COMPARISON BETWEEN CONVENTIONAL AND ORGANIC RICE USING PHOTOACOUSTIC TECHNIQUE

COMPARACIÓN ENTRE ARROZ CONVENCIONAL Y ORGÁNICO USANDO LA TÉCNICA FOTOACÚSTICA

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ABSTRACT: Rice (Oryza sativa) is staple food for more than half of the world population. This cereal contributes a considerable amount of calories to the consumer. Agrotoxics and synthetic fertilizers in agricultural practices have generated environmental damage and the pollution of fruits, which puts consumer health at risk. On the other hand, organic agricultural production requires certification, which frequently is a complicated and expensive process of inspection. For this reason, it is pertinent to look for a scientific discrimination criterion that allows for the certification procedure to be done in an efficient and economical way. In this paper, a photoacoustic spectroscopy study for husk and white grain rice samples of Combeima variety is shown. The samples were taken from crops of rice that were cultivated with organic and conventional techniques. Themophysical parameters of the same kind of samples were measured with the same technique, but in frequency - resolved configuration. Finally, rice grain cell morphology was studied by optical microscopy. The results show important differences among the samples for being used in a certification process.

KEYWORDS: Organic rice (Oryza sativa), Thermal diffusivity, Photoacoustic spectroscopy, Cellular morphology,

RESUMEN: El arroz (Oryza sativa) hace parte de los alimentos básicos para más de la mitad de la población mundial. Este cereal aporta grandes cantidades de calorías al consumidor. La utilización de herbicidas y de fertilizantes de origen sintético en los cultivos genera no sólo gran deterioro ambiental sino también la contaminación del fruto poniendo en riesgo la salud del consumidor. Por otro lado, la producción "orgánica" necesita de certificación, que normalmente se hace a través de un proceso de inspección que resulta ser engorroso y caro. Por esta razón es pertinente la búsqueda de criterios científicos de discriminación que permitan realizar este procedimiento con mayor garantía y a menor costo. En este trabajo se presentan los resultados obtenidos del análisis espectroscópico hecho a muestras de arroz variedad Combeima (cascarilla y grano blanco), recolectadas de cultivos tratados con técnicas orgánicas y convencionales, usando la técnica fotoacústica resuelta en longitud de onda. También se compararon sus parámetros termofísicos medidos con la misma técnica resuelta en frecuencia. Finalmente, se observó la morfología celular del grano a través de micrografías tomadas con microscopio óptico. Los resultados permitieron determinar diferencias importantes que pueden servir al propósito de la certificación.

PALABRAS CLAVE: Arroz orgánico (Oryza sativa), Difusividad térmica, Espectroscopia fotoacústica, Morfología celular.

1. INTRODUCTION

Currently, much research has been focused on the development of techniques that assure that there is an added value for agricultural products. Those techniques have been developed to promote the food security from a multidisciplinary approach. Rice is one of the products that have been base for this type of studies. These studies focus on the transformation processes of the rice grain after being roasted and ground. Also the use of organic rice growing techniques and the application of the rice husk in the industry of cements and activated carbons have been taken into consideration by other authors [1].

There are several types and levels of regulation for the production and processing of organic products. There is not a unique norm of organic certification on a global level and some countries have their own regulations.

However, the International Federation of Organic Agriculture Movements (IFOAM) and the Codex Alimentarius promote a global certification system. The certifier agency can work according to these general norms, or it may design its own norms to guarantee the characteristics of the origin of the products [2].

The rice crops are distributed in tropical and subtropical regions. The 91% of the global production takes place in Asia; America with 5%; Africa with 3%; and the European and Australian continents with 1% also contribute to the worldwide production. This sowing of rice dates from about 10,000 years ago in many humid regions of tropical and subtropical Asia, but it had his maximum development in China. Therefore, procedures have been studied for improving its quality, since rice is one of the main foods for the population of the planet. It contains carbohydrates, fiber, protein, fat, folic acid, iron, calcium, phosphorus, potassium, sodium, among others [3].

