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Sludge, treated biowaste and soil — Microwave digestion for the extraction of nitric acid soluble fraction of trace elements

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Foreword

This document Bt/TF151 WI CSS 99025A 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).

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	2 sludges	HORIZONTAL
Soil	2 soils	
Soil improvers		
Treated biowaste	Compost	
Waste		

Introduction

This document has been prepared as part of the project 'Horizontal'. It is the result of a desk study "Digestion of Solid Matrices – Desk study – Horizontal" and aims at evaluating the latest developments in the assessment of digestion methods for the determination of trace elements and other elements in sludge, soil, treated biowaste and neighbouring fields. 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.

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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.

This standard is a module for the analysis of inorganic parameters in solid matrices. The module concerns the digestion in microwave oven with nitric acid for the subsequent analysis of elements.

The texts of chapters 1 to 13 are normative; annexes are normative or informative, as stated in the top lines of the annexes.

SAFETY PRECAUTIONS — All this work has to be performed by skilled persons. The reagents used within this European Standard are strongly corrosive and partly very toxic. Safety precautions are absolutely necessary due not only to the strong corrosive reagents, but also to high temperature and high pressure.

The use of laboratory-grade microwave equipment with isolated and corrosion resistant safety devices is required. Domestic (kitchen) type microwave ovens should not be used, as corrosion by acid vapours may compromise the function of the safety devices and prevent the microwave magnetron from shutting off when the door is open, which could result in operator exposure to microwave energy.

All procedures have to be performed in a fume hood or in closed force-ventilated equipment. By the use of strong oxidising reagents, the formation of explosive organic intermediates is possible, especially when dealing with samples with a high organic content. Do not open pressurized vessels before they have cooled down. Avoid contact with the chemicals and the gaseous reaction products. Samples and solutions have to be disposed of according to regulations.

Toxic nitrogen oxide(s) and chlorine fumes are usually produced during digestion. Therefore, all steps involving open or the opening of microwave vessels must be performed in a proper fume ventilation system. The analyst should use protective gloves and face protection.

1 Scope

This part of CSS99025 specifies a method for microwave digestion of biowaste, sludge and soil by the use of nitric acid.

Digestion with nitric acid will not necessarily accomplish total decomposition of the sample; the extracted analyte concentrations may not necessarily reflect the total content in the sample. However, for most environmental applications the result is fit for the purpose. This method is applicable to microwave-assisted acid digestion of biowaste, sludge and soils for the following elements: Aluminium (Al), arsenic (As), barium (Ba), boron (B), cadmium (Cd), calcium (Ca), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), magnesium (Mg), manganese (Mn), mercury (Hg), molybdenum (Mo), nickel (Ni), potassium (K), selenium (Se), sodium (Na), strontium (Sr), thallium (Tl), vanadium (V) and zinc (Zn).

The method is intended to provide a rapid multi-element acid digestion prior to analysis. Solutions produced by the method are suitable for analysis by e.g. atomic absorption spectrometry (FAAS, HGAAS, CVAAS, and GFAAS), inductively coupled plasma emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS).

NOTE The degree to which analytes are brought into solution suitable for subsequent analysis may depend on the principle of the subsequent analysis. Some analytical methods require the element in solution independent of its chemical state, others require a specific valence or a specific ionic species, for instance hydride atomic spectrometry, photometry and electrochemical methods.

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 3696:1995, *Water for analytical laboratory use — Specification and test methods*.

CSS99022, *Solid materials. Determination of dry matter and water content on a mass basis — gravimetric method*.

CSS99031 *Sludge, treated biowaste, and soils in the landscape – Sampling – Framework for the preparation*

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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

For the purpose of this standard, the following terms and definitions apply.

3.1 digestion

mineralization of the organic matter of a sample and dissolution of its mineral part, more or less complete, when reacted with a reagent

3.2 sample

portion of material selected from a larger quantity of material

3.3 laboratory sample

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

3.4 test sample, analytical sample

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

3.5 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.

3.6 dry matter

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

3.7

digestion vessel

special flask that fits into the microwave oven and into which the test portion and acid are filled and the digestion is performed.

