

USING LEAST SQUARES METHOD FOR MINIMIZING THE TOTAL ENERGY VALUE MEASUREMENTS ERROR FOR OLIVE OIL AND ALCOHOLIC BEVERAGES WITH BOMB CALORIMETER

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Abstract– The scope of this paper is to investigate new ways of receiving data for several drinks, so as to be possible to apply the Least Squares Method (LSM) to the measurements. Using LSM in a sufficient number of measurements it is possible to take results with high accuracy. It is found that the ways for taking the measurements, with the appropriate amounts of substrates, give satisfying results and that using LSM it is possible to find the measured values with a measurement error less than 1%.

Keywords: Least Squares Method, drinks energy content, bomb calorimeter, minimum error

1. INTRODUCTION

Bomb calorimeter is a high precision instrument used for measuring the energy content of materials. In this paper bomb calorimeter is used to find the energy content of some edible liquids using LSM.

Benzoic acid is a substance which is used for the calibration of bomb calorimeter. It has a very stable energy content, equals to 6318 cal/g, and it is used always at the beginning of a cycle of measurements, after a pretesting cycle [1], [2].

Having a data of fifty measurements of benzoic acid energy content, the heat capacity of bomb calorimeter is estimated using LSM with variables ΔT (temperature change) and m_s (sample mass, here benzoic acid mass). Then the bomb calorimeter is used for the measurement of energy content of olive oil and of some alcoholic beverages. Several measurements for the gross heat of all samples used are taken and then using

LSM method the most precise value of the gross heat of each sample is estimated.

In all the cases the graphs (LSM is used again for these graphs) are plotted and the best fit of the results is obvious.

2. EXPERIMENTAL

For the estimation of the heat capacity of bomb calorimeter, benzoic acid is used. Using a data of fifty low deviation measurements for benzoic acid energy content, using LSM with variables ΔT (temperature change) and m_s (sample mass, here benzoic acid mass), bomb calorimeter heat capacity can be estimated as it is shown in (1) to (5). Generally it is [3]:

$$K_C \Delta T = (GH)_s m_s \quad (1)$$

and for benzoic acid:

$$K_C \Delta T = (GH)_{BA} m_{BA} \quad (2)$$

where K_C is bomb calorimeter heat capacity, ΔT is the bucket's temperature rise, $(GH)_s$ is the energy content of the sample, m_s is sample mass, $(GH)_{BA}$ is the energy content of benzoic acid and m_{BA} is the mass of benzoic acid.

From (2) it is obtained:

$$\Delta T = \frac{(GH)_{BA} m_{BA}}{K_C} \Rightarrow \Delta T = \frac{(GH)_{BA}}{K_C} \cdot m_{BA} \quad (3)$$

By matching with the equation of the straight line it is obtained:

$$\begin{aligned} m_{BA} &\rightarrow x \\ \Delta T &\rightarrow y \\ a &= 0 \end{aligned} \quad (4)$$

$$b = \frac{(GH)_{BA}}{K_C} \quad (5)$$

By applying the LSM for the measurements taken, the heat capacity of the bomb calorimeter is estimated. In the graph it is shown that there is a best fit of the measurements to the straight line of LSM.

For the measurement of energy content of olive oil and for all non-volatile liquids with the use of bomb calorimeter, it is used one substrate, sawdust. Then the energy content of such liquids is given by (6):

$$(GH)_s = \frac{(GH)_{tot} m_{tot} - (GH)_{sawd} m_{sawd}}{m_s} \quad (6)$$

where $(GH)_s$ is the energy content of sample, $(GH)_{tot}$ is the total energy content of the mixture (sample and sawdust), m_{tot} is the total mass of the mixture (sample and sawdust), $(GH)_{sawd}$ is the energy content of sawdust, m_{sawd} is the mass of sawdust and m_s is the mass of sample.

Generally it is:

$$K_C \Delta T = (GH)_{tot} m_{tot} \quad (7)$$

where K_C is bomb calorimeter heat capacity and ΔT is the bucket's temperature rise.

