Effect of Relative Humidity on the Antioxidant Activity of Spray-Dried Banana Passion Fruit - Coated Pulp: Measurement of the Thermodynamic Properties of Sorption

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Effect of Relative Humidity on the Antioxidant Activity of Spray-Dried Banana Passion Fruit - Coated Pulp: Measurement of the Thermodynamic Properties of Sorption

Shortened version of the title: Properties of Sorption of Spray-Dried Banana Passion Fruit Pulp.

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Abstract

The antioxidant activity of the spray-dried banana passion fruit – coated pulp with maltodextrin 10 DE was evaluated throughout 30 days of storage at a temperature of 25 °C for different relative humidity values. The antioxidant activity of spray-dried banana passion fruit pulp was influenced by the relative humidity throughout the 30 days of storage. In addition, the sorption equilibria of water for spray-dried banana passion fruit - coated pulp with maltodextrin 10 DE at 25, 35, 45 and 55 °C, over a range of relative humidity levels, from 0.113 to 0.843, was determined using a gravimetric static method. The isosteric heat and Gibbs free energy were calculated from the sorption equilibrium. The Guggenheim-Anderson-de Boer (GAB) and Brunauer-Emmett-Teller (BET) models were tested to fit the experimental data. The GAB model was found to be the most suitable for describing the sorption curves, exhibiting an error smaller than 10% and an *r* greater than 0.99. The monolayer moisture content values for the sorption at different temperatures that were calculated using the GAB model ranged between 0.05315 to 0.05716 g water / g dry matter. The sorption curves exhibited a Type III behavior. The isosteric heat decreased with increasing moisture content, while the Gibbs free energy increased.

Keywords: Spray-dried banana passion fruit, antioxidant activity, sorption equilibrium, thermodynamic properties.

Introduction

Colombia boasts a large number of underexploited native and exotic fruits that are of potential interest to the agroindustry and that constitute a promising source of income for the local population (Contreras-Calderon et al., 2010). These fruits represent an opportunity for local farmers to gain access to special markets, where the consumers recognize the value of the exotic character of the fruits, e.g., the presence of bioactive compounds useful in the prevention of degenerative diseases (Alves et al., 2008).

Several epidemiological studies indicate that a diet rich in fruits delays the aging process and reduces the risk of various lifestyle diseases, especially cardiovascular diseases and cancer, as well as other disorders such as Parkinson's or Alzheimer's disease, rheumatoid arthritis, pulmonary diseases lung diseases and cataracts. Compounds responsible for this protective effect are phytochemicals, such as polyphenols, carotenoids, vitamin C and tocopherols, with antioxidant properties due to the scavenging of reactive oxygen species (ROS) (Rice-Evans et al., 1996). The Passiflora family of fruit, in particular, banana passion fruit, has shown high phenolic content and excellent antioxidant capacity (Vasco et al., 2008). Banana Passion Fruit has large amounts of phenols, tannins and flavonoids, and an excellent ability to trap ROS, such as hydroxyl, superoxide and peroxyl radical (Rojano et al., 2012). However, fruits are quite perishable due to their high water content, because the majority of chemical and microbiological reactions occur in water.

Many methods have been implemented to extend the shelf life of perishable fruits and vegetables and maintain their nutraceutical properties, such as the antioxidant activity. One of these methods is spray drying, which is the transformation of material from a fluid state into a dried particle form by spraying it through a hot drying medium. This method is widely used in both food and pharmaceutical manufacturing processes. This technique can provide products with the following benefits: stability, ease of handling, ability to be transformed into reconstituted products with properties similar to the original juice, the ability to be used as food supplements and a long shelf life at normal temperatures (Gabas et al., 2009). However, drying processes that are subjected to the fruit juice and during storage and conditions such as humidity and time generate physicochemical changes. The antioxidant activity is an important indicator of these changes (Gutierrez et al., 2007; Aguayo et al., 2010).

