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

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National foreword

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The UK participation in its preparation was entrusted by Technical Committee B/508, Waste Management, to Subcommittee B/508/3, Characterization of waste.

A list of organizations represented on this subcommittee can be obtained on request to its secretary.

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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.

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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of an identical text or by endorsement, at the latest by April 2015, and conflicting national standards shall be withdrawn at the latest by April 2015.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].

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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.

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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.

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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.

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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;

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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.

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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.

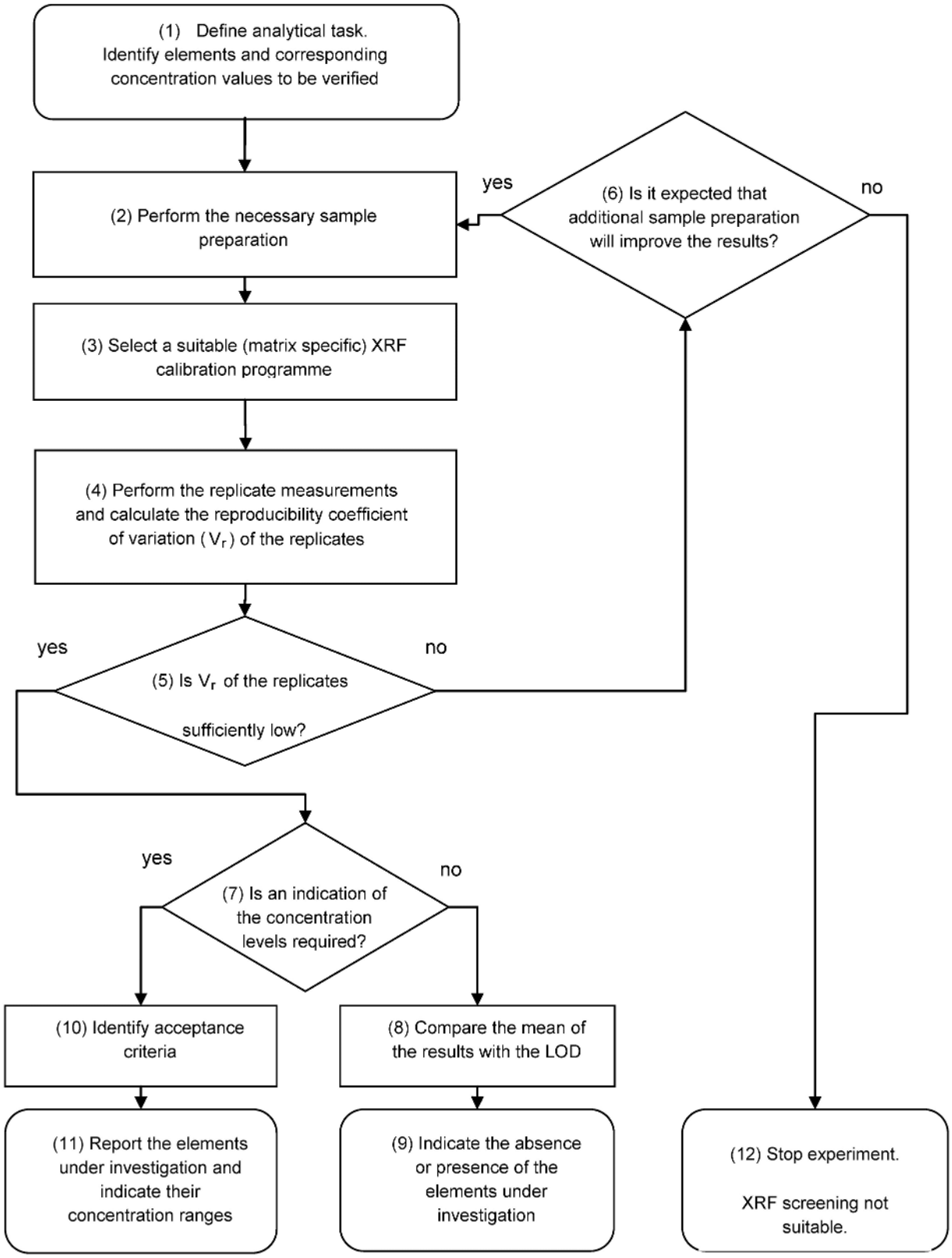

Figure 1 — Flowchart of the operational steps for screening experiments

9 Sample preparation

9.1 General

Milling and sieving are usually not applied because screening methods are used to obtain a preliminary result without or at least with limited sample preparation. Nevertheless in many cases the samples under investigation are very heterogeneous. Because XRF is a surface analysis technique, any sample preparation can improve the reliability of the results. The principles of EN 15002 shall be considered.

Be aware that the sample conditions, for example moisture content, organic content, particle size, high contents of some elements, have a significant influence on the quality of the results.

9.2 Sample preparation for direct measurement

In case of direct measurement (see 6.2) it is recommended to flatten and to compress the sample spot before measurement.

9.3 Sample preparation for filling cups

Sample cups provided with a suitable thin film foil are properly filled with sample material (as representative as possible) so that the bottom is completely covered. The material is shaken so that fine and coarse material are similarly distributed in the bottom of the cup. Use a spoon or a stamp to press the material tightly. Prepare at least three similar test samples from each sample spot.

9.4 Sample preparation for heterogeneous samples

Heterogeneous samples need further sample pretreatment if qualitative results with an indication of the concentration level are required. Drying of the collected sample and/or grinding of these sample using mortar and pestle might improve the quality of the results.

