
**Solid recovered fuels — Determination
of self-heating —**

**Part 1:
Isothermal calorimetry**

*Combustibles solides de récupération — Détermination de l'auto-
échauffement —*

Partie 1: Détermination calorimétrique isotherme

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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 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 materials, including solid recovered fuels*.

A list of all parts in the ISO 21911 series can be found on the ISO website.

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

There is a continuous global growth in the trading and use of solid recovered fuels (SRFs). This has resulted in an increased probability of fires, which has consequences for the handling, transporting and storage of SRFs.

SRFs can generate heat spontaneously by exothermic biological, chemical and physical processes. The heat build-up can be significant in large storage volumes if the heat conduction in the material is low. In some conditions the heat generation can lead to pyrolysis and spontaneous ignition. The potential for self-heating varies considerably for different types and qualities of SRFs and it is important to be able to identify SRF fractions with high heat generation potential to avoid fires in stored materials.

The increasing number of incidents is a clear indicator that safety needs to be prioritized, first of all for human safety and environmental concerns but also because interruptions in energy supply will have significant consequences. SRF fires throughout the supply chain will also, in addition to safety and environmental issues and direct economic losses, have a negative impact on the confidence in the SRFs as a reliable energy source. They can also lead to difficulties in obtaining insurance coverage.

It is difficult for SRF producers, logistics providers, SRF users, equipment suppliers and manufacturers, consultants, authorities and insurance providers to determine reasonable safety measures and an appropriate level of protection due to a lack of standards and recommendations.

As part of the determination and the assessment of risks for SRFs, defined test methods and standards are established or need to be developed. However, ageing and degradation due to the handling and storage of SRFs in actual environments affects their characteristics, so safety margins should be established in relation to actual analysis results.

The test method described in this document, isothermal calorimetry, is a method where the heat flow generated from the test portion is measured directly. The operating temperature for an isothermal calorimeter is normally in the range of 5 °C to 90 °C (some calorimeters can reach even higher temperatures) and can therefore measure low-temperature reactions, such as those from bacteria and other microbes. However, isothermal calorimetry is used for monitoring the thermal activity or heat flow of chemical, physical and biological processes. The technique is most commonly used in the fields of pharmaceuticals, energetic materials and cement. Isothermal calorimetry has also been applied for the measurement of heat flow from the self-heating of solid biofuel pellets^{[6]–[10]}.

For investigating heat generation at high temperatures, other types of test methods, such as basket heating tests, are possibly more suitable.

Data on spontaneous heat generation determined using this document are only associated with the specific quality, composition and age of the sample material.

The information derived using this document is for use in quality control and in hazard and risk assessments.

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Solid recovered fuels — Determination of self-heating —

Part 1: Isothermal calorimetry

1 Scope

This document specifies an analytical method for quantification of the spontaneous heat generation from solid recovered fuels using isothermal calorimetry.

This document gives guidance on the applicability and use of the specified analytical method. It further establishes procedures for sampling and sample handling of solid recovered fuels prior to the analysis of spontaneous heat generation.

The test procedure given in this document quantifies the thermal power (heat flow) of the sample during the test. It does not identify the source of self-heating in the test portion analysed.

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 — Vocabulary*

ISO 21645, *Solid recovered fuels — Methods for sampling*

3 Terms and definitions

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

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

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

3.1

analysis temperature

temperature of the analysis environment, i.e. the calorimeter temperature

3.2

self-heating

rise in temperature in a material resulting from an exothermic reaction within the material

[SOURCE: ISO 13943:2017, 3.341, modified — “<chemical>” removed from the definition.]

3.3

test portion

sub-sample of either a *laboratory sample* (3.5) or a *test sample* (3.4) required for the specific measurement

3.4

test sample

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

3.5

laboratory sample

part of the sample sent to or received by the laboratory

3.6

thermal power

rate of heat flow produced by the sample during the test

Note 1 to entry: Expressed in W or J/s.

Note 2 to entry: Commonly also expressed as specific thermal power with reference to the unit mass of solid recovered fuel in W/g or J/(s·g).