For heat and mass-transfer processes, knowledge of equilibrium data (sorption isotherms) and thermodynamic properties of adsorption (isosteric heat and Gibbs free energy) between the environment and food are essential in the successful applications of food science and technology (Comaposada et al., 2000). Therefore, sorption isotherms, isosteric heats of sorption and the Gibbs free energy are important parameters in the design and modeling of sorption and drying processes, food engineering and industrial quality control, predictions of the useful life and the storage stability of food (Lahsasni et al., 2003; Mulet et al., 2002).

The isotherms, isosteric heat and the Gibbs free energy of sorption provide information about sorption mechanisms and interactions between the components of food and water. Specifically, these values are used in the determination of the final moisture content of a product and in the calculation of the energy required during the operation of the drying unit (Gabas et al., 1999).

In the literature, numerous mathematical models that describe the sorption behavior of water in food had been reported (Belghit and Bennis, 2009; Iglesias and Chirife, 1982). Several of these models are based on theories of sorption mechanisms, while others are purely empirical or semi-empirical (Aviara et al., 2002). The most appropriate model must be selected by how well it fits the experimental data and its physical meaning. The model of Guggenheim, Anderson and Boer (GAB) (Van der Berg, 1984) and the model of Brunauer, Emmet and Teller (BET) (Brunauer et al., 1940) are the most popular of these models, due to their solid theoretical basis (Rahman, 1995; McMinn and Magee, 1999).

In this study, we report for the first time, thermodynamic properties of sorption and any changes in the antioxidant activity of stored spray-dried banana passion fruit coated-pulp in relation to the relative humidity.

The main objectives of this study were to address the following:

- Evaluate the effect of the relative humidity levels on the antioxidant activity of spray-dried banana passion fruit.
- Determine the effect of temperature on sorption isotherms of spray-dried banana passion fruit pulp in the temperature range of 25 - 55 °C.
- Analyze two sorption isotherm models available in the literature (GAB and BET).
- Find the most suitable model corresponding to the isotherms of the spray-dried banana passion fruit pulp.
- Compute the isosteric heat and the Gibbs free energy from the sorption equilibrium.

Materials and Methods

Materials

Banana passion fruit

Samples of banana passion fruit with no apparent physiological damage was purchased from a local market and was selected at random to ensure harvest maturity. The samples were washed in chlorinated water (100 ppm active chloride) and pulped. The pulp was stored at 4 °C until the analysis was performed.

Spray-dried banana passion fruit pulp

Before the spray-drying process, coat material (maltodextrin 10 DE) was added directly to the pulp and brought to complete dissolution using a magnetic stirrer bar. 700 g of pulp were mixed with 300 g of Maltodextrin 10 DE with constant agitation. The resulting preparation was homogenized with an Ultra-Turrax Brand: IKA-WERK © instrument operating at 10000 rpm for 5 min. The mixture was then fed to the spray dryer (B191 model, Büchi, Flawil, Switzerland). The inlet air temperature was 170 ºC, and the outlet air temperature varied from 91 °C to 102 ºC for each sample. The spray speed was 22000 rpm.

Static gravimetric method (sorption isotherms)

Dry samples were used in the sorption experiments. The samples were analyzed using the static gravimetric method to obtain the sorption isotherms at 25, 35, 45 and 55 °C. The method involves the determination of the equilibrium moisture content of the spray-dried banana passion fruit pulp at different water activities for each of the temperatures evaluated.

Eight saturated salt solutions were prepared (LiCl, CH_3COOK, $MgCl_2$, K_2CO3, NaBr, $NaNO_3$, NaCl and KCl) over a range of water activity between 0.113 and 0.843. The saturated salt solutions were selected to mimic different levels of relative humidity, over the range of 0.113–0.843, at different temperatures.

The samples of spray-dried banana passion fruit pulp were placed into eight containers with different saturated salt solutions and stored in a temperature-controlled cabinet at the selected temperatures with an accuracy of 1°C (Kaymak-Ertekin and Saltanoglu, 2001). The samples were weighed periodically until equilibrium in the weight was attained. Equilibrium in the weight was defined as the point at which the difference in weight between three consecutive measurements did not exceed 0.001 g.

