PROPULSION LAB MANUAL

Measurement of Calorific Value of a Solid Fuel Sample using a Bomb Calorimeter

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CONTENTS

1. INTRODUCTION

Abstract

In this experiment, we measure the calorific value of solid fuel by using a bomb calorimeter. We burn benzoic acid to find out the heat capacity of the equipment, this is called calibration of the system. After the calibration we put that calibrated value to the system as a reference for the further calculation of the fuel. We burn a small amount of solid fuel in isoperibol mode (17 minutes testing time) or dynamic mode (8 minutes). We get the result in any one mode and finally we can compare the experimental value with the theoretical heating value of the given fuel.

Introduction

In this experiment we will be using a bomb calorimeter. A bomb calorimeter measures the heat of combustion during a reaction. This will allow us to measure the calorific value of the solid fuel. We will first find out the heat capacity of the calorimeter using benzoic acid which will be fully combusts in oxygen. The bomb calorimeter is a closed system, therefore there is no heat transfer with the surroundings and we will be able to use the First Law of Thermodynamics: conservation of energy, to find out the necessary values. (Traum, 2009)

2. BACKGROUND AND THEORY

Bomb calorimetry is a process which can be used to determine the heat of combustion or calorific value of a solid or a liquid material. The Bomb Calorimeter was invented by a great chemist in the 18th century named Marcellin Berthelot. The sample is compressed with the oxygen inside a sample container or sample crucible within the bomb calorimeter. The bomb calorimeter is ignited with the help of nichrome wire which produces heat while supplying current and finally the heat produced by the wire will be transferred to the samples through the burning cotton thread. The burning sample generates heat and increase the temperature of the bomb which is inside the water jacket. The increase of temperature is measured by the thermometer or temperature sensor and ultimately finds the temperature difference of the water for the calculation. In figure 1 we can see that the system is a closed system there is no heat exchange between the surroundings and calorimeter, making it an adiabatic system. A water stirrer is used for the evenly distribution of heat in the water jacket of the calorimeter.

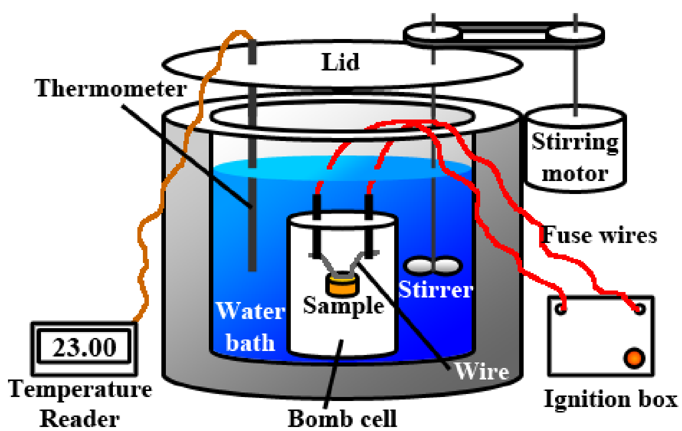


Figure: 1. Bomb calorimeter conceptual drawing [2].

Since volume does not change, a bomb calorimeter measures the heat evolved under constant volume, q_v,

$q_v = C * dT$, where dT is the temperature increase.

The q_v so measured is also called the change in internal energy, dU.

Note that $dU = q_v = C * dT$

The enthalpy (H), which in the present case is enthalpy of combustion, is defined as:

$$H = U + PV$$

and correspondingly a change in H (denoted by delta H) is given by:

$$dH = dU + (d(P\ V))$$
$$= dU + dn\ R\ T \qquad \text{(applying the ideal gas law)}$$

From the above expression, we see that delta U and delta H would be identical only if the pressure in the bomb remains constant. If the amount of gases in the bomb remain constant, delta P would be zero and thus delta U = delta H. However, in most combustion reactions the molar amounts of gases change and therefore a method for calculating the delta (PV) term is required.

where R is the gas constant (8.31 J mol−1 K−1). The term denoted by "small" can be neglected when changes in temperature are small (couple of ^{0}C). Note that delta n can be either positive (the amount of gaseous components increase) or negative (the amount of gaseous components decrease). Also the contribution of liquids and solids to the delta PV term is negligible.

Example 1:

When 0.1025 g of benzoic acid was burnt in a bomb calorimeter the temperature of the calorimeter increased by 2.165° C. For benzoic acid $dH°_{comb}$ = -3227 kJ mol^{-1}. Calculate the heat capacity of the calorimeter.

