



BSI Standards Publication

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

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National foreword

This British Standard is the UK implementation of EN 15410:2011. It supersedes DD CEN/TS 15410:2006 which is withdrawn.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 major elements (Al, Ca, Fe, K, Mg, Na, P, Si, Ti)

Combustibles solides de récupération - Pour la détermination de la teneur en éléments majeurs (Al, Ca, Fe, K, Mg, Na, P, Si et Ti)

Feste Sekundärbrennstoffe - Verfahren zur Bestimmung des Gehaltes an Hauptbestandteilen (Al, Ca, Fe, K, Mg, Na, P, Si, Ti)

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Foreword

This document (EN 15410:2011) 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of an identical text or by endorsement, at the latest by March 2012, and conflicting national standards shall be withdrawn at the latest by March 2012.

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This document differs from CEN/TS 15410:2006 only editorially.

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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. The determination of major elements such as Al, Ca, Fe, Mg, P, K, Si, Na and Ti can be helpful to predict the melting behaviour and slagging of the ash. 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, Flame Atomic Spectroscopy, Graphite Furnace Atomic Absorption Spectrometry and X-ray fluorescence spectrometry. X-ray fluorescence allows the simultaneous determination of these elements after ashing of solid recovered fuel (SRF). Direct analysis of the SRF material is not possible by XRF due to the sample inhomogeneity and because suitable certified reference materials for calibration are not available.

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 Si, Al, K, Na, Ca, Mg, Fe, P, and Ti is performed by Inductively Coupled Plasma Spectrometry with optical detection or other suitable spectroscopic techniques such as Flame Atomic Spectroscopy.

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) shall be used.

XRF can be used for the analysis of Si, Al, K, Na, Ca, Mg, Fe, P, Ti, after ashing (550 °C) of the sample: other elements can be analysed by XRF provided that the concentration levels are above the instrumental detection limits of the XRF instrumentation and after proper preliminary testing.

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 SRFs with high organic matter concentration that can be difficult to digest with the other methods.

Method c) is recommended for SRFs samples for which the other methods leave a significant insoluble residue.

All the listed methods are suitable for the determination of Si, provided that closed containers are used for sample dissolution. XRF is highly recommended for Si, P and Ti analysis.

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 (HNO₃) 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)*

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

EN ISO 12020, *Water quality — Determination of aluminium — Atomic absorption spectrometric methods (ISO 12020:1997)*

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

ISO 9964 (all parts), *Water quality — Determination of sodium and potassium*

3 Terms and definitions

For the purposes 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;
- The X-ray fluorescence spectrometers on the market are generally approved fully protected apparatus. This means that the user is not subjected to any radiation when operating the apparatus. All the apparatus are subject to specific official approval and acceptance conditions;
- The person responsible for managing or supervising the operation of X-ray equipment shall provide evidence of his knowledge of radiation protection according to national regulations.

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 inductively coupled plasma atomic emission spectroscopy.

For XRF analysis, the sample is ashed at 550 °C and the ash is homogenised in a ball mill to obtain a uniform size dimension of the particles. The ash is then pressed in the form of pellet or fused with tetraborate. Both techniques are suitable for the analysis by XRF. Coal ash and other ashes of various origins can be used for instrument calibration.

6 Apparatus

6.1 Microwave unit

Intended for laboratory use and preferably 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 quadrupole mass detector (ICP-OES, ICP-MS).

6.5 X-ray fluorescence spectrometer

Energy or wavelength dispersion system suitable for quantitative/qualitative analysis of the elements listed in this European Standard.

6.6 Atomic Absorption Spectrometer

Normal commercial instrumentation with air-acetylene burner or with graphite tube atomizer and background correction system and with hollow cathode lamps or electrodeless discharge lamp.

6.7 Press

6.8 Balance

Analytical balance with a resolution of $\pm 0,1$ mg.

6.9 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. When using hydrofluoric acid, a special fume cupboard can be required.

The glassware used in the digestion procedure should be accurately pre-cleaned with 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 should be of high purity. Redistilled acids are recommended because of the high sensitivity of ICP-MS. Nitric acid at less than 2 % (v/v) is required 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 (HNO₃), 65 % (w/w), $\rho = 1,40$ g/ml.