Stability during storage

For the storage stability tests, once the samples achieved equilibrium, they were removed and analyzed by measuring the antioxidant activity and phenolic content. The control samples were stored for 30 days under different relative humidity conditions before being subsequently removed and analyzed. All of the experiments were performed at 25 °C.

Mathematical model

Several models have been used in the literature to describe the sorption isotherms of water vapor in the foods (Lopes-Filho et al., 2002). In this paper, two models for describing the sorption equilibrium of spray-dried banana passion fruit pulp were selected.

The following models were selected from the literature: the GAB and BET models (see Equations 1 and 2).

BET:

$$X = \frac{X_m \cdot \alpha \cdot \mathrm{Aw}}{(1-\mathrm{Aw}) \cdot [1+(\alpha-1) \cdot \mathrm{Aw}]} \tag{1}$$

The GAB model has been widely used to correlate the experimental data of equilibrium sorption of food due to its theoretical basis. This model is a modification of the BET model. The GAB model is described by the following expression:

GAB

$$X = \frac{\alpha \cdot X_m \cdot K \cdot \mathrm{Aw}}{(1\text{-}K \cdot \mathrm{Aw}) \cdot [1+(\alpha-1) \cdot K \cdot \mathrm{Aw}]} \tag{2}$$

where X is the equilibrium moisture content; X_m is the moisture content (dry basis) for the monolayer; A, B and C are the fitting parameters for each of the models and T is the equilibrium temperature. K is a constant related to the effect of temperature (see Equations 3 and 4).

$$K = K_0 \exp\left(\frac{\Delta H_K}{RT}\right) \quad \text{where} \quad \Delta H_\alpha = H_m - H_n \tag{3}$$

$$\alpha = \alpha_0 \exp\left(\frac{\Delta H_\alpha}{RT}\right) \quad \text{where} \quad \Delta H_k = L_T - H_n \tag{4}$$

where ΔH_k, ΔH_α and heat are functions of the water sorption: $\Delta H_\alpha = H_m$ - H_n and $\Delta H_k = L_T$ - H_n. In the above equations, K_0 is a constant adjusted for the temperature and H_m and H_n are the heat of sorption of a monolayer and a multilayer, respectively. Finally, L_T is the latent heat of vaporization of pure water.

Thermodynamic properties of sorption

The sorption isosteric heat energy is dissipated during sorption (Cortes et al., 2009; Cortes et al., 2010a; Cortes et al., 2010b) and can be calculated based on the balance established between the condensed and gas phases using the Clapeyron equation for equilibrium sorption. This property is expressed thermodynamically as follows:

$$Q = \left(\frac{v_n}{v_g} - 1\right)\overline{R}Z\left(\frac{\partial \ln P}{\partial\left(1/T\right)}\right)_X = H_g - \overline{H_n} \qquad (5)$$

where P and T are the pressure and equilibrium temperature, respectively. R is the constant in the equation of state of the assessed gas, Z is the compressibility factor ($Z = 1$ for an ideal gas and $Z \neq 1$ for a real gas), and v_n y v_g denotes the partial volume of the adsorbed species and the stage gas. H_g and $\overline{H_n}$ are the molar enthalpy of the gas phase and the molar enthalpy of the adsorbed phase, respectively. Neglecting the molar volume of the condensed phase and the gas phase and assuming ideal gas behavior yields the Clausius-Clapeyron (see Equation 6).

$$Q = -R \cdot \left(\frac{\partial \ln \mathrm{Aw}}{\partial\left(1/T\right)}\right)_X = H_g - \overline{H_n} \qquad (6)$$