Solution:

The equation for the combustion is,

$$C_7H_6O_2(s) + 7.5\ O2(g) \rightarrow 7CO_2(g) + 3H_2O(l), \qquad dH° = 3227\ kJ$$

Since 7.5 moles of O_2 gas is needed, and 7 moles of CO_2 is produced, some pressure-volume work is done, to the calorimeter:

$P\ V = dn\ R\ T$, where dn = (7 - 7.5) = - 0.5 mol

$dU = dH - dn\ R\ T$

= - 3227 - (-0.5*8.314298*298)

= - 3226 kJ/mol (a small correction)

The amount of heat produced by 0.1025 g benzoic acid is

q = 0.1025/122.13 mol x 3226 (kJ/mol) = 2.680 kJ

Thus, the heat capacity is

$C = q / dT$ = 2.680 / 2.165 = 1.238 kJ / K.

After the heat capacity is determined, the calorimeter is ready to be used to measure the enthalpy of combustion of other substances.

Example 2:

A table of thermodynamic data gives dH_f = -285.8 kJ/mol for water. A bomb calorimeter measurement gives the heat of combustion for H_2 as -282.0 kJ/mol. Estimate the error of the enthalpy measurement.

Solution

Reinterpret the problem, we have

$H_2(g) + 0.5\ O_2(g) = H_2O(l)$, dU = 282.0 kJ/mol.

Furthermore,

$dn = -1.5$

$dH = dE + dn\ R\ T,$

$= -\ 282.0 + (-1.5\ \text{mol} * 8.314\ \text{J/(mol K)} * 298\ \text{K})$

$= (-282.0 - 3.72)\ \text{kJ}$

$= -285.7\ \text{kJ}$

The error is (285.8-285.7)/285.8 = 0.03%

3. IKA C200 CALORIMETRIC MESUREMENTS BASICS

Calculation

Combustion is carried out in a calorimeter under specific conditions. The decomposition vessel (bomb) is filled with a weighed fuel sample, the fuel sample is ignited and the temperature increase in the calorimeter system is measured. The specific calorific value of the sample is calculated as follows

$$HV = (C * dT - QExt1 - QExt2) / m \quad \{1\}$$

Where,

m- Weight of fuel sample

C- Heat capacity (C-value) of calorimeter system

DT - Calculated temperature increase of water in inner vessel of measuring cell

QExt1- Correction value for the heat energy generated by the cotton thread as ignition aid

QExt2- Correction value for the heat energy from other burning aids

The relevant standards are based on the following assumptions:

a. The temperature of the fuel and its combustion products is 25 °C.
b. The water contained in the fuel before combustion and the water formed whilst combusting the hydrogenous compounds of the fuel is in fluid form after combustion.
c. The atmospheric nitrogen has not oxidised.
d. The gaseous products after combustion consist of oxygen, nitrogen, carbon dioxide and sulphur dioxide.
e. Solid materials may form (e.g. ashes).

Calibration

The calorimeter system must be calibrated before accurate measurements are possible. This is done by combusting tablets made of certified benzoic acid with a known calorific value. The heat quantity required to raise the temperature of the calorimeter system by one Kelvin is used to determine the heat capacity of the so called "C value" of the system. For this calculation the equation1 is adapted:

$$C = (HV * m + QExt1 + QExt2) / dT \qquad \{2\}$$

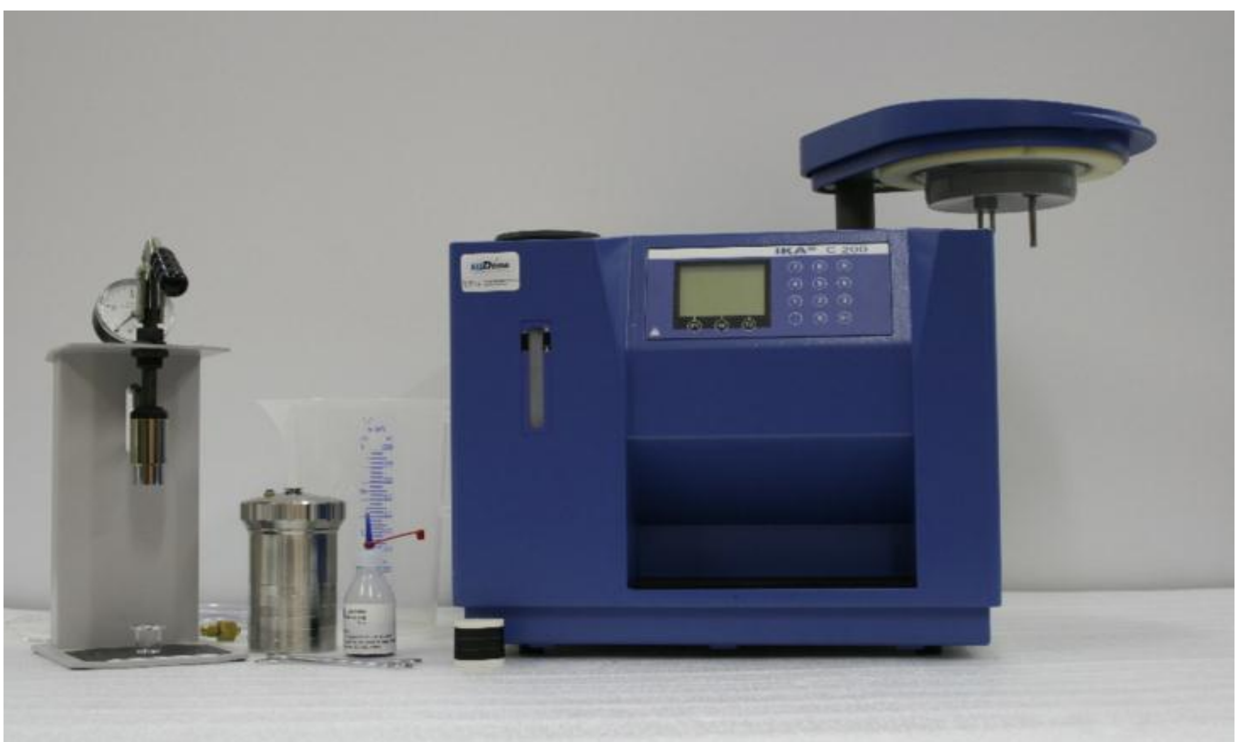
This value is used for determining the calorific values. The heat capacity is determined by the measuring cell and the decomposition vessel (bomb). It has a significant influence on the calorific value to be calculated and must be redetermined in particular when using for the first time, after servicing and when parts are replaced. A monthly control measurement is recommended.

Note: The system must be calibrated in every work mode used.

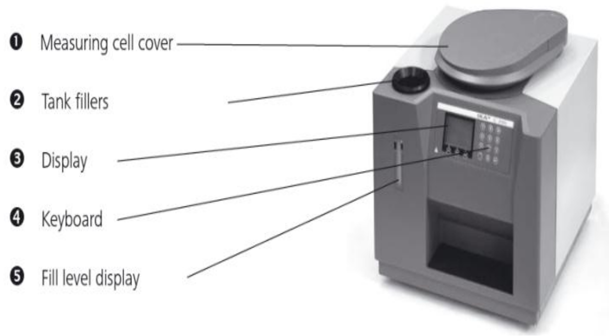
If a calorimeter is operated with several decomposition vessels, we will need to determine the heat capacity of the system for each decomposition vessel. Ensure that calibration is carried out under the same conditions as the subsequent tests. If substances are used in the decomposition vessel in combustion tests (e.g. distilled water or solutions), we must use exactly the same amount of this substance for calibration [3].

4. Calorimeter and its components

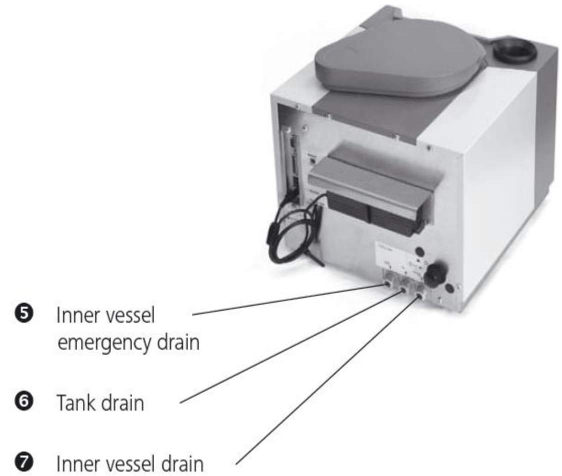
a. Calorimeter System IKA C 200, [3]



