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# Sludge, treated biowaste and soil – Determination of elements in aqua regia and nitric acid digests - Flame atomic absorption absorption spectrometry.

*Einführendes Element — Haupt-Element — Ergänzendes Element*

*Élément introductif — Élément central — Élément complémentaire*

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# Foreword

This document is a working document.

This document TF WI has been prepared by CEN/BT/Task Force 151 – Horizontal Standards in the Field of Sludge, Biowaste and Soil, the secretariat of which is held by Danish Standards.

This document has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association, and supports essential requirements of EU Directive(s).

For relationship with EU Directive(s), see informative Annex A, B, C or D, which is an integral part of this document.

This standard is applicable and validated for several types of matrices. The table below indicates which ones.

[table to be filled and amended by the standards writer]

| **Material** | **Validated for**<br><br>**(type of sample, e.g. municipal sludge, compost)** | **Reference** |
|---|---|---|
| Sludge | | (reference) |
| Soil | | |
| Biowaste | | |
| Waste | | |

# Contents

Page

# Introduction

NOTE: This is a draft version; the introduction will need to be adjusted….

This document is developed in the project 'Horizontal'. It is the result of a desk study "Horizontal no 20 AAS" and aims at evaluation of the latest developments in assessing cobalt, copper, iron, manganese, nickel and zinc in sludge, soil, treated biowaste and neighbouring fields. After discussion with all parties concerned in CEN and selection of a number of test methods described in this study the standard has been developed further as an modular horizontal method and has been validated within in the project 'Horizontal' .

A horizontal modular approach is being investigated and developed in the project 'Horizontal'. 'Horizontal' means that the methods can be used for a wide range of materials and products with certain properties. 'Modular' means that a test standard developed in this approach concerns a specific step in a test procedure and not the whole test procedure (from sampling to analyses).

The use of modular horizontal standards implies the drawing of test schemes as well. Before executing a test on a certain material or product to determine certain characteristics it is necessary to draw up a protocol in which the adequate modules are selected and together form the basis for the test procedure.

The other horizontal modules that will be available in due time are to be found in the informative annex [*xxx*] which contains a brief overview of the modules that will be worked out in the project 'Horizontal.'

The texts of the chapters 1 to 12 are normative; annexes are normative or informative, as stated in the top lines of the annexes.

# 1 Scope

This European Standard describes principles and procedures for the determination of metals in aqua regia and nitric acid digests of sludge, soil and treated biowaste and neigbouring samples, using flame atomic absorption.

The method detection limit for each element depends on the sample matrix as well as of the instrument. For water samples with a simple matrix (i.e. low concentration of dissolved solids and particles), the method detection limits will be close to instrument detection limits. In digests containing higher concentrations of dissolved solids, interference effects may lead to an increase in the method detection limit.

Table 1. Widely used detection limits and measurement ranges for direct determination.

| Element | Wavelength nm | Detection limit mg/l | Measurement range mg/l |
|---|---|---|---|
| Cobalt | 240,7 | 0,02 | 0,06 – 10 |
| Copper | 324,8 | 0,005 | 0,015 – 10 |
| Iron | 248,3 | 0,03 | 0,1 – 10 |
| Manganese | 279,5 | 0,01 | 0,3 – 5 |
| Nickel | 232,0 | 0,02 | 0,06– 10 |
| Zinc | 213,9 | 0,005 | 0,015 – 2 |

The optimum measurement range is from the limit of quantification (LOQ) (which is three times the limit of detection, LOD), and the upper limit for direct determination is corresponding to a concentration giving an absorbance about 1 abs/cm. For the determination of higher concentrations the sample has to be diluted.

NOTE This Horizontal Standard refers specifically to the use of atomic absorption spectrometry. Users of this Horizontal Standard are advised to operate their laboratories to accepted quality control procedures. Certified Reference Materials (CRM) should be used to establish the amounts of the relevant elements in in-house reference materials. The latter can be used for routine quality control of the procedures given in this Horizontal Standard. Results should be established with control charts, for each element, within the laboratory. No results should be accepted which falls outside an agreed limit. Quality control procedures based on a widely accepted statistical technique should be used to establish such limit, to ensure that these are stable and that no long-term drift is occurring. CRM's should be used regularly to maintain the integrity of the in-house reference materials and, thereby, the quality control system.

## 2 Normative references

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies (including amendments).

EN ISO 3696: 1997, *Water for analytical laboratory use - Specification and test methods.*

ISO 5725-1: 1994 Accuracy (trueness and precision) of measurement methods and results – Part 1: general principles and definitions.