Heterogeneity is identified by high standard deviation values of the replicates (see Clause 8).

The moisture content of the sample has also an influence on the calculation of the concentration. The estimated value may be based on the wet sample.

10 Analysis

10.1 General

Follow the instrument manufacturer's instructions for set-up, conditioning, preparation and maintenance of the XRF spectrometer. Each XRF instrument should be operated according to the manufacturer's recommendations.

Before analysis, quality control samples shall be measured to check the instrument stability and the quality of the calibration in accordance to the manufacturer's instructions.

Select the proper calibration programme.

10.2 Direct *in situ* measurement (hand-held method)

Direct the X-ray probe to the sample, measure the sample and record the data (see 6.2). Repeat the procedure at least 3 times, preferably 5, on different spots. Evaluate the recorded data, calculate the relative repeatability standard deviation (V_r) and perform the assessment of the XRF screening experiment according to Clause 12.

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NOTE Measurement time commonly used varies between 30 s and 90 s for each measurement.

10.3 Measurement by using a mounted hand-held XRF instrument or a small portable closed XRF instrument

Instead of measuring *in situ*, samples can be collected and placed into a sample cup.

Either a hand-held instrument mounted on a stand (see 6.3) or a small portable bench top instrument (see 6.4) can be used.

In case of a bench top system introduce the filled sample cup into the sample holder. In case of a mounted hand-held instrument place the sample cup in front of the X-ray window at a fixed position according to the technical notes of the instrument supplier.

Measure the sample and record the data. Repeat the procedure at least 3, preferably 5, times by collecting samples from different spots. Evaluate the recorded data, calculate the relative repeatability standard deviation (V_r) and perform the assessment of the XRF screening experiment according to Clause 12.

NOTE Measurement time commonly used varies between 30 s and 90 s for each measurement.

11 Calculation of the result

The concentrations of the analytes are calculated by the software programme from the measured intensity using the calibrations curves previously set up. The results are expressed as elements in terms of mg/kg or mass percentages.

12 Assessment of the XRF screening measurement

12.1 General

The XRF screening is performed in order to determine the elemental composition of waste materials for on-site verification, i.e. 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.

One of the following two issues is to be considered:

— identification of the presence or absence of the elements under investigation with respect to the set limit values;

— indication of the concentration range of the elements under investigation.

12.2 Identification of the presence or absence of the elements under investigation

The objective of the XRF screening methods is to identify the presence or absence of elements under investigation with respect to the set limit values. Therefore it is essential to avoid false negatives.

A limit value may be legally defined but it can be also any concentration value which is of interest in a specific investigation.

For this purpose, the experimental limit of detection (LOD) shall be known, or shall be determined from experimental results of at least three replicates. Calculate from the data of the replicate measurements the mean and the standard deviation for all relevant elements.

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The LOD is calculated as:

$$LOD = 3 \times s \quad (2)$$

where

LOD is the limit of detection

s is the standard deviation

If the calculated mean of the measured concentration is higher than the LOD, then this value indicates the presence of the element under consideration. Otherwise it should be stated that the indicative concentration value is less than the LOD.

12.3 Indication of the concentration range of the elements under investigation

If an indication of the concentration value is requested, the XRF screening method is able to give an overview of the elemental composition of the sample by expressing it in terms of concentration ranges.

Therefore it is necessary to define acceptance levels indicating the empirical tolerance of deviation of the determined mean result.

By comparing the measured XRF values of the elements under investigation with the indicated values (as defined in the basic characterization and/or described in the accompanying documents) and taking into consideration the defined acceptance criteria, it can be verified whether the waste composition is similar to what has been described in the documents.

In Annex C the relations between the elemental concentration determined and identification or acceptance criteria are explained.

13 Quality control

13.1 Drift correction procedure

XRF instruments, once calibrated, tend to be stable over long periods of time. Small amounts of instrumental drift can be corrected by analysing stable monitor samples as frequent as performance experience indicates.

For EDXRF spectrometers, an energy calibration shall be performed on a regular basis, as defined by the manufacturer’s instructions.

13.2 Blank test

Carry out a blank test to verify that no contamination exists in the spectrometer or on the probe window.

NOTE As blank sample a matrix adapted material, e.g. silicon dioxide, a polytetrafluoroethylene (PTFE) block or clean sand can be used.

13.3 Reference materials

Verify the trueness of the results by applying the procedure to one or more reference materials not used for calibration and covering the concentration range of interest (see also 7.4).

The element content of the reference material used shall be in accordance with the trigger values.

14 Test report

The test report shall include at least the following information:

a) a reference to this European Standard;

b) description and identification of the sample;

c) which processes (including sample preparation), procedures and apparatus were used;

d) documentation which XRF configuration was used (see 6.1 to 6.4);

e) a proof on the significance of true negatives and documentation of element specific LODs;

f) results of the determination expressed as mg/kg or mass percentages;

g) date(s) of performance(s) of test(s);

h) any details not specified in this European Standard or which are optional, and any other factors which may have affected the results.

Corrections or additions to a test report after issue shall be made only by a further document suitably marked, e.g. “Amendment/Addendum to test report serial number (or as otherwise identified)”, and shall meet the relevant requirements of the preceding paragraphs.

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Annex A
(informative)

Examples of instrumentation

In this annex examples are given of hand-held instruments and a compact bench top instrument, together with the different modes of operation.