The isosteric heat obtained by the Clausius-Clapeyron equation is independent of the temperature and pressure and is calculated based on the slope of a straight line (isosteric) in the plot of the relationship “ln Aw” vs. “$1/T$”. From a set of isosteric or experimental data for phase equilibrium between the food and water vapor, it is possible to fully describe the sorption equilibrium and evaluate the isosteric heat of sorption using equation 6. Based on the analogies between the processes of adsorption and condensation, the relationship between adsorption potential and the ambient pressure is inferred through the changes of Gibbs free energy based on the Polanyi theory (Polany, 1916). This relationship assumes the thermodynamic behavior of the adsorbed phase to be identical to the condensed phase; therefore, it is also known as the condensation approximation (see Equation 7).

$$\Delta G = \overline{R}T \ln\left(\frac{P}{P_s}\right) = -A \qquad (7)$$

where P_s is the saturation pressure, A is the molar work of sorption, which is a function of temperature, saturation and equilibrium pressure. ΔG is the Gibbs free energy.

Total phenolics and antioxidant activity

The extracts were obtained according to the method described by Kuskoski et al., (Kuskoski et al., 2005). 5.0 g of each dried sample were weighed in centrifuge tubes and extracted sequentially with 25-ml tri-distilled water at room temperature for 1 h. The tubes were centrifuged at 4000 rpm for 20 min, and the supernatant was recovered and stored at -20°C for the analysis.

FRAP assay

The antioxidant capacity of the phenolic extracts of spray-dried banana passion fruit pulp was estimated according to the procedure described by Benzie and Strain (Benzie and Strain, 1996), with some modifications. This method is based on the increase in absorbance due to the formation of 2,4,6-tripyridil-*s*-triazine (TPTZ)-Fe (II) in the presence of reducing agents. The FRAP reagent contained 2.5 mL of 10 μM TPTZ in 40 mM HCl. $FeCl_3$ (2.5 mL of 20 μM) and acetate buffer (25 ml of 0.3 μM, pH 3.6) were freshly prepared and warmed to 37 °C. A volume of 50 μl of extract were mixed with 950 μl FRAP reagent already dissolved in acetate buffer (pH 3.6). The absorbance increase was measured at 590 nm. The FRAP values were expressed as AEAC (ascorbic acid equivalent antioxidant capacity: mg ascorbic acid per 100 g dry powder) using an ascorbic acid standard curve (Rojano et al., 2008).

Total phenolic

The total phenolic content was determined according to the adapted Folin–Ciocalteu method (Singleton and Rossi, 1965). The extracts (50 μL) were mixed with 125 μL of Folin–Ciocalteu reagent and 400 μL of sodium carbonate solution (7.1 % p/v), and the resulting solution was brought to a final volume of 1000 μL. The mixture was stirred and stored at room temperature for 30 min in the dark. The absorbance was measured at 760 nm against a blank. Aqueous solutions of gallic acid were used for calibration. The results are expressed as g gallic acid equivalents (GAE)/100 g dry powder.

Statistical analysis

The identification of the parameters of each of the models was performed using the generalized gradient optimization method. The objective function was selected to minimize the differences between the experimental and theoretical moisture. The quality of the fits of the models used was evaluated using the results of the correlation coefficient (r) and the mean square error ($RME\ \%$).

$$RME\,\% = \frac{100}{n} \cdot \sum_{1}^{n} \left| \frac{X_{\exp} - X_{cal}}{X_{\exp}} \right| \qquad (8)$$

where $X_{\exp}$ and X_{cal} are the experimental and calculated moistures, respectively, and n is the number of observations. In the antioxidant methods, the tests were performed in triplicate, and the data are represented as the means ± the standard deviations.

All the experiments on antioxidant activity were performed four times. The data are presented as the mean ± the standard error and were processed by one-way analysis of variance (ANOVA). Multiple comparisons of the means were performed using Duncan's New Multiple Range Test ($p < 0.05$). All of the statistical analysis was performed using the Statgraphics Centurion V statistical package for Windows.

