SLOVENSKI STANDARD
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Karakterizacija odpadkov - Rešetalne metode za elementno sestavo z rentgensko fluorescenčno spektrometrijo na kraju samem

Characterization of waste - Screening methods for elemental composition by X-ray fluorescence spectrometry for on-site verification

Charakterisierung von Abfällen - Anwendung von Screening-Verfahren bei der Vor-Ort-Prüfung - Bestimmung der elementaren Zusammmensetzung mittels Röntgenfluoreszenzspektrometrie

Méthodes de dépistage pour la détermination de la composition élémentaire par spectrométrie à fluorescence de rayons X pour les vérifications in-situ

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Characterization of waste - Screening methods for elemental composition by X-ray fluorescence spectrometry for on-site verification

Caractérisation des déchets - Méthodes de dépistage pour la détermination de la composition élémentaire par spectrométrie à fluorescence de rayons X pour les vérifications in-situ

Charakterisierung von Abfällen - Anwendung von Screening-Verfahren bei der Vor-Ort-Prüfung - Bestimmung der elementaren Zusammmensetzung mittels Röntgenfluoreszenzspektrometrie

This draft Technical Report is submitted to CEN members for Technical Committee Approval. It has been drawn up by the Technical Committee CEN/TC 292.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
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Contents

Foreword

This document (FprCEN/TR 16176:2011) has been prepared by Technical Committee CEN/TC 292 “Characterization of Waste”, the secretariat of which is held by NEN.

This document is currently submitted to the Technical Committee Approval.

Introduction

Although bench-top instruments generally provide much more conclusive results, hand-held XRF instruments are becoming an interesting screening tool for a wide range of applications. Their portability and their ability to identify, characterise and also analyse a wide range of elements rapidly, along with the fact that little technical expertise is needed to operate them, make the hand-held XRF instruments very useful. The recent developments in the XRF technology tends to create hand-held instruments with performance levels approaching bench top equipment. Some years ago, hand-held instruments required the use of radioactive materials to provide a source of X-rays, resulting in very stringent regulatory demands. The development of miniaturised low-power X-ray tubes overcomes these problems and provides new opportunities for the hand-held instruments. Recent advances in the improvement of the detector efficiency led to a significant decrease in the detection limits for hand-held systems compared to the older ones. Due to the required compact configuration for hand-held XRF systems only energy dispersive X-ray fluorescence (EDXRF) are on the market. On the other hand wavelength dispersive XRFs (WDXRF) are generally more laborious.

The use of the XRF technique in field screening trials can provide a number of benefits compared to the traditional laboratory techniques. On-site analyses ensure a fast turnaround between the measurement itself and the availability of data results. Sample preparation is frequently unnecessary or will be limited. Screening can gain a large sample data set on a short time frame, but that can be at the expense of the accuracy and precision. When better accuracy is required confirmative analysis has to be performed. This approach will surely result in a significant reduction of analysis time and costs.

This report focuses on hand-held XRF instruments, although portable bench-top instruments are also on the market for this type of application. Whenever portable instruments are specifically addressed in this report, both types of instruments can be considered.

1 Purpose

In the framework of the EU Directive 99/31/EC on the landfill of waste and the EU Directive 2000/76/EC on the incineration of waste there is a growing need for fast, easy-to-handle screening tools. In this respect, low costs, fast analyses, control of truck loads and yes/no-acceptance decisions are relevant criteria. The X-ray fluorescence (XRF) technique meets these requirements as a screening tool for on-site verification on the landfill and for entrance control on the incineration plants.

Recent developments of the XRF technology have made this technique a method of choice for on-site analysis, namely miniaturisation of the XRF system (X-ray tube), the optimisation of the calibration programmes and the improvement of the detectors. Therefore, a state-of-the-art document on the current progress of the XRF technology and instruments available for on-site analysis shall support the key arguments, dealing with the pro’s and contra’s, and the performance of these systems to be expected.

The XRF standard EN 15309, is validated for Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, Sn, Sb, Te, I, Cs, Ba, Ta, W, Hg, Tl, Pb, Bi, Th and U, and describes in the informative annex the procedures for hand-held XRF systems together with the portable/transportable systems (placed in mobile labs). Although XRF can analyse a broad range of elements, the main focus of this document is on the series of elements that is also being covered by EN 15309. Of that series the following elements are related to the landfill directive: As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, Zn.

