BS EN 16192:2011

BSI Standards Publication

Characterization of waste — Analysis of eluates

bsi.

...making excellence a habit.™

National foreword

This British Standard is the UK implementation of EN 16192:2011. It supersedes BS EN 12506:2003 and BS EN 13370:2003 which are withdrawn.

The UK participation in its preparation was entrusted to Technical Committee B/508/3, Characterization of waste.

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

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

ISBN 978 0 580 72731 3

ICS 13.030.99

Compliance with a British Standard cannot confer immunity from legal obligations.

This British Standard was published under the authority of the Standards Policy and Strategy Committee on 30 April 2012.

Amendments issued since publication

Date	Text affected

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 16192

November 2011

ICS 13.030.99

Supersedes EN 12506:2003, EN 13370:2003

English Version

Characterization of waste - Analysis of eluates

Caractérisation des déchets - Analyse des éluats

Charakterisierung von Abfällen - Analyse von Eluaten

This European Standard was approved by CEN on 15 October 2011.

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 CEN-CENELEC 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 CEN-CENELEC Management Centre has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

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

Management Centre: Avenue Marnix 17, B-1000 Brussels

Contents

Page

Foreword

This document (EN 16192:2011) 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 May 2012, and conflicting national standards shall be withdrawn at the latest by May 2012.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

This document supersedes EN 12506:2003 and EN 13370:2003.

Details of significant technical changes between this European Standard and the previous edition are:

— This European Standard, EN 16192, is now a single document (instead of two) for the analysis of eluates specifying methods for the determination of the parameters pH, ammonium, AOX, As, Ba, Cd, Cl^-, easily liberatable CN^-, Co, Cr, Cr(VI), Cu, DOC/TOC, electrical conductivity, F^-, Hg, Mo, Ni, NO_2^-, Pb, phenol index, total S, Sb, Se, SO_4^{2-}, TDS, V and Zn in aqueous eluates for the characterization of waste.

— In Clause 7 the parameters, previously described in two documents, are now all integrated in Table 1.

— In Table 1 for all parameters EN and ISO standards are updated, removed if withdrawn and new relevant standards are added, i.e.:

  — addition of the parameters Sb and Se together with the related analytical methods;

  — revision of the standards EN ISO 11885 (ICP-OES) and EN ISO 10304-1 (IC);

  — addition of the ICP-MS method (EN ISO 17294-1:2006 and EN ISO 17294-2:2004);

  — addition of the AAS with graphite furnace technique (EN ISO 15586:2003);

  — addition of the flow analysis techniques for Cl^- (EN ISO 15682:2001), Cr(VI) (EN ISO 23913:2009) and SO_4^{2-} (ISO 22743:2006);

  — addition of the parameter TDS (total dissolved solids) together with the related analytical method;

  — addition of the parameter DOC (dissolved organic carbon) to the parameter TOC (total organic carbon);

  — revision of the standards EN ISO 11732 (ammonium by flow analyser);

  — replacement of EN 1485 (AOX) by EN ISO 9562:2004;

  — revision and addition of new standards for Hg determination – EN 1483 and EN ISO 17852.

— In Annex B (informative) additional validation data are added obtained from a round robin test for the determination of Ba, Cd, Cr, Mo, Sb and Se in eluates and from round robin tests in the framework of acceptability of waste at landfills, both organized in Belgium.

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

Introduction

This European standard is intended to be used for the characterization of waste as defined in the Council Directive 75/442/EEC on waste, as amended by Council Directive 91/156/EEC of 18th March 1991, and national regulations, whose final destination for disposal is landfill. In the Council Decision of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC, the test methods are described for determining the acceptability of waste at landfills. In section 3 of the Annex of this Decision the European standards EN 12506 and EN 13370 are included which are replaced by this European Standard.

This European Standard deals with the determination of chemical constituents, electrical conductivity, pH and total dissolved solids (TDS) in eluates which have been obtained by leaching of waste samples for example using EN 12457 “Characterization of waste - Leaching - Compliance test for leaching of granular waste materials and sludges” (Part 1 to Part 4). In principle, it may be used for the analysis of every kind of eluate as long as the performance characteristics of the applied analytical method fulfill the specific requirements.

1 Scope

This European Standard specifies methods for the determination of the parameters pH, ammonium, AOX, As, Ba, Cd, Cl^-, easily liberatable CN^-, Co, Cr, Cr(VI), Cu, DOC/TOC, electrical conductivity, F^-, Hg, Mo, Ni, NO_2^-, Pb, phenol index, total S, Sb, Se, SO_4^{2-}, TDS, V and Zn in aqueous eluates for the characterization of waste.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 1483:2007, *Water quality — Determination of mercury — Method using atomic absorption spectrometry*

EN 1484:1997, *Water analysis — Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC)*

EN 15216:2007, *Characterization of waste — Determination of total dissolved solids (TDS) in water and eluates*

EN 26777:1993, *Water quality — Determination of nitrite — Molecular absorption spectrometric method (ISO 6777:1984)*

EN 27888:1993, *Water quality — Determination of electrical conductivity (ISO 7888:1985)*

prEN ISO 5667-3, *Water quality — Sampling — Part 3: Preservation and handling of water samples (ISO/DIS 5667-3:2010)*

EN ISO 9562:2004, *Water quality — Determination of adsorbable organically bound halogens (AOX) (ISO 9562:2004)*

EN ISO 10304-1:2009, *Water quality — Determination of dissolved anions by liquid chromatography of ions — Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate (ISO 10304-1:2007)*

EN ISO 10304-3:1997, *Water quality — Determination of dissolved anions by liquid chromatography of ions — Part 3: Determination of chromate, iodide, sulfite, thiocyanate and thiosulfate (ISO 10304-3:1997)*

EN ISO 11732:2005, *Water quality — Determination of ammonium nitrogen — Method by flow analysis (CFA and FIA) and spectrometric detection (ISO 11732:2005)*

EN ISO 11885:2009, *Water quality — Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES) (ISO 11885:2007)*

EN ISO 11969:1996, *Water quality — Determination of arsenic — Atomic absorption spectrometric method (hydride technique) (ISO 11969:1996)*

EN ISO 13395:1996, *Water quality — Determination of nitrite nitrogen and nitrate nitrogen and the sum of both by flow analysis (CFA and FIA) and spectrometric detection (ISO 13395:1996)*

EN ISO 14402:1999, *Water quality — Determination of the phenol index by flow analysis (FIA and CFA) (ISO 14402:1999)*

EN ISO 14403:2002, *Water quality — Determination of total cyanide and free cyanide by continuous flow analysis (ISO 14403:2002)*

EN ISO 14911:1999, *Water quality — Determination of dissolved Li^+, Na^+, NH_4^+, K^+, Mn^{2+}, Ca^{2+}, Mg^{2+}, Sr^{2+} and Ba^{2+} using ion chromatography — Method for water and waste water (ISO 14911:1998)*

EN ISO 15586:2003, *Water quality — Determination of trace elements using atomic absorption spectrometry with graphite furnace (ISO 15586:2003)*

EN ISO 15682:2001, *Water quality — Determination of chloride by flow analysis (CFA and FIA) and photometric and potentiometric detection (ISO 15682:2000)*

EN ISO 17294-1:2006, *Water quality — Application of inductively coupled plasma mass spectrometry (ICP-MS) — Part 1: General guidelines (ISO 17294-1:2004)*

EN ISO 17294-2:2004, *Water quality — Application of inductively coupled plasma mass spectrometry (ICP-MS) — Part 2: Determination of 62 elements (ISO 17294-2:2003)*

EN ISO 17852:2008, *Water quality — Determination of mercury — Method using atomic fluorescence spectrometry (ISO 17852:2006)*

EN ISO 23913:2009, *Water quality — Determination of chromium(VI) — Method using flow analysis (FIA and CFA) and spectrometric detection (ISO 23913:2006)*

