BS EN 15411:2011

BSI Standards Publication

Solid recovered fuels — Methods for the determination of the content of major elements (As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mo, Mn, Ni, Pb, Sb, Se, Tl, V and Zn)

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National foreword

This British Standard is the UK implementation of EN 15411:2011. It supersedes DD CEN/TS 15411:2006 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee PTI/17, Solid biofuels.

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

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English Version

Solid recovered fuels - Methods for the determination of the content of trace elements (As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mo, Mn, Ni, Pb, Sb, Se, Tl, V and Zn)

Combustibles solides de récupération - Méthodes de détermination de la teneur en éléments à l'état de traces (As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mo, Mn, Ni, Pb, Sb, Se, Tl, V et Zn)

Feste Sekundärbrennstoffe - Verfahren zur Bestimmung des Gehaltes an Spurelementen (As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mo, Mn, Ni, Pb, Sb, Se, Tl, V und Zn)

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

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Foreword

This document (EN 15411:2011) has been prepared by Technical Committee CEN/TC 343 “Solid Recovered Fuels”, the secretariat of which is held by SFS.

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of an identical text or by endorsement, at the latest by March 2012, and conflicting national standards shall be withdrawn at the latest by March 2012.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 CEN/TS 15411:2006.

This document differs from CEN/TS 15411:2006 only editorially.

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 the United Kingdom.

Introduction

Accurate determination of trace element content in solid recovered fuels is important for environmental and technical reasons both in the production and combustion stage. After digestion of the solid recovered fuels using different methods, a number of analytical techniques can be used for the quantification of the trace element content. They include Inductively Coupled Plasma with optical or mass detection, graphite furnace Atomic Absorption Spectrometry and, when available, dedicated specific method (e.g. for mercury).

1 Scope

This European Standard specifies three methods of digestion for solid recovered fuels:

a) microwave assisted digestion with hydrofluoric, nitric and hydrochloric acid mixture;

b) hot water bath digestion of with hydrofluoric, nitric and hydrochloric acid mixture, after ashing of the SRFs sample;

c) oven digestion with nitric, perchloric and hydrofluoric acid mixture.

Instrumental determination of As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Sb, Se, Tl, V, Zn is performed by Inductively Coupled Plasma with optical or mass detection or graphite furnace Atomic Absorption Spectrometry. Hg can be analysed only after the microwave assisted procedure or, alternatively, by a direct analysis method (Hg direct – AMA).

The effectiveness of the digestion can be verified by qualitative X-ray fluorescence (XRF) analysis on the remaining residue. If necessary, an alternative digestion method (among those proposed) is used.

Method a) is recommended for general use, but the amount of the test portion can be very low in case of high concentration of organic matter.

Method b) is recommended for Solid Recovered Fuel (SRF) with high organic matter concentration that can be difficult to digest with the other methods. This method is not suitable for mercury.

Method c) is recommended for Solid Recovered Fuel (SRF) samples for which the other methods leave a significant insoluble residue.

Alternative digestion methods can be applied if their performance is proved to be comparable with those of the methods mentioned in a) to c) (see Annex C).

2 Normative references

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

EN 13656, *Characterization of waste — Microwave assisted digestion with hydrofluoric (HF), nitric (HNO_3) and hydrochloric (HCl) acid mixture for subsequent determination of elements*

EN 15357:2011, *Solid recovered fuels — Terminology, definitions and descriptions*

EN 15403, *Solid recovered fuels — Determination of ash content*

EN 15413, *Solid recovered fuels — Methods for the preparation of the test sample from the laboratory sample*

EN 15414-3, *Solid recovered fuels — Determination of moisture content using the oven dry method — Part 3: Moisture in general analysis sample*

EN ISO 3696:1995, *Water for analytical laboratory use — Specification and test methods (ISO 3696:1987)*

3 Terms and definitions

For the purpose of this document, the terms and definitions given in EN 15357:2011 and the following 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
microwave unit
whole microwave digestion system (oven and associated equipment)

4 Safety remarks

The safety in handling of potentially hazardous materials is dealt with by the relevant national and European regulations, which every laboratory should refer to.

In addition the following information is given:

- Only experienced personnel can use the microwave apparatus, following the operating instructions described in the manufacturer manual;
- Most of the reagents used within this European Standard are strongly corrosive and 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.

5 Principle

The test portion is digested using one of the proposed methods with a suitable acid mixture. The digested sample is then analysed by the most appropriate spectrometric technique, such as atomic absorption or emission spectroscopy.