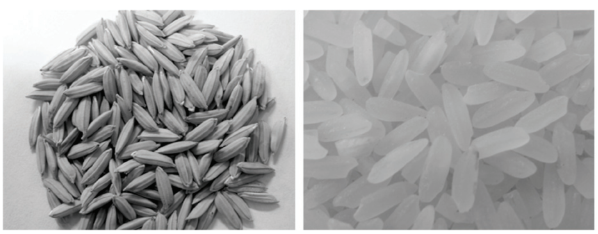

Figure 1. Rice seeds: a) with pericarp and b) without pericarp.

In the agricultural production of rice, the seeds of the plant, namely green paddy rice, are harvested. Its industrial processing includes a drying process of green paddy rice (dry paddy), descaling (threshing), and polishing in order to obtain consumption white rice and its derivatives like: divided rice, rice flour, crushed rice, and rice bran [4].

Figure 1 shows rice with (a) and without pericarp (b), respectively. The pericarp or husk can be reddish brown or violet. It is divided into three layers of cells that are the endocarp, the mesocarp, and the epicarp. The pericarp is known as the lemma or palea according to location in this surface. The rice grain is a caryopsis, which is called brown rice [5].

Transformation processes (roasted and ground) can be efficiently modeled with information about the thermal diffusivity of the raw material [6, 7]. This parameter is related to the speed of heat transference through a material. Therefore, knowledge of thermal diffusivity allows us to establish appropriate times and temperatures during these processes. On the other hand, the absorption spectrum is considered to be a fingerprint for identifying a material. These patterns allow for the comparison of products that have different characteristics. In this work, spectroscopic and thermal diffusivity measurements are reported in order to establish some differences between rice produced with the aid of chemical products and rice produced with the aid of organic fertilizer [8, 9].

2. METHODOLOGY

Paddy rice samples of the *combeima* variety were collected in random way from the municipality of Espinal - Tolima, Colombia, located at 323 m above the sea level, 4° 09' north latitude and 74° 53' to the west; dealt with organic and conventional techniques.

The comparison of the thermophysical parameters, absorption spectra and cellular morphology of the rice husk samples and rice without pericarp according to the type of treatment (synthetic or organic fertilizer) was made in the following way:

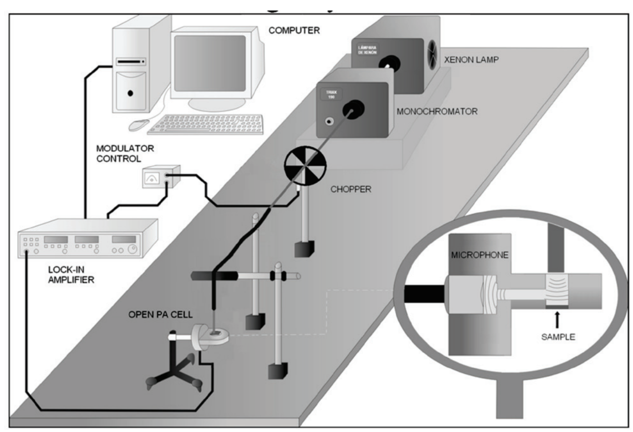

Figure 2. Photoacoustic spectroscopy system. The inset shows how the sample is putted into the cavity of a closed cell.

Photoacoustic spectroscopy (PAS) was used for the determination of pigments present in the sample using the experimental setup described in figure 2. The samples were rice grain powder and rice husk. In the first case, rice was roasted and ground; in the second husk was used without any previous process. The setup consists on a 1000 W Xenon lamp (ORIEL 66924), whose white light is focused onto a monochromator (Jobin Yvon - Pex Triax series 190) input slice after passing through a water filter used to eliminate the IR part of the spectrum that can heats the sample in an unwanted way. The output beam is modulated mechanically at a frequency of 17 Hz, and is led by an optical fiber onto the sample, which is placed within the cavity of a closed photoacoustic (PA) cell. Sample heating due to non-radiative de-excitations generates periodical heating that is transferred to a thin layer of air adjacent to the sample, which produces sound as described elsewhere [10]. For the detection of the acoustic signal an electret microphone was used as a transducer, and finally, this signal was measured using a Lock-in Amplifier (SR830), which uses the modulation frequency as a reference for minimizing the noise from other sources.