ISO 6439:1990, *Water quality — Determination of phenol index — 4-Aminoantipyrine spectrometic methods after distillation*

ISO 6703-2:1984, *Water quality — Determination of cyanide — Part 2: Determination of easily liberatable cyanide*

ISO 7150-1:1984, *Water quality — Determination of ammonium — Part 1: Manual spectrometric method*

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

ISO 9297:1989, *Water quality — Determination of chloride — Silver nitrate titration with chromate indicator (Mohr's method)*

ISO 9965:1993, *Water quality — Determination of selenium — Atomic absorption spectrometric method (hydride technique)*

ISO 10359-1:1992, *Water quality — Determination of fluoride — Part 1: Electrochemical probe method for potable and lightly polluted water*

ISO 10523:2008, *Water quality — Determination of pH*

ISO 11083:1994, *Water quality — Determination of chromium (VI) — Spectrometric method using 1,5-diphenylcarbazide*

ISO 22743:2006, *Water quality — Determination of sulfates — Method by continuous flow analysis (CFA)*

3 Terms and definitions

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

3.1
sample
portion of material selected from a larger quantity of material

3.2
eluate
solution obtained by a leaching test

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

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

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

NOTE 1 The test portion can 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, can be a test portion.

3.6
leachant
aqueous solution used in a leaching test

3.7
leaching test
laboratory test for the determination of the release of matter from a waste into water or an aqueous solution

4 Sample pretreatment

The eluate shall be analyzed for the total content of its constituents. If precipitation occurs between the preparation of the eluate and the analysis it is necessary to ensure by appropriate methods (e.g. redissolution, separate analysis of solution and precipitate) that the total content of the parameters of interest is determined. If the eluate results from a procedure including 0,45 µm membrane filtration analytical results refer to the content dissolved by the leaching process.

Eluates are susceptible to be changed to different extents as a result of physical, chemical or biological reactions which may take place between the time of leaching and the analysis. pH shall be determined immediately after preparation of the eluates and prior to sample pretreatment.

It is therefore essential to take the necessary precautions to minimize these reactions and in the case of many parameters to analyze the eluate sample with a minimum of delay. The maximum delay is given in prEN ISO 5667-3 or in the respective analytical standards.

Precautions should be taken before and during transport as well as during the time in which the samples are preserved in the laboratory before being analyzed, to avoid alteration of the test portion.

Split the eluate in an adequate number of test portions for different chemical analyses and preserve them according to the requirements in the analytical standards or prEN ISO 5667-3.

One specific test portion may be an untreated aliquot of the laboratory sample for the analysis of chromates such as chloride, fluoride, sulfate, nitrite and chromium(VI) as well as for the determination of electrical conductivity.

For trace metal analysis test portions usually need to be acidified to $pH \leq 2$.

NOTE 1 For safety reasons it is recommended to acidify the test portion under a hood as volatile toxic substances can be generated.

NOTE 2 In cases where high contents of soluble solids are leached, acidification of the eluates can lead to precipitation of salts. This can be avoided by dilution prior to acidification.

5 Blank determination

The blank contribution of the applied analytical procedures shall be determined as described in the analytical standards and considered in the calculation of the results when appropriate.

6 Interference

A large number of compounds can interfere with the determination of the parameters concerned. These potential interferences are listed in the individual standards in question.

Several types of interference effects can contribute to inaccuracies in the determination of the various parameters, especially at low concentrations. These potential interference effects are listed in the individual standards and shall be considered separately for each analytical technique.

Chemical interferences are characterized by molecular compound formation, ionization effects, solute vaporization, precipitation and effects of decomposition of organic matter. Addition of buffer and/or preservation methods may reduce these effects.

Physical interferences can be caused by changes of viscosity and surface tension. They can cause significant inaccuracies especially in eluate samples containing high concentrations of acids and/or dissolved components. The colour or turbidity of eluates can cause interference in spectrophotometric determination.

7 Selection of the suitable test method

Select the appropriate standardized test method listed in Table 1 according to the type of waste eluate, the concentration range of the parameter of interest and the expected interferences.

For analytical quality control purposes ENV ISO 13530 and EN ISO/IEC 17025 should be considered.

It is pointed out that the standardized test methods listed in Table 1 have primarily been developed for the analysis of water samples. Most of them were validated in an interlaboratory trial for a limited number of waste eluate matrices (see Annex A). Their suitability for other waste eluates shall be checked in the laboratory performing the analysis. Additional validation data obtained in the evaluation of the analytical performance of laboratories are given in Annex B.

Those standards cited in Table 1 that have not been validated in the CEN/TC 292 interlaboratory trial in 1999-2001, have the matrix waste water and/or leachates included in their scope, and they proved to be applicable for the analysis of eluates in routine analyses.

If the methods referred to in Table 1 are found to be inappropriate by reason of, for example, detection limits, repeatability or interferences, other methods validated for water analysis e.g. discrete analyzer, can be used. Their suitability for waste eluates shall be checked in the laboratory performing the analysis. The reason for the deviation shall be stated in the test report.

Table 1 — Parameters and test methods

Parameter	Test method
pH	ISO 10523:2008
Ammonium	EN ISO 11732:2005 EN ISO 14911:1999 ISO 7150-1:1984
AOX	EN ISO 9562:2004
As	EN ISO 11885:2009 EN ISO 11969:1996 EN ISO 15586:2003 EN ISO 17294-1:2006 EN ISO 17294-2:2004
Ba	EN ISO 11885:2009 EN ISO 17294-1:2006 EN ISO 17294-2:2004

Table 1 *(continued)*

Parameter	Test method
Cd	ISO 8288:1986 EN ISO 11885:2009 EN ISO 15586:2003 EN ISO 17294-1:2006 EN ISO 17294-2:2004
Cl^-	ISO 9297:1989 EN ISO 10304-1:2009 EN ISO 15682:2001
$CN^-_{easily\ liberatable}$	EN ISO 14403:2002[a] ISO 6703-2:1984
Co	EN ISO 11885:2009 EN ISO 15586:2003 EN ISO 17294-1:2006 EN ISO 17294-2:2004
Cr	EN ISO 11885:2009 EN ISO 15586:2003 EN ISO 17294-1:2006 EN ISO 17294-2:2004
Cr(VI)	ISO 11083:1994 EN ISO 10304-3:1997 EN ISO 23913:2009
Cu	ISO 8288:1986 EN ISO 11885:2009 EN ISO 15586:2003 EN ISO 17294-1:2006 EN ISO 17294-2:2004
DOC/TOC	EN 1484:1997
Electrical conductivity	EN 27888:1993
F^-	EN ISO 10304-1:2009[b] ISO 10359-1:1992
Hg	EN 1483:2007 EN ISO 17852:2008
Mo	EN ISO 11885:2009 EN ISO 15586:2003 EN ISO 17294-1:2006 EN ISO 17294-2:2004

Table 1 *(continued)*

Parameter	Test method
Ni	ISO 8288:1986 EN ISO 11885:2009 EN ISO 15586:2003 EN ISO 17294-1:2006 EN ISO 17294-2:2004
NO_2^-	EN 26777:1993 EN ISO 10304-1:2009 EN ISO 13395:1996
Pb	ISO 8288:1986 EN ISO 11885:2009 EN ISO 15586:2003 EN ISO 17294-1:2006 EN ISO 17294-2:2004
Phenol index	EN ISO 14402:1999[c] ISO 6439:1990
Total S	EN ISO 11885:2009
Sb	EN ISO 11885:2009 EN ISO 15586:2003 EN ISO 17294-1:2006 EN ISO 17294-2:2004
Se	EN ISO 11885:2009 EN ISO 15586:2003 EN ISO 17294-1:2006 EN ISO 17294-2:2004 ISO 9965:1993
SO_4^{2-}	EN ISO 10304-1:2009 ISO 22743:2006
TDS	EN 15216:2007
V	EN ISO 11885:2009 EN ISO 15586:2003 EN ISO 17294-1:2006 EN ISO 17294-2:2004
Zn	ISO 8288:1986 EN ISO 11885:2009 EN ISO 15586:2003 EN ISO 17294-1:2006 EN ISO 17294-2:2004

[a] free cyanide is equivalent to easily liberatable cyanide for eluates with low organic content after distillation.

