SLOVENSKI STANDARD
SIST EN 16424:2015

01-januar-2015

Karakterizacija odpadkov - Rešetalne metode za elementno sestavo s prenosnimi instrumenti za rentgensko fluorescenčno spektrometrijo

Characterization of waste - Screening methods for the element composition by portable X-ray fluorescence intruments

Charakterisierung von Abfällen - Screening-Verfahren zur Bestimmung der elementaren Zusammensetzung mit tragbaren Röntgenfluoreszenzspektrometern

Caractérisation des déchets - Méthode de dépistage pour la détermination de la composition élémentaire au moyen d'analyseurs portables de fluorescence X

Ta slovenski standard je istoveten z: **EN 16424:2014**

ICS:

13.030.01	Odpadki na splošno	Wastes in general

SIST EN 16424:2015 **en,fr,de**

EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

EN 16424

October 2014

ICS 13.030.01

English Version

Characterization of waste - Screening methods for the element composition by portable X-ray fluorescence instruments

Caractérisation des déchets - Méthode de dépistage pour la détermination de la composition élémentaire au moyen d'analyseurs portables de fluorescence X

Charakterisierung von Abfällen - Screening-Verfahren zur Bestimmung der elementaren Zusammensetzung mit tragbaren Röntgenfluoreszenzspektrometern

This European Standard was approved by CEN on 16 August 2014.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the CEN-CENELEC Management Centre or to any CEN member.

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.

CEN members are the national standards bodies of 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 United Kingdom.

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

CEN-CENELEC Management Centre: Avenue Marnix 17, B-1000 Brussels

Ref. No. EN 16424:2014 E

Contents

Foreword

This document (EN 16424:2014) has been prepared by Technical Committee CEN/TC 292 “Characterization of waste”, 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 2015, and conflicting national standards shall be withdrawn at the latest by April 2015.

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.

X-ray fluorescence spectrometry (XRF) is a fast and reliable method for the determination of the total content of certain elements within different matrices. Quantitative analysis using XRF is described in EN 15309 [2]. For screening purposes, portable instruments are often used, especially when only the absence or presence of elements is under investigation or qualitative results with an indication of the concentration level are requested. This standard is applicable for on-site verification at landfills (see CEN/TR 16130 [4]) and it is an exemplification of EN 16123 [3].

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.

1 Scope

This European Standard is dedicated to field portable X-ray fluorescence (XRF) equipment (hand-held or portable bench top) and specifies a screening method for the determination of the elemental composition of waste materials for on-site verification. Portable XRF spectrometers are used for a rapid and exploratory analysis of paste-like or solid materials. The absence or presence of specific elements is displayed qualitatively with an indication of the concentration level.

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 15002, *Characterization of waste — Preparation of test portions from the laboratory sample*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
field portable XRF spectrometer
XRF spectrometer for analyzing samples in the field, namely hand-held or portable bench top XRF spectrometers

3.2
hand-held XRF spectrometer
XRF spectrometer which can be used for in-situ analysis by direct probing or mounted on a stand

3.3
on-site verification
third level of inspection according to the Landfill Directive and the Landfill Decision to ensure that the waste accepted at a landfill is the same as described in the accompanying documents and that it is in accordance with the basic characterization and/or compliance testing

3.4
portable bench top spectrometer
compact bench top XRF spectrometer which can easily be carried into the field

3.5
screening
application of any analytical method for exploratory analysis

4 Principle

The sample can be measured directly or after a suitable sample preparation. In principle two different methods are used for probing the sample, either a pistol-like instrument is placed directly on the sample or a sufficient test portion is taken and put into a sample cup for measurement with the XRF instrument. The presence of a specific element is verified if a significant intensity for that element is measured. The intensities of the lines can be evaluated to indicate the concentration range.

5 Safety remarks

The X-ray fluorescence spectrometers on the market are generally fully protected apparatus which are subjected to specific official approval and acceptance conditions. This means that the user is not exposed to radiation when operating the apparatus correctly. Nevertheless while measuring in the field, scattering radiation can be produced when probing directly on the sample. Providing a protective radiation shield around the sample when measuring avoids these risks.

The person responsible for managing or supervising the operation of X-ray equipment shall provide evidence of his knowledge of radiation protection according to national regulations.

Proper safety precautions shall be considered when conducting field XRF measurements. The operator should always be aware that X-rays are produced during measurements. The operator should never point the open source at anyone and be aware that X-rays can penetrate through light atomic mass matrices. Proper training regarding handling of XRF instruments is an obligation.

