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Sludge, treated biowaste and soil — Determination of elements in aqua regia and nitric acid digests — Graphite furnace atomic absorption spectrometry

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Foreword

This document (BT/TF 151 WI CSS99029) 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 is a working document.

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).

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

Material	Validated for (type of sample, e.g. municipal sludge, compost)	Document
Sludge	#	(reference)
Soil	#	
Treated biowaste	#	
Sediment		
Waste		

Too limited number of data for validation

Introduction

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 silver, cadmium, cobalt, chromium, copper, nickel, lead, antimony, tellurium and vanadium in sludge, treated biowaste and soil. After an evaluation study, in which e.g. the ruggedness of the method was studied, a European wide validation of the draft standard has taken place. The results of the desk studies as well as the evaluation and validation studies have been subject to discussions with all parties concerned in CEN. The standard is part of a modular horizontal approach in which the standard belongs to the analytical step.

Until now test methods determining properties of materials were often prepared in Technical Committees (TCs) working on specific products or specific sectors. In those test methods often steps as sampling, extraction, release or other processing, analyses, etc were included. In this approach it was necessary to develop, edit and validate similar procedural steps over and over again for every material or product. Consequently this has resulted in duplication of work. To avoid such duplication of work for parts of a testing procedure references to parts of test methods from other TCs were introduced. However the following problems are often encountered while using references in this way: 1) The referenced parts are often not edited in a way that they could easily be referred to, 2) the referenced parts are often not validated for the other type of material and 3) the updates of such test standards on products might lead to inadequate references.

In the growing amount of product and sector oriented test methods it was recognised that many steps in test procedures are or could be used in test procedures for many products, materials and sectors. It was supposed that, by careful determination of these steps and selection of specific questions within these steps, elements of the test procedure could be described in a way that can be used for all materials and products or for all materials and products with certain specifications.

Based on this hypothesis 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 assessing a property and not the whole "chain of measurement" (from sampling to analyses). A beneficial feature of this approach is that "modules" can be replaced by better ones without jeopardizing the standard "chain".

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 modules that relates to this standard are specified in section XX Normative references.

An overview of modules and the manner, in which modules are selected will be worked out later, at which time proper reference in this standard will be provided.

1 Scope

This European Standard includes principles and procedures for the determination of trace metals in aqua regia and nitric acid digests of sludge, soil and treated biowaste and neighbouring samples, using atomic absorption spectrometry with electrothermal atomization in a graphite furnace. The method is applicable for determination of low concentrations of the following elements: Ag, Cd, Co, Cr, Cu, Ni, Pb, Sb, Tl, V.

The method detection limit for each element depends on the sample matrix as well as of the instrument, the type of atomizer and the use of chemical modifiers. 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. The values of Table 1 should at least be obtainable, using a 20 µl sample volume.

Table 1 — Approximate characteristic masses, instrument detection limits and optimum working ranges for water samples using a 20 µl sample volume.

Element	Characteristic mass (m_0) ^a (pg)	Detection limit ^b (µg/l)	Optimum working range ^c (µg/l)
Ag	1,5	0,2	0,6 - 10
Cd	0,7	0,1	0,3 - 4
Co	10	1	3 - 60
Cr	3	0,5	1,5 - 20
Cu	5 ^d	0,5	1,5 - 30
Ni	13	1	3 - 70
Pb	15	1	3 - 100
Sb	20	1	3 - 100
Tl	10 ^d	1	3 - 60
V	35	2	6 - 200

^a The characteristic mass (m_0) of an element is the mass in picograms, corresponding to a signal of 0,0044 seconds (s), using the integrated absorbance (peak area) for evaluation.

^b The detection limits are calculated as 3 times the standard deviation of repeated measurements of a blank solution.

^c The optimum working range is defined as the concentration range that corresponds to LOQ and up to an integrated absorbance reading 0,5.