[b] for eluates with low organic content.

[c] after distillation.

8 Expression of results

Specific instructions for the calculation of the results given in the individual analytical standards shall be strictly observed.

The results of the tests except for pH and electrical conductivity shall be expressed as a concentration of the constituents in the eluate, expressed in µg/l or mg/l. The amount of constituent leached relative to the total mass of the sample, in mg/kg of dry matter, can be calculated using the liquid to solid ratio of the leaching test.

9 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 information.

Each test report shall include at least the following information:

a) reference to this European Standard and supplementary standards;

b) name and address of testing laboratory;

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

d) description and identification of the laboratory sample;

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

f) identification of the test specification or description of the method or procedure;

g) description of eluate sampling and treatment, where relevant;

h) any deviations, additions to or exclusions from the test specification, and any other information relevant to a specific test;

i) measurements, examinations and derived results, supported by tables, graphs, sketches and photographs as appropriate, and any failures identified;

j) a statement on measurement uncertainty (where needed);

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

l) a statement that the test results relate only to the laboratory sample;

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

Annex A
(informative)

Validation of EN 12506:2003 and EN 13370:2003

A.1 General

During 1999 - 2001 a project for validation of these standards has been organized and carried out.

The validation included an interlaboratory study for evaluation of performance characteristics of methods included in these standards (reproducibility and repeatability).

A.2 Interlaboratory study

The purpose of the validation trial was to check the suitability of the cited standards for analysis of waste eluates.

A.3 Selection of laboratories

A questionnaire has been circulated by all CEN/TC 292/WG 2 and WG 3 members to collect a list of interested European laboratories. 41 laboratories gave their commitment to participate in the interlaboratory trial. All of them were asked to declare that they fulfil the minimum requirements to carry out the analyses according to the standards. According to ISO 5725 series no selection has been made in advance on the basis of the supposed "ability" of laboratories, their accreditation, etc. It is therefore legitimate to regard the participating laboratories as a good average of "normal" European laboratories.

A.4 Selection of samples

To test the analytical procedures on a proper number of eluates, four different materials were considered to produce bulk amounts of waste eluates:

— contaminated soil (COS),

— sewage sludge (SEW),

— sand blasting waste (SBW),

— fly ash filter cake from municipal solid waste incinerator (FFC),

Additionally, three synthetic solutions were prepared (SYN1, SYN2 and SYN3).

The analytical procedures mentioned in the cited standards require different conservation methods. Since it was impossible to produce waste eluates using all the different conservating agents and methods according to the corresponding standards, it was decided to use only two conservation methods:

— addition of HNO_3 to a pH of about 2,

— no conservation agents but storage of the eluates at 4°C in the dark.

The waste eluates and synthetic solutions stabilized with HNO_3 were filled into polyethylene bottles and other samples into glass bottles. Table A.1 shows the different conservation procedures as mentioned in the standards and used in this trial.

A.5 Validation scope

In this trial not all parameter/method combinations were validated for the different samples. In Table A.1 an overview is given of the validation scope.

The parameter/method combinations marked with an **x** in Table A.1 were successfully validated. A remark is given in Table A.1 for those parameter/method combinations where the validation was not successful, because:

— the element concentrations in some samples did not match the working range for the analytical method;

— the number of participants and/or the number of results was too low;

— matrix dependent interferences occured.

In the other cases no validation study was performed.

Complementarily some of the standards cited in EN 12506:2003 and EN 13370:2003 have been validated by ISO on waste water.

Table A.1 — Validated parameter/method/sample combinations

Parameter	Standard	Prescribed conservation in standard	Used Conservation in trial	COS	FFC	SBW	SEW	SYN 1	SYN 2	SYN 3		Validated by ISO on waste water
Ammonium NH_4	ISO 7150-1	Immediate analysis or H_2SO_4 pH 2	None, 4 °C				x		x			
Ammonium NH_4	EN ISO 11732	Immediate analysis or H_2SO_4 pH 2	None, 4 °C				x		x			x
AOX	EN 1485	HNO_3 pH 2	HNO_3 pH 2	x			x					x
As	EN ISO 11885	HNO_3 pH 2	HNO_3 pH 2	x			x			a		x
As	EN ISO 11969	HCl pH 2	HNO_3 pH 2	x			b					
Ba	EN ISO 11885	HNO_3 pH 2	HNO_3 pH 2		x	x				x		
Cd	ISO 8288	HNO_3 pH 2	HNO_3 pH 2	x				x	x			
Cd	EN ISO 11885	HNO_3 pH 2	HNO_3 pH 2	x						x		
Cl^-	ISO 9297	None, 4 °C	None, 4 °C		x	x						x
Cl^-	EN ISO 10304-1	None, 4 °C	None, 4 °C		x	x	x					x
Cyanide easily liberatable	ISO 6703-2	NaOH pH 8	None, 4 °C				c	a	x			
Cyanide easily liberatable	EN ISO 14403	NaOH pH 12	None, 4 °C					x	a			x
Co	EN ISO 11885	HNO_3 pH 2	HNO_3 pH 2	x						x		
Cr	EN ISO 11885	HNO_3 pH 2	HNO_3 pH 2		x					x		
Cr(VI)	ISO 11083	Buffer pH 7	None, 4 °C		x			x				x
Cu	ISO 8288	HNO_3 pH 2	HNO_3 pH 2	x				x	x			
Cu	EN ISO 11885	HNO_3 pH 2	HNO_3 pH 2	x		x				x		
Electrical conductivity	EN 27888	None, 4 °C	None, 4 °C	x	x	x	x	x	x			x
F^-	EN ISO 10304-1	None, 4 °C	None, 4 °C		x	x						
F^-	ISO 10359-1	None, 4 °C	None, 4 °C		x	x						
Hg	EN 1483	$K_2Cr_2O_7$ pH 1	HNO_3 pH 2				a		x			x
Mo	EN ISO 11885	HNO_3 pH 2	HNO_3 pH 2		x					x		
Ni	ISO 8288	HNO_3 pH 2	HNO_3 pH 2	x				x	x			

Table A.1 *(continued)*

Parameter	Standard	Prescribed conservation in standard	Used Conservation in trial	COS	FFC	SBW	SEW	SYN 1	SYN 2	SYN 3		Validated by ISO on waste water
Ni	EN ISO 11885	HNO_3 pH 2	HNO_3 pH 2	x			x			x		
NO_2^-	EN 26777	None, 4 °C within 24 hrs	None, 4 °C		x		c		x			x
NO_2^-	EN ISO 10304-1	None, 4 °C immediate analysis	None, 4 °C		a		a		x			x
NO_2^-	EN ISO 13395	None, 4 °C immediate analysis	None, 4 °C		a				x			x
Phenol index	ISO 6439	H_3PO_4 $CuSO_4$ pH 4	None, 4 °C			x			a			
Phenol index	EN ISO 14402	Immediatean alysis or H_2SO_4 pH 2	None, 4 °C			a			x			x
Pb	ISO 8288	HNO_3 pH 2	HNO_3 pH 2	x				x	x			
Pb	EN ISO 11885	HNO_3 pH 2	HNO_3 pH 2	x						x		
pH	ISO 10523	None, immediate analysis	None, 4 °C	x	x	x	x	x	x			
Total S	EN ISO 11885	HNO_3 pH 2	HNO_3 pH 2	x			x			x		
SO_4^{2-}	EN ISO 10304-1	None, 4 °C	None, 4 °C		x	x	x					x
DOC/TOC	EN 1484	H_3PO_4 pH 2	HNO_3 pH 2	x			x					x
V	EN ISO 11885	HNO_3 pH 2	HNO_3 pH 2							x		
Zn	ISO 8288	HNO_3 pH 2	HNO_3 pH 2	x				x	x			
Zn	EN ISO 11885	HNO_3 pH 2	HNO_3 pH 2	x	x	x				x		

a Validation failed because less than 6 labs and /or 18 valid results were available.

b Validation failed because of matrix interference or conservation problems (EN ISO 11969, see Clause 7).

c Validation failed because coloured solutions can not be analyzed by this method (see Clause 6).