4 Principle

Isothermal calorimetry is one of the sensitive techniques for studying heat production or heat consumption from samples of different kinds. It is non-destructive and non-invasive to the sample. Heat production due to any physical, chemical or biological changes in a sample can be measured. When heat is produced or consumed by any process, a temperature gradient is developed across the sensor. This will generate a voltage, which is proportional to the heat flow across the sensor and to the rate of the process taking place in the sample ampoule. The signal is recorded continuously and in real time.

NOTE 1 A commercial instrument for isothermal calorimetry normally has multiple channels and can thus be used for measurements of several samples simultaneously.

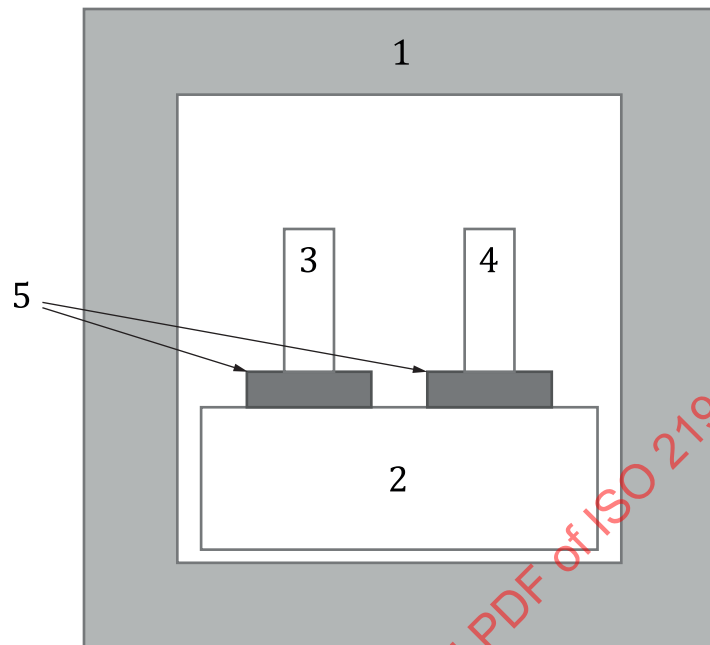
For each sample (channel) there is an inert reference that is on a parallel heat-flow sensor. During the time that the heat flow is monitored, any temperature fluctuations entering the instrument will influence both the sample and the reference sensors equally. This architecture allows a very accurate determination of heat that is produced or consumed by the sample alone while other non-sample-related heat disturbances are efficiently removed. The measured heat flow is normalized against the mass of the sample and the result is expressed in mW/g.

NOTE 2 The operating temperature for an isothermal calorimeter is typically in the range of 5 °C to 90 °C. However, there are calorimeters with a somewhat higher span for operating temperature.

5 Apparatus

The usual laboratory apparatus and, in particular, the following shall be used.

5.1 Isothermal calorimeter, consisting of a sample holder for the sample vial and the reference vial, each thermally connected to heat-flow sensors, which are thermally connected to a constant temperature sink. See example in [Figure 1](#).



Key

- | | | | |
|---|------------|---|-------------------|
| 1 | thermostat | 4 | reference |
| 2 | heat sink | 5 | heat-flow sensors |
| 3 | sample | | |

Figure 1 — Schematic drawing of an isothermal calorimeter

The calorimeter shall be calibrated for the analysis temperature according to [Annex A, Clauses A.1, A.2 and A.3](#). The analysis temperatures for the screening test procedure are 50 °C and 70 °C.

The data acquisition equipment shall be capable of performing continuous logging of the calorimeter output measured at time intervals of less than or equal to 10 s.

The baseline shall exhibit a low random noise level and be stable against drift, according to [Annex A, Clause A.4](#).

The minimum sensitivity for measuring power output shall be 100 µW.

5.2 Sample vial, made of glass with a minimum volume of 20 ml and provided with an airtight lid with an inert seal. Vials with volumes larger than 20 ml can be used if the sample loading is scaled accordingly (see [7.2.2](#)). In such cases, this deviation from the standard procedure is noted in the test report.

5.3 Balance, which should have a resolution of at least 10 mg.

6 Sample handling

6.1 General

Sample handling is important in maintaining the physical, chemical and biological properties of solid recovered fuel samples. The transport and storage (see [6.3](#)) is of especial importance for self-heating

properties, as the reactivity of the sample can be reduced from prolonged exposure to air or oxygen and/or elevated temperatures.