3.8

microwave unit

microwave digestion system (oven and associated equipment)

4 Principle

The test portion of 0,5 g is digested in 10 ml concentrated nitric acid for 10 min at $175\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$ by means of microwave heating with a suitable laboratory microwave unit. The samples and acid(s) are placed in a fluorocarbon polymer or quartz microwave vessel or vessel liner. The vessel is sealed and heated in the microwave unit. After cooling, the vessel contents are filtered, centrifuged or allowed to settle and then diluted to volume and analysed by the appropriate determinative method.

5 Interferences and sources of error

Due to the volatility of some compounds, it is of great importance to take care that the sample is not heated before the digestion and that any volatile reaction products formed during the digestion are not allowed to escape.

Grinding or milling of samples includes a risk of contamination of the sample from the environment (air, dust, wear of milling equipment). Due to elevated temperature, loss of volatile compounds is possible. For the determination of elements forming volatile compounds (e.g. Hg, As, Pb), take special care at the sample pre-treatment.

A few refractory sample matrix compounds, such as quartz, silicates, titanium dioxide, alumina and other oxides may not be dissolved. These bound elements are considered non-mobile in the environment and are excluded from most aqueous pollution transport mechanisms.

High acid and solute concentrations in the digest cause interferences need to be properly addressed during determination.

Be careful to ensure that all of the test portion is brought into contact with the acid mixture in the reaction vessel.

There is a potential for vigorous reaction, especially with samples containing volatile or easily oxidized species. When digesting a matrix of this type, use no more than 0,1 g sample to begin with. If a vigorous reaction occurs upon addition of reagent(s), allow the sample to predigest in the uncapped digestion vessel until the reaction ceases. Heat may be added in this step for safety considerations (for example, the rapid release of carbon dioxide from carbonates, easily oxidized organic matter etc.). Once the initial reaction has ceased, the sample may continue through the digestion procedure.

In the case of filtration of the digested solution, it is necessary to take care that the filtration procedure does not introduce contamination.

6 Reagents

Use only reagents of recognized analytical grade, unless otherwise specified.

6.1 Water, complying with grade 2 as defined in EN ISO 3696 or better. The water for preparation of reagent shall meet the requirement of the subsequent analysis. Verify their purity by performing a blank test.

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6.2 Nitric acid, $c(\text{HNO}_3) = 15 \text{ mol/l}$, $\rho = 1,4 \text{ kg/l}$. Sub-boiling distilled. or other grade may be used provided it is ascertained that the reagent is of sufficient purity to permit its use without decreasing the accuracy of the subsequent analysis.

7 Apparatus

Usual laboratory apparatus, and in particular the following:

7.1 Microwave unit, that is corrosion resistant and well ventilated.

All electronics shall be protected against corrosion for safe operation.

NOTE 1 A laboratory-grade microwave oven with temperature feedback control mechanisms is preferred.

The temperature performance requirements necessitate the microwave decomposition system to sense the temperature with an accuracy of $\pm 2,5 \text{ }^\circ\text{C}$ and automatically adjust the microwave field output power within 2 s of sensing. Temperature sensors shall be accurate to $\pm 2 \text{ }^\circ\text{C}$ (including the final reaction temperature of $175 \text{ }^\circ\text{C} \pm 5 \text{ }^\circ\text{C}$). Temperature feedback control provides the primary performance mechanism for the method. Due to the variability in sample matrix types and microwave digestion equipment (i.e. different vessel types and microwave designs), control of the temperature during digestion is important for reproducible microwave heating and comparable data.

Alternatively, for specific vessel types, specific sample types and specific sets of reagent(s) a calibration control mechanism could be developed that would allow the use of microwave systems with power programmable to within $\pm 12 \text{ W}$ of the required power. Typical systems provide a nominal 600 W to 1200 W. Calibration control provides a backward comparability with older laboratory microwave systems, which may not be equipped for temperature monitoring or feedback control. See 10.1 for calibration.

