Characterization of waste — Digestion for subsequent determination of aqua regia soluble portion of elements

The European Standard EN 13657:2002 has the status of a British Standard

ICS 13.030.40

British Standards

National foreword

This British Standard is the official English language version of EN 13657:2002.

The UK participation in its preparation was entrusted by Technical Committee B/508, Waste management, to Subcommittee B/508/3, Characterization of waste, which has the responsibility to:

- aid enquirers to understand the text;
- present to the responsible international/European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;
- monitor related international and European developments and promulgate them in the UK.

A list of organizations represented on this subcommittee can be obtained on request to its secretary.

Cross-references

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This British Standard, having been prepared under the direction of the Building and Civil Engineering Sector Policy and Strategy Committee, was published under the authority of the Standards Policy and Strategy Committee on 22 October 2002

Summary of pages

This document comprises a front cover, an inside front cover, the EN title page, pages 2 to 26, an inside back cover and a back cover.

The BSI copyright date displayed in this document indicates when the document was last issued.

Amendments issued since publication

Amd. No.	Date	Comments

ISBN 0 580 40624 5

EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

EN 13657

October 2002

ICS 13.030.40

English version

Characterization of waste - Digestion for subsequent determination of aqua regia soluble portion of elements

Caractérisation des déchets - Digestion en vue de la détermination ultérieure de la part des éléments solubles dans l'eau régale contenus dans les déchets

Charakterisierung von Abfällen - Aufschluss zur anschließenden Bestimmung des in Königswasser löslichen Anteils an Elementen in Abfällen

This European Standard was approved by CEN on 19 August 2002.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Management Centre or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Management Centre has the same status as the official versions.

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COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

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Ref. No. EN 13657:2002 E

Contents

Foreword

This document EN 13657:2002 has been prepared by Technical Committee CEN/TC 292 "Characterization of waste", the secretariat of which is held by NEN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by April 2003, and conflicting national standards shall be withdrawn at the latest by April 2003.

In this European Standard the annex A is normative and the annexe B is informative.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Malta, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

Introduction

The aim of this European Standard is to describe suitable methods for the extraction of elements in waste, soluble by digestion with aqua regia, i. e. aqua regia soluble elements.

For those types of waste, where the sample material by the described digestion with aqua regia are not brought totally in solution, the obtained results will not be the total amount of the elements in the waste.

The obtained results of aqua regia soluble elements cannot be regarded as available for leaching, as the digestion with aqua regia is too vigorous to represent natural processes.

1 Scope

This European Standard specifies methods of digestion with aqua regia. 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 will not necessarily release all elements completely. However for most environmental application and waste characterization the results fit for the purpose.

The method is applicable to the digestion of waste for example for the following elements: Al, Sb, As, B, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Mo, Ni, P, K, Se, Ag, S, Na, Sr, Sn, Te, Ti, Tl, V, Zn.

2 Normative references

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the 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).*

3 Terms and definitions

For the purposes of this European Standard, the following terms and definitions apply.

3.1
aqua regia
digestion solution obtained by mixing 1 volume of nitric acid (65 % m/m to 70 % m/m) and 3 volumes of hydrochloric acid (35 % m/m to 37 % m/m)

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

[ENV 12506:2001]

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

[ENV 12506:2001]

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

[ENV 12506:2001]

3.6

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

[ENV 12506:2001]

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 residue
dry matter expressed as a percentage by mass after drying at 105 °C ± 5 °C to the constancy of weight

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
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 Sample

5.1 Sample pre-treatment

The test portion should be transferred into the vessel as it is without any pre-treatment if possible.This is applicable only if the test portion is representative for the laboratory sample and the effectiveness of the digestion is proven.

If these conditions are not met a pre-treatment of the laboratory sample is necessary. 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 waste or homogenizing by use of a high speed mixer or sonification for liquid samples.

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

5.2 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 seperately. 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.

6 Equipment

6.1 Closed vessel system

6.1.1 Microwave unit

The microwave unit shall provide programmable power which can be programmed to within ± 10 W of the required power. Typical units provide a nominal 600 W to 1 200 W of power. If necessary (referring to manufactures specifications) calibration of the microwave unit has to be performed (see annex A).

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

The microwave unit 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.

All electronics are sufficiently protected against corrosion for safe operation. All parts which could have contact with acids or their vapours have to be corrosion resistant.

