INTERNATIONAL STANDARD

ISO 16993

Second edition
2016-07-01

Solid biofuels — Conversion of analytical results from one basis to another

Biocombustibles solides — Conversion de résultats analytiques d'une base en une autre base

Reference number
ISO 16993:2016(E)

ISO copyright office
Ch. de Blandonnet 8 • CP 401
CH-1214 Vernier, Geneva, Switzerland
Tel. +41 22 749 01 11
Fax +41 22 749 09 47
copyright@iso.org
www.iso.org

Contents

Page

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information.

The committee responsible for this document is ISO/TC 238, *Solid biofuels*.

This second edition cancels and replaces the first edition (ISO 16993:2015), of which it constitutes a minor revision.

Introduction

In the International Standards covering the analysis of solid biofuels, it is generally specified that the determination is intended to be carried out on the air-dried or in air-equilibrated general analysis test sample prepared according to ISO 14780. However, in making use of these analyses, it is necessary to express the results on dry basis and sometimes, also on some other basis. The bases in common use for solid biofuels are “air-dried” (sometimes stated as “as determined”), “as received” (sometimes stated “as sampled” or “as delivered”), “dry”, and “dry, ash free”.

Solid biofuels — Conversion of analytical results from one basis to another

1 Scope

This International Standard gives formulae which allow analytical data relating to solid biofuels to be expressed on the different bases in common use. Consideration is given to corrections that can be applied to certain determined values for solid biofuels prior to their calculation to other bases.

In Annex A, tools for integrity checks of analytical results are given. In Annex B, conversion factors for calculation into other units are given. Annex C is a guideline for the use of validation parameters as can be found in ISO/TC 238 analytical standards.

2 Normative references

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

ISO 16948:2015, *Solid biofuels — Determination of total content of carbon, hydrogen and nitrogen*

ISO 16994, *Solid biofuels — Determination of total content of sulphur and chlorine*

ISO 18122, *Solid biofuels — Determination of ash content*

ISO 18125[1)], *Solid biofuels — Determination of calorific value*

ISO 18134-1, *Solid biofuels — Determination of moisture content — Oven dry method — Part 1: Total moisture — Reference method*

ISO 18134-2, *Solid biofuels — Determination of moisture content — Oven dry method — Part 2: Total moisture — Simplified method*

ISO 18134-3, *Solid biofuels — Determination of moisture content — Oven dry method — Part 3: Moisture in general analysis sample*

3 Symbols and abbreviated terms

The symbols employed in the subsequent clauses are as follows, with the suffixes “ad” (air-dried), “ar” (as received), “d” (dry), and “daf” (dry, ash free), where appropriate.

A	ash (percentage by mass) according to ISO 18122
C	total carbon content (percentage by mass) according to ISO 16948
Cl	total chlorine content (percentage by mass) according to ISO 16994
$q_{p,net}$	net calorific value at constant pressure (J/g) according to ISO 18125
H	total hydrogen content (percentage by mass) according to ISO 16948

1) To be published.

M moisture content (percentage by mass) according to ISO 18134-1, ISO 18134-2, and ISO 18134-3

N total nitrogen content (percentage by mass) according to ISO 16948

O total oxygen content (percentage by mass)

S total sulfur content (percentage by mass) according to ISO 16994

4 Principle

In order to convert an analytical result expressed as one basis to another basis, it is multiplied by a factor calculated from the appropriate formulae (see Table 1), after insertion of the requisite numerical values into the formula in question.

5 Calculations for analyses of solid biofuels

5.1 General

Most analytical values on a particular basis can be converted to any other basis by multiplying it by a factor calculated from the appropriate formula given in Table 1, after insertion of the requisite numerical values into the formula in question. However, for some parameters, there is a direct involvement of the moisture content. In these cases, a correction (as specified in 5.2) of the air-dried result shall be carried out before calculation to dry basis or dry, ash-free basis. Also, if a result for these parameters expressed on a dry or a dry, ash-free basis is to be recalculated to a moist basis, the corrections stated in 5.2 shall be added back to the actual moist basis after applying the appropriate formula from Table 1.