NOTE 2 The accuracy of the temperature measurement system should be periodically controlled at an elevated temperature according to the manufactures instructions. If the temperature deviates by more than $1 \text{ }^\circ\text{C}$ to $2 \text{ }^\circ\text{C}$ from the temperature measured by an external, calibrated temperature measurement system, the microwave temperature measurement system should be calibrated.

7.2 Rotating turntable, with a minimum speed of 3 rpm.

7.3 Sample containers, plastic and glass containers are both suitable. All volumetric ware shall be adequately acid cleaned and stored in order to avoid any contamination.

7.4 Digestion vessels of microwave transparent and reagent and temperature resistant materials, such as fluorocarbon (e.g. PTA or TFM) or quartz. The vessels may be contained within layers of different microwave transparent materials for strength, durability and safety. The internal volume shall be at least 45 ml, and the vessel shall be capable of withstanding pressures of at least 30 atm and capable of controlled pressure relief. These specifications are to provide an appropriate, safe, and durable reaction vessel.

The inner wall of the vessel shall be inert and shall not release substances to the digest in excess of the purity requirements of the subsequent analysis. The vessel shall be suitable for the safe application in the temperature and pressure range applied.

Temperature control of closed vessel microwave instruments provides the main feedback performance mechanism for the method. Method control requires a temperature sensor in one or more vessels during the entire decomposition.

All digestion vessels shall be adequately acid cleaned and stored in order to avoid any contamination.

NOTE Digestion vessels may be cleaned in e.g. 10 % nitric acid.

7.5 Filter paper, cellulose-based ashless type, hardened and resistant to nitric acid.

7.6 Filter funnel, glass, polypropylene or other appropriate material.

7.7 Volumetric flask, usually of a nominal capacity of 50 ml or 100 ml.

7.8 Graduated pipettes or dispensers

7.9 Analytical balance, with an accuracy of 0,1 mg or better.

8 Sampling and sample pre-treatment

8.1 Sampling

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

Samples shall be stored in suitable plastic or glass containers (7.3) with an appropriate closure material.

Samples shall be kept cold (< 4°C).

8.2 Pre-treatment of test portion

The test portion shall be transferred into the digestion vessel (7.4) after a pre-treatment of the laboratory sample (CSS99034) that result in homogeneous and representative test portions out of the laboratory sample. This procedure shall not change the concentration of the elements of interest.

If the laboratory sample cannot be well mixed and homogenized as received, then air or oven dry at 60 °C or less, crush, sieve, grind and mix as necessary or homogenize the sample until the subsampling variance is less than the data quality objectives of the analysis. Be aware that in certain circumstances a loss of volatile metals (e.g. Hg, organometallics) could occur during sample preparation.

NOTE For soil samples it is common to use the fraction < 2 mm.

The mass of laboratory samples shall be sufficient for the multiple digestion procedures and the determination of the dry matter.

8.3 Mass of test portion

Select the mass of the test portion for a single digestion in a way, that:

- it is representative for the laboratory sample;
- it complies with the specifications of manufactures of the digestion unit.

9 Procedure

9.1 Calibration of microwave equipment

If the microwave unit (7.1) uses temperature feedback to control the performance specifications of the method, then performing the calibration procedure is not necessary.

NOTE 1 Calibration is the normalization and reproduction of microwave field strength to permit reagent and energy coupling in a predictable and reproducible manner. It balances reagent heating and heat loss from the vessels and is equipment dependent due to the heat retention and loss characteristics of the specific vessel. The available power is evaluated to permit the microwave field output in watts to be transferred from one microwave system to another. Use of calibration to control this reaction requires balancing output power, coupled energy and heat loss to reproduce the temperature heating profile as described by the procedure.

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Determine the conditions for each acid mixture and each batch containing the same specified number of vessels individually. Only identical acid mixtures and vessel models and specified numbers of vessels shall be used in a given batch.

Equilibrate a large volume of water (7.1) to room temperature. The initial temperature of the water should be $22\text{ }^{\circ}\text{C} \pm 3\text{ }^{\circ}\text{C}$ measured to $\pm 0,05^{\circ}\text{C}$. Weigh $1\ 000\text{ g} \pm 0,1\text{ g}$ of the water into a fluorocarbon beaker or a beaker made of some other material that does not significantly absorb microwave energy.

