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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 is a working document.

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

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

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

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	EN 13346, EN 13657
Soil		
Soil improvers	Method A validated for: Biowaste, composted sludge	EN 13650
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

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Introduction

This document is developed in the project 'Horizontal'. It is the result of a desk study "Digestion of Solid Matrices" and aims at evaluation of the latest developments in assessing digestion of sludge, soil, treated biowaste and neighbouring fields. After discussion with all parties concerned in CEN and selection of a number of test methods described in this study the standard has been developed further as an modular horizontal method and has been validated within in the project 'Horizontal'.

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

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

This standard is a module, for analysis of inorganic parameters in solid matrices. This module concerns the digestion with aqua regia for the subsequent analysis of elements.

This document is a horizontal draft standard composed of parts of the following existing standards:

- ISO 11466 Soil quality – Extraction of trace elements soluble in aqua regia
- EN 13346 Characterization of sludges Determination of trace elements and phosphorus Aqua regia extraction methods
- EN 13650 Soil improvers and growing media – Extraction of aqua regia soluble elements
- EN 13657 Characterization of waste - Digestion for subsequent determination of aqua regia soluble portion of elements

The horizontal draft standard was prepared by comparing the different paragraphs of the standards for digestion with aqua regia and trying to look for equivalence and find a compromise where differences were obvious. In some cases differences were necessary because of the different matrices – this is pointed out in the specific paragraphs.

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

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

1 Scope

This European Standard 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

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

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

EN 15002: 2005, *Characterization of waste – Preparation of test portion from the laboratory sample*

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

EN xxx *Determination of Dry matter (HORIZONTAL)*

EN *Determiniation of TOC (HORIZONTAL)*

EN *Sampling (HORIZONTAL)*

EN *Sample pre-treatment (HORIZONTAL)*

3 Terms and definitions

For the purpose of this European Standard, the following definitions apply:

3.1 aqua regia

digestion solution obtained by mixing 1 volume of nitric acid $w(HNO_3)$ = 65 - 70 % and 3 volumes of hydrochloric acid w(HCl) = 35 - 37 %.

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

the 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

is the whole microwave digestion system (oven and associated equipment).

4 Safety remarks

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.

5 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±5°C for 10 ± 1 min in a closed vessel followed by filtration and adjusting the volume in a volumetric flask (method C) ;

6 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.

7 Reagents

7.1 General

All reagents shall be of at least recognized analytical grade and shall meet the purity requirements of the subsequent analysis.

7.2 Water

Comply with grade 2 of EN ISO 3696 or better. The water for preparation of reagent shall meet the requirement of the subsequent analysis.

7.3 Hydrochloric acid

c(HCl) = 12 mol/l; ρ = 1,18 kg/L; w(HCL) = 37 %

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.

7.4 Nitric acid

c($HN0_3$) = 16 mol/L, ρ = 1,4 kg/L; w(HNO_3) = 65 %

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.

7.5 Nitric acid, diluted, c (HNO3) = 0,5 mol/l

dilute 35 ml nitric acid (7.4) to one litre with water

7.6 Antifoaming agent

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

8 Apparatus

8.1 General

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.

8.2 Method A - Thermal heating reflux method:

8.2.1 Digestion vessel

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

NOTE1 Quartz vessels can be used instead of glass vessels.

NOTE2 It can be necessary to periodically clean the reaction vessels with a suitable surfactant to remove stubborn deposits.

8.2.2 Reflux condenser with vapour recovery system (non-return type)

Reflux condenser with a vapour recovery system capable of absorbing volatile compounds in diluted nitric acid (7.5), - see figure 1 (ISO 11466)

Materials in contact with the acid vapours shall be inert and shall meet the purity requirements of the subsequent analysis

Adaptable to digestion vessels (8.2.1) used in method A.

8.2.3 Absorption vessel

Volatile species trap, in an open digestion system capable of trapping one or more volatile measurement species, which may pass through the vapour recovery system (8.2.2).

