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Stationary source emissions — Determination of the biogenic fraction in CO_2 in stack gas using the balance method

National foreword

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Stationary source emissions — Determination of the biogenic fraction in CO_2 in stack gas using the balance method

Émission des sources fixes — Détermination de la fraction biogénique de CO_2 dans les gaz de cheminées en utilisant la méthode des bilans

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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

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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).

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The committee responsible for this document is ISO/TC 146, *Air quality*, Subcommittee SC 1, *Stationary source emissions*.

Introduction

During the combustion of solid fuels, O_2 is consumed and CO_2 is simultaneously produced. Biogenic and fossil organic matter do not only show strong differences regarding O_2 consumption and CO_2 production, but also differences in their respective calorific value and carbon content are observable.

The balance method can be used when the elementary composition of moisture and ash free biomass and fossil matter present in the fuel used is known and online stack gas composition measurements (O_2 and CO_2) are available at high accuracy. It will enable online modelling of biomass fossil ratio's in stack gas giving the user the opportunity to control or report that ratio. The generated model data can be verified using the radiocarbon (^{14}C) determined biomass fuel ratio. The results obtained using this document will be complementary to the results obtained with ISO 13833. In ISO 13833, the biogenic fraction in stack gas from plants with unknown fuel composition is determined using the ^{14}C method. If the chemical composition of pure biogenic and fossil matter (contents of C, H, N, S, O referred of moisture and ash free biomass and fossil organic matter, respectively) present in the fuel used is known, the biogenic CO_2 fraction can be calculated utilizing different operating data of the Waste for Energy (WfE) plant. When the chlorine content is sufficiently high, it can be additionally used to optimize the mass balances.

Stationary source emissions — Determination of the biogenic fraction in CO_2 in stack gas using the balance method

1 Scope

This document enables the determination of the biogenic fraction in CO_2 in stack gas using the balance method. The balance method uses a mathematical model that is based on different operating data of the Waste for Energy (WfE) plant (including stack gas composition) and information about the elementary composition of biogenic and fossil matter present in the fuel used.

NOTE Use only mixed fuels when using the calculation method.

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 12039, *Stationary source emissions — Determination of carbon monoxide, carbon dioxide and oxygen — Performance characteristics and calibration of automated measuring systems*

EN 14181, *Quality assurance of automated measuring systems*

EN 15259, *Air quality — Measurement of stationary source emissions — Requirements for measurement sections and sites and for the measurement objective, plan and report*

EN 15267-3, *Air quality — Certification of automated measuring systems — Part 3: Performance criteria and test procedures for automated measuring systems for monitoring emissions from stationary sources*

3 Terms and definitions

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

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

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

3.1
biogenic
produced in natural processes by living organisms but not fossilized or derived from fossil resources

3.2
biomass
material of biological origin excluding material embedded in geological formation or transformed to fossil

3.3
radiocarbon
radioactive isotope of the element carbon, ^{14}C, having 8 neutrons, 6 protons, and 6 electrons

3.4
sample
quantity of material, representative of a larger quantity for which the property is to be determined

3.5

sample preparation

all the actions taken to obtain representative analyses, *samples* (3.4) or *test portions* (3.6) from the original sample

3.6

test portion

quantity of material drawn from the test sample (or from the laboratory sample if both are the same) and on which the test or observation is actually carried out

3.7

balance method

numerical procedure to calculate the fraction of *biogenic* (3.1) matter in waste continuously by solving a set of equations

4 Symbols and abbreviated terms

$C^{(f)}$	organic carbon content of the waste fuel derived from operating data (kg C/kg waste fuel)
ΔH	net enthalpy of steam cycle of the Waste for Energy (WfE) plant (MJ/kg)
$\boldsymbol{J}_x$	Jacobian matrix of range 6xN, with N representing the number of the measured variables
$\boldsymbol{J}_y$	Jacobian matrix of range 6xK, with K representing the number of the unknown variables
L_{vap}	evaporation heat (MJ/kg)
w_B, w_F, w_{H_2O}, w_I	mass fractions of moisture and ash free biogenic and fossil matter, water and inert matter (kg/kg waste fuel)
M_C	relative molecular mass of carbon (12,010 7 g/mol)
M_H	relative molecular mass of hydrogen (1,007 94 g/mol)
M_O	relative molecular mass of oxygen (15,999 4 g/mol)
M_N	relative molecular mass of nitrogen (14,006 7 g/mol)
M_S	relative molecular mass of sulfur (32,065 g/mol)
M_{gas}	molecular weight of auxiliary gas fuel (g/mol)
M_{H_2O}	molecular weight of water (g/mol)
$O^{(f)}$	oxygen consumption of the waste fuel derived from operating data (mol O_2/kg waste fuel);
p_v	vapour pressure of the inlet combustion air (Pa);
$\bar{q}_{LHV_w}$	average lower heating value of the waste feed within a defined period Δt (MJ/kg)
$\bar{q}_{LHV_k}$	elemental lower heating value of the combustible fractions (*k* is carbon, hydrogen, oxygen, nitrogen and sulfur) (MJ/kg)
$\bar{q}_{LHV_{gas}}$	average lower heating value of the auxiliary gas fuel (MJ/$m^3_{273,15\ K,\ 1,013\ 25\ bar}$)

$\bar{q}_{\mathrm{LHV}_{\mathrm{oil}}}$	average lower heating value of the auxiliary oil fuel (MJ/kg)
$R_{\mathrm{as}}{}^{*}$	specific gas constant for the dry air [287,0558 14 J/(kg K)]
S_{vap}	steam production of the Waste for Energy (WfE) plant within a defined period (kg/Δt)
Δt	defined time period (arbitrary time unit, e.g. days)
T_{air}	temperature of the inlet combustion air (°C);
V_{air}	volume of the inlet combustion air ($\mathrm{m}^3{}_{273.15\ \mathrm{K},\ 1.01325\ \mathrm{bar}}$);
V_{fg}	dry flue gas volume of the Waste for Energy (WfE) plant within a defined period ($\mathrm{m}^3{}_{273,15\ \mathrm{K},\ 1,013\ 25\ \mathrm{bar}}/\Delta t$)
V_{gas}	auxiliary gas fuel volume into the Waste for Energy (WfE) plant within a defined period ($\mathrm{m}^3{}_{273,15\ \mathrm{K},\ 1,013\ 25\ \mathrm{bar}}/\Delta t$)
V_{m}	molar volume of ideal gas under standard temperature and pressure (22,414 $\mathrm{dm}^3{}_{273,15\ \mathrm{K},\ 1,013\ 25\ \mathrm{bar}}$/mol)
m_{oil}	mass of auxiliary oil fuel into the Waste for Energy (WfE) plant within a defined period (kg/Δt)
m_{tot}	mass of waste feed into the Waste for Energy (WfE) plant within a defined period (kg/Δt)
W_{v}	vapour mass in the combustion air
ΣW_{S}	sum of solid residues (dry substance) of the Waste for Energy (WfE) plant within a defined period (kg/Δt)
c_{B}^{k}	elemental concentration of the combustible fractions of the biogenic matter (ash and moisture free; *k* is carbon, hydrogen, oxygen, nitrogen and sulfur) (kg/kg)
c_{F}^{k}	elemental concentration of the combustible fractions of the fossil organic matter (ash and moisture free; *k* is carbon, hydrogen, oxygen, nitrogen and sulfur) (kg/kg)
c_{gas}^{k}	elemental concentration of the auxiliary gas fuel (*k* is carbon, hydrogen, oxygen, nitrogen and sulfur) (kg/kg)
c_{oil}^{k}	elemental concentration of the auxiliary oil fuel (*k* is carbon, hydrogen, oxygen, nitrogen and sulfur) (kg/kg)
$x_{\mathrm{O_2,fg}}$, $x_{\mathrm{CO_2,fg}}$	average O_2 and CO_2 content in the dry flue gas of the Waste for Energy (WfE) plant within a defined period Δt (vol %)
$x_{\mathrm{O_2,air}}$, $x_{\mathrm{CO_2,air}}$	average O_2 and CO_2 content of dry combustion air of the Waste for Energy (WfE) plant within a defined period Δt (vol %)
$x_{\mathrm{H_2O}}$	average water content in the flue gas of the Waste for Energy (WfE) plant within a defined period Δt (vol %)
$\boldsymbol{x}_{\mathrm{S}}$	vector of N estimated values of the measured variables
$\boldsymbol{y}_{\mathrm{S}}$	vector of the K unknown variables
η	energy efficiency of the steam boiler of the Waste for Energy (WfE) plant

ε	vapour molecular weight/dry air molecular weight (0,621 98)
σ_{B}^{k}	weighted standard deviation for the *k*-th content of the moisture and ash free biogenic matter present in the waste feed (*k* = C, O, N, H, S)
σ_{F}^{k}	weighted standard deviation for the *k*-th content of the moisture and ash free fossil matter present in the waste feed (*k* = C, O, N, H, S)
σ_{wk}	standard deviation associated to the mass flow of the k-th type of waste
SRF	solid recovered fuel
WfE	waste for energy plant

5 Requirements

5.1 Input stream parameters

For the application of the balance method, the following input parameters are required:

- mass of waste feed (within a defined period, Δt);
- mass/volume of auxiliary fuels such as fuel oil or gas (within a defined period, Δt);
- elemental composition of the auxiliary fuels (fuel oil or gas) used (for carbon, hydrogen, oxygen, nitrogen and sulfur);
- total mass and elementary composition of fuels that are either composed of biogenic matter or fossil matter only (e.g. sewage sludge, wood waste);
- elemental composition (probable range) of moisture and ash free biogenic and fossil organic matter (with respect to the content of carbon, hydrogen, oxygen, nitrogen and sulfur) present in the waste feed;
- ratio of different waste types present in the waste feed such as municipal solid waste (MSW) or hospital waste (in case that the waste types are characterized by different elemental composition of biogenic and fossil organic matter);
- energy efficiency of the boiler;
- average temperature of feed water for the boiler (within defined period, Δt);
- amount of air used for the combustion (within defined period, Δt), not compulsory.

5.2 Output stream parameters

For the application of the balance method, the following output stream parameters are required:

- CO_2 concentration in dry flue gas (within defined period, Δt);
- O_2 concentration in dry flue gas (within defined period, Δt);
- flue gas flow volume within defined period, Δt (standardized to 273 K and 101,325 kPa);
- moisture content within defined period, Δt;
- temperature in stack at measurement point of flue gas flow, within defined period, Δt (in order to convert flue gas flow to standard temperature of 273 K), not compulsory;
- pressure in stack at measurement point of flue gas flow, within defined period, Δt (in order to convert flue gas flow to standard pressure of 101,325 kPa), not compulsory;

- total dry mass of solid residues (e.g. bottom ash, boiler ash and fly ash) produced within defined period, Δt;
- steam produced within defined period, Δt;
- temperature of steam produced within defined period, Δt;
- pressure of steam produced within defined period, Δt.

