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LABORATORY INSTRUCTION NO. 5-BK

DETERMINING THE HEAT OF COMBUSTION OF SOLID FUELS WITH A CALORIMETER

Purpose of exercise:
the purpose of the exercise is to calculate the studied solid fuel's heat of combustion.

A calorimeter is used for determining the heat of combustion of solid fuels, such as:

- peat,
- brown coal,
- bituminous coal,
- brown coal briquette,
- bituminous coal briquette,
- coke,
- semicoke,
- non-explosive, flammable organic compounds.

The method of measurement is in accordance with the Polish PN standard.

The measurement involves completely burning the fuel sample in a pressurized oxygen atmosphere, inside a calorimetric bomb submerged in water, and measuring the water's temperature increment. A heat exchange occurs between the calorimetric vessel and a thermostat, through heat radiation, conduction and convection. This exchange is considered in calculations as the heat exchange adjustment.

Construction of a calorimeter

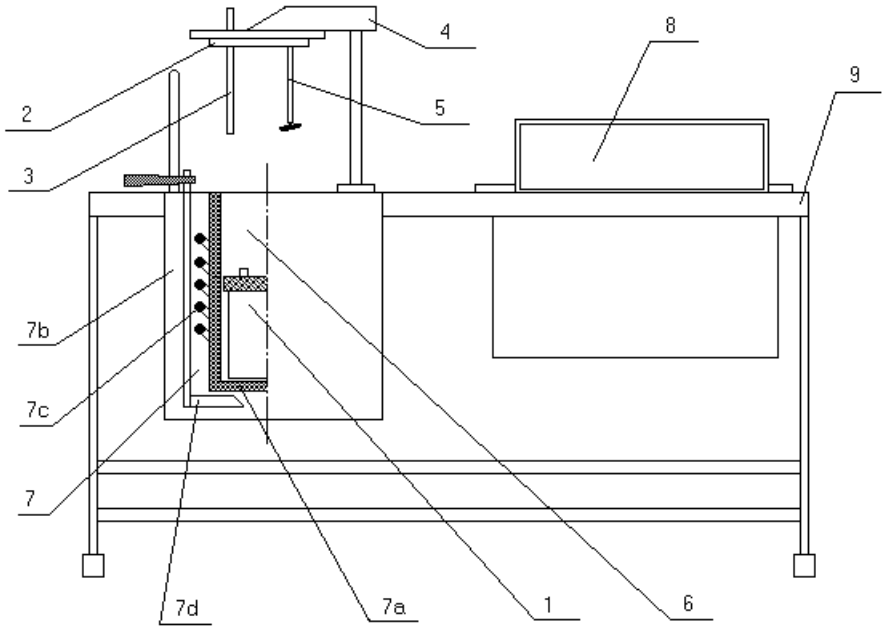


Fig. 1

1 calorimetric bomb
2 calorimeter cover
3 heat sensor
4 cover stand with the mechanical stirrer's drive
5 mechanical stirrer
6 calorimetric vessel
7 calorimeter mantle, including:
  7a inside wall
  7b outside wall
  7c pipe coil
  7d manual stirrer
8 calorimeter control desktop
9 calorimeter table with a frontal panel containing connection sockets and temperature sensor's output

The main element of the calorimeter, allowing safe combustion of fuels, is a specialized acid-proof steel vessel, known as **the calorimetric bomb** (fig.1 pos.1). The bomb is enclosed with a circular, self-sealing cap which does not require a wrench.
The self-sealing occurs due to internal pressure. The bomb's head contains two, automatic non-return valves: intake and exhaust, as well as an electrode. The intake valve is opened by turning the regulator in its upper part.

The calorimetric vessel (fig.1 pos.6) is placed within **the calorimeter's mantle - a water thermostat** (fig.1 pos.7) on an insulated base. The thermostat's purpose is to isolate the measurement from the surrounding's external heat influences. Within its space, there's a **pipe coil** (fig.1 pos.7c), used to regulate the water's temperature by introducing a heating or a cooling medium (preferably - also water). Next to the pipe coil, there's a **manual stirrer** (fig.1 pos.7d), used to equalize the mantle's water temperature. During measurement, thermostat must be enclosed with a **cover** (fig.1 pos.2).

Manual stirrer with a rotor (rys.1 poz.5) is powered by an electric engine and is used to stir water in the calorimetric vessel. The engine's rotation speed is set by the manufacturer. Measurement of temperature increment is carried out with a specialized, precise sensor (fig.1 pos.3), embedded in the calorimetric vessel.

