
Živila - Določevanje kalcija, bakra, železa, magnezija, mangana, fosforja, kalija, natrija, žvepla in cinka z ICP-OES

Foodstuffs - Determination of calcium, copper, iron, magnesium, manganese, phosphorus, potassium, sodium, sulfur and zinc by ICP-OES

Lebensmittel - Bestimmung von Calcium, Kupfer, Eisen, Magnesium, Mangan, Phosphor, Kalium, Natrium, Schwefel und Zink mit ICP-OES

Produits alimentaires - Dosage du calcium, du cuivre, du fer, du magnésium, du manganèse, du phosphore, du potassium, du sodium, du soufre et du zinc par ICP-OES

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General methods of tests and
analysis for food products

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EUROPEAN STANDARD

EN 16943

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This European Standard was approved by CEN on 20 February 2017.

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European foreword

This document (EN 16943:2017) 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of an identical text or by endorsement, at the latest by November 2017, and conflicting national standards shall be withdrawn at the latest by November 2017.

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EN 16943:2017 (E)

1 Scope

This European Standard describes a method for the determination of calcium, copper, iron, magnesium, manganese, phosphorus, potassium, sodium, sulfur and zinc in different foodstuffs using optical emission spectrometry with inductively coupled plasma (ICP-OES) after pressure digestion.

This method has been validated in an interlaboratory study according to ISO 5725 [1] on infant formula soya based, cheese, chicken meat, wheat flour, apple juice, lobster and milk (see elements ranges Table 1 and validation data in Annex B).

HorRat values greater than 2 have been observed for certain analyte/matrix combinations during the validation study.

Table 1 — Validated element ranges

Element	Range mg/kg
Calcium	70 to 7178
Copper	0,60 to 16,40
Iron	0,88 to 77
Magnesium	45 to 1 174
Manganese	0,44 to 5,12
Phosphorus	72 to 9 708
Potassium	605 to 14 312
Sodium	11 to 2 220
Sulfur	26 to 8 542
Zinc	0,16 to 43,5

At European or International level, vertical standards for the determination of specific minerals can exist, e.g. for milk and milk products or for animal and vegetable fats and oils [2].

2 Normative references

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

EN 13804, *Foodstuffs - Determination of elements and their chemical species - General considerations and specific requirements*

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

3 Principle

After digestion of the sample with the pressure digestion process described in EN 13805, calcium, copper, iron, magnesium, manganese, phosphorus, potassium, sodium, sulfur and zinc are determined quantitatively with the ICP-OES [2]. The digestion solution is nebulized, the aerosol is directed into an inductively coupled argon plasma, where the elements are atomized and excited for radiation. The emission radiation is resolved spectrally and its intensity determined at element-specific wavelengths with a detector system. Ionization interference can be minimized using an ionization buffer.

4 Reagents

The concentration of the elements to be determined shall be low enough in the reagents and water not to affect the results.

4.1 Nitric acid, minimum $w = 65\%$ ¹, density about 1,4 g/ml

4.2 Hydrochloric acid, $w = 30\%$, density = 1,15 g/ml

4.3 Hydrogen peroxide, $w = 30\%$

Hydrogen peroxide (4.3) can contain phosphoric acid as a stabilizing agent. Hydrogen peroxide stabilized with phosphoric acid contaminates the samples with phosphorus and thus leads to incorrect results.

4.4 Caesium chloride solution as ionization buffer, e.g. $w = 10\%$ (see 6.2.2)

4.5 Internal standard, e.g. scandium, ytterbium, yttrium

Depending on the matrix, e.g. for samples with high total salt content, the application of an internal standard can be advantageous in order to reduce physical interference. In doing so, it shall be ensured that no faults from line interference result due to the internal standard.

NOTE It has been shown that if an internal standard is used, it is applicable to all elements mentioned in the scope.

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4.6 Stock solutions, $\rho = 1\ 000\ \text{mg/l}$ ² per element

Calcium, copper, iron, magnesium, manganese, phosphorus, potassium, sodium, sulfur and zinc individual element stock solutions and internal standard used.

The individual element stock solutions may not contain any of the elements to be determined here as accompanying substances or impurities, which could affect the correctness of the results.

Alternatively, commercial mixed stock solutions can also be used.

4.7 Standard solutions, $\rho = 100\ \text{mg/l}$ per element

Copper, iron, manganese and zinc standard solution, produced by dilution of the respective stock solution (4.6).

Pour 10 ml of water into a 50-ml volumetric flask, add 2 ml of nitric acid (4.1) and mix. After cooling to room temperature, add exactly 5 ml respectively of the copper, iron, manganese and zinc stock solution (4.6) by pipette and fill up with water to the mark. These standard solutions are stable for at least six months.

4.8 Element reference solutions

4.8.1 General

The concentrations of the reference solutions indicated in 4.8.3 to 4.8.6 serve as examples and shall be modified corresponding to the instrument sensitivity, the direction of viewing (axial or radial) and the concentration range to be examined, if necessary. If possible, the calibration shall be performed in the

¹ w = mass fraction

² ρ = mass concentration

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linear range. Minimum 3, in the nonlinear range 5, reference solutions of different concentrations should be prepared for the calibration. The concentration of the reagents (acids, if applicable ionization buffer and internal standard) shall correspond to the sample measuring solution.

