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Specific heat measurement of organic and conventional coffee samples by thermal relaxation

Medición del calor específico de muestras de café orgánico y convencional por relajación térmica

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ABSTRACT

The specific heat at constant pressure (*Cp*) is a necessary thermal parameter in the description of the heat transport in a material, related to the adaptation to changes of temperature, which is very important in the valuation and inspection of inputs for the construction, adhesives, insulators thermal and electronic devices. In this work, a thermal relaxation system with infrared thermometry was used to determine the *Cp* of green coffee beans, measuring the temperature of the material placed inside a vacuum chamber that reaches a pressure of 10^{-2} Torr. The sample was heated by radiation with laser light and the data was obtained by means of an acquisition card. The calibration of the system was made comparing the values obtained of *Cp* of Zinc, Tungsten, Titanium and Steel sheets with those reported and similarity was found. This method was used to measure the *Cp* of samples of organic and conventional coffee; these values were subjected to an analysis of variance and significant differences were found with a confidence level of 95 %. This technique could be used for the discrimination of organic coffee in the certification process.

Keywords:

Coffee
Specific heat
Differentiation
Instrumentation

RESUMEN

El calor específico a presión constante (*Cp*) es un parámetro térmico necesario en la descripción del transporte de calor en un material, relacionado con la adaptación a cambios de temperatura, lo que es importante en la valoración e inspección de insumos para la construcción, pegantes, aislantes térmicos y dispositivos electrónicos. En este trabajo se utilizó un sistema de relajación térmica con termometría infrarroja para determinar el *Cp* de granos de café verde, midiendo la temperatura del material colocado dentro de una cámara de vacío que alcanza una presión de 10^{-2} Torr. La muestra se calentó por radiación con luz láser y los datos fueron obtenidos mediante una tarjeta de adquisición. La calibración del sistema se hizo comparando los valores obtenidos de *Cp* de láminas de Zinc, Wolframio, Titanio y Acero con los reportados y se encontró similitud. Este método se usó para medir el *Cp* de muestras de café orgánico y convencional; estos valores se sometieron a un análisis de varianza y se hallaron diferencias significativas con un nivel de confianza del 95%, lo que permite afirmar que la técnica podría ser utilizada para la discriminación de café orgánico en el proceso de certificación.

Palabras clave:

Café
Calor específico
Diferenciación
Instrumentación

1. Introduction

The fundamentals of heat transfer were established with Fourier's first works [1]. The thermal characteristics of solids determine their behaviour to a temperature difference [2], which is important in industry and material sciences. In particular, specific heat expresses the amount of heat dissipated in a unit volume sample when its temperature varies by one degree [3].

The development of simple systems for measuring this parameter is a matter of interest, since commercial equipment is high cost and analytical methods and calculations are restricted to initial conditions and different temperature ranges; however, the thermal relaxation technique is one of the simplest and most functional [4, 5]. This

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method is based on the disturbance of the state of thermodynamic equilibrium, by means of constant illumination, of a sample suspended adiabatically inside a vacuum chamber and on the measurement of the variation of its absolute temperature as a function of time [6]. Infrared radiometry is often used to measure the temperature of the sample, taking into account the influence of convection and radiation heat losses. The analytical solution of the heat diffusion equation allows to obtain the Cp of the material through the analysis of the temperature evolution between two parallel surfaces of the solid sample [7]. In recent years this method has been used for the thermal characterization of semiconductor materials, food, wood, zeolites, clays and polymers [3] and to develop discrimination criteria [8], since the specific heat depends on the internal structure of the material and is characteristic of each substance.

On the other hand, in organic coffee cultivation, environmentally friendly practices bring this activity closer to being sustainable, because they give added value to the product [9]. However, the commercialization of this product requires the intervention of certifying bodies that inspect and guarantee its denomination, through a costly and lengthy process that is based on on-site inspection and testing on each farm. For this reason, the use of a quantitative method, such as the one that can be visualized from the results of this work, could support the discrimination of organic coffee, since it is made from a precise measurement that does not require sample preparation and a quick and low-cost analysis. In this work, the thermal relaxation method was used to measure the Cp of organic and conventional coffee samples for differentiation purposes. The single factor analysis of variance (ANOVA) led to a significant difference between the data for the two types of coffee. In the implementation of the measurement system it was guaranteed that the sensed temperature was acquired and saved as a data in function of time, using programming and synchronization of the algorithms in the interfaces.