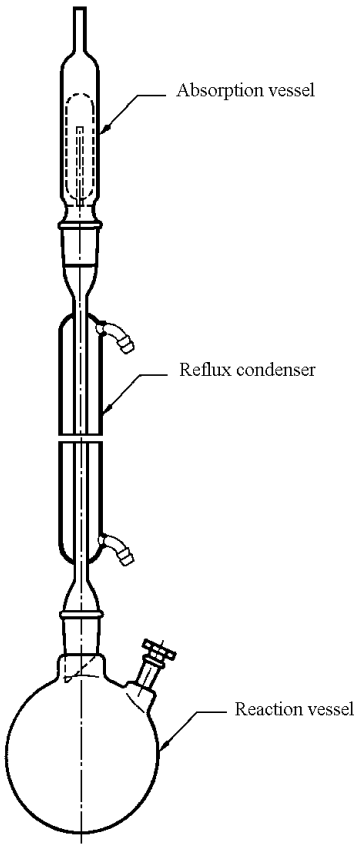

Figure 1 Reaction vessel, reflux condenser und absorption vessel (assembled)

8.2.4 Heating devices

heating mantle, thermostatic controlled or aluminium block thermostat

8.3 Method B Microwave heating with power control

8.3.1 Digestion vessel

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 should be at least 45 mL, and the vessel must 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.

8.3.2 Microwave oven

Corrosion resistant and well ventilated. All electronics must 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 of power. If necessary (referring to manufactures

specifications) calibration of the microwave unit has to be performed. A procedure to establish the relationship between microwave power and temperature is given in annex A.

The microwave oven has to comply to European and national regulations relevant to microwave radiation.

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.

8.4 Method C - Microwave heating with temperature control at 175±5°C

8.4.1 Digestion vessel

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

8.4.2 Heating devices

Corrosion resistant and well ventilated. All electronics must 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 seconds of sensing. Temperature sensors should be accurate to ± 2 °C (including the final reaction temperature of 175 ± 5 °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 ±12 W of the required power. Typical systems provide a nominal 600 W to 1400 W of power. 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 shall be periodically controlled at an elevated temperature according to the manufactures instructions. If the temperature deviates by more than 1 to 2 °C from the temperature measured by an external, calibrated temperature measurement system, the microwave temperature measurement system should be calibrated.

8.4.3 Rotating turntable

The speed of the turntable should be a minimum of 3 rpm. Other types of equipment used to assist in achieving uniformity of the microwave field may also be appropriate.

8.5 Sample containers

plastic and glass containers are both suitable

8.6 Filter papers

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

8.7 Volumetric flasks

capacity 25 ml, 50 ml or 100 ml.

8.8 Analytical balance

with an accuracy of 0,1 mg or better.

8.9 Boiling aids

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

9 Sampling and sample pre-treatment

9.1 Sampling

Sampling should be carried out in accordance with EN yyyy:200X (Horizontal standard module(s) for sampling of sludge, soil and treated biowaste).

Samples should 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.

9.2 Sample pre-treatment

The test portion should 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.

9.3 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: 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.

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.

10 Procedure

10.1 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.

10.2 Method A: Thermal heating under reflux conditions

10.2.1 Amount of test portion

Weigh approximately 3 g, to the nearest 0,001 g, of the prepared sample (9) and transfer to the 250 ml reaction vessel (8.2).

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.

10.2.2 Digestion

Moisten the sample with about 0,5 ml to 1,0 ml of water (7.2) and add, with mixing, 21 (± 0,1) ml of hydrochloric acid (7.3) followed by 7 (± 0,1) ml of nitric acid (7.4) drop wise if necessary to reduce foaming. Connect the condenser (8.2.2) to the reaction vessel; fill the absorption vessel (8.2.3) with nitric acid (7.4). 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 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 (8.2.4) 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 (7.5) or with 10 ml of water (7.2).

NOTE: 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 (8.7). In case of filtering dilute the content of the vessel, filter through the filter paper (8.4.3), and wash the insoluble residue with a diluted nitric acid (7.5). The method used has to be reported in the test report.

Transfer the digested sample into a suitable sized volumetric flask (8.7) and dilute to the mark with water (7.2).