6 Apparatus

6.1 Microwave unit

Intended for laboratory use and preferably equipped with temperature control.

6.2 Resistance heating oven

A resistance heated oven or heating block that can be used at a temperature of at least 220 °C and an accuracy of ± 10 °C.

6.3 Digestion vessels

The vessels used in the microwave unit shall be equipped with a pressure relieve valve or another technical equipment which avoids the bursting of the vessels at suddenly occurring 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.

6.4 Inductively coupled plasma

Normal commercial instrumentation with optical or mass spectrometric detector (ICP-OES, ICP-MS).

6.5 Atomic absorption spectrophotometer

Normal commercial instrumentation, equipped with graphite furnace or hydride generation systems or cold vapour (GF-AAS, HG-AAS, CV-AAS).

6.6 X-ray fluorescence spectrometer

Energy or wavelength dispersion system suitable for qualitative analysis of the elements listed in this European Standard (with the exception of beryllium).

6.7 Balances

Analytical balance resolution ± 0,1 mg.

6.8 General equipment

General laboratory equipment, including volumetric graduated flasks and pipettes of adequate size.

Filter equipment of adequate chemical resistance and purity or centrifuge.

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

The glassware used in the digestion procedure should be carefully pre-cleaned with for example 10 % nitric acid solution.

7 Reagents

All reagents shall be at least of analytical grade and suitable for their specific purposes. Other specific reagents are listed and described in the reference methods for digestion or instrumental determination listed in Clause 2.

NOTE Acids used in the preparation of standards and for sample processing are of high purity. Redistilled acids are recommended because of the high sensitivity of ICP-MS. Nitric acid at less than 2 % (v/v) is recommended for ICP-MS to minimize damage to the interface and to minimize isobaric molecular-ion interferences with the analytes. Many more molecular-ion interferences are observed when hydrochloric and sulphuric acids are used.

7.1 Water of grade 1 as specified by EN ISO 3696:1995.

7.2 Nitric acid (HNO_3), 65 % (w/w), ρ 1,40 g/ml.

7.3 Hydrofluoric acid (HF), 40 % (w/w), ρ 1,14 g/ml.

7.4 Perchloric acid ($HClO_4$), 70 % (w/w), ρ 1,62 g/ml.

7.5 Hydrochloric acid (HCl), 65 % (w/w), ρ 1,40 g/ml.

8 Procedure

8.1 Sample conservation and pre-treatment

The laboratory samples shall be stored according to guidelines defined in Annex A.

It is advisable to contact the people performing the sampling in order to agree a procedure for the laboratory sample preparation and storage before delivering to the laboratory. In particular, any treatment procedure which can increase the temperature of the material above 40 °C should be avoided, in order to avoid significant loss of mercury or other volatile compounds.

Furthermore, any possible source of contamination during the laboratory sample preparation (e.g. grinding with metallic apparatus) shall be avoided or reduced as much as possible.

The laboratory sample should be stored and delivered in sealed high-density plastic containers.

8.2 Sample preparation

The test portion shall be prepared from the laboratory sample according to EN 15413.

In addition, for the purposes of this method, the target size should be 1 mm or below.

Depending on the used digestion method, the amount of test portion ranges between 0,2 g and 0,5 g.

Whereas the determination is carried out on a dry basis, the moisture content shall be determined according to EN 15414-3.

9 Digestion procedure

9.1 Method A

Weigh between 0,2 g to 0,5 g of the sample, to the nearest 0,1 mg, prepared according to Clause 8 and transfer it into the vessel. If necessary, the sample may be moistened with a minimum amount of water. Proceed according to the general principle of EN 13656.

After cooling, the solutions are transferred to volumetric flasks of suitable volume (e.g. 50 ml). Any residue shall be separated by filtration or centrifugation and the composition is controlled by XRF or any other suitable technique: if a significant amount of the elements of interested is detected, an alternative digestion method for the dissolution of the residual material is necessary. The control on the residue can be avoided if its composition is known from previous analysis of the same kind of materials or on the basis of experience.

9.2 Method B (informative)

Weigh 0,2 g of ashed sample according to EN 15403 in a low pressure teflon bomb with relief valve and proceed according to the general principle of method reported in EN 13656. 4 ml aqua regia and 1 ml concentrated HF are added. After closing, the bombs are placed in a water bath at 90 °C for 3 h.

