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Sludge, treated biowaste and soil — Digestion for the extraction of aqua regia 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)**	**Reference**
Sludge	Method A and B validated for: Municipal sludge, Industrial sludge, sludge from electronic industry, ink waste sludge 2 sewage sludges	EN 13346, EN 13657 Horizontal validation report
Soil	2 soils	Horizontal validation report
Soil improvers	Method A validated for: Biowaste, composted sludge 2 compost	EN 13650 Horizontal validation report
Sediment		
Waste	Method A and B validated for: City waste incineration fly ash, city waste incineration bottom ash, ink waste sludge, electronic industry sludge	EN 13657

Introduction

This standard is developed in the European project 'HORIZONTAL'. It is the result of a desk study "Horizontal European standard for digestion by aqua regia" which aimed at evaluating the latest developments in digestion of sludge, soil, treated biowaste and neighbouring fields. After an evaluation study, in which e.g. the ruggedness of the method was studies, 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.

WARNING — All the work has to be performed by skilled persons.

The reagents used within this EN are strongly corrosive and partly very harmful. Safety precautions are absolutely necessary due to strong corrosive reagents, high temperature and high pressure.

All procedures have to be performed in a 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 pressurised 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.

1 Scope

This European Standard specifies methods for digestion of sludge, treated biowaste and soil by the use of aqua regia. Solutions produced by the methods are suitable for analysis e.g. by atomic absorption spectrometry (FAAS, HGAAS, CVAAS, GFAAS), inductively coupled plasma emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) for the following elements: arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), mercury (Hg), molybdenum (Mo), nickel (Ni), selenium (Se), strontium (Sr), thallium (Tl), vanadium (V) , zinc (Zn), phosphorous (P) and sulphur (S).

The digestion with aqua regia is operationally defined and will not necessarily release all elements completely. However for most environmental applications the results are fit for the purpose.

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.*

ISO 11464: 2006, *Soil quality — Pretreatment of samples for physico-chemical analysis.*

CSS99022, *Sludge, treated biowaste and soil — Determination of dry matter (HORIZONTAL).*

CSS99024, *Sludge, treated biowaste and soil — Determiniation of TOC (HORIZONTAL).*

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

For the purposes of this document, the following terms and definitions apply:

3.1
aqua regia
digestion solution obtained by mixing one volume of nitric acid and three volumes of hydrochloric acid

3.2
digestion
mineralization of the organic matter of a sample and dissolution of its mineral part, more or less completely, when reacted with a reagent mixture

3.3
sample
portion of material selected from a larger quantity of material

3.4
laboratory sample
sample or sub sample(s) sent to or received by the laboratory

3.5
test sample
analytical sample
sample, prepared from the laboratory sample, from which test portions are removed for testing or analysis

3.6
test portion
analytical portion
amount 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 pre-treated test sample.

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

3.7
dry matter
remaining mass fraction of a sample after the specified drying process. It is expressed in percentage or as grams per kilogram

(EN xxxx 200X – horizontal standard)

3.8
digestion vessel
special flask where the test portion and the acid mixture are filled in and the digestion is performed

3.9
microwave unit
microwave digestion system (oven and associated equipment)

4 Principle

The laboratory sample is prepared in order to obtain a representative test portion which is extracted with aqua regia according to one of the following heating procedures:

— boiling under reflux for 2 h, followed by filtration and adjusting the volume in a volumetric flask (method A);

— microwave digestion for 20 min in a closed vessel followed by filtration and adjusting the volume in a volumetric flask (method B);

— microwave digestion at 175 °C ± 5 °C for 10 min ± 1 min in a closed vessel followed by filtration and adjusting the volume in a volumetric flask (method C).

5 Interferences and sources of errors

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 the volatile reaction products which might be formed during the digestion are not allowed to escape.

The container in which the sample is delivered and stored can be a source of errors. Its material shall be chosen according to the elements to be determined (e.g. elemental Hg can penetrate polyethylene walls very fast in both directions. Glass can contaminate samples with elements contained: e.g. B, Na, K, Al).

Grinding or milling samples includes a risk of contamination of the sample by the environment (air, dust, wear of milling equipment). Due to elevate temperature losses of volatile compounds are possible (e.g.drying temperature over 40 ° C may result in losses of mercury).

For the determination of elements forming volatile compounds (e.g. Hg, As) special care has to be taken at sample pre-treatment. The preparation of test portions should be done according to the principles of EN 15002 or ISO 11464.

The use of the described digestion procedures may leave large parts of the sample undissolved. This includes the risk of bad repeatability.

High acid and solute concentrations in the digest may cause interferences at determination.

Contamination must be avoided. Depending on the concentration of the element of interest a particular caution to the cleaning the laboratory equipment shall be taken. It is recommended to clean the laboratory equipment thoroughly by e.g. standing overnight in 10 % nitric acid.

Care shall be taken to ensure that all of the test portion is brought into contact with the acid mixture in the reaction vessel.

Some elements of interest can be lost due to precipitation with ions present in the digest solution, e.g. low soluble chlorides, fluorides and sulphates. During filtration of the digested solution it is necessary to take care that the filtration procedure does not introduce contaminants.

6 Reagents

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

All reagents shall meet the purity requirements of the subsequent analysis.

6.1 Water, complying with grade 2 as defined in EN ISO 3696 or better.

6.2 Hydrochloric acid, c(HCl) = 12 mol/l; ρ = 1,18 kg/l. Sub-boiling distilled. 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.

6.3 Nitric acid, $c(HNO_3)$ = 16 mol/l, ρ = 1,4 kg/l. Sub-boiling distilled. 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.

6.4 Nitric acid, $c(HNO_3)$ = 0,5 mol/l. Dilute 35 ml nitric acid (0) to 1 l with water (6.1).

6.5 Antifoaming agent,e.g. n-dodecane ($C_{12}H_{26}$) or Triton X-100 is suitable.

7 Apparatus

All glassware and plastic ware shall be adequately cleaned and stored in order to avoid any contamination.

NOTE Depending on the concentration of the element of interest, a particular caution to the cleaning of the vessels shall be taken. It is recommended to clean the vessels by cooking with aqua regia or with 10 % nitric acid.

7.1 Apparatus used for method A

7.1.1 Digestion vessel, temperature- and pressure-resistant and capable of containing the mixture of sample and digest solution, for example a glass flask of 250 ml. 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.

NOTE 1 Quartz vessels can be used instead of glass vessels.

NOTE 2 It can be necessary to periodically clean the reaction vessels with a suitable surfactant to remove stubborn deposits.

7.1.2 Reflux condenser with a vapour recovery system (non-return type) capable of absorbing volatile compounds in diluted nitric acid, see figure 1, and adaptable to the digestion vessel (0).

7.1.3 Absorption vessel, volatile species trap, in an open digestion system capable of trapping one or more volatile measurement species, adaptable the vapour recovery system (0).

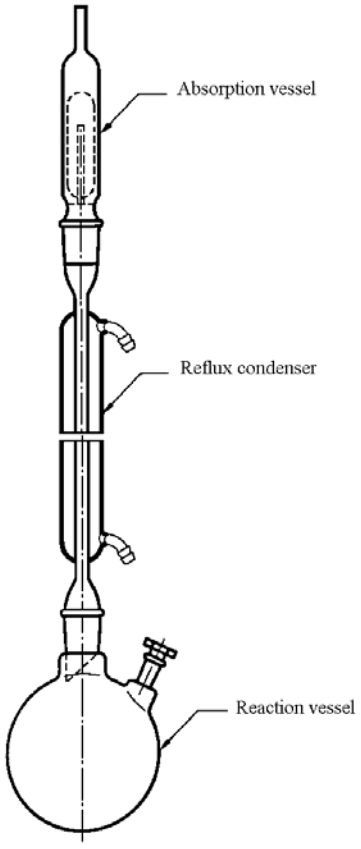

Figure 1 — Reaction vessel (7.1.1), reflux condenser (7.1.2) and absorption vessel (7.1.3) (assembled)

7.2 Apparatus used for method B

7.2.1 Heating device, for example a heating mantle, thermostatic controlled, or an aluminum block thermostat

7.2.2 Digestion vessel 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 (435 psi) 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.

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

7.2.3 Microwave oven, that is corrosion resistant and well ventilated. All electronics shall be protected against corrosion for safe operation.

The microwave oven shall provide programmable power which can be programmed to within ± 10 W of the required power. Typical units provide a nominal 600 W to 1200 W. If necessary (referring to manufactures specifications) calibration of the microwave unit has to be performed.