The analysis of the recorded PA spectra has been performed using both a first derivative criterion and analysis of variance (ANOVA).

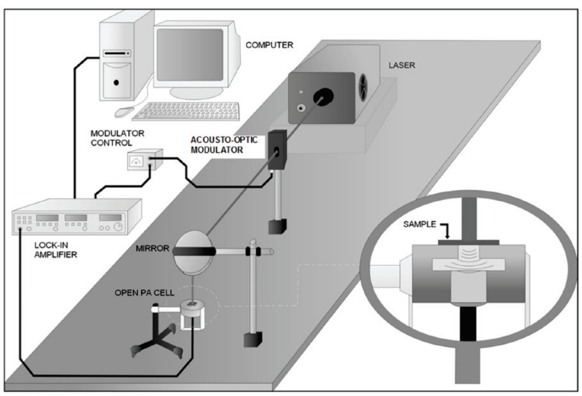

Figure 3. System used for the measurement of thermal diffusivity. The inset shows how the sample is putted on an open PA cell (OPC).

For thermal diffusivity measurement the rice grain samples were cut in disk shape of 600µm thickness and 2mm diameter approximately. The experimental setup is shown in figure 3. Light from an Argon laser (Modu-laser) was modulated in intensity through an acousto-optic modulator; the modulated light beam impinges on the sample, which is placed on an open PA cell (OPC), directly upon the orifice of a common electret microphone [10]. When modulated light is absorbed by the sample, its surface is periodically warmed up, and heat is transported to the gas in the cell generating pressure changes that are detected as sound by the microphone. The resultant signal is measured as a function of the modulation frequency using a lock-in amplifier. From the obtained graph the thermal diffusivity can be obtained straightforwardly using the model of Rosencwaig-Gersho [10, 11].

Finally, rice grains morphology observations were made to examine the cellular structure by means of the cross section of 15 randomly selected samples. The cells coloration with a lugol's solution showed the presence of some polysaccharides like starch and glycogen. This observation was done through micrographs that were taken with an optical microscope. A count of the amount of dyed cells was made taking into account the distribution within the epidermis, endosperm, and the central part of the grain.

3. RESULTS AND DISCUSSION

3.1. Morphology and composition analysis of the rice grain

A lugol's solution was used to dye the rice grain cells and to examine them with the optical microscope. This coloration is frequently used to observe the presence of some polysaccharides like starch and glycogen.

The micrographs of 10 grains showed that the organic rice contains a homogenous distribution of its nutrients. 66.7% of the studied area showed starch presence. From this percentage, 33.3% was in endosperm. This indicates a high amount of polysaccharides in the grain. On the other hand, the samples of conventional rice exhibited heterogeneity in the content of nutrients. In this case, 36.7% of the studied area contained starches in the central part and in the endosperm, and a 26.7% in the epidermis.

In figure 4, the darkness gray spots correspond to homogenous distribution regions where there are polysaccharides [4]. These micrographs were taken on transversal cuts of the organic rice samples from *combeima* variety plants. On the other hand, in figure 5 a non-homogenous distribution of polysaccharides in the endosperm of conventional rice grains of this same variety is observed.

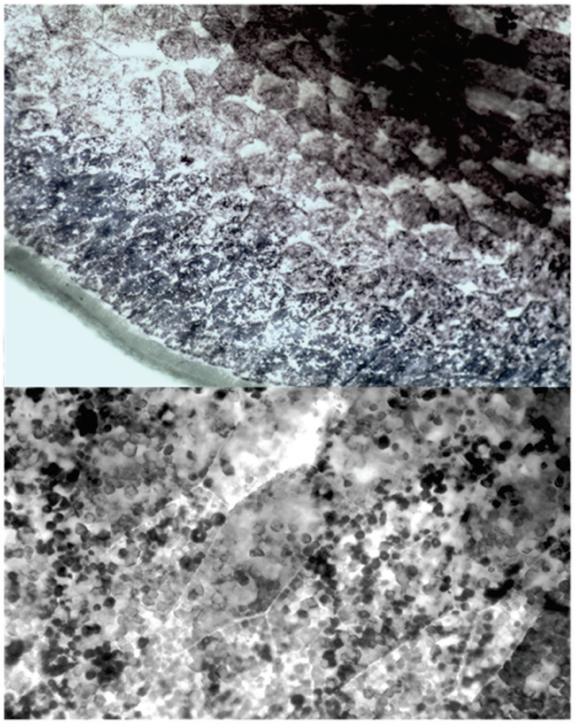

Figure 4. Microphotography with a zoom of a) 10X and b) 40X for a sample of organic rice. Zone with darkness gray corresponds to polysaccharides distribution.