6 Sampling

6.1 Sampling of input streams

For determining of the necessary input stream parameters, use the following procedures:

- amount of waste combusted (by crane weight data and the adjustment of this data to the waste amount delivered into the waste bunker within a longer time period);
- amount of auxiliary fuels (by volume flow measurements);
- ratio of different waste types present in the waste feed [data provided by trucks delivering waste to the Waste for Energy (WfE) plant];
- elemental composition of biogenic and fossil organic matter present in the waste feed (either reference data provided in Annex A).

6.2 Sampling of output streams

For determination of the necessary output streams parameters, use the following procedures:

- amount of flue gas (by volume flow measurements);
- amount of CO_2 and O_2 in the dry flue gas (by concentration);
- amount of residues (all kind of ashes, by content);
- amount of steam (by content).

7 Test methods

7.1 General

In this subclause, methods are described which define how data shall be generated and collected when they exist. However, more data might be needed than what appears below which is mainly due to lack of relevant method descriptions and standards for data generation and collection.

For all data not covered specifically below, it is expected that these will be generated and collected according to established industry standards and an acceptable level of accuracy. This shall be documented.

7.2 Process input

7.2.1 Amount of fuel that is combusted

The amount of fuel that is combusted is continuously determined by the crane weight which is calibrated according to internal procedures. More precise results might be produced using the weighbridge data for a period (e.g. yearly) and this is calibrated using relevant CEN and ISO standards, e.g. EN 45501.

7.2.2 Amount of combustion air

The amount of air used for combustion is determined using a calculation including the measured flue gas flow and the combustion products (this is more precise than the regular measurement data available). For an average combustion air temperature (15 °C) and average relative humidity (70 %), the relationship between combustion air and flue gas flow is the following: Wet combustion air flow = 1,035 times the dry flue gas flow.

7.2.3 Auxiliary fuel or oxygen enrichment

Metering of auxiliary fuel or oxygen enrichment shall be in accordance with industry best practice and undergo regular maintenance and periodic calibration.

7.3 Process output

7.3.1 Stack emissions

The quality of all air emissions shall follow EN 14181 or similar national or industry equivalents (needs documentation and evaluation of differences).

Determine the concentration of water, CO_2, CO and O_2 in the stack gas using ISO 12039.

Determine the stack gas flow using EN 15259 and EN 15267-3 or similar national or industry equivalents (needs documentation and evaluation of differences).

7.3.2 Energy production

Metering of steam and feed-water shall be in accordance with industry best practice and undergo regular maintenance and periodic calibration.

The energy efficiency of the boiler is typically only measured at the guarantee test of the facility. This value can be used if no other and more recent value is available and if the following is ensured: a) the boiler is well maintained, b) the boiler is cleaned according to industry practice, and c) the boiler design is unchanged. If a measurement is not available, a total energy balance including all energy losses and a detailed flue gas loss calculation can be used to establish a boiler efficiency. The value used shall always be documented together with its source.

7.3.3 Solid outputs

The production of bottom ash and fly ash is to be measured periodically and documented. The method of measurement shall be in accordance with industry best practice or follow a relevant standard if available.

8 Balance calculation

8.1 General

The balance calculation is a method to calculate the fraction of biogenic matter in waste continuously by solving a set of formulae. All data required are either available from literature or from operating data routinely measured (see 5.1 and 5.2).

When hydrogen is used as auxiliary fuel, special care should be taken regarding the use of the different balance formulae.

The balance method is based on five mass balances and one energy balance. If combustion air data are available, an additional water balance formula can be included. The result of each balance, which describes a certain waste characteristic (e.g. content of organic carbon, heating value), are attuned to physical or chemical waste characteristics derived from routinely measured operating data. In order to set up the theoretical balance formulae, the different materials comprised in the waste are virtually divided into four “groups”: inert (w_I), biogenic and fossil organic materials (w_B, w_F) and water $\left(w_{H_2O}\right)$, which represents the unknowns in the set of formulae that are to be determined. Inert materials include all incombustible solid residues such as glass, stones, ashes or other inorganic matter from bio wastes and plastics (e.g. kaolin in paper). Biogenic and fossil organic material groups refer only to the moisture free and ash free organic matter.

8.2 Mass balance

w_I, w_B, w_F and w_{H_2O} represent the mass fraction of each material group. The sum of all mass fractions should be equal to 1 as shown in Formula (1):

$$w_I + w_B + w_F + w_{H_2O} = 1 \tag{1}$$

8.3 Ash balance

The mass fraction of the inert (inorganic) material w_I (the ash content of the waste) corresponds approximately to the quotient of the measured mass flow of solid residues ΣW_S and the waste input m_{tot} of the Waste for Energy (WfE) plant. As a matter of fact, it can be shown that mass losses or increases of inorganic matter due to, e.g. the decomposition of lime ($CaCO_3 \rightarrow CaO + CO_2$) or the oxidation of metals ($4Al + 3O_2 \rightarrow 2Al_2O_3$), are insignificant for the ash balance, mainly in cases where typical municipal solid waste is incinerated. The contribution to solid residues ΣW_S is also neglected, so it is assumed that:

$$w_I = \frac{\sum W_S}{m_{tot}} \tag{2}$$

8.4 Carbon balance

The average content of organic carbon of the waste feed derived from the operating data of the plant (i.e. volume flow of flue gas V_{fg}, the CO_2 concentration in the flue gas $x_{CO_2,fg}$ and in the combustion air $x_{CO_2,air}$ and the mass flow of the waste input m_{tot}), subtracting the contribution of auxiliary fuel, equals the product of the organic mass fractions (biomass w_B and fossil matter m_F) and their carbon contents $\left(c_B^C, c_F^C\right)$. The mass flow of carbon due to emissions of CO and hydrocarbons is neglected since its share of the total mass flow of carbon is negligible in a well-controlled combustion system.

$$w_B c_B^C + w_F c_F^C = \frac{\left[V_{fg}\left(x_{CO_2,fg} - x_{CO_2,air}\frac{100 - x_{O_2,fg} - x_{CO_2,fg}}{100 - x_{O_2,air} - x_{CO_2,air}}\right)\frac{M_C}{100\,V_m}\right]}{m_{tot}} - \frac{\frac{M_{gas}}{V_m}c_{gas}^C V_{gas} + c_{oil}^C m_{oil}}{m_{tot}} \tag{3}$$

8.5 Energy balance

The lower heating value of the waste, $\bar{q}_{LHV_w}$, which is determined by applying approximation formulae using the elementary content of C, H, O, N and S, corresponds to the calorific value derived from operating data of the plant (steam production S_{vap}, the net enthalpy of steam cycle, ΔH, the mass flow of the waste input m_{tot} and the energy efficiency of the boiler η).

$$
\begin{aligned}
& w_{\mathrm{B}}\left(\bar{q}_{\mathrm{LHV_C}}\, c_{\mathrm{B}}^{\mathrm{C}} + \bar{q}_{\mathrm{LHV_H}}\, c_{\mathrm{B}}^{\mathrm{H}} - \bar{q}_{\mathrm{LHV_O}}\, c_{\mathrm{B}}^{\mathrm{O}} + \bar{q}_{\mathrm{LHV_N}}\, c_{\mathrm{B}}^{\mathrm{N}} + \bar{q}_{\mathrm{LHV_S}}\, c_{\mathrm{B}}^{\mathrm{S}}\right) + \\
& w_{\mathrm{F}}\left(\bar{q}_{\mathrm{LHV_C}}\, c_{\mathrm{F}}^{\mathrm{C}} + \bar{q}_{\mathrm{LHV_H}}\, c_{\mathrm{F}}^{\mathrm{H}} - \bar{q}_{\mathrm{LHV_O}}\, c_{\mathrm{F}}^{\mathrm{O}} + \bar{q}_{\mathrm{LHV_N}}\, c_{\mathrm{F}}^{\mathrm{N}} + \bar{q}_{\mathrm{LHV_S}}\, c_{\mathrm{F}}^{\mathrm{S}}\right) - L_{\mathrm{vap}} w_{\mathrm{H_2O}} = \\
& \frac{\left(S_{\mathrm{vap}} \dfrac{\Delta \mathrm{H}}{\eta}\right)}{m_{\mathrm{tot}}} - \frac{\bar{q}_{\mathrm{LHV_{gas}}} V_{\mathrm{gas}} + \bar{q}_{\mathrm{LHV_{oil}}} m_{\mathrm{oil}}}{m_{\mathrm{tot}}}
\end{aligned}
\qquad (4)
$$

The lower heating terms for biogenic and fossil fractions can be evaluated considering different expressions including different elemental values of lower heating. Currently, three relations can be considered in the model, depending on the chemical characterization of the fuel.

— Dulong

$$\bar{q}_{\mathrm{LHV}} = 34{,}0x_{\mathrm{C}} + 101{,}6x_{\mathrm{H}} + 6{,}3x_{\mathrm{N}} + 19{,}1x_{\mathrm{S}} - 9{,}8x_{\mathrm{O}} - 2{,}5M_{\mathrm{H_2O}} \left(\mathrm{MJ} / \mathrm{kg}\right)$$

— Boie

$$\bar{q}_{\mathrm{LHV}} = 34{,}834x_{\mathrm{C}} + 93{,}868x_{\mathrm{H}} - 10{,}802x_{\mathrm{O}} + 6{,}28x_{\mathrm{N}} + 10{,}467x_{\mathrm{S}} - 2{,}449M_{\mathrm{H_2O}} \left(\mathrm{MJ} / \mathrm{kg}\right)$$

— Chang

$$
\begin{aligned}
\bar{q}_{\mathrm{LHV}} = {} & 8\,561{,}11x_{\mathrm{C}} + 179{,}72x_{\mathrm{H}} - 63{,}89x_{\mathrm{S}} + 111{,}17x_{\mathrm{O}} + 91{,}11x_{\mathrm{Cl}} - \\
& 64{,}94x_{\mathrm{N}} - 597{,}114\,75M_{\mathrm{H_2O}} \left(\mathrm{kcal} / \mathrm{kg}\right)
\end{aligned}
$$

Currently, the Boie formulation is considered as default.