7.3 Hydrofluoric acid (HF), 40 % (w/w), $\rho = 1,14$ g/ml.

7.4 Perchloric acid (HClO₄), 70 % (w/w), $\rho = 1,62$ g/ml.

7.5 Hydrochloric acid (HCl), 36 % (w/w), $\rho = 1,179$ g/ml.

7.6 Helium (He), minimum 99,99 purity for use as a chamber purge gas for the analysis of light elements when the vacuum is not used.

7.7 Argon (Ar), with a minimum purity of 99,99 %.

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 and 0,5 g.

Ash sample for XRF analysis are prepared as described in the method reported in EN 15403, starting from a quantity of material to obtain the amount of ash sufficient for the analysis (ash content can be as low as few percent on dry basis).

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: if a significant amount (5 % of the measured amount) of the elements of interested is detected, an alternative digestion method for the dissolution of the residual material is necessary.

9.2 Method B

Weight 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 (5 % of the measured amount) of the elements of interested is detected, an alternative digestion method for the dissolution of the residual material is necessary.

NOTE This method has been validated (see Annex B) only using XRF as instrumental analytical technique.

9.3 Method C (informative)

Weight 0,5 g of sample in a teflon bomb. Add 10 ml of a 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.

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

Inductively coupled plasma atomic emission spectroscopy according to EN ISO 11885, Flame Spectroscopy according to ISO 9964 (all parts), EN ISO 12020 and EN ISO 15586 shall be used for the analysis of the digested solution following the general principles outlined in the above mentioned methods.

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

10.3 XRF analysis on ashed samples – sample preparation

The sample is prepared following the general principle of EN 15403. A sufficient amount of sample shall be ashed in order to obtain a suitable amount of sample (at least 1 g to 2 g of ash): the total ash content can be very low for some type a sample (5 % or less).

The sample preparation is a critical stage for the analysis by x-ray fluorescence. The quality of the sample preparation will strongly influence the standard deviation on repeated measurements.

The available preparation techniques for solids are powder, pressed pellets and fused glass disc.

NOTE 1 The error of the light elements Na to S decreases with pressed pellets in the preparation technique.

NOTE 2 By using a fused glass, particle size effects are eliminated.

NOTE 3 The particle size of the solid sample will strongly influence the standard deviation on repeated measurements.

In order to achieve a homogeneous and representative test portion and to reduce the standard deviation on repeated measurements, the solid sample should be crushing and/or milling directly or after a drying stage.

The resulting ashes are analysed in the form of pressed pellets or fused glass disc.

The analysis of the sample prepared as described can be performed following the general principles of several methods.

NOTE 4 An example of such methods is ASTM D4326.

With the used procedure the results are referred to the ashed sample: calculation on dry basis of the original sample is performed using the equation reported in Clause 11.

11 Expression of results

The results shall be expressed in milligrams per kilogram on a dry basis.

For XRF procedure 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 the concentration on dry basis in the original sample;

C_{ash} is the concentration in the ash;

A_{ash} is the 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 15410;
- 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 (chromatograms, 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 Methods A and B, according to ISO 5725-2, are presented in Tables B.1 to B.17. The statistical evaluation for other methods was not significant due to 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 AI – Method A

Sample	Matrix	<i>l</i>	<i>n</i>	<i>o</i>	<i>x_{ref}</i>	\bar{x}	η	<i>s_R</i>	<i>CV_R</i>	<i>S_r</i>	<i>CV_r</i>
				%	%	mg/kg	%	mg/kg	%	mg/kg	%
A	SRF from shredded tyres	36	6	14	na	428	na	132	31	88	21
B	SRF from demolition wood	36	6	14	na	693	na	601	87	552	80
C	SRF from sewage sludge	42	7	0	na	31 630	na	21 219	67	2 851	9
D	SRF from municipal waste	42	7	0	na	6 014	na	1 898	32	1 898	32
E	SRF from municipal waste (paper and plastic reach)	42	7	0	na	10 475	na	2 826	27	2 826	27

Definition of symbols

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

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

Sample	Matrix	<i>l</i>	<i>n</i>	<i>o</i> %	<i>x_{ref}</i> %	\bar{x} mg/kg	η %	<i>s_R</i> mg/kg	<i>CV_R</i> %	<i>S_r</i> mg/kg	<i>CV_r</i> %
A	SRF from shredded tyres	48	8	0	na	2 385	na	1 264	53	807	34
B	SRF from demolition wood	42	7	13	na	2 870	na	548	19	383	13
C	SRF from sewage sludge	48	8	0	na	67 564	na	33 656	50	4 622	7
D	SRF from municipal waste	48	8	0	na	22 272	na	5 356	24	3 427	15
E	SRF from municipal waste (paper and plastic reach)	48	8	0	na	24 836	na	3 145	13	3 145	13
Definition of symbols: see Table B.1.											

