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Solid recovered fuels — Methods for the determination of carbon (C), hydrogen (H), nitrogen (N) and sulphur (S) by the instrumental method

Combustibles solides de récupération — Méthodes de détermination de la teneur en carbone (C), hydrogène (H), azote (N) et soufre (S) par la méthode instrumentale

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Contents

Page

Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 300 *Solid recovered fuels*.

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

The determination of total content of carbon, hydrogen, nitrogen and sulfur is usually performed using instrumental methods. Depending on the amount of test portion used two different types of instrumental methods can be used: micro methods require few milligrams of sample; macro methods use grams of sample. Micro methods require a very careful preparation of the test sample for Solid Recovered Fuel (SRF) analysis.

Solid recovered fuels — Methods for the determination of carbon (C), hydrogen (H), nitrogen (N) and sulphur (S) by the instrumental method

1 Scope

This document specifies the determination of total content of carbon, hydrogen, nitrogen and sulfur in solid recovered fuels by instrumental method. Depending on the amount of test portion, micro or macro instrumental apparatus are used.

This method is applicable for concentrations on dry matter basis of C > 0,1 %, N > 0,1 %, H > 0,1 % and S > 0,05 %.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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.

ISO 21637, *Solid recovered fuels — Terminology, definitions and descriptions*

ISO 21660-3[1], *Solid recovered fuels — Determination of moisture content using the oven dry method — Part 3: Moisture in general analysis sample*

ISO 21646[2], *Solid recovered fuels — Sample preparation*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 21637 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at http://www.electropedia.org/

3.1
coefficient of variation
estimate of the standard deviation of a population from a *sample* (3.10) of n results divided by the mean of that sample

Note 1 to entry: Frequently stated as a percentage.

Note 2 to entry: Adapted from Eurachem/Citac Guide CG 4.

3.2
dry basis
calculation basis in which the material is considered free from *moisture* (3.6)

[SOURCE: ISO 21637, 3.20]

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[1] Under preparation. Stage at the time of publication ISO/FDIS 21660-3.

[2] Under preparation. Stage at the time of publication ISO/DIS 21646.

3.3
dry matter

material remaining after removal of *moisture* (3.6) under specific condition

[SOURCE: ISO 21637, 3.22]

3.4
general analysis sample

sub-sample of a laboratory sample having a *nominal top size* (3.7) of 1 mm or less and used for a number of chemical and physical analyses

3.5
laboratory sample

combined sample received by the laboratory on which sample preparation procedures are undertaken

Note 1 to entry: When the laboratory sample is further prepared (reduced) by subdividing, mixing, grinding, or by combinations of these operations, leading to a nominal top size ≤ 1mm, the result is the general analysis sample. A test portion is removed from the general analysis sample for the performance of the test or for analysis. When no preparation of the laboratory sample is required, the laboratory sample may become the test portion.

Note 2 to entry: The laboratory sample is the final sample from the point of view of sample collection, but it is the initial sample from the point of view of the laboratory.

Note 3 to entry: Several laboratory samples are prepared and sent to different laboratories or to the same laboratory for different purposes. When sent to the same laboratory, the set is generally considered as a single laboratory sample and is documented as a single sample.

3.6
moisture

water removable under specific conditions

[SOURCE: ISO 21637, 3.46]

3.7
nominal top size

smallest aperture size of the sieve used for determining the particle size distribution of solid recovered fuels through which at least 95 % by mass of the total material passes through the sieve

[SOURCE: ISO 21637, 3.48]

3.8
particle size

size of the fuel particles as determined in a solid fuel

Note 1 to entry: Different methods of determination can give different results.

3.9
precision

closeness of agreement between independent test/measurement results obtained under stipulated conditions

[SOURCE: ISO 21637, 3.57]

3.10
sample

quantity of material, from a larger amount for which the quality is to be determined

Note 1 to entry: See also increment (3.39), stratified sample (3.78), stratified random sample (3.80), stratified arbitrary sample (3.79), sub-sample (3.82) and test sample (3.84) in ISO 21637.

[SOURCE: ISO 21637, 3.63, modified — Notes 1 - 3 to entry were removed and new note 1 to entry was added]

3.11

test portion

sub-sample either of a laboratory sample or a *test sample* (3.12) required for the specific measurement

[SOURCE: ISO 21637, 3.83]

3.12

test sample

laboratory sample (3.5) after an appropriate preparation made by the laboratory

[SOURCE: ISO 21637, 3.84]

4 Safety remarks

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

In addition, the following information is given:

- only experienced personnel, following the safety instructions of the manufacturer, shall use instruments for carbon, hydrogen, nitrogen and sulfur determination.