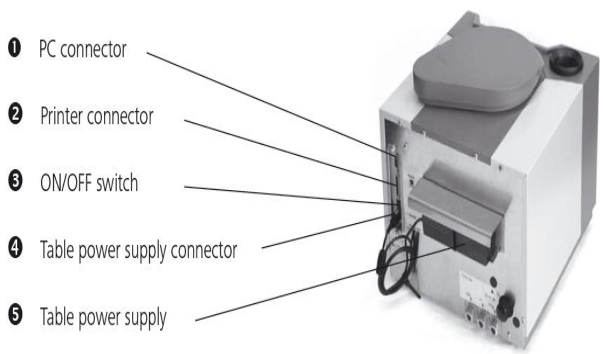
b. Calorimeter



c. Water connections

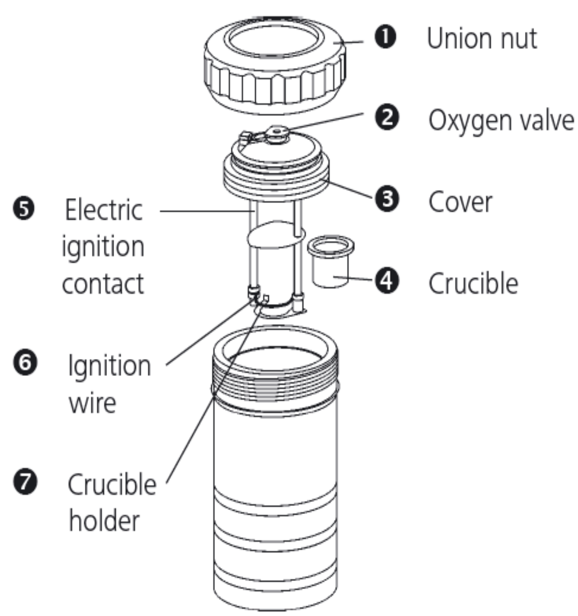


d. Electrical connections



e. Oxygen filling station

f. Decomposition vessel or bomb



5. PROCEDURES

1. Switch on the chiller unit and fix the temperature to 18 deg C.
2. Clean the calorimeter decomposition vessel (bomb), crucible, and other components.
3. Pour 5.0 ml of deionized water into the bomb to absorb the oxides of nitrogen formed from nitrogen present in the oxygen mixture.
4. Take out the thread from the plastic packet by forceps and tie it with the ignition wire.
5. Care must be taken to avoid overweight the sample, it must be realized that the peak pressure developed during combustion is proportional to the size of the sample and the initial oxygen pressure. Pellet size should be limited; not more than 1.1 g.
6. After keeping the fuel pellet in the pellet holder, make sure that the cotton thread is touching the pellet and then close the bomb with the top cover by screwing the union nut.
7. Hold the bomb carefully and keep it on the circle which is located on the oxygen station base. Be sure that the oxygen nozzle is aligned with the bomb valve and then rotate the top lever of the oxygen station in downward direction. Fill the bomb with oxygen at 30 bars and keep it at this pressure atleast for one minute and then free the bomb from the oxygen station.
8. Now switch on the IKA C200 bomb calorimeter: press ON (F1) to work with the appliance and then the start screen will appear. If the system is going to start first time, the system asks for 1st fill. Fill the outer tank with the chiller water and make sure that the tank level is in between the min & max range of the water level which is displayed on the left corner of the system. Then press F2 and go to prepare column.
9. Now go to weight column and put the weight of the sample, then come down to calibration column: 0- for calculation, 1- for calibration, then come down to vessel column: this is asking the name of the vessel (for single bomb- press 1), for Q_{Ext} press 50 J/g (calorific value of cotton thread), and finally in the test no press date of the experiment with the test serial no (like- 15122501= 25/12/15-01). After filling all, place the bomb inside the calorimeter, close the upper cover and press OK. The system starts and will be worked automatically [3].
10. The temperature rise is displayed on the screen and the result comes after sometimes based on mode setting (dynamic or isoperibol). The modes timings are such that, Dynamic modes takes 8 minutes and Isoperibol modes gives result in 17 minutes.
11. In order to ensure that the appliance works properly, we must set some parameters if uses in the first time. Press F3 button before pressing OK in the serial no 9. Now go to settings; it is displayed in this way: General, Calibration values, Unit, Language, Operation, and Service.