A.6 Results and statistics

The data from the interlaboratory study have been assessed according to ISO 5725-2. Furthermore the results have been filtered by acceptance criteria.

The tested parameters, the accepted combinations of method/parameter/sample, and the results of the statistical evaluation are given in Table A.2 to Table A.8.

Results from rejected combinations of method/parameter/sample are not shown in the result tables.

The acceptance criteria were:

— Minimum number of laboratories: 6

— Minimum number of results (outliers excluded): 18

If applicable, for a given parameter a F-test on the sR values and a t-test for the means have been run for comparing alternative methods at the 99 % confidence interval. Where one of the tests failed, a remark is given in the tables.

Table A.2 — Results of the interlaboratory study on validation of methods for eluate analysis– Contaminated soil eluate (COS)

Parameter	Standard	Units	Number of					Mean	s_r	s_R	S_r	S_R	Remarks
			Labs total	Labs accepted	Values total	Values accepted	Outliers				%	%	
AOX	EN 1485	µg/l	14	13	42	38	4	27,8	2,43	7,73	8,75	27,8	
As – hydride AAS	EN ISO 11969	µg/l	13	13	39	39	-	17,4	0,92	5,90	5,32	33,9	Sample stabilized with HNO_3, HCl is prescribed
As – ICP-OES	EN ISO 11885	µg/l	12	11	36	33	3	20,6	0,98	5,79	4,76	28,1	
Cd – ICP-OES	EN ISO 11885	µg/l	17	17	51	51	-	207	4,72	13,5	2,28	6,5	
Cd – ICP-OES/ AAS	ISO 8288	µg/l	8	8	24	24	-	208	7,42	14,6	3,57	7,02	
Co - ICP-OES	EN ISO 11885	µg/l	16	14	48	42	6	74,4	1,41	11,8	1,9	15,9	
Cu – ICP-OES	EN ISO 11885	µg/l	17	16	51	48	3	358	5,98	28,4	1,67	7,94	
Cu - AAS	ISO 8288	µg/l	8	8	24	23	1	363	2,40	18,2	0,66	5,01	
Electrical conductivity	EN 27888	µS/cm	12	11	36	30	6	2450	7,35	207,8	0,3	8,48	
Ni - ICP-OES	EN ISO 11885	µg/l	16	14	47	41	6	49,3	1,43	4,77	2,91	9,68	F-test failed
Ni - AAS	ISO 8288	µg/l	7	7	21	21	-	49,4	1,55	1,67	3,14	3,38	F-test failed
Pb - ICP-OES	EN ISO 11885	µg/l	17	16	51	48	3	324	7,00	19,9	2,16	6,13	F-test failed
Pb - AAS	ISO 8288	µg/l	8	8	24	24	-	326	7,79	48,9	2,39	15	F-test failed
pH - Electrode	EN ISO 10523	-	13	12	38	32	6	6,14	0,025	0,287	0,41	4,68	
DOC/TOC	EN 1484	mg/l	15	13	45	39	6	16,3	0,30	1,54	1,82	9,42	
Total S - ICP-OES	EN ISO 11885	µg/l	10	8	30	24	6	451000	8344	44649	1,85	9,9	
Zn - ICP-OES	EN ISO 11885	µg/l	17	16	51	48	3	49600	719	4052	1,45	8,17	
Zn - AAS	ISO 8288	µg/l	8	8	24	24	-	49500	782	3569	1,58	7,21	

S_r relative repeatability
S_R relative reproducibility

Table A.3 — Results of the interlaboratory study on validation of methods for eluate analysis – Sewage sludge eluate (SEW)

Parameter	Standard	Units	Number of					Mean	s_r	s_R	S_r	S_R	Remarks
			Labs total	Labs accepted	Values total	Values accepted	Outliers				%	%	
NH_4 – FIA/CFA	ISO EN 11732	mg/l	11	11	34	34	-	401	5,77	81,3	1,44	20,28	F-test failed
NH_4 - Photometry	ISO 7150-1	mg/l	11	10	33	30	3	360	8,03	152	2,23	42,11	F-test failed
AOX	EN 1485	mg/l	13	11	39	32	7	0,153	0,011	0,061	7,16	39,95	
As - ICP-OES	EN ISO 11885	µg/l	13	11	39	33	6	139	10,6	26,9	7,66	19,38	
Cl^- - IC	EN ISO 10304-1	mg/l	13	13	40	40	-	92,2	3,45	18,7	3,75	20,26	
Electrical conductivity	EN 27888	µS/cm	13	10	37	28	9	3530	11,6	469	0,33	13,3	
Ni - ICP-OES	EN ISO 11885	µg/l	16	16	48	48	-	117	5,52	11,5	4,72	9,8	
pH - Electrode	ISO 10523	-	14	12	40	34	6	6,29	0,048	0,34	0,76	5,34	
SO_4^{2-} - IC	EN ISO 10304-1	mg/l	12	12	37	37	-	53,9	1,61	8,49	2,98	15,75	
DOC/TOC	EN 1484	mg/l	15	13	47	41	6	1560	40,3	99,7	2,58	6,39	
Total S - ICP-OES	EN ISO 11885	µg/l	10	7	29	20	9	62700	552	1568	0,88	2,5	

Table A.4 — Results of the interlaboratory study on validation of methods for eluate analysis – Sand blasting waste eluate (SBW)

Parameter	Standard	Units	Number of					Mean	s_r	s_R	S_r	S_R
			Labs total	Labs accepted	Values total	Values accepted	Outliers				%	%
Ba - ICP-OES	EN ISO 11885	µg/l	16	15	47	44	3	80,4	1,51	10,1	1,88	12,59
Cl^- – IC	EN ISO 10304-1	mg/l	12	11	36	33	3	20,2	1,00	2,20	4,96	10,87
Cl^- - Titration	ISO 9297	mg/l	8	8	24	24	-	22	1,38	2,82	6,27	12,84
Cu - ICP-OES	EN ISO 11885	µg/l	16	15	48	45	3	102	4,29	12,4	4,21	12,17
Electrical conductivity	EN 27888	µS/cm	12	11	33	31	2	530	2,12	23,5	0,4	4,43
F^- - Electrode	ISO 10359-1	mg/l	10	10	30	30	-	7,66	0,060	0,99	0,78	12,91
F^- - IC	EN ISO 10304-1	mg/l	11	11	33	33	-	7,42	0,153	1,23	2,06	16,57
pH - Electrode	ISO 10523	-	13	13	35	35	-	6,99	0,055	0,18	0,79	2,54
Phenol index - Photometry	ISO 6439	mg/l	8	8	24	24	-	0,246	0,0187	0,095	7,62	38,6
SO_4^{2-} - IC	EN ISO 10304-1	mg/l	12	9	36	27	9	108	2,53	2,94	2,34	2,72
Zn - ICP-OES	EN ISO 11885	µg/l	16	16	48	48	-	260	7,25	26,1	2,79	10,02

Table A.5 — Results of the interlaboratory study on validation of methods for eluate analysis – Fly ash filter cake eluate (FFC)