2. Materials and methods

Coffee Samples

Using the thermal relaxation technique, Cp measurements were taken in triplicate from 10 samples of organic coffee and 10 samples of conventional coffee, chosen at random. The fruits of coffee plants (Coffea arabica) of the Castillo variety were collected in farms located in the municipality of Salento in the department of Quindío, at an altitude between 1721 and 1756 msm. The mucilage was removed from the seeds by fermentation [10] during 24 hours and then the grain was dried until reaching a humidity between 14.1 and 14.4 %, measured with a UNIMETER DIGITAL equipment. The samples were transformed into sheets with thickness between 0.6 and 0.75 mm, by means of a transversal cut using a rotary microtome.

Cp Measurement

Figure 1 presents the general scheme of the assembly of the measuring system; the sample is heated by radiating its upper surface with a laser beam and the temperature gradient is measured as a function of time, using infrared thermometry. The sample was placed inside a cylindrical stainless steel chamber 400 mm high and 250 mm in diameter in which a vacuum was made, using a Leybold Trivac D 2.5 E pump, until reaching a pressure around 10^{-2} Torr.

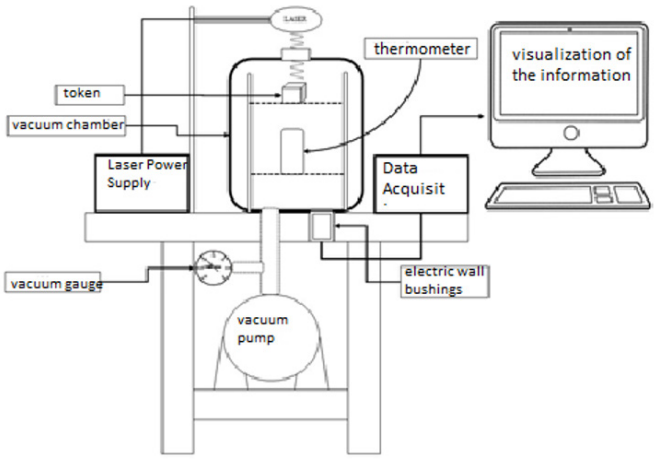

Figure 1. Scheme of the experimental set-up

A computer was used to acquire the temperature, measured with an infrared reference thermometer TM-908 LUTRON, located at the back of the sample. The data were recorded through a programmable development card, with a synchronized speed between receiving the temperature and sending data to the computer, which is crucial to avoid loss or latency of information that would cause an erroneous taking of data.

The front surface of the samples (where the laser beam strikes) was dyed with a thin layer of carbon paint to ensure uniform heating and heat transfer. The light absorbed by the solid is converted, in whole or in part, to heat by non-radiative de-excitation processes. Assuming a known heat source, called Q, which radiates a sample of thickness L and mass m, the temperature variation is found.

ΔT. Assuming that it is adiabatically suspended at atmospheric pressure, it has to be:

$$Q=C\Delta T \qquad (1)$$

Where C is the heat capacity, related to the specific heat as follows:

$$Cp=C/m \qquad (2)$$

The heat variation in the sample depends on the time of exposure to the heat source and is expressed as:

$$\partial Q/\partial t=P_{o-P} \qquad (3)$$

Where Po is the absorbed power of the incident radiation and P symbolizes the losses of heat by conduction, convection and radiation. On the other hand, radiation, R, which represents energy losses, is defined in the following equation:

$$R=A\epsilon\sigma(T^4-T_{0^4}) \qquad (4)$$

Where A is the sample area, ϵ is the emissivity, σ the Stefan-Boltzmann constant and T the absolute temperature, related to the ambient temperature at which the sample is found (thermal equilibrium). If the temperature variations ΔT are close to the ambient temperature, you can write:

$$T=T_0+\Delta T \qquad (5)$$

Where T_0 is the ambient temperature. In this way, equation (4) can be reduced to:

$$R=4A\epsilon\sigma(T_{0^3}\,\Delta T) \qquad (6)$$

With regard to convection, applying Newton's cooling law (the loss of heat from a body is proportional to the difference in temperature between the body and its surroundings), one has to:

$$dQ/dt=hA(T_{fluid\text{-}T\text{-}sample}) \qquad (7)$$

Where h is the coefficient of convection that quantifies the influence of the properties of the fluid (in this case the air inside the chamber), of the surface and of the flow when heat transfer occurs. Therefore:

$$Q=\rho cV\Delta T=CV\Delta T \qquad (8)$$

Where ρ is the density and V is the volume of the sample.

Deriving (8) with respect to time and replacing in (3) has to be:

$$\partial(\Delta T)/\partial t+\beta/C\,\Delta T-P_{o/C}=0 \qquad (9)$$

Where $\beta= A(4\epsilon\sigma T_{0^3}+h)$.

With the initial condition $\Delta T(0)=0$, the solution to equation (9) is:

$$\Delta T(t)=P\_o/\beta[1-[exp]^{(-t/\tau)}] \qquad (10)$$

Where thermal relaxation time, τ, is given by:

$$\tau=LC/2(4\epsilon\sigma T_{0^3}+h) \qquad (11)$$

Respuestas, 24 (3), pp. 65-71, 2019, ISSN 0122-820X - E ISSN: 2422-5053

When the heat source does not radiate the sample, equation (10) changes because the temperature of the sample is saturated by a value $P_{o/\beta}$; so when the temperature decreases it is obtained (12).

$$\Delta T(t)=P\_o/\beta\ [[exp]^{(-t/\tau)}\ ] \qquad (12)$$

When the sample is placed inside the chamber and the air is emptied into it, the heat transfer by convection tends to zero, so that the thermal relaxation time is mainly influenced by radiation and the parameter h can be neglected; thus, C can be calculated through (13).

$$C=[8\epsilon\sigma T_{0\text{^}3}\ \tau]_{R/L} \qquad (13)$$

3. Results and Discussion

Table I shows the dimensions and mass of the samples in sheet form, obtained by grain cuts. It can be noted that the two types of coffee are in the same size and weight range.

Table I. Average size and mass of coffee samples (lamines)

token	length (mm)	wide (mm)	thickness (mm)	lump (g)
Conventional	8,70±0,01	5,87±0,01	0,72± 0,001	0,0269±0,0001
Orgánic	7,63±0,01	5,76±0,01	0,66± 0,001	0,0220±0,0001

Calibration of the thermal relaxation system

Starting from equations 10 and 12, which describe respectively the evolution of the temperature of the sample when it is heated by the laser and when it cools down to return to its initial temperature, the thermal relaxation time is obtained, which indicates how long it takes for the sample to reach its thermal equilibrium. For vacuum measurements it is assumed that τ is equivalent to τ_R (heat transfer only by radiation) and applying equation 13 the value of *C* and *Cp* is calculated, considering the mass and volume of the samples shown in Table II.

To test the system, the parameter τ_R was found, based on the vacuum measurement of the temperature evolution of samples of zinc, tungsten, titanium and steel as a function of time, during the heating and cooling process (when the sample is not irradiated). The curves are shown in Figures 2 a) and 2 b), respectively.

Table II. Dimensions of the zinc, tungsten, titanium and steel samples

Samples	Long (mm)	Wide (mm)	Thickness (mm)	Lump (g)
Zinc 99% (Zn)	14,16±0,01	14,15±0,01	0,71±0,001	0,94±0,0001
Wolframe 99% (W)	15,00±0,01	15,56±0,01	0,96±0,001	3,70±0,0001
Titanium 99% (Ti)	20,08±0,01	20,52±0,01	1,03±0,001	1,86±0,0001
steel 99%	19,72±0,01	18,7±0,01	0,81±0,001	2,34±0,0001