NOTE 2 Glass adsorbs microwave energy and is not recommended.

The covered beaker is circulated continuously (in the normal sample path) through the microwave field for 120 s at the desired partial power setting with the system's exhaust fan on maximum (as it will be during normal operation). The beaker is removed and the water vigorously stirred. Use a magnetic stirring bar inserted immediately after microwave irradiation (irradiation with the stirring bar inserted could cause electrical arcing). Record the maximum temperature within the first 30 s to $\pm 0,05\text{ }^{\circ}\text{C}$. Make three measurements at each power setting.

Determine the absorbed power (P) using the following equation:

$$P = \frac{C_p \times m \times (T_2 - T_1)}{t} \quad (1)$$

where

P is the apparent power absorbed by the sample, in W;

C_p is the specific heat capacity of water, in $\text{J g}^{-1}\text{ }^{\circ}\text{C}^{-1}$;

m is the mass of the water, in g;

T_1 is the initial temperature of the water, in $^{\circ}\text{C}$;

T_2 is the final temperature of the water, in $^{\circ}\text{C}$;

t is the time, in s.

Using the experimental conditions of 120 s and 1 000 g of water (7.1) and the heat capacity of water at $25\text{ }^{\circ}\text{C}$ ($4,1827\text{ J g}^{-1}\text{ }^{\circ}\text{C}^{-1}$) the equation simplifies to:

$$P = (T_2 - T_1) \times 34,86$$

The multiple point calibration involves the measurement of absorbed power over a large range of power settings. Typically, for a 600 W unit, the following power settings are measured: 100 %, 99 %, 98 %, 97 %, 95 %, 90 %, 80 %, 70 %, 60 %, 50 %, and 40 %. This data is clustered about the customary working power ranges. Non-linearity has been encountered at the upper end of the calibration. If the system's electronics are known to have non-linear deviations in any region of proportional power control, it will be necessary to make a set of measurements that bracket the power to be used. The final calibration point shall be at the partial power setting that will be used in the test. Check this setting periodically to evaluate the integrity of the calibration. If a significant change is detected ($\pm 10\text{ W}$), then the entire calibration should be re-evaluated.

The three-point calibration involves the measurement of absorbed power at three different power settings. Measure the power at 100 % and 50 %. From this 2-point line, determine the partial power setting that corresponds to the power, in W, specified in the procedure to reproduce the heating profiles specified in 9.2. Measure the absorbed power at that partial power setting. If the measured absorbed power does not correspond to the specified power within $\pm 10\text{ W}$, use the multiple point calibration. Use this point to periodically verify the integrity of the calibration.

9.2 Digestion

Weigh an amount equal to 0,25 g – 0,5 g dried sample accurately at 0,001 g and transfer it into the digestion vessel (7.4). Add 10 ml \pm 0,1 ml of concentrated nitric acid (6.2) to the digestion vessel with test portion in a fume hood (or fume exhausted enclosure). Swirl and allow the mixture to stand until any visible reaction has stopped.

Cap the digestion vessel according to the manufacturer's directions. Weigh the digestion vessel before digestion. Place the vessel in the microwave system (7.1) according to the manufacturer's recommended specifications and, when applicable, connect appropriate temperature and pressure sensors to vessels according to the manufacturer's specifications.

This method is a performance based method, designed to achieve or approach consistent leaching of the sample by achieving specific reaction conditions. The temperature of each sample shall rise to 175 °C \pm 5 °C in approximately 5,5 min \pm 0,25 min and remain at 175 °C \pm 5°C for 4,5 min, or for the remainder of 10 min digestion period.

At the end of the microwave programme, allow the vessels to cool for a minimum of 5 min before removing them from the microwave system. Cooling of the vessels may be accelerated by internal or external cooling devices. When the vessels have cooled to near room temperature, determine if the microwave vessels have maintained their seal throughout the digestion. Due to the wide variety of vessel designs, a single procedure is not appropriate. Weigh the vessel after digestion to evaluate seal integrity. If the weight loss of the sample exceeds 1 % of the weight of the sample and reagents, then the sample is considered compromised.