Results and discussion

Sorption isotherms fitted with models

Figure 1 shows the experimental isotherms for spray-dried Banana Passion Fruit pulp at 25, 35, 45 and 55 °C. The range of water activities was between 0.113 and 0.843, and the humidity at equilibrium was between 0.027 and 0.296 (g water/g dry).

[Figure 1 near here]

In addition, the isotherms shift to the right with an increase in the storage temperature, which indicates that the adsorbed water amount decreases as the temperature increases. In general, other investigators have also reported this phenomenon; at higher temperatures the water molecules are activated at energy levels that allow the breaking of their adsorption sites. If the water activity is maintained at a constant level, the temperature increase weakens the interaction between the pair of adsorptive molecules, causing a decrease in the amount of water retained. (Palipane and Driscoll, 1992). It is important to determine the effect of temperature on the amount of water adsorbed by food matrices, because the food is exposed not only to humidity but also to a specific range of temperatures during storage and processing, both of which can cause physicochemical and microbiological changes.

All of the sorption isotherms exhibited type III behavior; according to the classification recommended by the International Union of Pure and Applied Chemistry (IUPAC), this behavior occurs in macroporous materials, when there is little affinity between the adsorbate and adsorbent and the interactions between the adsorptive couple are weak, which mainly leads to a coating of several layers of water, and a reduced value of the monolayer (Mathlouthi and Roge, 2003). Most of the sorption isotherms exhibited a plateau at high Aw values, indicating saturation of all binding sites in the adsorbent material and hence cessation of the adsorption phenomenon. However, Type III isotherms are particular to products that contain mostly water-soluble components, such as sugars, organic acids, amino acids and salts (Rahman, 1995) because these components are likely to leach at high water activity levels (> 0.8). Initially, the polymers experience swelling, followed by rupture and leaching (Maskan and Gogus, 1997). These water-soluble components, particularly sugars, first form a compact crystalline structure, but then undergo leaching and transform into an expanded amorphous state, which causes an increase in the number of adsorption sites, thereby allowing them to continue to attract water, even in high humidity conditions. This transformation has been validated by several studies with fruit pulp and sugar-rich products, including potato and pineapple (Yanniotis and Zambouits, 1996; Rao and Rizvi, 1995; Kaymak-Ertekin and Gedik, 2004). The sorption isotherms were modeled using the BET and GAB models for each of the temperatures. The parameters identified for the isotherms are presented in Table 1 and 2 and the calculated curves are shown in Figure 2.

[Table 1 near here],

[Table 2 near here],

[Figure 2 near here],

The quality of the fit was evaluated using the linear correlation coefficient (*r*) and the mean square error (*RME %*). The BET and GAB models exhibited a percentage error (% RME) of less than 10% and *r* greater than 0.99 for the four temperatures. Although both models adjusted the experimental data, the GAB model better describes the relationship between the equilibrium moisture content and relative humidity in the spray-dried banana passion fruit for all the temperatures. This result corroborates the information on the utility of the GAB model in powder food (Gálvez et al., 2006; Toloba et al., 2004). The monolayer value (Xm), one of the parameters determined by the models, is a measure of the availability of active sites in the material for absorbing water. Determining the value of Xm is of particular interest because it indicates the amount of water that is strongly adsorbed on specific sites of the surface of the food. By determining the optimum value of Xm to ensure the stability of food, the "water linked" value can predict the useful life of a food product; unlike the overall water content, this water fraction is capable of keeping food safe.

Both models determined that for spray-dried Banana Passion Fruit pulp, the monolayer value (Xm) is in the range of 0.045 and 0.057 g water / g dry matter. The values obtained for the monolayer using the GAB equation were higher than those obtained using the BET equation. Similar results have been reported by other authors for dried foods, such as grains, corn and flour, and both models offer a good approximation for Xm (Sopade and Ajisegiri, 1994; Timmermann et al., 2001).

The moisture content of the monolayer exhibited a tendency to decrease with increasing temperatures over the range from 25 to 55 °C. This behavior reflects the decreases in the interaction force between the adsorptive couple at higher temperatures, which facilitates the tendency of water to leak absorption sites to the minimum value of Xm (Garcia-Perez et al., 2008; Westgate et al., 1992).