5.2 Extra calculations for hydrogen, oxygen, and net calorific value

5.2.1 Hydrogen

The hydrogen content determined on the air-dried basis (H_{ad}, as analysed) includes both the hydrogen content of the combustible part of the solid biofuel, as well as the hydrogen present in the sample as moisture (total hydrogen content). Before calculation to any other basis, the determined hydrogen content, H_{ad}, shall be corrected of the moisture-bound hydrogen by calculation to dry basis, H_d, as shown in Formula (1):

$$H_d = \left(H_{ad} - \frac{M_{ad}}{8,937} \right) \times \frac{100}{\left(100 - M_{ad}\right)} \quad (1)$$

This hydrogen content, related to the combustible part of the solid biofuel, can be converted to any other basis using the formulae in Table 1.

With the constant factor 8,937, the hydrogen concentration in the water that is present in the sample is calculated. The factor is obtained from the molar formula of water (H_2O) and the atomic weight of hydrogen (1,008) and oxygen (15,999 4).

5.2.2 Oxygen

The oxygen content related to the combustible part of the solid biofuel can be calculated by difference on the dry basis using Formula (2):

$$O_d = 100 - C_d - H_d - N_d - S_d - Cl_d - A_d \quad (2)$$

If high precision is required, the values of S_d and Cl_d should be corrected for eventual remaining contents of sulfur and chlorine in the ash (A_d).

5.2.3 Net calorific value

The net calorific value at constant pressure on a moist basis ($q_{p,net,M}$) includes a correction for the heat of vaporization concerning the actual moisture content, M (M being e.g. M_{ad} or M_{ar}). Before conversion to any other basis, using the formulae in Table 1, this correction corresponding to 24,43 J/g per weight percent moisture (24,43 × M) shall be undone by adding 24,43 × M to the value of the net calorific value. After multiplying this sum with the appropriate formula from Table 1, the obtained value is to be corrected for the heat of vaporization concerning the new moisture content, M^*, by subtracting the value 24,43 × M^*. These corrections are illustrated in Formula (3) concerning the conversion of the net calorific value for a moisture content M ($q_{p,net,M}$ in J/g) to the net calorific value for a moisture content M^* (q_{p,net,M^*} in J/g), both at constant pressure.

$$q_{p,net,M^*} = \left[q_{p,net,M} + \left(24,43 \times M\right)\right] \times \frac{100 - M^*}{100 - M} - \left(24,43 \times M^*\right) \tag{3}$$

For the conversion of, e.g. the net calorific value on dry basis ($q_{p,net,d}$ in J/g) to the net calorific value on as received basis, ($q_{p,net,ar}$ in J/g) Formula (3) can be simplified into Formula (4):

$$q_{p,net,ar} = q_{p,net,d} \times \frac{100 - M_{ar}}{100} - 24,43 \times M_{ar} \tag{4}$$

as in this case, $M = 0$ and $M^* = M_{ar}$.

The net calorific value at a constant pressure for a dry sample ($q_{p,net,d}$) is derived from the corresponding gross calorific value at a constant volume according to ISO 18125.

5.3 General formulae for the conversion from one basis to another basis

After applying eventual corrections according to 5.2, analytical values on a particular basis can be converted to any other basis by multiplying it by a factor calculated from the appropriate formula given in Table 1, after insertion of the requisite numerical values into the formula in question.

Table 1 — Formulae for calculating conversion factors to convert analytical results from one basis to another

Given	Wanted			
	As analysed (air-dried) (ad)	**As received**[a] (ar)	**Dry** (d)	**Dry, ash free** (daf)
As analysed (air-dried, ad)		$\frac{100 - M_{ar}}{100 - M_{ad}}$	$\frac{100}{100 - M_{ad}}$	$\frac{100}{100 - \left(M_{ad} + A_{ad}\right)}$
As received (ar)	$\frac{100 - M_{ad}}{100 - M_{ar}}$		$\frac{100}{100 - M_{ar}}$	$\frac{100}{100 - \left(M_{ar} + A_{ar}\right)}$
Dry (d)	$\frac{100 - M_{ad}}{100}$	$\frac{100 - M_{ar}}{100}$		$\frac{100}{100 - A_d}$
Dry, ash free (daf)	$\frac{100 - \left(M_{ad} + A_{ad}\right)}{100}$	$\frac{100 - \left(M_{ar} + A_{ar}\right)}{100}$	$\frac{100 - A_d}{100}$	

[a] Note that the formulae given for calculating results to the "as received" basis can be used to calculate them to any other moisture bases.