In Figure A.1 a direct measurement on the sample using a pistol-like hand-held XRF instrument is shown.

In Figure A.2 a direct measurement using a hand-held XRF instrument in direct contact with the sample, but with the aid of a stand, is presented.

In Figure A.3 and Figure A.4 hand-held XRF instruments mounted on a stand and using sample cups filled with the sample are shown. In Figure A.4 the XRF instrument is supplementary equipped with a protective radiation shield which shall be closed when measuring.

In Figure A.5 a compact portable bench top XRF instrument is presented.

Figure A.1 — Direct measurement – Hand-held setup

Figure A.2 — Direct measurement – Hand-held instrument mounted on a stand

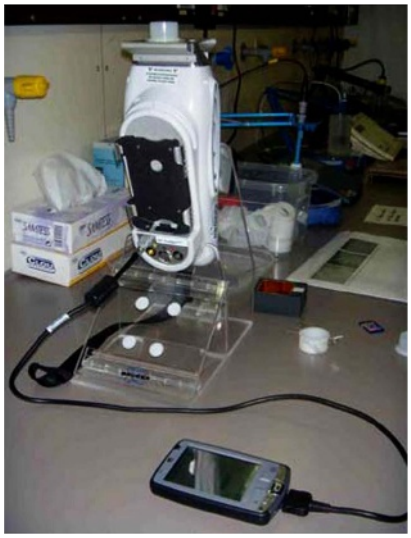

Figure A.3 — Measurement of a sample collected in a cup – Hand-held instrument mounted on a stand

Figure A.4 — Measurement of a sample collected in a cup – Hand-held instrument mounted on a stand – Using a radiation shield

Figure A.5 — Compact bench top XRF spectrometer

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Annex B
(informative)

List of analytical lines and spectral line overlaps

In Table B.1 an overview is given of analytical lines of selected elements and possible spectral line overlaps.

Table B.1 — Analytical lines and spectral line overlaps

Element	Line	Spectral line overlap
Na	Kα	ZnLβ
Mg	Kα	AsLα
Al	Kα	BrLα
Si	Kα	
P	Kα	
S	Kα	CoKα PbMα NbLβ
Cl	Kα	
K	Kα	
Ca	Kα	
Ti	Kα	BaLα ILβ
V	Kα	Ti Kβ
Cr	Kα	VKβ PbLα
Mn	Kα	CrKβ
Fe	Kα	MnKβ
Co	Kα	FeKβ
Ni	Kα	CoKβ
Cu	Kα	TaLα ThLβ
Zn	Kα	WLα
As	Kα Kβ	PbLα BrKα
Se	Kα	
Br	Kα	AsKβ
Rb	Kα	ULα BrKβ

Element	Line	Spectral line overlap
Sr	Kα	ULα
Y	Kα	RbKβ
Zr	Kα	SrKβ
Nb	Kα	YKβ ULβ
Mo	Kα	ZrKβ ULβ
Ag	Kα Lα	CrKβ
Cd	Kα Lα	AgLβ
Sn	Kα Lα	CoKα
Sb	Kα Lβ	CoKβ
Te	Kα Lα	SnLβ
I	Kα Lα	
Cs	Kα Lα	ZnKα ILβ
Ba	Kα Lα	TiKα ILβ CuKβ
Ta	Lα	CuKα NiKβ
W	Lα	TaLn
Hg	Lα	WLβ
Tl	Lβ	PbLβ
Pb	Lβ	ThLα BiLβ SnKα
Bi	Lα	TaLγ
Th	Lα	BiLβ PbLβ
U	Lα	BrKβ RbKα

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Annex C
(informative)

Evaluation of the acceptance criteria

C.1 Uncertainty

Any XRF measurement is characterized by an uncertainty in the resulting value of the concentration of an element in the sample. Uncertainty (U) is the parameter expressing the dispersion of the values that could reasonably be attributed to the measurand. Uncertainty of measurement comprises in general many components. Some of these components may be evaluated from the statistical distribution of the results of series of measurements and can be characterized by a standard deviation (s) of a series of repeated measurements. Other components may be evaluated from on the basis of experience or additional information.

C.2 Test of the absence of an element

It shall be identified whether or not an element is present in the sample. The basic criterion for 'absence' is that the calculated mean of the repeated measurements (M_{av}) is below the limit of detection (LOD), usually defined as 3 times the standard deviation (s):

$$M_{av} < 3 \times s \qquad \text{(C.1)}$$

C.3 Test of the documented concentration of an element

To decide whether or not an element is present in the waste sample with a concentration not higher than indicated in the document accompanying the waste (I_{doc}) the uncertainty (U) shall be estimated and used in the comparison of the average value of a series of repeated measurements (M_{av}). A condition is that both I_{doc} and M_{av} are higher than the limit of quantification (LOQ), commonly defined as 10 × s.

The basic acceptance criteria to decide whether an element is present in a sufficiently low concentration (lower than I_{doc}), is:

$$M_{av} + U \leq I_{doc} \qquad \text{(C.2)}$$

In this case, the waste involved can be accepted at the landfill.

In the case that $M_{av} - U < I_{doc} < M_{av} + U$ it cannot be decided whether the element concentration involved, is sufficiently low. If other evidence is present to accept the waste (e.g. more reliable results of repeated measurement after a sample preparation) a more accurate analytical method is necessary to enable a reliable decision.