Carefully uncap and vent each vessel in a chemical in a well-ventilated fume hood using the procedure recommended by the manufacturer. Quantitatively transfer or decant the sample into volumetric acid-cleaned ware and dilute the digest to a known volume (typically 50 ml or 100 ml).

The digest is now ready for analysis for elements of interest using appropriate elemental analysis techniques.

NOTE 1 If the digested sample contains particles which may clog nebulizers or interfere with an injection of the sample into the instrument, the sample may be centrifuged, allowed to settle, or filtered. Centrifugation at 2 000 rpm – 3 000 rpm for 10 min is usually sufficient to clear the supernatant. If undissolved material, such as SiO₂, TiO₂, or other refractory oxides, remains, it is recommended to allow the sample to stand until the supernatant is clear. Allowing a sample to stand overnight will usually accomplish this. If it does not, it is recommended to centrifuge or filter the sample. The filtering apparatus should be thoroughly cleaned and pre-rinsed with dilute (approximately 10 % V/V) nitric acid. It is recommended to filter the sample through qualitative filter paper into a second acid-cleaned container. The final solution typically requires nitric acid to maintain appropriate sample solution acidity and stability of the elements. Commonly, a 2 % (V/V) nitric acid concentration is desirable.

10 Quality control

10.1 Control charts

Record data from quality control for each control sample in control charts.

10.2 Duplicate samples

Process duplicate samples on a routine basis. A duplicate sample is a sample brought through the whole sample preparation and analysis process a second time. Process a duplicate sample with each analytical batch or every 20 samples, whichever is the greater number. Prepare a duplicate for each matrix type (i.e. soil, sludge, etc.).

Include spiked samples or standard reference materials with each group of samples processed, or every 20 samples, whichever is the greater number. Include a spiked sample for each new sample matrix.

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10.3 Blank test

Blank samples, reflecting blank values for the sampling bottles, reagents, digestion vessels and any contamination during the whole procedure, shall be prepared and digested in parallel with the batch of samples, by the same procedure, by the use of the same quantities of all the reagents as in the determination but omitting the test portion.

11 Precision data

The performance characteristics of the method (Annex A) data have been evaluated. Table 2 gives the resulting typical values for repeatability and reproducibility limits as their observed ranges. The typical value is derived from the data in Table A.2 in Annex A by taking the median value and rounding the numbers.

Table 2 — Typical values and observed ranges of the repeatability and reproducibility limits

The reproducibility limit provides a determination of the differences (positive and negative) that can be found (with a 95 % statistical confidence) between a single test result obtained by a laboratory using its own facilities and another test result obtained by another laboratory using its own facilities, both test results being obtained under the following conditions : The tests are performed in accordance with all the requirements of the present standard and the two laboratory samples are obtained from the same primary field sample and prepared under identical procedures. Conversely, the repeatability limit refers to measurements obtained from the same laboratory, all other conditions being identical. The reproducibility limit and the repeatability limit do not cover sampling but cover all activities carried out on the laboratory sample including its preparation from the primary field sample.		
Results of the validation of microwave digestion for the extraction of nitric acid soluble fraction of trace elements in soil, sludge and treated biowaste	Typical value %	Observed range %
Repeatability limit, r	15	11 - 22
Reproducibility limit, R	35	28 - 49

NOTE 1. The above results refer to the difference that may be found between two test results performed on two laboratory samples obtained under the same conditions. In the case when reference is made to the dispersion of the values that could reasonably be attributed to the parameter being measured, the above typical reproducibility values and observed reproducibility ranges should be divided by $\sqrt{2}$ to obtain the corresponding typical dispersion limit and its observed range. In the example of Pb in Sludge 2 the result and its dispersion limit is 80.2 ± 20 mg/kg ($2 * sR = 25 \%$ of 80). This means that with a 95 % statistical confidence, the values reasonably attributable to the measured parameter are larger than 59 mg/kg and lower than 100.

