SLOVENSKI STANDARD
SIST EN 16171:2017

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Nadomešča:
SIST-TS CEN/TS 16171:2013

Blato, obdelani biološki odpadki in tla - Določevanje elementov z masno spektrometrijo z induktivno sklopljeno plazmo (ICP/MS)

Sludge, treated biowaste and soil - Determination of elements using inductively coupled plasma mass spectrometry (ICP-MS)

Schlamm, behandelter Bioabfall und Boden - Bestimmung von Elementen mittels Massenspektrometrie mit induktiv gekoppeltem Plasma (ICP-MS)

Boues, bio-déchets traités et sols - Détermination des éléments en traces par spectrométrie de masse avec plasma induit par haute fréquence (ICPMS)

Ta slovenski standard je istoveten z: **EN 16171:2016**

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Supersedes CEN/TS 16171:2012

English Version

Sludge, treated biowaste and soil - Determination of elements using inductively coupled plasma mass spectrometry (ICP-MS)

Boues, bio-déchets traités et sols - Détermination des éléments en traces par spectrométrie de masse avec plasma induit par haute fréquence (ICP-MS)

Schlamm, behandelter Bioabfall und Boden - Bestimmung von Elementen mittels Massenspektrometrie mit induktiv gekoppeltem Plasma (ICP-MS)

This European Standard was approved by CEN on 19 March 2016.

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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-CENELEC Management Centre has the same status as the official versions.

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

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European foreword

This document (EN 16171:2016) has been prepared by Technical Committee CEN/TC 444 “Test methods for environmental characterization of solid matrices”, 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of an identical text or by endorsement, at the latest by April 2017, and conflicting national standards shall be withdrawn at the latest by April 2017.

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.

This document supersedes CEN/TS 16171:2012.

The preparation of the previous edition of this analytical method by CEN is based on a mandate by the European Commission (Mandate M/330), which assigned the development of standards on sampling and analytical methods for hygienic and biological parameters as well as inorganic and organic determinants, aiming to make these standards applicable to sludge, treated biowaste and soil as far as this is technically feasible.

This document contains the following technical changes in comparison with the previous edition:

- repeatability and reproducibility data have been added from a European interlaboratory comparison organized by the German Federal Institute for Materials Research and Testing BAM in 2013 (see Annex A).

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, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

Introduction

This European Standard is applicable and validated for several types of matrices as indicated in Table 1 (see Annex A for the results of validation).

Table 1 — Matrices for which this European Standard is applicable and validated

Matrix	Materials used for validation
Sludge	Municipal sludge
Biowaste	Compost
Soil	Soil

WARNING — Persons using this European Standard should be familiar with usual laboratory practice. This European Standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

IMPORTANT — It is absolutely essential that tests conducted according to this European Standard be carried out by suitably trained staff.

1 Scope

This European Standard specifies a method for the determination of the following elements in *aqua regia* or nitric acid digests of sludge, treated biowaste and soil:

Aluminium (Al), antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), bismuth (Bi), boron (B), cadmium (Cd), calcium (Ca), cerium (Ce), cesium (Cs), chromium (Cr), cobalt (Co), copper (Cu), dysprosium (Dy), erbium (Er), europium (Eu), gadolinium (Gd), gallium (Ga), germanium (Ge), gold (Au), hafnium (Hf), holmium (Ho), indium (In), iridium (Ir), iron (Fe), lanthanum (La), lead (Pb), lithium (Li), lutetium (Lu), magnesium (Mg), manganese (Mn), mercury (Hg), molybdenum (Mo), neodymium (Nd), nickel (Ni), palladium (Pd), phosphorus (P), platinum (Pt), potassium (K), praseodymium (Pr), rhenium (Re), rhodium (Rh), rubidium (Rb), ruthenium (Ru), samarium (Sm), scandium (Sc), selenium (Se), silicon (Si), silver (Ag), sodium (Na), strontium (Sr), sulfur (S), tellurium (Te), terbium (Tb), thallium (Tl), thorium (Th), thulium (Tm), tin (Sn), titanium (Ti), tungsten (W), uranium (U), vanadium (V), ytterbium (Yb), yttrium (Y), zinc (Zn), and zirconium (Zr).

The working range depends on the matrix and the interferences encountered.

