SLOVENSKI STANDARD
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Krma: metode vzorčenja in analize - Določevanje elementov v sledovih, težkih kovin in drugih elementov v krmi z ICP-MS (večelementna metoda)

Animal feeding stuffs: Methods of sampling and analysis - Determination of trace elements, heavy metals and other elements in feed by ICP-MS (multi-method)

Futtermittel - Probenahme- und Untersuchungsverfahren - Bestimmung von Spurenelementen, Schwermetallen und anderen Elementen in Futtermitteln mittels ICP-MS (Multimethode)

Aliments des animaux - Méthodes d'échantillonnage et d'analyse - Dosage par ICP-MS (multiméthode) des éléments traces, métaux lourds et autres éléments inorganiques présents dans les aliments

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Animal feeding stuffs: Methods of sampling and analysis - Determination of trace elements, heavy metals and other elements in feed by ICP-MS (multi-method)

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European foreword

This document (EN 17053:2018) has been prepared by Technical Committee CEN/TC 327 “Animal feeding stuffs - Methods of sampling and analysis”, the secretariat of which is held by NEN.

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of an identical text or by endorsement, at the latest by July 2018, and conflicting national standards shall be withdrawn at the latest by July 2018.

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WARNING — The method described in this standard implies the use of reagents that pose a hazard to health. The standard does not claim to address all associated safety problems. It is the responsibility of the user of this standard to take appropriate measures for the health and safety protection of the personnel prior to use of the standard and to ensure that regulatory and legal requirements are complied with.

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1 Scope

This European Standard specifies a method for the determination of trace elements, heavy metals and other elements in animal feed by inductively coupled plasma mass spectrometry (ICP-MS). The method is used to determine As, Cd, Co, Cu, Fe, Hg, Mn, Mo, Pb, Se, Tl, U and Zn in the extraction solution after pressurized digestion. For the determination of extractable lead in minerals and feeds containing phyllosilicates (e.g. kaolinite clay) wet digestion with nitric acid should be used. The method described is suitable for use in quadrupole instruments equipped either with or without additional technology to reduce molecular ion interferences (e.g. collision or reaction technologies) as well as in high-resolution sector-field systems.

The method was fully statistically tested and evaluated in a collaborative trial comprising eight animal feeding stuff samples for the elements As, Cd, Co, Cu, Fe, Hg, Mn, Mo, Pb, Se, Tl, U and Zn. For elements with a HORRAT value higher than 2 (e.g. mercury, see Annex A) the method is more applicable as a screening method and not for confirmatory purposes. High-resolution sector-field ICP-MS was not tested in the validation ring trial.

The limit of quantification for each element is dependent on the sample matrix as well as the instrument. For the elements Co, Mn, Mo, Pb, Tl, U a limit of quantification of 0,10 mg/kg should normally be obtained, for the elements Fe and Zn 5,0 mg/kg, while for Cd 0,03 mg/kg, Hg 0,04 mg/kg and As 0,05 mg/kg should normally be quantifiable.

Details on the successfully tested working range for each element are described in this standard.

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 ISO 3696, *Water for analytical laboratory use — Specification and test methods (ISO 3696)*

EN ISO 6498, *Animal feeding stuffs — Guidelines for sample preparation (ISO 6498)*

3 Principle

For the determination of As, Cd, Co, Cu, Fe, Hg, Mn, Mo, Pb, Se, Tl, U and Zn a test portion of the sample is digested with concentrated nitric acid under pressure.

For the determination of extractable lead in minerals and feeds containing phyllosilicates (e.g. kaolinite clay) wet digestion with nitric acid should be used.

The concentration of the elements is determined by inductively coupled plasma mass spectrometry (ICP-MS) using external calibration or standard addition technique. To reduce occurring mass interferences mathematical correction equations, physical or chemical technical solutions (see B.2) or high-resolution sector-field ICP-MS may be applied.

4 Reagents

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

Use only reagents of recognized analytical grade and water conforming to grade 2 of EN ISO 3696.

4.1 Nitric acid concentrated, not less than 65 % (mass fraction), $c(HNO_3) = 14,4$ mol/l, having a density of approximately $\rho(HNO_3) = 1,40$ g/ml.

4.2 Nitric acid solution of 5 % (mass fraction), Pipette 54 ml of nitric acid (4.1) into a 1 000 ml volumetric flask (5.4) and fill to the mark with water.