The interpretation of the parameters α and K are useful in understanding the moisture sorption behavior in any material. α is defined as the ratio between the heat of sorption of the first molecule adsorbed on a site (Hm) and the heat of sorption of the adsorbed molecules beyond the first molecule. In the multilayer, Hn is the natural enthalpy (Quirijns et al., 2005). K provides a measure of the interactions between the water molecules with the adsorbent multilayer. When K approaches one, there is no distinction between the multilayer molecules and molecules of pure liquid, as water molecules beyond the monolayer are not structured in a multilayer (Perez-Alonso, 2006); as a result, the sorption behavior is reduced to a monolayer and can be well modeled by the BET equation (Sobral et al., 1999). The values of α and K obtained using the models were between 2.6820 to 4.6462 and 0.9723 to 0.9738, respectively. Both parameters exhibited values close to 1, indicating a reduced value of the monolayer and multilayer molecules that exhibit characteristics of pure water molecules, which are prevalent in the multilayer adsorption.

Thermodynamic properties

The isosteric heat was obtained from the isostere slope for different humidity levels at equilibrium. The different isosteric values were derived from the experimental sorption isotherms at 25, 35, 45 and 55 °C. The isosteric heat values based on the equilibrium moisture of the product are shown in Figure 3.

[Figure 3 near here]

The isosteric heat of adsorption decreases exponentially as the moisture content increases. For a moisture content above 0.1 g / g dry matter, the isosteric heat falls in line with the heat of vaporization of pure water. By increasing the moisture content, higher activity sites are occupied and the absorption occurs in the lower activity sites, giving rise to a lower heat of sorption.

The water layers formed above the first layer, exhibit weak binding forces because they are not directly on the surface of the food molecule; thus, this is the portion of water that is available to be easily removed by heating or drying (Ajibola et al., 2003). When the water content is excessive, multilayer molecules exhibit characteristics similar to pure water molecules, and the isosteric heat of adsorption reduces the enthalpy of vaporization of water.

In this study, when the moisture content of the spray-dried Banana Passion Fruit pulp was close to the value of the monolayer, it was necessary to apply an amount of energy of approximately 400 J / g dry base, i.e., the additional heat of vaporization of pure water to dry the product, representing a significant amount of energy expenditure.

For low levels of moisture, adsorption occurs mainly in the monomolecular layer of the food, where the sorption sites tend to be more active in generating strong attractions. This first fraction of water is known as the monolayer, and it is directly related to the food components, thereby preventing diffusion and mobility. Removal of this monolayer requires large amounts of energy (Badui, 2006).

The isosteric heat magnitude and behavior as a function of moisture content are consistent with the behavior reported by several authors for powdered foods, including wheat semolina, and starch, and dehydrated foods, such as raisins, figs, prunes, and apricots (Erbas et al., 2005; Al-muhtaseb et al., 2004; Telis et al., 2000).

The Gibbs free energy is a criterion that defines the status of feasibility and spontaneity of thermodynamic processes, i.e., if a system naturally tends to undergo changes (Bulow, 2007). Figure 4 shows the variation of the Gibbs free energy of spray-dried Banana Passion Fruit pulp at different water activities. The Gibbs free energy increased from negative values to zero, which means that adsorption is a spontaneous and exothermic process.

[Figure 4 near here]

Effects of A_w on antioxidant activity during storage

Dry samples were equilibrated and stored at eight Aw levels, ranging from 0.114 to 0.843 at 25 ° C for 30 days. Table 3 shows the changes in the antioxidant activity expressed as FRAP and the total phenolic content.