For reasons of stability and purity, the phosphorus and sulfur reference solutions should be prepared separately from the multi-element reference solutions of the cations.

4.8.2 Preparation of the flask

Pour 10 ml to 20 ml of water into a 100-ml volumetric flask, add 10 ml of nitric acid (4.1) and 2 ml of hydrochloric acid (4.2) and mix. After cooling to room temperature, add stock (4.6) and standard solutions (4.7) by pipette. If using an ionization buffer, add 10 ml of 10 % caesium chloride solution (4.4). If using an internal standard (4.5), add the corresponding amount. Alternatively, the ionization buffer and/or the internal standard can be pumped via a Y-piece into the sample flow during the measurement.

These reference solutions are stable for a month.

The following data under 4.8.3 to 4.8.6 serve as examples and shall be adapted corresponding to the device sensitivity and the emission wavelength selected, and the direction of viewing (axial or radial), if necessary.

4.8.3 Reference solution 1

Pipette the following amounts of stock solutions (4.6) into the prepared 100-ml volumetric flask (4.8.2):

- 2,0 ml calcium → $\rho = 20$ mg/l calcium;
- 1,0 ml magnesium → $\rho = 10$ mg/l magnesium;
- 2,0 ml potassium → $\rho = 20$ mg/l potassium;
- 1,0 ml sodium → $\rho = 10$ mg/l sodium;

Furthermore, pipette the following amounts of standard solutions (4.7) into the same flask and fill up to the mark with water:

- 0,50 ml copper → $\rho = 0,5$ mg/l copper;
- 0,50 ml iron → $\rho = 0,5$ mg/l iron;
- 0,50 ml manganese → $\rho = 0,5$ mg/l manganese;
- 0,50 ml zinc → $\rho = 0,5$ mg/l zinc.

4.8.4 Reference solution 2

Pipette the following amounts of stock solutions (4.6) into the prepared 100-ml volumetric flask (4.8.2):

- 10,0 ml calcium → $\rho = 100$ mg/l calcium;
- 5,0 ml magnesium → $\rho = 50$ mg/l magnesium;
- 10,0 ml potassium → $\rho = 100$ mg/l potassium;
- 5,0 ml sodium → $\rho = 50$ mg/l sodium.

3) the sign "→" means: "which leads to a mass concentration of"

Furthermore, pipette the following amounts of standard solutions (4.7) into the same flask and fill up to the mark with water:

- 2,0 ml copper → $\rho = 2,0$ mg/l copper;
- 2,0 ml iron → $\rho = 2,0$ mg/l iron;
- 2,0 ml manganese → $\rho = 2,0$ mg/l manganese;
- 2,0 ml zinc → $\rho = 2,0$ mg/l zinc.

4.8.5 Reference solution 3

Pipette the following amounts of stock solutions (4.6) into the prepared 100-ml volumetric flask (4.8.2):

- 20,0 ml calcium → $\rho = 200$ mg/l calcium;
- 10,0 ml magnesium → $\rho = 100$ mg/l magnesium;
- 20,0 ml potassium → $\rho = 200$ mg/l potassium;
- 10,0 ml sodium → $\rho = 100$ mg/l sodium.

Furthermore, pipette the following amounts of standard solutions (4.7) into the same flask and fill up to the mark with water:

- 5,0 ml copper → $\rho = 5,0$ mg/l copper;
- 5,0 ml iron → $\rho = 5,0$ mg/l iron;
- 5,0 ml manganese → $\rho = 5,0$ mg/l manganese;
- 5,0 ml zinc → $\rho = 5,0$ mg/l zinc.

4.8.6 Reference solutions phosphorus and sulfur

Pipette the following amounts of stock solutions (4.6) into the prepared 100-ml volumetric flask (4.8.2) and fill up to the mark with water:

- 1,0 ml respectively phosphorus and sulfur → $\rho = 10,0$ mg/l phosphorus and sulfur;
- 5,0 ml respectively phosphorus and sulfur → $\rho = 50,0$ mg/l phosphorus and sulfur;
- 10,0 ml respectively phosphorus and sulfur → $\rho = 100,0$ mg/l phosphorus and sulfur.

4.9 Zero value solution

The zero value solution contains water, 10 ml of nitric acid (4.1), 2 ml of hydrochloric acid (4.2), if applicable 10 ml caesium chloride solution (4.4) and a corresponding amount of internal standard (4.5) in 100 ml.

5 Apparatus

5.1 General

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

5.2 ICP-OES, optical emission spectrometer with inductively coupled argon plasma, sample supply and atomization system as well as device control and evaluation unit.

EN 16943:2017 (E)**6 Procedure****6.1 Sample preparation**

Mineralize the sample in a pressure digestion corresponding to EN 13805.