The microwave unit 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.

6.1.2 Digestion vessels

The vessels used in the microwave unit shall be equiped with a pressure relieve valve or another technical equipment which avoids the bursting of the vessels at suddenly occuring excess pressure. The material of the vessels has to be inert to the acids used for digestion. The digestion vessel shall withstand the pressure of at least 8 bar. If the amount of organic carbon exceeds 100 mg it has to be ensured that the digestion vessel is capable of withstanding higher pressures.

6.2 Semi-open vessel system

6.2.1 Microwave unit

The microwave unit shall be equiped with power control. Typical unit provides a nominal 200 W or 300 W of released power. If necessary, calibration of the microwave unit has to be performed by the manufacturer.

The microwave unit shall comply with European and national regulations relevant to microwave radiation.

The microwave unit shall be designed for use in a laboratory hood.

Fume extraction equipment, used to extract acid vapours from the reaction vessels during the digestion program, shall have sufficient flow rate to prevent the release of dangerous vapours into the laboratory.

All electronics shall be sufficiently protected against corrosion for safe operation. All parts which can be in contact with acids or their vapours shall be corrosion resistant.

6.2.2 Digestion vessels

The vessel is working at atmospheric pressure and has to be connected with a reflux system to avoid losses of analytes. The vessel shall comply with the manufactures specifications and should have a minimum volume of 50 ml.

The material of the vessels has to be inert to the reagents used for digestion.

6.3 Apparatus for thermal heating digestion

6.3.1 Reaction vessels

The reaction vessel shall have a volume of at least 5 times of the volume of the aqua regia used.

6.3.2 Reflux condenser

Water-cooled reflux condenser, minimum assembled length 340 mm with conical ground joints.

6.3.3 Absorption vessel

Non-return type.

6.3.4 Roughened glass beards

Diameter 2 mm to 3 mm (or anti bumping granules), acid washed.

6.3.5 Temperature-controlled heating apparatus

Capable of heating the contents of the reaction vessel to reflux temperature.

6.4 General equipment

The following equipment is used by the systems described in 6.1, 6.2 and 6.3:

— volumetric graduated flasks and pipettes of adequate size;

— filter equipment of adequate chemical resistance and purity or centrifuge;

— analytical balance, with an error limit of 0,1 mg.

For the preparation of standards and the treatment and storage of samples for determination of boron the use of borosilicate glass shall be avoided.

7 Reagents

Use reagents of analytical grade quality or better and water of grade 1 according to EN ISO 3696:1995.

— Hydrochloric acid (HCl): a mass fraction of 35 % to 37 %;

— Nitric acid (HNO_3): a mass fraction of 65 % to 70 %;

— Diluted nitric acid: $c(HNO_3) = 0{,}5$ mol/l.

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 Semi-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 Procedure

9.1 Blank test

To detect possible contaminations from vessels and/or reagents, blank tests shall be carried out in parallel by the same digestion procedure and filtration if appropriate, using the same quantities of all reagents but omitting the test portion.

9.2 Procedure for microwave assisted digestion in closed vessels

Weigh between 0,2 g to 0,5 g of the sample, to the nearest 0,1 mg, prepared according to clause 5 and transfer it into the vessel. If necessary the sample may be moistened with a minimum amount of water. Then add seperately 6 ml of HCl and 2 ml of HNO_3.

It is necessary to use only one specific reaction mixture as well as the same kind of matrix in the same quantity of test portion in a single batch in the microwave unit cavity to ensure consistent reaction conditions.

If a vigorous reaction occurs, allow the reaction to lie down before capping the vessel. Transfer the digestion vessels into the microwave unit cavity 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 power programme (see Table 1) 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.

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.

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.

9.3 Procedure for microwave assisted digestion in semi-open vessels

9.3.1 Amount of samples

Weigh between 0,2 g to 1,0 g of the sample, to the nearest 0,1 mg, prepared according to clause 5 and transfer it into the vessel. If necessary the sample may be moistened with a minimum amount of water.

9.3.2 Digestion

Transfer the digestion vessels into the microwave unit cavity 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.

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.

9.3.3 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.

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.

9.4 Procedure for thermal heating digestion in reflux systems

9.4.1 Amount of samples

Weigh 1 g to 10 g, to the nearest 0,1 mg of the prepared sample and transfer to the reaction vessel.

