BS EN 13656:2002

Characterization of waste — Microwave assisted digestion with hydrofluoric (HF), nitric (HNO_3), and hydrochloric (HCl) acid mixture for subsequent determination of elements

The European Standard EN 13656:2002 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 13656:2002.

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

The British Standards which implement international or European publications referred to in this document may be found in the *BSI Catalogue* under the section entitled “International Standards Correspondence Index”, or by using the “Search” facility of the *BSI Electronic Catalogue* or of British Standards Online.

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

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 25 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 40625 3

EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

EN 13656

October 2002

ICS 13.030.40

English version

Characterization of waste - Microwave assisted digestion with hydrofluoric (HF), nitric (HNO_3) and hydrochloric (HCl) acid mixture for subsequent determination of elements

Caractérisation des déchets - Digestion assistée par micro-ondes avec un mélange d'acides fluorhydrique (HF), nitrique (HNO_3) et chlorhydrique (HCl) pour la détermination ultérieure d'éléments contenus dans les déchets

Charakterisierung von Abfällen - Aufschluss mittels Mikrowellengerät mit einem Gemisch aus Fluorwasserstoffsäure (HF), Salpetersäure (HNO_3) und Salzsäure (HCl) für die anschließende Bestimmung der Elemente im Abfall

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.

CEN members are the national standards bodies of Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Malta, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and United Kingdom.

EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: rue de Stassart, 36 B-1050 Brussels

Ref. No. EN 13656:2002 E

Contents

Foreword

This document EN 13656:2002 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 purpose of the method is to bring the elements to be determined in many types of waste into solution to provide a rapid digestion for analysis. Elements extractable by this procedure can in many instances be described as „total“. On another hand they cannot be regarded as available for leaching, as the extraction procedure is too vigorous to represent natural processes.

1 Scope

This European Standard specifies methods of microwave assisted digestion with hydrofluoric (HF), nitric (HNO_3) and hydrochloric (HCl) acid mixture. 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 method is applicable to the microwave assisted acid 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
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

3.2
sample
portion of material selected from a larger quantity of material

[ENV 12506:2001]

3.3
laboratory sample
sample or sub-sample(s) sent to or received by the laboratory

[ENV 12506:2001]

3.4
test sample; analytical sample
sample, prepared from the laboratory sample, from which test portions are removed for testing or analysis

[ENV 12506:2001]

3.5
test portion; analytical portion
quantity of material of proper size for measurement of the concentration or other properties of interest, removed from the test sample

[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.

3.6
dry residue
dry matter expressed as a percentage by mass after drying at 105 °C ± 5 °C to the constancy of weight

3.7
digestion vessel
special flask where the test portion and the acid mixture are filled in and the digestion is performed

3.8
microwave unit
whole microwave digestion system (oven and associated equipment)

3.9
microwave unit cavity
inner part of the microwave unit in which the digestion vessel is located and the microwave digestion is performed

3.10
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 European Standard 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.

People performing the test shall be informed on the specific risk of HF.

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.

NOTE Pre-treatment may 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 can 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 programme, 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.

NOTE Quartz or borosilicated glass digestion vessels are not useable when hydrofluoric acid is used. For example polytetrafluorethylen (PTFE) digestion vessels can be used.

6.3 General equipment

The following equipment is used by both systems described in 6.1 and 6.2:

- 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.

The use of glass ware shall be excluded when free hydrofluoric acid is present.

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 %;
- Hydrofluoric acid (HF): a mass fraction of 40 % to 45 %;
- Boric acid ($B(OH)_3$): solid.

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 procedure may leave parts of the sample undissolved. This includes the risk of low recoveries and of bad repeatability. If required the residue can be analysed separately e.g. by alkaline fusion.

High acid and solute concentration in the digest solution can cause interferences at determination. Depending on the content of the digest solution some equipment for determination is not applicable.

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

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 closed vessels

The following description have to be done step by step:

9.2.1 Amount of samples and reagents

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 HCl, 2 ml HNO_3 and 2 ml HF.

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.

9.2.2 Digestion

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.