Parameter	Standard	Units	Number of					Mean	s_r	s_R	S_r	S_R	Remarks
			Labs total	Labs accepted	Values total	Values accepted	Outliers				%	%	
Ba - ICP-OES	EN ISO 11885	µg/l	16	16	47	47	-	57,9	2,42	6,83	4,18	11,8	
Cl^- – IC	EN ISO 10304-1	mg/l	12	12	37	37	-	292	5,20	85,0	1,78	29,1	F-test failed
Cl^- - Titration	ISO 9297	mg/l	9	8	26	23	3	279	2,59	10, 7	0,93	3,83	F-test failed
Cr – ICP	EN ISO 11885	µg/l	16	15	48	45	3	1140	23,6	101	2,07	8,88	
Cr(VI) - Photometry	ISO 11083	µg/l	10	8	30	24	6	1150	8,86	132	0,77	11,51	
Electrical conductivity	EN 27888	µS/cm	12	12	33	33	-	2880	13,5	240	0,47	8,34	
F^- - Electrode	ISO 10359-1	mg/l	9	9	27	21	6	0,709	0,023	0,086	3,25	12,15	
F^- – IC	EN ISO 10304-1	mg/l	8	7	24	20	4	0,629	0,009	0,123	1,35	19,52	
Mo - ICP-OES	EN ISO 11885	µg/l	16	15	47	44	3	467	14,9	66,8	3,19	14,32	
NO_2^- - Photometry	EN 26777	mg/l	8	8	24	24	-	0,029	0,001	0,019	4,66	65,93	
pH - Electrode	ISO 10523	-	13	10	35	26	9	9,98	0,12	0,42	1,24	4,23	
SO_4^{2-} - IC	EN ISO 10304-1	mg/l	13	12	37	34	3	1350	18,5	85,7	1,37	6,35	
Zn - ICP-OES	EN ISO 11885	µg/l	16	16	48	48	-	281	8,88	37,7	3,16	13,42	

Table A.6 — Results of the interlaboratory study on validation of methods for eluate analysis – Synthetic eluate 1 (SYN1)

Parameter	Standard	Units	Number of					Mean	s_r	s_R	S_r	S_R	Remarks
			Labs total	Labs accepted	Values total	Values accepted	Outliers				%	%	
Cd - AAS	ISO 8288	µg/l	8	8	24	24	-	35,5	3,21	6,25	9,05	17,61	
CN – CFA	EN ISO 14403	mg/l	7	7	22	22	-	0,175	0,007	0,087	4,08	49,62	
Cr(VI) - Photometry	ISO 11083	mg/l	10	9	30	27	3	0,108	0,002	0,039	2,16	35,98	
Cu - AAS	ISO 8288	µg/l	8	8	24	24	-	19,2	1,22	2,92	6,35	15,2	
Electrical conductivity	EN 27888	µS/cm	13	11	37	31	6	353	5,26	17,4	1,49	4,92	
Ni - AAS	ISO 8288	µg/l	7	7	21	21	-	19	1,12	3,11	5,91	16,35	
Pb - AAS	ISO 8288	µg/l	8	8	24	24	-	13,8	0,73	8,16	5,29	59,14	Close to the detection limit
pH - Electrode	ISO 10523	-	14	13	40	37	3	6,68	0,081	0,63	1,22	9,46	
Zn - AAS	ISO 8288	µg/l	8	8	24	24	-	748	14,7	32,5	1,96	4,34	

Table A.7 — Results of the interlaboratory study on validation of methods for eluate analysis – Synthetic eluate 2 (SYN2)

Parameter	Standard	Units	Number of					Mean	s_r	s_R	S_r	S_R	Remarks
			Labs total	Labs accepted	Values total	Values accepted	Outliers				%	%	
NH_4 – FIA/CFA	EN ISO 11732	mg/l	10	8	32	26	6	0,248	0,013	0,067	5,22	27,17	F-test failed
NH_4 - Photometry	ISO 7150-1	mg/l	11	9	33	27	6	0,223	0,007	0,019	3,26	8,31	F-test failed
Cd - AAS	ISO 8288	µg/l	8	6	24	18	6	32,3	1,23	4,58	3,81	14,18	
CN^- Photometry	ISO 6703-2	mg/l	6	6	18	18	-	0,041	0,003	0,006	6,7	13,7	
Cu - AAS	ISO 8288	µg/l	8	6	24	18	6	19,7	0,99	2,44	5,05	12,39	
Electrical conductivity	EN 27888	µS/cm	13	13	36	36	-	478	2,92	21,6	0,61	4,51	
Hg - CV-AAS	EN 1483	µg/l	12	11	36	33	3	6,25	0,13	1,36	2,1	21,8	
Ni - AAS	ISO 8288	µg/l	7	7	21	21	-	19,5	0,96	2,39	4,93	12,25	
NO_2^- - FIA/CFA	EN ISO 13395	mg/l	11	9	33	26	7	0,132	0,001	0,049	0,98	37,17	
NO_2^- - IC	EN ISO 10304-1	mg/l	9	8	27	24	3	0,138	0,009	0,044	6,88	31,56	
NO_2^- - Photometry	EN 26777	mg/l	10	10	30	30	-	0,145	0,004	0,034	2,9	23,46	
Pb - AAS	ISO 8288	µg/l	8	7	24	21	3	14,7	0,82	8,86	5,57	60,25	Close to the detection limit
pH - Electrode	ISO 10523	-	14	13	38	35	3	6,94	0,054	0,22	0,78	3,13	
Phenol index – FIA/CFA	EN ISO 14402	mg/l	6	6	18	18	-	0,067	0,003	0,016	4,16	24,5	
Zn - AAS	ISO 8288	µg/l	8	8	24	24	-	807	14,8	57,7	1,84	7,15	

Table A.8 — Results of the interlaboratory study on validation of methods for eluate analysis – Synthetic eluate 3 (SYN3)

Parameter	Standard	Units	Number of					Mean	s_r	s_R	S_r	S_R	Remarks
			Labs total	Labs accepted	Values total	Values accepted	Outliers				%	%	
Ba - ICP-OES	EN ISO 11885	µg/l	15	15	42	41	1	27,1	1,07	3,48	3,95	12,85	
Cd - ICP-OES	EN ISO 11885	µg/l	16	14	48	42	6	365	7,34	29,5	2,01	8,09	
Co - ICP-OES	EN ISO 11885	µg/l	10	9	27	24	3	5,85	0,42	0,54	7,21	9,3	
Cr - ICP-OES	EN ISO 11885	µg/l	16	15	45	42	3	81,8	3,42	6,98	4,18	8,53	
Cu – ICP-OES	EN ISO 11885	µg/l	12	10	35	30	5	7,66	1,15	1,28	14,98	16,75	
Mo - ICP-OES	EN ISO 11885	µg/l	15	14	41	38	3	70,3	3,70	11,3	5,27	16,05	
Ni - ICP-OES	EN ISO 11885	µg/l	12	11	35	32	3	13,3	0,83	2,29	6,23	17,22	
Pb - ICP-OES	EN ISO 11885	µg/l	15	14	45	41	4	75,9	3,20	16,1	4,21	21,17	
S - ICP-OES	EN ISO 11885	µg/l	10	9	27	24	3	50500	747	3848	1,48	7,62	
V - ICP-OES	EN ISO 11885	µg/l	13	12	34	30	4	24,9	1,42	4,60	5,71	18,49	
Zn - ICP-OES	EN ISO 11885	µg/l	16	16	47	47	-	18600	616	1655	3,31	8,9	

A.7 Conclusion

The validation of the European Standards EN 12506:2003 and EN 13370:2003 was performed in the period 1999-2001 on a selection of waste and synthetic eluates. These data are still applicable for this European Standard because the same analytical methods (in some cases with minor revisions) are referred to.