9.4.2 Digestion

Add, while mixing, the appropriate amount of hydrochloric acid followed by nitric acid, dropwise if necessary to reduce foaming. The mass: volume ratio between sample and acid mixture shall be 1:10. Connect the condenser to the reaction vessel, fill the absorption vessel with aqua regia. Connect the absorption vessel to the condenser and allow to stand at room temperature until effervescence lies down to allow for slow oxidation of the organic matter in the test portion.

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.

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.

9.4.3 Preparation of the solution for analysis

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.

10 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 include at least the following information:

a) a reference to this European Standard;

b) name and address of the testing laboratory and location where the test was carried out when different from the address of the testing laboratory;

c) unique identification of report (such as serial number) and of each page, and total number of pages of the report;

d) identification and description of the laboratory sample(s);

e) quantity and date of receipt of the laboratory sample(s) and date(s) of performance of the test;

f) relevant information about the digestion procedure and the sample(s):

- quantity of each test portion;
- sample(s) pre-treatment (e.g. drying, milling);
  - reference to the actual digestion method (e.g. digestion system, reagents, microwave programme);
  - technique used for the separation of the solid residue, if any (e.g. centrifugation, filtering);
  - description and reasons for any deviation from the standard procedures;

- method and result of dry matter determination;

g) a signature and title or an equivalent marking of person(s) accepting technical responsibility for the test report and date of issue;

h) a statement, that the information contained in the report relate exclusively to the laboratory sample(s) tested;

i) a statement that the report shall not be reproduced except in full without the written approval of the testing laboratory.

The test report may include the following information:

1) information about the sampling;

2) 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.

A test report shall not include any advice or recommendation arising from the test results.

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

Annex A
(normative)

Calibration of the power adjustment

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 (see formula at the end of this annex).

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:

$$P = \frac{Cp \quad m \quad\quad T}{t}$$

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;

T 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:

$$P = \quad T \quad 34{,}87$$

Annex B
(informative)

Validation

During 1998 to1999 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).

B.1 Inter-laboratory study

B.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.

B.1.2 Selection of samples

The materials to be used in the inter-laboratory study had to satisfy all the following requisites:

— representative of a wide range of matrices, as much as possible;

— available in a homogeneous form or, alternatively, not too difficult to grind, sieve and homogenise;

— available in a sufficient quantity;

After a survey, the following materials have been found:

— city waste incineration fly ash ("oxidised" matrix) (CEN6/99 FLY ASH CW6 POWDER);

— city waste incineration bottom ash ("silicate" matrix) (CEN7/99 "ASH CW4 POWDER");

— ink waste sludge (organic matrix) (CEN8/99 "INK WASTE CW12 POWDER");

— electronic industry sludge ("metallic" matrix) (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 of the above four materials). This has been used as a tool for discarding from the evaluation laboratories that did not prove their analytical ability for some matrices/elements.

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

— BCR 146R (sewage sludge);

— BCR 176 (city waste incineration ash).

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

B.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).

B.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.

B.1.5 Conclusions

The performances of the three methods should 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.

Table B.1 – Sample CEN 6/99 "Fly ash cw 6 powder"