8.6 O_2 consumption balance

Information about the chemical composition of the fuel, with special reference to the concentration in the moisture and ash free biogenic (B) and fossil (F) material of carbon $\left(c_{\mathrm{B}}^{\mathrm{C}} \text{ and } c_{\mathrm{F}}^{\mathrm{C}}\right)$, hydrogen $\left(c_{\mathrm{B}}^{\mathrm{H}} \text{ and } c_{\mathrm{F}}^{\mathrm{H}}\right)$, oxygen $\left(c_{\mathrm{B}}^{\mathrm{O}} \text{ and } c_{\mathrm{F}}^{\mathrm{O}}\right)$, nitrogen $\left(c_{\mathrm{B}}^{\mathrm{N}} \text{ and } c_{\mathrm{F}}^{\mathrm{N}}\right)$ and sulfur $\left(c_{\mathrm{B}}^{\mathrm{S}} \text{ and } c_{\mathrm{F}}^{\mathrm{S}}\right)$, allows quantification of the consumption of oxygen in the combustion air. This amount (moles/kg) in the defined period Δt has to match with the oxygen depletion observable in the flue gas using operating data about the volume flow of flue gas V_{fg}, the O_2 and CO_2 concentration in the flue gas $\left(x_{\mathrm{O_2,fg}}, x_{\mathrm{CO_2,fg}}\right)$ and in the combustion air $\left(x_{\mathrm{O_2,air}}, x_{\mathrm{CO_2,air}}\right)$ and the mass flow of the waste input m_{tot}, accounting for the amount of oxygen consumed in the combustion of auxiliary fuel (gas or oil).

$$10^3 w_\mathrm{B} \left(\frac{c_\mathrm{B}^\mathrm{C}}{M_\mathrm{C}} + \frac{c_\mathrm{B}^\mathrm{H}}{4M_\mathrm{H}} - \frac{c_\mathrm{B}^\mathrm{O}}{2M_\mathrm{O}} + \frac{c_\mathrm{B}^\mathrm{N}}{M_\mathrm{N}} + \frac{c_\mathrm{B}^\mathrm{S}}{M_\mathrm{S}} \right) + 10^3 w_\mathrm{F} \left(\frac{c_\mathrm{F}^\mathrm{C}}{M_\mathrm{C}} + \frac{c_\mathrm{F}^\mathrm{H}}{4M_\mathrm{H}} - \frac{c_\mathrm{F}^\mathrm{O}}{2M_\mathrm{O}} + \frac{c_\mathrm{F}^\mathrm{N}}{M_\mathrm{N}} + \frac{c_\mathrm{F}^\mathrm{S}}{M_\mathrm{S}} \right) =$$

$$\frac{10^3 \left[V_\mathrm{fg} \left(x_{\mathrm{O_2,air}} \frac{100 - x_{\mathrm{O_2,fg}} - x_{\mathrm{CO_2,fg}}}{100 - x_{\mathrm{O_2,air}} - x_{\mathrm{CO_2,air}}} - x_{\mathrm{O_2fg}} \right) \frac{1}{100 V_\mathrm{m}} \right]}{m_\mathrm{tot}} - \qquad (5)$$

$$\frac{10^3 \frac{M_\mathrm{gas}}{V_\mathrm{m}} \left(\frac{c_\mathrm{gas}^\mathrm{C}}{M_\mathrm{C}} + \frac{c_\mathrm{gas}^\mathrm{H}}{4M_\mathrm{H}} + \frac{c_\mathrm{gas}^\mathrm{N}}{M_\mathrm{N}} \right) V_\mathrm{gas}}{m_\mathrm{tot}} - \frac{10^3 \left(\frac{c_\mathrm{oil}^\mathrm{C}}{M_\mathrm{C}} + \frac{c_\mathrm{oil}^\mathrm{H}}{4M_\mathrm{H}} + \frac{c_\mathrm{oil}^\mathrm{N}}{2M_\mathrm{O}} + \frac{c_\mathrm{oil}^\mathrm{N}}{M_\mathrm{N}} \right) m_\mathrm{oil}}{m_\mathrm{tot}}$$

The coefficients $+M_\mathrm{C}$, $+4M_\mathrm{H}$, $-2M_\mathrm{O}$, $+M_\mathrm{N}$ and $+M_\mathrm{S}$ in Formula (5) represent the mass of each element necessary to consume 1 mol of O_2 during the combustion process. The term $\left(100 - x_{\mathrm{O_2,fg}} - x_{\mathrm{CO_2,fg}}\right) / \left(100 - x_{\mathrm{O_2,air}} - x_{\mathrm{CO_2,air}}\right)$ is derived from the difference in volume between the dry flue gas and the dry combustion air, while the coefficients 10^3 account for the fact that the relative molecular mass are in g/moles unit and V_m in Ndm^3/moles.

8.7 Difference between O_2 consumption and CO_2 production

During the combustion of solid fuels, O_2 is consumed and CO_2 is simultaneously produced. Due to the difference in the chemical composition of biogenic and fossil organic matter (in particular, concerning the ratio of hydrogen and oxygen content), both materials show strong differences in their behaviour regarding O_2 consumption and CO_2 production. The chemical formula describing the combustion of characteristic biogenic and fossil materials (such as cellulose and polyethylene) illustrates this difference given in Formulae (6) and (7):

Combustion of cellulose (biomass fuel):

$$\left(\mathrm{C_6H_{10}O_5}\right)_\mathrm{n} + 6\mathrm{O_2} \rightarrow 6\mathrm{CO_2} + 5\mathrm{H_2O} \qquad (6)$$

Plastics: polyethylene (fossil fuel):

$$\left(-\mathrm{CH_2} - \mathrm{CH_2} -\right)_\mathrm{n} + 3\mathrm{O_2} \rightarrow 2\mathrm{CO_2} + \mathrm{H_2O} \qquad (7)$$

Whereas during the complete combustion of cellulose, the consumption of O_2 equals the amount (in moles) of CO_2 generated during the incineration of polyethylene more oxygen is consumed compared to the production of CO_2. This implies that in the case of cellulose combustion, the sum of O_2 and CO_2 concentration in the flue gas (referred to the dry gas) equals the addition of O_2 and CO_2 content in the combustion air, whereas when burning polyethylene, the sum of O_2 and CO_2 in flue gas is lower than that in the combustion air. The difference between O_2 consumption and CO_2 production can be assessed using information about the chemical concentration in the moisture and ash free biogenic (B) and fossil (F) material of hydrogen $\left(c_\mathrm{B}^\mathrm{H} \text{ and } c_\mathrm{F}^\mathrm{H}\right)$, oxygen $\left(c_\mathrm{B}^\mathrm{O} \text{ and } c_\mathrm{F}^\mathrm{O}\right)$, nitrogen $\left(c_\mathrm{B}^\mathrm{N} \text{ and } c_\mathrm{F}^\mathrm{N}\right)$ and sulfur $\left(c_\mathrm{B}^\mathrm{S} \text{ and } c_\mathrm{F}^\mathrm{S}\right)$. This result (moles/kg) is equated to the dry flue gas data obtained at the incineration plant, accounting for the amount of oxygen consumed and CO_2 produced in the combustion of auxiliary fuel (gas or oil).

$$10^3 m_\mathrm{B}\left(\frac{c_\mathrm{B}^\mathrm{H}}{4M_\mathrm{H}}-\frac{c_\mathrm{B}^\mathrm{O}}{2M_\mathrm{O}}+\frac{c_\mathrm{B}^\mathrm{N}}{M_\mathrm{N}}+\frac{c_\mathrm{B}^\mathrm{S}}{M_\mathrm{S}}\right)+10^3 m_\mathrm{F}\left(\frac{c_\mathrm{F}^\mathrm{H}}{4M_\mathrm{H}}-\frac{c_\mathrm{F}^\mathrm{O}}{2M_\mathrm{O}}+\frac{c_\mathrm{F}^\mathrm{N}}{M_\mathrm{N}}+\frac{c_\mathrm{F}^\mathrm{S}}{M_\mathrm{S}}\right)=$$

$$\frac{10^3\left\{V_\mathrm{fg}\left[\left(x_{\mathrm{CO_2,air}}+x_{\mathrm{O_2,air}}\right)\frac{100-x_{\mathrm{O_2,fg}}-x_{\mathrm{CO_2,fg}}}{100-x_{\mathrm{O_2,air}}-x_{\mathrm{CO_2,air}}}-\left(x_{\mathrm{CO_2,fg}}+x_{\mathrm{O_2,fg}}\right)\right]\frac{1}{100V_\mathrm{m}}\right\}}{m_\mathrm{tot}}-\frac{10^3\frac{M_\mathrm{gas}}{V_\mathrm{m}}\frac{c_\mathrm{gas}^\mathrm{H}}{4M_\mathrm{H}}V_\mathrm{gas}+\frac{c_\mathrm{oil}^\mathrm{H}}{4M_\mathrm{H}}m_\mathrm{oil}}{m_\mathrm{tot}} \qquad (8)$$

The coefficients $+4M_\mathrm{H}$, $-2M_\mathrm{O}$, $+M_\mathrm{N}$ and $+M_\mathrm{S}$ in Formula (8) refer to the amount (mole) of O_2 that is consumed by the "combustion" of H, O, N and S. Carbon is not included in Formula (8) because during its combustion, the amount of CO_2 produced equals the amount of O_2 consumption. The term $\left(100-x_{\mathrm{O_2,fg}}-x_{\mathrm{CO_2,fg}}\right)/\left(100-x_{\mathrm{O_2,air}}-x_{\mathrm{CO_2,air}}\right)$ is derived from the difference in volume between the dry flue gas and the dry combustion air, while the coefficients 10^3 account for the fact that the relative molecular mass are in g/moles unit and V_m in $\mathrm{Ndm^3}$/moles.