NOTE A procedure to establish the relationship between microwave power and temperature is given in annex A.

The microwave oven cavity has to be well ventilated. It has to have an exhaust air tube which is connected to a corrosion resistant laboratory air outlet system or the instrument is provided for use in a laboratory hood.

The microwave oven shall be designed in a way that guarantees homogeneous heating of the samples.

The microwave unit cavity has to be built in a way that even in case of leakage or explosion of the vessels the safety of the operators can be guaranteed. Household instruments are not suitable for laboratory use.

NOTE The microwave unit should include a temperature and/or pressure control system.

7.3 Apparatus used for method C

7.3.1 Digestion vessel, preferable of 100 ml volume, temperature- and pressure-resistant and capable of containing the mixture of sample and digest solution. Devices made of PFA, TMF, Quartz or glass equipped with a pressure releasing system to avoid explosion of the vessel can be used. The inner wall of the vessel shall be inert and shall not release contaminations to the digest.

NOTE It can be necessary to periodically clean the reaction vessels with a suitable surfactant to remove stubborn deposits.

7.3.2 Heating devices, corrosion resistant and well ventilated. All electronics shall be protected against corrosion for safe operation.

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 ± 2,5 °C and automatically adjust the microwave field output power within 2 s of sensing. Temperature sensors shall be accurate to ± 2 °C (including the final reaction temperature of 175 °C ± 5 °C).

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 ± 12 W of the required power. Typical systems provide a nominal 600 W to 1400 W.

Calibration control provides a backward comparability with older laboratory microwave systems, which may not be equipped for temperature monitoring or feedback control. See Annex A for calibration.

NOTE 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 °C to 2 °C from the temperature measured by an external, calibrated temperature measurement system, the microwave temperature measurement system should be calibrated.

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

7.3.4 Sample container, plastic and glass containers are both suitable.

7.3.5 Filter paper, cellulose based, hardened and resistant to aqua regia.

7.3.6 Volumetric flasks, capacity 25 ml, 50 ml or 100 ml.

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

7.3.8 Boiling aids, anti bumping granules or glass beads, diameter 2 mm to 3 mm, acid washed (for method A)

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 containers with an appropriate closure material. Samples should be kept cold (< 8 °C) the sample pre-treatment should take place within 1 month of sampling. Alternatively, samples may be frozen (-18 °C) directly after sampling and kept frozen before sample pre-treatment.

8.2 Sample pre-treatment

The test portion shall be transferred into the vessel after a pre-treatment according to EN yyyy:200X (Horizontal standard module(s) for sample pretreatment of sludge, soil and treated biowaste, respectively EN 15002 or ISO 11464, of the laboratory sample to result in homogeneous and representative test portions out of the laboratory sample. This procedure shall not change the concentration of the elements of interest.

Pre-treatment should include drying or grain size reduction below a particle size of 250 µm for solid materials or homogenizing by use of pestle and mortar for dried sludges or a high speed mixer or sonification for liquid samples.

NOTE For soil samples it is common to use the fraction < 2mm; if it is used without any particle size reduction, an influence of grain size on recovery rate of digestion cannot be excluded for some types of soil.

The mass of test samples shall be sufficient for the multiple digestion procedures and determination of the dry matter. Determination of dry matter according EN yyyy:200X (Horizontal standard module(s) of sludge, soil and treated biowaste shall be performed on a separate test sample.

8.3 Mass of test portion

The mass of test portion for a single digestion has to be selected in a way, that:

— it is representative for the laboratory sample

— it complies with the specifications of manufacturer of the digestion unit.

NOTE 1 If the representative test portion exceeds the manufacturer's specifications the test portion should be divided into smaller quantities and digested separately. The individual digests should be combined prior to analysis.

NOTE 2 For representativity reason, mass above 200 mg is to be preferred.

Unless recommended by the manufacturer, the amount of organic carbon shall not exceed 100 mg because of safety reasons in the case of closed digestion vessel.

9 Procedure

9.1 Blank test

The reagent blank test shall be carried out in parallel with the determination, by the same procedure, using the same quantities of all the reagents as in the determination but omitting the test portion.

NOTE The measurement of a blank is introduced to determine the contribution of the extracting solution, glassware and filter paper used.

9.2 Method A: Thermal heating under reflux conditions

9.2.1 Amount of test portion

Weigh approximately 3 g, to the nearest 0,001 g, of the prepared sample and transfer to the 250 ml reaction vessel (0).

NOTE If necessary it is possible to weigh 1 g to 10 g of the prepared sample and transfer it to the reaction vessel. In this case the appropriate amount of acid mixture should be added to obtain a mass to volume ratio between sample and acid mixture of 1:10.

9.2.2 Digestion

Moisten the sample with about 0,5 ml to 1,0 ml of water (0) and add, with mixing, 21 ml ± 0,1 ml of hydrochloric acid (0) followed by 7 ml ± 0,1 ml of nitric acid (0) drop wise if necessary to reduce foaming. Connect the condenser (0) to the reaction vessel (0). Fill the absorption vessel (0) with nitric acid (0). Connect the absorption vessel to the condenser, and let stand at room temperature until any effervescence almost ceases to allow for slow oxidation of the organic mass in the sample.

NOTE 1 The time of standing at room temperature may have an influence on the digestion rate of aqua regia. For comparison reason of the method it is recommended to start heating as soon as possible after the first strong reaction has ceased.

30 ml of aqua regia is sufficient only for the oxidation of about 0,5 g organic carbon. If there is any doubt of the amount of carbon present, estimate the amount of carbon in the sample or carry out a determination of TOC. If there is more than 0,5 g of organic carbon in the test portion, proceed as follows.

Allow first reaction with the aqua regia to subside. Then add an extra 1 ml of nitric acid only to every 0,1 g of organic carbon above 0,5 g. Do not add more than 10 ml of nitric acid at any time, and allow any reaction to subside before proceeding further.

Transfer to the heating device (0) and raise the temperature of the reaction mixture slowly to reflux conditions and maintain for 2 h ensuring that the condensation zone is lower than 1/3 of the height of the condenser, then allow to cool. Add the content of the adsorption vessel to the reaction vessel via the condenser, rinsing both the absorption vessel and condenser with further 10 ml of diluted nitric acid (0) or with 10 ml of water (0).

NOTE 2 If the digested sample contains particulates which may clog nebulisers or interfere with the injection of the sample into the instrument, the sample solution may be centrifuged, allowed to settle, or filtered before transferring into a suitable sized volumetric flask (0). In case of filtering dilute the content of the vessel, filter through the filter paper (0), and wash the insoluble residue with a diluted nitric acid (0). The method used has to be reported in the test report.

Transfer the digested sample into a suitable sized volumetric flask (0) and dilute to the mark with water (0).

9.3 Method B: Microwave heating with power control

9.3.1 Amount of test portion

Weigh 0,5 g of the prepared sample, accurately at 0,1 mg, and transfer it into the vessel (0).

The upper limits of mass of the test portion referring to the manufacturer's specifications have to be taken into account.

9.3.2 Digestion

If necessary the sample may be moistened with a minimum amount of water (0). Then add separately 6 ml ± 0,1 ml of hydrochloric acid (0) and 2 ml ± 0,1 ml of nitric acid (0) and mix well.

If a vigorous reaction occurs, allow the reaction to lie down before capping the vessel. Transfer the digestion vessels into the microwave oven (0) according to the manufactures instructions and start the following digestion procedure in case of using a power controlled microwave oven:

Table 1 — Power programme for power controlled microwave oven

Time min	Power W
2	250
2	0
5	250
5	400
5	500

The above power programme is intended to be used for batches of 6 samples. Commercial available microwave units may contain more or less sample positions. In order to ensure consistant reaction conditions in these cases the power programme has to be adjusted according to the manufactures instructions. For batches where all positions are not occupied either the empty positions shall be filled up with e.g. blanks or duplicates or the power programme shall be adjusted in accordance with the number of samples.

NOTE 1 Temperatures of about 115°C ± 5 °C should be reached with the power programme of table 1, otherwise the power should be adjusted to reach these temperatures

If a temperature controlled microwave unit is used, the appropiate temperatures of 115 °C ±5 °C shall be obtained for about 5 min after a heating period of 12 min ± 2 min.

Very reactive or volatile materials that may create high pressures when heated may cause a venting of the vessels with potential loss of sample and analytes. The complete decomposition of either carbonates, or carbon based samples, may cause enough pressure to vent the vessel.