NOTE 2. The repeatability limit (r) and the reproducibility limit (R) as given in Table A.2 (Annex A) and in this table are indicative values of the attainable precision if the microwave digestion for the extraction of nitric acid soluble fraction of trace elements is performed in accordance with this standard [CSS99025A].

NOTE 3 A limited number of materials and parameters were tested. Consequently, for other materials and parameters, performance characteristics may fall outside the limits as derived from the validation of the the microwave digestion for the extraction of nitric acid soluble fraction of trace elements in soil, sludge and treated biowaste.

NOTE 4 In particular for relatively heterogeneous materials, the repeatability and the reproducibility limits may be larger than the values given in Table A.2 (Annex A) and this table.

12 Test report

The work carried out by the testing laboratory shall be covered by a report that accurately, clearly and unambiguously presents the test results and all other relevant information. The test report shall include the following information:

- a) a reference to this European Standard including its date of publication;
- b) all information necessary for identification of the sample tested;
- c) information about the pre-treatment and digestion of the sample;
- d) any detail not specified in this European Standard, or which are optional;
- e) any other information pertinent to the quality of the analytical data.

NOTE 1 The test report may include information about the sampling and sample pre-treatment and the results of the analytical determinations carried out according to other methods on the same samples, if any.

The final report shall include all results and relevant information on the sampling, the digestion method and the analytical methods used.

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 reasons for the deviations.

Repeatability and reproducibility data

A.1 Performance characteristics

A.1.1 Objective of the interlaboratory comparison

In a European wide interlaboratory comparison study according to ISO 5725-2, the performance characteristics of the standard "Microwave digestion for the extraction of nitric acid soluble fraction of trace elements in soil, sludge and treated biowaste" were established.

A.1.2 Materials used in the interlaboratory comparison study

The interlaboratory comparison of microwave digestion for the extraction of nitric acid soluble fraction of trace elements in soil, sludge and treated biowaste was carried out with 7 European laboratories on 5 materials. The materials selected for the interlaboratory comparison were chosen to represent soil, sludge and biowaste as broad as possible, because the standard will find general application across different types of soil and soil related materials. (detailed information can be found in the final report on the Interlaboratory comparison study mentioned in the Bibliography).

In the interlaboratory comparison study the following starting points were used:

- The laboratory samples were all taken from one large batch of the different materials according to the normal practice. The normal size reduction and the normal repeated mixing were carried out as needed to obtain representative laboratory samples from the large batch sample (ref JRC).

Note : the samples provided for the validation should not be confused with reference samples provided for certification purposes, as the performance results obtained have to be directly applicable to daily practice (less rigorous sample preparation than for a reference material).

- The experimental plan was designed by project HORIZONTAL on the basis of each laboratory being given two laboratory samples of each material to be tested. This is in accordance with ISO 5725-2.

The materials examined cover all the grain size classes to which the the microwave digestion for the extraction of nitric acid soluble fraction of trace elements in soil, sludge and treated biowaste applies: very fine grained materials (like sludge: 0 µm to about 125 µm) and fine-grained materials (soil and compost: 0 mm to 4 mm).

Table A.1 provides a list of the types of materials chosen for testing and the selected components.

Table A.AD.1 — Material types tested and components analysed in the interlaboratory comparison of the microwave digestion for the extraction of nitric acid soluble fraction of trace elements in soil, sludge and treated biowaste.