4.3 Nitric acid solution (rinsing solution), Pipette 20 ml nitric acid (4.1) in a 1 000 ml volumetric flask (5.4). Fill up to the mark with water.

4.4 Hydrochloric acid concentrated, 30 % (mass fraction), $c(HCl) = 9,5$ mol/l, having a density of approximately $\rho(HCl) = 1,15$ g/ml.

4.5 Hydrogen peroxide, not less than 30 % (mass fraction), $c(H_2O_2) = 9,7$ mol/l, having a density of approximately $\rho(H_2O_2) = 1,12$ g/ml.

4.6 Single-element and multi-element stock solutions for ICP-MS, $\beta = 1\,000$ mg/l, It is advisable to use certified multi-element stock solutions. Stock solutions with concentrations different from 1 000 mg/l may be used as well. Stock solutions are considered to be stable for several months.

4.7 Calibration solutions, The concentrations of the calibration solutions depend on the element and the estimated concentration levels in the samples. When preparing calibration solutions care should be taken to pipette suitable volumes, intermediate dilution steps are recommended. If calibration solutions are prepared from single-element stock solutions, it should be checked whether they are chemically compatible and sufficiently pure (specification). Calibration solutions shall be prepared daily.

4.8 Internal standard stock solution, $\beta = 1000$ mg/l; As internal standard rhodium is recommended.

NOTE Alternatively, for low mass elements germanium, it is advised to use indium or scandium as internal standards. Rhenium, thulium and lutetium are beneficial for the quantification of high mass elements.

4.9 Internal standard working solution, $\beta = 1$ mg/l, Dilute 1 ml of the internal standard stock solution (4.8) to 1 000 ml with water.

4.10 Gold chloride stock solution, $AuCl_3$ (in 10 % HCl), $\beta = 10$ g Au/l.

4.11 Gold stability solution, $\beta = 200$ mg Au/l, Place 200 ml of water into a 500 ml volumetric flask (5.4), pipette 250 ml conc. HCl (4.4) and 10,0 ml gold chloride stock solution (4.10) and fill to the mark with water.

5 Apparatus

Usual laboratory apparatus and, in particular, the following:

5.1 Laboratory grinder

5.1.1 Laboratory grinder, capable of grinding to a particle size of less than or equal to 0,5 mm, e.g. a knife mill or equivalent.

5.1.2 Laboratory grinder, capable of grinding to a particle size of less than or equal to 0,1 mm, e.g. a ball mill or equivalent.

Check that the mill used does not influence the concentration of elements in the sample (e.g. adsorption, contamination) which shall be analysed.

5.2 Analytical balance, capable of weighing to an accuracy of 1 mg.

5.3 Pressure digestion apparatus, capable to reach temperatures above 210 °C. The apparatus shall be tested for safety pressure vessels made of acid-resistant materials and having vials for the sample of acid-resistant material with low level of contamination by elements to be determined. Instead of polytetrafluoroethylene (PTFE) vials, it is better to use graduated quartz vials, fluorinated ethylene propylene (FEP) vials or perfluoroalkoxy (PFA) vials. Quartz is advisable to be used for decomposition temperatures above 230 °C.

NOTE The use of a microwave heated pressure digestion apparatus is an option.

5.4 One-mark volumetric flasks;

5.5 Inductively Coupled Plasma Mass Spectrometer (ICP-MS);

5.6 Freeze-drying equipment, capable of freeze-drying liquid animal feeding stuffs;

5.7 Oven for pre-drying, capable to hold a temperature of 70 °C ± 5 °C;

5.8 Beaker, capacity 250 ml;

5.9 Electric hot plate, with temperature control.

6 Sampling

Sampling is not part of the method specified in this European Standard. A recommended sampling method is given in EN ISO 6497. It is important that the laboratory receives a sample which is truly representative and has not been damaged or changed during transport or storage.

7 Preparation and preservation of test samples

7.1 General

Prepare the test sample in accordance with EN ISO 6498:

- The grinding shall be done in conditions such that the substance is not appreciably heated and that no contamination takes place by the grinding tools;
- The operation shall be repeated as many times as is necessary and it shall be performed as quick as possible in order to prevent any gain or loss of constituents (water);

- The whole ground product is placed in a flask made of e.g. polypropylene, which can be stoppered and stored in such way to prevent any change in composition;
- Before any weighing is carried out for the analysis, the whole test sample shall be thoroughly mixed for reasons of homogeneity. Since a maximum of 0,5 g of sample is used for the digestion it is of the utmost importance to have a homogeneous sample in order to take a representative sub sample.