9.2.3 Complexation of HF

Carefully uncap and vent each vessel in a fume hood, then add a solution containing 650 mg of boric acid (e.g. 22 ml of 4 % m/m). Cap the vessels and put them into the microwave unit cavity and start the following programme:

— time 3 min ;

— power 300 W.

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

In this step the boron determination shall not be performed. In this case ensure that HF concentration in solution is low enough to avoid damage to measurement systems.

9.2.4 Preparation of the solution for analysis

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 up 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 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 and complexation of HF

Transfer the digestion vessels into the microwave unit cavity according to the manufactures instructions and start the following digestion procedure (see Table 2).

Table 2 — Microwave programme

Step	Acid	Volume ml	Power W	Time min
1	HCl	3	0	0
2	HNO_3	1	0	0
3	HF	5	70	10
4	HNO_3	5	70	5
5	HNO_3	5	70	5
6	HCl	5	70	5
7	H_3BO_3 (4 % m/m)	40	70	5

It is necessary not to let the digested solution cool down between the step 6 and the step 7. If the solution is cooled down between these two steps, the heating step 7 shall last 10 min.

For boron determination step 7 shall not be executed. In this case ensure that HF concentration in solution is low enough to avoid damage to measurement systems.

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.

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.

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 shall 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 with a limit deviation of ± 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 shall 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:

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

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 to 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).

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 didn't prove their analytical ability for some matrices/elements.

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

- BCR 146R (sewage sludge);
- BCR 176 (city waste incineration ash).

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

B.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 5725-2:1994, 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 two 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.

In some cases, mainly for low-concentration elements, poor values of reproducibility have been found; this might be due to the utilisation of different analytical techniques, with very different sensitivity and limits of detection.

B.1.5 Conclusions

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

Recovery rates of the two CRMs are generally good.

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

SAMPLE CEN6/99 "FLY ASH CW6 POWDER"

	Method D: Microwave assisted, with HF+HNO3+HCl in closed vessels								*Method E: Microwave assisted, with HF+HNO3+HCl in semi-open vessels*							
	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	69	17	0		39207		41,5	13,7	9	2	5		46451		0,5	2,1
Sb	46	11	0		1250,2		8,3	4,1	13	3	4		1226,8		5,1	4,5
As	66	15	0		40,59		31,4	16,6	13	3	0		36,27		64	40,8
B	0	0	0						0	0	0					
Ba	39	10	5		1130,6		31	9,7	13	3	0		846,9		64,6	25,1
Be	20	5	4		0,87		20,5	10,4	4	1	0		1,09		-	7,4
Cd	69	17	2		435,1		7,7	4,1	17	4	0		437,4		8	4,4
Ca	43	10	4		149675		6	4,2	13	3	4		144938		5,7	3,4
Cr	81	19	0		527,8		10,9	5,7	13	3	1		516,7		1,7	6,8
Co	63	15	0		31,34		32,3	6,5	13	3	0		26,16		29,1	8,2
Cu	77	18	9		2076,1		5,7	3,9	13	3	4		2035,2		2	3
Fe	66	16	1		10060		10,3	3,7	12	3	5		10213		3,9	3,3
Pb	84	20	1		10085		10,3	5,8	17	4	0		8470,9		32,1	12
Mg	42	10	8		11461		7,6	4,8	13	3	4		11937		3,6	6,7
Mn	58	14	18		541,2		3,4	4,3	13	3	4		515,4		5	3,4
Hg	36	9	5		6,04		7,3	5,1	13	3	0		5,53		22	20,9
Mo	54	13	5		37,77		70,3	11,2	8	2	1		25,61		5,5	15,8
Ni	68	16	4		77,63		15,7	5,2	8	2	0		59,45		41,4	28,5
P	25	6	8		5772,8		6,4	1,7	12	3	0		5056,8		17,1	20,4
K	34	8	0		65117		11,5	4,1	13	3	4		66814		6,5	3,3
Se	28	7	0		30,63		44	6,7	12	3	1		34,01		66,1	7,9
Ag	12	3	1		386,8		9,6	2,3	7	2	0		38,3		33,1	22,8
S	12	3	4		39249		0,9	4,8	4	1	0		18886		-	7,7
Na	28	7	5		63630		4,8	4,3	5	1	0		62542		-	2,5
Sr	20	5	0		276,9		15	2,8	13	3	0		248,9		24,3	6,5
Sn	36	9	5		1458,4		15	3,9	13	3	0		1137,8		53,6	7,1
Te	8	2	0		0,95		31,3	57,5	0	0	0					
Tl	12	3	0		7,09		99	16,2	7	2	1		10,02		117,4	5,4
Ti	46	11	0		9073,7		4,1	3	13	3	0		7709,1		6,9	4,1
V	66	16	9		25,6		31,6	13,7	13	3	0		25,41		40,9	27,6
Zn	85	20	0		30002		8,9	3,7	12	3	5		28165		4,2	6,7