After cooling, the solutions are transferred to volumetric flasks of suitable volume (e.g. 50 ml). Any residue shall be separated by filtration or centrifugation and the composition is controlled by XRF or any other suitable technique: if a significant amount of the elements of interested is detected, an alternative digestion method for the dissolution of the residual material is necessary. The control on the residue can be avoided if its composition is known from previous analysis of the same kind of materials or on the basis of experience.

9.3 Method C (informative)

Weight 0,5 g of sample in a teflon bomb. Add 10 ml of an acid mixture prepared by mixing 950 ml of nitric acid and 50 ml of perchloric acid. After closing the bombs are placed in an oven at 190 °C for at least 10 h (including heating up time). After cooling, the solutions are transferred to 50 ml plastic bottles and the bombs are washed with 5 ml of 0,1 M nitric acid solution and 0,5 ml of concentrated hydrofluoric acid. The solutions are taken to volume with 0,1 M nitric acid. In the case of incomplete digestion, the residue should be separated by filtration or centrifugation and then dissolved with nitric/perchloric/hydrofluoric acid mixture (5/0,5/4,5) in ultrasonic bath at 50 °C.

After cooling, the solutions are transferred to volumetric flasks of suitable volume (e.g. 50 ml). Any residue shall be separated by filtration or centrifugation and the composition is controlled by XRF or any other suitable technique: if a significant amount of the elements of interested is detected, an alternative digestion method for the dissolution of the residual material is necessary. The control on the residue can be avoided if its composition is known from previous analysis of the same kind of materials or on the basis of experience.

10 Analysis of the digestion solutions

10.1 Preparation of the solution for analysis

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.

Solution containing hydrofluoric acid shall be processed with HF resistant apparatus.

10.2 Analytical step

Different techniques can be used for the analysis of the digested solutions.

NOTE Examples of such techniques are ICP MS according to the general principle of the method reported in EN ISO 17294-2, GF-AAS and CV-AAS/HG-AAS (Cold Vapour and Hydride Generation Atomic Absorption) according to the principle of the method reported in ASTM E885-88 or direct mercury analysis according to the method reported in EPA Method 7473.

Instruments shall be set up and calibrated following the manufacturers' instructions and the used reference methods.

11 Expression of results

The results are expressed in milligram per kilogram on a dry basis.

For procedure B on SRF ash, the following equation shall be used to express the results on dry original matter:

$$C_d = C_{ash} \times \frac{A_{ash}}{100}$$

where

C_d is concentration on dry basis in the original sample;

C_{ash} is concentration in the ash;

A_{ash} is ash content (%).

12 Quality control

To detect possible contaminations from vessels and/or reagents, blank tests shall be carried out by the same sample preparation procedure, using the same quantities of reagents.

If available, the use of standard reference materials is recommended. The trueness of the analytical method shall be checked by applying it to a certified reference material (CRM) or a reference material (RM) if existing. Calculate the analytical result for the CRM/RM, and compare it with the reference or certified value.

13 Performance characteristics

Data about performances of the methods will be available after validation in QUOVADIS project.

14 Test report

The test report shall contain at least the following information:

a) name, address and location of any laboratory involved in the analysis;

b) description and identification of the laboratory sample;

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

d) reference to this European Standard, i.e. EN 15411;

e) reference to the analytical standard used for the determination for each element;

f) the analytical results, referring to Clause 11;

g) any details not specified in this European Standard or which are optional, and any other factors which may have affected the results;

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

The laboratory should keep a trace of any analytical steps and intermediate results (raw data and calculation details) that should be kept available in case of specific requirements.

Annex A
(normative)

Guidelines - Characteristics of the laboratory sample for chemical analysis of SRF

The following requirements apply when preparing the laboratory sample for the chemical characterisation of SRF samples according to this European Standard.

NOTE Equivalent requirements apply in all chemical test method specifications for SRF, i.e. EN 15407, EN 15408, EN 15410, EN 15411, CEN/TS 15412 and EN 15413.

A maximum amount of laboratory sample of 10 kg and maximum particle size of 1 cm is established on the basis of number and type of parameters to be determined, sample representativity and practical reasons for handling samples. In the following table the requirements are summarised both for single or grouped chemical parameters.