EN zzz: 200y (Hor.) Chemical analyses - Digestion of soil, sludge, biowaste and waste for the extraction of aqua regia soluble elements.

EN xxx: 200y (Hor.) Chemical analyses - Digestion of soil, sludge, biowaste and waste for the extraction of nitric acid soluble fraction of trace elements.

## 3 Terms and definitions

For the purpose of this European Standard, the following definition applies:

**3.1**

## 4 Safety remarks

## 5 Principle

The method is based on the atomic absorption spectrometric measurement of the concent-ration of the element in an aqua regia or nitric acid extract of the sample, prepared in accordance with the standards given under clause 2, using the instrumental conditions given in table 2.

Table 2. General conditions for flame atomic absorption spectrometry

| Element | Wavelength nm | Flame type | Lanthanum chloride | Main interferences | Background correction |
|---|---|---|---|---|---|
| Cobalt | 240,7 | Oxidizing air/acetyelene | No | | Deuterium |
| Copper | 324,8 | Oxidizing air/acetyelene | No | | Deuterium |
| Iron | 248,3 | Oxidizing air/acetyelene | No | Co, Ni, Si | Deuterium |
| Manganese | 279,5 | Oxidizing air/acetyelene or acetylene/$N_2O$ | Yes<br>No | Fe, Si | Deuterium |
| Nickel | 232,0 | Oxidizing air/acetyelene | No | Fe | Deuterium |
| Zinc | 213,9 | Oxidizing air/acetyelene | No | | Deuterium |

NOTE The wavelengths given are the most sensitive. Interferences are generally lower if the nitrous oxide flame is used for the determination of chromium and manganese. Users should be aware that small changes in gas volume ratios can have significant effects on the intensity of the analytical signal, and can also change the linearity of the instrument response. Also difference in acid strength, which will vary slightly from digest to digest, can have a measurable effect on some elements especially if background correction is not used. Users should, therefore, familiarize themselves with these aspects of their instrument's performance.

## 6 Interferences and sources of errors

Sample solutions of waste waters and digestions of sediments and soils, may contain large amounts of substances that may affect the results. Matrix effects may be overcome, partially or completely, by the use of a chemical modifier like lanthanum, the standard addition technique, and the use of background correction.

Nickel is affected a little by a high concentration of cobalt in aqua regia solution, however, the signal was increased by 10 % at a cobalt concentration of 1000 mg/l.

## 7 Reagents

Use only reagents of recognised analytical grade and water grade 1 in accordance with ISO 3696.

The metal contribution from water, reagents and gases should be significantly less than the lowest metal content to be determined. The overall metal content of water, chemicals, and gases shall be checked by measuring the total blank (see 8.2)

**6.1 Nitric acid**, $HNO_3$, □ = 1,42 g/ml, 65% (m/m) solution.

The same batch of nitric acid shall be used throughout the procedure.

**6.2 Nitric acid, diluted 1 + 3 (V/V)**

Add 250 ml of nitric acid (6.1) to 500 ml of water in a 1000 ml volumetric flask and fill to the mark with water.

**6.3 Hydrochloric acid, 37 %; ρ ~ 1,18 g/ml**

The same batch of hydrochloric acid shall be used throughout the procedure.

**6.4 Aqua regia, diluted ~ 1 + 3**

Dilute 210 ml of hydrochloric acid (6.3) and 70 ml of nitric acid (6.1) with about 500 ml of water in a 1000 ml volumetric flask, and dilute to the mark.

**6.5 Stock solutions**,

Both single-element stock solutions and multi-element stock solutions with adequate specification, stating the acid used and the preparation technique, are commercially available. These solutions are considered to be stable for more than one year, but in reference to guaranteed stability, the recommendations of the manufacturer should be considered.

Alternatively, the stock solutions may be prepared as indicated in table A1 in Annex A.

**6.5.1 Standard solutions**

Use the same acid and acid concentration as the digested samples when preparing the standard and the calibration solutions.

#### 6.5.2 Standard solution corresponding to 100 mg/l of element

Pipette 10,00 ml of the actual element stock solution (6.5) into a 100 ml volumetric flask. Add 20 ml of nitric acid (6.2) or 20 ml of aqua regia (6.4), fill to the mark with water and mix well.

#### 6.5.3 Standard solution corresponding to 10 mg/l of element

Pipette 10,00 ml of the element standard solution (6.5.1) into a 100 ml volumetric flask. Add 2 ml of nitric acid (6.2) or 2 ml of aqua regia (6.4), fill to the mark with water and mix well. Prepare this solution on the day of use.

