ICS

English version

Digestion of soil, sludge, and biowaste and waste for the extraction of aqua regia soluble elements

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Contents

Foreword

Introduction

This document is developed in the project 'Horizontal'. It is the result of the desk study digestion with aqua regia of solid matrices in the project and aims at an extraction standard for the subsequent analysis of elements. After discussion with all parties concerned in CEN and selection of a number of test methods described in this study will be developed further as an modular horizontal method and validated in the project 'Horizontal' .

Until now test methods determining properties of materials were often prepared in Technical Committees (TC's) 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 each other product. Consequently this resulted in a lot of duplicate work.

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 they 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 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.?Is this so in all cases?

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 D Bibliography which contains a brief overview of the modules that are or will be worked out in the project 'Horizontal.'

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

1 Scope

This standard specifies methods of digestion with aqua regia of the following materials: Soil, sludge, biowaste and waste. Solutions produced by the methods are suitable for analysis e.g. by atomic absorption spectrometry (FLAAS, HGAAS, CVAAS, GFAAS), inductively coupled plasma emission spectrometry (ICP-OES) and inductive coupled plasma mass spectrometry (ICP-MS).

The digestion with aqua regia is emperical 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 3696:1995	Water for analytical laboratory use - Specification and test methods (ISO 3696:1987)
EN xxx	Determination of dry matter (HORIZONTAL)
EN xxx	Determination of TOC (HORIZONTAL)

3 Definitions

For the purpose of this standard, the following definitions apply:

3.1 aqua regia

digestion solution obtained by mixing 1 volume of nitric acid (65 - 70 % m/m) and 3 volumes of hydrochloric acid (35 - 37 % m/m).

3.2 digestion

mineralization of the organic matter of a sample and dissolution of its mineral part, more or less completly, 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 subsample(s) sent to or received by the laboratory

3.5 test sample; analytical sample

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

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

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

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

3.7 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 XXXXX: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).

3.10 microwave unit cavity

the inner part of the microwave unit in which the digestion vessel is located and the microwave digestion is performed.

3.11 focused microwave unit

microwave unit in which a precise control of the electric field is made by using a wave guide

NOTE: Microwaves are focused at the bottom part of the digestion vessel.

4 Safety remarks

All this work has to be performed by skilled persons.

The reagents used within this EN are strongly corrosive and partly very toxic. 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 5 Principles

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 for about 2 h with a reflux condenser, followed by filtration and making up to volume in a volumetric flask (method A) ;
- _ microwave digestion for about 20 min in a closed vessel followed by filtration and making up to volume in a volumetric flask (method B) ;
- _ microwave digestion for about 30 min in an open vessel followed by filtration and making up to volume in a volumetric flask (method C).

NOTE: Other heating procedures can be used providing they demonstrate equivalent performance.

6 Reagents

6.1 General

All reagents used shall be of recognized analytical quality. Use water of grade 2 complying with EN ISO 3696.
Deionized water may be used, providing that it meets the requirements given above. It is recommended that the

same batch of water be used throughout a given batch of determinations and that blank determinations are carried out.

6.2 Water

Deionised or distilled water used shall conform to purity grade 2 of EN ISO 3696.

6.3 Hydrochloric acid

c(HCl) = 12 mol/l; _ _ 1,18 g/ml; 37 % mass/volume

6.4 Nitric acid

c(HNO3) = 15 mol/l; _ _ 1,42 g/ml; not less than 65 % mass/volume

6.5 Nitric acid, diluted

c (HNO3) = 0,5 mol/l, 35 ml nitric acid **(5.**4) is diluted to one litre of water

7 Apparatus

7.1 General

All glassware and plasticware 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 with 10 % nitric acid

7.2 Digestion vessel

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

Method A) glass flask, 250 ml for example ;
Method B) quartz or teflon vessel (at least 100 ml) equipped with a system capable of controlling overpressure in order to avoid explosion of the vessel

Method C) borosilicate glass vessel with a volume of at least 50 ml

> NOTE Quartz vessels can be used instead of glass vessels.NOTE: It can be necessary to periodically clean the reaction vessels with a suitable surfactant to remove stubborn deposits.