^d If Zeeman effect background correction is used, the m_0 value will be higher.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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

CSS99025A Soil, sludge and treated biowaste – Microwave digestion for the extraction of nitric acid soluble fraction of trace elements

CSS99025B Soil, sludge and treated biowaste – Digestion for the extraction of aqua regia soluble fraction of trace elements

CSS99031 *Sludge, treated biowaste, and soils in the landscape – Sampling – Framework for the preparation and application of a sampling plan*

CSS99058 Sludge, treated biowaste, and soils in the landscape – Sampling – Part 1: Guidance on selection and application of criteria for sampling under various conditions

CSS99057 Sludge, treated biowaste, and soils in the landscape – Sampling – Part 2: Guidance on sampling techniques

CSS99032 Sludge, treated biowaste, and soils in the landscape – Sampling - Part 3: Guidance on sub-sampling in the field

CSS99059 Sludge, treated biowaste, and soils in the landscape – Sampling – Part 4: Guidance on procedures for sample packaging, storage, preservation, transport and delivery

CSS99060 Sludge, treated biowaste, and soils in the landscape – Sampling – Part 5: Guidance on the process of defining the sampling plan

CSS99034 Soil, sludge and treated biowaste – Guidance for sample pre-treatment

3 Terms and definitions

3.1

sample

portion of material selected from a larger quantity of material

3.2

laboratory sample

sample or subsample(s) sent to or received by the laboratory

3.3

test sample, analytical sample

sample prepared from the laboratory sample from which test portions are removed for testing or analysis

3.4

test portion, analytical portion

quantity of material of proper size for measurement of the concentration, or other properties of interest, removed from the test sample

NOTE 1 The test portion may be taken from the laboratory sample directly if no preparation of sample is required (e.g. with liquids), but usually it is taken from the prepared test sample.

NOTE 2 A unit or increment of proper homogeneity, size and fineness, needing no further preparation, may be a test portion.

3.5

dry matter

remaining mass fraction of a sample after the specified drying process. It is expressed in percentage or as grams per kilogram

4 Safety remarks

5 Principle

In electrothermal atomization atomic absorption spectrometry, discrete sample aliquots are dispensed into a graphite tube (of which there are several types), which can be heated to over 2 800 °C very rapidly and in a controlled manner. By increasing the temperature stepwise, the processes of drying, thermal decomposition of

the matrix and thermal dissociation into free atoms occur. Atomic absorption spectrometry is based on the ability of free atoms to absorb light. A light source emits light specific for a certain element (or elements). When the light beam passes through the atom cloud in the heated graphite furnace, the light is selectively absorbed by atoms of the chosen element(s). The decrease in light intensity is measured with a detector at a specific wavelength. The concentration of an element in the sample is determined by comparing the absorbance of the sample with the absorbance of calibration solutions. The signal-peak produced is, under optimum conditions, sharp and symmetrical, and of narrow half-width. The height of the peak is, for most elements, proportional to the concentration of the element in solution, although in very many cases it is preferable to work with peak area. The measurements are made at the wavelengths given in Table 2.

Table 2 — Examples of general conditions for electrothermal atomic absorption spectrometry

Element	Wavelength	Atomization conditions	Recommended background correction technique
Silver	328,1	No platform	Zeeman, deuterium
Cadmium	228,8	Platform recommended	Zeeman, deuterium
Chromium	357,9	No platform	Zeeman or Smith-Hieftje
Cobalt	240,7	No platform	Zeeman, deuterium
Copper	324,8	Platform recommended	Zeeman or Smith-Hieftje
Lead	217,0	Platform recommended	Zeeman, deuterium
Nickel	232,0	No platform	Zeeman, deuterium
Antimony	217,6	No platform	Zeeman, deuterium
Thallium	276,8	No platform	Zeeman, deuterium
Vanadium	318,4	No platform	Zeeman, deuterium

If necessary, interferences may be overcome by adding a matrix modifier to the samples before analysis, or by performing the calibration with standard addition technique.

The results are given as the mass of analyte (micrograms or milligrams) per kilogram of dried sample materials.

6 Interferences and sources of errors

The sample solutions prepared from digestion of samples, may contain large amounts of substances that may affect the results. High concentrations of chloride may cause low results, because the volatility of many elements is increased and analyte loss may occur during the pyrolysis step. Matrix effects may be overcome, partially or completely, by optimization of the temperature programme, the use of pyrolytically coated tubes or platforms, the use of chemical modifiers, the standard addition technique and the use of background correction.

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 10.3)

The concentration of the element to be determined in the water used for blank determinations and for preparing reagents and standard solutions shall be negligible compared with the lowest concentration of that element in the sample solutions.

7.1 Hydrochloric acid, 37 % p.a.; $\rho \sim 1,18$ g/ml

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

7.2 Nitric acid, 65 % p.a.; $\rho \sim 1,42$ g/ml

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

7.3 Nitric acid, diluted 1 + 3 (V/V)

Add 250 ml of nitric acid (7.2) to 500 ml of water in a 1 000 ml volumetric flask and fill to the mark with water.