8.8 Water balance

During the combustion of solid fuels, an amount of water is produced in addition to that already contained in the waste together with that produced by the auxiliary fuel combustion. This amount equals the humidity content measured in the flue gas $M_{\mathrm{H_2O}}$ subtracting the humidity of the combustion air. This implies only for plants without wet flue gas scrubber, as the scrubber vaporized would significantly increase the water content of the flue gas given in Formula (9):

$$10^3 w_\mathrm{B}\frac{c_\mathrm{B}^\mathrm{H}}{2M_\mathrm{H}}+10^3 w_\mathrm{F}\frac{c_\mathrm{F}^\mathrm{H}}{2M_\mathrm{H}}+10^3\frac{M_{\mathrm{H_2O}}}{M_{\mathrm{H_2O}}}+\frac{10^3\frac{M_\mathrm{gas}}{V_\mathrm{m}}\frac{c_\mathrm{gas}^\mathrm{H}}{2M_\mathrm{H}}V_\mathrm{gas}+\frac{c_\mathrm{oil}^\mathrm{H}}{2M_\mathrm{H}}W_\mathrm{oil}}{m_\mathrm{tot}}=\frac{10^3\left(V_\mathrm{fg}\frac{M_{\mathrm{H_2O}}}{1-M_{\mathrm{H_2O}}}\frac{1}{V_\mathrm{m}}-\frac{W_\mathrm{v}}{M_{\mathrm{H_2O}}}\right)}{m_\mathrm{tot}} \qquad (9)$$

being

$$V_\mathrm{air}=\frac{\left(100-x_{\mathrm{O_2,fg}}-x_{\mathrm{CO_2,fg}}\right)}{V_\mathrm{fg}\left(100-x_{\mathrm{O_2,air}}-x_{\mathrm{CO_2,air}}\right)} \qquad (10)$$

$$W_\mathrm{v}=\frac{\varepsilon p_\mathrm{v}\left[1-\left(\varepsilon p_\mathrm{v}\right)/\left(R_\mathrm{as}T_\mathrm{air}\right)\right]V_\mathrm{air}}{R_\mathrm{as}T_\mathrm{air}} \qquad (11)$$

The vapour pressure is evaluated using the Magnus-Tetens relationship depending on air temperature and humidity, valid for temperature lower than 40 °C.

8.9 Composition of the organic matter

The chemical composition of the moisture and ash free biogenic and fossil matter, which is required as fixed input data, can be derived from various literature data regarding the composition of waste and single waste fractions, or from measurements performed on the basis of accepted standards defined in 6.1. The data are reported as average values and standard deviations, which are derived from the metering precision of the gauges. If the waste fuel is a mixture of different waste types, then the mass m_{tot} in the balance formulae as shown in Formula (12) can be determined using the sum of the partial waste fractions for the defined period Δt.

$$m_{\mathrm{tot}} = m_{\mathrm{tot1}} + m_{\mathrm{tot2}} + m_{\mathrm{tot3}} \tag{12}$$

The corresponding chemical composition in the biogenic (B) and fossil (F) material of carbon $\left(c_{\mathrm{B}}^{\mathrm{C}} \text{ and } c_{\mathrm{F}}^{\mathrm{C}}\right)$, hydrogen $\left(c_{\mathrm{B}}^{\mathrm{H}} \text{ and } c_{\mathrm{F}}^{\mathrm{H}}\right)$, oxygen $\left(c_{\mathrm{B}}^{\mathrm{O}} \text{ and } c_{\mathrm{F}}^{\mathrm{O}}\right)$, nitrogen $\left(c_{\mathrm{B}}^{\mathrm{N}} \text{ and } c_{\mathrm{F}}^{\mathrm{N}}\right)$ and sulfur $\left(c_{\mathrm{B}}^{\mathrm{S}} \text{ and } c_{\mathrm{F}}^{\mathrm{S}}\right)$ can be evaluated by the weighted average formula as shown in Formula (13):

$$\begin{aligned} c_{\mathrm{B}}^{k} &= \frac{c_{\mathrm{B1}}^{k} m_{\mathrm{tot1}} + c_{\mathrm{B2}}^{k} m_{\mathrm{tot2}} + c_{\mathrm{B3}}^{k} m_{\mathrm{tot3}}}{m_{\mathrm{tot1}} + m_{\mathrm{tot2}} + m_{\mathrm{tot3}}} \\ c_{\mathrm{F}}^{k} &= \frac{c_{\mathrm{F1}}^{k} m_{\mathrm{tot1}} + c_{\mathrm{F2}}^{k} m_{\mathrm{tot2}} + c_{\mathrm{F3}}^{k} m_{\mathrm{tot3}}}{m_{\mathrm{tot1}} + m_{\mathrm{tot2}} + m_{\mathrm{tot3}}} \end{aligned} \tag{13}$$

with corresponding standard deviations defined as shown in Formulae (14) and (15):

$$\sigma_{\mathrm{B}}^{k} = \left[\frac{\begin{gathered}\left(\frac{\sigma_{\mathrm{W1}}}{m_{\mathrm{tot1}}} + \frac{\sigma_{\mathrm{B1}}^{k}}{c_{\mathrm{B1}}^{k}}\right)\left(m_{\mathrm{tot1}} + c_{\mathrm{B1}}^{k}\right) + \left(\frac{\sigma_{\mathrm{W2}}}{m_{\mathrm{tot2}}} + \frac{\sigma_{\mathrm{B2}}^{k}}{c_{\mathrm{B2}}^{k}}\right)\left(m_{\mathrm{tot2}} + c_{\mathrm{B2}}^{k}\right) + \\ \left(\frac{\sigma_{\mathrm{W3}}}{m_{\mathrm{tot3}}} + \frac{\sigma_{\mathrm{B3}}^{k}}{c_{\mathrm{B3}}^{k}}\right)\left(m_{\mathrm{tot3}} + c_{\mathrm{B3}}^{k}\right)\end{gathered}}{c_{\mathrm{B1}}^{k} m_{\mathrm{tot1}} + c_{\mathrm{B2}}^{k} m_{\mathrm{tot2}} + c_{\mathrm{B3}}^{k} m_{\mathrm{tot3}}} + \frac{\sigma_{\mathrm{W1}} + \sigma_{\mathrm{W2}} + \sigma_{\mathrm{W3}}}{m_{\mathrm{tot1}} + m_{\mathrm{tot2}} + m_{\mathrm{tot3}}} \right] c_{\mathrm{B}}^{k} \tag{14}$$

$$\sigma_{\mathrm{F}}^{k} = \left[\frac{\begin{gathered}\left(\frac{\sigma_{\mathrm{W1}}}{m_{\mathrm{tot1}}} + \frac{\sigma_{\mathrm{F1}}^{k}}{c_{\mathrm{F1}}^{k}}\right)\left(m_{\mathrm{tot1}} + c_{\mathrm{F1}}^{k}\right) + \left(\frac{\sigma_{\mathrm{W2}}}{m_{\mathrm{tot2}}} + \frac{\sigma_{\mathrm{F2}}^{k}}{c_{\mathrm{F2}}^{k}}\right)\left(m_{\mathrm{tot2}} + c_{\mathrm{F2}}^{k}\right) + \\ \left(\frac{\sigma_{\mathrm{W3}}}{m_{\mathrm{tot3}}} + \frac{\sigma_{\mathrm{F3}}^{k}}{c_{\mathrm{F3}}^{k}}\right)\left(m_{\mathrm{tot3}} + c_{\mathrm{F3}}^{k}\right)\end{gathered}}{c_{\mathrm{B1}}^{k} m_{\mathrm{tot1}} + c_{\mathrm{B2}}^{k} m_{\mathrm{tot2}} + c_{\mathrm{B3}}^{k} m_{\mathrm{tot3}}} + \frac{\sigma_{\mathrm{W1}} + \sigma_{\mathrm{W2}} + \sigma_{\mathrm{W3}}}{m_{\mathrm{tot1}} + m_{\mathrm{tot2}} + m_{\mathrm{tot3}}} \right] c_{\mathrm{F}}^{k} \tag{15}$$

A reference chemical composition for different waste types is included in Annex A, while the chemical composition of the most common auxiliary fuels is included in Annex B.

8.10 Operating data of the Waste for Energy (WfE) plant and plausibility checks

The required operating data from the Waste for Energy (WfE) plant (waste amount, amount of solid residues, volume of flue gas, O_2 and CO_2 content in the flue gas, steam production, steam pressure and temperature, temperature of the feed water) shall be routinely measured and recorded. As for the chemical composition of the organic matter, the data are reported as average values and the uncertainties in the measurements.

When the plant is in continuous operation and reporting for this period (e.g. a year) is conducted at least 80 % of the data points shall pass the plausibility testing for the results to represent the period. If this is not the case, only sub-periods that individually pass the 80 % requirement can be reported and they cannot be said to cover the full period.

The operating data accuracy is important, but even where uncertainties are taken into account, gross errors due to sensor failure can occur so secondary checks need to be made to verify the data. A suggested approach is to verify if the oxygen consumption and organic carbon contents corresponding to the operating data recorded is in the range of theoretical values when only biogenic matter or only fossil matter is attributed to the waste mixture, both evaluated in correspondence of the theoretical lower heating value $\bar{q}_{\mathrm{LHV}}{}^{(\mathrm{f})}$, calculated as shown in Formula (16):

$$\bar{q}_{\mathrm{LHV}}{}^{(\mathrm{f})} = \frac{\left(S_{\mathrm{vap}}\dfrac{\Delta \mathrm{H}}{\eta}\right)}{m_{\mathrm{tot}}} - \frac{\bar{q}_{\mathrm{LHV}_{\mathrm{gas}}} V_{\mathrm{gas}} + \bar{q}_{\mathrm{LHV}_{\mathrm{oil}}} m_{\mathrm{oil}}}{m_{\mathrm{tot}}} \qquad (16)$$

The corresponding organic carbon contents and oxygen consumption are evaluated as shown in Formula (17):

$$\mathrm{C}^{(\mathrm{f})} = \frac{10^3\left[V_{\mathrm{fg}}\left(x_{\mathrm{CO_2,fg}} - x_{\mathrm{CO_2air}}\dfrac{100 - x_{\mathrm{O_2,fg}} - x_{\mathrm{CO_2,fg}}}{100 - x_{\mathrm{O_2,air}} - x_{\mathrm{CO_2,air}}}\right)\dfrac{M_{\mathrm{C}}}{100\,V_{\mathrm{m}}}\right]}{m_{\mathrm{tot}}} - \frac{10^3\left(\dfrac{M_{\mathrm{gas}}}{V_{\mathrm{m}}} c_{\mathrm{gas}}^{C} V_{\mathrm{gas}} + c_{\mathrm{oil}}^{C} m_{\mathrm{oil}}\right)}{m_{\mathrm{tot}}} \qquad (17)$$

and Formula (18):

$$\mathrm{O}^{(\mathrm{f})} = \frac{10^3\left[V_{\mathrm{fg}}\left(x_{\mathrm{O_2,air}}\dfrac{100 - x_{\mathrm{O_2,fg}} - x_{\mathrm{CO_2,fg}}}{100 - x_{\mathrm{O_2,air}} - x_{\mathrm{CO_2,air}}} - x_{\mathrm{O_2,fumi}}\right)\dfrac{1}{100\,V_{\mathrm{m}}}\right]}{m_{\mathrm{tot}}} - 10^3\left[\frac{\dfrac{M_{\mathrm{gas}}}{V_{\mathrm{m}}}\left(\dfrac{c_{\mathrm{gas}}^{\mathrm{C}}}{M_{\mathrm{C}}} + \dfrac{c_{\mathrm{gas}}^{\mathrm{H}}}{4M_{\mathrm{H}}} + \dfrac{c_{\mathrm{gas}}^{\mathrm{N}}}{M_{\mathrm{N}}}\right)V_{\mathrm{gas}}}{m_{\mathrm{tot}}}\right] - 10^3\left[\frac{\left(\dfrac{c_{\mathrm{oil}}^{\mathrm{C}}}{M_{\mathrm{C}}} + \dfrac{c_{\mathrm{oil}}^{\mathrm{H}}}{4M_{\mathrm{H}}} - \dfrac{c_{\mathrm{oil}}^{\mathrm{O}}}{2M_{\mathrm{O}}} + \dfrac{c_{\mathrm{oil}}^{\mathrm{N}}}{M_{\mathrm{N}}} + \dfrac{c_{\mathrm{oil}}^{\mathrm{S}}}{M_{\mathrm{S}}}\right)m_{\mathrm{oil}}}{m_{\mathrm{tot}}}\right] \qquad (18)$$