Table A.1 — Requirements for the laboratory sample for the analysis of SRF

Parameter (single or group)	**Minimum laboratory sample amount (g)** [a]	**Short term storage conditions before delivery to the lab**	**Long term storage condition before delivery to the lab**	**Container material**
C, H, N	100	In the same condition of SRF production	refrigeration 4 °C	plastic bottle or bag
Cl, S, Br, F	100	In the same condition of SRF production	refrigeration 4 °C	non-PVC plastic bottle or bag
Metallic Al	200	In the same condition of SRF production	refrigeration 4 °C	plastic bottle or bag
Major elements	400	In the same condition of SRF production	refrigeration 4 °C	plastic bottle or bag
Trace elements excluding Hg	200	In the same condition of SRF production	refrigeration 4 °C	plastic bottle or bag
Hg	100	In the same condition of SRF production	refrigeration 4 °C	Glass or PFA bottle
C, H, N, Cl, S, Br, F	150	In the same condition of SRF production	refrigeration 4 °C	non-PVC plastic bottle or bag
Major elements + Trace elements excluding Hg	500	In the same condition of SRF production	refrigeration 4 °C	plastic bottle or bag
Major elements + Trace elements + Hg	600	In the same condition of SRF production	refrigeration 4 °C	Glass bottle (100 g) + plastic bottle or bag

Table A.1 *(concluded)*

Major elements + Trace elements + Hg + metallic Al	700	In the same condition of SRF production	refrigeration 4 °C	Glass bottle (100 g) + plastic bottle or bag
Complete analysis	800	In the same condition of SRF production	refrigeration 4 °C	Glass bottle (100 g) + non-PVC plastic bottle or bag

[a] The maximum particle size (mm) is related to the laboratory sample amount (g) in order to guarantee sample homogeneity. It is established following the rules reported in EN 15413.

Annex B
(informative)

Performance data

Inter-laboratory trials were carried out by laboratories in Austria, Finland, France, Germany, Italy, the Netherlands, Poland, Sweden and the United Kingdom. The variety of instruments and other analytical conditions used conformed to the quality parameters specified in the method.

The performance data for Method A and direct determination of Hg, according to ISO 5725-2 are presented in Tables B.1 to B.17. The statistical evaluation for other methods was not significant due the too limited number of participating laboratories.

The data derive from laboratories participating in the above-mentioned inter-laboratory trials.

Table B.1 — Performance data for As – Method A

Sample	Matrix	l	n	o %	x_{ref} %	$\bar{\bar{x}}$ mg/kg	η %	s_R mg/kg	CV_R %	S_r mg/kg	CV_r %
A	SRF from shredded tyres	28	9	48	na	4.3	na	5	126	5	126
B	SRF from demolition wood	54	9	0	na	22.6	na	6	26	4	16
C	SRF from sewage sludge	42	9	22	na	8.6	na	4	43	2	20
D	SRF from municipal waste	32	9	41	na	2.4	na	2	63	2	63
E	SRF from municipal waste (paper and plastic reach)	25	9	54	na	2.5	na	2	68	2	68

Definition of symbols:

l	is the number of outlier-free individual analytical values per level;
n	is the number of laboratories after outlier elimination;
o	is the percentage of outlying values from the replicate determination;
x_{ref}	is the accepted reference value on dry matter base;
$\bar{\bar{x}}$	is the overall mean on dry matter base;
η	is the recovery rate;
s_R	is the reproducibility standard deviation on dry matter base;
CV_R	is the coefficient of the variation of the reproducibility;
S_r	is the repeatability standard deviation on dry matter base;
CV_r	is the coefficient of the variation of the repeatability
na	not applicable

Table B.2 — Performance data for Ba – Method A

Sample	Matrix	l	n	o %	x_{ref} %	$\overline{\overline{x}}$ mg/kg	η %	s_R mg/kg	CV_R %	S_r mg/kg	CV_r %
A	SRF from shredded tyres	54	9	0	na	6	na	2	33	2	33
B	SRF from demolition wood	54	9	0	na	152	na	92	61	90	59
C	SRF from sewage sludge	60	9	11	na	1 498	na	616	41	115	8
D	SRF from municipal waste	58	9	7	na	352	na	114	32	105	30
E	SRF from municipal waste (paper and plastic reach)	60	9	11	na	153	na	82	54	82	54

Definition of symbols: see Table B.1.

Table B.3 — Performance data for Be – Method A

Sample	Matrix	l	n	o %	x_{ref} %	$\overline{\overline{x}}$ mg/kg	η %	s_R mg/kg	CV_R %	S_r mg/kg	CV_r %
A	SRF from shredded tyres	11	7	80	na	0,56	na	0	35	0	35
B	SRF from demolition wood	20	7	63	na	0,34	na	0	119	0	13
C	SRF from sewage sludge	36	7	33	na	2,14	na	0	21	0	21
D	SRF from municipal waste	24	7	56	na	0,36	na	0	7	0	7
E	SRF from municipal waste (paper and plastic reach)	29	7	46	na	0,38	na	0	86	0	23

Definition of symbols: see Table B.1.