7.4 Aqua regia, diluted $\sim 1 + 3$

Dilute 210 ml of hydrochloric acid (7.1) and 70 ml of nitric acid (7.2) with about 500 ml of water in a 1 000 ml volumetric flask, and dilute to the mark.

7.5 Stock solutions

Both single-element stock solutions and multi-element stock solutions with concentration of 1 000 mg/l, 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 A.1 in Annex A.

7.6 Standard solutions

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

7.6.1 Standard solution corresponding to 10 mg/l of element

Pipette 10,00 ml of the actual element stock solution (7.5) into a 1000 ml volumetric flask. Add 20 ml of nitric acid (7.3) or 20 ml of aqua regia (7.4), fill to the mark with water and mix well.

7.6.2 Standard solution corresponding to 0,1 mg/l of element

Pipette 5,00 ml of the element standard solution (7.6.1) into a 500 ml volumetric flask. Add 10 ml of nitric acid (7.3) or 10 ml of aqua regia (7.4), fill to the mark with water and mix well. Prepare this solution on the day of use.

7.7 Calibration solutions

Before each batch of determinations, prepare, from the standard solutions of each element (7.6.1 or 7.6.2), 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.

7.8 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.

7.9 Palladium nitrate / magnesium nitrate modifier

$\text{Pd}(\text{NO}_3)_2$ solution is commercially available (10 g/l). Dissolve 0,259 g of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 100 ml of water. Mix the palladium nitrate solution with twice as much magnesium nitrate solution. 10 μl of the mixed solution is

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equal to 15 µg Pd and 10 µg Mg(NO₃)₂. The mixture is also commercially available. Prepare the solution freshly every month.

7.10 Magnesium nitrate modifier

Dissolve 0,865 g Mg(NO₃)₂•6H₂O in 100 ml of water. 10 µl of this solution is equal to 50 µg Mg(NO₃)₂.

7.11 Ammonium dihydrogen phosphate modifier

Dissolve 2,0 g of NH₄H₂PO₄ in 100 ml of water. 10 µl of this solution is equal to 200 µg NH₄H₂PO₄.

7.12 Ammonium dihydrogen phosphate / magnesium nitrate modifier

Dissolve 2,0 g of NH₄H₂PO₄ and 0,173 g of Mg(NO₃)₂•6H₂O in 100 ml of water. 10 µl of this solution is equal to 200 µg NH₄H₂PO₄ and 10 µg Mg(NO₃)₂.

7.13 Nickel modifier

Dissolve 0,200 g of nickel powder in 1 ml concentrated nitric acid (7.2) and dilute to 100 ml with water. 10 µl of this solution is equal to 20 µg Ni. Solutions of Ni(NO₃)₂ are also commercially available.

7.14 Purge gas

Argon, Ar (> 99,99 %).

8 Apparatus

8.1 Usual laboratory apparatus

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

NOTE It has been found convenient to to keep separate sets of glass or plastic ware for the determinations given in this standard, in order to reduce the possibility of within-laboratory contamination. Similarly, it can be convenient to carry out the acid cleaning step overnight. Certain kinds of plastic are effected by nitric acid, so care should be taken in the choice of plastic. Because of the high sensitivity of electrothermal atomic absorption spectrometry, stringent precautions should be taken to clean all glass or plastic ware and avoid contamination of sample, standard and calibration solutions from foreign material and dust from the laboratory atmosphere.

8.2 Atomic absorption spectrometer

This shall be equipped with an electrothermal atomizer, the necessary hollow cathod lamps or electrodeless discharge lamps appropriate to the element of interest and operated at a current recommended for the lamp by the instrument manufacturer, an automatic background correction device, and a computerized read-out or a high speed chart recorder. Background correction shall be used with electrothermal atomic absorption spectrometry, the minimum acceptable technical specification (below 350 nm wavelength) of which is that based on deuterium.

NOTE Deuterium background correction is appropriate for cadmium, zinc and lead, if the limited application of deuterium background correction for some instruments to about 0,6 to 0,8 absorbance is not exceeded. Smith-Hieftje or Zeeman background correction is required for all elements if the background signal is high. To increase the analyte-to-background-signal ratio, application of a graphite tube with a pyrolytic platform together with matrix modifiers such as diammonium hydrogen phosphate (NH₄)₂HPO₄, reduced palladium or other, plus peak integration read-out, are recommended for samples with high acid and matrix load. Pyrolytic graphite has the additional advantage that carry-over from sample to sample is likely to be greatly reduced for most elements, in comparison with non-pyrolytic graphite. Users of this standard should not assume that the routine instrumental settings recommended by the manufacturers will necessarily give the best results with complex matrices such as those dealt with in this standard. Careful development of temperature programmes is essential.