Annex A
(informative)

Tools for integrity check

A.1 General

In this Annex, three integrity checks are described. It helps users to evaluate analysis results. These tools are especially useful when larger series of results have to be checked on analysis/typing errors.

A.2 Integrity check based on the carbon results

Calculate the estimate, QB, expressed in MJ/kg, for the net calorific value at constant pressure on dry basis from the carbon content, using Formula (A.1)[3][8][9]:

$$QB = 0{,}274\,6 \times C_d + 5{,}79 \quad \text{(A.1)}$$

Compare this calculated QB value with the measured value $q_{p,net,d}$ in MJ/kg.

A.3 Integrity check based on the major elements and the ash results

Add the results of the major elements after conversion to their composition on oxide basis. The sum of these oxides (Mash) can then be compared to the ash content (550 °C). For samples with a high S and/or Cl content, these values should be added as well. The conversion factor for S is 2,50, while the conversion factor for Cl is 1.

The conversion factors for converting the major elements into their oxide forms are as follows.

Al → Al_2O_3 : 1,89

Ca → CaO : 1,40

Fe → Fe_2O_3 : 1,43

Mg → MgO : 1,66

P → P_2O_5 : 2,29

K → K_2O : 1,20

Si → SiO_2 : 2,14

Na → Na_2O : 1,35

Ti → TiO_2 : 1,67

Calculate the sum Mash (= Major element ash), in mass fraction (%), on dry basis according to Formula (A.2) using the element concentrations in mg/kg on dry basis.

$$\text{Mash} = \frac{\left(\begin{array}{l}\text{Al}_d \times 1,89 + \text{Ca}_d \times 1,40 + \text{Fe}_d \times 1,43 + \text{Mg}_d \times 1,66 + \text{P}_d \times 2,29 + \\ \text{K}_d \times 1,20 + \text{Si}_d \times 2,14 + \text{Na}_d \times 1,35 + \text{Ti}_d \times 1,67 + \text{Cl}_d + \text{S}_d \times 2,50\end{array}\right)}{10\ 000} \quad \text{(A.2)}$$

The ratio Mash/ash should be around 1 (from 0,8 to 1,2).

NOTE 1 If the sum of the oxides is less than the ash content, the explanation might be a high content of carbonates.

NOTE 2 With high S and/or Cl content, be aware that more than 50 % of these elements could be lost by ashing at 550 °C.

A.4 Integrity check based on the C H N O and ash results

This check is only possible if the O content has been determined.

Calculate the sum MB (= Mass Balance) according to Formula (A.3):

$$\text{MB} = \text{C}_d + \text{H}_d + \text{N}_d + \text{O}_d + \text{S}_d + \text{Cl}_d + \text{A}_d \quad \text{(A.3)}$$

All values are in %.

The MB value should be around 100.

In some types of solid biofuels, relative high amounts of F, Br, or I are found. In that case, the contribution of these elements shall be accounted for as well.