Figure 5. Microphotography with a zoom of 40X, sample of conventional rice. Zone with darkness gray corresponds to polysaccharides distribution.

3.2. Thermal diffusivity of the rice husk

The curves of PA signal amplitude as a function of the light modulation frequency were fitted to the Eq. (1) predicted by the Rosencwaig-Gersho model for opaque and thermally thick samples [12].

$$S = S_0(\omega)\exp j\left[-\frac{\pi}{2}\arctan\left(\frac{\tan\left(f/f_C\right)}{\tanh\left(f/f_C\right)}\right)\right] \qquad (1)$$

Here $f_c=\alpha/(\pi l^2)$ is the frequency for which the thermal diffusion length equals the sample thickness, l. This parameter, called the "cut-off frequency" was taken as a fit parameter. From it the thermal diffusivity is determined if the thickness is well known. In table 1 are shown the average values from measurements performed in seven rice grains.

From these results one can see that the thermal diffusivity of organic rice has a lower value than the one corresponding to conventional rice. This behavior can be related to the nutrients distribution observed and also to possible chemicals inoculation in the grain of plants cultivated in a conventional way.

Table 1. Values of thermal diffusivity (α), cut-off frequency (f_c), and sample thickness (l) for conventional and organic rice of the *combeima* variety.

Rice sample	f_c ± 0,02 (Hz)	l ±0,0004 (cm)	α ± 0,001 (cm^2/s)
Organic	0,58	0,0615	0,007
Conventional	0,91	0,0610	0,011

3.3. Spectroscopic study of the rice husk

The samples of husk and powder rice were located in the cavity of a closed PA cell. The sample was optically opaque (the optical penetration depth $\mu_\beta=1/\beta$, where β is the optical absorption coefficient, was much smaller than the sample´s thickness, l ($\mu_\beta \ll l$). For biological samples the thermal diffusivity is in general lower than 0.03 cm^2/s and its extinction coefficient is high ($10^4 \leq \varepsilon \leq 5x10^4$ $mol^{-1}cm^{-1}$). This allows to affirm that the measurements can be performed in the optically opaque and thermally thick sample regime for which: $\mu_S \ll l$, and $\mu_S \ll \mu_\beta$, where $\mu_S=(\alpha/\pi f)^{1/2}$. In this regime, in agreement to the Rosencwaig-Gersho model [11], the complex PA signal is directly proportional to the sample optical absorption coefficient, β, and therefore to the absorbance of the sample. This can be expressed in the following way:

$$Q = \frac{j\beta\mu_S\mu_g}{2}\left(\frac{\mu_S}{k_S}\right)Y \qquad (2)$$

Where, Q is the envelope of the sinusoidal pressure variation, which is produced by the PA effect. The subscripts s and g correspond to solid sample and gas in the cell, respectively; k is the material thermal conductivity; and Y is a constant factor. The amplitude and phase of this complex amount are proportional to the optical absorption coefficient and are respectively given by [13]:

$$S = \sqrt{Q^2{}_{real} + Q^2{}_{imag}} \qquad (3)$$

$$\phi = \arctan\left(Q_{imag}/Q_{real}\right), \qquad (4)$$

A spectroscopic study for rice husk samples from conventional and organic crop was made in order to study possible pigmentation changes. The spectra were the result of measuring average for ten samples, which were chosen randomly. The differences in the form of the spectra were quantified using the first derivative criterion and ANOVA [12].