8.3 Automated sample introduction system

Depending on the concentration levels to be determined, new autosampler cups may be cleaned with distilled water. The autosampler system shall be capable of delivering fixed volumes up to 70 μl .

8.4 Graphite tubes

Pyrolytically coated graphite tubes with platforms, or other corresponding tubes, are preferably used for high and medium volatile elements, while elements of low volatility should be atomized from the wall. Provided satisfactory results are achieved, manufacturers recommendations regarding the use of graphite tubes and platforms should be followed.

8.5 Chemical modification

Chemical modifiers are used to overcome spectral and/or non-spectral interferences in a sample (matrix effects). By measuring a sample with and without addition of an analyte, and compare the recovery of the analyte with a calibration standard, the existence of a non-spectral interference is often recognized. In order to ascertain that the modification works, the same procedure is repeated with the addition of a chosen chemical modifier.

In general, the aim of chemical modification is to allow a pyrolysis temperature that is high enough to remove the bulk of concomitants before the atomization step. The combination of Pd and $\text{Mg}(\text{NO}_3)_2$ is regarded as a "universal" modifier that is used for a lot of elements. The combination of Pd and a reducing agent, like ascorbic acid, is sometimes used instead of $\text{Pd}/\text{Mg}(\text{NO}_3)_2$. The background absorption tends to be high with $\text{Mg}(\text{NO}_3)_2$. Other modifiers are also used. Some of them (e.g. Ni compounds) may be disadvantageous, because they contain

Table 3 — Examples of chemical modifiers.

Element	Chemical modifiers (7.9 to 7.13)	Amounts, μg
Ag	Pd + $\text{Mg}(\text{NO}_3)_2$ or $\text{NH}_4\text{H}_2\text{PO}_4$	15 + 10 or 200
Cd	Pd + $\text{Mg}(\text{NO}_3)_2$ or $\text{NH}_4\text{H}_2\text{PO}_4$ + $\text{Mg}(\text{NO}_3)_2$	15 + 10 or 200 + 10
Co	$\text{Mg}(\text{NO}_3)_2$	50
Cr	$\text{Mg}(\text{NO}_3)_2$	50
Cu	Pd + $\text{Mg}(\text{NO}_3)_2$	15 + 10
Ni	$\text{Mg}(\text{NO}_3)_2$	50
Pb	Pd + $\text{Mg}(\text{NO}_3)_2$ or $\text{NH}_4\text{H}_2\text{PO}_4$ + $\text{Mg}(\text{NO}_3)_2$	15 + 10 or 200 + 10
Sb	Pd + $\text{Mg}(\text{NO}_3)_2$ or Ni (as nitrate)	15 + 10 or 20
Tl	Pd + $\text{Mg}(\text{NO}_3)_2$	15 + 10
V	No modifier required	

^a These amounts are only recommendations. Significantly lower amounts may be required in some atomizers. See also recommendations from instrument manufacturers.

Elements that are frequently determined with the same equipment and will cause contamination of the furnace. In Table 3 some examples of chemical modifiers are given for the elements in this standard. Other chemical modifiers may be used if they show consistent results.

If chemical modifiers are used, add them both to test samples, reagent blank solutions, blank test solutions, calibration solutions, and blank calibration solutions. To achieve the recommended amounts in Table 3, 10 μl of modifier solution shall be added. Preferably inject the modifier solution with the autosampler directly into the atomizer after the sample is delivered.

9 Sampling and sample pre-treatment

9.1 Sampling

Sampling shall be carried out in accordance with sampling standards CSS99031-32 and 99057-60.

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 h 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.

Transfer a sub-sample, homogenized according to CSS99034 (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.

9.2 Sample pre-treatment

Transfer a sub-sample, homogenized according to CSS99034 (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 Graphite furnace programme

A temperature programme for the graphite furnace usually includes four steps:

- Drying;
- pyrolysis;
- atomization;
- cleaning.

Examples of how to program the graphite furnace are given in Annex B.

Preferably, as a start, use the temperatures and times recommended by the manufacturer. Interrupt the argon flow during the atomization step. Always use background correction.

