Pipette 1 ml multi-element standard solution (5.3) into the 100-ml volumetric flask prepared according to 5.6 with water and nitric acid and follow the procedure described in 5.6.

ρ (silver, cadmium, cobalt, chromium, copper, manganese, molybdenum, nickel, lead, thallium and uranium) = 1 µg /l, ρ (arsenic, selenium and zinc) = 10 µg/l and internal standard ρ = 10 µg /l.

5.6.4 Calibration solution 3

Pipette 2 ml multi-element standard solution (5.3) into the 100-ml volumetric flask prepared according to 6.6 with water and nitric acid and follow the procedure described in 5.6.

ρ (silver, cadmium, cobalt, chromium, copper, manganese, molybdenum, nickel, lead, thallium and uranium) = 2 µg /l, ρ (arsenic, selenium and zinc) = 20 µg/l and internal standard ρ = 10 µg /l.

5.6.5 Zero-point solution

The zero-point solution contains 2 ml nitric acid (5.1) and internal standard (in the same concentration as the calibration solutions specified in 5.6) filled up with water to 100 ml.

Table 2 — Example of multi-element calibration solutions and zero-point solution

Calibration solution	Volume of multi-element standard solution (5.3) in 100 ml	Volume of internal standard solution (5.5) in 100 ml	Element concentration in the calibration solution[a] in µg /l
Calibration solution 1	0,5 ml	0,1 ml	0,5
Calibration solution 2	1,0 ml	0,1 ml	1,0
Calibration solution 3	2,0 ml	0,1 ml	2,0
Zero point solution	–	0,1 ml	–

[a] Concentration levels of arsenic, selenium and zinc are ten times higher.

6 Apparatus

6.1 General

All equipment and labware that come into direct contact with the sample and the solutions used shall be carefully pre-treated/cleaned according to EN 13804 to minimize the blank value.

It is recommended to only use vessels of quartz glass, perfluoroalkoxy alkane (PFA), fluorinated ethylene propylene (FEP) or polypropylene. It shall be ensured that the vessel materials do not release or absorb specific elements to prevent inaccurate analysis results.

6.2 ICP-MS

The mass spectrometer shall include an inductively coupled argon plasma, sample supply and nebulising system as well as instrument controlling and data acquisition. In order to avoid interferences of the atomic mass of all elements listed in this method, it is necessary to use a mass spectrometer that is able to eliminate or minimize interferences (e.g. reaction and/or collision cell, tandem MS, resolution above 4 000 m/z).

7 Sampling

The sampling procedure is not part of the method of analysis defined in this official method.

The sampling shall be carried out in such a way to avoid any contamination with or loss of analytes.

8 Procedure

8.1 Digestion

The sample is mineralized with nitric acid, in the case of foodstuffs with a low water content, after adding water, using the pressure digestion process described in EN 13805.

After the spontaneous reaction with the sample matrix caused by nitric acid has taken place, the digestion vessel is closed and the pressure digestion process is started.

The digestion conditions depend on the manufacturer's specifications, the reactivity of the sample, the maximum pressure stability of the digestion vessels and the temperature reached.

NOTE Depending on the natural chloride content of the samples, the recovery of silver could be affected. Therefore, the addition of hydrochloric acid could be beneficial. Also, in case of using HCl additional interferences could be occurring.

The digestion solution obtained by pressure digestion is filled up to a defined volume, e.g. 20 ml. It can be used for the subsequent element determination directly or after dilution. To minimize the signal suppression, dilution by a factor of ten, but at least by a factor of 2,5, is recommended. All test solutions shall have a similar concentration of acid and exactly the same concentration of internal standard as the calibration solutions.

8.2 Inductively coupled plasma mass spectrometry (ICP-MS)

8.2.1 ICP-MS working conditions

Set the instrument according to the manufacturer's specifications and ignite the plasma. After sufficient warming-up and stabilisation of the instrument (approximately 20 min to 30 min), the settings are optimized.

Select the instrument settings in such a way that not only high sensitivity is achieved, but also a low amount of molecule ion interferences (e.g. oxide ratio, double charged ions).

For this purpose, an optimization solution is measured that contains e.g. Mg, Rh, Pb and Ce (ρ = 10 µg /l). The formation rate of oxides and double charged ions should be lower than 3 %, for example, depending on the recommendations of the instrument manufacturer.

If a collision or reaction cell is used in order to reduce polyatomic interferences, the flow rate of the cell gas(es) should be optimized taking the matrix into account. The recommendations of the instrument manufacturer shall be observed during optimization. When cell gases are used, they shall also be applied to at least one internal standard and the correction shall be carried out with that internal standard.

When applying different resolutions[1] of the mass spectrometer, the mass windows shall be adjusted for each of the selected resolutions to make sure that the isotope to be determined is positioned in the centre of the window. At least one internal standard shall be measured at each resolution level.

Commercially available mass spectrometers often use different detectors or detector operating modes to cover a larger linear concentration range. In such cases, it shall be able to ensure that the sensitivity transitions of the detectors or operating modes are continuous and without any leaps.

8.2.2 Determination by ICP-MS

After optimizing the instrument, the measurements are started. It is recommended to use the isotopes listed in Annex A to determine the analytes. Generally, only isotopes that are not prone to be affected by interferences should be selected. To remove interferences, instrument systems should be used that are capable of working with collision or reaction cells or with a higher physical resolution. If such corrections are not possible, the interferences can also be reduced by using correction equations. For a plausibility check, simultaneous measurement of the uncorrected signals is advisable.

The interferences indicated in Annex A shall be taken into account.