The evaluation of the theoretical range is performed starting from the consideration that the combustion of 1 g of carbon corresponds to a total amount of energy evaluated by the energy balance, between 33,25 kJ and 44 kJ, and similarly to 1 mol of consumed oxygen corresponds an amount of energy between 360 kJ and 400 kJ. Therefore, evaluated the theoretical lower heating value from Formula (16), the corresponding carbon content evaluated from Formula (17) shall be in the range:

$$\mathrm{C}^{(\mathrm{f})}{}_{\mathrm{min}} = 250 + 50\left[\bar{q}_{\mathrm{LHV}}{}^{(\mathrm{f})} - 10\right]/\,3 \text{ and } \mathrm{C}^{(\mathrm{f})}{}_{\mathrm{max}} = 260 + 90\left[\bar{q}_{\mathrm{LHV}}{}^{(\mathrm{f})} - 9/4\right] \qquad (19)$$

while the oxygen consumed evaluated from Formula (18) shall be in the range:

$$\mathrm{O}^{(\mathrm{f})}{}_{\mathrm{min}} = 25 + 15\left[\bar{q}_{\mathrm{LHV}}{}^{(\mathrm{f})} - 10\right]/\,6{,}2 \text{ and } \mathrm{O}^{(\mathrm{f})}{}_{\mathrm{max}} = 30 + 2{,}5\left[\bar{q}_{\mathrm{LHV}}{}^{(\mathrm{f})} - 11\right] \qquad (20)$$

8.11 Mathematical solution with data reconciliation

Because the set of formulae applied in the balance method is over determined (i.e. number of formulae > number of unknowns), data reconciliation has to be performed to improve the accuracy of the measurements (chemical compositions and operating data) accounting for the corresponding uncertainties, currently with the exception of chemical composition and operating data of auxiliary fuel, having no uncertainties. Subsequently, the improved values are used to calculate the unknown quantities (w_I, w_B, w_F, w_{H_2O}) including their uncertainties. The quantities of w_I, w_B, w_F, w_{H_2O} including their uncertainties are subsequently used by inserting into the respective balance formula to compute the ratio of biogenic or fossil CO_2 (using the carbon balance) or the ratio of energy from biogenic sources (using the energy balance). All these final results of the balance method are characterized by a mean value and a statistically derived uncertainty.

The mathematical solution of the equation system shall take into account that the formula of difference between O_2 consumption and CO_2 production can also be considered as the linear combination of the carbon balance and the oxygen consumption formulae, so one of them shall be omitted in the numerical equation system. Furthermore, the water balance formula is not essential for the system solution, but it can be added to the numerical equation system if the required data are available in order to improve accuracy.

8.12 Calculation model

The balance method combines the standard data of the chemical composition of biogenic and fossil organic matter with routinely measured operating data of the incineration plant. The method is based on six mass balances and one energy balance, whereby the result of each balance describes a certain waste characteristic (e.g. content of organic carbon, heating value, ash content, etc.). Each balance formula encompasses a theoretically derived term that has to be reconciled with measured data of the plant.

In order to set-up the theoretical formulae, the different materials comprised in the waste are virtually divided into four “groups”: inert (w_I), biogenic and fossil organic material (w_B, w_F) and water $\left(w_{H_2O}\right)$ that are the unknown variables. Inert materials include all incombustible matter from bio wastes and plastics (e.g. kaolin in paper). Biogenic and fossil organic material groups refer only to the moisture and ash free organic matter.

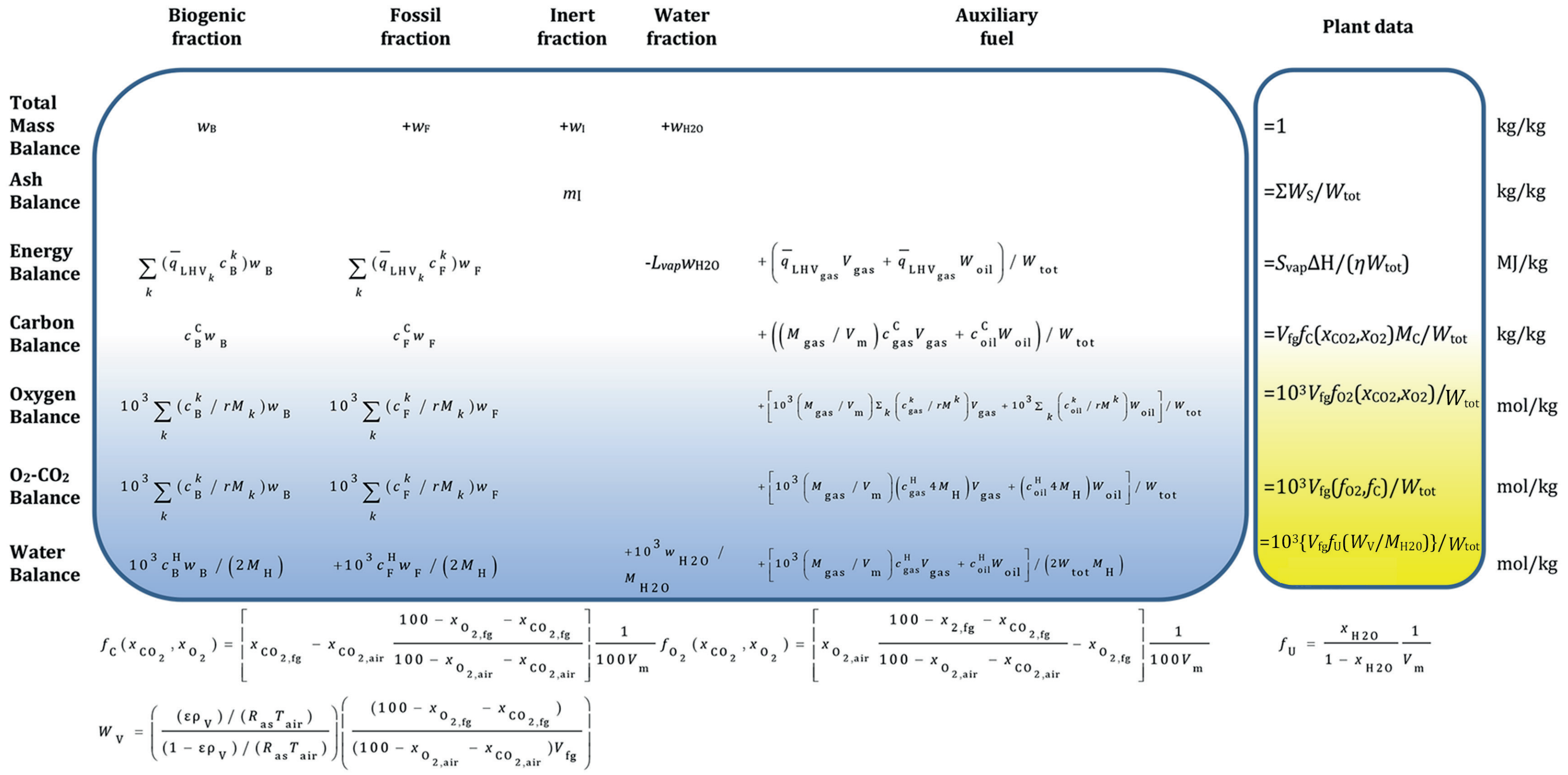
Due to the fact that the qualitative composition of organic materials in waste is well known [e.g. biogenic matter encompasses paper, wood, kitchen waste, etc. and fossil organic matter includes polypropylene (PP), polyethylene (PE), polyethylene terephthalate (PET), polyvinyl chloride (PVC), etc.], typical ranges for the content of carbon (C) hydrogen (H), oxygen (O), nitrogen (N) and sulfur (S) biogenic and fossil organic materials can be taken from literature.

The balance formulae considered, as detailed in 8.2 to 8.8, are summarized in Figure 1, accounting for the fact that the O_2-CO_2 balance is not an independent formula being the linear combination of carbon balance and oxygen balance, so only two of these three formulae can be considered simultaneously.

Each balance formula encompasses at least one of the mass fractions (w_I, w_B, w_F, w_{H_2O}), that represent therein the four unknowns of the nonlinear set of formulae, that can be solved using a data reconciliation algorithm being the system over determined (six formulae with four unknowns). It is also important to clarify the variable classification of data reconciliation technique, for which measured variables are classified as redundant and non-redundant, whereas unmeasured variables are classified as observable and non-observable, being:

- a redundant variable is a measured variable that can be estimated by other measured variables via process models, in addition to its measurement;
- a non-redundant variable is a measured variable that cannot be estimated other than by its own measurement;
- an observable variable is an unmeasured variable that can be estimated from measured variables through physical models;
- a non-observable variable is a variable for which no information is available.

More precisely, the calculation model refers to a condition of steady-state nonlinear model including redundant measured variables and observable unmeasured variables, since their values can be estimated by the data reconciliation algorithm.