The method detection limit of the method is between 0,1 mg/kg dry matter and 2,0 mg/kg dry matter for most elements. The limit of detection will be higher in cases where the determination is likely to be interfered (see Clause 4) or in case of memory effects (see e.g. EN ISO 17294-1:2006, 8.3).

The method has been validated for the elements given in Table A.1 (sludge), Table A.2 (compost) and Table A.3 (soil). The method is applicable for the other elements listed above, provided the user has verified the applicability.

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 15934, *Sludge, treated biowaste, soil and waste — Calculation of dry matter fraction after determination of dry residue or water content*

EN 16173, *Sludge, treated biowaste and soil — Digestion of nitric acid soluble fractions of elements*

EN 16174, *Sludge, treated biowaste and soil — Digestion of aqua regia soluble fractions of elements*

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

EN ISO 17294-1:2006, *Water quality — Application of inductively coupled plasma mass spectrometry (ICP-MS) — Part 1: General guidelines (ISO 17294-1:2004)*

3 Principle

Digests of sludge, treated biowaste or soil with nitric acid or *aqua regia* (see EN 16173 and EN 16174) are analysed by ICP-MS to get a multi-elemental determination of analytes.

The method measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in the digest solution are nebulised and the resulting aerosol is transported by argon gas into the plasma. The ions produced by the high temperatures of the plasma are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer, sorted according to their mass-to-charge ratios and quantified with a detector (e.g. channel electron multiplier).

NOTE For the determination of tin only *aqua regia* extraction applies (EN 16174).

4 Interferences

4.1 General

Interferences shall be assessed and valid corrections applied. Interference correction shall include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.

Detailed information on spectral and non-spectral interferences is given in EN ISO 17294-1:2006, Clause 6.

4.2 Spectral interferences

4.2.1 Isobaric elemental interferences

Isobaric elemental interferences are caused by isotopes of different elements of closely matched nominal mass-to-charge ratio and which cannot be separated due to an insufficient resolution of the mass spectrometer in use (e.g. ^{114}Cd and ^{114}Sn).

Element interferences from isobars may be corrected by taking into account the influence from the interfering element (see EN ISO 17294-1:2006). The isotopes used for correction shall be free of interference if possible. Correction options are often included in the software supplied with the instrument. Common isobaric interferences are given in Table B.1.

4.2.2 Isobaric molecular and doubly-charged ion interferences

Isobaric molecular and doubly-charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Examples include ^{40}Ar^{35}Cl^{+} and ^{40}Ca^{35}Cl^{+} ion on the ^{75}As signal or ^{98}Mo^{16}O^{+} ions on the ^{114}Cd^{+} signal. Natural isotope abundances are available from the literature.

The accuracy of correction equations is based upon the constancy of the observed isotopic ratios for the interfering species. Corrections that presume a constant fraction of a molecular ion relative to the "parent" ion have not been found to be reliable, e.g. oxide levels can vary with operating conditions. If a correction for an oxide ion is based upon the ratio of parent-to-oxide ion intensities, this shall be determined by measuring the interference solution just before the sequence is started. The validity of the correction coefficient should be checked at regular intervals within a sequence.

Another possibility to remove isobaric molecular interferences is the use of an instrument with collision/reaction cell technology. The use of high resolution ICP-MS allows the resolution of these interferences and additionally double-charged ion interferences.

The response of the analyte of interest shall be corrected for the contribution of isobaric molecular and doubly charged interferences if their impact can be higher than three times the detection limit or higher than half the lowest concentration to be reported.

More information about the use of correction factors is given in EN ISO 17294-1.

4.2.3 Non-spectral interferences

Physical interferences are associated with sample nebulisation and transport processes as well as with ion-transmission efficiencies. Nebulisation and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement. Solids can be deposited on the nebuliser tip of a pneumatic nebuliser and on the cones.

It is recommended to keep the level of total dissolved solids below 0,2 % (2 000 mg/l) to minimise deposition of solids in the sample introduction system of the plasma torch. An internal standard can be used to correct for physical interferences if it is carefully matched to the analyte, so that the two elements are similarly affected by matrix changes. Other possibilities to minimise non-spectral interferences are matrix matching, particularly matching of the acid concentration, and standard addition.

When intolerable physical interferences are present in a sample, a significant suppression of the internal standard signals (to less than 30 % of the signals in the calibration solution) will be observed. Dilution of the sample (e.g. fivefold) usually eliminates the problem.