NOTE Alternative wavelengths (with different sensitivities) may be used. E.g. for lead, the wavelength 217,0 nm may be used, where the sensitivity is about twice of that at 283,3 nm. However, the noise is higher and the risk for interferences is greater. In case of high concentrations a wavelength with lower sensitivity may be used. For evaluation the integrated absorbance (peak area) is recommended.

10.2 Test sample solution

Extract the solid samples with aqua regia or nitric acid in accordance with CSS99025A or B, respectively. To cover the calibration range of the very sensitive electrothermal absorption method and to protect the graphite tubes from high acid concentrations, it is recommended to dilute the sample solutions 1 + 3 with water, as follows. Pipette 25,00 ml of each sample solution into a 100 ml volumetric flask and fill to the mark with water.

10.3 Blank test solution

Prepare the blank test solution at the same time as the extraction with aqua regia or nitric acid was performed. Follow the same procedure, using the same quantities of all reagents for the determination, but omit the test sample. To prepare the diluted blank test solutions 1 + 3, pipette 25,00 ml of the above solution into a 100 ml volumetric flask and fill to the mark with water.

10.4 Determination

Set up the instrument parameters and align the electrothermal atomizer according to the manufacturer's instructions to take full advantage of the background correction system. Set up the sampler similarly. Determine the optimum electrothermal atomizer parameters for the particular type of atomizer and sample volume (up to 70 μ l) as recommended by the instrument manufacturer to cover the optimal working range. Set the instrument baseline to zero. Check the zero stability within the atomization system by running the pre-set heating programme for blank firing of the graphite atomizer. Check the lack of spectral interferences by running real sample solutions with standard additions. Repeat the blank firing to ensure baseline stability.

Using the autosampler, inject into the atomiser the predetermined volume (up to 70 μ l) of each of the diluted test solutions. Add a fixed volume of modifier solution, atomize and note the instrument response. If possible, sort the test solutions into groups of three or four with similar concentrations of the analyte, starting with the lowest. Be careful to note any memory effects caused by particular samples, especially at high analyte levels.

Using an autosampler, inject a fixed volume of solution. Add a fixed volume of modifier solution and atomize the diluted blank calibration solution (7.8), the calibration solutions (7.7), the diluted blank test solution (10.3) and the diluted test sample solutions (10.2) in order of increasing instrument response. If the peak height (or peak area) of the test portion exceeds the value of the highest calibration solution, a smaller volume of the test portion shall be used.

Atomize each solution at least twice and, if the reproducibility is acceptable according to the quality control system in use in the laboratory, average the readings. Check the instrument again for absence of memory effects, especially at high analyte levels, by running the blank firing programme after high readings. Reset the baseline to zero if necessary.

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

NOTE The reproducibility of the instrument readings expressed as an absolute difference, coefficient of variation, or a standard deviation, will vary depending on the concentration of the element in the extracts.

10.5 Calibration

10.5.1 Standard calibration technique

Perform the calibration with a blank calibration solution (7.8) and four equidistant calibration solutions (7.7) for an appropriate concentration range. It should be stressed that the linearity of the calibration curve is often limited.

Correct the absorbance values of the calibration solutions by subtracting the absorbance value of the blank calibration solution. For plotting a calibration curve or for calculation of the calibration function, use the resulting values together with the analyte concentrations of the calibration solutions.

10.5.2 Standard addition technique

To reduce the effect of non-spectral interferences, if chemical modification is not used or does not eliminate matrix effects, the standard addition technique may be applied provided the calibration curve is linear in the absorbance range used. The standard addition technique cannot be used to correct for spectral interferences, such as unspecific background absorption, and shall not be used if interferences are changing the signal with a factor of more than three.

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Transfer equal volumes of the test sample to three vessels (e.g. autosampler cups). Add a small amount of standard solution to two of the vessels, calculated that the resulting concentration in the samples will be respectively about 100 % and 200 % higher than what is expected in the original sample. Add an equal amount of water to the third vessel. Mix the solutions well. Measure the integrated absorbance of each solution, and plot a diagram where the concentration added is given on the abscissa and the measured absorbance on the ordinate. Determine the analyte concentration in the reagent blank solution or blank test solution in the same way.

10.6 Quality Assurance of the overall procedure

10.6.1 Analysis of CRM

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

10.6.2 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 (7.5) to an aliquot of a test sample. Establish a control limit for recovery of the spike based for example on precision data in Annex C(to be incorporated) or on laboratory precision data.