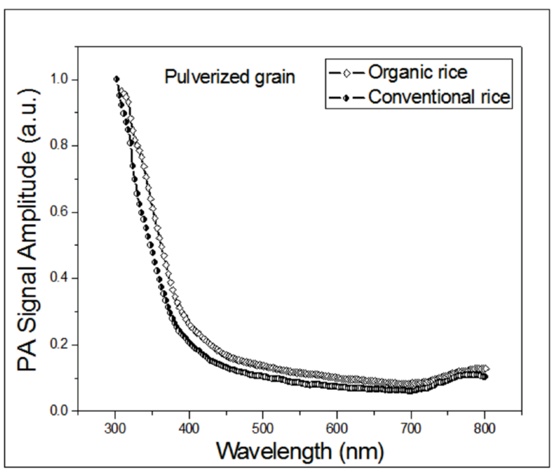

Figure 6. PA absorption spectra for samples of conventional and organic rice, after being ground. Empty squares symbols correspond to organic sample, while open circles correspond to a conventional sample.

The spectra of ground rice from roasted and non-roasted samples are showed in figures 6 and 7, respectively. In these results are not observed significant differences in the light absorption behavior according to the type of the applied fertilizer in the cultivation. This indicates that the samples have similar pigments distribution.

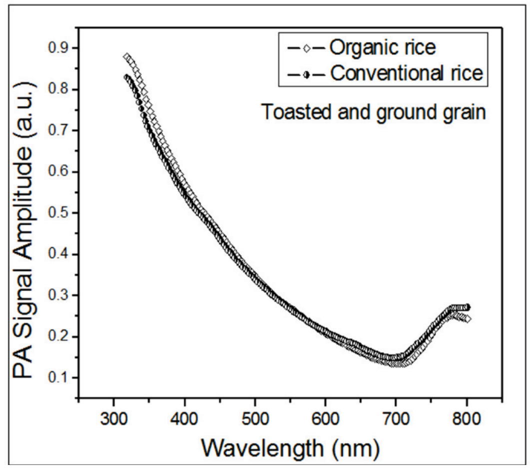

Figure 7. PA absorption spectra for samples of conventional and organic rice after roasting and ground process. Empty squares and open circles correspond to organic and conventional sample respectively.

The resolved-wavelength PA signal amplitudes in figure 8 correspond to the pericarp (husk) of the organic and conventional sample. These spectra show a wide absorption center situated between 320 and 380 nm that is related to the capsaicin presence; and other one, between 380 and 458 nm corresponding to the presence of β-carotene, lutein, violaxanthin and neoxanthin, with a maximum intensity value in 411 nm attributed to the absorption of the capsorubin pigment. A considerable difference between derivative of both spectra in the ranges 320-430 nm and 450-670 nm can be seen from figure 9. The absorption center in the infrared region above 720 nm can be related to the morphologic structure of the sample. This behavior is the same for the two considered kinds of samples.

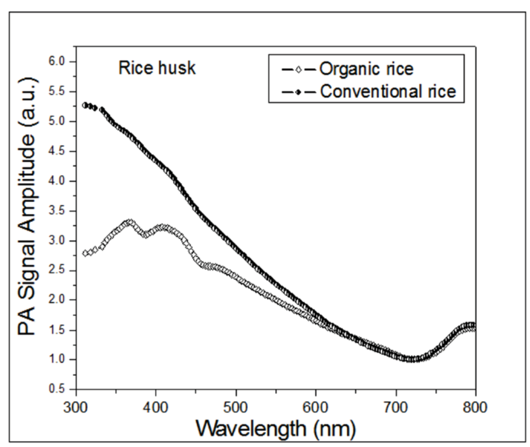

Figure 8. PA absorption spectra for husk samples of conventional and organic rice. Empty squares correspond to organic sample, while semi-full circles correspond to conventional sample.

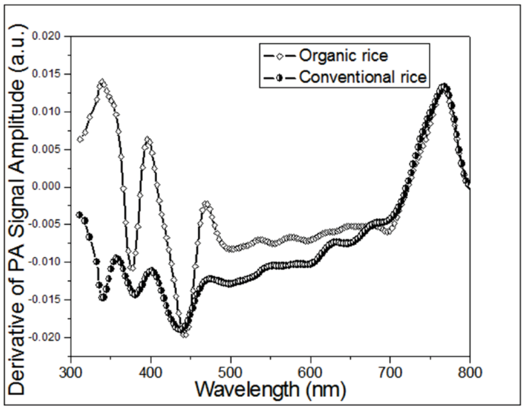

Figure 9. Derivatives of PA absorption spectra amplitude. Empty squares correspond to organic sample, while semi-full circles correspond to conventional sample.