### 6.6 Calibration solutions

Before each batch of determinations, prepare, from the standard solutions of each element (6.5.1 or 6.5.2), at least four calibration solutions covering the range of concentrations to be determined, the optimum working range being indicated in table 1. Calibration solutions shall be prepared on the day of use. Use the set of standard solutions containing the same acid as the digested samples.

#### 6.6.1 Blank calibration solutions

Prepare a blank calibration solution in the same way as the calibration solutions, but add no standard solution. Use a 100 ml volumetric flask. Add acid in correspondence to the samples that the solution will be analysed together with. Cool if necessary and dilute to volume with water.

#### 6.6.2 Lanthanum chloride solution, 37 g/l lanthanum

Dissolve 100 g lanthanum(III) chloride, $LaCl_3.7H_2O$, in 700 ml water. Then quantitatively transfer it to a 1000 ml volumetric flask and fill to the mark with water.

#### 6.6.3 Blank solution without lanthanum, aqua regia

Dilute 210 ml of hydrochloric acid (6.3) and 70 ml of nitric acid (6.1) with 500 ml water in a 1000 ml volumetric flask and fill to the mark with water.

#### 6.6.4 Blank solution without lanthanum, nitric acid

Dilute 200 ml of nitric acid (6.1) with 500 ml water in a 1000 ml volumetric flask and fill to the mark with water.

#### 6.6.5 Blank solution with lanthanum, aqua regia

Dilute 210 ml of hydrochloric acid (6.3) and 70 ml of nitric acid (6.1) with 500 ml water in a 1000 ml volumetric flask. Add 100 ml lanthanum chloride solution (6.6.2) and fill to the mark with water.

#### 6.6.6 Blank solution with lanthanum, nitric acid

Dilute 200 ml of nitric acid (6.3) with 500 ml water in a 1000 ml volumetric flask. Add 100 ml lanthanum chloride solution (6.6.2) and fill to the mark with water.

## 8 Apparatus

### 8.1 Usual laboratory equipment

All glass or plastic ware shall be cleaned carefully before trace element determinations, e.g. by immersion in warm 5 % (*V/V*) aqueous nitric acid solution for a minimum of 6 hours, followed by rinsing with water before use. The nitric acid shall be replaced each week.

NOTE It has been found conveniant to to keep separate sets of glass or plastic ware for the determinations given in this Horizontal Standard, in order to reduce the possibility of within-laboratory contamination. Similarly, it can be conveniant to carry out the acid cleaning step overnight.

### 8.2 Atomic absorption spectrometer

This shall be equipped with a hollow cathod lamp or electrodeless discharge lamp appropriate to the element of interest and operated at a current recommended for the lamp by the instrument manufacturer, a background correction system, a burner suitable for an air/acetylene or nitrous oxide/acetylene flame (operated according to the manufacturer's instructions). Deuterium background correction is the minimum technical specification acceptable for background correction for measurement wavelengths below 350 nm and a halogen lamp for measurement wavelengths above 350 nm. Other systems (e.g. Zeeman polarization, Smith-Hieftje) are equally acceptable and, in certain circumstances, can be superior.

**WARNING – It is essential that the manufacturer's safety recommendations are strictly observed when using these flames.**

## 9 Sampling and sample pre-treatment

### 9.1 Sampling

Sampling should be carried out in accordance with EN yyyy:2003 (Horizontal standard module(s) for sampling of sludge, soil and waste).

Samples should be stored in suitable containers with an appropriate closure material such as PTFE. Samples to be frozen may be stored in aluminium containers pre-cleaned by heating to 450°C for minimum 4 hours or by rinsing with a non-chlorinated solvent.

Samples should be kept cold (< 8°C) and in the dark. The sample pre-treatment should take place within 24 hours of sampling. Alternatively, samples may be frozen (-18 °C) directly after sampling and kept frozen for a maximum of one month before sample pre-treatment.

### 9.2 Sample pre-treatment

Transfer a sub-sample, homogenized according to EN wwww:2003 (Horizontal standard module(s) for pre-treatment of solid materials) of approximately 100 g to a porcelain dish.

Store the ground material in a desiccators or a tightly closed glass container.

## 10 Procedure

### 10.1 Test solution

The solid samples shall be extracted with aqua regia or nitric acid in accordance with EN xxx 200y (Hor.) or EN zzz 200y (Hor.), respectively. The nitric acid or aqua regia digested samples are transferred to 100 ml volumetric flasks and filled to the mark with water, thus giving the test solutions.