Table B.4 — Performance data for Cd – Method A

Sample	Matrix	l	n	o %	x_{ref} %	$\bar{\bar{x}}$ mg/kg	η %	s_R mg/kg	CV_R %	S_r mg/kg	CV_r %
A	SRF from shredded tyres	37	9	31	na	3,6	na	3	78	3	78
B	SRF from demolition wood	30	9	44	na	0,7	na	0	33	0	33
C	SRF from sewage sludge	54	9	0	na	4,6	na	0	7	0	7
D	SRF from municipal waste	47	9	13	na	2,3	na	1	60	1	57
E	SRF from municipal waste (paper and plastic reach)	54	9	0	na	2,3	na	1	51	1	33
Definition of symbols: see Table B.1.											

Table B.5 — Performance data for Cr – Method A

Sample	Matrix	l	n	o %	x_{ref} %	$\bar{\bar{x}}$ mg/kg	η %	s_R mg/kg	CV_R %	S_r mg/kg	CV_r %
A	SRF from shredded tyres	54	9	0	na	48	na	20	42	15	31
B	SRF from demolition wood	54	9	0	na	28	na	5	18	5	18
C	SRF from sewage sludge	54	9	0	na	178	na	8	4	8	4
D	SRF from municipal waste	53	9	2	na	89	na	18	20	17	19
E	SRF from municipal waste (paper and plastic reach)	54	9	0	na	132	na	208	158	208	158
Definition of symbols: see Table B.1.											

Table B.6 — Performance data for Co – Method A

Sample	Matrix	l	n	o %	x_{ref} %	$\bar{\bar{x}}$ mg/kg	η %	s_R mg/kg	CV_R %	S_r mg/kg	CV_r %
A	SRF from shredded tyres	48	8	11	na	100,9	na	20	19	20	19
B	SRF from demolition wood	35	8	35	na	1,5	na	1	43	0	24
C	SRF from sewage sludge	48	8	11	na	20	na	3	16	3	16
D	SRF from municipal waste	42	8	22	na	4,6	na	2	34	1	23
E	SRF from municipal waste (paper and plastic reach)	43	8	20	na	5,1	na	5	94	5	94
Definition of symbols: see Table B.1.											

Table B.7 — Performance data for Cu – Method A

Sample	Matrix	l	n	o %	x_{ref} %	$\bar{\bar{x}}$ mg/kg	η %	s_R mg/kg	CV_R %	S_r mg/kg	CV_r %
A	SRF from shredded tyres	60	9	0	na	255	na	77	30	77	30
B	SRF from demolition wood	54	9	10	na	58	na	52	89	52	89
C	SRF from sewage sludge	54	9	10	na	183	na	7	4	7	4
D	SRF from municipal waste	57	9	5	na	564	na	2 077	368	2 067	367
E	SRF from municipal waste (paper and plastic reach)	60	9	0	na	748	na	1 736	232	1736	232
Definition of symbols: see Table B.1.											

Table B.8 — Performance data for Hg – Method A

Sample	Matrix	l	n	o	x_{ref}	$\bar{\bar{x}}$	η	s_R	CV_R	S_r	CV_r
				%	%	mg/kg	%	mg/kg	%	mg/kg	%
A	SRF from shredded tyres	18	8	67	na	0,35	na	0	126	0	126
B	SRF from demolition wood	16	8	70	na	0,25	na	0	72	0	72
C	SRF from sewage sludge	42	8	22	na	1,41	na	1	92	1	92
D	SRF from municipal waste	31	8	43	na	0,49	na	1	133	1	133
E	SRF from municipal waste (paper and plastic reach)	36	8	33	na	0,63	na	0	17	0	17
Definition of symbols: see Table B.1.											

Table B.9 — Performance data for Mn – Method A

Sample	Matrix	l	n	o	x_{ref}	$\bar{\bar{x}}$	η	s_R	CV_R	S_r	CV_r
				%	%	mg/kg	%	mg/kg	%	mg/kg	%
A	SRF from shredded tyres	54	9	0	na	560	na	264	47	264	47
B	SRF from demolition wood	54	9	0	na	73	na	5	7	5	7
C	SRF from sewage sludge	54	9	0	na	529	na	18	3	18	3
D	SRF from municipal waste	60	9	11	na	152	na	21	14	21	14
E	SRF from municipal waste (paper and plastic reach)	54	9	0	na	195	na	98	50	89	46
Definition of symbols: see Table B.1.											