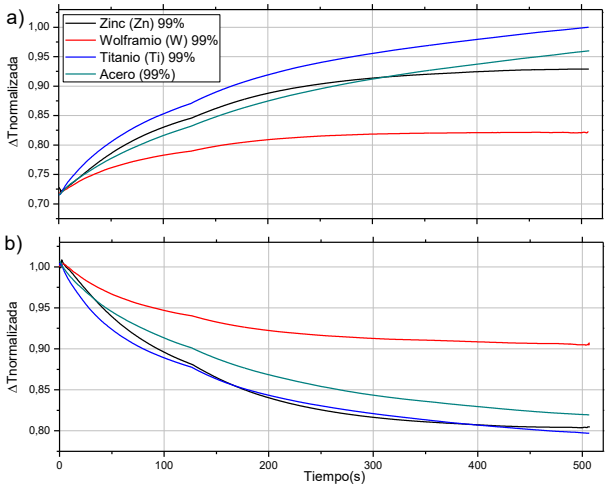

Figure 2. Evolution of temperature, normalized with the maximum value reached, corresponding to samples of zinc, tungsten, titanium and steel with 99 % purity, taken in vacuum under a) incidence and b) without incidence of laser light.

The relaxation time was estimated as a parameter of adjustment to equations (10) and (12) and the results are presented in Table III.

Table III. Obtained results of Cp, through the thermal relaxation technique and values reported by other authors

Samples	*Cp* garnered (J g^{-1} K^{-1})	*Cp* reported (J g^{-1} K^{-1})
Zinc 99% (Zn)	0,384 ± 0,005	0,389 [11]
Wolframe 99% (W)	0,11 ± 0,02	0,133 [12]
Titanium 99% (Ti)	0,56 ± 0,01	0,543 [13]
steel 99%	0,46 ± 0,01	0,460 [14]

Cp measurement of organic and conventional coffee

The *Cp* of ten samples of each type of coffee was determined with the thermal relaxation technique. Figures 3 a) and 3 b) show the evolution of temperature as a function of time, with and without the incidence of laser light, respectively. The curves correspond to a sample of conventional coffee and one of organic coffee, but this behavior was similar in all cases.

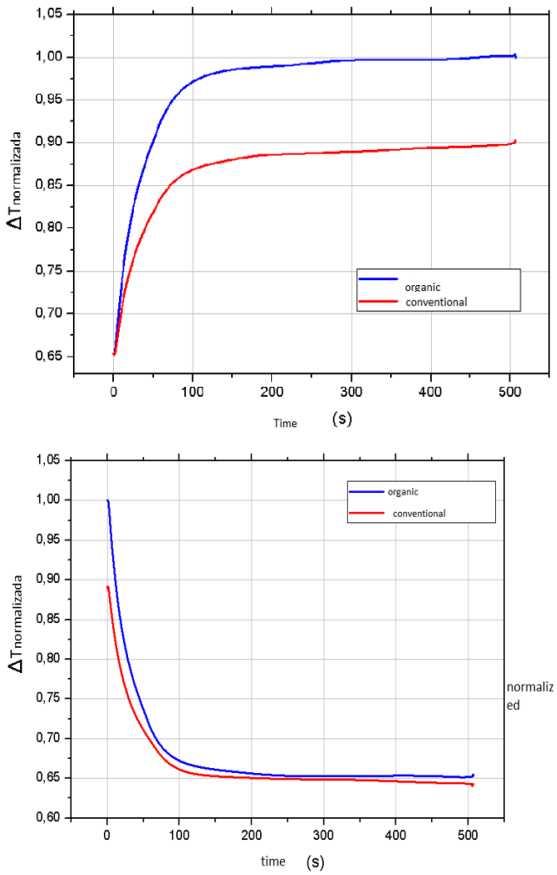

Figure 3. Evolution of the temperature, normalized with the maximum value reached, corresponding to a sample of organic coffee and a sample of conventional coffee, taken in vacuum under a) incidence and b) without incidence of laser light.

Application of single factor ANOVA

A single factor analysis of variance was applied to the results obtained, shown in Table IV.