The sample history and the conditions for sample handling should be stated as thoroughly as possible in the test report.

6.2 Sampling

Sampling of SRF shall be made in accordance with the procedures prescribed in ISO 21645.

The minimum volume of the laboratory sample shall be 500 ml.

6.3 Sample transport and storage

The laboratory sample shall be transported in a closed airtight sample container.

NOTE 1 The requirement of an airtight container is to limit the chemical or biological reactions that can take place in the presence of oxygen.

The container shall be completely filled with sample.

NOTE 2 A completely filled container limits the amount of air in the container (i.e. the amount of oxygen) and further reduces deterioration of the sample from physical wear (i.e. reduces the amount of fine fraction).

The time between sampling and analysis shall be minimized and elevated temperatures shall be avoided.

6.4 Sample preparation

SRF can be a mixture of many different materials and the stream can be heterogenous, making it difficult to derive a representative sample to use for testing. One way to handle this is to mill and homogenize the material.

The milling process chosen should not increase the temperature above the ambient temperature, in order not to accelerate the self-heating reactions.

7 Test procedure

7.1 Temperature stabilization

Set the instrument temperature to the selected analysis temperature. The standard analysis temperatures for screening are 50 °C and 70 °C.

Follow the manufacturer's procedure to ascertain the temperature stability.

NOTE The values for stability criterion vary for different calorimeters and are usually decided by the software.

7.2 Sample vial preparation

7.2.1 Preparation procedure

A sufficient amount of the sample should be taken out 3 h to 4 h before testing, if stored in a freezer, to reach thermal equilibrium with the room temperature before testing.

The test portion shall be put into a glass vial with a minimum volume of 20 ml.

Handle the sample using a pair of tweezers or rubber gloves to avoid contamination of the sample.

Add to the sample vial a test portion corresponding to approximately 50 % of the vial volume. Note the mass of the test portion added to the glass vial.

NOTE Since the density of different types of SRFs can differ significantly, it is not possible to specify an exact sample mass to add to the vial. ISO 20049-1, which is a corresponding isothermal calorimetry standard for pelletized biofuels, specifies that $4 \text{ g} \pm 0,1 \text{ g}$ pellets are added to a 20 ml glass vial. This corresponds to approximately 50 % of the vial volume.

The lid of the standard glass vial shall be tightened after sample loading.

The prepared sample vial shall not be pre-heated.

If oxygen deficiency, which influences the test results, occurs in the closed ampoule during measurement, follow the procedure in 7.2.2. A method to detect significant oxygen deficiency is given in 8.1.

7.2.2 Procedure to find proper test portion in case of influence from oxygen deficiency

To find the proper sample volume for avoiding the influence of oxygen deficiency, first run tests with sample volumes corresponding to approximately 50 % and 25 % of the sample vial volume. If the difference in normalized total heat production between the two sample volumes (normalized by the sample mass) is non-significant (less than 10 relative-% difference) no more tests are required; 50 % sample volume is proper to use. If, however, the difference is significant, additional tests with smaller sample portions (less mass or volume) shall be made to find the sample volume where the effect of oxygen deficiency is non-significant.

7.3 Reference vial preparation

Prepare two reference vials for each sample vial (for each channel).

The portion of reference material shall have the same total heat capacity as the test portion. Water is recommended as reference material, although other non-reactive materials can be used, for example dry quartz sand.

NOTE The heat capacity of a mixture of municipal solid waste (mass fraction of ≈ 10 % moisture content) has been reported to be $1,4 \text{ J}/(\text{g}\cdot\text{K})$.^[9] If specific heat capacity of the SRF or waste sample is not available, a value of $1,4 \text{ J}/(\text{g}\cdot\text{K})$ can be assumed and Formula (1) can be used for the calculations.

$$M_r \times C_{pr} = M_w \times C_{pw} \quad (1)$$

where

M_r is the mass of the reference;

C_{pr} is the specific heat of the reference;

M_w is the mass of the waste sample;

C_{pw} is the specific heat of the waste sample.