Table B.10 — Performance data for Mo – Method A

Sample	Matrix	l	n	o	x_{ref}	$\bar{\bar{x}}$	η	s_R	CV_R	S_r	CV_r
				%	%	mg/kg	%	mg/kg	%	mg/kg	%
A	SRF from shredded tyres	42	9	22	na	4,4	na	2	47	2	47
B	SRF from demolition wood	24	9	56	na	11,3	na	11	95	11	95
C	SRF from sewage sludge	54	9	0	na	34,6	na	4	12	4	12
D	SRF from municipal waste	35	9	35	na	2	na	0	22	0	22
E	SRF from municipal waste (paper and plastic reach)	36	9	33	na	3,3	na	1	18	1	18
Definition of symbols: see Table B.1.											

Table B.11 — Performance data for Ni – Method A

Sample	Matrix	l	n	o	x_{ref}	$\bar{\bar{x}}$	η	s_R	CV_R	S_r	CV_r
				%	%	mg/kg	%	mg/kg	%	mg/kg	%
A	SRF from shredded tyres	42	8	22	na	31,2	na	10	32	10	32
B	SRF from demolition wood	35	8	35	na	55,2	na	74	134	29	53
C	SRF from sewage sludge	42	8	22	na	184,9	na	24	13	24	13
D	SRF from municipal waste	42	8	22	na	18,6	na	16	86	16	86
E	SRF from municipal waste (paper and plastic reach)	48	8	11	na	34,9	na	8	23	7	20
Definition of symbols: see Table B.1.											

Table B.12 — Performance data for Pb – Method A

Sample	Matrix	l	n	o %	x_{ref} %	$\bar{\bar{x}}$ mg/kg	η %	s_R mg/kg	CV_R %	S_r mg/kg	CV_r %
A	SRF from shredded tyres	54	9	0	na	18	na	4	22	4	22
B	SRF from demolition wood	47	9	13	na	17	na	11	65	11	65
C	SRF from sewage sludge	54	9	0	na	117	na	5	4	5	4
D	SRF from municipal waste	60	9	11	na	163	na	257	158	257	158
E	SRF from municipal waste (paper and plastic reach)	54	9	0	na	145	na	80	55	77	53
Definition of symbols: see Table B.1.											

Table B.13 — Performance data for Sb – Method A

Sample	Matrix	l	n	o %	x_{ref} %	$\bar{\bar{x}}$ mg/kg	η %	s_R mg/kg	CV_R %	S_r mg/kg	CV_r %
A	SRF from shredded tyres	39	8	28	na	7,28	na	4	49	4	49
B	SRF from demolition wood	29	8	46	na	1,46	na	1	61	1	51
C	SRF from sewage sludge	42	8	22	na	10,31	na	5	47	3	27
D	SRF from municipal waste	43	8	20	na	18,2	na	15	80	15	80
E	SRF from municipal waste (paper and plastic reach)	47	8	13	na	22,71	na	29	128	29	128
Definition of symbols: see Table B.1.											

Table B.14 — Performance data for Se – Method A

Sample	Matrix	l	n	o %	x_{ref} %	$\overset{=}{x}$ mg/kg	η %	s_R mg/kg	CV_R %	S_r mg/kg	CV_r %
A	SRF from shredded tyres	23	8	57	na	3,29	na	6	170	2	49
B	SRF from demolition wood	26	8	52	na	1,24	na	1	56	1	40
C	SRF from sewage sludge	25	8	54	na	2,16	na	1	56	0	14
D	SRF from municipal waste	19	8	65	na	1,12	na	1	63	1	63
E	SRF from municipal waste (paper and plastic reach)	19	8	65	na	0,89	na	0	34	0	34

Definition of symbols: see Table B.1.

Table B.15 — Performance data for V – Method A

Sample	Matrix	l	n	o %	x_{ref} %	$\overset{=}{x}$ mg/kg	η %	s_R mg/kg	CV_R %	S_r mg/kg	CV_r %
A	SRF from shredded tyres	27	9	50	na	4,8	na	1	27	1	27
B	SRF from demolition wood	23	9	57	na	5,9	na	3	57	3	57
C	SRF from sewage sludge	54	9	0	na	611,6	na	93	15	46	8
D	SRF from municipal waste	29	9	46	na	4,1	na	0	11	0	11
E	SRF from municipal waste (paper and plastic reach)	32	9	41	na	4,8	na	1	18	1	17

Definition of symbols: see Table B.1.