SAMPLE CEN6/99 "FLY ASH CW6 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	71	18	0		40382		25,4	4,6	24	6	2		39559		5,2	4,6	38	9	0		41811		20,2	2,8
Sb	52	12	0		980,8		24,4	4,6	12	4	0		945,4		28,2	3,7	18	4	0		800,1		21,2	2
As	57	14	0		41,67		30,6	8,5	9	3	1		39,99		17,4	1,5	36	8	0		35,22		26,5	7,7
B	37	9	1		210,2		16,2	3,7	13	3	0		209,6		13,6	10,8	19	4	0		269,6		25,1	6,8
Ba	58	14	1		844,3		36,8	11,3	20	5	0		971,9		33,5	4,9	19	4	5		196,6		29,5	14,7
Be	26	6	5		0,92		11,7	5,9	4	1	0		1,04		-	2,2	9	2	0		0,91		9,6	2,6
Cd	105	26	0		419,7		14,1	3,6	26	7	5		407,9		5,1	2,6	45	10	5		441,4		7,5	3,1
Ca	50	12	5		144174		14,2	4,6	24	6	0		145420		5,1	2,8	27	6	6		154346		10	5,1
Cr	103	25	0		422,5		12,1	4,8	22	6	5		390,0		11,5	1,7	54	12	0		386,2		20,6	3,4
Co	81	20	0		24,77		27,9	6,3	22	6	0		25,51		20	7,3	46	10	0		20,25		29,3	4,2
Cu	104	25	0		1868,5		20,3	4,4	31	8	0		2038,8		12,8	4,1	49	11	5		1983,8		15,4	6,1
Fe	83	21	0		9574,8		12,6	3,7	27	7	3		9449,0		11,3	4,1	44	10	5		9416,9		14	5,5
Pb	96	24	0		10035		11,5	4,4	26	7	0		9990,7		6,1	2,6	51	12	1		10448		12,8	4,1
Mg	51	12	5		9936,5		8,8	2,7	23	6	3		10489		6,6	6,6	33	7	0		10198		16,9	5,6
Mn	91	23	0		489,8		12,7	3,8	31	8	0		477,7		9,7	3,3	50	11	0		471,1		15,4	5
Hg	42	11	0		5,56		37,4	5,3	14	4	6		5,26		12,5	5,6	31	7	0		5,01		29,9	11,5
Mo	38	9	8		24,77		9,6	8,3	18	5	0		42,7		34,7	4	15	3	4		26,43		1,6	7
Ni	93	23	5		58,2		13	6,3	25	6	0		55,41		9,8	4	49	11	0		52,44		22,2	6,6
P	32	7	0		5706,7		5,8	2,9	17	4	12		5296,1		0,8	4,4	14	3	0		5195,9		4,9	4,8
K	57	14	1		64277		9,5	3,9	19	5	0		61282		26,7	4	26	6	0		56012		15,2	9,8
Se	22	5	4		37,33		8,9	12,4	10	3	0		30,62		39	2,4	14	3	0		31,53		24,2	6,5
Ag	33	8	5		354,1		17,3	6	13	3	0		379,0		23,1	17,2	29	6	0		343,1		17,8	6,8
S	24	5	0		37148		10,3	1,5	7	2	0		41960		14,3	3,8	10	2	0		35858		11	6,3
Na	58	14	0		60057		12,5	3,4	11	3	0		49587		32,1	1,1	37	8	1		58956		24,6	5,2
Sr	50	12	1		266,0		11,5	3,8	15	4	0		270,3		11,7	4,2	14	3	5		271,4		2,8	8,5
Sn	39	9	1		1252,9		7,9	4,3	15	4	0		1317,1		20,4	2,4	13	3	1		1351,6		3,4	3,6
Te	0	0	0						0	0	0						0	0	0					
Tl	6	2	0		22,98		82,8	9,2	8	2	0		22,71		105,5	8,2	9	3	0		2,45		67,6	60,3
Ti	26	6	4		5129,7		14,2	8,4	14	4	0		3142,3		20,5	3,9	14	3	0		3350,9		2,5	8
V	46	11	4		22,12		14,9	4,8	19	5	0		33,18		67,6	5,4	22	5	5		19,31		46	3
Zn	102	24	2		27244		9,9	3,6	27	7	2		27925		9,7	2,4	53	12	1		25886		20,9	5,9