General:

- Reference- (reference calorific value for benzoic acid- given to the benzoic acid tablet strip = 26461 J/g)

- One way crucible- (without- for the case when sample burns under non combustible crucible, with- for the case when sample burns with combustible crucible)
- Date & time- (one time input)
- Operation- (no of operation like- 1,2,3,.....)

Calibration values:
- Vessel 1-
- Vessel 2-
- Vessel 3-
- Vessel 4-

(Values which comes from calibration by benzoic acid)

Unit:
- Unit- J/g or Cal/g

Language:
- English

Operation:
- Isoperibol/Manual/Dynamic/Time control

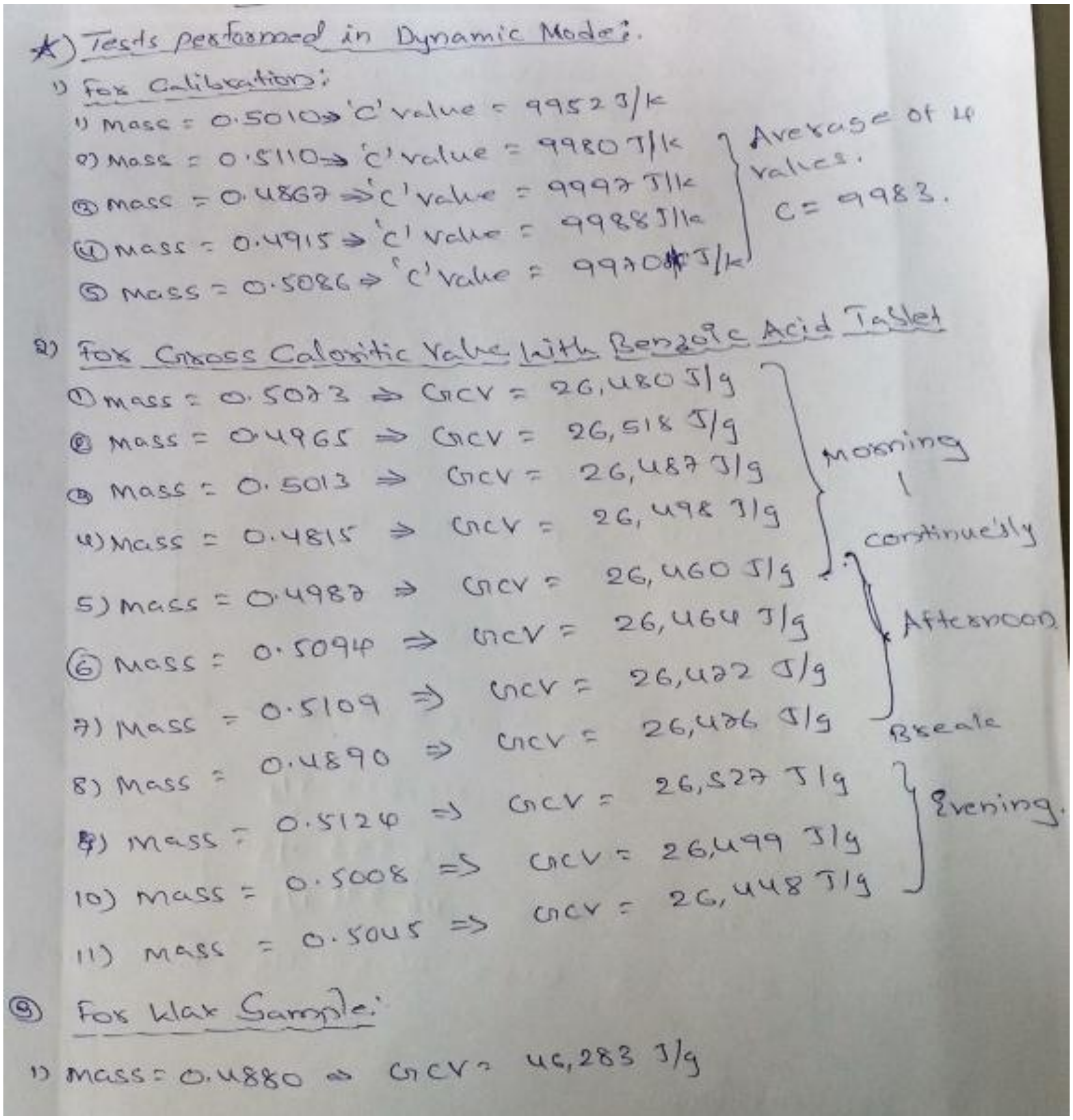
Service:
- Ignition off- (To check whether ignition is working or not)
- Fill off- (To check whether water flows from outer tank to inner vessel or not)
- Empty off- (To check whether water flows from inner vessel to outside the calorimeter or not)
- Stirrer off- (To check whether stirrer is working or not)
- Pump off- (To check whether pump is working or not: sound comes if working)
- Outer vessel off- (To check whether water flows from outer vessel to inner vessel or not)
- Reset- (Reset all settings)
- Reinitiating- (If AD board does not work which is inside the top cover, then select this option)
- Contrast- (This is for contrast setting of the screen, generally takes 50)