### 10.2 Blank test

Carry out a blank test at the same time as the extraction with aqua regia or nitric acid following the same procedure, using the same quantities of all reagents for the determination, but omitting the test sample. Transfer the digested blank solution to a 100 ml volumetric flask and fill to the mark with water. (10.2 -

### 10.3 Calibration and determination

Set up the atomic absorption spectrometer according to the manufacturer's instructions at the appropriate wavelength using appropriate conditions (see table 1), and with the suitable background correction system in operation. Aspirate a calibration solution (6.6) and optimize the aspiration conditions, burner height and flame conditions. Adjust the response of the instrument to zero absorbance whilst aspirating water.

Aspirate the set of calibration solutions in ascending order and, as a zero member, the blank solution (6.6.3 or 6.6.4, alternatively 6.6.5 or 6.6.6 when lanthanum is added to the test solution). After a delay of more than 10 seconds, read the absorbance of each solution at least twice and, if the values fall with an accepted range, average the values. Care should be taken to ensure that, when using the more concentrated standards, the absorbance is < 1, and preferably not more than 0,7.

NOTE 1 Nickel shows severe curvature above about 0,5 absorbance units even with a spectral bandwidth of 0,2 nm.

NOTE 2 The definition of an accepted range is outside the scope of this Horizontal Standard. However, users are reminded of NOTE 1 in clause 1, concerning quality control procedures. Whatever the basis for the latter in the laboratory, it should conform to well-established practices, such as those based on control charts, confidence limits, and the statistics of normal and non-normal distributions.

### 10.4 Plotting the graph

Plot a graph for each element with the concentrations of the 6.6.3 or6.6.4, alternatively 6.6.5 or 6.6.6)), in milligrams per litre, as abscissa, and the corresponding absorbance values as ordinate, alternatively calculate the correlation coefficients and slope for each element. (or determine the calibration function)

### 10.5 Determination of the element content of the test portion

Aspirate the blank test solution (8.2) and the test portion (8.1) separately into the flame, and measure the absorbance for that element. Read the solutions at least twice and, if the values fall within an accepted range, average the values (see NOTE 2 in 10.3). After each measurement, aspirate water and re-adjust the zero if necessary. In case of re-adjusting the zero the calibration has to be re-checked (e.g. by measuring a standard solution with intermediate element content). If the concentration of the element in the test portion exceeds the calibration range, dilute the test solution with the blank solution (6.6.3 or 6.6.4, alternatively 6.6.5 or 6.6.6) accordingly. Particular elements might need special precautions (10.6).

If an unknown type of sample is to be handled, determine the concentration of each element by the standard addition method. If the analytical result according to the standard addition method and the calibration curve are equal, the calibration curve method can be applied.

NOTE The temperature of all calibration and test solutions should be within 1 °C of each other at the time of atomic absorption measurement.

### 10.6 Special factors

#### 10.6.1 Chromium

For measurement with an air/acetylene flame, add 10 ml of lanthanum chloride solution (6.6.5 or 6.6.6) to the blank, each standard and sample flask.

NOTE The efficiency of the extraction of chromium from soils by aqua regia or nitric acid depends strongly on the nature of chromium compounds present, and the analytical signal is strongly affected by matrix elements (see table 1) in the extract.

#### 10.6.2 Manganese

For measurement with an air/acetylene flame, add 10 ml of lanthanum chloride solution (6.6.5 or 6.6.6) to the blank, each standard and sample flask.

**10.6.3 Nickel**

For wavelength λ = 232,0 nm, select a spectral bandwidth of 0,2 nm to separate the analytical line from adjacent non-absorbing lines.

**10.1 Quality Assurance of the overall procedure**

**10.1.1 Analysis of CRM**

Analyse a test sample of a certified reference material with matrix comparable to the samples to be analysed.

**10.1.2 Analysis of spiked natural samples**

Analyse at least one spiked natural sample for each 20 samples in each series of samples:

Spike 50 µl or 100 µl of the metal stock solution (6,5) to an aliquot of a test sample. Establish a control limit for recovery of the spike based for example on precision data in Annex ? or on laboratory precision data.

NOTE If the recovery is outside the control limits, the whole series of analyses should be repeated.