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

10.6.3 Duplicate determination

Analyse two individual test samples of each dried, homogenised sample submitted for analysis. Establish a control limit for the difference between results for the two sub-samples based for example on precision data in Annex C or on laboratory precision data.

11 Expression of results

11.1 Method of calculation

Read the analyte concentrations of the test sample solutions and blank test solution from the calibration graph or calculate them from the calibration function. If necessary, correct the analyte concentrations of the test sample solutions by subtracting the analyte concentration of the test blank solution.

Calculate the analyte content of the test samples, when the determination is performed on a dried material, from the formulae

$$w_{(M)} = \frac{\rho \times f \times V}{m}$$

or when the determination is performed on wet sample

$$w_{(M)} = \frac{f \times V \times 100}{(j \times k)}$$

where

$w_{(M)}$ is the mass fraction of the element M in the sample, in mg/kg;

ρ is the concentration of the element, in micrograms per liter, of the digested and diluted sample, corrected for the blank test solution;

f is the dilution factor of the diluted test portion (10.2);

V is the volume, in litres, of the test portion taken for the analysis, e.g. 0,1 l;

m is the mass of the dried sample, in mg;

i is the mass of the wet sample, in mg;

k is the content of dried material in the wet sample, in %.

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: $w(\text{Cu}) = 8,5 \text{ mg/kg}$

$w(\text{Cu}) = 0,3 \text{ mg/kg}$

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 11.2;
- 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 xxx:2007 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

The interlaboratory test has resulted in too limited number of data to derive performance data. Results of the comparison between GFAAS and ICP will be given in Annex C.

Annex A (informative)

Preparation of stock solutions, 1 000 mg/l

A.1 General information

The following procedures for preparation of stock solutions are taken from [1] and [2].

All salts should be dried for one hour at 105 °C, unless otherwise is specified. It is also possible to use commercial standard stock solutions as an alternative.

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

Element	Compound	Formulae	Amount (g)
Ag	Metal	Ag	1,000
Cd	Metal ^a	Cd	1,000
Co	Metal ^a	Co	1,000
Cr	Chromium trioxide	CrO ₃	1,923
Cu	Metal ^b	Cu	1,000
Ni	Metal	Ni	1,000
Pb	Lead nitrate	Pb(NO ₃) ₂	1,599
Sb	Metal powder	Sb	1,000
Tl	Thallium nitrate	TlNO ₃	1,303
V	Metal ^a	V	1,000

^a Acid cleaned with (1 + 9) HNO₃

^b Acid cleaned with (1 + 1) HCl

A.2 Ag stock solution

Dissolve the metal in 80 ml (1 + 1) HNO₃ with heating to effect dissolution. Cool and dilute to volume with water in a 1 000 ml volumetric flask. Store the solution in amberbottle or wrap bottle completely with aluminium foil to protect from light.

A.3 Cd, Co, Cu, and V stock solution

Dissolve the metal in 50 ml (1 + 1) HNO₃ with heating if necessary to effect dissolution. Cool and dilute to volume with water in a 1 000 ml volumetric flask.

A.4 Cr stock solution

Dissolve the metal compound in 120 ml (1 + 5) HNO₃. Dilute to volume with water in a 1 000 ml volumetric flask.

A.5 Ni stock solution

Dissolve the metal in 20 ml hot concentrated HNO₃. Cool and dilute to volume with water in a 1 000 ml volumetric flask.

A.6 Pb stock solution

Dissolve the metal compound in minimum amount of (1 + 1) HNO₃. Add 20 ml (1 + 1) HNO₃ and dilute to volume with water in a 1 000 ml volumetric flask.

A.7 Sb stock solution

Dissolve the metal powder in 20 ml (1 + 1) HNO₃ and 10 ml concentrated HCl. Add 100 ml water and 1,50 g tartaric acid. Warm solution slightly to effect complete dissolution. Cool and dilute to volume with water in a 1 000 ml volumetric flask.

A.8 Tl stock solution

Dissolve the metal compound in water. Add 10 ml concentrated HNO₃. Dilute to volume with water in a 1 000 ml volumetric flask.

Annex B (informative)

Examples of instrumental parameter settings

There may be great differences between instruments from different manufacturers, and between old and new models. It is recommended to use the temperatures proposed by the manufacturers as a start.