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

Sample	Matrix	<i>l</i>	<i>n</i>	<i>o</i> %	<i>x_{ref}</i> %	\bar{x} mg/kg	η %	<i>s_R</i> mg/kg	<i>CV_R</i> %	<i>S_r</i> mg/kg	<i>CV_r</i> %
A	SRF from shredded tyres	48	8	0	na	106 166	na	48 077	45	48 077	45
B	SRF from demolition wood	48	8	0	na	558	na	741	133	739	132
C	SRF from sewage sludge	48	8	0	na	30 761	na	1 553	5	1 553	5
D	SRF from municipal waste	48	8	0	na	2 606	na	634	24	634	24
E	SRF from municipal waste (paper and plastic reach)	48	8	0	na	4 818	na	1 215	25	1 215	25
Definition of symbols: see Table B.1.											

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

Sample	Matrix	<i>l</i>	<i>n</i>	<i>o</i>	<i>x_{ref}</i>	\bar{x}	η	<i>s_R</i>	<i>CV_R</i>	<i>S_r</i>	<i>CV_r</i>
				%	%	mg/kg	%	mg/kg	%	mg/kg	%
A	SRF from shredded tyres	42	7	13	na	520	na	165	32	165	32
B	SRF from demolition wood	45	7	6	na	1 994	na	598	30	598	30
C	SRF from sewage sludge	48	8	0	na	5 527	na	2 260	41	293	5
D	SRF from municipal waste	48	8	0	na	2 367	na	237	10	237	10
E	SRF from municipal waste (paper and plastic reach)	48	8	0	na	3 502	na	365	10	365	10

Definition of symbols: see Table B.1.

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

Sample	Matrix	<i>l</i>	<i>n</i>	<i>o</i>	<i>x_{ref}</i>	\bar{x}	η	<i>s_R</i>	<i>CV_R</i>	<i>S_r</i>	<i>CV_r</i>
				%	%	mg/kg	%	mg/kg	%	mg/kg	%
A	SRF from shredded tyres	48	8	0	na	309	na	81	26	47	15
B	SRF from demolition wood	48	8	0	na	10 993	na	1 613	15	1 204	11
C	SRF from sewage sludge	48	8	0	na	6 383	na	1 932	30	544	9
D	SRF from municipal waste	48	8	0	na	2 521	na	393	16	393	16
E	SRF from municipal waste (paper and plastic reach)	48	8	0	na	2 441	na	743	30	343	14

Definition of symbols: see Table B.1.

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

Sample	Matrix	l	n	o %	x_{ref} %	\bar{x} mg/kg	η %	s_R mg/kg	CV_R %	S_r mg/kg	CV_r %
A	SRF from shredded tyres	42	7	13	na	409	na	132	32	62	15
B	SRF from demolition wood	42	7	13	na	474	na	101	21	47	10
C	SRF from sewage sludge	48	8	0	na	5 136	na	1 222	24	269	5
D	SRF from municipal waste	42	7	13	na	5 165	na	517	10	517	10
E	SRF from municipal waste (paper and plastic reach)	42	7	13	na	10 112	na	1 686	17	1 489	15
Definition of symbols: see Table B.1.											

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

Sample	Matrix	l	n	o %	x_{ref} %	\bar{x} mg/kg	η %	s_R mg/kg	CV_R %	S_r mg/kg	CV_r %
A	SRF from shredded tyres	30	6	29	na	209	na	62	30	62	30
B	SRF from demolition wood	30	6	29	na	86	na	50	58	18	21
C	SRF from sewage sludge	42	7	0	na	3 701	na	1 716	46	243	7
D	SRF from municipal waste	36	6	14	na	618	na	95	15	95	15
E	SRF from municipal waste (paper and plastic reach)	36	6	14	na	991	na	154	16	154	16
Definition of symbols: see Table B.1.											