Equations (6) and (7) give:

$$\begin{aligned} K_C \Delta T &= \\ &= (GH)_s m_s + (GH)_{sawd} m_{sawd} = \\ &= \Delta T = \frac{(GH)_s m_s}{K_C} + \frac{(GH)_{sawd} m_{sawd}}{K_C} = \\ &= \Delta T = \frac{(GH)_s}{K_C} \cdot m_s + \frac{(GH)_{sawd} m_{sawd}}{K_C} \quad (8) \\ y &= b \cdot x + a \quad (9) \end{aligned}$$

It is necessary that a in (9) is constant, which means that:

$$\frac{(GH)_{sawd} m_{sawd}}{K_C} = \text{const} \quad (10)$$

That is it must be:

$$\frac{4330 \text{ cal/g} \cdot m_{sawd}}{922 \text{ cal/grad}} = \text{const} \quad (11)$$

[($GH)_{sawd}$ =4330 cal/g and K_C =922 cal/grad have been estimated using LSM.]

Then m_{sawd} must be constant.

The measurements for this paper have been done by using constant mass for the sawdust (equals to 0,15 g).

According to (8), using LSM it is obtained:

$$m_s \rightarrow x$$

$$a = \frac{\Delta T \rightarrow y}{\frac{(GH)_{sawd} m_{sawd}}{K_C}} \quad (12)$$

$$b = \frac{(GH)_s}{K_C} \quad (13)$$

From (13) it derives:

$$(GH)_s = b \cdot K_C \quad (14)$$

It is obvious that from (15), using LSM, the sample energy content can be estimated in high accuracy.

From the corresponding LSM graph it is found that there is a best fit of the measurements to the LSM straight line (linear module).

For the measurement of energy content of alcoholic beverages and for all volatile liquids with the use of bomb calorimeter, it is necessary to use two substrates, such as sawdust and membrane. It is:

$$(GH)_s = \frac{(GH)_{tot} m_{tot} - (GH)_{sawd} m_{sawd} - (GH)_{memb} m_{memb}}{m_s} \quad (15)$$

where $(GH)_s$ is the energy content of sample, $(GH)_{tot}$ is the total energy content of the mixture (sample, sawdust and membrane), m_{tot} is the total mass of the mixture (sample, sawdust and membrane), $(GH)_{sawd}$ is the energy content of sawdust, m_{sawd} is the energy content of sawdust, $(GH)_{memb}$ is the energy content of membrane, m_{memb} is the mass of membrane and m_s is the mass of sample.

Equations (7) and (15) give:

$$\begin{aligned} K_C \Delta T &= \\ &= (GH)_s m_s + (GH)_{sawd} m_{sawd} + (GH)_{memb} m_{memb} \Rightarrow \\ &\Rightarrow \Delta T = \frac{(GH)_s m_s}{K_C} + \frac{(GH)_{sawd} m_{sawd} + (GH)_{memb} m_{memb}}{K_C} \Rightarrow \\ &\Rightarrow \Delta T = \frac{(GH)_s}{K_C} \cdot m_s + \frac{(GH)_{sawd} m_{sawd} + (GH)_{memb} m_{memb}}{K_C} \quad (16) \\ y &= b \cdot x + a \end{aligned}$$

It is necessary in (16) that a will be constant, which means that:

$$\frac{(GH)_{sawd} m_{sawd} + (GH)_{memb} m_{memb}}{K_C} = \text{const} \quad (17)$$

That is, it must be:

$$\frac{4330 \text{ cal/g} \cdot m_{sawd} + 11000 \text{ cal/g} \cdot m_{memb}}{922 \text{ cal/grad}} = \text{const} \quad (18)$$

[($GH)_{sawd}$ =4330 cal/g, $(GH)_{memb}$ =11000 cal/g and K_C =922 cal/grad have been estimated using LSM.]

Then m_{sawd} and m_{memb} must be constant.

The measurements for this paper have been done by using always constant mass of sawdust (0,3 g) and constant mass of membrane (0,09 g).

According to (16), using LSM it is obtained:

$$a = \frac{m_{\text{sample}} \rightarrow x \cdot \Delta T \rightarrow y}{K_C \cdot m_{\text{sawd}} + (GH)_{\text{memb}} \cdot m_{\text{memb}}} \quad (19)$$

$$b = \frac{(GH)_s}{K_C} \quad (20)$$

From (20) it derives:

$$(GH)_s = b \cdot K_C \quad (21)$$

It is obvious that from (21), using LSM, the sample energy content can be estimated in high accuracy [5].