At the end of the programme let the vessels cool down to room temperature. If not, losses of certain elements, particularly volatile elements as mercury or arsenic can occur. Confirm that no losses of digestion solution occured during the procedure (e.g. by control of burstmembran referring to the manufactures specifications or controll of mass). Otherwise the samples have to be discarded. Carefully uncap and vent each vessel in a fume hood.

If the digested sample contains particulates which may clog nebulisers or interfere with the injection of the sample into the instrument, the sample solution may be centrifuged, allowed to settle, or filtered before transferring into a suitable sized volumetric flask (0). In case of filtering dilute the content of the vessel, filter through the filter paper (0), and wash the insoluble residue with a diluted nitric acid (0). The method used has to be reported in the test report.

Transfer the digested sample into a suitable sized volumetric flask (0) and dilute to the mark with water (0).

9.4 Method C: Microwave heating with temperature control at 175 °C ± 5 °C

9.4.1 Amount of test portion

Weigh 0,5 g of the prepared sample, accurately at 0,1 mg, and transfer it into the vessel (0).

Referring to the manufacturer's specifications, the upper limits of mass of the test portion have to be taken into account.

9.4.2 Digestion

Moisten the sample with two drops of water (0). Then add separately 6 ml ± 0,1 ml of hydrochloric acid (0) and 2 ml ± 0,1 ml of nitric acid (0) and mix well.

If a vigorous reaction occurs, allow the reaction to lie down before capping the vessel. If excessive foaming occurs, add a drop of anti-foaming agent (6.5).

The amount of nitric acid is sufficient for approx. 20 % organic carbon in the sample. If the organic carbon is higher, than add additionally 0,5 ml to 1 ml nitric acid (0) for samples up to 40 % organic carbon.

Cap the extraction vessel (7.3.1) and weigh it. Connect the extraction vessel to the microwave equipment or place it into the carrousel. Always fill all positions of the microwave equipment (usually 6, 12, 16 or 40 positions). If not all positions are occupied by samples, fill the remaining digestion vessels with the same amount of aqua regia as in the sample vessels to make sure that the energy is evenly absorbed.

Increase the temperature of the extraction mixture with a rate of approx. 15 °C/min to a temperature of 175 °C ± 5 °C.

NOTE 1 Too fast increase of the temperature may lead to exothermic reactions which can result in a release through the pressure safety valve and loss of analytes.

Maintain the extraction for a period of at least 10 min ± 1 min at 175 °C. Then allow the extraction vessel to cool to room temperature. Weigh the extraction vessels and accept the extract if the mass loss is lower than 3 %. Otherwise a release of fumes has ocurred and volatile analytes may be lost. These samples have to be discarded. Uncap and vent the extraction vessel in a fume hood.

Transfer quantitatively, by decanting, the extract into a clean volumetric flask. If appropriate, add releasing agents or internal standards necessary for the determination method and fill up to the mark with water. Centrifuge or filtrate the extract before subsequent measurement.

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

NOTE 2 Centrifugation at 2000 rpm – 3000 rpm for 10 min is usually sufficient to clear the supernatant. If un-dissolved material, such as SiO_2, TiO_2, 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, 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 a quantative filter paper into a second acid cleaned container or use membrane filtration.

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 whenever a new sample matrix is being analysed.

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 C) 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 C.2 in Annex C by taking the median value and rounding the numbers.

Table C.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 digestion for the extraction of aqua regia soluble fraction of trace elements in soil, sludge and treated biowaste	Typical value %	Observed range %
Repeatability limit, r (Reflux)	14	*7 - 21*
Reproducibility limit, R (Reflux)	27	*15 - 37*
Repeatability limit, r (MW 115 C)	19	*7 - 22*
Reproducibility limit, R (MW 115C)	23	*16 - 33*
Repeatability limit, r (all AR)	17	*10 - 21*
Reproducibility limit, R (all AR)	34	*30 - 59*

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 Cu in Sludge 2 the result and its dispersion limit is 429 ± 72 mg/kg (2 * sR = 16.8 % of 429). This means that with a 95 % statistical confidence, the values reasonably attributable to the measured parameter are larger than 356 mg/kg and lower than 501 mg/kg.

NOTE 2. The repeatability limit (r) and the reproducibility limit (R) as given in Table C.2 (Annex C) and in this table are indicative values of the attainable precision if the digestion for the extraction of aqua regia soluble fraction of trace elements is performed in accordance with this standard [CSS99025B].

NOTE 3 A limited numbe

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 C.2 (Annex C) and this table.

12 Test report

The work carried out by the testing laboratory shall be covered by a report which accurately, clearly and unambiguously presents the test results and all other relevant informations. The test report shall be issued separately or in conjunction with the report from the subsequent analytical method.

The test report shall include at least 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 extraction 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.

The traceability of the work carried out by the testing laboratory (e.g. instruments, worksheets, printouts, forms with samples weight) shall be recorded and stored. This information shall be available on customers request.

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

NOTE 2 The final report should include all results and relevant information on the sampling, the digestion method and the analysis 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 deviation.

Annex A
(normative)

Procedure to establish the relationship between microwave power and temperature for power-controlled systems with pressure measurement

A.1 General

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

Several closed microwave-assisted extraction and digestion systems control power rather than temperature. These instruments have facilities to measure the pressure of the vessel. The procedure to establish the relationship between digestion temperature and power setting is given in A.1.1. and A.1.2.

A.2 Power calibration

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.

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 may be used in a given batch.

Equilibrate a large volume of water (6.1) to room temperature (22 °C ± 3 °C). The initial temperature of the water should be 22 ºC ± 3 ºC measured to ± 0,05ºC. Weigh 1 000 g ± 0,1 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 ± 0,05 °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 J g^{-1} $^oC^{-1}$;

m is the mass of the water, in g;

T_1 is the initial temperature of the water, in ^oC;

T_2 is the final temperature of the water, in ^oC;

t is the time, in s.

Using the experimental conditions of 120 s and 1 000 g of water (6.1) and the heat capacity of water at 25 ^oC (4,1827 J g^{-1} $^oC^{-1}$) 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, is will be necessary to make a set of measurements that bracket the power to be used. The final calibration point should be at the partial power setting that will be used in the test. This setting should be checked periodically to evaluate the integrity of the calibration. If a significant change is detected (± 10 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 watts, specified in the procedure to reproduce the heating profiles specified in section 10.3.2. Measure the absorbed power at that partial power setting. If the measured absorbed power doeses not correspond to the specified power within ± } 10 W, use the multiple point calibration. This point should also be used to periodically verify the integrity of the calibration.

A.3 Temperature calibration

At constant room temperature, T_{RT}, measure the digestion pressure P, expressed in kilo-Pascal (kPa), at different power settings using 25,0 ml ± 0,1 ml (blank) grade 1 water (6.1) mixed with exactly the same volume of freshly prepared aqua regia as used for extraction of samples.

Use all extraction positions of the microwave oven and use an identical test portion for every position. Calculate the digestion temperature T_d, in ^oC, corresponding to the pressure P, expressed in kPa, of diluted aqua regia using the approximation:

$$T_d = 38{,}9 + 3 \times (\ln P)^2 \qquad (2)$$

Obtain for every power setting the corresponding microwave power from equation (1). Establish the relationship between the digestion temperature and the microwave power in the calibration graph. Re-evaluate the temperature calibration graph each time changes are made in the microwave system, for instance for the type of extraction vessel (geometry, material), composition of extracted sample or extraction volume. Use the relationship for sample analysis in the following way.

— Choose the temperature T_d for sample digestion.

— Obtain the required microwave power using the temperature calibration graph determined above.

— Obtain the power setting using the power calibration graph of A.1.1.

NOTE 1 Applicability of the procedure is limited to temperatures less than 120 °C due to the influence of air expansion inside the vessel.

NOTE 2 Power-controlled microwave energy raises the digestion temperature above room temperature. Therefore, the temperature calibration graph is valid for the room temperature during the calibration ($T_{RT,cal}$). If room temperature ($T_{RT,sample}$) during digestion of samples differs, the actual temperature will be ($T_{RT,sample}$- $T_{RT,cal}$) differend than calculated.

In order to compare the power adjustment of different apparatus among themselves, determine the actually supplied (effective) power. Also the relationship between the supplied power and the adjustment scale shall be controlled. Furthermore the effective power shall be checked periodically.