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

Sample	Matrix	<i>l</i>	<i>n</i>	<i>o</i> %	<i>x_{ref}</i> %	\bar{x} mg/kg	η %	<i>s_R</i> mg/kg	<i>CV_R</i> %	<i>S_r</i> mg/kg	<i>CV_r</i> %
A	SRF from shredded tyres	35	6	17	na	16 266	na	5 723	35	1 839	11
B	SRF from demolition wood	35	6	17	na	1 650	na	490	30	334	20
C	SRF from sewage sludge	42	7	0	na	73 228	na	23 582	32	5 979	8
D	SRF from municipal waste	42	7	0	na	24 713	na	3 952	16	3 952	16
E	SRF from municipal waste (paper and plastic reach)	42	7	0	na	37 587	na	8 909	24	6 236	17

Definition of symbols: see Table B.1.

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

Sample	Matrix	<i>l</i>	<i>n</i>	<i>o</i> %	<i>x_{ref}</i> %	\bar{x} mg/kg	η %	<i>s_R</i> mg/kg	<i>CV_R</i> %	<i>S_r</i> mg/kg	<i>CV_r</i> %
A	SRF from shredded tyres	42	7	13	na	47	na	28	60	12	26
B	SRF from demolition wood	42	7	13	na	643	na	304	47	140	22
C	SRF from sewage sludge	48	8	0	na	2 262	na	1 165	52	149	7
D	SRF from municipal waste	42	7	13	na	1 374	na	315	23	315	23
E	SRF from municipal waste (paper and plastic reach)	48	8	0	na	784	na	347	44	133	17

Definition of symbols: see Table B.1.

Table B.10 — Performance data for Al– Method B

Sample	Matrix	<i>l</i>	<i>n</i>	<i>o</i> %	<i>x_{ref}</i> %	\bar{x} mg/kg	η %	<i>s_R</i> mg/kg	<i>CV_R</i> %	<i>S_r</i> mg/kg	<i>CV_r</i> %
A	SRF from shredded tyres	15	3	38	na	626	na	951	152	41	7
B	SRF from demolition wood	14	3	42	na	204	na	293	144	11	5
C	SRF from sewage sludge	24	4	0	na	19 132	na	22 172	116	542	3
D	SRF from municipal waste	24	4	0	na	1 936	na	2 309	119	97	5
E	SRF from municipal waste (paper and plastic reach)	24	4	0	na	3 446	na	3 972	115	252	7

Definition of symbols: see Table B.1.

Table B.11 — Performance data for Ca– Method B

Sample	Matrix	<i>l</i>	<i>n</i>	<i>o</i> %	<i>x_{ref}</i> %	\bar{x} mg/kg	η %	<i>s_R</i> mg/kg	<i>CV_R</i> %	<i>S_r</i> mg/kg	<i>CV_r</i> %
A	SRF from shredded tyres	21	3	13	na	4545	na	4652	102	386	8
B	SRF from demolition wood	16	3	33	na	1423	na	1703	120	54	4
C	SRF from sewage sludge	24	4	0	na	45368	na	52845	116	443	1
D	SRF from municipal waste	24	4	0	na	15076	na	17427	116	369	2
E	SRF from municipal waste (paper and plastic reach)	24	4	0	na	17113	na	19752	115	312	2

Definition of symbols: see Table B.1.

Table B.12 — Performance data for Fe– Method B

Sample	Matrix	<i>l</i>	<i>n</i>	<i>o</i> %	<i>x_{ref}</i> %	\bar{x} mg/kg	η %	<i>s_R</i> mg/kg	<i>CV_R</i> %	<i>S_r</i> mg/kg	<i>CV_r</i> %
A	SRF from shredded tyres	21	3	13	na	20 374	na	27 245	134	1 421	7
B	SRF from demolition wood	16	3	33	na	211	na	283	134	11	5
C	SRF from sewage sludge	24	4	0	na	16 710	na	20 570	123	158	1
D	SRF from municipal waste	24	4	0	na	1 331	na	1 808	136	59	4
E	SRF from municipal waste (paper and plastic reach)	24	4	0	na	2 758	na	3 736	135	95	3

Definition of symbols: see Table B.1.