In the case that $M_{av} - U > I_{doc}$ the indication is given that the element concentration of the element involved is too high to be accepted on the landfill. The waste should be refused at the landfill until an element determination with a well prepared sample in a laboratory will falsify the on-site result.

C.4 Estimation of uncertainty

To estimate the uncertainty (U) for XRF measurements in the field, the only parameter present is usually the standard deviation of the repeated measurements (s_r).

Based on s_r a number of methods to derive a value for U are possible. Some methods are presented.

a) Under regular laboratory condition and/or in case of a well-prepared (homogenized, small particles, flat) sample, it is generally accepted that a fair estimation of U is:

$$U = 2 \times s_r$$

In this particular case, and assuming a normal distribution of the measured values, the chance that the true value is in the range $M_{av} \pm U$ is 96 %. This percentage increases to 99 % for $U = 3 \times s_r$. As under field conditions during on-site verification, the well-preparedness of the sample is often not possible, and additional factors such as heterogeneity of the sample will enlarge the value of the uncertainty.

In those cases $U = k \times 2 \times s_r$ where the value of k can be a number based on expert view. Often a value of 2 or 3 is adopted.

b) Except for very low concentrations close to the LOD, the standard deviation in analytical measurements is dependent on the concentration of the measurand, as a result of the variability in the calibration function, according to $s = f\left(c^{1/2}\right)$.

To perform this dependence, either the variation in the calibration function should be known or repeated measurements at different element concentrations should be performed. Under conditions of on-site verification, these possibilities are usually not realizable.

To reckon with a higher s at higher element concentrations, a rough, practical ('quick and dirty') approach can be applied:

1) for M_{av} < 500 mg/kg, set the uncertainty range at $\frac{1}{5} \times M_{av}$ to $5 \times M_{av}$,

2) for 500 < M_{av} < 5 000 mg/kg, set the uncertainty range at: $\frac{1}{2} \times M_{av}$ to $2 \times M_{av}$,

3) for M_{av} > 5 000 mg/kg, set the uncertainty range at: $\frac{1}{1{,}3} \times M_{av}$ and $1{,}3 \times M_{av}$.

These numbers follow a Horwitz-like function [8].

When selecting identification criteria in case of applying XRF as a screening method at landfills, one should keep in mind to aim a control of documented values that should performed sufficiently quick while simultaneously protecting the environment.

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Annex D
(informative)

Validation

A validation trial was performed to prove the capability of portable XRF systems for screening waste and contaminated soil. Five manufacturers were invited to participate in the validation trial. It was performed as a workshop where 6 different waste samples were analysed with in total 8 different portable XRF instruments. During the validation workshop the selected waste samples were identically prepared and presented in 6 different rooms (one room for each sample) in order to guarantee similar test conditions for all samples and for all manufactures. The participants of the trial were asked one by one to analyse all samples in fivefold (probing different spots). One manufacturer with a hand-held system measured directly on the sample while the others used the hand-held instrument in a bench top stand. In the latter case, a test portion was taken five times from the sample to be analysed and filled into a sample cup provided with a thin foil.

For details of the study see Reference [7]. The conclusions of this study are reported in CEN/TR 16176:2011 [5].

The following samples representative for landfills and waste incineration plants were selected. Sample material have been provided by waste handling plants from Germany and Belgium.

— sample 1: Pb granulate (particle size: 0 mm - 8 mm);

— sample 2: recycled construction waste (particle size: 0 mm - 10 mm);

— sample 3: waste wood (particle size: 0 mm - 2 mm);

— sample 7: shredder material (particle size: 0 mm - 2 mm);

— sample 8: contaminated soil;

— sample 11: slag from a municipal incineration waste (particle size: 0 mm - 8 mm).

As the samples S3 and S7 already had a particle size of less than 2 mm, no additional sample preparation was performed on these samples. From the other samples 2 subsamples were taken from the homogenized batches. One subsample was considered as the field study sample (conditions closely related to real field conditions). These samples were further indicated as ‘coarse’ samples. The second subsample was dried and finely ground with a planetary ball mill (indicative particle size < 250 µm) and are also further indicated as ‘fine’ samples.

Reference values (m_{REF}) for all elements were determined using the following methods:

— $HF:HNO_3$:HCl digestion (in triplicate) according to EN 13656 [1] and subsequent analysis of the digestion solution with ICP-AES, and

— EDXRF or WDXRF analysis according to EN 15309 [2]. The waste wood sample S3 was analysed with WDXRF using a semiquantitative measurement programme. These results can only be considered as indicative. The other samples were analysed with the EDXRF system with polarized light using a precalibrated geological calibration programme.

If elemental results were available from ICP-AES analyses, these values were used as reference values, otherwise the XRF results were defined as reference values.

The results are presented in Tables D.1, D.2, D.3, D.4, D.5, D.6, D.7, D.8, D.9 and D.10. More details related to the evaluation according to predefined acceptance levels are reported in CEN/TR 16176:2011 [5].