7.3 Vapour recovery system

Vapour recovery system, capable of recovering the evaporated digest during open digestion (e.g. reflux condenser) and designed to minimise losses

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

Adaptable to reaction vessels used in method A or C.

7.4 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 (7.3).

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7.5 Heating devices

Method A) a heating mantle or aluminium block heater;
Method B) a focused microwave oven with programmable power to control fast exothermic reaction . Method C) a microwave oven with a programmer module

> NOTE: For example an apparatus with microwave frequencies 2,45 GHz, electronic automatic power control which can be pilot-operated from 10 % to 99 % with 5 % increment for maximal power released of 200 W and a pump for reagent.

7.6 Filter papers

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

7.7 Volumetric flasks

capacity 25 ml, 50 ml or 100 ml.

7.8 Analytical balance

with an accuracy of 0,1 mg or better.

7.9 Boiling aids

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

8 Interferences and sources of error

8.1 General informations

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.

For the determination of elements forming volatile compounds (e.g. Hg, As, Pb) special care has to be taken at sample pre-treatment.

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.

Depending on the concentration of the element of interest and the wanted precision, a particular caution to the cleaning of the vessels shall be taken. It is recommended to clean the vessels with 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 because of precipitation with some ions of the solution. It is the case for insoluble chlorides, fluorides and sulphates for example. In this case the precipitate can be analysed separately.

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

8.2 Closed vessel system

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

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.

After digestion, the vessel shall be cooled to room temperature before opening. If not, losses of certain elements, particulary volatile elements as mercury or arsenic can occur.

8.3 Open vessel system for microwave or thermal heating digestion

Depending on the volatility of some elements of interest, the reflux system can be inefficient to condense the vapours and losses of some elements of interest can happen.

9 Pretreatment

9.1 Pretreatment of test portion

The test portion should be transferred into the vessel after a pre-treatment 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.

Pretreatment 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

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

9.2 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 manufacturers specifications the test portion should be devided 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 (7.2).

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 : 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 (6.2) and add, with mixing, 21 (± 0,1) ml of hydrochloric acid (6.3) followed by 7 (± 0,1) ml of nitric acid (6.4) dropwise if necessary to reduce foaming. Connect the condenser (7.3) to the reaction vessel, fill the absorption vessel (7.4) with aqua regia. 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.

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, carry out a determination. 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 preceeding further.

Transfer to the heating device (7.5) 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 (6.5) or with 10 ml of water (6.2).

NOTE: If the digested sample contains particulates which can clog nebulisers or interfere with injection of the sample, the sample can be centrifuged, allowed to settle, or filtered before transferring into a suitable sized volumetric flask (7.7). For example, the solution should be allowed to pass through the filter paper (7.6), then the insoluble residue washed onto the filter paper with a minimum of water (6.2). The method used has to be reported in the test report.

Transfer the digested sample into a suitable sized volumetric flask (7.7) and dilute to the mark with water (6.2).

10.3 Method B: Microwave assisted digestion in closed vessels

10.3.1 Amount of test portion

Weigh between 0,2 g to 1 g of the sample, accurately at 0,1 mg, prepared according to clause 9 and transfer it into the vessel (7.2).

10.3.2 Digestion

If necessary the sample may be moistened with a minimum amount of water (6.2). Then add separately 6 ml of HCl (6.3) and 2 ml of HNO_3 (6.4).

If a vigorous reaction occurs, allow the reaction to lie down before capping the vessel. Transfer the digestion vessels into the microwave oven (7.5) according to the manufactures instructions and start the following digestion procedure.

Table 1: Power programme

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 samplesNOTE If a temperature controlled microwave unit is used the appropiate temperatures may be calculated analogous to Annex A.

At the end of the programme let the vessels cool down to room temperature. 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, then transfer quantitatively the content of the vessels into a suitable sized volumetric flask and fill to the mark.

NOTE: If the digested sample contains particles which might clog the nebulizers of the measurement apparatus or which might interfere with the injection of the sample into the instrument, the sample solution may be centrifuged, allowed to settle or be filtered. In the case of filtration, dilute the content of the vessel before filtering, rinse and then fill to the mark of the volumetric flask. The method used has to be reported in the test report.