Grain size class	Sample code	Material type tested	Parameters/congeners
Sludge (<0.5 mm) Fine grained (< 2 mm)	Sludge 1	Mix 1 of municipal WWTP sludges from North Rhine Westphalia, Germany	Cd, Cr, Cu, Fe, Ni, Pb, Zn
	Sludge 2	Mix 2 of municipal WWTP sludges from North Rhine Westphalia, Germany	Cd, Cr, Cu, Fe, Ni, Pb, Zn
	Compost 1	Fresh compost from Vienna, Austria	Cd, Cr, Cu, Fe, Ni, Pb, Zn
	Compost 2	Compost from Germany	Cd, Cr, Cu, Fe, Ni, Pb, Zn
	Soil 1	A sludge amended soil from Pavia	Cd, Cr, Cu, Fe, Ni, Pb, Zn
	Soil 2	A sludge amended soul from Düsseldorf	Cd, Cr, Cu, Fe, Ni, Pb, Zn

A.1.3 Interlaboratory comparison results

The statistical evaluation was conducted according to ISO 5725-2. The average values, the repeatability standard deviation (s_r) and the reproducibility standard deviation (s_R) were obtained (Table A.2).

The repeatability is determined as an interval around a measurement result (i.e. "repeatability limit"). This interval corresponds to the maximum difference that can be expected (with a 95% statistical confidence) between one test result and another, both test results being obtained under the following conditions: The tests are performed in accordance with all the requirements of the present standard by the same laboratory using its own facilities and testing laboratory samples obtained from the same primary field sample and prepared under identical procedures.

The repeatability limit was calculated using the relationship : $r_{\text{test}} = f \cdot \sqrt{2} \cdot s_{r,\text{test}}$ with the critical range factor $f = 2$.

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For instance, the repeatability limit around a measurement result of 50 mg Pb /kg is ± 7.6 mg Pb/kg (i.e. ± 15 % of 50)

NOTE The above relationship refers to the difference that may be found between two measurement results performed each on two laboratory samples obtained under the same conditions. The value $f = 2$ used in the factor $f \cdot \sqrt{2}$ corresponds to the theoretical factor of 1,96 for a pure normal distribution at 95 % statistical confidence. Also, this value $f = 2$ corresponds to the usual value $k = 2$ of the coverage factor recommended in the Guide to the expression of Uncertainty in Measurement (GUM). However it may be necessary to use a larger value for f in situation as described in clause 11.

The reproducibility, like repeatability is also determined as an interval around a measurement result (i.e. "reproducibility limit"). This interval corresponds to the maximum difference that can be expected (with a 95% statistical confidence) between one test result and another test result obtained by another laboratory, both test results being obtained under the following conditions : The tests are performed in accordance with all the requirements of the present standard by two different laboratories using their own facilities and testing laboratory samples obtained from the same primary field sample and prepared under identical procedures.

The reproducibility limit was calculated using the relationship: $R = f \cdot \sqrt{2} \cdot s_R$ with the critical range factor $f = 2$.

For instance, the reproducibility limit around a measurement result 50 mg Pb /kg is ± 17.4 mg Pb /kg (i.e. ± 35 % of 50).

NOTE The above relationship refers to the difference that may be found between two measurement results performed each on two laboratory samples obtained under the same conditions. The value $f = 2$ used in the factor $f \cdot \sqrt{2}$ corresponds to the theoretical factor of 1,96 for a pure normal distribution at 95 % statistical confidence. Also, this value $f = 2$ corresponds to the usual value $k = 2$ of the coverage factor recommended in the Guide to the expression of Uncertainty in Measurement (GUM). In the case when reference is made to the dispersion of the values that could reasonably be attributed to the parameter being measured, the dispersion limit is equal to $k \cdot s_R$ with the usual value $k = 2$, resulting in a dispersion limit lower than the reproducibility limit (i.e. a ratio of $\sqrt{2}$). However it may be necessary to use a larger value $f \cdot \sqrt{2}$ (or k) in situation as described in clause 11 .

In case of relatively heterogeneous materials, the repeatability and the reproducibility limits may be larger than the values given in Tables A.2 (this means that the value chosen for the critical range factor f is larger than 2 as well as for the coverage factor k for dispersion). This is because the extreme results may have been obtained in accordance with the present standard and/or be caused by the variability within, or in between, the laboratory samples.

Table A.AD.2 — Results of the interlaboratory comparison studies of the microwave digestion for the extraction of nitric acid soluble fraction of trace elements. All concentrations in mg/kg.