Table D.1 — Validation data of sample 1 (Pb granulate, coarse)

Element	*l*	*n*	m_{REF} mg/kg dm	mm_{XRF} mg/kg	mS_r mg/kg	mV_r %	mV_r < 30 %?	mm_{XRF} above LOD? > 3 × mS_r	Indication of concentration level? m_{REF} between $mm_{XRF} \pm 3 \times mS_r$
S	7	35	2 358	108 573	12 243	10	YES	> LOD	NO
Cl	6	30	< 10	27 076	4 735	14	YES	> LOD	NO
V	5	25	282	263	32	25	YES	> LOD	YES
Cr	8	40	1 830	1 579	179	12	YES	> LOD	YES
Mn	8	40	9 597	21 667	604	5	YES	> LOD	NO
Fe	8	40	240 000	277 478	11 367	4	YES	> LOD	NO
Co	4	20	300	5 134	226	19	YES	> LOD	NO
Ni	5	25	286	131	17	36	NO	-	-
Cu	7	35	538	583	88	17	YES	> LOD	YES
Zn	8	40	118 000	142 814	4 350	3	YES	> LOD	NO
As	8	40	4 450	9 488	1 531	13	YES	> LOD	NO
Br	2	10	19	91	5	22	YES	> LOD	NO
Mo	8	40	272	260	22	13	YES	> LOD	YES
Cd	1	5	5,9	31	2	56	NO	-	-
Sn	8	40	1 650	2 077	125	6	YES	> LOD	NO
Sb	8	40	2 480	2 562	263	10	YES	> LOD	YES
Ba	5	25	1 930	2 314	83	7	YES	> LOD	NO
Pb	8	40	94 600	89 744	8 911	10	YES	> LOD	YES

l number of accepted laboratories
n number of accepted results
m_{REF} content of elements specified determined by reference method (see above), in mg/kg dry matter
mm_{XRF} mean of the mean content of elements specified calculated from N data sets, in mg/kg
mS_r mean repeatability standard deviation
mV_r mean relative repeatability standard deviation
LOD limit of detection
Limit value set limit value (see 12.2)

Table D.2 — Validation data of sample 1 (Pb granulate, fine)

Element	*l*	*n*	m_{REF} mg/kg dm	mm_{XRF} mg/kg	mS_r mg/kg	mV_r %	mV_r < 30 %?	mm_{XRF} above LOD? > 3 × mS_r	Indication of concentration level? m_{REF} between $mm_{XRF} \pm 3 \times mS_r$
S	7	35	2 358	80 010	4 547	9	YES	> LOD	NO
Cl	6	30	< 10	26 416	2 195	8	YES	> LOD	NO
V	5	25	282	267	31	20	YES	> LOD	YES
Cr	8	40	1 830	2 230	112	5	YES	> LOD	NO
Mn	8	40	9 597	21 205	400	3	YES	> LOD	NO
Fe	8	40	240 000	287 991	7 190	3	YES	> LOD	NO
Co	4	20	300	4 160	156	11	YES	> LOD	NO
Ni	4	20	286	166	10	9	YES	> LOD	NO
Cu	7	35	538	546	49	10	YES	> LOD	YES
Zn	8	40	118 000	143 504	4 558	3	YES	> LOD	NO
As	8	40	4 450	8 562	349	4	YES	> LOD	NO
Br	1	5	19	230	4	15	YES	> LOD	NO
Mo	8	40	272	254	19	10	YES	> LOD	YES
Cd	1	5	5,9	127	3	47	NO	-	-
Sn	8	40	1 650	1 957	87	4	YES	> LOD	NO
Sb	8	40	2 480	2 645	143	5	YES	> LOD	YES
Ba	5	25	1 930	2 022	88	8	YES	> LOD	YES
Pb	8	40	94 600	94 370	4 252	4	YES	> LOD	YES

l number of accepted laboratories
n number of accepted results
m_{REF} content of elements specified determined by reference method (see above), in mg/kg dry matter
mm_{XRF} mean of the mean content of elements specified calculated from N data sets, in mg/kg
mS_r mean repeatability standard deviation
mV_r mean relative repeatability standard deviation
LOD limit of detection
Limit value set limit value (see 12.2)

Table D.3 — Validation data of sample 2 (recycled construction waste, coarse)

Element	*l*	*n*	m_{REF} mg/kg dm	mm_{XRF} mg/kg	mS_r mg/kg	mV_r %	mV_r < 30 %?	mm_{XRF} above LOD? > 3 × mS_r	Indication of concentration level? m_{REF} between $mm_{XRF} \pm 3 \times mS_r$	$m_{verification}$ mg/kg	Present with respect to $m_{verification}$? [$mm_{XRF} - 3 \times mS_r$] > $m_{verification}$
S	6	30	3 780	5 671	1 246	18	YES	PRESENT	YES		
Cl	3	15	451	1 338	60	10	YES	PRESENT	NO		
V	5	25	84	93	21	33	NO	-	-	30	-
Cr	7	35	125	119	40	28	YES	< LOD	-	120	NO
Mn	7	35	1 370	923	161	18	YES	PRESENT	YES		
Fe	7	35	20 300	15 907	1 873	12	YES	PRESENT	YES		
Co	3	15	10	223	42	60	NO	-	-	5	-
Ni	4	20	41	34	7	42	NO	-	-	100	-
Cu	7	35	40	37	8	24	YES	PRESENT	YES	80	NO
Zn	7	35	272	226	43	19	YES	PRESENT	YES	300	NO
As	3	15	13	24	3	24	YES	PRESENT	NO	10	YES
Br	1	5	< 3	6	0,1	9	YES	PRESENT	NO		
Mo	1	5	2,5	8	0,5	31	NO	-	-	2	-
Cd	1	5	0,7	11	1	54	NO	-	-	10	-
Sn	3	15	4,9	31	4	29	YES	PRESENT	NO		
Ba	5	25	416	491	77	22	YES	PRESENT	YES		
Pb	7	35	191	102	33	28	YES	PRESENT	YES	40	NO

l number of accepted laboratories
n number of accepted results
m_{REF} content of elements specified determined by reference method (see above), in mg/kg dry matter
mm_{XRF} mean of the mean content of elements specified calculated from N data sets, in mg/kg
mS_r mean repeatability standard deviation
mV_r mean relative repeatability standard deviation
LOD limit of detection
Limit value set limit value (see 12.2)

NOTE $m_{verification}$: values serve as example, to be substituted in according to the requirements.