The information in this document will be useful in all cases in which on-site determination of the elemental compositions of waste is needed and hand-held instrumentation is therefore used. These cases may include, beside landfills and incineration plant, also waste treatment plants, contaminations soil sites and controls of transports of waste.

2 Description of the XRF technique

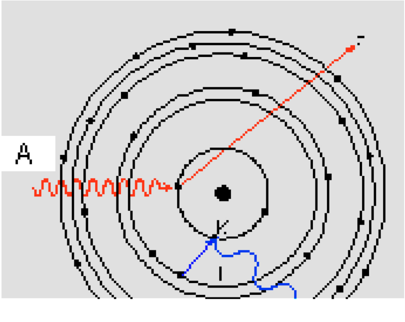
2.1 General

X-ray fluorescence spectrometry is a fast and reliable method for the analysis of the total content of certain elements within different matrices. The quality of the results obtained depends very closely on the type of instrument used, e.g. hand-held, bench top. When selecting a specific instrument several factors have to be considered, such as the matrices to be analysed, elements to be determined, detection limits required and the measuring time. The quality of the results depends on the element to be determined and on the surrounding matrix, together with the applied sample preparation method, and the heterogeneity of the test sample.

2.2 Principle of XRF

An electron can be ejected from its atomic orbital by the absorption of a light wave (photon) of sufficient energy [1]. The energy of the photon ($h\nu$) must be greater than the energy with which the electron is bound to the nucleus of the atom. When an inner orbital electron is ejected from an atom, an electron from a higher energy level orbital will be transferred to the lower energy level orbital. During this transition a photon maybe emitted from the atom. This fluorescent light is called the characteristic X-ray of the element (Figure 1). The energy of the emitted photon will be equal to the difference in energies between the two orbitals occupied by the electron making the transition. Because the energy difference between two specific orbital shells, in a given element, is always the same (i.e. characteristic of a particular element), the photon emitted when an electron moves between these two levels, will always have the same energy. Therefore, by determining the energy (wavelength) of the X-rays (photon) emitted by a particular element, it is possible to determine the identity of that element.

For a particular energy (wavelength) of fluorescent light emitted by an element, the number of photons per unit time (generally referred to as peak intensity or count rate) is related to the amount of that analyte in the sample. The counting rates for all detectable elements within a sample are usually calculated by counting, for a set amount of time, the number of photons that are detected for the various analytes’ characteristic X-ray energy lines. It is important to note that these fluorescent lines are actually observed as peaks with a semi-Gaussian distribution depending on the resolution of modern detector technology. Therefore, by determining the energy of the X-ray peaks in a sample's spectrum, and by calculating the count rate of the various elemental peaks, it is possible to qualitatively establish the elemental composition of the samples and to quantitatively measure the concentration of these elements.

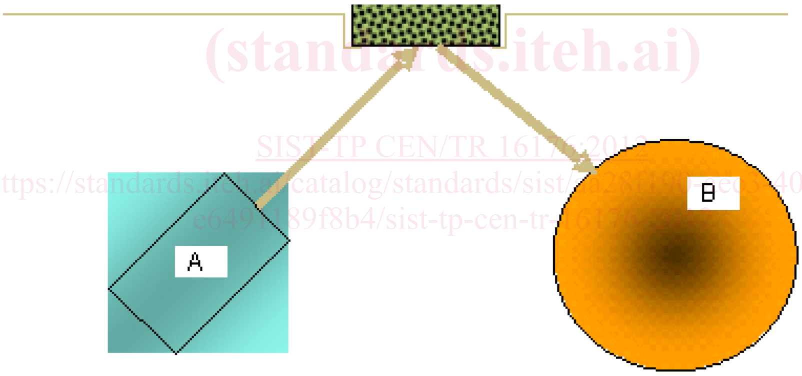


Key

A excitation: X-rays from X-ray source
B fluorescence: Characteristic X-ray

Figure 1 — Principle of XRF

The basic configuration of an EDXRF system consists of an excitation source and a detector, coupled to data processing unit, as shown in Figure 2.



Key

A X-ray source
B detector

Figure 2 — Basic configuration of an XRF system

2.3 Interferences

Interferences in X-ray fluorescence spectrometry are due to 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. Corrections for these interferences are made using the algorithms provided with the software.

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. In the case of complex matrices these effects generally have to be corrected.

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 spectrometry.

Particle size effects can be reduced by milling the sample, and both particle size and mineralogical effects can be eliminated by preparing bead samples. It is vital for quantitative analysis that the same sample preparation procedure is applied to both the standards and the samples to be analysed.