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 D: Microwave assisted, with HF+HNO3+HCl in closed vessels								*Method E: Microwave assisted, with HF+HNO3+HCl in semi-open vessels*							
	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	63	16	0		71894		37,2	5,8	17	4	0		80767		3,4	4,3
Sb	44	11	1		318,3		11,8	4,6	17	4	0		333,4		12,6	4,5
As	59	14	0		82,44		14,2	6,3	14	4	0		72,2		45,7	12,4
B	0	0	0						0	0	0					
Ba	51	13	1		2579,6		54,9	11,7	13	3	0		2206,8		85,7	22,5
Be	28	7	0		2,28		35,2	7	4	1	0		2,46		-	7,5
Cd	70	17	5		530,7		6,5	3,2	17	4	0		538,4		4,6	2,8
Ca	53	13	1		66125		47,1	4,5	13	3	4		82261		2,3	3,1
Cr	86	20	0		304,5		13,5	5,3	17	4	0		266,5		3,4	5,8
Co	66	16	0		36,32		30,3	5,2	12	3	0		26,72		36,2	12,2
Cu	92	22	6		1294,2		8,8	4	13	3	4		1269,7		1,1	2,7
Fe	75	18	1		20258		8,9	4,6	17	4	0		20039		6,2	6,4
Pb	88	21	2		11526		9,3	4,7	16	4	0		9670,3		20,1	9,8
Mg	41	10	4		17561		14,9	4,4	16	4	1		18048		2	2,9
Mn	74	18	6		1301,1		7,1	3,3	17	4	0		1329,3		11,4	6,6
Hg	38	9	6		31,15		8,2	4,1	13	3	0		27,68		15,4	6,7
Mo	54	13	4		52,19		44,5	15,1	9	2	0		44,19		0,5	4,3
Ni	88	21	0		115,4		23,2	4,9	13	3	0		109,3		9	6,5
P	34	8	0		6322,0		12,4	3,9	12	3	0		5528,6		12,9	14,6
K	23	6	14		40426		1,6	3,4	17	4	0		30996		44,1	4,3
Se	26	6	4		40,64		12,8	5,3	9	2	0		47,84		3,7	4,9
Ag	17	4	0		68,59		11,7	34	8	2	0		21,79		11,5	40
S	16	4	0		34020		7,4	2,1	0	0	0					
Na	38	9	0		28931		21,3	7,5	13	3	0		30498		9,7	2,9
Sr	21	5	2		333,7		19,8	1,6	13	3	0		354,8		8,9	7,6
Sn	42	10	4		2551,5		12,6	4,7	13	3	0		2274,1		18,6	23
Te	8	2	0		1,09		12,6	33,4	0	0	0					
Tl	12	3	0		5,71		76,5	15,4	0	0	1					
Ti	50	12	0		9089,5		11,3	4	17	4	0		7470,9		9,7	8,6
V	66	16	8		41,97		24,4	5,2	13	3	0		66,42		56,7	10,4
Zn	84	20	1		27791		8,7	3,2	17	4	0		26268		4,6	5,6