	Biogenic fraction	Fossil fraction	Inert fraction	Water fraction	Auxiliary fuel	Plant data	
Total Mass Balance	w_B	$+w_F$	$+w_I$	$+w_{H2O}$		$=1$	kg/kg
Ash Balance			m_I			$=\Sigma W_S/W_{tot}$	kg/kg
Energy Balance	$\sum_k (\bar{q}_{LHV_k} c_B^k) w_B$	$\sum_k (\bar{q}_{LHV_k} c_F^k) w_F$		$-L_{vap}w_{H2O}$	$+\left(\bar{q}_{LHV_{gas}} V_{gas} + \bar{q}_{LHV_{gas}} W_{oil}\right)/W_{tot}$	$=S_{vap}\Delta H/(\eta W_{tot})$	MJ/kg
Carbon Balance	$c_B^C w_B$	$c_F^C w_F$			$+\left(\left(M_{gas}/V_m\right)c_{gas}^C V_{gas} + c_{oil}^C W_{oil}\right)/W_{tot}$	$=V_{fg}f_C(x_{CO2},x_{O2})M_C/W_{tot}$	kg/kg
Oxygen Balance	$10^3\sum_k (c_B^k/rM_k)w_B$	$10^3\sum_k (c_F^k/rM_k)w_F$			$+\left[10^3\left(M_{gas}/V_m\right)\Sigma_k\left(c_{gas}^k/rM^k\right)V_{gas}+10^3\Sigma_k\left(c_{oil}^k/rM^k\right)W_{oil}\right]/W_{tot}$	$=10^3V_{fg}f_{O2}(x_{CO2},x_{O2})/W_{tot}$	mol/kg
O2-CO2 Balance	$10^3\sum_k (c_B^k/rM_k)w_B$	$10^3\sum_k (c_F^k/rM_k)w_F$			$+\left[10^3\left(M_{gas}/V_m\right)\left(c_{gas}^H 4M_H\right)V_{gas}+\left(c_{oil}^H 4M_H\right)W_{oil}\right]/W_{tot}$	$=10^3V_{fg}(f_{O2},f_C)/W_{tot}$	mol/kg
Water Balance	$10^3 c_B^H w_B/(2M_H)$	$+10^3 c_F^H w_F/(2M_H)$		$+10^3 w_{H2O}/M_{H2O}$	$+\left[10^3\left(M_{gas}/V_m\right)c_{gas}^H V_{gas}+c_{oil}^H W_{oil}\right]/\left(2W_{tot}M_H\right)$	$=10^3\{V_{fg}f_U(W_V/M_{H2O})\}/W_{tot}$	mol/kg

$$f_C(x_{CO_2},x_{O_2}) = \left[x_{CO_{2,fg}} - x_{CO_{2,air}}\frac{100 - x_{O_{2,fg}} - x_{CO_{2,fg}}}{100 - x_{O_{2,air}} - x_{CO_{2,air}}}\right]\frac{1}{100V_m} \quad f_{O_2}(x_{CO_2},x_{O_2}) = \left[x_{O_{2,air}}\frac{100 - x_{2,fg} - x_{CO_{2,fg}}}{100 - x_{O_{2,air}} - x_{CO_{2,air}}} - x_{O_{2,fg}}\right]\frac{1}{100V_m} \quad f_U = \frac{x_{H2O}}{1 - x_{H2O}}\frac{1}{V_m}$$

$$W_V = \left(\frac{(\varepsilon\rho_V)/(R_{as}T_{air})}{(1 - \varepsilon\rho_V)/(R_{as}T_{air})}\right)\left(\frac{(100 - x_{O_{2,fg}} - x_{CO_{2,fg}})}{(100 - x_{O_{2,air}} - x_{CO_{2,air}})V_{fg}}\right)$$

Figure 1 — Formulae used for the balance method for determining the biogenic fraction in CO_2 in stack gas

The nonlinear data reconciliation problem is essentially a weighted least squares optimization problem:

$$\mathrm{Min}\left[\left(\boldsymbol{x}_\mathrm{m}-\boldsymbol{x}\right)^\mathrm{T}\boldsymbol{\Sigma}^{-1}\left(\boldsymbol{x}_\mathrm{m}-\boldsymbol{x}\right)\right] \tag{21}$$

with the associated constraint conditions:

$$f\,(\boldsymbol{x},\boldsymbol{y},\boldsymbol{z})=0 \tag{22}$$

being $\boldsymbol{x}$ is the vector of N measured variables $\left(c_\mathrm{B}^k, c_\mathrm{F}^k, m_\mathrm{tot}, V_\mathrm{fg}, x_{\mathrm{O_2},\mathrm{CO_2},\mathrm{air}}, x_{\mathrm{O_2},\mathrm{CO_2},\mathrm{fg}}, \Sigma W_\mathrm{s}, S_\mathrm{vap}, \eta, \Delta\mathrm{H}\right)$, $\boldsymbol{x}_\mathrm{m}$ is the vector of corresponding N measured values, $\boldsymbol{y}$ is the vector of K unmeasured variables (w_I, w_B, w_F, $w_{\mathrm{H_2O}}$), $\boldsymbol{z}$ is the vector of M constant values and $\boldsymbol{\Sigma}$ is the NxN covariance matrix of the measured variables.

Since the constraints are partly nonlinear, the data reconciliation shall be necessarily carried out iteratively, performing the linearization of formulae and performing a sequence of consecutive linear reconciliations until a convergence condition is achieved. The idea is that the nonlinear constraints $f\,(\boldsymbol{x},\boldsymbol{y},\boldsymbol{z})$ can be linearized using a first order Taylor's around an estimation of the variables:

$$f\,(\boldsymbol{x},\boldsymbol{y},\boldsymbol{z})=\boldsymbol{J}_\mathrm{y}\,(\boldsymbol{y}-\boldsymbol{y}_\mathrm{S})+\boldsymbol{J}_\mathrm{x}\,(\boldsymbol{x}-\boldsymbol{x}_\mathrm{S})+f\,(\boldsymbol{x}_\mathrm{S},\boldsymbol{y}_\mathrm{S},\boldsymbol{z})=0 \tag{23}$$

where $\boldsymbol{x}_\mathrm{S}$ is the vector of N estimated values of the measured variables, $\boldsymbol{y}_\mathrm{S}$ is the vector of the K estimated values of the unmeasured variables, $\boldsymbol{J}_\mathrm{x}$ is the Jacobian matrix of range 6xN of the measured variables and $\boldsymbol{J}_\mathrm{y}$ is the Jacobian matrix of range 6xK of the unmeasured variables. The equation system can then be written in the matrix form:

$$\begin{vmatrix}\boldsymbol{J}_\mathrm{y} & \boldsymbol{J}_\mathrm{x} & f\end{vmatrix}\begin{vmatrix}(\boldsymbol{y}-\boldsymbol{y}_\mathrm{s})\\(\boldsymbol{x}-\boldsymbol{x}_\mathrm{s})\\1\end{vmatrix}=0 \tag{24}$$

being

$$\boldsymbol{J}_\mathrm{y}=\begin{vmatrix}\dfrac{\partial f_1}{\partial y_1} & \dfrac{\partial f_1}{\partial y_2} & \cdots & \dfrac{\partial f_1}{\partial y_K}\\ \dfrac{\partial f_2}{\partial y_1} & \dfrac{\partial f_2}{\partial y_2} & \cdots & \dfrac{\partial f_2}{\partial y_K}\\ \cdots & \cdots & \cdots & \cdots\\ \dfrac{\partial f_6}{\partial y_1} & \dfrac{\partial f_6}{\partial y_2} & \cdots & \dfrac{\partial f_6}{\partial y_K}\end{vmatrix} \tag{25}$$

and

$$\boldsymbol{J}_\mathrm{x}=\begin{vmatrix}\dfrac{\partial f_1}{\partial x_1} & \dfrac{\partial f_1}{\partial x_2} & \cdots & \dfrac{\partial f_1}{\partial x_N}\\ \dfrac{\partial f_2}{\partial x_1} & \dfrac{\partial f_2}{\partial x_2} & \cdots & \dfrac{\partial f_2}{\partial x_N}\\ \cdots & \cdots & \cdots & \cdots\\ \dfrac{\partial f_6}{\partial x_1} & \dfrac{\partial f_6}{\partial x_2} & \cdots & \dfrac{\partial f_6}{\partial x_N}\end{vmatrix} \tag{26}$$

The weighted least squares relationship in Formula (20), together with the constraints of Formula (21), as shown in Formula (22), allow to rewrite the data reconciliation problem as:

$$\text{Min}\left[\left(\boldsymbol{x}_{\text{m}}-\boldsymbol{x}\right)^{\text{T}}\Sigma^{-1}\left(\boldsymbol{x}_{\text{m}}-\boldsymbol{x}\right)\right] \tag{27}$$

$$\boldsymbol{J}_{\text{x}}\boldsymbol{x}+\boldsymbol{J}_{\text{y}}\boldsymbol{y}=\boldsymbol{b}$$

The matrices $\boldsymbol{J}_{\text{x}}$ and $\boldsymbol{J}_{\text{y}}$ are the incidence matrices in Jacobian form of the balance formulae, the first one related to the vector of measured variables and the second one related to the vector of the unmeasured variables. The right side term $\boldsymbol{b}$ can be evaluated as:

$$\boldsymbol{b}=\boldsymbol{J}_{\text{x}}\boldsymbol{x}_{\text{s}}^{(n-1)}+\boldsymbol{J}_{\text{y}}\boldsymbol{y}_{\text{s}}^{(n-1)}-f\left[\boldsymbol{x}_{\text{s}}^{(n-1)},\boldsymbol{y}_{\text{s}}^{(n-1)},\boldsymbol{z}\right] \tag{28}$$

where $\boldsymbol{x}_{\text{s}}{}^{(n-1)}$ and $\boldsymbol{y}_{\text{s}}{}^{(n-1)}$ are the estimated values of measured variables at the iteration (n–1)-th of the iterative cycle, with the Jacobian matrices $\boldsymbol{J}_{\text{x}}$ [Formula (26)] and $\boldsymbol{J}_{\text{y}}$ [Formula (25)] also evaluated using the estimated values $\boldsymbol{x}_{\text{s}}{}^{(n-1)}$ and $\boldsymbol{y}_{\text{s}}{}^{(n-1)}$; the measured values $\boldsymbol{x}_{\text{m}}$ are used as estimated values $\boldsymbol{x}_{\text{s}}{}^{(n-1)}$ at the first iteration, while to the unmeasured variables $\boldsymbol{y}_{\text{s}}{}^{(n-1)}$, arbitrary guess values are assigned.