2.4 Measurement

All X-ray spectrometers are supplied with a spectrometer software programme to operate the instrument. The software packages are manufacturer depended and contain two major modules:

- analytical measurement programme for data collection. This module controls the measurement of a sample using a certain set of measurement parameters e.g. tube setting (kV, mA), targets and crystals, detectors, measurement times. The analytical programme is always linked to a selected evaluation and calibration programme. Actually, the same measurement conditions have to be applied for both the standards of the calibration curve and the samples. Because in screening analysis the measurements will be performed with the predefined analytical programmes, no further detailed descriptions will be given of the analytical measurement parameters. Follow the manufacturer's instruction for further operation and handling of the analytical software package;

- evaluation programme for data processing. This module converts the measured intensities of the different element lines to elemental concentrations taking all corrections into account. There are various types of evaluation programmes available and each manufacturer has set up his own programmes for data processing based on the XRF principles.

Sensitivity, instrumental detection limits and precision are instrument dependent and should therefore be investigated and established for each individual analyte line on that particular instrument, and, if relevant, as a function of matrix type and sample preparation procedure.

The XRF systems (hand-held as well as bench top) for screening purposes are all provided with precalibrated measurement programmes, setup by the manufacturer, and therefore the user does not need to calibrate the system itself. The user may be able to calibrate the XRF system itself, but it is not a requirement. It should be stressed out that the user needs to verify the calibration programme using reference samples in order to gain insights in the expected accuracy and precision of the XRF calibration programme. More information about the validation will be described in 2.6.

2.5 Calibration/evaluation

For calibration purposes the measurement of analyte lines of samples of known composition is needed. The basic equation implies a linear relationship between the intensity and the concentration.

$$c_i = a_{i,0} + a_{i,1} \times I_i \tag{1}$$

where

c_i is the concentration of the element of interest, expressed as mg/kg or percentage dry matter;

$a_{i,0}$ 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, expressed as counts per second.

Matrix effects have to be taken into account in X-ray spectrometry according to the following equation:

$$c_i = (a_{i,0} + a_{i,1} \times I_i) \times M \tag{2}$$

where

M is the correction term due to the matrix effects.

Different procedures for correcting matrix effects may be used according to the analytical accuracy required:

- the scattered radiation method is based on the principle that the intensities of the analyte line and of the Compton line are affected in the same proportion due to the overall mass absorption coefficient of the sample. This linear relationship holds when all analytes are at low concentrations (trace elements) and their absorption coefficients are not affected by an adjacent absorption edge. In this case an internal Compton correction can be used. Beside that, a correction method using the Compton intensity with mass absorption coefficients (MAC) is also applicable. In this method, the intensities of the major elements are measured to apply a jump edge correction for the analysed trace elements;

- correction using the fundamental parameter approach;

- correction using theoretical correction coefficients (alphas) taking basic physical principles, instrumental geometry etc. into account;

- correction using empirical correction coefficients (alphas) based on regression analysis of standards with known elemental concentrations.

For more information about the various calibration procedures is referred to EN 15309.

2.6 Validation

Prior to analysis of a sample, the available pre-calibrated analytical method has to be validated. The validation can be performed on different levels. First of all, and this is also a requirement when performing screening analysis, a verification of the calibration programme using a reference material with known composition has to be carried out on a regular base in order to follow-up the stability and drift of the system. Secondly, control analyses can be performed by using reference samples with a similar composition as the samples under investigation to gain insights in the expected measurement uncertainty. If no reference materials with a comparable matrix are available, only a qualitative analysis with indicative concentration values can be performed.

The reference sample can consist of:

- in-house or commercially available reference materials - if possible certified - with matrices similar to that of the sample;

- synthetic samples, made by weighing the appropriate amount of each pure reagent;

- site specific or batch specific samples, similar to the matrix of the sample;

- 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 needs to match that of the sample.

The element concentrations of the reference samples have to be known by certification or by determination with a different analytical technique.

The reference samples have to be analysed under the same analytical conditions as the sample, meaning the same sample preparation (pellet, powder etc.), the same analytical measurement method etc.

3 Overview XRF applications

An overview of 'portable/benchtop' and 'hand-held' instruments that are at present commercially available, is given in Annex A. The 'hand-held' instruments are generally less than 2 kg in weight, whereas the 'portable/benchtop' instruments are not below 9 kg.