Annex B
(informativ)

Validation of methods – Data of EN 13657

B.1 General

For information purposes validation data of EN 13657 for sewage sludge are listed below, additional data for soil and biowaste will be added when available.

During 1998-1999 a project for validation of EN 13657 has been carried out. The validation included an inter-laboratory study for evaluation of performance characteristics of methods included in the standard (reproducibility, repeatability, accuracy where applicable), and a robustness study (i. e. the evaluation of the influence of some defined operational parameters on the methods).

B.2 Inter-laboratory study

B.2.1 Selection of laboratories

A questionnaire has been circulated by all CEN/TC 292/WG 3 members to collect a list of interested European laboratories. About seventy laboratories gave their availability to participate to the inter-laboratory trial. All of them were asked to declare that they fulfill the minimum requirements to carry out digestion and analyses according to EN 13657. According to ISO 5725 series no selection has been made in advance on the basis of the supposed "ability" of laboratories, their certifications, etc: it's therefore possible to assume that participating laboratories are a rather good "sample" of "normal" European laboratories.

B.2.2 Selection of samples

Sewage sludge was one of the selected materials of this validation trial:(CEN9/99 "SEWAGE SLUDGE SL11 POWDER");

For the evaluation of performances of digestion procedures, independently from the subsequent analyses performed on digested samples, all laboratories have been asked to analyse some already-prepared aqueous solutions with different degrees of difficulty (clean synthetic solutions, acid digested solutions). This has been used as a tool for discarding from the evaluation laboratories that didn't prove their analytical ability for some matrices/elements.

For accuracy evaluation, two certified reference material (CRM) have been also included:

— BCR 146R (sewage sludge);

— BCR 176 (city waste incineration ash).

All samples, including the two CRMs, have been delivered to laboratories in anonymous form.

B.2.3 Experimental

Preparation and homogenisation of samples, packaging, delivering, collection and evaluation of results have been carried out by Environmental Monitoring Sector of European Commission Joint Research Centre in Ispra (Italy).

B.2.4 Results

About fifty laboratories have actually returned results for the inter-laboratory study. The evaluation of results has been performed by following these steps:

— removing of "obviously erroneous data", both means and single data according to ISO 5725-2:1994, see 7.2.6;

— results from laboratories failing to correctly measure some elements in "clean metals" solution were removed from the whole data set (for the failed elements only);

— results from laboratories failing to correctly measure some elements in digested aqueous solutions were removed from the whole data set (for the failed elements only);

— the remaining data sets were evaluated according to ISO 5725 series, with calculation of repeatability, reproducibility and, where a "conventional true value" was available, accuracy (recovery); results of this evaluation are reported in the tables below.

The inter-laboratory study involved a large number of laboratories, performing analyses in four replicates on several samples (five aqueous, six powders), for the determination of a large number of elements (up to 31), by using one to three digestion methods: this led to a very large data set. For some digestion methods and for some elements determination, only few data were available (a minimum of 24 outlyer-free results is generally required); anyway, even for these methods and elements, useful information on performance have been obtained.

B.2.5 Conclusions

The performances of the three methods have to be compared on an element-by-element, matrix-by-matrix basis, in the tables below. In general words, performances are actually well comparable, especially for most environmentally-sensitive elements.

Recovery rates for CRM: sewage sludge (BCR 146 R, non-refractory matrix) are in generally high, for CRM: city waste incineration ash (BCR 176, refractory matrix) in many cases low. Digestion with aqua regia will not necessarily release elements completely.

SAMPLE CEN9/99 "SEWAGE SLUDGE SL11 POWDER"

	Method A: Microwave assisted with aqua regia in closed vessel								*Method - B: Microwave assisted, with aqua regia in semi-open vessel*								*Method C: Thermal heating, with aqua regia in reflux systems*							
	N	L	NA	XREF mg/kg	Mean mg/kg	Recov %	Reprod %	Repeat %	N	L	NA	XREF mg/kg	Mean mg/kg	Recov %	Reprod %	Repeat %	N	L	NA	XREF mg/kg	Mean mg/kg	Recov %	Reprod %	Repeat %
Al	67	16	5		81848		6,7	2,5	21	6	1		77368		16,7	1,7	29	7	0		79678		24,6	6,4
Sb	16	4	0		19,49		103,9	25,6	5	2	1		2,57		29,7	0,5	3	1	1		2,2		-	8,6
As	19	5	4		4,43		78,1	22,2	4	1	0		5,55		-	10,1	17	5	0		4,03		58,5	16,2
B	33	8	2		279,9		15,6	3,4	12	3	1		282,6		14,1	0,9	19	4	0		328,1		28,4	16,6
Ba	51	12	8		76,52		8,6	2,7	22	6	4		75,52		4,5	1,2	27	6	0		61,8		18,9	7,9
Be	13	3	0		1,79		147,8	29,3	0	0	0						5	1	0		1,45		-	17,6
Cd	30	7	20		0,23		32,1	16	14	3	0		0,9		153,6	29,5	14	3	4		0,74		142,8	73,8
Ca	60	14	0		57232		11	5,9	19	5	5		58797		4	5,8	21	5	0		58521		17,2	2,6
Cr	92	23	10		77,24		10,2	4	31	8	0		73,0		10,2	2,9	40	9	4		78,47		19,6	5,8
Co	39	11	4		4,59		24,9	8,6	12	4	0		5,43		48,1	52,5	26	6	0		3,16		53,5	12,4
Cu	96	23	5		96534		13,2	3,5	31	8	0		93526		6,3	1,4	31	7	13		91351		3,3	2,6
Fe	81	20	7		4440,3		11	3,6	26	7	0		4437,7		4,2	2,3	43	10	4		4021,1		10,6	7,2
Pb	96	23	7		9327,5		11,2	2,9	31	8	0		9323,8		3,5	1,2	33	8	14		9305,6		5,6	3,6
Mg	60	14	0		2309,1		14,2	4,2	21	6	4		2177,3		5	2,9	21	5	0		1992,1		19	5,6
Mn	92	23	5		590,2		12,2	3	31	8	0		583,8		3,6	1,4	46	11	5		587,6		9	2,8
Hg	27	7	12		0,14		52,7	10,8	10	2	0		0,33		21,8	8,4	15	3	4		0,19		46,7	9,7
Mo	22	6	1		4,33		11,1	6,4	14	3	0		4,59		62,2	11,9	13	3	0		3,56		6,8	7,4
Ni	100	25	5		1729,6		10,6	3,3	26	7	5		1720,0		5,5	1,7	40	9	9		1568,6		18,7	6,1
P	18	4	10		4724,5		3,8	6,3	22	5	0		5834,6		33,9	5,6	13	3	0		4012,9		24,7	6,7
K	48	12	4		629,5		39,1	6,8	11	3	0		436,3		31,7	5,5	21	5	0		467,8		58,6	3,8
Se	8	2	0		7,03		110,2	14	0	0	0						0	0	0					
Ag	28	7	0		10,53		14,7	13,1	18	4	0		7,73		20,5	11,8	18	4	0		9,68		21	7
S	26	6	0		61982		8,8	1,7	7	2	0		60496		2,6	2,5	10	2	0		59698		12,8	1,8
Na	64	15	0		11041		22,7	6	7	2	0		12596		7,7	1,3	28	6	1		11805		10,8	4,3
Sr	41	10	10		200,8		5,6	2,4	15	4	0		197,3		3,3	2,2	18	4	0		195,2		9,5	2,2
Sn	35	8	5		19155		5,2	6,6	15	4	0		16768		15,1	5,1	14	3	0		17840		18,2	1,8
Te	0	0	0						0	0	0						0	0	0					
Tl	6	2	0		18,65		203	9,6	0	0	0						0	0	0					
Ti	21	5	0		29,78		28,2	8,9	8	3	4		26,34		10,1	0,5	12	3	0		24,64		35,7	3
V	25	7	14		6,36		17,6	2,3	15	4	0		8,09		63,9	28,8	18	4	5		6,83		77,1	32,3
Zn	99	24	4		228,1		34,9	5,5	31	8	0		323,3		44,6	7	48	11	5		209,6		35,5	23

N = Number of results, L = Number of laboratories, NA = Number of outliers, XREF = Conventional true value (where applicable)

SAMPLE CEN10/99 "SEWAGE SLUDGE" (BCR 146R)