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 D: Microwave assisted, with HF+HNO3+HCl in closed vessels								*Method E: Microwave assisted, with HF+HNO3+HCl in semi-open vessels*							
	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	57	14	1		2056,2		31,2	8,7	13	3	3		1966,9		10,6	9,7
Sb	21	5	0		69,61		100,2	17,8	4	1	0		0,46		-	40,2
As	30	7	0		7,48		25	15,4	6	2	0		3,19		83,3	11,5
B	0	0	0						0	0	0					
Ba	29	7	8		101,2		8,2	5,1	13	3	4		103,5		2	6,1
Be	16	4	0		0,47		90,9	11,5	3	1	0		0,08		-	23,2
Cd	21	5	10		0,5		30,7	15,7	4	1	0		2,1		-	10,3
Ca	43	10	8		111589		5,4	2,9	17	4	0		125086		41,2	9,1
Cr	89	21	0		3638,3		7,6	4,4	17	4	0		3081,8		27,1	10,3
Co	46	11	9		14,59		18,9	5	13	3	0		12,9		15,3	9,1
Cu	92	22	1		12487		8,5	3,1	17	4	0		12970		15,6	4,4
Fe	67	16	10		76239		4,7	2,8	17	4	0		73737		20,5	6,2
Pb	85	20	4		5945,1		7,2	4,6	17	4	0		5639,4		6,3	6,9
Mg	45	11	14		976,5		7,8	3,5	17	4	0		905,9		12,8	11,4
Mn	70	17	6		543,3		5,8	2,5	17	4	0		501,8		14,5	7,8
Hg	35	8	0		1,93		17,4	15,2	9	2	0		1,8		4,1	4,7
Mo	35	9	0		5,55		85,3	15,5	9	2	0		2,93		21,7	5,1
Ni	58	14	10		23,67		23,2	15	12	3	1		19,32		25,2	8,7
P	30	7	0		14352		7	2,4	12	3	0		13139		10,6	13,5
K	41	10	1		971,7		33,3	19,1	13	3	0		944,3		19	9,4
Se	4	1	0		3,53		-	20,4	4	1	0		11,27		-	20,6
Ag	3	1	1		1,32		-	8,3	3	1	0		2,0		-	35,3
S	16	4	0		33032		11,5	2,3	0	0	0					
Na	39	9	0		7013,3		38	13,3	5	1	0		5018,0		-	4,5
Sr	12	3	0		113,6		18,3	7,2	13	3	0		119,5		7,6	3,2
Sn	12	3	4		2,06		81,6	38	0	0	0					
Te	0	0	0						0	0	0					
Tl	8	2	0		2,19		108,7	18,5	0	0	0					
Ti	33	8	5		244,0		12,6	7,4	17	4	0		182,6		22,1	11,8
V	45	11	5		14,64		12,3	4,9	4	1	0		11,93		-	60,3
Zn	85	21	6		1210,0		9,3	3,8	13	3	0		1172,7		15,6	4,4