For most analytical methods validation data are available for at least two eluates per parameter. In the case of As (EN ISO 11969:1996), easily liberatable CN^- (EN ISO 14403:2002 and ISO 6703-2:1984), Hg (EN 1483:2007), NO_2^- (EN ISO 10304-1:2009 and EN ISO 13395:1996), phenol index (EN ISO 14402:1999 and ISO 6439:1990) and V (EN ISO 11885:2009) only one matrix was validated.

For some parameters different analytical methods were validated. In any case, for the analysis of a given parameter within a specific matrix, it is the responsibility of the laboratory to choose the appropriate analytical method depending on the expected interferences and concentration range as mentioned in the respective standards.

There is no international standard on equivalence testing between alternative physical or chemical methods available. However based on the F-test and the t-test for means (used are the s_R values) there is a realistic chance to prove equivalence between the following method/matrix combinations:

— for COS: As – ICP-OES (EN ISO 11885), As – AAS (EN ISO 11969),

Cd – ICP-OES (EN ISO 11885), Cd – AAS (ISO 8288),

Cu – ICP-OES (EN ISO 11885), Cu – AAS (ISO 8288),

Zn – ICP-OES (EN ISO 11885), Zn – AAS (ISO 8288);

— for SBW Cl^- – IC (EN ISO 10304-1), Cl^- - Titration (ISO 9297),

F^- – Electrode (ISO 10359-1), F^- - IC (EN ISO 10304-1);

— for FFC F^- – Electrode (ISO 10359-1), F^- - IC (EN ISO 10304-1);

— for SYN2 NO_2^- – FIA/CFA (EN ISO 13395), NO_2^- - IC (EN ISO 10304-1),
NO_2^- – Photometry (EN 26777).

Annex B
(informative)

Additional validation data

B.1 Round robin test for the determination of Ba, Cd, Cr, Mo, Sb and Se in eluates

B.1.1 General

In 2004 - 2005 a round robin test was organized by the Flemish Institute for Technological Research (VITO, Belgium) in commission of the Public Waste Agency of Flanders (OVAM) to evaluate the analytical performance of laboratories for the determination of Ba, Cd, Cr, Mo, Sb and Se in eluates. Nineteen laboratories (from Flanders/Belgium and the Netherlands) with recognized expertise for eluate analysis participated in this round robin test and analyzed four samples spiked with the elements at relevant concentration levels.

B.1.2 Round robin samples

Eluate samples were prepared from two waste samples i.e. a blasting grit (eluate 1) and a contaminated soil (eluate 2). To these eluate matrices the elements Ba, Cd, Cr, Mo, Sb and Se were added to get four concentration levels (low and high region). The reference values for these spiked eluates are presented in Table B.1.

Table B.1 — Reference values of round robin samples

Element	Eluate 1-1 µg/l	Eluate 1-2 µg/l	Eluate 2-1 µg/l	Eluate 2-2 µg/l
Mo	54,8	1175	43	494
Sb	7,5	79	101	12,4
Se	12	59	15,5	79
Ba	1275	2937	996	1977
Cr	39	1174	3921	26
Cd	2,95	117	4,96	147

B.1.3 Results of the round robin test

The results of the round robin test were subjected to a Grubbs outlier test (95 % confidence level, 2-sided). The outliers were removed and from the remaining values the average, the reproducibility coefficient of variation (% CV_R) and the bias towards the reference value were calculated.

For the elements Mo, Ba, Cr and Cd an overview of the obtained results is presented in Table B.2. Combining the results of both ICP-MS and ICP-OES, results in a reproducibility coefficient of variation for all elements and type of eluates of less than 7 %. The bias of the average is within acceptable limits. Only for the element Cd in eluate 2-1 an increased negative bias of -12 % is observed.

Evaluation of the dataset as a function of the applied analytical technique (i. e. ICP-MS and ICP-OES) results in comparable measurement uncertainties.

Table B.2 — Overview of the round robin results for Mo, Ba, Cr and Cd

Eluate		Refer. value	All results				ICP-MS		ICP-OES	
				$\bar{x}$	CV_R	Bias		CV_R		CV_R
		µg/l	n / o	µg/l	%	%	n / o	%	n / o	%
1-1	Mo	54,8	19/2	54	4,0	-0,8	4/0	5,0	15/2	3,6
	Ba	1275	21/0	1258	3,2	-1,3	4/0	3,0	17/0	3,2
	Cr	39	21/0	39	6,5	0,1	4/0	5,2	17/0	6,9
	Cd	2,95	18/3	2,9	5,2	-3,1	5/1	7,7	13/2	4,3
1-2	Mo	1175	20/1	1178	5,4	0,2	4/0	6,0	16/1	5,2
	Ba	2937	21/0	2988	4,6	1,7	4/0	6,7	17/0	3,9
	Cr	1174	20/1	1191	4,3	1,5	4/0	5,1	16/1	4,0
	Cd	117	20/1	115	3,4	-1,4	6/0	3,7	14/1	2,9
2-1	Mo	43	19/2	46	6,3	6,9	4/0	7,1	15/2	6,3
	Ba	996	21/0	961	5,3	-3,5	4/0	6,5	17/0	5,2
	Cr	3921	21/0	4048	3,5	3,3	4/0	4,2	17/0	3,5
	Cd	4,96	19/2	4,3	7,2	-12	6/0	4,8	13/2	7,9
2-2	Mo	494	20/1	472	6,3	-4,5	4/0	6,9	16/1	6,0
	Ba	1977	21/0	1948	4,6	-1,4	4/0	5,8	17/0	5,4
	Cr	26	20/1	26	6,1	0,8	4/0	7,3	16/1	6,0
	Cd	147	20/1	143	4,5	-3,0	6/0	4,3	14/1	4,2

n: number of accepted results;
o: number of outliers;
CV_R: reproducibility coefficient of variation;
$\bar{x}$: mean.

Based on these results it can be concluded that for the elements Mo, Ba, Cr and Cd accurate and reproducible data can be obtained, independent of the applied technique (ICP-MS or ICP-OES).

For the elements Sb and Se an overview of all the results is given in Table B.3. These results show that for low levels of Sb and Se (7,5 µg/l to 15,5 µg/l) rather large reproducibility coefficient of variation of up to ±17 % were obtained. And although the concentration level of Sb in eluate 2-1 was higher, an even larger reproducibility coefficient of variation of 25 % is observed.

Table B.3 — Overview of the round robin results for Sb and Se

Eluate		Refer. value	All results			
				$\bar{x}$	CV_R	Bias
		µg/l	n / o	µg/l	%	%
1-1	Sb	7,5	19/2	7,2	16	-4,4
	Se	12	18/3	12	11	-1,7
1-2	Sb	79	19/2	77	8,7	-2,8
	Se	59	21/0	59	7,6	0,1
2-1	Sb	101	19/2	109	25	7,7
	Se	15,5	20/1	16	16	1,8
	Cr	3921	21/0	4048	3,5	3,3
2-2	Sb	12,4	20/1	11,6	17	-6,2
	Se	79	20/1	81	6,2	2,1

n: number of accepted results;
o: number of outliers;
CV_R: reproducibility coefficient of variation;
$\bar{x}$: mean.

Evaluation of the results as a function of the applied analytical technique shows that the analyses performed with ICP-MS (Table B.4) result in values with the lowest measurement uncertainty and the lowest bias towards the reference values.

Table B.4 — Overview of the ICP-MS results for Sb and Se

Eluate		Refer. value	ICP-MS results		
			$\bar{x}$	CV_R	Bias
		µg/l	µg/l	%	%
1-1	Sb	7,5	7,4	4,4	-1,4
	Se	12	11	6,4	-4,9
1-2	Sb	79	77	5,1	-1,9
	Se	59	57	4,6	-2,8
2-1	Sb	101	103	6,3	1,6
	Se	15,5	15,5	6,4	0,0
	Cr	3921	4079	4,2	4,0
2-2	Sb	12,4	13,0	6,9	4,9
	Se	79	79	3,7	-0,3

5 results of Sb; 6 results of Se;
no outliers detected;
CV_R: reproducibility coefficient of variation;
$\bar{x}$: mean.