	Method A: Microwave assisted with aqua regia in closed vessel								*Method - B: Microwave assisted, with aqua regia in semi-open vessel*								*Method C: Thermal heating, with aqua regia in reflux systems*							
	N	L	NA	XREF mg/kg	Mean mg/kg	Recov %	Reprod %	Repeat %	N	L	NA	XREF mg/kg	Mean mg/kg	Recov %	Reprod %	Repeat %	N	L	NA	XREF mg/kg	Mean mg/kg	Recov %	Reprod %	Repeat %
Al	79	20	0	25130	20652	82,2	19	6,1	20	6	1	25130	18943	75,4	13,7	2,1	37	9	0	25130	21230	84,5	25,4	5,4
Sb	29	7	2	16,25	9,33	57,4	21,5	7,6	13	4	0	16,25	11,28	69,4	31,9	5,2	19	5	0	16,25	7,24	44,6	55,8	4,8
As	29	8	4	6,3	5,52	87,6	31	11,6	13	3	0	6,3	8,39	133,3	34,9	12,5	29	7	0	6,3	6,32	100,3	53,3	40,3
B	23	6	0		38,7		37,3	15	11	3	0		30,87		33,8	6	15	4	0		21,9		15	16,8
Ba	63	15	0	735	572,8	77,9	20	4,6	19	5	1	735	391,8	53,3	16,9	7,7	23	5	0	735	479,3	65,2	13,9	13,7
Be	22	5	4		0,75		5,7	6,1	4	1	0		1,09		-	9,1	13	3	0		0,88		21,7	10,2
Cd	82	20	14	18,76	17,15	91,4	8,8	4,5	22	6	4	18,76	15,75	84	13	2,3	45	11	0	18,76	16,26	86,7	14,8	9,6
Ca	60	14	0	154600	140455	90,9	8,7	3,7	18	5	5	154600	145312	94	7,3	1,4	27	6	1	154600	154356	99,8	17	4,4
Cr	103	25	0	196	164,6	84	13,6	3,4	27	8	4	196	157,5	80,3	12,3	4,4	45	10	4	196	163,6	83,4	13,7	3,3
Co	64	17	0	7,39	6,08	82,3	19,2	5,7	22	7	0	7,39	7,59	102,8	37,4	22,5	31	8	0	7,39	6,49	87,8	35,1	8,4
Cu	112	27	0	837,9	806,7	96,3	13,3	7,3	35	10	5	837,9	798,9	95,3	9,4	2,3	30	7	9	837,9	765,6	91,4	3	2,7
Fe	89	22	0	16100	13889	86,3	11,7	3,6	21	6	5	16100	13922	86,5	6,8	1,9	34	8	5	16100	13500	83,9	12,2	5
Pb	98	24	0	608,7	530,8	87,2	13,3	3,4	31	8	0	608,7	562,9	92,5	7,6	1,7	42	10	5	608,7	534,0	87,7	10,1	3,3
Mg	64	15	0	10460	9031,3	86,3	9,3	3,3	21	6	5	10460	8449,2	80,8	8,1	1,9	30	7	1	10460	9446,1	90,3	17,8	8,5
Mn	92	23	0	323,5	274,4	84,8	10,9	2,8	37	9	0	323,5	281,4	87	8,6	1,6	43	10	0	323,5	262,9	81,3	14,3	3,1
Hg	41	10	0	8,62	7,39	85,7	25,1	10,8	18	5	0	8,62	8,73	101,3	16,8	6,9	31	7	0	8,62	7,06	81,9	27,2	12,2
Mo	32	8	4		7,95		8,1	5,2	15	4	0		8,51		21,3	5,7	16	4	0		8,67		13,2	2,9
Ni	105	26	0	69,7	62,54	89,7	21,7	4,6	31	8	0	69,7	59,17	84,9	15,3	2,7	49	11	0	69,7	58,08	83,3	18,1	5,4
P	31	7	1	25600	27658	108	2,4	2,8	24	6	0	25600	30286	118,3	17,5	5	14	3	0	25600	28756	112,3	11,3	9,3
K	56	14	0	5240	2025,6	38,7	34,7	17,3	16	5	1	5240	1306,2	24,9	24,8	9,4	30	7	5	5240	1313,8	25,1	33,7	5,3
Se	13	3	0		4,74		60	12,3	4	1	0		3,33		-	7,9	2	1	0		2,67		-	-
Ag	38	9	0		190,9		23,1	1,9	24	6	0		205,9		6,6	5,2	18	4	1		198,8		4,4	1,1
S	26	6	0	10620	9188,4	86,5	17,7	2,4	2	1	0	10620	9180,0	86,4	-	-	10	2	0	10620	9021,6	84,9	15,4	8,7
Na	44	11	6	1804	777,0	43,1	28,1	4,3	6	2	0	1804	481,8	26,7	5,9	10,1	41	9	0	1804	701,3	38,9	55,2	18,3
Sr	46	11	5	1179	1027,2	87,1	4,9	2	11	3	1	1179	975,1	82,7	4,4	2,4	19	4	0	1179	1019,6	86,5	10,6	1,3
Sn	30	7	3	95,8	59,79	62,4	32,5	6,3	15	4	0	95,8	61,15	63,8	33	3,8	14	3	0	95,8	63,94	66,7	28,6	4,6
Te	0	0	0						0	0	0						0	0	0					
Tl	4	1	0		4,12		-	8,7	4	1	0		0,55		-	11,9	4	1	0		0,5		-	7,7
Ti	30	7	0	2771	299,8	10,8	57,6	21,5	21	6	0	2771	182,8	6,6	59,4	19	14	3	0	2771	183,6	6,6	34,1	7,2
V	50	12	8	42,7	34,14	80	8,6	3,3	14	4	8	42,7	27,76	65	3,4	2,8	26	6	0	42,7	46,25	108,3	47,9	4,8
Zn	108	26	0	3061	2813,5	91,9	10,8	4,5	31	8	0	3061	2761,8	90,2	7,1	3,1	43	10	6	3061	2810,0	91,8	12,1	6,5

N = Number of results, L = Number of laboratories, NA = Number of outliers, XREF = Conventional true value (where applicable)

SAMPLE CEN10/99 "SEWAGE SLUDGE" (BCR 146R)