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

SAMPLE CEN7/99 "ASH CW4 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	77	19	2		55564		17,7	7,5	25	7	1		46200		9,1	1,7	38	9	0		53085		22,3	7,3
Sb	55	13	0		255,9		20	9,6	14	4	0		263,9		12,5	3	22	5	0		226,5		13,8	10,1
As	68	17	0		83,77		27,6	8	14	4	0		88,29		8,9	1,9	28	6	4		78,88		6,6	5,2
B	38	9	5		176,4		9,4	3,4	13	3	0		188,6		7,3	15,6	19	4	0		164,1		6,1	2,9
Ba	65	16	0		1320,5		108,8	15,4	20	5	0		2053,0		84,2	17,4	14	3	4		163,2		17,2	47,1
Be	36	9	0		1,78		17,4	4,5	4	1	0		1,8		-	10,7	13	3	0		1,87		9,4	3,9
Cd	111	27	1		513,2		12,7	4,9	31	8	0		526,9		5,7	1,6	45	10	0		514,9		15,2	4,6
Ca	56	13	4		79614		12,9	6,7	23	6	1		83128		5,8	1,5	24	5	5		83584		4,7	1,7
Cr	107	26	0		206,9		17,6	9	17	5	14		157,1		1,5	5,6	49	11	5		186,9		13,3	5,2
Co	76	19	4		26,73		22,6	5,8	20	5	0		30,15		17,3	6,3	45	10	4		23,25		27	7,1
Cu	115	28	1		1135,8		13	4,5	31	8	0		1142,0		6,9	2,1	45	10	5		1149,5		18,4	4,3
Fe	91	23	1		18024		11	5,4	24	7	2		17419		4,2	1,8	44	10	5		17644		14,5	3,5
Pb	103	26	1		11044		10,8	4,6	30	8	1		11225		4,2	1,7	52	12	0		11816		16,5	4,5
Mg	64	15	0		11916		12,6	6,9	22	6	1		11047		2,8	1,9	34	7	0		13072		17,4	4,3
Mn	98	25	1		1173,6		12	4,8	30	8	1		1178,1		4,8	2,1	52	12	0		1249,7		17,4	3,9
Hg	52	13	0		29,82		17,2	6,9	20	5	0		28,45		18,1	6,3	30	7	0		31,31		20,2	10,9
Mo	41	10	1		42,84		9,8	4,9	17	5	0		52,31		18,8	2,4	14	3	1		46,37		13,1	2,9
Ni	110	28	0		86,63		19,2	6,4	31	8	0		77,75		10,7	3,5	45	10	5		84,76		11	3,8
P	27	6	5		6074,1		2,3	2,2	24	6	0		5914,5		5,2	5,9	19	4	0		5839,1		5,8	2,4
K	61	15	1		33445		12,2	2,9	21	6	0		29187		38,1	2,5	31	7	5		26720		32,4	3,8
Se	29	7	1		40,49		12,1	10,2	10	3	0		33,71		45,9	5,4	8	2	1		30,54		6,1	8,2
Ag	38	9	0		65,12		24,9	7,9	13	3	0		70,87		8,9	4,9	24	5	0		63,05		7,8	6,6
S	26	6	0		29916		24,2	6,6	5	1	0		23754		-	2,7	10	2	0		32304		7,3	1,9
Na	62	15	2		28404		20,1	5,3	7	2	0		24694		25	1	33	7	5		30315		12,9	5,9
Sr	50	12	1		316,2		13,5	2,4	15	4	0		311,7		12,6	3,5	17	4	1		273,8		8	3,7
Sn	44	10	0		2196,2		10,6	7,3	15	4	0		2269,9		7,1	7,8	14	3	0		2346,1		10	4,1
Te	0	0	0						0	0	0						0	0	0					
Tl	10	3	0		29,69		103,8	3,2	4	1	0		2,23		-	10,2	4	1	0		2,36		-	11,4
Ti	30	7	0		3462,1		23,8	8,9	19	5	0		2422,7		11	7,4	13	3	0		2750,9		4,8	4,7
V	54	13	4		37,73		13,1	5,4	22	6	0		45,58		38,3	4,3	27	6	5		30,46		45,6	4,4
Zn	105	26	2		24716		12,1	2,6	28	7	1		24402		9,5	1,6	54	12	0		23795		23,1	7,8