Analytical results obtained with ICP-OES (Table B.5) reveal high measurement uncertainties for samples with a low concentration level of Sb and Se. This can be attributed to the fact that the concentration levels of both Sb and Se were close to the method-specific limits of determination for these elements.

For eluate 2-1 with a higher content of Sb (101 µg/l) a significant exceeding of the reference value (bias of 22 %) was observed. This overestimation can be attributed to the interference of Cr on the Sb spectral line of 206,833 nm. If no interelement correction is applied or no other spectral line of Sb (217,581 nm) is selected, there will be an overestimation of the Sb value.

Table B.5 — Overview of the ICP-OES results for Sb and Se

Eluate		Refer. Value	ICP-OES results			
				$\bar{x}$	CV_R	Bias
		µg/l	n / o	µg/l	%	%
1-1	Sb	7,5	7/2	7,6	19	0,8
	Se	12	7/3	12	15	0,7
1-2	Sb	79	10/2	79	9,7	-0,4
	Se	59	11/0	60	9,5	1,1
2-1	Sb	101	10/2	124	20	22
	Se	15,5	8/1	16	22	5,8
	Cr	3921	17/0	4041	3,5	3,1
2-2	Sb	12,4	9/1	10,9	23	-13
	Se	79	10/1	82	7,5	3,4

n: number of accepted results;
o: number of outliers;
CV_R: reproducibility coefficient of variation;
$\bar{x}$: mean.

Results for Sb and Se obtained after hydride generation and detection with ICP-OES or ICP-MS and with graphite furnaceatomic absorption spectrometry (GF-AAS) are shown in Table B.6. Applying these analytical methods results in lower measurement uncertainties compared to direct analysis with ICP-OES. However, for Sb a tendency to a negative bias towards the reference value was observed when applying hydride generation technique, although this phenomenon seems to be laboratory-dependent. This indicates, that the procedure for hydride generation has to be optimized in order to obtain maximum yields.

The results obtained for both elements with GF-AAS were in good agreement with the corresponding reference values.

Table B.6 — Overview of results for Sb and Se obtained with hydride generation - ICP-OES/ICP-MS and GF-AAS

Eluate		Refer. value	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Average	CV_R	Bias
		µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	%	%
1-1	Sb	7,5	5,3	6,5	5,9	6,7	7,5	6,4	13	-15
	Se	12	-	12,8	12,0	10,4	12,4	12	8,9	-1,1
1-2	Sb	79	70,2	73	65,5	-	75,5	71	6,0	-10
	Se	59	-	61	58,9	-	60,5	60	1,9	1,9
2-1	Sb	101	101	**42**	81	-	94	92	11	-9,0
	Se	15,5	-	17	14,3	14,7	13,9	15	9,3	-3,4
2-2	Sb	12,4	12,0	12	10,6	12,3	11,5	11,7	5,7	-5,9
	Se	79	-	81	76,2	-	85,9	81	6,0	2,6
Technique			A	B,C	B, E	B,C	D, E			

Bold: outlier, not included in the statistical evaluation;
A: Sb: hydride – ICP-MS; B: Sb: hydride – ICP-OES; C: Se: hydride – ICP-OES; D: Sb: GF-AAS;
E: Se: GF-AAS
CV_R: reproducibility coefficient of variation

B.1.4 Conclusion from the round robin test

Based on obtained results it can be concluded that:

For the determination of the elements Sb and Se the ICP-MS technique is the method of choice, especially if concentrations in the lower µg/l - range have to be determined with minimum measurement uncertainty.

Using the ICP-OES technique, the limit of detection for Sb and Se is too high to verify the lowest limit values with an acceptable confidence level. Be aware that Cr interferes on the spectral line of Sb (206,836 nm), therefore an interelement correction has to be performed or an alternative line for Sb has to be taken.

The hydride generation ICP-OES/ICP-MS techniques can be used to measure Sb and Se, provided that the hydride generation procedure is capable of obtaining maximum yields for these elements.

GF-AAS can also be considered as a suitable alternative for the determination of Sb and Se in eluates.

B.2 Round robin tests in the framework of acceptability of waste at landfills

On a regular base, the Flemish Institute for Technological Research (VITO, Belgium) organizes in commission of the Public Waste Agency of Flanders (OVAM) round robin tests for the recognition of laboratories. The analysis of waste samples and/or eluates in the framework of the acceptability of waste at landfills is included in these round robin tests. In Table B.7 an overview is given of the round robin results of 2007 - 2010, respectively, for the parameters of interest. The laboratories were free to choose analytical methods cited in this European Standard. For the elements of interest the following methods were used by the participating laboratories: ICP-OES, ICP-MS, GF-AAS and hydride generation-ICP-OES.

As reference value either the spiked value or the average of all the laboratory results was taken. If the reference value was obtained from a spiked sample, the bias was calculated between the reference value and the average of the various laboratory results. The results of 6 to 13 laboratories were processed and the reproducibility coefficient of variation were calculated.

Table B.7 — Results of round robin tests in the framework of acceptability of waste at landfills

		Period: 03.2010					Period: 03.2009			Period: 03.2008					Period: 03.2007				
	Unit	Refer. value	n/o	$\bar{x}$	CV_R %	Bias %	n/o	$\bar{x}$	CV_R %	Refer. value	n/o	$\bar{x}$	CV_R %	Bias %	Refer. value	n/o	$\bar{x}$	CV_R %	Bias %
Antimony	µg/l		9/1	266	22		9/1	22,14	11		8/2	95,7	4			13/0	37	21	
Arsenic	µg/l		8/1	77,8	133		10/0	76,7	8	-	-	-	-		150	12/1	152	5	1
Barium	µg/l	3461	9/1	3398	3	-2	10/0	1032	3		10/0	721	5			13/1	158	15	
Cadmium	µg/l		9/1	2282	7		10/0	6,71	4	25	8/2	24,8	5	-1	12,5	13/0	12,7	6	1
Chloride	mg/l		10/0	529	10		10/0	77	4		10/0	156	9			12/1	907	3	
Chromium tot	µg/l	126	9/1	124	5	-1	9/1	65,6	4	300	10/0	303	4	1		12/1	122	10	
Chromium VI	µg/l	375	6/1	374	1	0,2	7/1	443	4	191	9/0	185	9	-3		11/0	104	35	
Copper	µg/l	714	9/1	709	2	-1	10/0	1273	6		10/0	12,2	17			13/0	6300	8	
Cyanide	µg/l	1125	10/0	1146	8	2	10/0	1280	9	750	10/0	778	6	4		12/0	819	4	
DOC	mg/l	143	10/0	137	6	-4	10/0	94,8	4		8/2	84,4	5			10/0	287	9	
Fluoride	mg/l		8/1	5,87	3		9/0	0,808	17	3,24	9/0	3,39	10	5	2,5	13/0	2,5	6	0
Lead	µg/l	176	9/1	171	4	-3	10/0	75,6	3	500	10/0	492	4	-2	250	12/1	241	5	-3
Mercury	µg/l	3,72	10/0	3,48	9	-6	9/1	1,35	11	7,5	10/0	7,43	9	-1	10	13/0	9,73	14	-3
Molybdenum	µg/l	127	9/1	129	3	1	10/0	130	5		10/0	597	8			13/0	178	6	
Nickel	µg/l	83	9/1	82,5	4	-1	10/0	46,2	5		10/0	30,1	13			13/0	26,1	8	
pH			9/1	9,24	2		10/0	8,33	1		10/0	11,7	1			11/2	10,7	2	
Selenium	µg/l		10/0	3397	58		10/0	16,4	20	65	10/0	66,4	12	2	35	12/1	35,2	18	0
Sulfate (SO_4)	mg/l		10/0	1865	3		9/1	495	5		10/0	1423	7			13/0	549	11	
TDS	mg/l		10/0	3958	4		10/0	1204	5		9/1	3019	4			10/3	3304	6	
Zinc	µg/l	1664	9/1	1627	3	-2	10/0	61,4	32		10/0	545	45		10000	13/0	9542	6	-5

Reference value: spiked value; n: number of accepted results; o: number of outliers; Average: average results of x labs;CVR: reproducibility coefficient of variation; % bias: difference between reference value and average

.