10.3 Method B Microwave heating with power control

10.3.1 Amount of test portion

Weigh 0,5 g of the sample, accurately at 0,1 mg, prepared according to clause 9 and transfer it into the vessel (8.3.1).

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

10.3.2 Digestion

If necessary the sample may be moistened with a minimum amount of water (7.2). Then add separately 6± 0,1 ml of HCl (7.3) and 2± 0,1 ml of HNO3 (7.4) 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 (8.3.2) 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:Temperatures of about 115±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±5°C should be obtained for about 5 minutes after a heating period of 12±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.

NOTE: 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 (8.7). In case of filtering dilute the content of the vessel, filter through the filter paper (8.4.3), and wash the insoluble residue with a diluted nitric acid (7.5). The method used has to be reported in the test report.

Transfer the digested sample into a suitable sized volumetric flask (8.7) and dilute to the mark with water (7.2).

10.4 Method C - Microwave heating with temperature control at 175±5°C

10.4.1 Amount of test portion

Weigh 0,5 g of the sample, accurately at 0,1 mg, prepared according to clause 9 and transfer it into the vessel (8.3.1).

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

10.4.2 Digestion

Moisten the sample with two drops of water (7.2). Then add separately 6± 0,1 ml of HCl (7.3) and 2± 0,1 ml of HNO3 (7.4) 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 (7.6)

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 (7.4) for samples up to 40 % organic carbon.

Cap the extraction vessel (8.3.1) 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 ± 5 °C.

> NOTE: 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 ± 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 1: Centrifugation at 2000 – 3000 rpm for ten minutes is usually sufficient to clear the supernatant.

NOTE 2: Settling: If un-dissolved material, such as SiO_2, TiO_2, or other refractory oxides, remains, 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.

NOTE 3: Filtering: If necessary, the filtering apparatus must be thoroughly cleaned and pre-rinsed with dilute (approximately 10 % V/V) nitric acid. Filter the sample through a quantative filter paper into a second acid cleaned container or use membrane filtration.

11 Quality control

11.1 Control charts

Data from quality control should be recorded for each control sample in control charts.

11.2 Duplicate samples

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

Spiked samples or standard reference materials should be included with each group of samples processed, or every 20 samples, whichever is the greater number. A spiked sample should also be included whenever a new sample matrix is being analysed.

11.3 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.

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 ;

b) complete identification of the sample ;

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 test report may include the following information:

information about the sampling and sample pretreatment;

results of the analytical determinations carried out with other methods on the same samples, if any.

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: 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.

13 Performance characteristics

Performance data in terms of repeatability and reproducibility will be available after validation by a round robin test.

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.1.1 Power calibration

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. The conditions for each acid mixture and each batch containing the same specified number of vessels must be determined individually. Only identical acid mixtures and vessel models and specified numbers of vessels may be used in a given batch. For cavity type microwave equipment, calibration is accomplished by measuring the temperature rise in 1 kg of water exposed to microwave radiation for a fixed period of time. The analyst can relate power in watts to the partial power setting of the system. The calibration format required for laboratory microwave systems depends on the type of electronic system used by the manufacturer to provide partial microwave power. Few systems have an accurate and precise linear relationship between percent power settings and absorbed power. The calibration curve can be determined by a three-point calibration method or by the multiple point calibration. In calibrating the microwave unit, the power absorbed (for each power setting) by 1 kg of reagent water exposed to 120 seconds of microwave energy is determined by the expression

$$\text{Power (in watts)} = (T_1 - T_2) \times (34,.86)$$

where:

T_1 = Initial temperature of water (between 21 and 25 °C to nearest 0.1 °C)

T_2 = Final temperature of water (to nearest 0.1 °C)

Plot the power settings against the absorbed power to obtain a calibration relationship. Alternatively, use a microwave calibration program to analyse the calibration data. Interpolate the data to obtain the instrument settings needed to provide the wattage levels.