Table B.13 — Performance data for K– Method B

Sample	Matrix	<i>l</i>	<i>n</i>	<i>o</i> %	<i>x_{ref}</i> %	\bar{x} mg/kg	η %	<i>s_R</i> mg/kg	<i>CV_R</i> %	<i>S_r</i> mg/kg	<i>CV_r</i> %
A	SRF from shredded tyres	15	3	38	na	256	na	64	25	64	25
B	SRF from demolition wood	16	3	33	na	401	na	482	120	13	3
C	SRF from sewage sludge	18	3	25	na	2 529	na	3 574	141	27	1
D	SRF from municipal waste	24	4	0	na	1 821	na	156	9	156	9
E	SRF from municipal waste (paper and plastic reach)	24	4	0	na	4 268	na	6 137	144	172	4

Definition of symbols: see Table B.1.

Table B.14 — Performance data for Mg– Method B

Sample	Matrix	<i>l</i>	<i>n</i>	<i>o</i> %	<i>x_{ref}</i> %	\bar{x} mg/kg	η %	<i>s_R</i> mg/kg	<i>CV_R</i> %	<i>S_r</i> mg/kg	<i>CV_r</i> %
A	SRF from shredded tyres	21	3	13	na	481	na	637	132	281	58
B	SRF from demolition wood	14	3	42	na	3 490	na	3 048	87	78	2
C	SRF from sewage sludge	24	4	0	na	2 866	na	3 626	127	149	5
D	SRF from municipal waste	24	4	0	na	1 805	na	2 434	135	2 434	135
E	SRF from municipal waste (paper and plastic reach)	24	4	0	na	1 058	na	1 675	158	89	8
Definition of symbols: see Table B.1.											

Table B.15 — Performance data for P– Method B

Sample	Matrix	<i>l</i>	<i>n</i>	<i>o</i> %	<i>x_{ref}</i> %	\bar{x} mg/kg	η %	<i>s_R</i> mg/kg	<i>CV_R</i> %	<i>S_r</i> mg/kg	<i>CV_r</i> %
A	SRF from shredded tyres	21	3	13	na	158	na	160	101	12	8
B	SRF from demolition wood	16	3	33	na	59	na	7	12	7	12
C	SRF from sewage sludge	24	4	0	na	2 426	na	2 829	117	89	4
D	SRF from municipal waste	24	4	0	na	415	na	18	4	18	4
E	SRF from municipal waste (paper and plastic reach)	24	4	0	na	845	na	992	117	33	4
Definition of symbols: see Table B.1.											

Table B.16 — Performance data for Si– Method B

Sample	Matrix	<i>l</i>	<i>n</i>	<i>o</i> %	<i>x_{ref}</i> %	\bar{x} mg/kg	η %	<i>s_R</i> mg/kg	<i>CV_R</i> %	<i>S_r</i> mg/kg	<i>CV_r</i> %
A	SRF from shredded tyres	21	3	13	na	26 016	na	27 835	107	600	2
B	SRF from demolition wood	16	3	33	na	1 286	na	1 528	119	17	1
C	SRF from sewage sludge	24	4	0	na	39 553	na	47 499	120	695	2
D	SRF from municipal waste	24	4	0	na	10 062	na	12 542	125	193	2
E	SRF from municipal waste (paper and plastic reach)	24	4	0	na	13 913	na	18 152	130	392	3
Definition of symbols: see Table B.1.											

Table B.17 — Performance data for Ti– Method B

Sample	Matrix	<i>l</i>	<i>n</i>	<i>o</i> %	<i>x_{ref}</i> %	\bar{x} mg/kg	η %	<i>s_R</i> mg/kg	<i>CV_R</i> %	<i>S_r</i> mg/kg	<i>CV_r</i> %
A	SRF from shredded tyres	21	3	13	na	84	na	90	107	20	24
B	SRF from demolition wood	16	3	33	na	318	na	385	121	9	3
C	SRF from sewage sludge	24	4	0	na	868	na	26	3	26	3
D	SRF from municipal waste	24	4	0	na	527	na	674	128	11	2
E	SRF from municipal waste (paper and plastic reach)	24	4	0	na	382	na	469	123	12	3
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 — Major 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 major elements according to Method A of EN 15410 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.

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 major 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.