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 D: Microwave assisted, with HF+HNO3+HCl in closed vessels								Method E: Microwave assisted, with HF+HNO3+HCl in semi-open vessels							
	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	17	0		73799		33,8	5,1	17	4	0		82229		7	3,5
Sb	8	2	0		21,37		53,5	16,3	8	2	0		19,22		96	26,3
As	24	6	0		4,65		77,9	39,7	6	2	0		2,18		25,3	13,2
B	0	0	0						0	0	0					
Ba	41	10	4		70,55		32,9	12,4	15	4	1		74,55		14,1	2,6
Be	20	5	0		0,65		71,7	9,6	4	1	0		0,53		-	5,9
Cd	12	3	1		0,56		91,5	14,2	0	0	1					
Ca	39	9	4		53986		11,8	10,5	17	4	0		54327		11,9	7,9
Cr	73	17	0		86,24		14,2	5,9	12	3	1		78,66		4,9	5
Co	29	7	4		3,67		18,1	11,6	13	3	0		4,01		12,8	18,8
Cu	84	20	7		94981		7,4	3	17	4	0		97289		10,7	2,7
Fe	73	17	4		5065,3		15,6	5,2	17	4	0		4954,2		5,6	4,1
Pb	86	21	6		9455,4		6,7	3,9	17	4	0		9054,9		7,8	2,2
Mg	41	10	0		2143,7		36,7	11,9	17	4	0		2210,4		5,5	2,9
Mn	76	18	5		622,3		7,4	3,2	16	4	1		618,1		3,3	1,4
Hg	26	6	0		0,18		20,1	13,5	0	0	0					
Mo	25	6	5		4,47		20,1	7,5	8	2	0		3,75		38,3	7,7
Ni	89	21	1		1750,6		7,5	3,3	17	4	0		1621,8		3,7	2,8
P	30	7	0		5142,5		13,6	2,3	12	3	0		4169,0		22,6	13,6
K	37	9	1		3137,5		14,1	12	11	3	1		2519,2		55,7	6,6
Se	2	1	0		1,0		-	14,1	4	1	0		3,8		-	23,2
Ag	11	3	1		8,82		9,9	8,5	8	2	0		9,47		5,7	9,3
S	16	4	0		68041		8,9	0,8	0	0	0					
Na	35	8	4		13232		7,5	8,5	5	1	0		13032		-	4,6
Sr	21	5	0		157,2		36,7	8,6	13	3	0		202,6		5,4	2,6
Sn	36	9	6		18756		8,7	4,3	13	3	0		13711		43,7	10,8
Te	0	0	0						0	0	0					
Tl	8	2	0		1,13		87,2	17,6	2	1	0		0,08		-	23,9
Ti	39	10	5		118,1		21,8	6,7	17	4	0		109,8		40	21,7
V	44	11	9		4,91		41,4	17,8	8	2	0		6,88		19,5	8,4
Zn	77	18	4		230,6		34,5	4,3	17	4	0		331,7		31,4	9,3

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 D: Microwave assisted, with HF+HNO3+HCl in closed vessels								*Method E: Microwave assisted, with HF+HNO3+HCl in semi-open vessels*							
	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	61	15	0	25130	28658	114	22,8	8,9	12	3	5	25130	27496	109,4	1,1	3,5
Sb	25	6	0	16,25	12,55	77,2	21	7,6	8	2	0	16,25	12,85	79,1	5,1	3,8
As	34	8	0	6,3	6,89	109,4	42,5	21,6	6	2	0	6,3	3,1	49,2	95,6	6,2
B	4	1	0		3610,0		-	19,5	0	0	0					
Ba	49	12	4	735	659,8	89,8	16,3	3,9	13	3	0	735	662,6	90,1	8,5	2,4
Be	28	7	0		0,98		38,1	12,1	4	1	0		0,95		-	6,4
Cd	66	16	1	18,76	16,01	85,3	13,5	6,9	13	3	0	18,76	17,87	95,2	5,6	3,7
Ca	46	11	4	154600	134370	86,9	7,4	4,9	16	4	1	154600	133679	86,5	7,4	3,9
Cr	81	19	5	196	178,3	91	7,4	4,3	8	2	5	196	175,1	89,3	0,3	3,2
Co	42	10	4	7,39	7,93	107,2	26,6	17,1	13	3	0	7,39	8,04	108,7	21,2	10,2
Cu	92	22	2	837,9	809,6	96,6	8,7	6	8	2	5	837,9	826,8	98,7	2,3	1,5
Fe	81	19	0	16100	14215	88,3	11,9	4,2	16	4	1	16100	14527	90,2	1	3,8
Pb	76	18	0	608,7	556,1	91,4	10	4,9	17	4	0	608,7	536,1	88,1	7,8	3,5
Mg	58	14	5	10460	9384,6	89,7	17,2	3	16	4	1	10460	9274,8	88,7	3,3	3,6
Mn	80	19	4	323,5	304,9	94,2	6,7	2,1	17	4	0	323,5	290,6	89,8	7,1	2,2
Hg	44	10	0	8,62	7,23	83,8	21,8	13,7	12	3	0	8,62	6,51	75,5	25,4	6,9
Mo	35	9	12		7,81		21,5	6,3	8	2	0		7,99		1,9	12,5
Ni	80	19	0	69,7	65,01	93,3	18,6	6,6	15	4	1	69,7	63,35	90,9	9,8	11,5
P	25	6	5	25600	27479	107,3	3	1,8	12	3	0	25600	25186	98,4	5,8	11,6
K	42	10	0	5240	5465,9	104,3	16,4	10,8	9	2	0	5240	4969,4	94,8	0,7	2,7
Se	9	2	0		2,84		37,6	26,9	4	1	0		11,84		-	13,2
Ag	12	3	0		215,0		4	3,5	4	1	0		91,71		-	11,7
S	11	3	4	10620	10049	94,6	3,8	1,1	0	0	0	10620				
Na	35	8	0	1804	2710,1	150,2	54,4	11,6	17	4	0	1804	1665,6	92,3	47,8	4,1
Sr	21	5	0	1179	972,0	82,4	12	2	13	3	0	1179	1010,4	85,7	8,8	2,7
Sn	28	7	2	95,8	75,58	78,9	13,6	5	9	2	1	95,8	77,12	80,5	3,8	23,8
Te	0	0	0						0	0	0					
Tl	12	3	0		2,33		130,3	16,7	4	1	0		0,51		-	23,5
Ti	45	11	5	2771	2313,9	83,5	7,6	2,9	15	4	1	2771	1737,7	62,7	12,3	7,9
V	76	18	0	42,7	38,14	89,3	23,5	9,4	17	4	0	42,7	40,0	93,7	40,1	8,2
Zn	93	22	0	3061	2848,0	93	7,3	4,1	17	4	0	3061	2702,1	88,3	9,5	2,7