If the calorimeter is equipped with a fixed reference, then either the reference or sample mass needs to be optimized accordingly. If the sample mass is higher than the aforesaid range, the fixed reference in the calorimeter is optimized.

7.4 Measurement

7.4.1 First baseline measurement

Start the test with a baseline measurement:

- a) Put a reference vial in the reference position. This reference shall be kept stationary for the complete test.
- b) Put a second reference vial in the measurement position for the baseline measurement.
- c) When the instrument has reached stable conditions, run a 30-min baseline measurement.

NOTE This applies for all channels that are used for measurement.

The baseline measurement data shall be included in the measurement data file.

7.4.2 Sample measurement

When the first baseline measurement is completed, replace the reference vial in the measurement position with the sample vial.

Measure the heat flow from the sample vial and save to the measurement data file. The measurement shall be run for at least 24 h.

If the heat production rate has not declined to be relatively insignificant at 24 h, the measurement should be continued until that time.

NOTE The procedure for starting the test and saving data to the measurement data file can differ between different brands of isothermal conduction calorimeters.

7.4.3 Second baseline measurement

After completion of the measurement on the sample:

- a) remove the sample vial from the measurement position;
- b) put a second reference vial in the measurement position;
- c) when the instrument has reached stable conditions, run a 30-min baseline measurement.

NOTE The baseline measured after the test is to ensure that the instrument has the same stability as before the test started. There is software for some instruments that by default measure the baseline before and after the test.

7.4.4 Measurement data file

The resulting data file shall include the data from the sample measurement as well as the data from both the baseline measurements. The file shall be stored with a unique name identifying the test portion measured.

8 Results

8.1 Test data

The data recorded is the thermal power (heat flow) in mW. The test data shall be presented as a plot of specific thermal power in mW/g versus time.

Investigate the thermal power data plot for signs of oxygen deficiency in the ampoule during the test (see NOTE). If such signs are present, additional tests shall be made according to 7.2.2.

NOTE A typical sign of significant oxygen deficiency in a test is a sharp break in the heat-flow curve (i.e. an abrupt reduction in heat flow).

[Annex B](#) shows an example of isothermal calorimetric measurements of solid recovered fuel.

8.2 Reported data

The maximum peak in specific thermal power (mW/g) and the specific total heat produced (J/g) during the test (24 h) shall be reported.

The specific total heat is calculated by integrating the specific thermal power curve from the time 45 min until the time 24 h.

9 Test report

The test report shall include the following information:

- a) test laboratory
 - 1) name and address of the laboratory;
 - 2) isothermal calorimetry instrument used;
- b) sample description
 - 1) sample ID;
 - 2) type of product (and, for example, brand name, material groups and waste code numbers, if appropriate and available);
 - 3) sample selection process (e.g. random);
 - 4) product history (dates of production, sampling, transport and arrival at the test laboratory);
 - 5) type of package for the sample during transport;
 - 6) relevant fuel parameters when available and applicable (e.g. calorific value, water content, particle size distribution);
- c) sample preparation
 - 1) sample storage prior to sample preparation (e.g. temperature);
 - 2) date and time of unpacking and sample preparation (hour, day, month and year);
 - 3) type of sample preparation before taking out test portions;
- d) reference to this document (i.e. ISO 21911-1:2022)
 - 1) analysis temperature of the isothermal calorimeter;
 - 2) use of the test results: screening tests or tests for calculation of kinetic parameters;
- e) any deviations from the procedure;
- f) any unusual features noted during the determination which possibly affected the result;
- g) results of the test, including units and the basis they are given, e.g. original or dry substance;
- h) date of the test.

Annex A (normative)

Calibration of the calorimeter

A.1 General

The instrument shall be calibrated according to the manufacturer's recommendations whenever there are questions about performance, for example when the drift is above the recommended value (see [Clause A.4](#)).

A.2 Calibration or validation of temperature

The instrument shall be calibrated for the selected analysis temperature.

NOTE 1 The measurement procedure in this document can be applied for different analysis temperatures, for example for extended measurements at several temperatures for deriving a kinetic model of heat production.

The set temperature shall be validated by an independent measurement of the temperature in the thermostat media. The temperature shall not deviate more than 0,2 K from the set temperature.

NOTE 2 The temperature calibration is made using a calibrated thermocouple device.