Bibliography

[1] EN 12457-1:2002, *Characterization of waste — Leaching — Compliance test for leaching of granular waste materials and sludges — Part 1: One stage batch test at a liquid to solid ratio of 2 l/kg for materials with high solid content and with particle size below 4 mm (without or with size reduction)*

[2] EN 12457-2:2002, *Characterization of waste — Leaching — Compliance test for leaching of granular waste materials and sludges — Part 2: One stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 4 mm (without or with size reduction)*

[3] EN 12457-3:2002, *Characterization of waste — Leaching — Compliance test for leaching of granular waste materials and sludges — Part 3: Two stage batch test at a liquid to solid ratio of 2 l/kg and 8 l/kg for materials with high solid content with particle size below 4 mm (without or with size reduction)*

[4] EN 12457-4:2002, *Characterization of waste — Leaching — Compliance test for leaching of granular waste materials and sludges — Part 4: One stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 10 mm (without or with size reduction)*

[5] EN 12506:2003, *Characterization of waste — Analysis of eluates — Determination of pH, As, Ba, Cd, Cl-, Co, Cr, Cr VI, Cu, Mo, Ni, NO2-, Pb, total S, SO42-, V and Zn*

[6] EN 12920:2006+A1:2008, *Characterization of waste — Methodology for the determination of the leaching behaviour of waste under specified conditions*

[7] EN 13370:2003, *Characterization of waste — Analysis of eluates — Determination of Ammonium, AOX, conductivity, Hg, phenol index, TOC, easily liberatable CN-, F-*

[8] CEN/TS 14405:2004, *Characterization of waste — Leaching behaviour tests — Up-flow percolation test (under specified conditions)*

[9] CEN/TS 14429:2005, *Characterization of waste — Leaching behaviour tests — Influence of pH on leaching with initial acid/base addition*

[10] CEN/TS 14997:2006, *Characterization of waste — Leaching behaviour tests — Influence of pH on leaching with continuous pH-control*

[11] EN 15002, *Characterization of waste — Preparation of test portions from the laboratory sample*

[12] CEN/TR 16184, *Characterization of waste — State-of-the-art document – Analysis of eluates*

[13] ENV ISO 13530:1998, *Water quality — Guide to analytical quality control for water analysis (ISO/TR 13530:1997)*

[14] EN ISO/IEC 17025:2005, *General requirements for the competence of testing and calibration laboratories (ISO/IEC 17025:2005)*

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

[16] 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*

[17] 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*

[18] 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*

[19] ISO 5725-5:1998, *Accuracy (trueness and precision) of measurement methods and results — Part 5: Alternative methods for the determination of the precision of a standard measurement method*

[20] ISO 5725-6:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 6: Use in practice of accuracy values*

[21] NEN 6604:2007, *Water — Bepaling van het gehalte aan ammonium, nitraat, nitriet, chloride, ortho-fosfaat, sulfaat en silicaat met een discreet analysesysteem en spectrofotometrische detectie; Water Quality — Determination of ammonium, nitrate, nitrite, chloride, ortho-phosphate, sulphate and silicate by a discrete analyzer system and spectrophotometric detection*

[22] 2003/33/EC, Council Decision of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC

[23] 75/442/EEC, Council Directive of 15 July 1975 on waste

[24] 91/156/EEC, Council Directive of 18 March 1991 amending Directive 75/442/EEC on waste (91/156/EEC)

[25] H.A. van der Sloot, O. Hjemar, J. Bjerre-Hansen, P. Woitke, P. Lepom, R. Leschber, B. Bartet, B. Leathem: Validation of CEN/TC 292 Leaching tests and eluate analysis methods prEN 12457 part 1-4, ENV 13370 and ENV 12506 in Co-operation with CEN/TC 308, May 2001

[26] C. Vanhoof and K. Tirez, VITO report 2002/MIM/R/060, Waste on landfills: determination of analytical methods for new parameters, May 2005 (in Dutch)

[27] V. Hermans, H. Van den Broeck, VITO report 2007/MIM/R/98, AARDE 2007: Acceptance criteria for waste on landfills, July 2007 (in Dutch)

[28] V. Hermans, C. Kenis, H. Van den Broeck, VITO report 2008/MIM/R/108, AARDE 2008: Acceptance criteria for waste on landfills, October 2008 (in Dutch)

[29] C. Kenis, V. Hermans, H. Van den Broeck, VITO report 2009/MANT/R/071, AARDE 2009: Acceptance criteria for waste on landfills, December 2009 (in Dutch)

[30] T. De Ceuster, C. Kenis, S. Hofman, H. Van den Broeck, VITO report 2011/REE/R/01, AARDE 2010: Acceptance criteria for waste on landfills, Maart 2011 (in Dutch)

This page deliberately left blank

British Standards Institution (BSI)

BSI is the national body responsible for preparing British Standards and other standards-related publications, information and services.

BSI is incorporated by Royal Charter. British Standards and other standardization products are published by BSI Standards Limited.

About us

We bring together business, industry, government, consumers, innovators and others to shape their combined experience and expertise into standards -based solutions.

The knowledge embodied in our standards has been carefully assembled in a dependable format and refined through our open consultation process. Organizations of all sizes and across all sectors choose standards to help them achieve their goals.

Information on standards

We can provide you with the knowledge that your organization needs to succeed. Find out more about British Standards by visiting our website at bsigroup.com/standards or contacting our Customer Services team or Knowledge Centre.

Buying standards

You can buy and download PDF versions of BSI publications, including British and adopted European and international standards, through our website at bsigroup.com/shop, where hard copies can also be purchased.

If you need international and foreign standards from other Standards Development Organizations, hard copies can be ordered from our Customer Services team.

Subscriptions

Our range of subscription services are designed to make using standards easier for you. For further information on our subscription products go to bsigroup.com/subscriptions.

With **British Standards Online (BSOL)** you'll have instant access to over 55,000 British and adopted European and international standards from your desktop. It's available 24/7 and is refreshed daily so you'll always be up to date.

You can keep in touch with standards developments and receive substantial discounts on the purchase price of standards, both in single copy and subscription format, by becoming a **BSI Subscribing Member**.

PLUS is an updating service exclusive to BSI Subscribing Members. You will automatically receive the latest hard copy of your standards when they're revised or replaced.

To find out more about becoming a BSI Subscribing Member and the benefits of membership, please visit bsigroup.com/shop.

With a **Multi-User Network Licence (MUNL)** you are able to host standards publications on your intranet. Licences can cover as few or as many users as you wish. With updates supplied as soon as they're available, you can be sure your documentation is current. For further information, email bsmusales@bsigroup.com.

BSI Group Headquarters

389 Chiswick High Road London W4 4AL UK

Revisions

Our British Standards and other publications are updated by amendment or revision.

We continually improve the quality of our products and services to benefit your business. If you find an inaccuracy or ambiguity within a British Standard or other BSI publication please inform the Knowledge Centre.

Copyright

Useful Contacts:

Customer Services
Tel: +44 845 086 9001
Email (orders): orders@bsigroup.com
Email (enquiries): cservices@bsigroup.com

Subscriptions
Tel: +44 845 086 9001
Email: subscriptions@bsigroup.com

Knowledge Centre
Tel: +44 20 8996 7004
Email: knowledgecentre@bsigroup.com

Copyright & Licensing
Tel: +44 20 8996 7070
Email: copyright@bsigroup.com

bsi.

...making excellence a habit.™