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 D: Microwave assisted, with HF+HNO3+HCl in closed vessels								*Method E: Microwave assisted, with HF+HNO3+HCl in semi-open vessels*							
	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	54	13	0	101600	83828	82,5	14,7	3	13	3	4	101600	81990	80,7	0,5	3,7
Sb	44	11	4	412	329,3	79,9	8,8	4,4	13	3	4	412	330,7	80,3	1,9	3,1
As	60	14	0	93,3	82,69	88,6	21,1	7,7	13	3	0	93,3	85,26	91,4	15,6	15,4
B	3	1	0		2468,0		-	10,8	4	1	1		102,4		-	1,2
Ba	53	13	0	4500	2755,8	61,2	60,8	12,7	13	3	0	4500	2106,6	46,8	101,6	7,1
Be	24	6	0		2,54		22,6	6	4	1	0		2,44		-	5,3
Cd	72	18	2	470	450,1	95,8	5,5	3,8	17	4	0	470	455,0	96,8	8	2,5
Ca	39	9	0	88016	83821	95,2	6,7	3,7	17	4	0	88016	81419	92,5	5,5	3,5
Cr	71	18	4	863	321,9	37,3	14,6	5,7	17	4	0	863	271,7	31,5	4,1	5,9
Co	58	14	0	30,9	71,58	231,6	137,4	7,3	13	3	0	30,9	31,34	101,4	17,5	6,7
Cu	88	21	1	1302	1293,5	99,3	7,2	4,8	8	2	6	1302	1275,0	97,9	0,6	4
Fe	78	19	1	21300	20946	98,3	9,1	3,3	12	3	1	21300	21014	98,7	2,5	2,4
Pb	87	21	4	10870	10609	97,6	6,6	5,3	17	4	0	10870	7963,2	73,3	24	9,7
Mg	46	11	0	21720	17583	81	20,5	4,3	13	3	4	21720	18103	83,3	0,4	3,2
Mn	82	20	0	1500	1370,0	91,3	7,6	3,7	17	4	0	1500	1304,4	87	8,3	2
Hg	35	8	5	31,4	30,76	98	5,9	5,5	13	3	0	31,4	25,87	82,4	20,8	5,7
Mo	50	12	4		47,19		21,8	5,3	13	3	0		51,74		23,1	2,8
Ni	66	16	14	123,5	122,9	99,5	7,6	3,8	17	4	0	123,5	113,3	91,7	7,8	5
P	29	7	5		6369,0		9,8	3,9	12	3	0		5370,8		8	13,6
K	41	10	0	44986	35759	79,5	13,4	3,3	9	2	0	44986	38498	85,6	4,2	3,7
Se	28	7	2	41,2	38,06	92,4	14,5	5,4	8	2	0	41,2	46,82	113,6	1,3	5,4
Ag	12	3	0	60	57,61	96	10,5	4,3	8	2	0	60	34,45	57,4	9,6	68,6
S	16	4	0	44600	32965	73,9	6,7	1,3	0	0	0	44600				
Na	38	9	0	42920	27152	63,3	17,9	5,6	7	2	1	42920	28321	66	5,2	0,6
Sr	13	3	6	433	392,4	90,6	2,3	2,5	13	3	0	433	370,2	85,5	8,2	3
Sn	37	9	4		2664,0		11,9	4,3	9	2	0		2647,8		3	3,1
Te	8	2	0		1,93		45,3	9,2	0	0	0					
Tl	17	4	0		3,71		38	9,9	4	1	0		2,2		-	11,2
Ti	44	11	5	8520	8990,2	105,5	7,7	3,6	17	4	0	8520	7366,3	86,5	13,1	5,5
V	75	18	0	41	47,19	115,1	31,8	5,3	9	2	0	41	45,6	111,2	2,3	3,3
Zn	87	21	0	25770	26198	101,7	9,2	4,3	16	4	1	25770	25300	98,2	1,8	3,2