Equilibrate a large volume of water to room temperature (22 ± 3°C). One kg of reagent water is weighed (1 000,0 ± 0,1 g) into a fluorocarbon beaker or a beaker made of some other material that does not significantly absorb microwave energy (glass adsorbs microwave energy and is not recommended). The initial temperature of the water should be 22 ± 3 °C measured to ± 0,05°C. The covered beaker is circulated continuously (in the normal sample path) through the microwave field for 2 minutes 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 seconds to ± 0,05 °C. Three measurements at each power setting should be made. The absorbed power is determined by the following relationship:

(1) $$P = \frac{K \bullet C_p \bullet m \bullet \Delta T}{t}$$

(K)(C)(m)(T)
P p □
□
where

P = the apparent power absorbed by the sample in watts (W) (joule/sec)

K = the conversion factor for thermochemical calories sec^{-1} to watts (K = 4,184)

C_p = the heat capacity, thermal capacity, or specific heat [cal/g o°C)] of water

m = the mass of the water sample in grams (g)

ΔT= the final temperature minus the initial temperature (o°C)

t = the time in seconds (s)

Using the experimental conditions of 2 minutes (120 sec) and 1 kg (1000 g) of distilled water [heat capacity at 25 °oC is 0,.9997 cal/(g °oC)] the calibration equation simplifies to:

(2) P = (ΔT)•(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.1.2 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 (7.2) 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 Td, expressed in degrees Celsius, corresponding to the pressure p, expressed in kilo-Pascal, of diluted aqua regia using the approximation:

(3) $T_d = 38{,}9 + 3{,}00 \times (\ln p)^2$

Obtain for every power setting the corresponding microwave power from the relationship established in (1) A.1.1. 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, the actually supplied (effective) power must be determined. Also the relationship between the supplied power and the adjustment scale should be controlled. Furthermore the effective power should be checked periodically.

Calibration is carried out by heating a known amount of water during a fixed time period (e.g. 2 min) at different microwave power rates. Each raise of temperature has to be measured accuratly to ± 0,1 °C after each heating cycle. The absorbed power is calculated from the raise of temperature (formula see at the end of annex A).

Put e.g. 1 kg of water in a plastic beaker (or a beaker made of other material that does not absorb or reflect microwave energy, glass beaker must be avoided), stir and measure the temperature. Place the beaker in the microwave oven. Do always select the same position. Set the microwave during 2 min at full power. Remove the beaker, stir and measure the final temperature. Repeat this procedure also at lower power rates.

The power absorbed is calculated with the following formula:

$$P = \frac{Cp \cdot m \cdot \Delta T}{t}$$

where:

P is the power absorbed by the water in W (J/s)

Cp is the specific heat for water J/kg °C (= 4184 J/kg °C)

m is the mass of the water that is used for the calibration in kg

ΔT is the difference between initial and final temperature in °C

t is the time period in s

If in the described procedure 2 min and 1 kg water are used, the formula can be simplified to:

$$P = \Delta T \cdot 34{,}87$$

Annex B
(informative)

Validation of methods – Data of EN 13657

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 this standard has been organised and 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).

C.1 Inter-laboratory study

C.1.1 Selection of laboratories

A questionnaire has been circulated by all CEN/TC292/WG3 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 this standard. 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.

C.1.2 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.

C.1.3 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).

C.1.4 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, part 2, 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.