Take care when handling samples that may contain sharps or are of a dusty nature. Handling of samples should be performed with gloves and in the case of dusty materials with respiratory mask and gloves.

Take special precautions with samples from potentially hazardous waste. Avoid any contact with the skin and/or inhaling of dust.

6 Apparatus and equipment

6.1 X-ray fluorescence spectrometer

The X-ray fluorescence spectrometer shall comply with European and national regulations relevant to radiation protection.

The X-ray fluorescence spectrometer shall be able to analyse the relevant elements. The following types of X-ray fluorescence spectrometers are applicable:

- energy dispersive X-ray fluorescence spectrometer (EDXRF) which gains the dispersion of the emitted X-ray fluorescence radiation by an energy dispersive detector;
- wavelength dispersive X-ray fluorescence spectrometer (WDXRF) which gains the dispersion of the emitted X-ray fluorescence radiation by diffraction by a crystal.

For screening analysis generally EDXRF instruments are applied.

Portable spectrometers comprise mainly the following components:

- a primary X-ray source, a miniaturised X-ray tube with a low voltage generator;
- a detector unit including electronic equipment;
- a power supply including rechargeable batteries;
- a radiation shield according to safety regulations;
- optional source modifiers to modify the shape or intensity of the source spectrum or the beam shape e.g. primary source filters.

Portable spectrometers are mostly hand-held instruments which may be mounted on a stand. Alternatively small bench top systems are available which are equipped with a sample holder. In general, the weight of portable instruments should be below 10 kg and the size should be less than 500 mm wide, 500 mm deep and 200 mm high.

The detector unit is different for wavelength dispersive (WDXRF) and for energy dispersive (EDXRF) spectrometers. WDXRF spectrometers take advantage of the dispersion of the emitted radiation by scattering by a crystal. EDXRF spectrometers are using an energy dispersive detector. The detector current pulses, a measure for the energy of the incoming X-rays, are segregated into channels according to energy using a multi-channel analyser (MCA).

6.2 Direct measurement using a hand-held instrumentation in direct contact with the sample

When using a pistol-like instrument, direct probing of the sample is possible (see Figure A.1 and Figure A.2). To avoid uncertainties due to different measurement geometry such as distance to sample, angle between sample and incident beam, the measuring window of the instrument should be in close contact to the sample.

6.3 Hand-held instrumentation mounted on a stand using sample cups filled with the sample

For practical reasons or to improve the accuracy of the results due to different measurement geometries, hand-held instruments may be mounted in a stand to operate with a well-defined geometry. Sample cups containing the material under investigation are placed into the instrument at a fixed position (see Figure A.3 and Figure A.4).

6.4 Portable bench top XRF instrument

Portable bench top XRF systems equipped with a sample holder for positioning sample cups may show improved repeatability of the results compared to hand-held instruments. A mounted shield against X-ray radiation provides a higher safety protection (see Figure A.5).

6.5 Spoon, stamp and/or hammer

Tool to prepare (e.g. compress, flatten) the sample prior to the measurement.

6.6 Mortar and pestle

Tool to grind the sample, if required.

6.7 Thin-film support

Select a thin film support that provides maximum transmittance and is resistant to the components in the sample (e.g. Mylar, polypropylene). Preferably samples are analysed using the same film that was previously used for calibration. The selected thin film shall be contaminant-free with respect to the elements of interest.

6.8 Sample cups

Select a sample cup suitable to be positioned in the applied XRF system. The sample cup needs to be assembled using an appropriate thin film support.

7 Calibration

7.1 General

The calibration strategy is comparable for energy dispersive and wavelength dispersive technique.

When using energy dispersive instruments, deconvolution of the spectra is needed when analysing complex samples with overlapping lines. Usually XRF instruments are supplied with a specific software module for that purpose.

The calibration procedures for screening purposes are dependent on the analytical software package of the instrument. Most of them use a programme which contain calibration curves previously set-up; often by the manufacturer. In most cases the user can also set-up calibration programmes or improve the existing ones.

7.2 Interferences

Interferences in X-ray fluorescence spectrometry consists of spectral line overlaps, matrix effects, spectral artefacts and particle size or mineralogical effects.