In the case of dry, powdery or free-flowing materials (water content below 20 %), add 2 ml of water in relation to a test portion of 400 mg, and mix intensively so that the sample is well suspended in the water. Add nitric acid (4.1) and mix. For the determination of iron in order to avoid adsorption losses, add 0,5 ml to 1 ml of hydrochloric acid (4.2) to the digestion vessel, in addition to the nitric acid (4.1). The amount of hydrochloric acid depends on the amount of nitric acid used. Do not add the hydrochloric acid before/until the termination/expiration of the spontaneous reaction caused by the nitric acid. Seal the digestion vessel immediately after addition of the hydrochloric acid. The pressure digestion should be started shortly afterwards. Use digestion conditions according to the device manufacturer, the reactivity of the sample, the maximum pressure stability of the digestion vessel and the attainable temperature.

NOTE The trueness of the determination of the other elements is not impaired by the addition of hydrochloric acid during the digestion.

Fill up the digestion solution obtained according to EN 13805 after the pressure digestion to a definite volume, e.g. 20 ml. It can be used directly or after dilution for the following element determinations. The same concentration of acids, if applicable internal standard and ionization buffer, shall be present in all measuring solutions as in the reference solutions.

6.2 Optical emission spectrometry with inductively coupled plasma**6.2.1 ICP-OES working conditions**

Ensure that the device is set corresponding to the manufacturer's data and the plasma is ignited. After sufficient heating and stabilization of the device, optimize the settings [3], [4].

6.2.2 Determination with ICP-OES

Start the measurements after optimizing the device. The following wavelengths (Table 2), which have been tested for possible interference (see Table A.1), are recommended for determination of elements and for internal standards (Table 3). The wavelength data in the device-specific spectral libraries can deviate. Further wavelengths can be used, although these shall be tested for potential interference in individual cases.

Table 2 — Recommended wavelengths for element determination

Element	Wavelengths nm	Possible interference
Calcium	317,93 315,89 422,67	Ce, Fe, Mo, V Co, Mo, OH band Mo, V, Zr
Copper	324,75 327,40	Cr, Fe, Mo, Nb, Ti, U Co, Nb, Ti, U
Iron	259,94 238,20	Co, Mn, Nb Co
Magnesium	279,08 285,21	Fe, Nb, Rh Cr, Fe, Mo, W
Manganese	257,61 293,31	Cr, Fe, Mo, W Al, Cr, Fe, Ti
Phosphorus	213,62 214,91 177,43	Co, Cu, Fe, Mo, Zn Al, Cu, Fe, Mg Cu
Potassium	766,49 769,90 404,72	Ar, Ba, Mg, Ba Ba
Sodium	589,59 330,24	Ar, Ba, V Zn
Sulfur	181,97 180,67 182,56	B, Nb, Ni, Pb As, Ca, Co, Ni, Si B, Cu, Mg
Zinc	213,86 206,20	Al, As, Cu, Fe, Mg, Ni Cr, Nb

Table 3 — Recommended wavelengths for internal standards

Element	Wavelength nm
Scandium	361,38
Ytterbium	328,94
Yttrium	371,03

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When determining sodium and potassium, ionization interferences are generally present. In general, an ionization buffer, e.g. caesium chloride ($w = 1\%$ in the measurement solution), should be used for the axial recording of the plasma emission. In the case of radial recording of the emission intensity, the user of this standard shall establish whether the use of an ionization buffer can be omitted by optimizing the observation height and the gas settings. If element lines below 190 nm are applied, ensure sufficient inert gas purging between the plasma and inlet gap as well as the spectrometer so that oxygen absorption cannot cause any drifting of intensities.

If the ionization buffer is added via a Y-piece, adjust volume ratios so that the solution that enters the atomizer or plasma contains an excess of caesium chloride.

Measure zero value solution (4.9) and reference solutions (4.8) and prepare a calibration curve using emission intensities or peak areas and concentrations. In the case of complex matrices, the standard addition method may be necessary.

Aspirate sample solution and measure it. The determined peak areas or intensities are converted via calibration curve using linear regression into concentration units.

Ensure sufficient time for rinsing before the next measurement in case of samples with high element concentrations. Rinse performance can be monitored with zero value solution (4.9).

When making dilutions, ensure that the diluted measuring solutions have the same concentrations of reagents as the original measuring solutions.

6.3 Quality control of the analysis

For quality control, analyse control samples with reliably known contents of the elements to be determined in parallel to every measurement series. The control samples should pass through all analytical steps, beginning with the digestion. Likewise, prepare reagent blank solutions and measure for every digestion series, taking into account all process steps.

To check for matrix effect spiking experiments should be performed by adding a known concentration of the elements to the measurement solution.

7 Calculation

Calculate the mass fraction w in milligrams per kilogram or litre of sample according to Formula (1):

$$w = \frac{a \cdot V \cdot F}{m} \quad (1)$$

where

a	is the mass fraction of the element in the sample solution in milligrams per litre;
V	is the volume of the sample solution after digestion in millilitres;
F	is the dilution factor of the sample measuring solution;
m	is the mass of the test portion in grams or the sample volume in millilitres used for digestion.

Causes of increased element contents in the blank value solution shall be clarified and, if necessary, deducted from the calculation of the results.