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Table D.4 — Validation data of sample 2 (recycled construction waste, fine)

Element	*l*	*n*	m_{REF} mg/kg dm	mm_{XRF} mg/kg	mS_r mg/kg	mV_r %	mV_r < 30 %?	mm_{XRF} above LOD? > 3 × mS_r	Indication of concentration level? m_{REF} between $mm_{XRF} \pm 3 \times mS_r$	$m_{verification}$ mg/kg	Present with respect to $m_{verification}$? $mm_{XRF} - 3 \times mS_r > m_{verification}$
S	7	35	3 780	6 205	723	13	YES	PRESENT	NO		
Cl	3	15	451	1 337	75	13	YES	PRESENT	NO		
V	4	20	84	122	10	26	YES	PRESENT	NO	30	YES
Cr	7	35	125	148	15	13	YES	PRESENT	YES	120	NO
Mn	8	40	1 370	3 945	143	5	YES	PRESENT	NO		
Fe	8	40	20 300	21 245	842	4	YES	PRESENT	YES		
Co	3	15	10	208	23	61	NO	-	-	5	-
Ni	5	25	41	33	7	35	NO	-	-	100	-
Cu	8	40	40	39	13	32	NO	-	-	80	-
Zn	8	40	272	271	51	20	YES	PRESENT	YES	300	NO
As	4	20	13	12	3	53	NO	-	-	10	-
Br	1	5	< 3	5	0,1	22	YES	PRESENT	NO		
Mo	2	10	2,5	51	1	9	YES	PRESENT	NO	2	YES
Cd	2	10	0,7	28	5	100	NO	-	-	10	-
Sn	4	20	4,9	172	9	30	YES	PRESENT	NO		
Ba	5	25	416	507	30	9	YES	PRESENT	NO		
Pb	8	40	191	124	29	24	YES	PRESENT	YES	40	NO

l number of accepted laboratories
n number of accepted results
m_{REF} content of elements specified determined by reference method (see above), in mg/kg dry matter
mm_{XRF} mean of the mean content of elements specified calculated from N data sets, in mg/kg
mS_r mean repeatability standard deviation
mV_r mean relative repeatability standard deviation
LOD limit of detection
Limit value set limit value (see 12.2)

NOTE $m_{verification}$: values serve as example, to be substituted in according to the requirements.

Table D.5 — Validation data of sample 3 (waste wood)

Element	*l*	*n*	m_{REF} mg/kg dm	mm_{XRF} mg/kg	mS_r mg/kg	mV_r %	mV_r < 30 %?	mm_{XRF} above LOD? > 3 × mS_r	Indication of concentration level? m_{REF} between mm_{XRF} ± 3 × mS_r
S	3	15	536	863	87	27	YES	PRESENT	NO
Cl	3	15	387	400	26	15	YES	PRESENT	YES
Cr	6	30	65	40	7	26	YES	PRESENT	NO
Mn	8	40	112	222	15	6	YES	PRESENT	NO
Fe	8	40	1 154	1 177	256	17	YES	PRESENT	YES
Ni	2	10	25	40	14	69	NO	-	-
Cu	7	35	19	125	14	29	YES	PRESENT	NO
Zn	8	40	184	290	44	20	YES	PRESENT	YES
As	3	15	1,8	24	1	14	YES	PRESENT	NO
Sn	5	25	338	124	84	101	NO	-	-
Sb	2	10	44	42	2	21	YES	PRESENT	YES
Ba	5	25	159	322	81	26	YES	PRESENT	YES
Pb	8	40	180	189	72	42	NO	-	-

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Table D.6 — Validation data of sample 4 (shredder material)

Element	*l*	*n*	m_{REF} mg/kg dm	mm_{XRF} mg/kg	mS_r mg/kg	mV_r %	mV_r < 30 %?	mm_{XRF} above LOD? > 3 × mS_r	Indication of concentration level? m_{REF} between mm_{XRF} ± 3 × mS_r
S	6	30	5 788	18 623	1 663	13	YES	PRESENT	NO
Cl	6	30	4 500	6 134	753	17	YES	PRESENT	YES
V	6	30	54	447	82	21	YES	PRESENT	NO
Cr	8	40	597	867	157	17	YES	PRESENT	YES
Mn	8	40	1 740	2 193	279	13	YES	PRESENT	YES
Fe	8	40	114 000	127 542	8 322	6	YES	PRESENT	YES
Co	4	20	61	1 240	90	21	YES	PRESENT	NO
Ni	8	40	657	373	63	18	YES	PRESENT	NO
Cu	8	40	3 050	3 290	816	25	YES	PRESENT	YES
Zn	8	40	16 400	23 940	2 202	9	YES	PRESENT	NO
As	4	20	26	276	28	42	NO	-	-
Br	5	25	333	672	203	45	NO	-	-
Mo	6	30	67	96	16	27	YES	PRESENT	YES
Ag	6	30	84	72	8	30	YES	PRESENT	YES
Cd	7	35	40	60	13	26	YES	PRESENT	YES
Sn	8	40	338	564	152	27	YES	PRESENT	YES
Sb	8	40	335	447	99	20	YES	PRESENT	YES
Ba	6	30	3 680	3 759	312	11	YES	PRESENT	YES
Pb	8	40	6 080	6 038	742	12	YES	PRESENT	YES