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

SAMPLE CEN8/99 "INK WASTE CW12 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	72	18	2		1387,8		22,5	8,7	22	6	4		1250,9		10,6	3	37	9	0		1225,2		26,9	8,1
Sb	28	7	0		53,65		89,8	12,4	6	2	0		23,58		64,4	15,8	8	2	0		30,3		116,9	1,4
As	30	7	5		5,71		34,1	14,6	5	2	1		5,74		17,3	0,8	22	6	4		6,33		10,6	4,1
B	24	6	4		44,06		68,7	6	13	3	0		113,7		76,4	21,4	11	3	0		22,06		75,5	18,9
Ba	64	15	0		97,43		19,1	8,3	24	6	2		75,61		25,2	7,6	23	5	0		80,11		9,6	12,9
Be	13	3	0		0,42		116,9	8,9	0	0	0						9	2	0		0,17		44,8	31,2
Cd	70	18	6		4,59		117,3	12,1	18	4	5		0,99		79,5	24,3	21	5	0		0,72		58,9	40,9
Ca	56	13	0		115640		8,5	5,2	24	6	0		120616		6,3	4,9	33	7	0		116663		7,3	4,8
Cr	104	25	5		3624,0		11,4	4,9	30	8	1		3710,9		11,4	2,3	54	12	0		3529,9		12,4	6,6
Co	67	17	4		14,56		23,1	5,8	13	4	5		16,55		19,9	6,4	40	9	0		14,3		19,1	10,1
Cu	113	27	2		12285		10,3	3,1	31	8	0		12703		9,1	2,4	53	12	1		12782		14,5	6,6
Fe	87	21	0		76961		9,7	4,9	26	7	0		78738		8,3	1,6	44	10	0		73215		10,8	9,6
Pb	99	24	0		5855,9		7,9	4	27	7	4		6033,8		8,3	1,9	52	12	0		6042,2		13,5	5,7
Mg	57	14	2		1039,5		22	5	25	7	1		954,7		11,8	2,7	24	5	0		942,9		13,6	8
Mn	97	24	4		544,3		8,7	4	31	8	0		558,8		10,8	2,5	52	12	0		521,1		7,7	4
Hg	45	12	5		2,0		41,3	14,9	15	4	1		2,29		27,7	3	27	6	0		1,94		18,3	14,1
Mo	16	4	0		3,95		39,9	14,9	9	3	5		3,2		14,8	3,5	14	3	0		3,3		1,4	19,7
Ni	91	23	9		20,67		31,8	10,5	21	5	0		21,14		13,7	5	45	10	1		22,49		39	23,4
P	28	6	0		14215		3,2	2,2	24	6	0		13350		18	2,6	19	4	0		13305		6,2	2,5
K	56	14	1		997,3		47,9	14,2	17	5	0		875,5		44,4	4,3	26	7	0		661,5		75,6	8,6
Se	7	2	1		5,67		2,1	13,3	4	1	0		3,55		-	21,1	4	1	0		2,9		-	10,7
Ag	17	5	0		4,34		72	58,6	5	1	0		0,78		-	1,6	7	2	0		1,79		3,8	4,6
S	23	5	1		28708		9,4	2,4	0	0	0						10	2	0		27399		11,2	1,6
Na	54	13	5		4664,4		22,4	2,6	7	2	0		5685,4		17,3	2,5	33	7	0		5265,5		32,9	8,4
Sr	47	11	0		121,5		14,5	3,4	17	5	0		112,6		7	2,4	18	4	0		108,4		9,4	1,3
Sn	12	3	0		8,64		110,8	2,7	0	0	0						2	1	0		1,18		-	2,2
Te	0	0	0						5	1	0		20,8		-	7,9	0	0	0					
Tl	13	3	0		62,47		75,8	4,4	0	0	0						3	1	0				-	32,7
Ti	18	5	5		96,75		4,2	5,5	11	4	1		71,82		11,2	2,6	14	3	0		78,84		5,3	27,8
V	43	10	1		16,18		34,2	5,9	16	4	0		17,24		28,9	13,3	22	5	5		16,97		33,2	20,5
Zn	103	25	7		1173,2		11,5	3,2	31	8	0		1346,6		13,2	5,8	44	10	6		1136,5		9,3	6,6

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

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)

B.2 Robustness study

B.2.1 General

Two key variables have been taken into account: particle size and mass of test portions; their influence on microwave-assisted digestion method in closed vessels (see 9.2) has been independently evaluated; each variable has been varied on different levels and each digestion has been performed at least in four replicates on a portion of the same original sample (coal bottom ash); all digested solutions and blanks have been analyzed for the determination of Al, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Ni, Pb, Se, Sn, Ti, V, Zn. A sequential inductively coupled plasma optical emission spectrometer (ICP-OES) with pneumatic nebulizer was used for determination of most elements; As, Cd, and Se were determined with both ICP-OES and a graphite furnace atomic absorption spectrometer (GFAAS) with Zeeman background correction system; Hg was determined by using a cold vapour atomic absorption spectrometer (CVAAS). Evaluation has not been possible for As, Cd, Hg and Se because of their very low concentration (below limits of detection).

Levels of variables:

— sample particle size (digestions performed by weighing a test portion of 300 mg):

(1) below 90 µm (4 replicates);

(2) between 400 and 560 µm (8 replicates).