Matrix	Parameter	Mean mg/kg	sr	sR	r	R	p	Outliers	Used number of data	Number of data reported below detection
Sludge 1	NA Cd	2.20	4.09%	6.24%	0.252	0.384	4	2	29	
Sludge 2	NA Cd	2.70	5.33%	9.76%	0.403	0.739	5	1	41	
Compost 2	NA Cd	0.65	6.11%	7.38%	0.111	0.133	4	2	29	
Soil 1	NA Cd	0.24	14.0%	15.43%	0.095	0.105	4	2	27	
Soil 2	NA Cd	0.41	6.08%	6.51%	0.070	0.074	4	2	29	
Sludge 1	NA Cr	54.39	3.75%	8.05%	5.712	12.263	5	2	29	
Sludge 2	NA Cr	46.02	2.69%	27.14%	3.461	34.973	5	2	43	
Compost 2	NA Cr	20.72	8.31%	24.58%	4.820	14.260	6	2	35	
Soil 1	NA Cr	43.94	5.29%	20.97%	6.504	25.801	4	2	37	
Soil 2	NA Cr	17.69	10.0%	37.29%	4.952	18.468	6	0	51	
Sludge 1	NA Cu	376.3	8.48%	11.24%	89.385	118.447	5	2	35	
Sludge 2	NA Cu	399.6	4.43%	9.15%	49.574	102.339	5	2	35	
Compost 2	NA Cu	37.83	6.90%	10.51%	7.314	11.137	6	2	39	
Soil 1	NA Cu	27.13	4.03%	5.62%	3.062	4.271	4	2	33	
Soil 2	NA Cu	9.01	9.37%	13.69%	2.365	3.457	6	0	57	
Sludge 1	NA Fe	47492	2.49%	9.50%	3310	12639	5	2	29	
Sludge 2	NA Fe	44532	2.73%	10.05%	3400	12530	6	1	41	
Compost 2	NA Fe	9533	7.50%	18.19%	2002	4855	8	0	51	
Soil 1	NA Fe	24171	1.90%	12.40%	1288	8394	4	2	27	
Soil 2	NA Fe	7554	3.59%	17.05%	759	3606	5	1	39	
Sludge 1	NA Ni	44.53	2.59%	9.11%	3.226	11.353	5	2	29	
Sludge 2	NA Ni	36.64	3.48%	13.82%	3.573	14.174	6	1	47	
Compost 2	NA Ni	11.74	6.63%	17.37%	2.180	5.707	6	2	47	
Soil 1	NA Ni	30.91	2.58%	11.04%	2.230	9.558	4	2	27	
Soil 2	NA Ni	3.68	15.5%	38.50%	1.600	3.963	5	1	53	
Sludge 1	NA Pb	145.5	3.77%	10.16%	15.358	41.385	5	2	43	
Sludge 2	NA Pb	80.20	5.49%	12.69%	12.327	28.498	7	0	53	
Compost 2	NA Pb	39.73	6.08%	17.51%	6.769	19.480	6	2	35	
Soil 1	NA Pb	25.31	7.78%	16.39%	5.514	11.613	6	0	51	
Soil 2	NA Pb	28.30	8.00%	13.04%	6.338	10.332	6	0	51	
Sludge 1	NA Zn	1231	2.42%	7.74%	83.633	266.856	5	2	29	
Sludge 2	NA Zn	737	2.15%	15.42%	44.438	318.464	5	2	29	
Compost 2	NA Zn	184.8	5.41%	13.54%	27.982	70.082	7	1	51	
Soil 1	NA Zn	74.45	7.38%	10.39%	15.379	21.654	6	0	57	
Soil 2	NA Zn	52.26	6.97%	8.39%	10.202	12.276	6	0	57	

Abbreviations: sr Repeatability standard deviation; SR Reproducibility standard deviation; r Repeatability limit (comparing two measurements); R Reproducibility limit (comparing two measurements); p Number of labs.

Bibliography

- [1] US EPA Method 3051A. Microwave assisted acid digestion of sediments, sludges, soils, and oils. Rev. 1. January 1998.
- [2] EN 14888:2005, *Fertilizers and liming materials – Determination of cadmium contents.*