C.1.5 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*							
	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
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
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
B	23	6	0		38,7		37,3	15	11	3	0		30,87		33,8	6
Ba	63	15	0	735	572,8	77,9	20	4,6	19	5	1	735	391,8	53,3	16,9	7,7
Be	22	5	4		0,75		5,7	6,1	4	1	0		1,09		-	9,1
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
Ca	60	14	0	154600	140455	90,9	8,7	3,7	18	5	5	154600	145312	94	7,3	1,4
Cr	103	25	0	196	164,6	84	13,6	3,4	27	8	4	196	157,5	80,3	12,3	4,4
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
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
Fe	89	22	0	16100	13889	86,3	11,7	3,6	21	6	5	16100	13922	86,5	6,8	1,9
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
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
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
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
Mo	32	8	4		7,95		8,1	5,2	15	4	0		8,51		21,3	5,7
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
P	31	7	1	25600	27658	108	2,4	2,8	24	6	0	25600	30286	118,3	17,5	5
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
Se	13	3	0		4,74		60	12,3	4	1	0		3,33		-	7,9
Ag	38	9	0		190,9		23,1	1,9	24	6	0		205,9		6,6	5,2
S	26	6	0	10620	9188,4	86,5	17,7	2,4	2	1	0	10620	9180,0	86,4	-	-
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
Sr	46	11	5	1179	1027,2	87,1	4,9	2	11	3	1	1179	975,1	82,7	4,4	2,4
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
Te	0	0	0						0	0	0					
Tl	4	1	0		4,12		-	8,7	4	1	0		0,55		-	11,9
Ti	30	7	0	2771	299,8	10,8	57,6	21,5	21	6	0	2771	182,8	6,6	59,4	19
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
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

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:*		
	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
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
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
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
B	23	6	0		38,7		37,3	15	11	3	0		30,87		33,8	6	15	4	0
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
Be	22	5	4		0,75		5,7	6,1	4	1	0		1,09		-	9,1	13	3	0
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
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
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
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
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
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
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
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
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
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
Mo	32	8	4		7,95		8,1	5,2	15	4	0		8,51		21,3	5,7	16	4	0
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
P	31	7	1	25600	27658	108	2,4	2,8	24	6	0	25600	30286	118,3	17,5	5	14	3	0
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
Se	13	3	0		4,74		60	12,3	4	1	0		3,33		-	7,9	2	1	0
Ag	38	9	0		190,9		23,1	1,9	24	6	0		205,9		6,6	5,2	18	4	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
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
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
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
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
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
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
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

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" (B

	Method A: Microwave assisted with aqua regia in closed vessel								*Method - B: Microwave assisted, with aqua regia in semi-open vessel*							
	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
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
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
B	33	8	4		173,1		21,3	2,3	13	3	0		169,8		11,8	6,8
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
Be	30	9	1		1,89		15,9	10,4	4	1	0		1,75		-	4,4
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
Ca	48	11	0	88016	83012	94,3	8,2	3	24	6	0	88016	83050	94,4	5,3	3
Cr	106	26	1	863	210,7	24,4	17,7	6,5	30	8	1	863	164,7	19,1	15	2,6
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
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
Fe	92	23	0	21300	18866	88,6	10,5	3,2	26	7	0	21300	18598	87,3	4,3	2,2
Pb	101	25	3	10870	10146	93,3	8,7	2,5	31	8	0	10870	10206	93,9	8,7	2,7
Mg	56	13	4	21720	11731	54	10,7	6	26	7	5	21720	10851	50	5,8	2,4
Mn	94	24	0	1500	1269,3	84,6	8,4	2,3	22	6	4	1500	1245,1	83	2,1	2,1
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
Mo	42	10	4		43,58		13,5	5,8	17	5	5		49,6		15,9	2,4
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
P	32	7	0		6212,5		5,3	2,3	24	6	0		6114,7		14,8	3,3
K	58	14	0	44986	31613	70,3	16,7	5	13	4	0	44986	35334	78,5	20,5	1,5
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
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
S	26	6	0	44600	29051	65,1	14,2	5,2	0	0	0	44600				
Na	64	15	0	42920	26037	60,7	19	2,6	7	2	0	42920	32251	75,1	11,2	0,2
Sr	50	12	1	433	335,2	77,4	14,1	2,4	13	4	2	433	335,1	77,4	10	2,5
Sn	38	9	5		2500,4		5,1	2,8	11	3	4		2418,7		0,8	0,5
Te	0	0	0						5	1	0		24,2		-	5,4
Tl	7	3	0		5,74		69,8	6,5	4	1	0		1,44		-	9,1
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
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
Zn	109	26	3	25770	23851	92,6	9,8	2,9	24	6	0	25770	23202	90	6,8	1,9

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

Annex C
(informative)

The modular horizontal system

Annex D
(informative)

Information on WP xx and the project Horizontal

Bibliography

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