From the corresponding LSM graph everyone can see the best fit of the measurements to the LSM straight line (linear module).

3. RESULTS AND DISCUSSION

In this research it was found that the heat capacity of bomb calorimeter in use is 922 cal/grad and the values of energy contents of the edible liquids were measured are presented in Table 1.

Table 1. Experimental results for the energy content of some liquid foods (in cal/g)

Liquid food	Energy content
Olive oil	9500
Ouzo	2100
Tsipouro	2150
Red wine	850
White wine	830
Whiskey	2500
Cognac	2300
Vodka	2300
Beer	430
Light beer	290
Champagne	840

For example, for tsipouro without anise all the measurements and the estimations are presented below [4]. In Table 2 the values of energy content of tsipouro without anise are shown. These have been found by replacing the measurement given from bomb calorimeter to (15).

Table 2. Energy content found for benzoic acid (instrument calibration) and for tsipouro without anise using bomb calorimeter (in cal/g)

Sample ID	Energy content	Residue
BENZOIC-184	6315,8848	No residue
TS-CONF-1	1997,0569	Zero smut
TS-CONF-2	2147,9903	Zero smut
TS-CONF-3	2248,5766	Zero smut
TS-CONF-4	2240,9496	Zero smut
TS-CONF-5	2286,7506	Zero smut
TS-CONF-6	2256,3330	Beige water, a little smut
TS-CONF-7	2272,8865	Clear water, three small black like dust grains, almost zero smut
TS-CONF-8	2160,6322	Clear water, zero smut
TS-CONF-9	2122,1428	Beige water, a little smut
TS-CONF-10	2096,0936	Beige water, a little smut

Average $(GH)_s = 2182,9412$ cal/g

Table 3. Measurements table for LSM application

Sample ID	Sample mass (g) $m_s \rightarrow x$	Temperature change (grad) $\Delta T \rightarrow y$
TS-CONF-1	0,1847	2,9222
TS-CONF-2	0,2516	3,1014
TS-CONF-3	0,3866	3,4557
TS-CONF-4	0,3168	3,2877
TS-CONF-5	0,3649	3,4182
TS-CONF-6	1,0311	5,0213
TS-CONF-7	0,4845	3,7048
TS-CONF-8	0,7999	4,3800
TS-CONF-9	0,8833	4,5371
TS-CONF-10	0,9319	4,6204

Table 4. Application of LSM

x	y	x^2	xy
0,1847	2,9222	0,034114	0,53973
0,2516	3,1014	0,063303	0,780312
0,3866	3,4557	0,14946	1,335974
0,3168	3,2877	0,100362	1,041543
0,3649	3,4182	0,133152	1,247301
1,0311	5,0213	1,063167	5,177462

0,4845	3,7048	0,23474	1,794976
0,7999	4,3800	0,63984	3,503562
0,8833	4,5371	0,780219	4,00762
0,9319	4,6204	0,868438	4,305751

For N=10 it is found that $a=2,5376$ and $b=2,3197$. From (21) by replacing $b=2,3197$ it is found that $(GH)_s=2138,7634$ cal/g. The LSM graph is shown in Fig. 1.

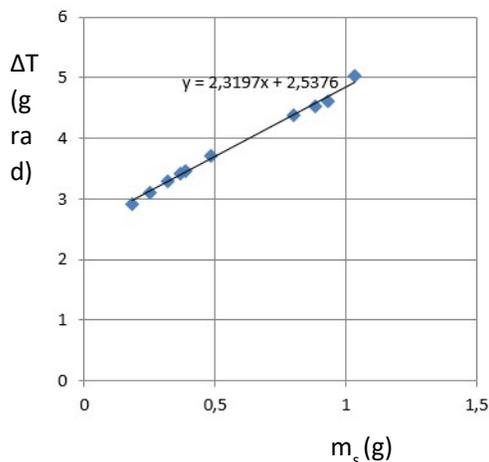


Figure 1. LSM graph for tsipouro without anise

In Fig. 1 the best fit of the measurements to the LSM straight line is shown.

4. CONCLUSIONS

Best fit of the measurements to the LMS graph in all cases under investigation was realized. Using LSM in data obtained with the use of suitable substrates it was possible to estimate the energy content of some edible liquids in high accuracy with a deviation between theoretical and experimental values less than 1%.

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