	Method A: Microwave assisted with aqua regia in closed vessel								*Method - B: Microwave assisted, with aqua regia in semi-open vessel*								*Method C: Thermal heating, with aqua regia in reflux systems*							
	N	L	NA	XREF mg/kg	Mean mg/kg	Recov %	Reprod %	Repeat %	N	L	NA	XREF mg/kg	Mean mg/kg	Recov %	Reprod %	Repeat %	N	L	NA	XREF mg/kg	Mean mg/kg	Recov %	Reprod %	Repeat %
Al	79	20	0	25130	20652	82,2	19	6,1	20	6	1	25130	18943	75,4	13,7	2,1	37	9	0	25130	21230	84,5	25,4	5,4
Sb	29	7	2	16,25	9,33	57,4	21,5	7,6	13	4	0	16,25	11,28	69,4	31,9	5,2	19	5	0	16,25	7,24	44,6	55,8	4,8
As	29	8	4	6,3	5,52	87,6	31	11,6	13	3	0	6,3	8,39	133,3	34,9	12,5	29	7	0	6,3	6,32	100,3	53,3	40,3
B	23	6	0		38,7		37,3	15	11	3	0		30,87		33,8	6	15	4	0		21,9		15	16,8
Ba	63	15	0	735	572,8	77,9	20	4,6	19	5	1	735	391,8	53,3	16,9	7,7	23	5	0	735	479,3	65,2	13,9	13,7
Be	22	5	4		0,75		5,7	6,1	4	1	0		1,09		-	9,1	13	3	0		0,88		21,7	10,2
Cd	82	20	14	18,76	17,15	91,4	8,8	4,5	22	6	4	18,76	15,75	84	13	2,3	45	11	0	18,76	16,26	86,7	14,8	9,6
Ca	60	14	0	154600	140455	90,9	8,7	3,7	18	5	5	154600	145312	94	7,3	1,4	27	6	1	154600	154356	99,8	17	4,4
Cr	103	25	0	196	164,6	84	13,6	3,4	27	8	4	196	157,5	80,3	12,3	4,4	45	10	4	196	163,6	83,4	13,7	3,3
Co	64	17	0	7,39	6,08	82,3	19,2	5,7	22	7	0	7,39	7,59	102,8	37,4	22,5	31	8	0	7,39	6,49	87,8	35,1	8,4
Cu	112	27	0	837,9	806,7	96,3	13,3	7,3	35	10	5	837,9	798,9	95,3	9,4	2,3	30	7	9	837,9	765,6	91,4	3	2,7
Fe	89	22	0	16100	13889	86,3	11,7	3,6	21	6	5	16100	13922	86,5	6,8	1,9	34	8	5	16100	13500	83,9	12,2	5
Pb	98	24	0	608,7	530,8	87,2	13,3	3,4	31	8	0	608,7	562,9	92,5	7,6	1,7	42	10	5	608,7	534,0	87,7	10,1	3,3
Mg	64	15	0	10460	9031,3	86,3	9,3	3,3	21	6	5	10460	8449,2	80,8	8,1	1,9	30	7	1	10460	9446,1	90,3	17,8	8,5
Mn	92	23	0	323,5	274,4	84,8	10,9	2,8	37	9	0	323,5	281,4	87	8,6	1,6	43	10	0	323,5	262,9	81,3	14,3	3,1
Hg	41	10	0	8,62	7,39	85,7	25,1	10,8	18	5	0	8,62	8,73	101,3	16,8	6,9	31	7	0	8,62	7,06	81,9	27,2	12,2
Mo	32	8	4		7,95		8,1	5,2	15	4	0		8,51		21,3	5,7	16	4	0		8,67		13,2	2,9
Ni	105	26	0	69,7	62,54	89,7	21,7	4,6	31	8	0	69,7	59,17	84,9	15,3	2,7	49	11	0	69,7	58,08	83,3	18,1	5,4
P	31	7	1	25600	27658	108	2,4	2,8	24	6	0	25600	30286	118,3	17,5	5	14	3	0	25600	28756	112,3	11,3	9,3
K	56	14	0	5240	2025,6	38,7	34,7	17,3	16	5	1	5240	1306,2	24,9	24,8	9,4	30	7	5	5240	1313,8	25,1	33,7	5,3
Se	13	3	0		4,74		60	12,3	4	1	0		3,33		-	7,9	2	1	0		2,67		-	-
Ag	38	9	0		190,9		23,1	1,9	24	6	0		205,9		6,6	5,2	18	4	1		198,8		4,4	1,1
S	26	6	0	10620	9188,4	86,5	17,7	2,4	2	1	0	10620	9180,0	86,4	-	-	10	2	0	10620	9021,6	84,9	15,4	8,7
Na	44	11	6	1804	777,0	43,1	28,1	4,3	6	2	0	1804	481,8	26,7	5,9	10,1	41	9	0	1804	701,3	38,9	55,2	18,3
Sr	46	11	5	1179	1027,2	87,1	4,9	2	11	3	1	1179	975,1	82,7	4,4	2,4	19	4	0	1179	1019,6	86,5	10,6	1,3
Sn	30	7	3	95,8	59,79	62,4	32,5	6,3	15	4	0	95,8	61,15	63,8	33	3,8	14	3	0	95,8	63,94	66,7	28,6	4,6
Te	0	0	0						0	0	0						0	0	0					
Tl	4	1	0		4,12		-	8,7	4	1	0		0,55		-	11,9	4	1	0		0,5		-	7,7
Ti	30	7	0	2771	299,8	10,8	57,6	21,5	21	6	0	2771	182,8	6,6	59,4	19	14	3	0	2771	183,6	6,6	34,1	7,2
V	50	12	8	42,7	34,14	80	8,6	3,3	14	4	8	42,7	27,76	65	3,4	2,8	26	6	0	42,7	46,25	108,3	47,9	4,8
Zn	108	26	0	3061	2813,5	91,9	10,8	4,5	31	8	0	3061	2761,8	90,2	7,1	3,1	43	10	6	3061	2810,0	91,8	12,1	6,5

N = Number of results, L = Number of laboratories, NA = Number of outliers, XREF = Conventional true value (where applicable)

SAMPLE CEN11/99 "CITY WASTE INCINERATION ASH" (BCR 176)

	Method A: Microwave assisted with aqua regia in closed vessel								*Method - B: Microwave assisted, with aqua regia in semi-open vessel*								*Method C: Thermal heating, with aqua regia in reflux systems*							
	N	L	NA	XREF mg/kg	Mean mg/kg	Recov %	Reprod %	Repeat %	N	L	NA	XREF mg/kg	Mean mg/kg	Recov %	Reprod %	Repeat %	N	L	NA	XREF mg/kg	Mean mg/kg	Recov %	Reprod %	Repeat %
Al	65	16	4	101600	57116	56,2	15,7	5,2	21	6	5	101600	48606	47,8	6,9	3,2	29	7	5	101600	53275	52,4	12,9	2
Sb	42	10	5	412	262,5	63,7	13,9	7,5	19	5	0	412	277,0	67,2	1,6	3,2	18	4	0	412	242,9	59	6,1	1,8
As	67	17	1	93,3	85,2	91,3	28,2	5,9	10	3	0	93,3	88,57	94,9	4,6	2,9	36	8	0	93,3	74,93	80,3	26,8	4,1
B	33	8	4		173,1		21,3	2,3	13	3	0		169,8		11,8	6,8	19	4	0		192,7		18,2	4
Ba	62	15	0	4500	1329,6	29,5	119,6	11,2	21	6	0	4500	1811,4	40,3	103,5	21,1	23	5	0	4500	280,6	6,2	73,8	12
Be	30	9	1		1,89		15,9	10,4	4	1	0		1,75		-	4,4	12	3	1		1,79		5,4	1,6
Cd	107	26	1	470	422,7	89,9	13,7	3,2	31	8	0	470	428,3	91,1	7,9	2,1	38	9	5	470	446,7	95	3,9	1,7
Ca	48	11	0	88016	83012	94,3	8,2	3	24	6	0	88016	83050	94,4	5,3	3	26	6	10	88016	83516	94,9	5,7	2,1
Cr	106	26	1	863	210,7	24,4	17,7	6,5	30	8	1	863	164,7	19,1	15	2,6	48	11	0	863	190,6	22,1	18,7	3,7
Co	72	18	8	30,9	26,62	86,1	21,6	5,1	22	6	0	30,9	27,24	88,2	19,7	7,7	39	9	0	30,9	22,1	71,5	38,3	6,2
Cu	115	28	1	1302	1154,1	88,6	11,1	3,1	30	8	1	1302	1143,5	87,8	6,3	4,1	38	9	0	1302	1125,2	86,4	7,3	2,3
Fe	92	23	0	21300	18866	88,6	10,5	3,2	26	7	0	21300	18598	87,3	4,3	2,2	38	9	5	21300	18679	87,7	13,7	3,5
Pb	101	25	3	10870	10146	93,3	8,7	2,5	31	8	0	10870	10206	93,9	8,7	2,7	48	11	0	10870	10843	99,7	16,5	3,4
Mg	56	13	4	21720	11731	54	10,7	6	26	7	5	21720	10851	50	5,8	2,4	27	6	5	21720	13020	59,9	8,3	5,3
Mn	94	24	0	1500	1269,3	84,6	8,4	2,3	22	6	4	1500	1245,1	83	2,1	2,1	43	10	5	1500	1318,3	87,9	11	3
Hg	52	13	0	31,4	29,86	95,1	24,9	7,7	22	6	0	31,4	25,57	81,4	31,6	4,3	29	7	0	31,4	32,79	104,4	24,2	10,5
Mo	42	10	4		43,58		13,5	5,8	17	5	5		49,6		15,9	2,4	17	4	0		47,49		12,5	4,1
Ni	100	25	0	123,5	91,42	74	14,6	4,9	31	8	0	123,5	78,43	63,5	16,5	4,2	38	9	9	123,5	83,31	67,5	5,7	2,9
P	32	7	0		6212,5		5,3	2,3	24	6	0		6114,7		14,8	3,3	27	6	0		12655		89,8	7,4
K	58	14	0	44986	31613	70,3	16,7	5	13	4	0	44986	35334	78,5	20,5	1,5	15	3	4	44986	31861	70,8	8,7	1,8
Se	30	7	0	41,2	41,66	101,1	14,5	5,4	6	2	0	41,2	36,92	89,6	7,3	8,5	13	3	0	41,2	33,86	82,2	15	6,3
Ag	37	9	0	60	55,75	92,9	23,3	5,2	22	5	0	60	69,13	115,2	19,3	3,5	24	5	0	60	59,12	98,5	3,8	2,6
S	26	6	0	44600	29051	65,1	14,2	5,2	0	0	0	44600					10	2	0	44600	30770	69	6,7	1,1
Na	64	15	0	42920	26037	60,7	19	2,6	7	2	0	42920	32251	75,1	11,2	0,2	27	6	5	42920	28524	66,5	8,2	4,8
Sr	50	12	1	433	335,2	77,4	14,1	2,4	13	4	2	433	335,1	77,4	10	2,5	18	4	0	433	285,5	65,9	6,4	1,5
Sn	38	9	5		2500,4		5,1	2,8	11	3	4		2418,7		0,8	0,5	13	3	1		2481,5		9,7	1,2
Te	0	0	0						5	1	0		24,2		-	5,4	0	0	0					
Tl	7	3	0		5,74		69,8	6,5	4	1	0		1,44		-	9,1	4	1	0		1,54		-	2,8
Ti	26	6	1	8520	3538,2	41,5	21,8	3,1	19	5	0	8520	2604,4	30,6	11,1	1,7	13	3	0	8520	2871,3	33,7	3,6	2,3
V	47	12	7	41	37,44	91,3	11,3	2,2	13	4	9	41	34,79	84,9	8,3	1,6	21	5	0	41	39,72	96,9	23,1	3,1
Zn	109	26	3	25770	23851	92,6	9,8	2,9	24	6	0	25770	23202	90	6,8	1,9	34	8	9	25770	24205	93,9	4,8	3,8