Waste samples can consist of different matrix types, each of them may require an appropriate sample preparation. See Annex B in EN 15309, where five different types are described: 1. soil, sediment, fly ash and sludge samples, 2. samples consisting of carbon matrices, 3. liquid samples, 4. paste-like materials, 5. scrap samples. The procedures of the different sample preparation techniques are described in ISO 11464, EN 15002.

Application of XRF in 'on-site' verification at the entrance of landfill or a waste incinerator, will usually consist of the check of the presence of one or more components in solid material, with relatively low carbon content. For large landfills en plants, limited laboratory facilities will be present for sample preparation and 'portable/benchtop' instruments available.

Application of XRF during transport in traffic, will require a hand-held instruments at different sizes and forms of load must be approached.

Applications of XRF 'in the field', e.g. looking for hot spots in suspected areas; hand-held instruments are preferred because of their mobility.

4 Influence of the sample preparation on the result

Although the XRF technique is a non-destructive technique and it is often stated that no or only a limited sample preparation is required, the applied sample preparation method plays an important role in the final quality of the obtained results. The moisture content and the particle size of a solid sample have a significant influence on the obtained quality of the results. The highest quality can be obtained when the samples are dried and finely ground. However, on the field it is not always possible to perform an extended sample pretreatment.

XRF analysis can be performed on samples with different levels of pretreatment resulting in different quality of result:

- In situ analysis: The XRF is placed directly onto the sample and the analysis is performed without any sample preparation (Figure 3). A limited handling of the sample (flattening, make it more compact) can improve the quality of the obtained results. Nevertheless, the obtained results will only be qualitative and can only be considered as indicative.

Figure 3 — *In situ* analysis

- Analysis of a bagged sample: A simple way of improving the quality of the XRF results can be achieved by homogenisation of the sample. When putting the sample in a plastic bag, the sample can be homogenised roughly and crushed into smaller parts by hand. The XRF measurement can be performed directly on the bagged sample (Figure 4).

Figure 4 — Analysis of a bagged sample

- Analysis of a wet sieved sample: Although a wet sample is not easy to sieve, it can significantly improve the XRF data quality. The sieved sample can be put in a bag and analysed as such or it can be placed in a sample cup and analysed with the XRF in stand mode (Figure 5). Using this procedure the XRF results can be considered as semi-quantitative.

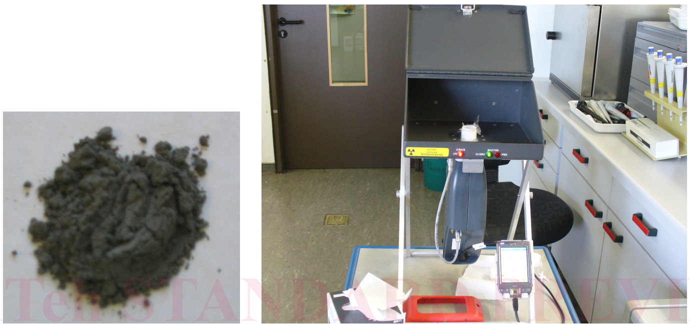


Figure 5 — Analysis of a wet sieved sample

- Analysis of a dried and ground sample: If a mobile lab is present at the site under investigation, it can be equipped with a drying oven (e.g. microwave) and grinding tools. Analysing a dried and finely ground sample will significantly improve the accuracy and precision of the XRF results. The prepared sample can be analysed with the XRF in stand mode (Figure 6). Using this procedure, one have to keep in mind that longer testing times are required and that the sample throughput will be lower compared to the direct XRF analysis.

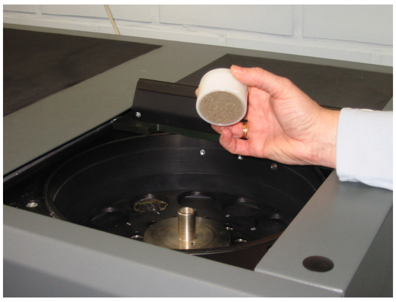


Figure 6 — Analysis of a dried and ground sample

In a publication of C. Vanhoof *et al* [2] several types of XRF instruments were compared, together with the influence of the applied preparation method on the acquired data using a field portable instrument. The influence of the pretreatment on the acquired data is shown in Figure 7. Performing *in situ* analysis with the field portable Spectrace 9000 resulted in low regression coefficients R^2 of 0,7 for both elements. Also the slopes were very low, therefore, the XRF values with a low concentration level were overestimated while the higher levels were underestimated. A limited homogenisation (sieving over 2 mm) of the soil sample significantly improved the regression parameters resulting in more comparable results.