10.4 Method C: Microwave assisted digestion in open vessels

10.4.1 Amount of samples

Weigh between 0,2 g to 1,0 g of the sample, accurately at 0,1 mg, prepared according to clause 9 and transfer it into the vessel (7.2). If necessary the sample may be moistened with a minimum amount of water (6.2).

10.4.2 Digestion

Transfer the digestion vessels into the microwave oven (7.5) according to the manufactures instructions and start the following digestion procedure.

Table 2: Microwave programme

Step	Acid	Volume (ml)	Power (W)	Time (min)
1	HCl	9	0	0
2	HNO_3	3	40	15
3	HCl	9	0	0
4	HNO_3	3	40	15

NOTE: Introduction of the digestion vessel into the microwave cavity, reagent injection into the digestion vessel, temperature and/or power control can be done automatically or manually depending on the apparatus used.

NOTE If a temperature controlled microwave unit is used the appropiate temperatures may be calculated analogous to Annex A.

24 ml of aqua regia is sufficient only for the oxidation of about 0,4 g organic carbon. If there is any doubt of the amount of carbon present, carry out a determination. If there is more than 0,4 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 0,4 g. Do not add more than 10 ml of nitric acid at any time, and allow any reaction to subside before preceeding further.

At the end of the programme let the vessels cool down to room temperature.

10.4.3 Preparation of the solution for analysis

Transfer quantitatively the solution content of each vessel into a suitable sized volumetric flask and dilute to the mark.

NOTE: If the digested mixture contains particles which might clog the nebulizers of the measurement apparatus or which might interfere with the injection of the sample into the instrument, the sample may be centrifuged, allowed to settle or be filtered. In the case of filtration, dilute the content of the vessel before filtering, rinse and then dilute to the mark of the volumetric flask. The method used has to be reported in the test report.

11 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:

(a) information about the sampling and sample pretreatment;

(b) 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.

Annex A (normative): Calibration of the power adjustment for the microwave oven

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 data

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.

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

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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 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 D (informative): Bibliography

EN 45001:1989	General criteria for the operation of testing laboratories
EN 1233:1997	Water quality - Determination of chromium - Atomic Absorption Spectrometric Methods
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ISO 5725-2:1994	Accuracy (trueness and precision) of measurement methods and results - Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method
ISO 5725-3:1994	Accuracy (trueness and precision) of measurement methods and results - Part 3: Intermediate measures of the precision of a standard measurement method
ISO 5725-4:1994	Accuracy (trueness and precision) of measurement methods and results - Part 4: Basic methods for the determination of the trueness of a standard measurement method
ISO 5725-5:1994	Accuracy (trueness and precision) of measurement methods and results - Part 5: Alternative methods for the determination of the precision of a standard measurement method
ISO 5725-6:1994	Accuracy (trueness and precision) of measurement methods and results - Part 6: Use in practice of accuracy values
ISO 11466:1995	Soil quality - Extraction of trace elements soluble in aqua regia
EN 13346:2000	Characterization of sludges Determination of trace elements and phosphorus Aqua regia extraction methods
EN 13650:2001	Soil improvers and growing media – Extraction of aqua regia soluble elements
EN 13657:2002	Characterization of waste - Digestion for subsequent determination of aqua regia soluble portion of elements
EN ISO 5961:1995	Water quality - Determination of cadmium
EN ISO 11969:1997	Water quality - Determination of arsenic - Atomic Absorption Spectrometry method (hydride technique)
ISO 8288:1986	Water quality - Determination of cobalt, nickel, copper, zinc, cadmium and lead - Flame atomic absorption spectrometric methods
ISO 11885:1996	Determination of 33 elements by ICP-AES
EPA Method 3015:1990	Microwave assisted acid digestion of aqueous samples and extracts
EPA Method 3051:1994	Microwave assisted acid digestion of sediments, sludges, soils and oils
EPA Method 3052:1995	Microwave assisted acid digestion of siliceous and organically based materials