Table A.1 — Examples of the integrity checks according to A.1, A.2, and A.3

Element	C	H	N	O	Al	Ca	Fe	K	Na	Mg	Si	P	Ti	S	Cl	Ash	$q_{p,net,d}$	MB	Mash	QB
Unit	%	%	%	%	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	%	MJ/kg	%	%	MJ/kg
Wood+bark	46,4	6,20	0,01	42,5	44	1 398	46	637	25	175	236	65	3	75	11	0,6	19,2	96	0,4	18,5
Straw	44,4	5,86	0,65	43,7	71	2 829	87	10 770	70	754	11 130	706	25	1 008	1 112	5,6	17,9	100	4,8	18,0
Bark	46,5	5,38	0,56	41,4	536	45 290	297	2 080	115	531	3 175	196	41	741	40	13,3	16,5	107	7,8	18,6
Rapestraw	44,8	5,69	0,34	44,7	34	11 100	25	8 970	653	567	194	551	2	1 943	2 814	4,8	17,7	100	3,9	18,1
Thistle	43,0	5,73	1,03	41,8	411	13 380	238	13 130	12 310	2 308	1 074	795	10	2 002	17 280	9,9	16,8	101	8,3	17,6
Fir without bark	47,8	6,10	0,05	43,9	51	784	15	311	3	103	25	23	3	41	3	0,3	19,2	98	0,2	18,9
Exhausted olive residue	46,0	5,45	1,37	38,7	2 214	13 860	1512	23 870	166	2 955	10 060	1 474	133	1 336	2 074	11,5	19,3	103	9,1	18,4
Wood with glue	50,7	5,78	0,25	42,9	39	4 180	52	944	83	484	80	6	4	167	89	1,5	20,5	101	0,9	19,7
Seaweed	32,3	4,20	2,49	36,1	11 250	19 230	4 440	9 885	11 505	7 620	74 880	1 433	321	20 525	1 847	31,5	12,8	107	32,2	14,6
Coconut shells	49,2	5,54	0,22	45,0	263	697	164	3 410	1 900	575	1 785	128	12	380	1 788	2,1	19,6	102	1,6	19,3
Almond kernels	49,1	6,17	0,22	47,3	108	2 765	237	4 165	49	313	2 430	199	14	177	93	1,9	19,5	105	1,6	19,3
Palm pit kernels	50,8	5,87	0,32	42,8	619	5 460	487	1 240	92	517	8 010	272	31	310	149	3,1	20,2	103	3,1	19,7

NOTE All results are on dry basis,

where

MB are the calculated values according to A.3;

Mash are the calculated values according to A.2;

QB are the calculated values according to A.1.

Annex B
(informative)

Tables with units and conversion factors

Table B.1 — Conversion factors 1

	toe[a]	MWh	GJ	Gcal
toe[a]	1	11,63	41,868	10,0
MWh	0,085 98	1	3,600	0,859 8
GJ	0,023 88	0,277 8	1	0,238 8
Gcal	0,1	1,163 0	4,186 8	1

[a] Tonne oil equivalent.

EXAMPLE 1 toe = 11,63 MWh.

Table B.2 — Conversion factors 2

To convert from	To	Multiply by
g/cm^3	lb/ft^3	62,427 974
lb/ft^3	kg/m^3	16,018 46
lb/in^3	kg/m^3	27 679,90
lb/ft^3	g/cm^3	0,016 018 46
cm	mil	393,70
joule (J)	BTU	$9,484\ 5 \times 10^{-4}$
BTU	joule (J)	1 054,350

A mil, also known as a “thou” or a “point”, is a measurement unit of length equal to 0,001 inch (a “milli-inch”, one thousandth of an inch).

Annex C
(informative)

Guideline for the use of validation parameters

A laboratory has to prove the accuracy of a method in its own laboratory, e.g. either by using Certified Reference Materials (CRM's) or by participation in round robins. When comparing obtained results with validation data presented in the ISO/TC 238 analytical standards, it has to be taken into account that the concentration of a component might vary over orders of magnitudes in different biomass samples. When measuring close to the detection limits of instruments for elements in very low concentrations, standard deviation and errors usually increase. Furthermore, some solid biofuels are difficult to homogenize or contain impurities and the sample homogeneity, as well as the biomass type, can influence the performance of the method[1][5][7].

Validation data can include the parameters listed in Table C.1.

Table C.1 — Validation parameters

Symbol	Meaning
n	is the number of laboratories after outlier elimination
l	is the number of outlier-free individual analytical values
o	is the percentage of outlying values from replicate determination
x	is the overall mean
s_R	is the reproducibility standard deviation
CV_R	is the coefficient of the variation of the reproducibility
s_r	is the repeatability standard deviation
CV_r	is the coefficient of the variation of the repeatability
r	is the repeatability limit
R	is the reproducibility limit

If the r and R values are not included in presented validation data, they can be calculated from the standard deviations as follows.