## 11 Expression of results

**11.1 Method of calculation**

By reference to the calibration graph obtained, determine the concentration of the element corresponding to the absorbance of the test portion (10.1) and of the blank test solution (10.2). Calculate the content (*w*) of the element in the sample using the following equation:

$$w_{(M)} = (\rho_1 - \rho_0).f.V/m$$

where

$w_{(M)}$ is the mass fraction of the element M in the sample, in milligrams per kilogram;

$\rho_1$ is the concentration of the analyte, in milligrams per litre, in the diluted test sample solution;

$\rho_0$ is the concentration of the analyte, in milligrams per liter, in the blank test solution with the same dilution factor as for the test sample solution;

f is the dilution factor of the diluted test portion (10.1), if applicable;

V is the volume, in litres, of the test portion taken for the analysis;

m is the mass of the sample, in kilograms, corrected for water content;

**11.2 Expression of results**

The measurement uncertainty reported for the results should reflect the results from the quality control measures and incorporate the deviation between the individual readings for the sample in question. In general, values shall not be expressed to a greater degree of accuracy than two significant figures. The rounding of values will depend on the statistics of the quality control procedures mentioned earlier, and the requirements of the analysis.

Example: *w*(Co) = 8,5 mg/kg

*w*(Co) = 0,3 mg/kg

## 12 Test report

The test report shall contain the following information:

a) a reference to this European Standard including its date of publication;

b) precise identification of the sample;

c) expression of results, according to ;

d) any deviation from this standard, and any facts which may have influenced the result. Where the test is not carried out in accordance with this standard, reference may only be made to EN xxxx:2003 in the report in case all deviations from the procedures prescribed in this standard are indicated in the report stating the reason for deviation.

## 13 Performance characteristics

An interlaboratory test has to be performed to yield precision data.

# Annex A
**(informative)**

**Preparation of stock solutions, 1000 mg/l**

The following procedures for preparation of stock solutions are taken from U.S. Environmental Protection Agency, Method 200.9 – Determination of Trace Elements by Stabilized Temperature Graphite Furnace Atomic Absorption, Rev. 2.2, 1994, and Method 200.7 - Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry, Rev. 4.4, 1994 (V). All salts should be dried for one hour at 105 °C, unless otherwise is specified.

Table A.1 – Amount of metals and metal salts for preparation of stock solutions

| Element | Compound | Formulae | Amount, g |
|---|---|---|---|
| Co | Metal [a] | Co | 1,000 |
| Cu | Metal [b] | Cu | 1,000 |
| Fe | Metal | Fe | 1,000 |
| Mn | Electrolytic metal | Mn | 1,000 |
| Ni | Metal | Ni | 1,000 |
| Zn | Metal | Zn | 1,000 |

[a] Acid cleaned with (1 + 9) $HNO_3$. [b] Acid cleaned with (1 + 1) HCl.

Co and Cu stock solution: Dissolve the metal in 50 ml (1 + 1) $HNO_3$ with heating if necessary to effect dissolution. Cool and dilute to volume with water in a 1000 ml volumetric flask.

Fe stock solution: Weigh, to the nearest ± 0,0002 g, approximately 1,0000 g iron metal (minimum purity 99,5 %) and dissolve it in a covered 250 ml glass beaker with 10 ml nitric acid. Then add 100 ml of water. Boil to expel nitrous fumes, cool, transfer to a 1000 ml volumetric flask and fill to the mark with water.

Mn stock solution: Clean manganese metal by transferring several grams of electrolytic manganese (minimum purity 99,5 %) and dissolve it in a covered 250 glass beaker containing about 150 ml dilute sulfuric acid. Stir and allow the manganese to settle for several minutes. Decant, wash several times with water and finally with acetone. Decant the surplus acetone, dry the metal for 2 minutes at 105 °C and cool in a desiccator.

Weigh, to the nearest ± 0,0002 g, approximately 1,0000 g of such cleaned manganese metal and dissolve it in a covered 250 ml glass beaker with 20 ml hydrochloric acid and 20 ml nitric acid. Then add 100 ml of water. Boil to expel nitrous fumes, cool, transfer to a 1000 ml volumetric flask and fill to the mark with water.

Ni stock solution: Dissolve the metal in 20 ml hot concentrated $HNO_3$. Cool and dilute to volume with water in a 1000 ml volumetric flask.

Zn stock solution: Weigh, to the nearest ± 0,0002 g, approximately 1,0000 g zinc metal (minimum purity 99,5 %) and dilute it in a covered 250 ml glass beaker with 40 ml nitric acid. Then add 100 ml of water. Boil to expel nitrous fumes, cool, transfer to a 1000 ml volumetric flask and fill to the mark with water.

# Annex B
(informative)

# The modular horizontal system

# Annex C
(informative)

## Information on WP xx and the project Horizontal

# Bibliography