— mass of test portion (digestions performed on the < 90 µm fraction of the sample):

(1) 100 mg (4 replicates);

(2) 300 mg (4 replicates);

(3) 500 mg (4 replicates).

B.2.2 Analytical method

Table B.7 — Analytical results (values in mg/kg)

mg	µm	Al	StdDev	Ba	StdDev	Be	StdDev	Mg	StdDev
100	90	108614	7001	1400	89	6,7	0,4	615,5	34,0
300	90	100263	4301	1162	22	5,7	0,2	560,0	18,6
500	90	100365	4642	1137	65	5,6	0,2	545,8	21,7
300	560	81163	8667	949	77	4,5	0,4	420,1	42,9

mg	µm	Co	StdDev	Cr	StdDev	Cu	StdDev	Fe	StdDev
100	90	30,9	2,2	40,7	2,1	26,5	0,9	24873	1946
300	90	25,2	1,0	34,5	1,3	22,6	1,0	22021	690
500	90	24,3	0,8	34,3	1,4	22,9	0,5	20751	745
300	560	18,3	2,3	24,7	3,5	18,3	1,4	15725	1948

mg	µm	Mn	StdDev	Mo	StdDev	Ni	StdDev	Pb	StdDev
100	90	339	13	2,6	0,4	122	5	22,5	1,2
300	90	287	13	2,3	0,2	108	7	20,4	0,8
500	90	279	13	2,0	0,1	116	8	18,2	0,6
300	560	224	24	1,9	0,5	91	9	15,3	2,8

mg	µm	Sn	StdDev	Ti	StdDev	V	StdDev	Zn	StdDev
100	90	5,5	1,8	5020	423	249	6	38,7	1,6
300	90	3,7	1,1	3749	116	223	6	25,7	1,1
500	90	3,6	1,0	3481	74	226	9	24,8	1,5
300	560	3,4	2,6	2689	437	196	15	28,7	4,1

B.2.3 Results

Influence of mass of test portion and sample particle size has been evaluated both visually and statistically. Statistical evaluation has been carried out by using a "data pair comparison" criterion: for each digestion method and element, recovery values in mg/kg have been paired for each level variation and the following parameters have been calculated:

— the differences from recovery value at level A and level B: $d_i = x_{A,i} - x_{B,I}$;

— the mean m_d of values d_i;

— the standard deviation s of values d_i;

— the number n of valid available results (4 in most cases);

— the distribution-t, with the formula $\hat{t} = \frac{m_d \times \sqrt{n}}{s}$;

— the degree of freedom $= n - 1$.

All distribution-t values, calculated as above, have been matched against tabled values t shown in Table B.9; when $\hat{t} > t$, we assume that the differences between the two series of values (recovery at level 1 and recovery at level 2) are significant, otherwise we assume that the difference is only casual (see Table B.8).

A qualitative evaluation of the overall robustness of the method with respect to a variable might be performed by simply counting the number of elements that are not significantly affected by that variable.

Table B.8 — Results of "data pair comparison" t-tests

Element	100 mg 300 mg	300 mg 500 mg	100 mg 500 mg	90 µm 560 µm
Al	-	-	-	-
Ba	X	-	X	X
Be	X	-	X	X
Mg	-	-	X	X
Co	X	-	X	X
Cr	X	-	X	X
Cu	X	-	X	X
Fe	-	-	X	X
Mn	X	-	X	X
Mo	-	-	-	-
Ni	X	-	-	-
Pb	X	X	X	-
Sn	-	-	X	-
Ti	X	X	X	X
V	X	-	X	-
Zn	X	-	X	-
Total affected	11	2	13	9
Total unaffected	5	14	3	7

"X" means that the element recovery is significantly influenced by the corresponding level variation.

Table B.9 — Tabled values used for "data pair comparison" tests

(n - 1)	$\hat{t}$
1	12,706
2	4,303
3	3,182
4	2,776
5	2,571
6	2,447
7	2,365

B.2.4 Conclusion

Most elements behave in a very consistent way, showing small but significant effect of both variables: recovery rate decreases slightly with the mass of test portion in almost all cases, and decreases slightly with increasing particle size in most cases. Within the range specified by the standard (200 mg to 500 mg, < 250 µm), both variables have a very small influence. It is important to stress that the study has been carried out on a sample with refractory matrix. Most other kinds of samples are much less affected by both mass of test portion and particle size.

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