7.2 Animal feeding stuff, which can be ground as such

Grind the laboratory sample (usually 500 g), using a laboratory grinder (5.1) or mortar, until a particle size of 0,5 mm or less has been reached.

7.3 Mineral animal feeding stuffs

Mineral compounds, except mineral products containing crystalline water, e.g. $MgCl_2 \cdot 6H_2O$, shall be ground using a laboratory grinder (5.1.2) or mortar until a particle size of 0,1 mm or less has been reached. Mineral products containing crystalline water such as phyllosilicates should not be ground.

8 Procedure

8.1 Pressure digestion

8.1.1 General

Match the initial sample mass to the capacity of the digestion vessel, with the manufacturer's instructions being strictly followed for safety reasons.

8.1.2 Example of a high pressure digestion

When using a 100 ml vial, weigh about 0,5 g of the prepared test sample to the nearest 1 mg. Add 3 ml of nitric acid (4.1) and seal the digestion vial and the pressure vial in the correct manner. Leave to pre-digest for about 30 min and heat it in a pressure digestion apparatus (5.3) from room temperature to 150 °C in 60 min, then to at least 210 °C in 40 min and keep this temperature for 90 min before cooling down. Dilute the digestion solution accordingly with water. Treat a blank in the same way.

8.1.3 Example of microwave digestion

When using 100 ml vials, weigh about 0,5 g of the prepared test sample to the nearest 1 mg. Add 3 ml of nitric acid (4.1) and 0,5 ml of hydrogen peroxide (4.5), seal the digestion vial and the pressure holders in the correct manner. Leave to pre-digest outside the microwave oven (5.3) for about 30 min. Apply low microwave energy at the beginning of the digestion and slowly raise the energy to the maximum power, to reach at least 210 °C. Hold this temperature for at least 20 min, cool down for minimum 20 min to 25 min. Dilute the digestion solution accordingly with water. Treat a blank in the same way.

8.2 Extractable lead in minerals and feeds containing phyllosilicates (e.g. kaolinite clay) – extraction with diluted nitric acid

Weigh about 2 g of the prepared test sample to the nearest 1 mg into a beaker of 250 ml (5.8). Add 85 ml diluted nitric acid (4.2). Cover the beaker with a watch-glass and boil for 30 min on a hot plate (5.9). Allow to cool. Transfer the liquid into a 100 ml volumetric flask (5.4), rinse the beaker and the watch-glass several times with water. Dilute to the mark with water. After homogenizing, filter through a dry folded filter paper into a dry conical flask. Use the first portion of the filtrate to rinse the glassware and discard that part. If the determination is not carried out immediately, the conical flask with the filtrate shall be stoppered. Treat a blank in the same way.

8.3 Calibration

8.3.1 General

The concentration of elements in the extraction solution is quantified against element calibration solutions (4.7) by means of external calibration or standard addition technique.

Usually, there exists a stable linear relationship over several decimal powers between the signal measured by the detector and the concentration of elements in the analyte solution.

8.3.2 External calibration

For the calibration at least five calibration solutions are recommended, of which one is a blank calibration solution. Due to different element concentrations in the feeding stuff the calibration range is to adjust, considering the resulting count rate. If the linearity of the calibration is proved, further a two-point-calibration, of which one is a blank solution, is allowed.

Appropriate matrix matching at least in acid composition and concentration of the calibration solutions to that of the sample solutions shall be performed if an external calibration method is used.

8.3.3 Standard addition technique

The standard addition curve should consist of at least four points, of which three are additions. For those elements whose concentration is near the limit of quantification, the standard addition curve should consist of at least three points, of which two are additions. If three additions are used, the concentration of the highest standard should be 3 to 5 times the concentration in the sample solution.

8.4 Preparation of measurement solutions

8.4.1 General

The element concentrations in feed can vary in a wide range. Therefore suitable dilution steps of the sample solutions, obtained from the pressure digestion (8.1) or extraction procedure (8.2), can be necessary. The sample solutions should be diluted to a level that ensures that the salt concentration in the measuring solutions is below 0,2 %.

Internal standard (4.9) is added to all measuring solutions taking care that the resultant concentration of internal standard is matched in all solutions (e.g. β = 10 µg/l). Alternatively, it may be worthwhile to add the internal standard online during measurement.