Table B.16 — Performance data for Zn – Method A

Sample	Matrix	l	n	o %	x_{ref} %	$\overset{=}{x}$ mg/kg	η %	s_R mg/kg	CV_R %	S_r mg/kg	CV_r %
A	SRF from shredded tyres	60	9	0	na	11 020	na	2 956	27	1 935	18
B	SRF from demolition wood	54	9	10	na	147	na	116	79	116	79
C	SRF from sewage sludge	54	9	10	na	1 183	na	116	10	69	6
D	SRF from municipal waste	60	9	0	na	573	na	1 371	239	1 371	239
E	SRF from municipal waste (paper and plastic reach)	54	9	10	na	431	na	268	62	267	62
Definition of symbols: see Table B.1.											

Table B.17 — Performance data for Hg – direct (AMA)

Sample	Matrix	l	n	o %	x_{ref} %	$\overset{=}{x}$ mg/kg	η %	s_R mg/kg	CV_R %	S_r mg/kg	CV_r %
A	SRF from shredded tyres	48	2		na	0,02	na	0	50	0	50
B	SRF from demolition wood	48	2		na	0,01	na	0	60	0	40
C	SRF from sewage sludge	48	2		na	1	na	0	15	0	8
D	SRF from municipal waste	48	2		na	0,28	na	0	20	0	20
E	SRF from municipal waste (paper and plastic reach)	48	2		na	0,62	na	0	19	0	14
Definition of symbols: see Table B.1.											

Annex C
(informative)

Major results of ruggedness testing

The design of the ruggedness testing was carried out by applying the analytical method(s) to be validated with some controlled variations of analytical parameters in repeatability conditions, in order to evaluate separately the influence of each varying parameter on the final results.

— **Method A - Trace elements by EN 13656 (aqua regia + HF + boric acid, microwave) + ICP-OES/MS or GFAAS**

Tests have been performed to evaluate the effects of grain size, of the amount of test portion and composition on the determination of trace elements according to Method A of EN 15411 in SRF samples.

Four different sample types were considered:

- QR-A: shredded tyre;
- QR-B: demolition wood;
- QR-C: dried sludge;
- QR-E: paper plastic fluff.

Grain size effect

Sample QR-E, in particular, has been analyzed at three different grain size: 0,5, 1 and 1,5 mm.

No significant differences are observed in the average values of samples QR-E at different grain size levels. RSD values in general are between 3 and 20%; higher values of RSD were explained by lower content of element, i.e. Pb.

Amount of test portion effect

Sample QR-E, has been analyzed at three different amount of test portion: 0,1, 0,2 and 0,4 g.

Test portion effect is not evident in recovery of elements. CV values in general are between 4 and 26% for QR-E samples; lower values were explained by higher amounts of test portion.

Composition effect

Four kinds of SRF were used to tested the composition effect: QR-A (shredded tyre), QR-B (demolition wood), QR-C (sludge) and QR-E (paper-plastic fluff) at 0,2 g of test portion and 1 mm of grain size (except sludge samples that have been analysed as is). Method A results to be applicable for each kind of matrix tested; higher values of RSD were explained by lower contents of elements.

— **Method B - Trace elements by ashing (EN 15403) + EN 13656 + ICP-OES/MS or GFAAS**

Tests have been performed to evaluate the effects of grain size on the determination of elements according to Method B of EN 15411 in SRF samples. Sample type of SRF considered in this test was QR-A (shredded tyre).

Grain size effect

Sample QR-A (shredded tyre) has been analyzed at three different grain size: 0,5, 1 and 1,5 mm.

Some influence of grain size was observed; lower values of recovery rate were explained by larger grain size. This behaviour was expected for this kind of matrix (oxides, refractory).

- **Method C - Trace elements by ICP-OES/MS after nitric-perchloric acid dissolution**

The time of heating for SRF dissolution was the only factor under investigation. Elements were determined in the final solution. SAMPLE QR-E (paper/plastic) in the form of 1 mm grain size was used.

Time of heating effect

For most of the elements, 6 hours heating is not sufficient for the recovery of the elements from the SRF sample.

For most of the element, it seems that 10 hours of heating are sufficient for the extraction of the element of interest, while in some cases a little lower recovery is obtained. However, it is also evident that for element such as Zn, Sr, and Mo there is a trend demonstrating that 10 hours are not enough for the extraction. In particular, the behaviour of Ti is very significant: for 6, 10 and 14 hours heating time the recovery is 1/3 of that at 20 hours. For Ti it is likely that the difficult to destroy compounds present in the SRF matrix can be dissolved only with a long time procedure.