A.3 Calibration of thermal power

The thermal power measurement of the instrument shall be calibrated at the analysis temperature.

The calorimeter shall be at equilibrium with no significant signal drift prior to the initiation of the calibration process.

NOTE 1 The measurement procedure in this document can be applied for different analysis temperatures, for example for extended measurements at several temperatures for deriving a kinetic model of heat production.

NOTE 2 The purpose of calibration is to compare the calorimeter signal with the thermal power or enthalpy change of a well-defined process, i.e. a calibration process, after which the calorimeter signal is adjusted in order to be accurate within defined and tolerable limits. The result from the calibration measurement is compared with the theoretical value that has been assigned to the calibration process and a calibration constant is calculated.

Heat-flow calorimeters can be sensitive to systematic errors due to the fact that a fraction of the generated heat escapes the heat-flow sensors, the magnitude of which depends on the design of the instrument. It is thus important that the calibration process is designed in such a way that it closely mimics the real sample measurement. Calibration can be made electrically by generating a known amount of Joule heat in a well-positioned resistor or chemically by a reaction of well-established thermal power or enthalpy change.

Many commercial heat-flow calorimeters are equipped with an inbuilt electrical heater (calibration heater) that is used to calibrate the instrument. It is noted that the placement of the calibration heater in relation to the positioning of the sample and heat-flow sensor can be critical for the calorimetric accuracy. The instrument manufacturer normally specifies the accuracy of the calorimeter when calibrated according to the manufacturer's instructions.

Due to minor sensitivity of the heat flow sensors within a narrow temperature range, the calorimeter shall be calibrated at the same set temperature at which the sample measurement is to be conducted. The accuracy achieved is validated by the calibration by use of a well-characterized independent test process^[11].

A.4 Noise level and drift requirements

Requirements on noise and drift shall be verified on a new instrument and whenever there are questions about performance.

The rate of change of the baseline measured during a time period of 3 days shall be $\leq 20 \mu\text{J/s}$ per gram sample per hour of the test and a baseline random noise level of $\leq 10 \mu\text{J/s}$ per gram sample.

NOTE 1 In practice, the baseline is measured for 3 days and a straight line is fitted to the power $[\text{J}/(\text{g}\cdot\text{s})]$ versus time (h) data using a linear regression procedure. The long-term drift is then the slope in the line $[\text{J}/(\text{g}\cdot\text{s}\cdot\text{h})]$ and the baseline noise level is the standard deviation $[\text{J}/(\text{g}\cdot\text{s})]$ around this regression line.

NOTE 2 The rationale for these limits is found in Reference [12].

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Annex B (informative)

Example of isothermal calorimetric measurements of solid recovered fuel

Finely cut sorting solid recovered fuels produced from sorting residues of lightweight packaging materials were investigated using isothermal calorimetry. Material properties of the tested sample are listed in [Table B.1](#).

Table B.1 — Material properties of tested SRF (sorting residues of lightweight packaging)

Parameter	Unit	Mean value 2020
Net calorific value (original substance)	MJ/kg	23,8
Water (original substance)	%	11,7
Ash (original substance)	%	9,3
Volatile (original substance)	%	78,3
Carbon (dry substance)	%	55,8
Hydrogen (dry substance)	%	9,3
Nitrogen (dry substance)	%	1,0

Investigations within the framework of an ILS have shown that the measured heat flows depend significantly on the properties of the sample and especially on the moisture content. The time course of the measured heat flows can provide indications of a possible risk of spontaneous combustion.

If large heat flows occur after a comparatively short storage period, this can be an indication of significant reactions taking place at low storage temperatures (e.g. microbial activities). These reactions can bring a bulk to a higher temperature level in a short time, which can cause a subsequent spontaneous combustion process. To assess the overall risk of spontaneous combustion, the results of isothermal calorimetry should be combined with those of basket heating tests^[3].

NOTE 1 ISO/TS 21911-2 includes a test method to determine self-heating of solid recovered fuels using basket heating.

[Figure B.1](#) shows exemplary test results of tested SRF with moisture contents of 13 % (as-delivered condition), 19,8 %, 24,4 % and 31,1 % (artificially moistened) at a calorimeter temperature of 50 °C.