The values of Cp and C of the 10 samples of coffee of each type were analyzed. Table IV shows the average values obtained with their respective standard deviation and coefficient of variation. The coefficient of variation for the two grain classes is very low, which is related to the precision of the measuring instrument and the homogeneity of the data. The average Cp value of the conventional and organic coffee samples was 1,320±0,003 and 1,157±0,003 J g-1 K-1, respectively.

Table IV. results of the Cp annova of the coffee samples

Type of coffe	Recount	Average ($J\ g^{-1}\ K^{-1}$)	Standard deviation ($J\ g^{-1}\ K^{-1}$)	Coefficient of variation
Conventional	10	1,32	0,01	0,99%
Orgánic	10	1,16	0,01	1,28%
Total	20	1,24	0,08	6,85%

The main intention of the ANOVA of a factor is to compare the means; therefore to determine the discrimination potential of the parameter *Cp* a null hypothesis H_o and an alternative hypothesis H_A were raised.

$$H_o: Cp_{conventional} = C[p\ ]_{organic} = Cp \qquad (15)$$

The null hypothesis defines that the mean of the Cp of the coffee samples, $Cp_{conventional}$ and $Cp_{organic}$ (conventional and organic) are equal; whereas with the alternative hypothesis H_A defined in (16), it is specified that the value of the parameter *Cp* is different in both cases.

$$H_A: Cp_{convencional} \neq Cp_{orgánico} \neq Cp \qquad (16)$$

Table V. Anova applied to the Cp of coffee samples

Fountain	Sum of squares ($J\ g^{-1}\ K^{-1}$)	Levels of freedom	Cuadrado medio ($J\ g^{-1}\ K^{-1}$)	Reason-F	Value-P
Cultivation method	0,133188	1	0,133188	683,72	0,0000
Miscarriage	0,003506	18	0,0001947		
Total	0,136694	19			

Table V shows the ANOVA data; the total variation of the 20 analyzed data was 0.136694 J g-1 K-1. Weighing these values with the corresponding degrees of freedom, we obtained the mean squares that reflect the real magnitude of each source of variation. It is noted that the difference due to the culture mode is 0.133188 J g-1 K-1 and that the error is 0.0001947 J g-1 K-1; therefore, the mean square of the culture mode is approximately 683.72 times greater than the mean square of the error; this indicates that the differences observed between the two types of culture are significant and are not due to small variations in the samples. As the P value is less than 5 %, the null hypothesis is rejected and it is concluded that there is no equality between the means for each cultivation mode. In order to verify

Respuestas, 24 (3), pp. 65-71, 2019, ISSN 0122-820X - E ISSN: 2422-5053

the presence of significant differences between the Cp means of the samples of both types of crops, the hypotheses were tested using the method of minimum significant difference (LSD).

Table VI. Values resulting from the application of the LSD test according to the mode of cultivation of the coffee bean

Contrast	Sig.	Variance	+/- Límits
Conventional organic coffee	*	0,16321	0,0131135

Table VI shows the data from the LSD test, from which it is determined that the means are significantly different with a 95% confidence level.

4. Conclusions

The Cp value of zinc sheets, tungsten, titanium and steel, measured with the thermal relaxation system was close to that reported by other authors. This served to establish the reliability of the method.

The ANOVA applied to the *Cp* data, obtained through the thermal relaxation technique, allowed establishing a difference between samples of organic and conventional coffee. This single factor analysis, in which the response variable was the value of this parameter, led to define that this magnitude ranged between 1.3165 and 1.3233 J g-1 K-1 and between 1.1538 and 1.1596 J g-1 K-1, for conventional and organic coffee beans, respectively. On the other hand, information was obtained on the precision of the measurements, which had a coefficient of variation of less than 1%.

Possibly the Cp of conventional coffee is higher due to the different content of lipids, proteins and acids [15].

The electronic instrumentation implemented was of low cost and easy commercial acquisition, which gives added value to the development of the *Cp* measurement system and makes it a viable option for the purpose of supporting the organic coffee certification process.

5. Acknowledgements

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