Element	Wave-length (nm)	Slit width (nm)	Pyrolysis temperature (°C)		Atomization temperature (°C)	
			Without modifier	With modifier ^a	Without modifier	With modifier ^a
Ag	328,1	0,7	650	1000 / 650	1600	2200 / 2200
Cd	228,8	0,7	300	900 / 900	1250	1100 / 1800
Cr	357,9	0,7	1050	1650	2300	2600
Co	240,7	0,2	1100	1400	2200	2400
Cu	324,8	0,7	1100	1100	2300	2600
Pb	217,0	0,7	600	1200 / 600	1500	2000 / 1900
Ni	232,0	0,2	1100	1400	2400	2400
Sb	217,6	0,7	900	1200 / 1100	1900	1900 / 2400
Tl	276,8	0,7	600	1000	1350	1650
V	318,4	0,7	1400	-	2650	-

^a The alternate temperature values are for the cases where two alternative chemical modifiers are recommended

Annex C (informative)

Performanc data

There were insufficient data to derive performance characteristics. In table 1 the comparison of provided test data with performance of the ICP/ AES and ICP/MS results. These results indicate that the limited data provided match well with the ICP data.

	Cd ICP			Cd GFAAS	Cd GFAAS min lab 1			
Compost2	Mean =	0.64453	mg/kg	Avg n	0.651503 5		0.663373	
	S2r =	0.00876						
	Sr =	0.09357	-->	14.52%				
	S2L =	0.00472						
	S2R =	0.01347						
	SR =	0.11606	-->	18.01%	Stdev	0.115088	17.66	0.072277
Sludge 1	Mean =	2.12062	mg/kg	Avg n	2.149657 5		2.272962	
	S2r =	0.03146						
	Sr =	0.17737	-->	8.36%				
	S2L =	0.04052						
	S2R =	0.07198						
	SR =	0.26830	-->	12.65%	Stdev	0.54002	25.12	0.320173
Sludge 2	Mean =	2.63033	mg/kg	Avg n	2.404733 5		2.665785	
	S2r =	0.04076						
	Sr =	0.20189	-->	7.68%				
	S2L =	0.06857						
	S2R =	0.10933						
	SR =	0.33065	-->	12.57%	Stdev	0.771985	32.10	0.212766
Soil 1	Mean =	0.23303	mg/kg	Avg n	0.212415 5		0.225816	
	S2r =	0.00338						
	Sr =	0.05814	-->	24.95%				
	S2L =	0.00230						
	S2R =	0.00568						
	SR =	0.07536	-->	32.34%	Stdev	0.064005	30.13	0.047188
Soil 2	Mean =	0.41096	mg/kg	Avg n	0.382122 5		0.41052	
	S2r =	0.00119						
	Sr =	0.03449	-->	8.39%				
	S2L =	0.00297						
	S2R =	0.00416						
	SR =	0.06447	-->	15.69%	Stdev	0.093861	24.56	0.053513

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Ag ICP			Ag GFAAS		
Mean =	0.25073	mg/kg	Avg	0.19	
			n	1	
S2r =	0.00760				
Sr =	0.08717	--> 34.77%			
S2L =	0.00363				
S2R =	0.01123				
SR =	0.10598	--> 42.27%	Stdev	0.078419	40.72 %
Mean =	7.48938	mg/kg	Avg	7.06	
S2r =	0.48235				
Sr =	0.69451	--> 9.27%			
S2L =	0.22044				
S2R =	0.70279				
SR =	0.83833	--> 11.19%	Stdev	0.265	3.76 %
Mean =	5.22952	mg/kg	Avg	5.14	
S2r =	0.63738				
Sr =	0.79836	--> 15.27%			
S2L =	1.90231				
S2R =	2.53969				
SR =	1.59364	--> 30.47%	Stdev	0.144802	2.82 %
Mean =	0.44732	mg/kg	Avg	0.40	
S2r =	0.00099				
Sr =	0.03145	--> 7.03%			
S2L =	0.00091				
S2R =	0.00190				
SR =	0.04358	--> 9.74%	Stdev	0.040342	10.20 %
Mean =	0.34649	mg/kg	Avg	DTL	
S2r =	0.00333				
Sr =	0.05766	--> 16.64%			
S2L =	0.09540				
S2R =	0.09872				
SR =	0.31420	--> 90.68%	Stdev		