More precisely, for each n-th step of the iterative cycle, the first task is the evaluation of the new values of the measured variables $\boldsymbol{x}_{\text{s}}{}^{(n)}$ through Formula (26) and considering the corresponding constraint condition. Being $\boldsymbol{F}$ [$\boldsymbol{x}_{\text{s}}{}^{(n)}$, $\boldsymbol{y}_{\text{s}}{}^{(n)}$], the function for which the minimum condition shall be searched, Formula (26) can be written as:

$$\begin{gathered}\boldsymbol{F}\left[\boldsymbol{x}_{\text{s}}^{(n)},\boldsymbol{y}_{\text{s}}^{(n)}\right]=\left[\boldsymbol{x}_{\text{m}}-\boldsymbol{x}_{\text{s}}^{(n)}\right]^{\text{T}}\sum{}^{-1}\left[\boldsymbol{x}_{\text{m}}-\boldsymbol{x}_{\text{s}}^{(n)}\right]\\ \boldsymbol{J}_{\text{x}}\boldsymbol{x}_{\text{s}}^{(n)}+\boldsymbol{J}_{\text{y}}\boldsymbol{y}_{\text{s}}^{(n)}=\boldsymbol{b}\end{gathered} \tag{29}$$

The data reconciliation problem can be solved by first eliminating the unmeasured variables $\boldsymbol{y}_{\text{s}}$ from the constraint formulae multiplying both sides by a projection matrix $\boldsymbol{P}$ such that:

$$\boldsymbol{P}\boldsymbol{J}_{\text{y}}=0 \tag{30}$$

Then, the data reconciliation problem becomes:

$$\boldsymbol{F}\left[\boldsymbol{x}_{\text{s}}^{(n)}\right]=\left[\boldsymbol{x}_{\text{m}}-\boldsymbol{x}_{\text{s}}^{(n)}\right]^{\text{T}}\sum{}^{-1}\left[\boldsymbol{x}_{\text{m}}-\boldsymbol{x}_{\text{s}}^{(n)}\right] \tag{31}$$

$$\left(\boldsymbol{P}\boldsymbol{J}_{\text{y}}\right)\boldsymbol{x}_{\text{s}}^{(n)}=\boldsymbol{P}\boldsymbol{b}$$

The solution of this optimization problem can be performed using the Lagrange multipliers technique. This approach allows to reduce the stationary points of a function $\boldsymbol{F}$ ($\boldsymbol{x}$), defined by a set of I variables associated to J boundary constraints $\boldsymbol{f}$ ($\boldsymbol{x}$) = 0, to the stationary points of a further not constrained function $\Lambda(\boldsymbol{x},\boldsymbol{\lambda})$ having I+J variables, named “Lagrangian function”, where $\boldsymbol{\lambda}$ is the multiplier vector:

$$\Lambda\left(\boldsymbol{x},\boldsymbol{y}\right)=\boldsymbol{F}\left(\boldsymbol{x}\right)+\text{»}f\left(\boldsymbol{x}\right)=\boldsymbol{F}\left(\boldsymbol{x}\right)+\sum\nolimits_{j=1}^{J}\lambda_j f_j\left(\boldsymbol{x}\right) \tag{32}$$

Applying this technique to Formula (30), the corresponding Lagrangian function will be:

$$\boldsymbol{F}\left(\boldsymbol{x}\right)=\left[\boldsymbol{x}_{\mathrm{m}}-\boldsymbol{x}_{\mathrm{s}}^{(n)}\right]^{\mathrm{T}}\sum^{-1}\left[\boldsymbol{x}_{\mathrm{m}}-\boldsymbol{x}_{\mathrm{s}}^{(n)}\right]-2\lambda^{\mathrm{T}}\left[\left(\boldsymbol{PJ}_{\mathrm{x}}\right)s_{\mathrm{s}}^{(n)}-\boldsymbol{Pb}\right] \qquad (33)$$

The necessary conditions to obtain the minimum of this function are:

$$\begin{aligned}&\frac{\partial F}{\partial x}=-2\sum^{-1}\left[\boldsymbol{x}_{\mathrm{m}}-\boldsymbol{x}_{\mathrm{s}}^{(n)}\right]-2\left(\boldsymbol{PJ}_{\mathrm{x}}\right)^{\mathrm{T}}\lambda=0\\&\frac{\partial F}{\partial \lambda}=\left(\boldsymbol{PJ}_{\mathrm{x}}\right)\boldsymbol{x}_{\mathrm{s}}^{(n)}-\boldsymbol{Pb}=0\end{aligned} \qquad (34)$$

Multiplying each term by the covariance matrix **Σ** in Formula (33) yields:

$$\left[\boldsymbol{x}_{\mathrm{m}}-\boldsymbol{x}_{\mathrm{s}}^{(n)}\right]+\sum\left(\boldsymbol{PJ}_{\mathrm{x}}\right)^{\mathrm{T}}\lambda=0 \qquad (35)$$

and multiplying again both the terms by $\boldsymbol{PJ}_{\mathrm{x}}$, Formula (34) becomes:

$$\left(\boldsymbol{PJ}_{\mathrm{x}}\right)\boldsymbol{x}_{\mathrm{m}}+\boldsymbol{Pb}+\boldsymbol{PJ}\sum\left(\boldsymbol{PJ}_{\mathrm{x}}\right)^{\mathrm{T}}\lambda=0 \qquad (36)$$

being the term $(\boldsymbol{PJ}_{\mathrm{x}})\,\boldsymbol{x}_{\mathrm{S}}^{(n)}$ is equal to $-\boldsymbol{Pb}$ from Formula (33). Rearranging Formula (35), the vector of Lagrange multiplier $\boldsymbol{\lambda}$ is evaluated:

$$\lambda=-\left[\left(\boldsymbol{PJ}_{\mathrm{x}}\right)\sum\left(\boldsymbol{PJ}_{\mathrm{x}}\right)^{\mathrm{T}}\right]^{-1}\left[\left(\boldsymbol{PJ}_{\mathrm{x}}\right)\boldsymbol{x}_{\mathrm{m}}-\boldsymbol{Pb}\right] \qquad (37)$$

Substituting the $\boldsymbol{\lambda}$ values in Formula (34), the vector of the estimated measured variables $\boldsymbol{x}_{\mathrm{S}}^{(n)}$ at the *n*-th iteration can be evaluated:

$$\boldsymbol{x}_{\mathrm{s}}^{(n)}=\boldsymbol{x}_{\mathrm{m}}-\sum\left(\boldsymbol{PJ}_{\mathrm{x}}\right)^{\mathrm{T}}\left[\left(\boldsymbol{PJ}_{\mathrm{x}}\right)\sum\left(\boldsymbol{PJ}_{\mathrm{x}}\right)^{\mathrm{T}}\right]^{-1}\left[\left(\boldsymbol{PJ}_{\mathrm{x}}\right)\boldsymbol{x}_{\mathrm{m}}-\boldsymbol{PJ}\right] \qquad (38)$$

Now it is necessary to evaluate the projection matrix ***P***. There are more methods to obtain a matrix satisfying the requirements of Formula (29). In this model, the projection matrix ***P*** is evaluated by the ***QR*** factorization technique applied to the matrix $\boldsymbol{J}_{\mathrm{y}}$. Being $\boldsymbol{J}_{\mathrm{y}}$, a 6xK matrix having linearly independent columns so its rank is equal to the number K of unknowns, it can be proven that it can be found a matrix ***Q*** (6x6) satisfying Formula (39):

$$\boldsymbol{J}_\mathrm{y} = \boldsymbol{Q}\boldsymbol{R} \tag{39}$$

and satisfying also the orthogonality condition:

$$\boldsymbol{Q}^\mathrm{T}\boldsymbol{Q} = \boldsymbol{I} \tag{40}$$

whereas $\boldsymbol{R}$ is characterized as:

$$\boldsymbol{R} = \begin{bmatrix} \boldsymbol{R}_1 \\ 0 \end{bmatrix} \tag{41}$$

being $\boldsymbol{R}_1$, an upper triangular and non-singular matrix with dimension (KxK), 0 the null matrix of dimension (2xK) and $\boldsymbol{I}$ the identity matrix. The matrix $\boldsymbol{Q}$ can then be partitioned into two other matrices $\boldsymbol{Q} = [\boldsymbol{Q}_1 \quad \boldsymbol{Q}_2]$, where $\boldsymbol{Q}_1$ is a matrix of dimension (6xK) while $\boldsymbol{Q}_2$ is a matrix of dimension (6x2), so Formula (38) becomes:

$$\boldsymbol{J}_\mathrm{y} = \begin{bmatrix} \boldsymbol{Q}_1 \boldsymbol{Q}_2 \end{bmatrix} \begin{bmatrix} \boldsymbol{R}_1 \\ 0 \end{bmatrix} \tag{42}$$

Multiplying both the sides by $\boldsymbol{Q}_2^\mathrm{T}$:

$$\boldsymbol{Q}_2^\mathrm{T} \boldsymbol{J}_\mathrm{y} = \boldsymbol{Q}_2^\mathrm{T} \begin{bmatrix} \boldsymbol{Q}_1 \boldsymbol{Q}_2 \end{bmatrix} \begin{bmatrix} \boldsymbol{R}_1 \\ 0 \end{bmatrix} \tag{43}$$

and being $\boldsymbol{Q}$ an orthogonal matrix, the matrix $\boldsymbol{Q}_2$ assumes the following property:

$$\boldsymbol{Q}_2^\mathrm{T} \begin{bmatrix} \boldsymbol{Q}_1 & \boldsymbol{Q}_2 \end{bmatrix} \begin{bmatrix} \boldsymbol{R}_1 \\ 0 \end{bmatrix} = \begin{bmatrix} 0 & 1 \end{bmatrix} \begin{bmatrix} \boldsymbol{R}_1 \\ 0 \end{bmatrix} = 0 \tag{44}$$

that is:

$$\boldsymbol{Q}_2^\mathrm{T} \boldsymbol{J}_\mathrm{y} = 0 \tag{45}$$

Therefore, the $\boldsymbol{Q}_2^\mathrm{T}$ matrix is the searched projection matrix $\boldsymbol{P}$ so starting from Formula (37), it is possible to evaluate the vector of the estimated values for the measured variables $\boldsymbol{x}_\mathrm{s}^{(n)}$ at the n-th iteration knowing the measured values $\boldsymbol{x}_\mathrm{m}$

$$\boldsymbol{x}_\mathrm{s}^{(n)} = \boldsymbol{x}_\mathrm{m} - \Sigma\left(\boldsymbol{Q}_2^\mathrm{T}\boldsymbol{J}_\mathrm{x}\right)^\mathrm{T} \left[\left(\boldsymbol{Q}_2^\mathrm{T}\boldsymbol{J}_\mathrm{x}\right)\Sigma\left(\boldsymbol{Q}_2^\mathrm{T}\boldsymbol{J}_\mathrm{x}\right)^\mathrm{T}\right]^{-1} \left[\left(\boldsymbol{Q}_2^\mathrm{T}\boldsymbol{J}_\mathrm{x}\right)\boldsymbol{x}_\mathrm{m} - \boldsymbol{Q}_2^\mathrm{T}\boldsymbol{b}\right] \tag{46}$$

whereas the solution for the unmeasured variables can be obtained from Formula (28) rewritten as

$$\boldsymbol{J}_\mathrm{y}\boldsymbol{y}_\mathrm{s}^{(n)} = \boldsymbol{b} - \boldsymbol{J}_\mathrm{x}\boldsymbol{x}_\mathrm{s}^{(n)} \tag{47}$$

where the terms at the right side can be evaluated from Formula (45) and Formula (27), so the vector of estimated unmeasured variables at the n-th iteration can be evaluated as:

$$\boldsymbol{y}_\mathrm{s}^{(n)} = \left(\boldsymbol{J}_\mathrm{y}^\mathrm{T}\boldsymbol{J}_\mathrm{y}\right)^{-1}\boldsymbol{J}_\mathrm{y}^\mathrm{T}\boldsymbol{b} - \left(\boldsymbol{J}_\mathrm{y}^\mathrm{T}\boldsymbol{J}_\mathrm{y}\right)^{-1}\boldsymbol{J}_\mathrm{y}^\mathrm{T}\left[\boldsymbol{J}_\mathrm{x}\boldsymbol{x}_\mathrm{s}^{(n)}\right] \tag{48}$$