Grain size effect

In order to check the influence of the grain size, 2 test were performed on a 0,5 grinded aliquot of the same SRF sample (E). The results clearly show that the situation is similar to that of 1 mm grain size:

As expected, the RSD values are generally better at 0,5 mm than at 1 mm grain size, both at 10 and 20 hours heating: but, as already found in previous studies for some elements the RSD is worse at 0,5 mm. As regards the average values, those obtained for 0,5 mm are significantly larger for Cr, Cu, Sr and Pb at 10 hours heating, while they are more similar at 20 hours heating.

From a repeatability (as SD value) point of view there are no differences between the two series of data (at 6 and 14 hours heating time): SD values are larger for some elements for 6 hours heating but they are smaller for other elements.

- **Method D - Trace elements by EN 13657 (aqua regia, microwave) + ICP-OES/MS**

Tests have been performed to evaluate the effects of grain size, of the amount of test portion and composition on the determination of elements according to this method in SRF samples.

Four different sample types were considered:

- QR-A: shredded tyre;
- QR-B: demolition wood;
- QR-C: dried sludge;
- QR-E: paper plastic fluff.

Grain size effect

Sample QR-E has been analyzed at three different grain size: 0,5, 1 and 1,5 mm.

No significant differences are observed in the average values of samples QR-E at different grain size levels. RSD values in general are included between 3 and 20%, higher values of RSD were explained by lower content of element, i.e. Pb.

Amount of test portion effect

Sample QR-E has been analyzed at three different amount of test portion: 0,1, 0,2 and 0,4 g. Test portion effect is not evident in recovery of trace elements. CV values in general are between 4 and 26% for QR-E samples, lower values were explained by higher amount of test portion.

Composition effect

Four kinds of SRF were used to tested the composition effect: QR-A (shredded tyre), QR-B (demolition wood), QR-C (sludge) and QR-E (paper-plastic fluff) at 0,2 g of test portion and 1 mm of grain size (except sludge samples that has been analysed as is).

Method D results to be applicable for each kind of matrix tested. For a better evaluation of performances of Method D, the ratio between recovery rate of elements with Method D (aqua regia digestion) and Method A (Hydrofluoric acid and aqua regia digestion) was calculated. Recovery rate is well comparable between the two digestion procedures for almost all elements, except for Sb.

Hg by direct method (AMA)

Tests have been performed to evaluate the effects of grain size and amount of test portion on the instrumental direct determination of mercury in SRF samples.

Two different sample types were considered:

- QR-B: demolition wood;
- QR-E: paper plastic fluff.

Amount of test portion effect

Both samples have been analyzed at three different amount of test portion (grain size 1,0 mm): 50-75-100 mg.

Test portion effect is not evident in determination of mercury; there are not significant differences on Hg content. CV values are included between 13 and 34 % for QR-B samples, higher values were related to lower amount of test portion (RSD=34% if test portion=50mg); samples QR-E showed smaller RSD values (between 4 and 13 %) without any relation with the amount of test portion.

Grain size effect

Sample QR-E has been analyzed at three different grain size: 0,5, 1 and 1,5 mm.

No significant difference are observed in the average values of samples QR-E at different grain size levels; the RSD values are good (between 4 and 11%).

Bibliography

[1] EN 15407, *Solid recovered fuels — Methods for the determination of carbon (C), hydrogen (H) and nitrogen (N) content*

[2] EN 15408, *Solid recovered fuels — Methods for the determination of sulphur (S), chlorine (Cl), fluorine (F) and bromine (Br) content*

[3] EN 15410, *Solid recovered fuels — Methods for the determination of the content of major elements (Al, Ca, Fe, K, Mg, Na, P, Si, Ti)*

[4] CEN/TS 15412, *Solid recovered fuels — Methods for the determination of metallic aluminium*

[5] EN 15442, *Solid recovered fuels — Methods for sampling*

[6] EN 15443, *Solid recovered fuels — Methods for the preparation of the laboratory sample*

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

[8] ISO 5725-2, *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*

[9] ASTM D3683 - 04, *Standard Test Method for Trace Elements in Coal and Coke Ash by Atomic Absorption*

[10] ASTM E885-88(2004), *Standard Test Methods for Analyses of Metals in Refuse-Derived Fuel by Atomic Absorption Spectroscopy*

[11] EPA Method 7473, *Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation and Atomic Absorption Spectrophotometry*

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