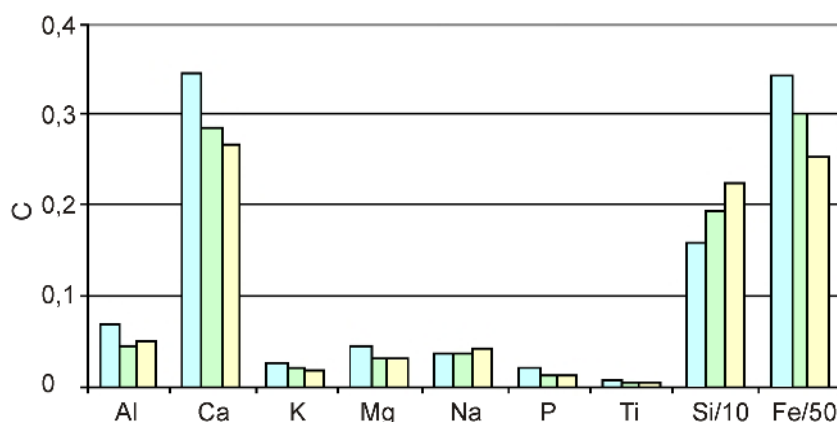
— **Method B - Major elements by ashing (EN 15403) + EN 13656 + ICP-OES/MS or GFAAS**

Tests have been performed to evaluate the effects of grain size on the determination of major elements according to Method B of EN 15410 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.

The data related to determination of major elements are graphically summarized in Figure C.1, where the mean values and the standard deviation are compared.



Key
 c concentration in %
 QR-A 0,5 mm
 QR-A 1,0 mm
 QR-A 1,5 mm

Figure C.1 — Grain size effect on determination of major elements by Method B

Some influence of grain size was observed for some elements (Fe, Ca, Al, K, Mg, P); lower values of recovery rate were explained by larger grain size. This behaviour was expected for this kind of matrix (oxides, refractory).

— **Method B — Major elements by XRF analysis of ashed samples**

Sample QR-E (paper plastic fluff) in the form of 1 mm grain size was ashed according to EN 15403. Ash was mixed with boric acid and pressed pellets were prepared (4 replicates for each run). Standard materials in the same form (ash.) were used for the calibration of the instrument. Standards and samples were distributed among the three laboratories involved in the robustness testing for elements determination by XRF. Furthermore, these laboratories use three different technologies of XRF analysis:

- WD-XRF: wavelength dispersive X-ray fluorescence spectrometry;
- EDP-XRF: energy dispersive X-ray fluorescence spectrometry whit polarized X-ray radiation Spectro X-Lab 2000;
- ED-XRF: energy dispersive X-ray fluorescence spectrometry Spectrace QuanX.

As far as QR-E is concerned, the analyses show good RSD% values for most of the elements (less than 5%).

The same ashed sample was analysed after grinding in agate mortar in order to check if particle size of the sample affects the quality of results of XRF analysis.

Grinded ash shows generally lower RSD%, but in the case of sodium RSD is generally lower for non grinded ash. The average concentration values for the major and minor elements are similar for grinded and non grinded ash, thus showing that the ash is sufficiently fine to be analysed as such by XRF. Some differences are observed between XRF results from the three labs even if calibrants and samples were prepared in only one lab; this might be due to the different technologies of the instruments used. Furthermore, it appears that there is no “best” XRF technology for this kind of application.

— Method C — Major elements by ICP-OES/MS after nitric-perchloric acid dissolution

The time of heating for SRF dissolution was the only factor under investigation. Major 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. But it is also evident that for element such as Al, Ba, Ca, K, Mg and Ti 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 longer time procedure (to be tested by the laboratory).

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: Na, Mg, Ca and K tend to be higher at 20 hours heating, but in particular Ba and Ti show a significant tendency to higher elements recoveries with increasing time of heating. For Ti the behaviour is completely the same as for 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 Mg, Ca, Cr, Cu, Sr, P and Pb at 10 hours heating, while they are more similar at 20 hours heating (in this case the same differences are observed for Ca and Mg, while the Cu value is much lower at 0,5 mm than at 1 mm).

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 - Major 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 major 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.

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 major elements.

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 Si, Ti and Sb (and Al in sewage sludge QR-C only). Recovery of Si with EN 13656 is not guaranteed because of volatility of SiF_4 (tetrafluorosilane).

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