5 Reagents

For the determination of elements at trace and ultra-trace level, the reagents shall be of adequate purity. The concentration of the analyte or interfering substances in the reagents and the water should be negligible compared to the lowest concentration to be determined.

5.1 Water, grade 1 as specified in EN ISO 3696 for all sample preparations and dilutions.

5.2 Nitric acid, HNO_3, $\rho(HNO_3)$ = 1,4g/ml, $c(HNO_3)$ = 15 mol/l, $w(HNO_3)$ = 650 g/kg.

5.3 Hydrochloric acid, HCl, ρ(HCl) = 1,18 g/ml, c(HCl) = 12 mol/l, w(HCl) = 370 g/kg.

5.4 Single-element standard stock solutions

Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, S, Sb, Sc, Se, Si, Sm, Sn, Sr, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr, ρ(element) = 1 000 mg/l each.

Preferably, nitric acid preservation should be applied in order to minimise interferences by chloropolyatom molecules. Bi, Hf, Hg, Mo, Sn, Sb, Te, W and Zr may need hydrochloric acid for preservation.

Both single-element standard stock solutions and multi-element standard stock solutions with adequate specification stating the acid used and the preparation technique are commercially available.

These solutions are considered to be stable for more than one year, but in reference to guaranteed stability, the recommendations of the manufacturer should be considered.

5.5 Anion standard stock solutions

Cl^-, PO_4^{3-}, SO_4^{2-}, ρ(anion) = 1 000 mg/l each.

Prepare these solutions from the respective acids. The solutions are commercially available.

These solutions are considered to be stable for more than one year, but in reference to guaranteed stability, the recommendations of the manufacturer should be considered.

5.6 Multi-element standard stock solutions

Depending on the analytes to be determined, different multi-element standard stock solutions may be necessary. In general, when combining multi-element standard stock solutions, their chemical compatibility and the possible hydrolysis of the components shall be regarded. Care shall be taken to prevent chemical reactions (e.g. precipitation).

The multi-element standard stock solutions are considered to be stable for several months if stored in the dark. This does not apply to multi-element standard stock solutions that are prone to hydrolysis, in particular solutions of Bi, Mo, Sn, Sb, Te, W, Hf and Zr.

Mercury standard stock solutions can be stabilised by adding 1 mg/l Au in nitric acid (5.2) or by adding hydrochloric acid (5.3) up to 0,6 %.

NOTE When Au is to be used as a modifier, it cannot be determined accurately itself in the same analysis run.

Multi-element standard stock solutions with more elements are allowed, provided that these solutions are stable.

5.6.1 Multi-element standard stock solution A at the mg/l level may contain the following elements:

Ag, Al, As, B, Ba, Be, Bi, Cd, Ce, Co, Cr, Cu, Fe, Hg, Li, Mn, Nd, Ni, Pb, Pr, Sc, Se, Si, Sm, Sr, Te, Th, Ti, Tl, U, V, Zn.

Use nitric acid (5.2) for stabilisation of multi-element standard stock solution A.

Other elements of interest may be added to the standard stock solution, provided that the resulting multi-element solution is stable.

5.6.2 Multi-element standard stock solution B at the mg/l level may contain the following elements:

Mo, Sb, Si, Sn, W, Zr.

Use hydrochloric acid (5.3) for stabilisation of multi-element standard stock solution B.

Other elements of interest may be added to the standard stock solution, provided that the resulting multi-element solution is stable.

5.6.3 Multi-element standard stock solution C at the mg/l level may contain the following elements:

Ca, Mg, Na, K, P, S.

Use nitric acid (5.2) for stabilisation of multi-element standard stock solution C.

5.7 Multi-element calibration solutions

Prepare in one or more steps calibration solutions at the highest concentration of interest. If more concentration levels are needed prepare those similarly.

Add acids (5.2 and/or 5.3) to match the acid concentration of samples closely.

If traceability of the values is not established check the validity by comparison with a (traceable) independent standard.

Check the stability of the calibration solutions.

5.8 Internal standard solution

Internal standards can either be added to every flask or added online. It is essential that the same concentration of internal standard is added to all measurement solutions. The elements In, Lu, Re, Ge and Rh have been found suitable for this purpose.

The choice of elements for the internal standard solution depends on the analytical problem. The solution of this/these internal standard(s) should cover the mass range of interest. The internal standards elements shall not be analytes and the concentrations of the selected elements should be negligibly low in the digests of samples.