NOTE 1 Measurements in HR-ICP-MS systems generally use lower concentrations of internal standard (e.g. β = 1 µg/l).

NOTE 2 To reduce matrix effects it can be worthwhile to assay higher dilution steps when adequate system sensitivity and clean lab environment are ensured (low blanks). If using HR-ICP-MS systems higher dilutions are required to achieve lower salt concentrations (e.g. ≤ 0,05 %).

8.4.2 Mercury

If the determination of mercury is desired, an additional activity is needed to prevent both mercury adsorption to surfaces and memory effects. An effective method is to increase the concentration of HCl to 0,5 or 1 % in all measuring solutions by adding the appropriate volume of HCl (4.4).

Another possible activity to prevent adsorption is the addition of gold (4.11) to all measuring solutions. Every solution should contain a gold concentration of at least c = 0,2 mg Au/l.

8.5 Determination

8.5.1 ICP-MS Optimization

The ICP-MS system is optimized and checked in accordance with the instructions given by the supplier's user manual. In doing so, care should be taken to ensure that system sensitivity and signal stability are adequate. With quadrupole-equipped mass spectrometers, the rate of both oxide ions and double charged ions formation should be kept below 3 % and held as constant as possible. With sector-field high-resolution ICP-MS systems adequate resolution shall be ensured.

To avoid memory effects, the nebulizer is thoroughly rinsed with a rinsing solution (4.3).

It is recommended to check by control measurements on a blank whether the purging time selected is appropriate following the analysis of a sample solution.

8.5.2 Interferences

Interferences in ICP-MS are caused when ions generated from the plasma, the sample, or a combination of the two carry a mass-to-charge ratio that is identical to that of the analyte ion. A short description of interferences and a survey of techniques for lowering are shown in Annex B.

8.5.3 Analyte isotopes

Table 1 shows recommended analyte isotopes, selected isobaric and molecular ion interferences and recommended techniques.

Table 1 — Recommended analyte isotopes, selected isobaric and molecular ion interferences and recommended techniques