After the evaluation of the estimated variables, the iteration loop continues with the (n+1)-th iteration starting from the calculation of the matrices $\boldsymbol{J}_\mathrm{x}$ and $\boldsymbol{J}_\mathrm{y}$ and of the known term $\boldsymbol{b}$ using the estimated values $\boldsymbol{x}_{\mathrm{S}}{}^{(n)}$ and $\boldsymbol{y}_{\mathrm{S}}{}^{(n)}$, evaluating a new set of estimated values of measured variables $\boldsymbol{x}_{\mathrm{S}}{}^{(n+1)}$ and unmeasured variables $\boldsymbol{y}_{\mathrm{S}}{}^{(n+1)}$. If n is the current iteration step, the calculation cycle continues until the relationships:

$$\left\|\boldsymbol{x}_{\mathrm{s}}^{(n)}-\boldsymbol{x}_{\mathrm{s}}^{(n-1)}\right\|<\varepsilon \text{ and } \left\|\boldsymbol{y}_{\mathrm{s}}^{(n)}-\boldsymbol{y}_{\mathrm{s}}^{(n-1)}\right\|<\varepsilon \tag{49}$$

satisfied, where ε is the value of the assigned convergence criterion.

Now it is possible to evaluate the covariance matrix of the reconciliated data rewriting Formula (45) as

$$\begin{aligned}\boldsymbol{x}_{\mathrm{s}}^{(n)}=&\left\{\mathbf{I}-\sum\left(\boldsymbol{Q}_2^{\mathrm{T}}\boldsymbol{J}_{\mathrm{x}}\right)^{\mathrm{T}}\left[\left(\boldsymbol{Q}_2^{\mathrm{T}}\boldsymbol{J}_{\mathrm{x}}\right)\sum\left(\boldsymbol{Q}_2^{\mathrm{T}}\boldsymbol{J}_{\mathrm{x}}\right)^{\mathrm{T}}\right]^{-1}\left(\boldsymbol{Q}_2^{\mathrm{T}}\boldsymbol{J}_{\mathrm{x}}\right)\right\}\boldsymbol{x}_{\mathrm{m}}+\\&\sum\left(\boldsymbol{Q}_2^{\mathrm{T}}\boldsymbol{J}_{\mathrm{x}}\right)^{\mathrm{T}}\left[\left(\boldsymbol{Q}_2^{\mathrm{T}}\boldsymbol{J}_{\mathrm{x}}\right)\sum\left(\boldsymbol{Q}_2^{\mathrm{T}}\boldsymbol{J}_{\mathrm{x}}\right)^{\mathrm{T}}\right]^{-1}\boldsymbol{Q}_2^{\mathrm{T}}\boldsymbol{b}\end{aligned} \tag{50}$$

where $\boldsymbol{I}$ is the identity matrix. Assuming that

$$W=\left\{\boldsymbol{I}-\sum\left(\boldsymbol{Q}_2^{\mathrm{T}}\boldsymbol{J}_{\mathrm{x}}\right)^{\mathrm{T}}\left[\left(\boldsymbol{Q}_2^{\mathrm{T}}\boldsymbol{J}_{\mathrm{x}}\right)\sum\left(\boldsymbol{Q}_2^{\mathrm{T}}\boldsymbol{J}_{\mathrm{x}}\right)^{\mathrm{T}}\right]^{-1}\left(\boldsymbol{Q}_2^{\mathrm{T}}\boldsymbol{J}_{\mathrm{x}}\right)\right\} \tag{51}$$

$$\boldsymbol{H}=\sum\left(\boldsymbol{Q}_2^{\mathrm{T}}\boldsymbol{A}_{\mathrm{x}}\right)^{\mathrm{T}}\left[\left(\boldsymbol{Q}_2^{\mathrm{T}}\boldsymbol{A}_{\mathrm{x}}\right)\sum\left(\boldsymbol{Q}_2^{\mathrm{T}}\boldsymbol{A}_{\mathrm{x}}\right)^{\mathrm{T}}\right]^{-1}\boldsymbol{Q}_2^{\mathrm{T}}\boldsymbol{b}$$

then, Formula (49) becomes

$$\boldsymbol{x}_{\mathrm{s}}^{(n)}=W\boldsymbol{x}_{\mathrm{m}}+\boldsymbol{H}\,\boldsymbol{x}_{\mathrm{s}}^{(n)}=W\boldsymbol{x}_{\mathrm{m}}+\boldsymbol{H} \tag{52}$$

Therefore, being the $\boldsymbol{H}$ matrix a constant matrix, the covariance matrix of the measured variables can be given as

$$\operatorname{cov}(\boldsymbol{x})=W\operatorname{cov}(\boldsymbol{x}_{\mathrm{m}})W^{\mathrm{T}}=W\sum W^{\mathrm{T}} \tag{53}$$

and for the unmeasured variables

$$\operatorname{cov}(\boldsymbol{y})=\left[\left(\boldsymbol{J}_{\mathrm{y}}^{\mathrm{T}}\boldsymbol{J}_{\mathrm{y}}\right)^{-1}\boldsymbol{J}_{\mathrm{y}}^{\mathrm{T}}\boldsymbol{J}_{\mathrm{x}}\right]\operatorname{cov}(\boldsymbol{x})\left[\left(\boldsymbol{J}_{\mathrm{y}}^{\mathrm{T}}\boldsymbol{J}_{\mathrm{y}}\right)^{-1}\boldsymbol{J}_{\mathrm{y}}^{\mathrm{T}}\boldsymbol{J}_{\mathrm{x}}\right] \tag{54}$$

9 Operating the model

9.1 Installation routines

When installing the method at a given facility, great care shall be taken to ensure that the measurements used do not contain systematic errors and the facility specific constants shall be collected. Furthermore, documentation of measurements, constants and uncertainties shall be collected and stored for easy access during any validation.

Validating the installation of the model is required as it will provide certainty that errors do not exist with the model at a given facility.

9.2 Ongoing operation calculation routines

When this document is used to report the fossil CO_2 emission by the year, the calculations and input data quality have to be monitored continuously throughout the year (minimum monthly evaluations) to ensure countermeasures are put into force if/when measurements become untrustworthy. Therefore, the method shall be used running continuously or at least on a monthly basis. Furthermore, the following shall be available to allow the user to interpret results find mistakes and act accordingly:

- the software shall produce warnings and error messages based on the plausibility testing;
- user interface shall contain results for all plant lines (numeric and graphical representation) for comparison and the warnings and error messages;
- the user shall be able to see both results and inputs (ideally both before and after the reconciliation routine);
- the user shall be able to extract the results to a database program.

10 Uncertainty budget methodology and interpretation

The input for the uncertainty calculation is the actual uncertainty on the measurement including both systematic and random uncertainty. If this is not measured and meters are well maintained and calibrated (hence without systematic uncertainty), the meter nameplate uncertainty could be used.

The procedures applicable in the area where the measurement is performed shall be followed. The procedures followed shall be documented together with the results.

For example, in the EU the QAL1 measurement, uncertainty is to be used according to EN 14181 for CEMS measurements and systematic uncertainty can be neglected if QAL2 calibrations are performed for, as minimum, O_2, CO_2. The procedure for flow and moisture is described in EN 14181.

When performing calibrations and using calibration factors identified (difference between reference method and plant method), it has to be tested if the results are still equal and within theoretical limits. For mixed waste, the CO_2 measurement corrected to 0 % H_2O and 0 % O_2 shall always be between 16 % and 19 %. When feeding two lines from a common waste storage, the corrected CO_2 (0 % H_2O and 0 % O_2) shall be very similar (if not identical).

Annex A
(informative)

Reference chemical compositions of moisture and ash free biogenic and fossil organic matter

Content	Unit	Biogenic matter			Fossil organic matter		
		Symbol	**Mean**	**Standard-deviation**	**Symbol**	**Mean**	**Standard-deviation**
C	kg/kg moisture and ash free matter	C_{CB}	0,483	0,004	C_{CF}	0,777	0,016
H		C_{HB}	0,065	0,001	C_{HF}	0,112	0,006
O		C_{OB}	0,443	0,007	C_{OF}	0,061	0,013
N		C_{NB}	0,007	0,002	C_{NF}	0,014	0,005
S		C_{SB}	0,001	0,000 4	C_{SF}	0,003	0,001

Source: United Nations. Clan Development Mechanism. *Large Scale Consolidated Methodology. ACM0022: Alternative Waste Treatment Processes. Version 02.0. Sectorial scope: 01 and 13* – CDM-EB81-A13 (2013). Page 76

Annex B
(informative)

Reference chemical compositions for the auxiliary fuels

Fuel	**C** (g/kg)	**H** (g/kg)	**N** (g/kg)	**O** (g/kg)	**S** (g/kg)	$\bar{q}_{\text{LHV}}$ (MJ/kg)	$\bar{q}_{\text{LHV}}$ (MJ/Nm^3)
Low sulfur oil	864	127	1	1	7	41,87	—
High sulfur oil	856	117	3	4	20	41,03	—
Heavy oil	857	105	5	4	29	40,49	—
Standard oil	862	123	0	0	0	41,85	—
Natural methan	745,9	250,3	0	0	0	—	34,54
Pure methan	750	250	0	0	0	—	35,838

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