12. Results shows on the screen then open the top cover of the calorimeter, once the cover opens water start draining from inner vessel to the chiller unit. After draining of water, take out bomb from the calorimeter.
13. Write down the result in the record, then release the pressure of the bomb by using pressure release tool and at the same time clean the bomb and other involved parts carefully by a good quality tissue paper.
14. Switch off calorimeter, chiller unit, and finally close the top cover of the calorimeter. It is advised to cover the calorimeter by a clean cloth to protect it from the dust particles.

6. RESULTS

Some results are shown here for dynamic and isoperibol mode of operation for IKA C200: the present calorimeter what we discussed so far. The fuel is both benzoic acid and paraffin wax.

a. Calibration and calculation results for Dynamic mode of operation



*) Tests performed in Dynamic Mode:

1) For Calibration:

1) Mass = 0.5010 ⇒ 'C' value = 9952 J/K
2) Mass = 0.5110 ⇒ 'C' value = 9980 J/K
3) Mass = 0.4867 ⇒ 'C' value = 9997 J/K
4) Mass = 0.4915 ⇒ 'C' value = 9988 J/K
5) Mass = 0.5086 ⇒ 'C' value = 9970 J/K

} Average of 4 values. C = 9983.

2) For Gross Calorific Value With Benzoic Acid Tablet

1) mass = 0.5023 ⇒ GCV = 26,480 J/g
2) mass = 0.4965 ⇒ GCV = 26,518 J/g
3) mass = 0.5013 ⇒ GCV = 26,487 J/g
4) mass = 0.4815 ⇒ GCV = 26,498 J/g

} Morning continuously

5) mass = 0.4987 ⇒ GCV = 26,460 J/g
6) mass = 0.5094 ⇒ GCV = 26,464 J/g
7) Mass = 0.5109 ⇒ GCV = 26,422 J/g

} Afternoon

Break

8) Mass = 0.4890 ⇒ GCV = 26,527 J/g
9) mass = 0.5124 ⇒ GCV = 26,499 J/g
10) mass = 0.5008 ⇒ GCV = 26,448 J/g