N = Number of results, L = Number of laboratories, NA = Number of outliers, XREF = Conventional true value (where applicable)

Annex C
(informative)

Repeatability and reproducibility data

C.1 Performance characteristics

C.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 “Digestion for the extraction of aqua regia soluble fraction of trace elements in soil, sludge and treated biowaste” were established.

C.1.2 Materials used in the interlaboratory comparison study

The interlaboratory comparison of digestion for the extraction of aqua regia soluble fraction of trace elements in soil, sludge and treated biowaste was carried out with 20 -23 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 digestion for the extraction of aqua regia 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.CD.1 — Material types tested and components analysed in the interlaboratory comparison of the digestion for the extraction of aqua regia 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)	Sludge 1	Mix 1 of municipal WWTP sludges from North Rhine Westphalia, Germany	As,Cd, Cr, Cu, Fe, Mn, Ni, P, Pb, Zn
	Sludge 2	Mix 2 of municipal WWTP sludges from North Rhine Westphalia, Germany	As,Cd, Cr, Cu, Fe, Mn, Ni, P, Pb, Zn
Fine grained (< 2 mm)	Compost 1	Fresh compost from Vienna, Austria	As,Cd, Cr, Cu, Fe, Mn, Ni, P, Pb, Zn
	Compost 2	Compost from Germany	As,Cd, Cr, Cu, Fe, Mn, Ni, P, Pb, Zn
	Soil 1	A sludge amended soil from Pavia	As,Cd, Cr, Cu, Fe, Mn, Ni, P, Pb, Zn
	Soil 2	A sludge amended soul from Düsseldorf	As,Cd, Cr, Cu, Fe, Mn, Ni, P, 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 : $r_{test} = f \cdot \sqrt{2} \cdot s_{r,test}$ with the critical range factor f = 2.

For instance, the repeatability limit around a measurement result of 50 mg Cu /kg is ± 8.2 mg Cu/kg (i.e ± 16 % 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 Cu /kg is ± 11.8 mg Cu /kg (i.e ± 24 % 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.CD.2 — Results of the interlaboratory comparison studies of the digestion for the extraction of aqua regia soluble fraction of trace elements. All concentrations in mg/kg.

Total P by AR digestion method

Matrix	Parameter	Mean mg/kg	sr	sR	r	R	p	Outliers	Used number of data	Number of data reported below detection	Total no of data
Sludge 1	ICP P	28265	2.7%	14.3%	2112	11291	8	1	46	0	50
Sludge 2	ICP P	24359	1.7%	8.7%	1135	5914	7	2	42	0	50
Compost 2	ICP P	3129	4.2%	8.1%	365	707	8	1	48	0	52
Soil 1	ICP P	694	3.8%	7.2%	74	139	7	1	42	0	46
Soil 2	ICP P	739	5.4%	8.9%	111	184	8	0	47	0	47

Aqua regia Reflux

Matrix	Parameter	Mean mg/kg	sr	sR	r	R	p	Outliers	Used number of data	Number of data reported below detection	Total no of data
Sludge 1	Ref As	5.66	4.6%	24.1%	0.74	3.82	7	2	44	0	52
Sludge 2	Ref As	5.98	10.8%	32.8%	1.80	5.49	8	2	50	0	58
Compost 2	Ref As	3.64	9.7%	28.1%	0.99	2.87	9	1	58	0	62
Soil 1	Ref As	20.66	3.1%	8.1%	1.80	4.69	8	1	56	0	60
Soil 2	Ref As	7.20	6.3%	13.9%	1.28	2.79	7	2	50	0	58
Sludge 1	Ref Cd	2.13	5.4%	12.6%	0.32	0.75	7	4	38	0	54
Sludge 2	Ref Cd	2.58	11.2%	17.4%	0.81	1.25	9	2	53	0	61
Compost 2	Ref Cd	0.59	8.0%	13.0%	0.13	0.22	8	2	42	0	50
Soil 1	Ref Cd						0	7	41	0	69
Soil 2	Ref Cd	0.38	5.0%	20.1%	0.05	0.21	7	2	36	0	44

Sludge 1	Ref Cr	64.82	3.7%	7.0%	6.72	12.68	9	1	53	0
Sludge 2	Ref Cr	50.45	5.8%	9.7%	8.15	13.72	8	0	56	0
Compost 2	Ref Cr	24.31	5.7%	7.2%	3.90	4.89	8	2	58	0
Soil 1	Ref Cr	51.19	5.5%	8.1%	7.86	11.67	8	1	62	0
Soil 2	Ref Cr	18.07	5.7%	7.0%	2.86	3.56	8	1	62	0
Sludge 1	Ref Cu	399.26	3.2%	7.8%	35.23	87.22	9	1	56	0
Sludge 2	Ref Cu	429.14	6.2%	8.4%	74.59	101.05	10	2	60	0
Compost 2	Ref Cu	38.81	9.7%	11.2%	10.58	12.16	8	2	57	0
Soil 1	Ref Cu	26.41	5.9%	7.9%	4.34	5.82	9	0	68	0
Soil 2	Ref Cu	8.75	5.8%	9.7%	1.43	2.37	7	2	54	0
Sludge 1	Ref Ni	47.90	3.1%	8.7%	4.11	11.71	9	1	62	0
Sludge 2	Ref Ni	37.27	3.4%	12.8%	3.51	13.41	10	2	56	0
Compost 2	Ref Ni	13.59	6.2%	10.4%	2.34	3.95	9	2	64	0
Soil 1	Ref Ni	34.73	4.6%	6.0%	4.46	5.81	9	0	68	0
Soil 2	Ref Ni	4.12	9.9%	20.0%	1.14	2.30	8	2	62	0
Sludge 1	Ref Pb	143.45	3.1%	7.3%	12.54	29.46	10	0	66	0
Sludge 2	Ref Pb	79.93	3.3%	9.5%	7.39	21.19	10	1	61	0
Compost 2	Ref Pb	43.80	8.8%	12.5%	10.77	15.35	7	2	51	0
Soil 1	Ref Pb	25.30	4.4%	13.8%	3.11	9.79	6	2	44	0
Soil 2	Ref Pb	28.48	3.6%	7.1%	2.90	5.70	6	2	44	0
Sludge 1	Ref V	17.80	2.4%	14.4%	1.17	7.16	7	1	38	0
Sludge 2	Ref V	29.60	3.2%	14.4%	2.69	11.95	8	1	42	0
Compost 2	Ref V	16.87	6.1%	9.6%	2.87	4.53	9	0	54	0
Soil 1	Ref V	43.16	3.2%	9.5%	3.89	11.48	9	0	58	0
Soil 2	Ref V	32.21	1.9%	9.9%	1.69	8.97	7	2	40	0
Sludge 1	Ref Zn	1340.56	2.5%	9.6%	93.03	361.08	8	2	50	0
Sludge 2	Ref Zn	828.44	3.9%	8.4%	89.83	195.77	10	2	59	0
Compost 2	Ref Zn	206.98	7.7%	13.3%	44.39	77.19	8	2	55	0
Soil 1	Ref Zn	79.99	3.0%	5.5%	6.82	12.38	8	1	60	0
Soil 2	Ref Zn	58.65	4.8%	6.1%	7.90	10.00	9	1	66	0