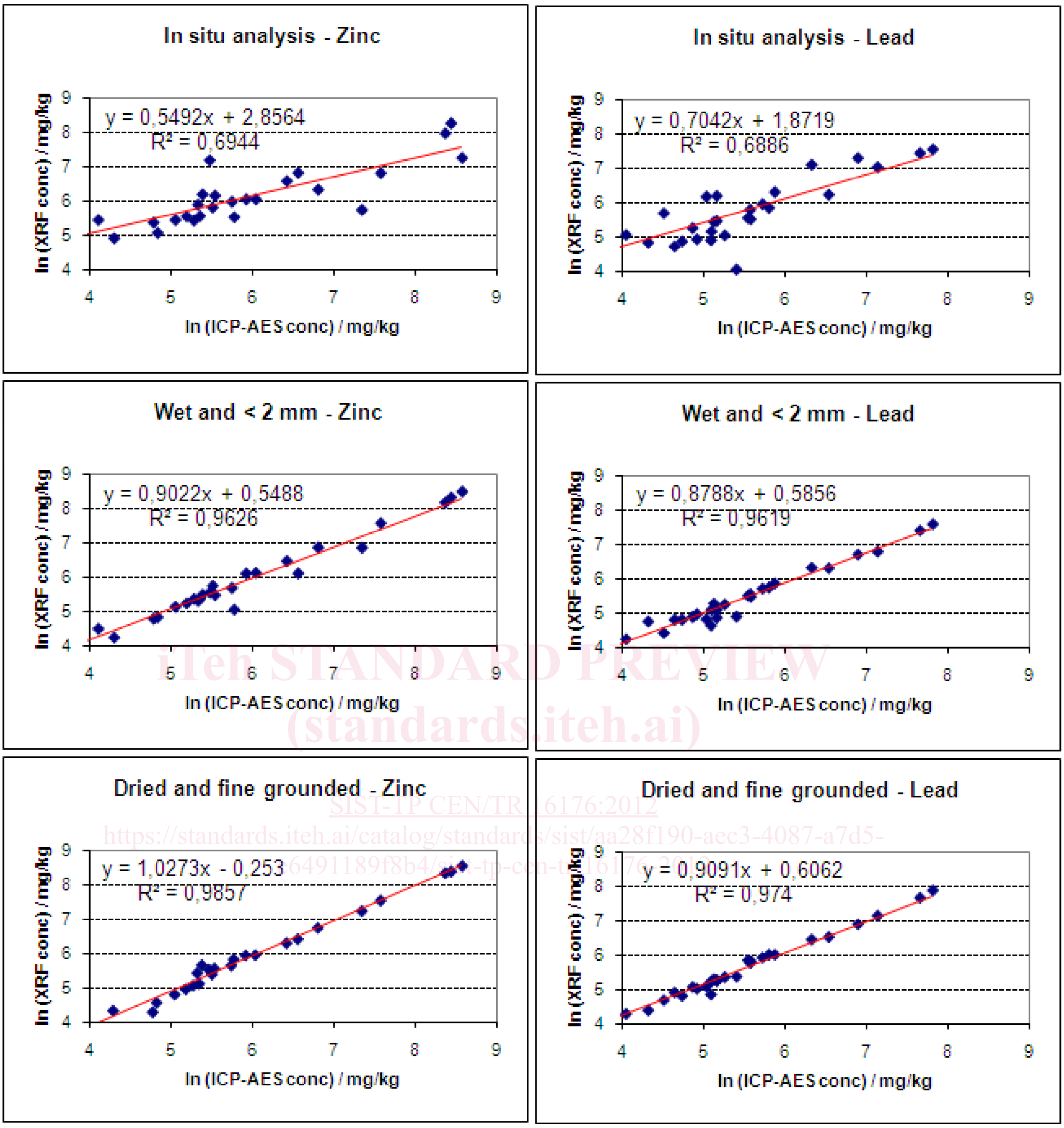


Figure 7 — Method comparison for the elements Zn and Pb, measured with the field portable EDXRF, as a function of the pretreatment

These results confirm that *in situ* analyses are strongly influenced by the heterogeneity of the samples. A limitation of the *in situ* analysis, without any homogenisation, is that only the surface top layer is analysed on just a small soil area (± 5 cm^2) corresponding to the XRF measuring window. Furthermore, the homogenisation process also assure that the same sample will be analyzed by the XRF system and the reference ICP-AES technique, while *in situ* analysis can be regarded as a one point surface analysis.