Crucial elements of the **frontal panel**, presented in fig.2, are:

1 - front panel with the device's name
2 - control desktop (opened)
3 - temperature sensor wire outlet
4 - mechanical stirrer control input connection socket
5 - ignition (sample combustion) wire connection socket
6 - power supply signal diode – calorimeter is turned on with the POWER switch (fig.3 pos.1)

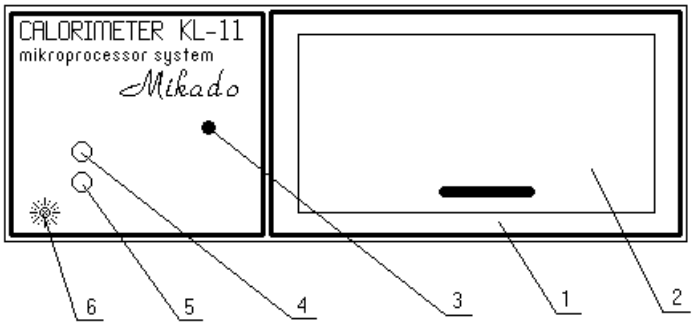


Fig.2

Control desktop, containing the following elements (visible when the desktop is opened) (fig.3):

1 - power supply switch - POWER
2 - START button, initiating the calorimeter's automatic work cycle
3 - two buttons for switching the information displayed on the digital display
4 - digital display for reading work parameters and calculated heat of combustion
5 - a series of 8 diodes corresponding to the information being displayed
6 - a series of 5 diodes displaying the current work cycle phase

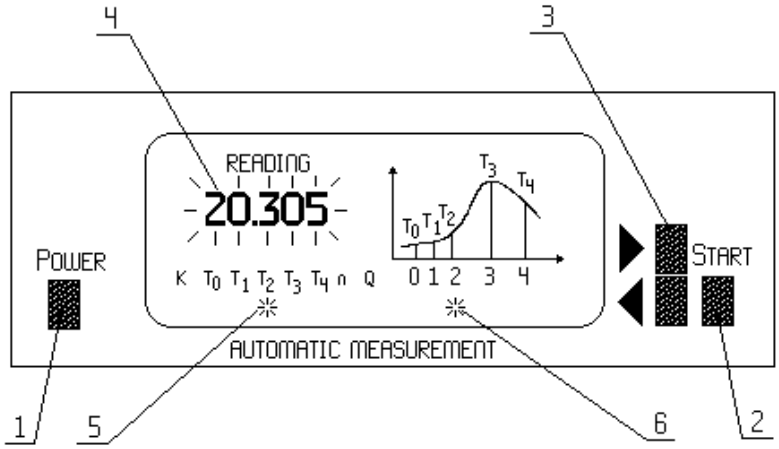


Fig.3

Optical indicators, placed on the desktop, provide complete information on the calorimeter's work. Under the following signatures:

T	- current temperature
K	- calorimeter constant
T_1,T_2,T_3,T_4	- specific measuring cycle temperatures
n	- duration of cycle no. 2 (main)

a series of diodes is placed, which indicate what kind of information is presented on display. To switch the type of information being displayed, use the buttons with a left or right arrow (fig.3 pos.3). The information on the calorimeter's status is provided by diodes, placed under the indicators of different cycles (**0**, **1**, **2**, **3**, **4**).
After completely opening the desktop, a switch for selecting **Joule/calorie** units can be reached.

Technical parameters of the calorimeter

calorimetric bomb sample pressure	19.62 MPa (200 atm)
calorimetric bomb volume	0.35 dm³ (350 ml)
calorimetric vessel volume	4.4 dm³ (4.4 l)
calorimetric mantle volume	15.5 dm³ (15.5 l)
power supply voltage	230V ±10%
device dimensions in mm	approx. 1100x600x750
whole calorimeter mass, excluding water	approx. 75 kg
digital temperature measurement precision	0.001 K (°C)

parameters of the resistance wire, used for sample combustion:

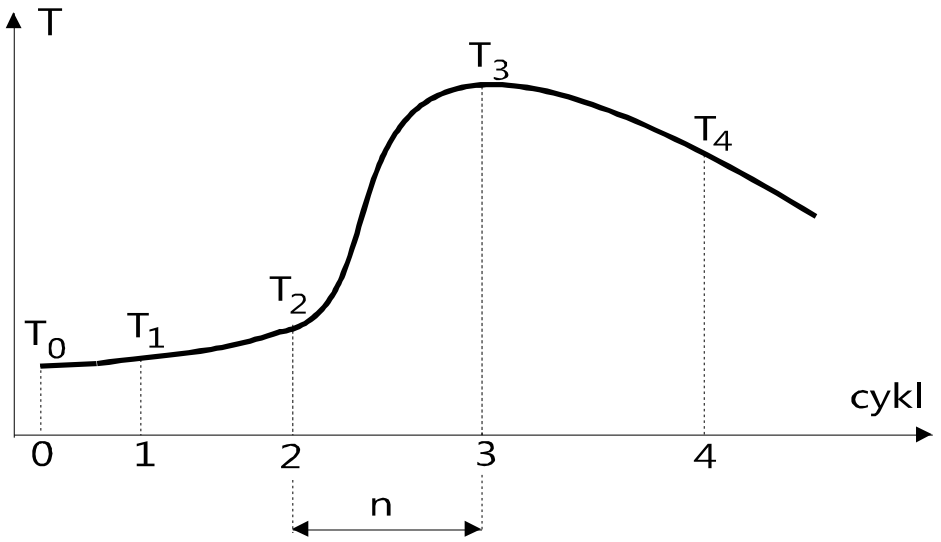
diameter	≤0.2 mm
length	100 mm
mass	< 10 mg
own heat of combustion	approx. 6698.9 kJ/kg

TABLE 1. Heat of combustion of benzoic acid in different temperatures

Temperature [K]	Heat of combustion [J/g]
273	26,469
288	26,456
289	26,455
290	26,454
291	26,453
293	26,451

Measurement

The measurement process is presented on the following graph:



Heat, emitted during fuel sample combustion, is calculated according to the following method:

$$Q = K \cdot (T_3 - T_2 - k)$$

where:

K - calorimeter constant
T_2,T_3 - specific temperatures of the balance
k - - adjustment for heat exchange with the surroundings

$$k = 0.5 \cdot [0.2 \cdot (T_2 - T_1) + 0.2 \cdot (T_4 - T_3)] + 0.2 \cdot (n-1) \cdot (T_4 - T_3)$$

where:

n - number of minutes in cycle no. 2 (main cycle)
T_1,T_4 - specific temperatures of the balance

Calorimetric constant is determined through the comparative measurements. This method involves directly comparing the substance's heat of combustion with the heat of combustion of a standard substance. Both results must be obtained from measurements carried out in identical conditions.

The baseline thermochemical standard substance, approved by the International Union of Pure and Applied Chemistry (IUPAC), is **benzoic acid $C_7H_6O_2$**.

Order of principle operations

(the measurement cycle is conducted twice: burning the standard substance sample and burning the studied fuel sample)

1. Set the Joule/calorie switch in proper position.

2. Prepare and **weigh** a tablet of the studied fuel (approx. 1g).

   The tablet, prepared on a specialized press and containing the resistance wire, is put in a crucible. Ends of the wire must be attached to the electrodes. Lift the electrode's clasping tubes, insert the wires in the indentations and lower the clasps. Electrodes should be cleaned. Incorrect wire insertion into the electrodes may cause the formation of an electric arch, critically distorting measurement results.

3. Prepare the bomb for measurement.
   Using a pippete, pour 0.002÷0.005 dm^3 (2÷5 cm^3) of distilled water into the bomb.
   Moments before beginning the measurement, fill the bomb with oxygen up to a pressure of: 2.0 MPa $\pm$ 0.2 MPa (20 $\pm$ 2 kG/cm^2).
   To do so:
   - Carefully carry the bomb in a vertical position to the oxygen container.
   - Unscrew the pin from the bomb's inlet valve.
   - Screw the connection pipe's loose end onto the bomb's inlet valve.
   - Unscrew the bomb inlet's regulator by turning it once clockwise, to open the inlet valve.
   - After opening the oxygen container's valve, set the container's output pressure on the limiter to 2.0 MPa (20 atm).
   - Open the limiter's outlet valve, and then close the bomb's outlet valve by screwing in the valve regulator counterclockwise as far as possible. Time between the opening of the limiter's outlet valve and closing the bomb's outlet valve is used to push the air out of the calorimetric bomb and substitute it with oxygen.
   - After achieving required pressure inside the calorimetric bomb, close the oxygen feed by closing the outlet valve on the limiter and then - closing the oxygen container's main valve.
   - Separate the connection pipe from the bomb by unscrewing it from the bomb's inlet valve, and replace it with a screwed-in valve pin.
   - Carefully move the bomb in a vertical position to the calorimeter and place it into the calorimetric vessel, holding the bomb by the valves.
4. Insert the calorimetric bomb into the vessel and connect the ignition wires to electrode pins.