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);

(1) 300 mg (4 replicates);

(2) 400 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	162888	3983	2088	101	8,9	0,3	876,2	43,0
300	90	152504	3781	1798	109	8,4	0,2	734,1	44,6
400	90	160125	4122	1875	69	8,2	0,1	799,3	32,6
500	90	159060	11191	1817	17	7,9	0,4	755,2	15,9
300	560	119963	18421	1577	153	9,0	0,2	600,7	127,2

mg	µm	Co	StdDev	Cr	StdDev	Cu	StdDev	Fe	StdDev
100	90	47,5	2,3	131,1	5,8	40,3	1,1	35766	2572
300	90	43,9	1,0	122,1	1,4	38,1	0,8	34535	1311
400	90	42,2	0,6	116,1	2,2	37,4	0,7	30883	1397
500	90	41,2	2,0	112,8	6,7	36,9	2,4	31749	2446
300	560	44,9	0,8	122,6	1,8	38,2	1,0	34025	1308

mg	µm	Mn	StdDev	Mo	StdDev	Ni	StdDev	Pb	StdDev
100	90	431	16	3,0	0,8	152	17	28,6	2,6
300	90	413	6	2,5	0,4	148	5	29,4	4,6
400	90	404	8	2,1	0,2	135	8	29,4	1,2
500	90	389	18	2,2	0,3	133	9	25,9	1,8
300	560	426	7	2,1	0,3	151	8	25,4	1,7

mg	µm	Sn	StdDev	Ti	StdDev	V	StdDev	Zn	StdDev
100	90	13,7	1,5	8459	230	293	14	47,7	3,7
300	90	8,9	1,1	8299	268	279	3	41,7	4,0
400	90	7,5	0,3	8237	184	277	7	35,6	0,4
500	90	6,6	0,8	8346	505	267	13	34,5	2,5
300	560	9,1	1,6	8589	219	281	8	44,0	3,4

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 $\hat{t} = \frac{m_d \quad \sqrt{n}}{s}$;

— 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	X	-	-	-
Ba	X	-	X	X
Be	-	-	X	X
Mg	X	-	X	-
Co	-	X	X	-
Cr	-	-	X	-
Cu	X	-	X	-
Fe	-	-	X	-
Mn	X	X	X	-
Mo	-	-	-	-
Ni	-	X	X	-
Pb	-	-	-	-
Sn	X	X	X	-
Ti	-	-	-	-
V	-	-	X	-
Zn	-	X	X	-
Total affected	6	5	12	2
Total unaffected	10	11	4	14
"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 some effect of both variables: recovery rate decreases slightly with the mass of test portion in many cases (actually, only Sn appears to be significantly affected), and decreases slightly with large particle size only in some cases. Within the range specified by the standard (200 mg to 500 mg, < 250 µm), both variables have a very small or no 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.