Pb ICP			Pb GFAAS		
Mean =	44.04575	mg/kg	Avg	55.19	
			n	4	
S2r =	31.88539				
Sr =	5.64671	--> 12.82%			
S2L =	24.75824				
S2R =	56.64363		Stdev	14.6	26.49 %
SR =	7.52620	--> 17.09%			
Mean =	147.13154	mg/kg	Avg	166.3765	
S2r =	40.80966				
Sr =	6.38824	--> 4.34%			
S2L =	141.78476				
S2R =	182.59442		Stdev	10.64392	6.40 %
SR =	13.51275	--> 9.18%			
Mean =	84.35929	mg/kg	Avg	93.56756	
S2r =	13.36038				
Sr =	3.65518	--> 4.33%			
S2L =	47.41796				
S2R =	60.77833		Stdev	8.4144	8.99 %
SR =	7.79605	--> 9.24%			
Mean =	25.12887	mg/kg	Avg	25.07	
S2r =	3.86095				
Sr =	1.96493	--> 7.82%			
S2L =	4.79373				
S2R =	8.65468		Stdev	1.1911	4.75 %
SR =	2.94188	--> 11.71%			
Mean =	29.36478	mg/kg	Avg	28.58429	
S2r =	4.71331				
Sr =	2.17102	--> 7.39%			
S2L =	4.01956				
S2R =	8.73287		Stdev	2.2663	7.93 %
SR =	2.95514	--> 10.06%			

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Co ICP			Co GFAAS		
Mean =	4.41258	mg/kg	Avg	3.661667	
			n	1	
S2r =	0.28470				
Sr =	0.53357	--> 12.09%			
S2L =	0.29939				
S2R =	0.58409				
SR =	0.76426	--> 17.32%	Stdev	0.308183	8.42 %
Mean =	14.51671	mg/kg	Avg	NA	
S2r =	0.43400				
Sr =	0.65878	--> 4.54%			
S2L =	1.52785				
S2R =	1.96185				
SR =	1.40066	--> 9.65%	Stdev		
Mean =	10.30984	mg/kg	Avg	8.665	
S2r =	0.57553				
Sr =	0.75864	--> 7.36%			
S2L =	1.28061				
S2R =	1.85614				
SR =	1.36240	--> 13.21%	Stdev	0.503895	5.82 %
Mean =	10.87827	mg/kg	Avg	8.576667	
S2r =	0.17180				
Sr =	0.41448	--> 3.81%			
S2L =	0.62665				
S2R =	0.79845				
SR =	0.89356	--> 8.21%	Stdev	0.40322	4.70 %
Mean =	2.17791	mg/kg	Avg	2.061667	
S2r =	0.03165				
Sr =	0.17789	--> 8.17%			
S2L =	0.06942				
S2R =	0.10106				
SR =	0.31790	--> 14.60%	Stdev	0.564603	27.39 %

Cr ICP			Cr GFAAS		
Mean =	24.57666	mg/kg	Avg	41.57	
			n	1	
S2r =	10.51429				
Sr =	3.24257	--> 13.19%			
S2L =	12.52553				
S2R =	23.03983				
SR =	4.79998	--> 19.53%	Stdev	7.1	17.12 %
Mean =	67.07854	mg/kg	Avg	94.56	
S2r =	34.12863				
Sr =	5.84197	--> 8.71%			
S2L =	71.84066				
S2R =	105.96929				
SR =	10.29414	--> 15.35%	Stdev	3.577094	3.78 %
Mean =	52.88061	mg/kg	Avg	79.67	
S2r =	16.88381				
Sr =	4.10899	--> 7.77%			
S2L =	74.04082				
S2R =	90.92463				
SR =	9.53544	--> 18.03%	Stdev	4.7121	5.91 %
Mean =	49.15201	mg/kg	Avg	87.35	
S2r =	8.59801				
Sr =	2.93224	--> 5.97%			
S2L =	72.25273				
S2R =	80.85074				
SR =	8.99170	--> 18.29%	Stdev	3.9004	4.47 %
Mean =	18.48901	mg/kg	Avg	33.82	
S2r =	3.95507				
Sr =	1.98874	--> 10.76%			
S2L =	14.43296				
S2R =	18.38803				
SR =	4.28813	--> 23.19%	Stdev	3.2322	9.56 %

Bibliography

- [1] U.S. Environmental Protection Agency, Method 200.9 – Determination of Trace Elements by Stabilized Temperature Graphite Furnace Atomic Absorption, Rev. 2.2, 1994,
- [2] U.S. Environmental Protection Agency, 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).
- [3] ISO 5725-1:1994, Accuracy (trueness and precision) of measurement methods and results — Part 1: general principles and definitions.