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Table D.7 — Validation data of sample 5 (contaminated soil, coarse)

Element	*l*	*n*	m_{REF} mg/kg dm	mm_{XRF} mg/kg	mS_r mg/kg	mV_r %	mV_r < 30 %?	mm_{XRF} above LOD? > 3 × mS_r	Indication of concentration level? m_{REF} between mm_{XRF} ± 3 × mS_r	$m_{verification}$ mg/kg	Present with respect to $m_{verification}$? mm_{XRF} – 3 × mS_r > $m_{verification}$
S	6	30	12 400	8 849	1 008	12	YES	PRESENT	NO		
Cl	7	35	21 050	25 329	3 688	11	YES	PRESENT	YES		
V	3	15	53	38	3	18	YES	PRESENT	NO	30	YES
Cr	8	40	266	208	47	28	YES	PRESENT	YES	120	NO
Mn	7	35	638	349	37	9	YES	PRESENT	NO		
Fe	8	40	25 200	16 035	1 331	8	YES	PRESENT	NO		
Co	3	15	15	271	18	35	NO	-	-	5	-
Ni	7	35	129	61	17	32	NO	-	-	100	-
Cu	8	40	541	313	30	10	YES	PRESENT	NO	80	YES
Zn	8	40	2 870	2 122	189	8	YES	PRESENT	NO	300	YES
As	3	15	22	13	3	68	NO	-	-	10	-
Br	5	25	103	88	6	9	YES	PRESENT	YES		
Mo	7	35	40	26	6	26	YES	PRESENT	YES	2	YES
Cd	5	25	11	30	6	35	NO	-	-	10	-
Sn	8	40	93	193	63	26	YES	PRESENT	YES		
Sb	6	30	60	168	48	35	NO	-	-	1	-
Ba	5	25	413	302	36	17	YES	PRESENT	NO		
Pb	8	40	739	367	41	10	YES	PRESENT	NO	40	YES

l number of accepted laboratories
n number of accepted results
m_{REF} content of elements specified determined by reference method (see above), in mg/kg dry matter
mm_{XRF} mean of the mean content of elements specified calculated from N data sets, in mg/kg
mS_r mean repeatability standard deviation
mV_r mean relative repeatability standard deviation
LOD limit of detection
Limit value set limit value (see 12.2)

NOTE $m_{verification}$: values serve as example, to be substituted in according to the requirements.

Table D.8 — Validation data of sample 5 (contaminated soil, fine)

Element	*l*	*n*	m_{REF} mg/kg dm	mm_{XRF} mg/kg	mS_r mg/kg	mV_r %	mV_r < 30 %?	mm_{XRF} above LOD? > 3 × mS_r	Indication of concentration level? m_{REF} between mm_{XRF} ± 3 × mS_r	$m_{verification}$ mg/kg	Present with respect to $m_{verification}$? mm_{XRF} – 3 × mS_r > $m_{verification}$
S	6	30	12 400	14 736	1 561	11	YES	PRESENT	YES		
Cl	7	35	21 050	31 061	3 383	6	YES	PRESENT	YES		
V	3	15	53	59	2	10	YES	PRESENT	NO	30	YES
Cr	8	40	266	288	49	14	YES	PRESENT	YES	120	YES
Mn	8	40	638	573	36	6	YES	PRESENT	YES		
Fe	8	40	25 200	24 758	833	3	YES	PRESENT	YES		
Co	3	15	15	302	19	32	NO	-	-	5	-
Ni	8	40	129	104	16	16	YES	PRESENT	YES	100	NO
Cu	8	40	541	492	24	5	YES	PRESENT	YES	80	YES
Zn	8	40	2 870	3 134	99	3	YES	PRESENT	YES	300	YES
As	3	15	22	15	2	30	NO	-	-	10	-
Br	5	25	103	132	3	4	YES	PRESENT	NO		
Mo	7	35	40	42	3	12	YES	PRESENT	YES	2	YES
Cd	6	30	11	39	9	28	YES	PRESENT	NO	10	YES
Sn	8	40	93	206	37	16	YES	PRESENT	NO		
Sb	7	35	60	148	41	28	YES	PRESENT	YES	1	YES
Ba	6	30	413	547	45	11	YES	PRESENT	YES		
Pb	8	40	739	578	27	5	YES	PRESENT	NO	40	YES

l number of accepted laboratories
n number of accepted results
m_{REF} content of elements specified determined by reference method (see above), in mg/kg dry matter
mm_{XRF} mean of the mean content of elements specified calculated from N data sets, in mg/kg
mS_r mean repeatability standard deviation
mV_r mean relative repeatability standard deviation
LOD limit of detection
Limit value set limit value (see 12.2)

NOTE $m_{verification}$: values serve as example, to be substituted in according to the requirements.