$r = 2\sqrt{2} \times s_r = 2,8 \times s_r$ (absolute comparison of two measurements at repeatability conditions)

$r = 2\sqrt{2} \times CV_r = 2,8 \times CV_r$ (relatively comparison of two measurements at repeatability conditions)

$R = 2\sqrt{2} \times s_R = 2,8 \times s_R$ (absolute comparison of two measurements at reproducibility conditions)

$R = 2\sqrt{2} \times CV_R = 2,8 \times CV_R$ (relatively comparison of two measurements at reproducibility conditions)

Available performance/validation data for a method (as can be found in ISO/TC 238 analytical standards) or the data from other reliable round robin investigations of the method may be used as one of the sources when determining the expanded uncertainty of measurement.

In that case, it should be assured that:

— the method used by the laboratory performs as good as or better than the performance data given in the standards (usually, common quality assurance methods for laboratories such as control cards, use of CRM's, proficiency test, or round robins, are necessary to document this);

— the types of samples analysed are within the scope of the samples for which the data are valid (e.g. the type of samples investigated in the performed round robin);

— the analysis method included by the budget is the same method for which the data are valid (e.g. the method used by the participants in the performed round robin).

EXAMPLE 1 Use of validation data for the estimation of expanded uncertainty of measurement.

A laboratory wants to determine the expanded uncertainty of measurement of their carbon determination in wood and wants to include general accepted method specific data as part of that budget.

The intralab reproducibility of this laboratory, calculated from internal validation studies and control charts, was determined to be 0,82 % (CV_R).

The performance data presented in ISO 16948:2015, Table A.1 state a CV_R (between laboratories) at 1,1 % relative (wood chip sample).

Then,

$$u_{c,rel} = \sqrt{\left(0,82^2 + 1,1^2\right)} = 1,37\,\% \text{ relative}$$

$$U_{rel} = 2 \times u_{c,rel} = 2,7\,\% \text{ relative}$$

where

$u_{c,rel}$ is the combined uncertainty of measurement;

U_{rel} is the expanded uncertainty of measurement using a coverage factor of 2 (approximately 95 % confidence interval).

EXAMPLE 2 Use of validation data for evaluation of double determinations.

Available performance/validation data for a method may also be used for a control of the actual level of precision for the method, e.g. according to the following example.

In ISO 16967:2015, Table B.5, the following performance data shown in Table C.2 are presented for the determination of phosphorous.

Table C.2 — Examples validation parameters

Sample	n	l	o	x	s_R	CV_R	s_r	CV_r
			%	mg/kg	mg/kg	%	mg/kg	%
Wood chips	11	53	3,6	74	5	6,7	2	3,4
Olive residues	13	65	0	1 490	127	8,5	58	3,9

When analysing a sample of solid biofuel, two results for the phosphorus content were obtained: 810 mg P/kg and 1 180 mg P/kg. The difference between these two results is 370 mg P/kg or 37 % of the mean value, 995 mg P/kg. At this level, the repeatability limit (r), as calculated from the performance data presented in ISO 16967 (r = 2,8 × CVr), is expected to be 10 % to 11 % of the mean value. As the actual difference exceeds this interval significant, the results should not be accepted and the determination should be repeated after a survey of the procedure.

Bibliography

[1] 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*

[2] ISO 14780[2)], *Solid biofuels —Sample preparation*

[3] ISO 16948, *Solid biofuels — Determination of total content of carbon, hydrogen and nitrogen*

[4] ISO 16967, *Solid biofuels — Determination of major elements — Al, Ca, Fe, Mg, P, K, Si, Na and Ti*

[5] ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories*

[6] ISO 17225-1, *Solid biofuels — Fuel specifications and classes — Part 1: General requirements*

[7] Harmonized protocols for the adoption of standardized analytical methods for the presentation of their performance characteristics. Pure Appl. Chem. 1990, **62** (1) pp. 149–162

[8] *Calculation of the upper heating value of biomass*, H. Bayer, W. Schaller, 12th European Conference on Biomass for Energy, Industry and Climate protection,17-21 June 2002, Amsterdam, The Netherlands

[9] *Thermal Data for Natural and Synthetic Fuels*, Marcel Dekker, 1998

2) To be published.

ICS 27.190; 75.160.10

Price based on 10 pages