5 Principle

A known mass of sample is treated with oxygen, or in an oxygen/carrier gas mixture, under conditions such that it is converted into gaseous products of combustion or decomposition. These consist mainly of carbon dioxide, water vapour, elemental nitrogen and/or nitrogen oxides, oxyacids and oxides of sulfur and hydrogen halides. The products are treated to ensure that any hydrogen associated with sulfur or halides are converted, through a catalytic process, into water vapour. Nitrogen oxides are reduced to nitrogen, and the products of combustion which can interfere with the subsequent gas-analysis procedures are properly removed. The carbon dioxide, water vapour and nitrogen mass fractions in the gas stream are then determined quantitatively by appropriate instrumental gas analysis procedures after separation by trapping or suitable chromatographic column.

The samples are held in a suitable container (tin or other crucible) and then dropped inside the quartz tube furnace at about 1 250 °C in an oxygen stream for complete oxidation in the presence of a catalyst layer.

6 Reagents and calibration standards

All reagents shall be at least of analytical grade and suitable for their specific purposes.

6.1 Carrier gas: Helium, 99,99 % volume fraction or other gases as specified by the instrument manufacturer.

6.2 Oxygen, free of combustion material, purity 99,95 % volume fraction, or as specified by the instrument manufacturer.

6.3 Additional reagents: as specified by the instrument manufacturer.

6.4 Calibration standards

Examples of pure organic substances suitable for calibration are given in Table 1.

Examples of certified biomass sample with metrological traceability are given in Table 2.

The two tables refer to different types of materials: Table 1 refers to pure substances to be used primary calibration standards while Table 2 refers to biomass materials which can be used as controls since the content depends on the batch.

Table 1 — Calibration standards

Name	Formula	C %	H %	N %	S %
Acetanilide	C_8H_9NO	71,1	6,7	10,4	
Antipyrine	$C_{11}H_{12}N_2O$	70,19	6,43	14,88	
Atropine	$C_{17}H_{23}NO_3$	70,6	8,0	4,8	
Benzoic acid	$C_7H_6O_2$	68,8	5,0	0,0	
Cystine	$C_6H_{12}N_2O_4S_2$	30,0	5,0	11,7	26,7
Diphenylamine	$C_{12}H_{11}N$	85,2	6,5	8,3	
EDTA	$C_{10}H_{16}N_2O_8$	41,1	5,5	9,6	
Phenylalanine	$C_9H_{11}NO_2$	65,4	6,7	8,5	
Sulfanil amide	$C_6H_8N_2O_2S$	41,8	4,7	16,3	18,6
Sulfanilic acid	$C_6H_7NO_3S$	41,6	4,1	8,1	18,5
Thiourea	CH_4N_2S	15,78	5,3	36,8	42,12
TRIS	$C_4H_{11}NO_3$	39,7	9,1	11,6	
2,5-Bis(5-tert-butyl-benzoxazol-2-yl)thiophene (BBOT)	$C_{26}H_{26}N_2O_2S$	72,5	6,0	6,5	7,4

Table 2 — Examples of certified biomass sample with metrological traceability

Name	C %	H %	N %	S %
Alfalfa	45,05		3,6	0,38
Oat meal	45,8	6,7	2,8	0,25
Rye Flour	45	6,4	1,7	0,14
Wheat Flour	45,3	6,4	2,7	0,19

NOTE Certified value for biomass samples is only indicative, depending on the batch.

7 Apparatus

Various instrumental configurations are available. The general requirements for a suitable apparatus are:

a) the combustion conditions shall be such that all carbon, hydrogen, nitrogen and sulfur are converted to carbon dioxide, water vapour, nitrogen oxides or elemental nitrogen and sulfur oxides;

b) for the determination of sulfur, the instrumental configuration shall be able to reach adequate conditions of temperature and combustion time to allow to convert all the chemical compounds that can be present in the sample (e.g. metal sulphides require a temperature of 1 000 °C and calcium sulfate a temperature > 1250 °C);

c) Tungsten wire may not be used for the determination of sulfur because it is a sulfur trap. For instance, copper wire can be used as an alternative;