Table D.9 — Validation data of sample 6 (slag, coarse)

Element	*l*	*n*	m_{REF} mg/kg dm	mm_{XRF} mg/kg	mS_r mg/kg	mV_r %	mV_r < 30 %?	mm_{XRF} above LOD? > 3 × mS_r	Indication of concentration level? m_{REF} between mm_{XRF} ± 3 × mS_r
S	5	25	13 400	29 648	1 893	10	YES	PRESENT	NO
Cl	7	35	17 020	20 771	3 772	33	NO	-	-
V	4	20	52	193	41	37	NO	-	-
Cr	8	40	503	1 258	1 987	68	NO	-	-
Mn	8	40	1 390	1 153	554	40	NO	-	-
Fe	8	40	68 500	41 589	12 164	32	NO	-	-
Co	4	20	45	563	105	30	NO	-	-
Ni	8	40	228	183	174	88	NO	-	-
Cu	8	40	3 130	2 813	2 229	60	NO	-	-
Zn	8	40	4 190	4 339	1 058	24	YES	PRESENT	YES
As	5	25	26	71	17	35	NO	-	-
Br	5	25	38	45	5	18	YES	PRESENT	YES
Mo	7	35	22	33	20	50	NO	-	-
Ag	7	35	21	54	11	42	NO	-	-
Cd	4	20	12	116	6	35	NO	-	-
Sn	8	40	186	311	161	46	NO	-	-
Sb	8	40	138	205	47	26	YES	PRESENT	YES
Ba	6	30	3 100	3 396	810	30	YES	PRESENT	YES
Pb	8	40	2 037	976	234	22	YES	PRESENT	NO

l number of accepted laboratories
n number of accepted results
m_{REF} content of elements specified determined by reference method (see above), in mg/kg dry matter
mm_{XRF} mean of the mean content of elements specified calculated from N data sets, in mg/kg
mS_r mean repeatability standard deviation
mV_r mean relative repeatability standard deviation
LOD limit of detection
Limit value set limit value (see 12.2)

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Table D.10 — Validation data of sample 6 (slag, fine)

Element	*l*	*n*	m_{REF} mg/kg dm	mm_{XRF} mg/kg	mS_r mg/kg	mV_r %	mV_r < 30 %?	mm_{XRF} above LOD? > 3*mS_r	Indication of concentration level? m_{REF} between $mm_{XRF} \pm 3 \times mS_r$
S	6	30	13 400	30 656	1 688	7	YES	PRESENT	NO
Cl	7	35	17 020	21 466	1 260	5	YES	PRESENT	NO
V	5	25	52	240	27	18	YES	PRESENT	NO
Cr	8	40	503	664	108	16	YES	PRESENT	YES
Mn	8	40	1 390	1 523	131	8	YES	PRESENT	YES
Fe	8	40	68 500	61 527	3 329	5	YES	PRESENT	YES
Co	5	25	45	765	74	23	YES	PRESENT	NO
Ni	8	40	228	177	37	19	YES	PRESENT	YES
Cu	8	40	3 130	3 089	468	14	YES	PRESENT	YES
Zn	8	40	4 190	5 073	536	11	YES	PRESENT	YES
As	5	25	26	42	10	40	NO	-	-
Br	5	25	38	46	3	11	YES	PRESENT	YES
Mo	6	30	22	35	5	16	YES	PRESENT	YES
Ag	7	35	21	57	5	17	YES	PRESENT	NO
Cd	4	20	12	33	9	42	NO	-	-
Sn	8	40	186	317	78	22	YES	PRESENT	YES
Sb	8	40	138	235	60	18	YES	PRESENT	YES
Ba	6	30	3 100	2 865	109	5	YES	PRESENT	YES
Pb	8	40	2 037	1 268	105	8	YES	PRESENT	NO

l number of accepted laboratories
n number of accepted results
m_{REF} content of elements specified determined by reference method (see above), in mg/kg dry matter
mm_{XRF} mean of the mean content of elements specified calculated from N data sets, in mg/kg
mS_r mean repeatability standard deviation
mV_r mean relative repeatability standard deviation
LOD limit of detection
Limit value set limit value (see 12.2)

Bibliography

[1] EN 13656:2002, *Characterization of waste - Microwave assisted digestion with hydrofluoric (HF), nitric (HNO3) and hydrochloric (HCl) acid mixture for subsequent determination of elements*

[2] EN 15309:2007, *Characterization of waste and soil - Determination of elemental composition by X-ray fluorescence*

[3] EN 16123:2013, *Characterization of waste - Guidance on selection and application of screening methods*

[4] CEN/TR 16130:2011, *Characterization of waste - On-site verification*

[5] CEN/TR 16176:2011, *Characterization of waste - Screening methods for elemental composition by X-ray fluorescence spectrometry for on-site verification*

[6] ISO 13196:2013, *Soil quality - Screening soils for selected elements by energy-dispersive X-ray fluorescence spectrometry using a handheld or portable instrument*

[7] BUND/LÄNDER-ARBEITSGEMEINSCHAFT ABFALL (LAGA), ed. LAGA Project L.2.08 Applicability of handheld XRF system for waste characterisation

[8] Horwitz W., Kamps L.R., Boyer K.W. Quality assurance in the analysis of food and trace constituents. *J. Assoc. Off. Anal. Chem.* 1980, 63 pp. 1344–1354

[9] Vanhoof C., Holschbach-Bussian K.A., Bussian B.M., Cleven R. and Furtmann K., *Applicability of portable XRF systems for screening waste loads on hazardous substances as incoming inspection at waste handling plants*, accepted for publication in X-Ray Spectrom., 2013

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