Spectral line overlaps occur when an analytical line cannot be resolved from the line of a different element. In general, these interferences are removed using the algorithms provided with the software. However, due to the complexity of waste samples optimal matrix calibration is in most cases not affordable for screening experiments. Therefore the user shall be aware of those characteristic interferences which may occur in waste samples under investigation. A list of characteristic interferences is given in Annex B.

Matrix effects occur when the X-ray fluorescence radiation from the analyte element is absorbed or enhanced by other elements in the sample before it reaches the detector.

Spectral artefacts (e.g. escape peaks, sum peaks, pulse pile up lines, dead time, bremsstrahlung correction) are accounted for by the provided software. Spectral artefacts differ for energy-dispersive and wavelength-dispersive XRF.

7.3 Calibration procedure

Calibration involves the measurement of emitted intensities of characteristic lines for specimens of known composition. The basic formula implies a linear relationship between the intensity and the concentration.

$$C_i = a_{i,0} + a_{i,1} \times I_i \quad (1)$$

where

C_i is the concentration of the element of interest;

$a_{i,0}$ is the offset of the calibration curve;

$a_{i,1}$ is the slope of the calibration curve;

I_i is the net intensity of the element of interest.

Different calibration procedures can be applied for the determination of the element concentration according to EN 15309 [2].

It is a necessity to select a calibration programme which is able to handle the sample matrices under investigation, meaning performing the deconvolution, the interelement corrections and the calculation of the element concentration in a proper way. This can be done by using a universal or matrix-specific calibration programme. It is the task of the XRF user to validate the system with representative reference samples.

7.4 Validation of the calibration

The calibration shall fit with the concentration values to be verified by the investigation. The calibration protocol should be able to verify the lowest (highest) values within the calibration range.

The available precalibrated analytical method shall be validated using reference materials with a similar composition as the unknown samples. Based on the obtained results an estimation of the uncertainty range for each analyte can be defined. The reference sample can consist of:

a) certified reference materials with matrices similar to that of the unknown sample;

b) in-house made reference materials with matrices similar to that of the unknown sample;

c) synthetic standard samples, made by weighing the appropriate amount of each pure reagent;

d) site specific or batch specific samples, similar to the matrix of the unknown sample;

e) standard addition method or spiked samples may also be used to create standards for which appropriate reference materials are not available for an element of interest; the matrix material shall match that of the unknown sample.

The element concentrations of these reference samples shall be known, by certification, or by determination with another analytical technique.

The reference materials shall be analysed under the same analytical conditions as the unknown sample, meaning the same sample preparation (pellet, powder, etc.), the same analytical measurement method, etc.

If no reference materials with a comparable matrix as the unknown sample are available, only a qualitative analysis with indicative concentration values can be performed. A method can be defined as (semi)-quantitative when the uncertainty ranges can be defined.

8 Screening strategy

The operational steps for screening experiments are defined below and presented in the flowchart in Figure 1.

Step 1: Define analytical task. Identify the elements including the corresponding concentration values to be verified and/or decision values.

Elements of interest are listed in the European and national legislation. In case of landfills the European Landfill Directive mentions these elements as relevant: As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, Zn, (Cl).

Step 2: Perform the necessary sample preparation.

The sample preparation technique depends on the selected measurement procedure. See Clause 9.

Step 3: Select a suitable (matrix specific) XRF calibration programme (see Clause 7).

Step 4: Perform the replicate measurements (see Clause 10) and calculate the relative repeatability standard deviation (V_r) of the replicates.

Step 5: Is V_r of the replicates sufficiently low? If no, go to step 6; if yes, continue with Step 7.

When evaluating the resulting concentration values, the V_r in relation with the concentrations to be verified and/or decision values shall be considered.

Usually a V_r of less than 30 % is a proper criterion to decide between acceptable or not acceptable results.

Step 6: If V_r is not sufficiently low, the sample preparation needs to be improved. Check, if the results are getting acceptable by repeated sample preparation. If yes, repeat from step 2. If no, go to Step 12.

Improved sample preparation can include homogenization, and drying.

Step 7: Is an indication of the concentration level required? If no, go to Step 8; if yes, continue with Step 10.

Step 8: Compare the mean of the results with the limit of detection (LOD) (see 12.2).

Step 9: Indicate the absence or presence of the elements under investigation with respect to the set limit values (see 12.2).

Step 10: Identify the acceptance criteria (see 12.3).

Step 11: Report the elements under investigation and indicate their concentration ranges.

Step 12: XRF screening is not suitable. Stop experiment.