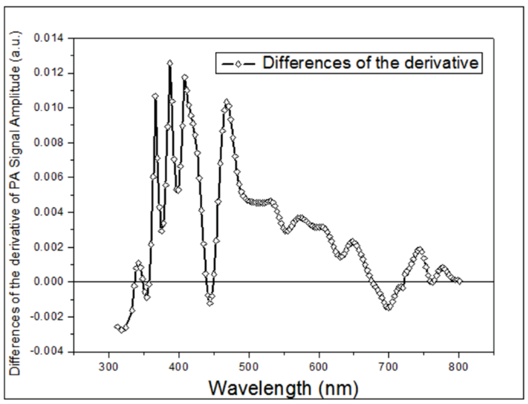

Figure 10. Subtraction of the PA absorption spectra derivative for husk samples of conventional and organic rice.

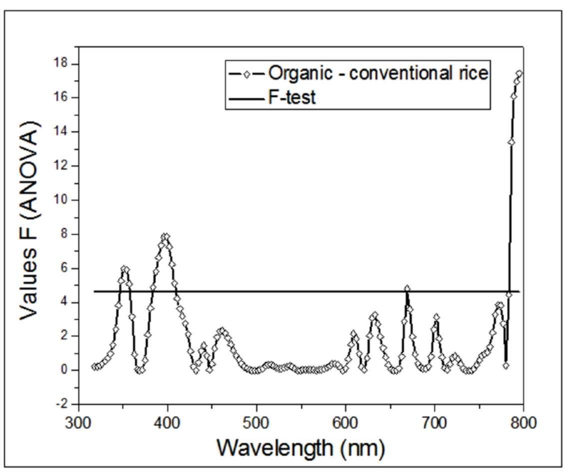

Figure 11. Analysis of variance (ANOVA) between PA spectra of organic and conventional rice husk.

In figure 10, the difference between the spectra for the organic and conventional samples of rice husk is evidenced through subtraction of PA signal amplitude derivatives. Maxima in this curve indicate the wavelength values for which light absorption by pigments is better resolved for organic rice husk. It is probably due to a less homogenous distribution of pigments in the conventional sample.

In figure 11 the ANOVA for the rice husk spectra shows significant differences between the organic and conventional treatments. The F-test was 4.6 according to Fisher distribution with a significance level of 5% [14]. This curve corresponds to the theoretical determined F for each wavelength. The ranges 348 to 356 nm, 383 to 408 nm and 786 to 795 nm have a theoretical F greater than that of the F-test. Therefore, the null hypothesis is rejected, assuring a significant difference in these wavelength ranges.

3. CONCLUSIONS

The differences in microphotographies and thermal diffusivity values of the rice according to type of growing treatment demonstrated the homogenous distribution of the nutrients and pigments in the organic rice. Thermal diffusivity was approximately 40% lower for the organic samples.

The apparent presence of starch was almost two times higher in organic rice that in conventional sample. These results can be explained by different internal distribution of components evidenced in micrographs.

It was possible to identify certain characteristics of the rice growing with organic techniques through PAS, when the presence of rice pigments such as capsaicin, β-carotene, lutein, violaxanthin and neoxanthin are considered. From the criteria of the first derivative and the analysis of variance important differences in the form of PA spectra corresponding to the cultivated samples with both types of treatment were determined.

According to spectroscopy results, both conventional and organic rice have similar pigments content. However, the spectra corresponding to husk show different pigments distribution in each case. Capsaicin and capsorubin were specially identified in husk of organic rice around 360 and 411 nm, respectively; which characterizes the origin of the sample.

These results guarantee the use of PA technique as a tool that would allow discrimination of rice growing by organic practices. On the other hand, the study of the physical properties of the rice grain and the rice husk opens the way to future applications of this raw material in transformation processes.

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