Element	Isotope	Interferenced by	Recommended technique to overcome interferences [a]
As	$^{75}\mathrm{As}$	$^{40}\mathrm{Ar}^{35}\mathrm{Cl}^{+}$, $^{40}\mathrm{Ca}^{35}\mathrm{Cl}^{+}$, $^{36}\mathrm{Ar}^{39}\mathrm{K}^{+}$, $^{59}\mathrm{Co}^{16}\mathrm{O}^{+}$	Math. Corr. ($^{35}\mathrm{Cl}/^{37}\mathrm{Cl}$), KED, RM
	($^{91}\mathrm{AsO}$)	$^{91}\mathrm{Zr}^{+}$	RM ($^{75}\mathrm{As}^{16}\mathrm{O}^{+}$), Math. Corr. ($^{90}\mathrm{Zr}$)
Cd	$^{111}\mathrm{Cd}$	$^{95}\mathrm{Mo}^{16}\mathrm{O}^{+}$, $^{94}\mathrm{Mo}^{16}\mathrm{O}^{1}\mathrm{H}^{+}$, $^{94}\mathrm{Zr}^{16}\mathrm{O}^{1}\mathrm{H}^{+}$	KED, RM
Cd	$^{112}\mathrm{Cd}$	$^{112}\mathrm{Sn}^{+}$, $^{96}\mathrm{Ru}^{16}\mathrm{O}^{+}$	Math. Corr. ($^{118}\mathrm{Sn}$), KED, RM
Cd	$^{114}\mathrm{Cd}$	$^{114}\mathrm{Sn}^{+}$, $^{98}\mathrm{Mo}^{16}\mathrm{O}^{+}$, $^{98}\mathrm{Ru}^{16}\mathrm{O}^{+}$	Math. Corr. ($^{118}\mathrm{Sn}$), KED, RM
Co	$^{59}\mathrm{Co}$	$^{43}\mathrm{Ca}^{16}\mathrm{O}^{+}$, $^{42}\mathrm{Ca}^{16}\mathrm{O}^{1}\mathrm{H}^{+}$, $^{24}\mathrm{Mg}^{35}\mathrm{Cl}^{+}$, $^{36}\mathrm{Ar}^{23}\mathrm{Na}^{+}$,$^{40}\mathrm{Ar}^{18}\mathrm{O}^{1}\mathrm{H}^{+}$	Math. Corr. ($^{43}\mathrm{Ca}$), KED, RM
Cu	$^{63}\mathrm{Cu}$	$^{40}\mathrm{Ar}^{23}\mathrm{Na}^{+}$, $^{31}\mathrm{P}^{16}\mathrm{O}^{16}\mathrm{O}^{+}$, $^{26}\mathrm{Mg}^{37}\mathrm{Cl}^{+}$, $^{47}\mathrm{Ti}^{16}\mathrm{O}^{+}$, $^{40}\mathrm{Ca}^{23}\mathrm{Na}^{+}$	KED
Cu	$^{65}\mathrm{Cu}$	$^{130}\mathrm{Ba}^{2+}$, $^{49}\mathrm{Ti}^{16}\mathrm{O}^{+}$, $^{40}\mathrm{Ar}^{25}\mathrm{Mg}^{+}$	KED
Fe	$^{56}\mathrm{Fe}$	$^{40}\mathrm{Ar}^{16}\mathrm{O}^{+}$, $^{40}\mathrm{Ca}^{16}\mathrm{O}^{+}$	KED, RM
Hg	$^{201}\mathrm{Hg}$	$^{184}\mathrm{W}^{16}\mathrm{O}^{1}\mathrm{H}^{+}$, $^{185}\mathrm{Re}^{16}\mathrm{O}^{+}$	
Mn	$^{55}\mathrm{Mn}$	$^{40}\mathrm{Ar}^{14}\mathrm{N}^{1}\mathrm{H}^{+}$, $^{40}\mathrm{Ar}^{15}\mathrm{N}^{+}$	KED
Mo	$^{95}\mathrm{Mo}$	$^{40}\mathrm{Ar}^{39}\mathrm{K}^{16}\mathrm{O}^{+}$	KED
	$^{98}\mathrm{Mo}$	$^{98}\mathrm{Ru}^{+}$, $^{41}\mathrm{K}^{41}\mathrm{K}^{16}\mathrm{O}^{+}$	Math. Corr. ($^{101}\mathrm{Ru}$), KED
Pb	$^{206}\mathrm{Pb}$		measure all three isotopes and sum the signal intensities
	$^{207}\mathrm{Pb}$		
	$^{208}\mathrm{Pb}$		
Se	$^{78}\mathrm{Se}$	$^{78}\mathrm{Kr}^{+}$, $^{38}\mathrm{Ar}^{40}\mathrm{Ar}^{+}$, $^{38}\mathrm{Ar}^{40}\mathrm{Ca}^{+}$, $^{156}\mathrm{Gd}^{2+}$	Math. Corr. ($^{83}\mathrm{Kr}$), KED, RM
	$^{80}\mathrm{Se}$	$^{80}\mathrm{Kr}^{+}$, $^{40}\mathrm{Ar}^{40}\mathrm{Ar}^{+}$, $^{40}\mathrm{Ar}^{40}\mathrm{Ca}^{+}$	Math. Corr. ($^{83}\mathrm{Kr}$), KED, RM
	$^{82}\mathrm{Se}$	$^{82}\mathrm{Kr}^{+}$,$^{12}\mathrm{C}^{35}\mathrm{Cl}^{35}\mathrm{Cl}^{+}$	Math. Corr. ($^{83}\mathrm{Kr}$, $^{35}\mathrm{Cl}$), KED, RM
Tl	$^{205}\mathrm{Tl}$		
U	$^{238}\mathrm{U}$		
Zn	$^{66}\mathrm{Zn}$	$^{50}\mathrm{Ti}^{16}\mathrm{O}^{+}$, $^{32}\mathrm{S}^{34}\mathrm{S}^{+}$, $^{34}\mathrm{S}^{16}\mathrm{O}^{16}\mathrm{O}^{+}$, $^{32}\mathrm{S}^{16}\mathrm{O}^{18}\mathrm{O}^{+}$	KED
	$^{68}\mathrm{Zn}$	$^{34}\mathrm{S}^{34}\mathrm{S}^{+}$, $^{34}\mathrm{S}^{16}\mathrm{O}^{18}\mathrm{O}^{+}$ $^{32}\mathrm{S}^{18}\mathrm{O}^{18}\mathrm{O}^{+}$, $^{40}\mathrm{Ar}^{14}\mathrm{N}^{14}\mathrm{N}^{+}$, $^{36}\mathrm{Ar}^{32}\mathrm{S}^{+}$	KED

[a] KED – Kinetic Energy Discrimination; RM – Reaction Mode.