Combination of all Aqua regia methods

Matrix	Parameter	Mean mg/kg	sr	sR	r	R	p	Outliers	Used number of data	Number of data reported below detection	T
Sludge 1	AR As	6.16	8.6%	30.4%	1.48	5.25	14	3	113	0	
Sludge 2	AR As	7.67	7.8%	14.3%	1.68	3.08	12	5	105	0	
Compost 2	AR As	4.22	12.0%	24.6%	1.42	2.91	15	2	125	0	
Soil 1	AR As	21.26	5.8%	15.3%	3.43	9.09	16	2	131	0	
Soil 2	AR As	7.81	8.0%	20.6%	1.76	4.50	15	2	124	0	
Sludge 1	AR Cd	2.12	7.7%	13.1%	0.45	0.78	17	5	122	0	
Sludge 2	AR Cd	2.63	8.2%	13.4%	0.61	0.99	19	4	135	0	
Compost 2	AR Cd	0.64	12.4%	17.6%	0.22	0.32	18	3	127	0	
Soil 1	AR Cd	0.28	21.8%	36.6%	0.17	0.29	13	4	85	0	

Soil 2	AR Cd	0.42	8.2%	16.6%	0.10	0.19	15	4	91	0	107
Sludge 1	AR Cr	69.48	9.0%	13.1%	17.49	25.48	21	2	162	0	170
Sludge 2	AR Cr	53.89	5.7%	16.4%	8.58	24.77	24	2	151	0	159
Compost 2	AR Cr	25.48	12.6%	15.5%	8.96	11.07	23	2	183	0	191
Soil 1	AR Cr	52.19	5.7%	13.1%	8.32	19.12	21	3	138	0	150
Soil 2	AR Cr	19.23	7.7%	18.0%	4.15	9.68	22	2	146	0	154
Sludge 1	AR Cu	398.42	3.3%	8.4%	37.33	93.72	20	2	122	0	130
Sludge 2	AR Cu	433.71	5.9%	8.8%	71.48	106.46	23	2	168	0	176
Compost 2	AR Cu	40.35	7.7%	10.0%	8.72	11.35	22	2	175	0	183
Soil 1	AR Cu	27.51	6.1%	9.2%	4.72	7.08	21	2	170	0	178
Soil 2	AR Cu	9.29	6.6%	14.6%	1.72	3.79	21	2	167	0	175
Sludge 1	AR Co	14.60	4.1%	9.9%	1.66	4.03	18	2	133	0	141
Sludge 2	AR Co	10.42	7.2%	13.2%	2.11	3.85	19	2	143	0	151
Compost 2	AR Co	4.53	11.8%	17.4%	1.50	2.20	18	2	145	0	153
Soil 1	AR Co	11.01	3.4%	7.6%	1.04	2.34	16	4	110	0	126
Soil 2	AR Co	2.23	7.4%	12.8%	0.46	0.80	16	4	130	0	146
Sludge 1	AR Fe	53503	2.6%	8.4%	3964.50	12547	18	3	109	0	121
Sludge 2	AR Fe	51183	2.8%	8.9%	3944.52	12701	19	4	119	0	135
Compost 2	AR Fe	10200	6.1%	14.4%	1733.63	4102	21	1	144	0	148
Soil 1	AR Fe	26029	3.6%	10.6%	2607.91	7754	17	3	116	0	128
Soil 2	AR Fe	8622	5.8%	9.4%	1402.15	2263	19	1	133	0	137
Sludge 1	AR Mn	906.00	2.2%	8.8%	55.36	224.2	19	2	107	0	115
Sludge 2	AR Mn	1407.34	4.1%	8.1%	162.42	318.78	21	2	153	0	161
Compost 2	AR Mn	447.74	4.8%	9.0%	60.70	113.38	22	1	166	0	170
Soil 1	AR Mn	504.36	4.7%	9.1%	65.87	128.09	21	1	161	0	165
Soil 2	AR Mn	410.74	3.9%	7.2%	44.55	82.50	19	3	114	0	126
Sludge 1	AR Ni	51.09	4.9%	7.7%	6.98	11.03	19	3	147	0	159
Sludge 2	AR Ni	41.12	4.7%	7.8%	5.46	9.02	20	4	161	0	177
Compost 2	AR Ni	14.52	9.1%	10.2%	3.70	4.14	19	4	155	0	171
Soil 1	AR Ni	35.33	4.5%	7.1%	4.45	7.04	21	1	174	0	178
Soil 2	AR Ni	4.46	11.1%	18.4%	1.38	2.30	19	3	128	0	140
Sludge 1	AR Pb	148.07	3.9%	8.4%	16.26	34.96	19	2	146	0	154
Sludge 2	AR Pb	84.72	4.0%	8.1%	9.39	19.19	21	1	160	0	164
Compost 2	AR Pb	44.55	10.2%	13.9%	12.74	17.35	20	2	167	0	175
Soil 1	AR Pb	25.25	7.6%	9.9%	5.40	7.01	19	2	153	0	161
Soil 2	AR Pb	29.59	3.9%	8.0%	3.21	6.64	19	2	125	0	133
Sludge 1	AR Sb	7.81	4.6%	11.7%	1.02	2.57	11	2	82	0	90
Sludge 2	AR Sb	9.11	8.5%	23.5%	2.16	5.99	11	3	84	0	96
Compost 2	AR Sb	1.16	24.0%	34.1%	0.78	1.11	10	2	73	0	81
Soil 1	AR Sb	1.01	8.8%	17.6%	0.25	0.50	7	5	53	0	73
Soil 2	AR Sb	0.39	12.7%	17.3%	0.14	0.19	5	3	42	0	54
Sludge 1	AR V	19.05	3.7%	13.2%	1.98	7.03	16	2	98	0	106
Sludge 2	AR V	32.26	6.2%	21.1%	5.57	19.10	17	2	103	0	111
Compost 2	AR V	17.91	7.6%	16.3%	3.79	8.15	16	2	96	0	104
Soil 1	AR V	43.24	5.3%	10.8%	6.38	13.09	15	3	90	0	102

Soil 2	AR V	33.50	7.6%	12.3%	7.13	11.50	16	2	131	0
Sludge 1	AR Zn	1350.01	4.8%	9.6%	180.52	363.75	21	2	152	0
Sludge 2	AR Zn	842.27	5.1%	9.2%	121.22	217.13	24	2	167	0
Compost 2	AR Zn	205.44	7.3%	12.0%	42.25	69.02	23	2	170	0
Soil 1	AR Zn	80.47	5.0%	7.8%	11.16	17.59	22	2	174	0
Soil 2	AR Zn	59.45	5.0%	8.3%	8.27	13.90	22	2	162	0

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Matrix	Parameter	Mean	sr	sR	r	R	p	Outliers	Used number of data	Number of data reported below detection
Compost 2	AR2 Cd	0.71	8.9%	14.3%	0.18	0.29	4	1	30	0
Sludge 2	A2 Cd	2.78	6.9%	7.9%	0.54	0.61	4	1	30	0
Soil 2	Cd AR2	0.47	7.7%	10.9%	0.10	0.14	4	1	19	0
Compost 2	Cr AR2	27.18	8.8%	14.8%	6.72	11.24	4	1	36	0
Sludge 2	A2 Cr	65.33	3.9%	13.6%	7.08	24.86	6	0	42	0
Soil 2	Cr AR2	20.48	9.3%	16.4%	5.31	9.37	5	0	39	0
Compost 2	Cu AR2	42.51	6.5%	6.9%	7.71	8.16	5	0	43	0
Sludge 2	Cu AR2	438.89	5.4%	7.1%	65.98	87.70	5	0	42	0
Soil 2	Cu AR2	9.14	6.8%	8.2%	1.75	2.09	4	1	32	0
Compost 2	Pb AR2	46.55	7.6%	9.0%	9.87	11.79	5	0	41	0
Sludge 2	Pb AR2	90.57	4.3%	5.7%	10.90	14.42	4	1	30	0
Soil 2	Pb AR2	30.46	5.1%	5.7%	4.38	4.86	4	1	27	0
Compost 2	Zn AR2	216	7.9%	11.7%	48.02	71.09	5	0	43	0
Sludge 2	Zn AR2	891	2.6%	6.8%	64.37	169.84	4	1	30	0
Soil 2	Zn AR2	56.9	4.9%	6.9%	7.81	10.99	4	1	27	0

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.

Note: The aqua regia microwave method at 175 °C has not been validated due to too limited number of results.

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