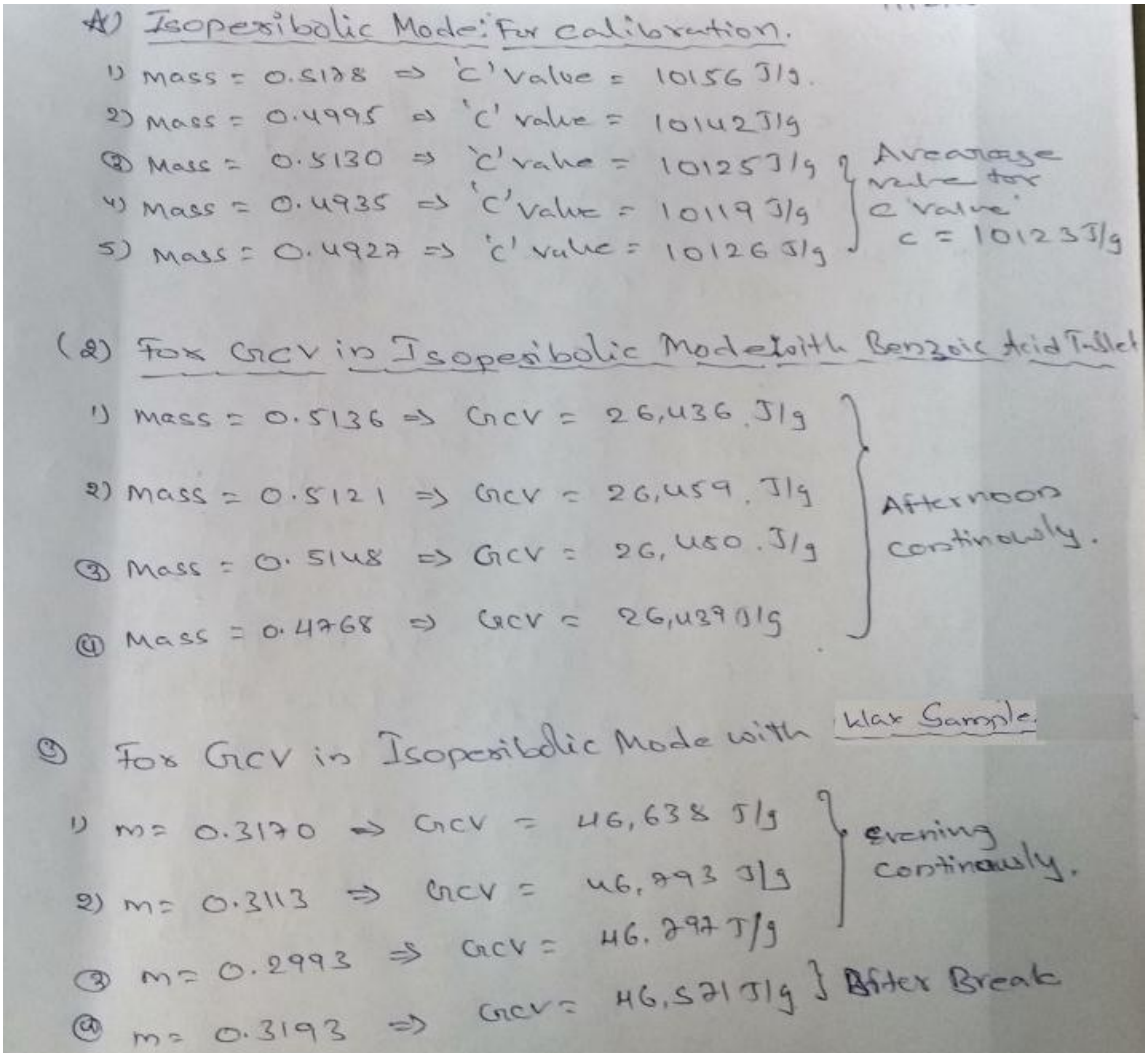
} Evening.

11) mass = 0.5045 ⇒ GCV =

3) For Wax Sample:

1) mass = 0.4880 ⇒ GCV = 46,283 J/g

b. Calibration and calculation results for Isoperibol mode of operation



A) Isoperibolic Mode: For calibration.

1) mass = 0.5128 => 'C' value = 10156 J/g.
2) Mass = 0.4995 => 'C' value = 10142 J/g
3) Mass = 0.5130 => 'C' value = 10125 J/g
4) Mass = 0.4935 => 'C' value = 10119 J/g
5) Mass = 0.4927 => 'C' value = 10126 J/g

} Avearage value for 'C value' c = 10123 J/g

(2) For GCV in Isoperibolic Mode with Benzoic Acid Tablet

1) mass = 0.5136 => GCV = 26,436 J/g
2) mass = 0.5121 => GCV = 26,459 J/g
3) Mass = 0.5148 => GCV = 26,450 J/g
4) Mass = 0.4768 => GCV = 26,439 J/g

} Afternoon continously.

3) For GCV in Isoperibolic Mode with Wax Sample

1) m = 0.3170 => GCV = 46,638 J/g
2) m = 0.3113 => GCV = 46,793 J/g
3) m = 0.2993 => GCV = 46,797 J/g
4) m = 0.3193 => GCV = 46,521 J/g

} evening continously. (1, 2)

} After Break (3, 4)

7. REFERENCES

[1]. Traum, D. M. (2009). Bomb Calorimetry

[2].https://www.google.co.in/search?q=ika+c200+isoperibol&biw=1440&bih=775&source=lnms&tbm=isch&sa=X&ved=0ahUKEwjKoO2EqJfKAhXFCI4KHSzsCP4Q_AUIBigB#tbm=isch&q=bomb+calorimeter&imgrc=V3huOJZBZ0jJSM%3A

[3]. http://www.ika.com