The zero-point solution (5.6.5) and the calibration solutions (5.6) are measured and a calibration curve is created from the count rates (counts/sec) and concentrations. For complex matrices and high total salt concentrations, using the standard addition method may be advantageous.

The linear range of the calibration function shall be determined and checked on a regular basis.

The sample test solution is aspirated and measured. It is recommended that only diluted sample solutions are measured (see 8.1). When preparing dilutions, attention shall be paid that the diluted test solutions have the same concentration of acids and internal standard as the original test solutions as well as the calibration solutions. The internal standard can be mixed with the test solution via a separate channel of the hose pump using a Y-piece and then nebulized. In this case, no internal standard is added to the test and calibration solutions. When using this approach, attention shall be paid that the solutions are sufficiently mixed before they are nebulized and that the pump rate of both channels is constant.

The measured count rate is converted into units of concentration using the calibration curve.

Depending on the matrix effects, the count rate of internal standards in individual test solutions could be reduced or increased compared to that of pure calibration solutions.

If the count rate of the internal standards is reduced by more than 20 %, the digestion solution should be diluted further. To recognize potential interference effects on the element contents measured in the test solutions, measuring different dilutions of the digestion solution is generally recommended.

If the count rate of the internal standards is increased by more than 20 %, the cause should be identified as well. Continuous changes in intensity occur, for example, in the event of deposits on the sampling cones. If the count rate is increased, it should also be checked whether the internal standard was not already contained in the sample.

Matrix effects due to large amounts of salts (usually above 0,1 %) in the test solution can lead to heavy deposits, for example on the sampling cone, causing so called memory effects in the sample introduction system. In the case of samples with high element concentrations, attention shall therefore be paid to adequate flushing before analysing the next test solution. The flush-out behaviour can be checked with zero-point solution (5.6.5).

The consistence of the calibration functions shall be checked at sufficient intervals (e.g. after ten samples) by measuring a calibration solution. If necessary, the system shall be recalibrated.

[1] Spectrometer specific value: Resolution = m/(delta-m). This information is given for the convenience of the users applying this document.

8.3 Quality control of the analysis

For quality control, samples with reliably known contents of the analysed elements shall be analysed in parallel to every measurement series, including all process steps, starting with digestion. Prepare and measure blank solutions for every digestion series, also including all steps of the procedure.

It is recommended to use a certified reference material that is comparable to the sample in terms of matrix and concentration range and has a low uncertainty interval.

9 Evaluation

9.1 Calculation of element contents in foodstuffs

The content ω is calculated for each element as mass fraction in milligrams per kilogram (Formula 1) or litre (Formula 2) of sample using:

$$\omega = \frac{a \times V \times F}{1000 \times m} \quad (1)$$

$$\omega = \frac{a \times V \times F}{1000 \times v} \quad (2)$$

where

a is the element content in the test solution, in micrograms per litre;

V is the volume of the sample test solution after digestion, in millilitres;

F is the dilution factor of the test solution;

m is the sample weight, in grams;

v is the sample volume, in millilitres.

Factors of 1 000 required for unit conversion other than those shown above were cancelled with each other in both formulae (for a more detailed representation, see sample calculation of limit of quantification in 9.2).

Blank subtraction is not recommended. In the case of contaminations that have an influence on the contents in the digestion solutions, the whole series shall be generally discarded. Before starting a new digestion series, the source of contamination shall be identified and its cause eliminated.

9.2 Limits of quantification

The limit of quantification shall be calculated for each element. It is a laboratory-specific value and depends on the following factors:

a) method used to calculate the limit of quantification;

b) food matrix and water content of the foodstuff;

c) sample weight and sample volume;

d) volume of the sample test solution after digestion;

e) vessel materials;

f) purity of the chemicals;

g) ICP-MS instrument;

h) technique;

i) laboratory environment.

The limit of quantification in foodstuffs is calculated according to the formulae specified in 9.1. The element content in micrograms per litre of test solution obtained when calculating the limit of quantification is used for *a*. The dilution factor is the minimum factor by which each sample is diluted routinely, e.g. 10. Higher dilutions that are necessary due to too-high contents in the samples are not taken into account in calculating the limit of quantification. Higher dilutions that become necessary due to matrix effects shall be taken into account in calculating the limit of quantification.

Sample calculation of limit of quantification of lead in milk in mg/kg:

Example values:	Calculated limit of quantification *a*:	0,05 µg /l test solution
	Volume of digestion solution *V*:	20 ml
	Dilution factor *F*:	10
	Sample weight *m*:	2 g

Calculation using the example values with their units in the formula specified in 9.1 (Formula 1):

$$\omega = \frac{0,05\ \mu g / l \times 20 ml \times 10}{1000 \times 2 g} = 0,005\ mg / kg$$

More detailed representation of the calculation showing the unit conversion:

$$\omega = \frac{0,05\ \mu g \times 20\ ml \times 10 \times 1\ l \times 1\ mg \times 1000\ g}{1\ l \times 2\ g \times 1000\ ml \times 1000\ \mu g \times 1\ kg} = 0,005\ mg / kg$$

9.3 Reliability of the method

The present method was validated in a collaborative study (in 2017) with 18 participating laboratories.

A total of eleven samples with ten different matrices (banana, cocoa powder, wheat noodles, currant nectar, milk powder, oyster, celery, dogfish liver, liver, kale) were used, each with different contents of the individual elements.

In two of these eleven samples, the sample material was identical, namely wheat noodles. Each quantitative value of a laboratory is obtained from duplicate measurement or, in the case of wheat noodles (double blank), from quadruplicate measurement.

10 Precision

10.1 General

Details of the inter-laboratory test of the precision of the methods are summarized in Annex B. The values derived from this test may not be applicable to analyte concentration ranges and matrices other than given in Annex B.