5. Close the calorimeter cover by shifting it on the outrigger and then - lowering it.

6. If the frontal panel wires are disconnected, connect them.

7. Turn the calorimeter on with the POWER switch (fig.3 pos.1), placed on the desktop.
8. Wait 15 minutes to allow the thermal work conditions to stabilize before starting the measurement cycle.

9. Enable the automatic measurement cycle with the START button (fig.3 pos.2).
   The following operations are carried out automatically:
   1) mechanical stirrer is enabled;
   2) diode indicating cycle 0 lights up;
   3) after approx. 1 minute, cycle 1 starts (proper signal diode lights up);
   4) after 5 minutes, diode indicating the start of cycle 2 lights up. The fuel sample is ignited an maximum temperature T_3 is achieved;
   5) after recording maximum temperature T_3 and time *n* minutes, diode indicating the start of cycle 3 lights up.
   6) after 5 minutes, diode indicating work's end lights up. Temperature T_4 is recorded and the mechanical stirred shuts down automatically.

Attention: Early end of work is a sign of an operational error. The cause of error is displayed on the desktop, but all possible parameters need to be checked in search for a notice: Error. A list of errors has been provided in the manual.

10. Turn off the calorimeter power supply with the POWER button (fig.3 pos.1).

11. Final operations.

After the measurement, open the calorimetric vessel cover, disconnect the electrode wires from the bomb and remove the bomb from the vessel, first lifting it by the valves and later - holding the bomb by the body. Dry the bomb with a cloth and release the exhaust gasses by screwing in the outlet valve regulator, clockwise, as far as possible. Put the calorimetric bomb on the base (fig.5 pos.2), unscrew the self-sealing ring and remove it. Remove the bomb's head and put in on the stand (fig.5 pos.1). Then, check the crucible and the inside of the bomb to make sure that the fuel combustion was complete. If there's unburnt residue present, the measurement should be repeated. Remove the crucible from the crucible handle in the bomb's head.

Calculation methodology

The amount of heat *Q*, emitted during combustion, is a sum of:

A - heat of combustion of sample material,

B - heat of combustion/formation of other substances, such as: combustion of the wire, formation of nitric acid etc.

If the marginal amount of heat mentioned in point B is omitted, then the heat emitted during combustion of a sample with a mass of m is:

$$Q = m \cdot Q_s = K \cdot (T_3 - T_2 - k),$$

where: Q_S- heat of combustion [J/g], can be compared to heat emitted during combustion of the standard material.

This returns:

$$Q_2 = \frac{m_1 Q_1 \left(T_{3_2} - T_{2_2} - k_2\right)}{m_2 \left(T_{3_1} - T_{2_1} - k_1\right)},$$

where:
Q_1 and Q_2 - values of heat of combustion for the standard and the studied material [J/g],
m_1 and m_2 - sample masses for the standard and the studied material [g],
T_2 and T_3 - specific temperatures for both measurement cycles
k_1, k_2 - adjustments for heat exchange with the surroundings during both cycles.

Based on the results of calculation, identify the studied material.

List of possible measurements errors

Err 1 - temperature range exceeded.
Err 2- exceeded (more than 35 minutes) or too short (less than 1 minute) time of achieving maximum temperature T_3. The experiment should be repeated.
Err 3 - no ignition. Check if the wire was attached properly and repeat the experiment.
Err 4 - system error. Turn of the power supply for a short time period. If the error persists after turning on the power, contact service & maintenance.
Err 5 - calorimetric constant input error. Turn off the calorimeter's power supply and initiate calorimeter constant K setup. Enter the correct value. If the error persists, contact service & maintenance.

Supplementary equipment

1) press
2) stand (fig.4 pos.1)
3) calorimetric bomb opener base (fig.4 pos.2)
4) device used to fill the bomb with oxygen, including:
   - limiter
   - connection pipe (fig.4 pos.3)

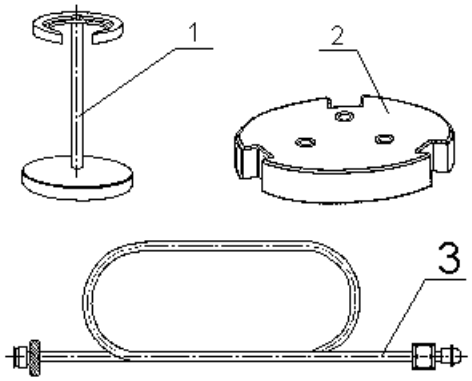


Fig. 4

Stand - used for holding the bomb's head when setting in the crucible and attaching the ignition wires to the electrodes.

Opener base - when attached to a steady surface, used to position, open and close the calorimetric bomb.

Connection pipe - used for connecting the limiter with the bomb, when filling the bomb with oxygen.