Bibliography

EN 1233:1997, *Water quality - Determination of chromium - Atomic Absorption Spectrometric Methods.*

EN 1483:1997, *Water quality - Determination of mercury.*

ENV 12506, *Characterization of waste - Analysis of eluates - Determination of pH, As, Cd, Cr, Cr VI, Cu, Ni, Pb, Zn,* Cl^-, NO^{2-}, SO_4^{2-}.

EN 45001:1989, *General criteria for the operation of testing laboratories.*

EN ISO 5961:1995, *Water quality - Determination of cadmium by atomic absorption spectrometrie (ISO 5961:1994).*

EN ISO 11969:1996, *Water quality - Determination of arsenic - Atomic Absorption Spectrometry method (hydride technique) (ISO 11696:1996).*

ISO 5725-1:1994, *Accuracy (trueness and precision) of measurement methods and results - Part 1: General principles and definitions.*

ISO 5725-1/C1:1998, *Accuracy (trueness and precision) of measurement methods and results - Part 1: General principles and definitions; Technical Corrigendum 1.*

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 8288:1986, *Water quality - Determination of cobalt, nickel, copper, zinc, cadmium and lead - Flame atomic absorption spectrometric methods.*

ISO 11466:1995, *Soil quality - Extraction of trace elements soluble in aqua regia.*

ISO 11885:1996, *Determination of 33 elements by inductively coupled plasma atomic emission spectroscopy.*

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.*

BSI — British Standards Institution

BSI is the independent national body responsible for preparing British Standards. It presents the UK view on standards in Europe and at the international level. It is incorporated by Royal Charter.

Revisions

British Standards are updated by amendment or revision. Users of British Standards should make sure that they possess the latest amendments or editions.

It is the constant aim of BSI to improve the quality of our products and services. We would be grateful if anyone finding an inaccuracy or ambiguity while using this British Standard would inform the Secretary of the technical committee responsible, the identity of which can be found on the inside front cover.
Tel: +44 (0)20 8996 9000. Fax: +44 (0)20 8996 7400.

BSI offers members an individual updating service called PLUS which ensures that subscribers automatically receive the latest editions of standards.

Buying standards

Orders for all BSI, international and foreign standards publications should be addressed to Customer Services. Tel: +44 (0)20 8996 9001.
Fax: +44 (0)20 8996 7001. Email: orders@bsi-global.com. Standards are also available from the BSI website at http://www.bsi-global.com.

In response to orders for international standards, it is BSI policy to supply the BSI implementation of those that have been published as British Standards, unless otherwise requested.

Information on standards

BSI provides a wide range of information on national, European and international standards through its Library and its Technical Help to Exporters Service. Various BSI electronic information services are also available which give details on all its products and services. Contact the Information Centre.
Tel: +44 (0)20 8996 7111. Fax: +44 (0)20 8996 7048. Email: info@bsi-global.com.

Subscribing members of BSI are kept up to date with standards developments and receive substantial discounts on the purchase price of standards. For details of these and other benefits contact Membership Administration.
Tel: +44 (0)20 8996 7002. Fax: +44 (0)20 8996 7001.
Email: membership@bsi-global.com.

Information regarding online access to British Standards via British Standards Online can be found at http://www.bsi-global.com/bsonline.

Further information about BSI is available on the BSI website at http://www.bsi-global.com.

Copyright

This does not preclude the free use, in the course of implementing the standard, of necessary details such as symbols, and size, type or grade designations. If these details are to be used for any other purpose than implementation then the prior written permission of BSI must be obtained.

Details and advice can be obtained from the Copyright & Licensing Manager.
Tel: +44 (0)20 8996 7070. Fax: +44 (0)20 8996 7553.
Email: copyright@bsi-global.com.

BSI
389 Chiswick High Road
London
W4 4AL