d) one or more separation steps are usually included to commercial devices, depending on the detector used, to reduce or eliminate any possible interference during the subsequent determination;

e) nitrogen oxides shall be converted to the nitrogen before detection;

f) hydrogen associated with sulfur or halides are converted, through a catalytic process, into water vapour

g) the detection system shall provide response, that correlate directly with the concentrations of the combustion gases, over the full range applicable and preferable in a linear manner;

h) if a nonlinear response is provided by a detection system, it shall include provisions for evaluating that response in a manner which correlates accurately with the concentration of the combustion gas;

i) it shall include a means of displaying the detector responses or of calculating and presenting the concentrations of carbon, hydrogen, nitrogen and sulfur in the sample following the input of other appropriate data as necessary;

j) analytical balance, resolution of at least 1 part per thousand of the weighted amount.

8 Procedure

8.1 Sample conservation and pre-treatment

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

8.2 Sample preparation

The test sample shall be prepared from the laboratory sample according to ISO 21646.

The nominal top size of the test sample shall be 1 mm or less. For some instruments it may be necessary to prepare a test sample with a lower nominal top size than 1 mm in order to keep the desired precision. For “new products” an adequate particle size shall be determined by validation experiments.

The size of test portion depends on the particular instrument used.

For some types of instruments, it is necessary to carry out the determination of hydrogen on dried analysis samples.

Whereas the determination is carried out on dry sample, the moisture content shall be determined according to ISO 21660-3.

8.3 Preparation of the test portion

Weigh the appropriate amount of test sample as recommended by the instrument manufacturer as appropriate for the type of instrument and the expected content of carbon, hydrogen, nitrogen and sulfur.

The test portion shall be weighed directly into the sample capsule in the case of a micro- or semi-micro analyser. Otherwise it may be weighed directly or transferred from a suitable weighing container.

8.4 Calibration

Set up the instrument following the manufacturer instructions.

Stabilize the furnace and analyser.

Select 3 to 5 calibration standards (6.4) with increasing concentration of nitrogen, hydrogen, carbon and sulfur. Calibrate the instruments for nitrogen, hydrogen, carbon and sulfur determination following the manufacturer instructions. Use the same procedure as for sample analysis (see below). Alternatively, different amounts of the same substance may be used to prepare the calibration.

Verify the calibration by analysing as a test sample a portion of a suitable standard, preferably with a different material than that used for the calibration.

Verification of the calibration is necessary if operating with pre-calibrated instruments.

Check the performance of the instrument using the accepted standard procedures like replicate analysis, use of CRM and/or Standard Reference Material (SRM), control samples and create control charts. The calibration and quality control scheme shall be organized and maintained in such a way that the required uncertainty of measurement can be obtained. The results of the validation study QUOVADIS (Annex B) demonstrate what is achievable with commercial instruments that are used by experienced laboratories.

Major results of robustness testing are reported in Annex C.

8.5 Analysis of samples

Depending on the internal laboratory quality requirements, at least two independent replicates shall be analysed for each laboratory sample. In the case that the variability between replicates is larger than the established limit larger number of replicates shall be processed. In the following formulas the average values shall be used for calculation.

Weigh the test portion and transfer it into the instrumental apparatus. Start the cycle following the operating instruction for the specific instruments.

The total carbon, hydrogen, nitrogen and sulfur contents of the solid recovered fuels shall be expressed as a percentage by mass on the dry basis. Most commercially available instruments can give the results directly.

The following Formulae shall be used:

for the carbon content:

$$w_d(C)=w_{ad}(C)\times\frac{100}{100-w_{ad}(H_2O)} \quad (1)$$

for the nitrogen content:

$$w_d(N)=w_{ad}(N)\times\frac{100}{100-w_{ad}(H_2O)} \quad (2)$$

for the sulfur content:

$$w_d(S)=w_{ad}(S)\times\frac{100}{100-w_{ad}(H_2O)} \quad (3)$$

for the hydrogen content:

$$w_d(H)=\left(w_{ad}(H)-\frac{w_{ad}(H_2O)}{8{,}94}\right)\times\frac{100}{100-w_{ad}(H_2O)} \quad (4)$$

where:

d is dry basis;

ad is as determined;

$w_{ad}(H_2O)$ is the moisture content of the general analysis sample when analysed.

9 Performance characteristics

Data on performance characteristics of the present method are given in Annex B which presents the results of CHNS from the QUOVADIS validation project (Quality Management, Organization, Validation of standards, Developments and Inquiries for Solid Recovered Fuel - SRF) or other resources.

10 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) a reference to this document, i.e. ISO 21663: 2020;

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

f) the analytical results, referring to Clause 8;

g) any details not specified in this document 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 (e.g. accreditation).

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 characterization of Solid Recovered Fuel (SRF) samples according to this document.

NOTE Equivalent requirements apply in all chemical test method specifications for SRF, i.e. this document, EN 15408:2011, EN 15410:2011, EN 15411:2011, CEN/TS 15412:2010[4],[5],[6],[7] and ISO 21646.

A minimum 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 representativeness and practical reasons for handling samples. In Table A.1, the requirements are summarized 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)	Long term storage condition before delivery to the lab	Container material
C, H, N, S	100	refrigeration 3–5 °C	plastic bottle or bag

Annex B
(informative)

Data on performance characteristics

The method described in this document has been validated within the QUOVADIS project[8]. In this validation project several SRF were selected to provide a reasonable coverage of SRF. They were tested according to the present standardised method. Results and robustness, repeatability and reproducibility data are reported in the document: "EUR 23552 EN — Organization of Validation Exercises — JRC Scientific and Technical Reports — ISBN 978-92-79-10396-4 — Luxembourg: Office for Official Publications of the European Communities".

Inter-laboratory trials were carried out by laboratories in Austria, Belgium, France, Germany, Italy, the Netherlands 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 according to ISO 5725-2[2] are presented in Tables B.1 to B.3.

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

Table B.1 — Performance data for carbon

Sample	**Matrix**	l	n	o %	x_{ref} %	$\bar{\bar{x}}$ %	η %	s_R %	$C_{V,R}$ %	S_r %	$C_{V,r}$ %
A	SRF produced from shredded tyres	81	14	3,6	na	71,6	na	5,12	7,10	5,12	7,10
B	SRF produced from demolition wood	80	14	4,8	na	47,7	na	2,33	4,85	0,26	0,54
C	SRF produced from sewage sludge	84	14	0	na	30,5	na	0,43	1,43	0,43	1,43
D	SRF produced from municipal waste	84	14	0	na	46,4	na	2,23	4,85	1,63	3,54
E	SRF produced from municipal waste (paper and plastic reach)	84	14	0	na	45,4	na	2,97	6,60	1,71	3,80

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;

$C_{V,R}$ is the coefficient of the variation of the reproducibility;

S_r is the repeatability standard deviation on dry matter base;

$C_{V,r}$ is the coefficient of the variation of the repeatability;

na not applicable.

Table B.2 — Performance data for hydrogen

Sample	**Matrix**	l	n	o %	x_{ref} %	$\bar{\bar{x}}$ %	η %	s_R %	$C_{V,R}$ %	S_r %	$C_{V,r}$ %
A	SRF produced from shredded tyres	63	12	12,5	na	6,83	na	0,91	13,4	0,30	4,40
B	SRF produced from demolition wood	66	13	15,4	na	6,14	na	0,73	12,0	0,07	1,10
C	SRF produced from sewage sludge	60	12	16,7	na	2,28	na	0,04	1,70	0,04	1,70
D	SRF produced from municipal waste	70	13	10,2	na	6,53	na	0,76	11,7	0,24	3,70
E	SRF produced from municipal waste (paper and plastic reach)	72	13	7,7	na	6,73	na	1,20	17,9	0,43	6,40

Definition of symbols: see Table B.1.

Table B.3 — Performance data for nitrogen

Sample	**Matrix**	l	n	o %	x_{ref} %	$\bar{\bar{x}}$ %	η %	s_R %	$C_{V,R}$ %	S_r %	$C_{V,r}$ %
A	SRF produced from shredded tyres	53	12	26,4	na	0,55	na	0,20	36,4	0,07	12,7
B	SRF produced from demolition wood	64	13	17,9	na	0,71	na	0,18	25,4	0,06	8,5
C	SRF produced from sewage sludge	58	12	19,4	na	1,02	na	0,02	2,0	0,02	2,0
D	SRF produced from municipal waste	62	13	20,5	na	1,83	na	0,12	6,6	0,12	6,6
E	SRF produced from municipal waste (paper and plastic reach)	58	13	25,6	na	0,95	na	0,14	14,7	0,06	6,3

Definition of symbols: see Table B.1.

Performance data for sulfur are not available at the time of publication of this document.