[Table 3 near here],

The antioxidant activities of spray-dried Banana Passion Fruit pulp at different water activities determined by the FRAP assay ranged between 4845.92 and 7783.90 mg ascorbic acid equivalents /100 g dried powder, and the total phenol content varied between 4067.66 and 7083.56 mg gallic acid equivalents /100 g dried powder. In the Aw range between 0.114 and 0.843, the FRAP values and the phenolic content exhibited statistically significant differences. In general, both the antioxidant capacity and the phenolic content decreased as the relative humidity increased from 11.3 to 68.0%; above these values, the antioxidant properties improved, up to a maximum value of 84.3% humidity (Figure 5 and 6). The results indicated that the critical relative humidity range is 57.6 - 75.3%.

[Figure 5 near here],

[Figure 6 near here],

Conservation in antioxidant capacity coincides with the transition of the sample from a glassy state to a rubbery state. Most amorphous powders possess a conversion point that indicates a thermodynamic pseudo-transition from solid (glassy) to liquid (sticky) by heat and moisture (Roos and Karel, 1991). Under storage, this type of food is likely to become sticky.

Food is a multiphase material that may undergo phase changes in the range of temperatures or pressures in which it is processed, stored or consumed. The temperature at which the material becomes gummy and acquires certain elasticity is known as the glass transition temperature (Tg). The glass transition temperature of food is generally high, but decreases with increasing water content. The water in the food acts as a plasticizer, separating chemical bonds between chains and facilitating movement of the material. The plasticization results in physical and chemical changes in low moisture foods. These physical changes, such as stickiness and collapse, are related to the product behavior against certain stresses or strains, while the chemical changes reflect the speed with which some degradation reactions occur: non-enzymatic browning, loss of metabolites and lipids oxidation, enzymatic reactions, etc. (Bhandari et al., 1997; Ling et al., 2005; Telis and Martinez-Navarrete, 2009). These changes affect the sensory quality of food and can determine the processing and storage conditions.

In spray-dried Banana Passion Fruit pulp, the rubbery state transition not only had an impact on the physical structure but also exhibited a reduction in the degradation of the phenolic compounds and the consequent preservation of antioxidant activity. In the collapse (sticky side) of the powder, which occurred for relative humidity values greater than or equal to 57.6%, a decrease occurred in the micropores through which oxygen can enter the core of the food matrix of the samples, which resulted in reduced oxidation of the metabolites responsible for the antioxidant activity (total phenols, total flavonoids, condensed tannins, ascorbic acid and B-carotene).

In the collapsed foods, a physical impediment to the diffusion of oxygen contained in the water exists, and in the absence of this oxygen, the antioxidants are more stable metabolites. The porosity effect can be important in diffusion-controlled reactions, such as oxidation, where the movement of reagents may occur in the pores more easily than in the rest of the solid matrix. The collapse results in the loss of some of the desirable qualities, such as the appearance of the product (Bhandari et al., 1997). However, previous studies have shown that the collapse of food matrices can reduce the rate of decay reactions because a decrease in the porosity of the matrices reduces the diffusion of oxygen (water).

To evaluate the internal structure of the samples subjected to different humidity conditions and evaluate the porosity, a visual analysis was performed by scanning electron microscopy (SEM). Figure 7 compares the micro surface of the spray-dried Banana Passion Fruit pulp stored at different values of relative humidity. Samples stored at relative humidity levels below or equal to 57.6% exhibit porous and rough surfaces, whereas samples stored at relative humidity levels higher than 57.6% exhibit soft and smooth surfaces.

[Figure 7 near here],

Conclusion

The behavior described by all the sorption isotherms for spray-dried Banana Passion Fruit pulp at 25, 35, 45 and 55 ° C was type III, which is particular to products containing mostly water soluble components, such as sugars. The GAB model best describes the relationship between the equilibrium moisture content and relative humidity for curuba powder. The isosteric heat of adsorption decreased exponentially with the increase of moisture content. For moisture contents above 0.1 g / g dry base, the isosteric heat falls in line with the heat of vaporization of pure water. The ΔG was negative, which means that the process of adsorption of water is a spontaneous reaction. The storage humidity and the moisture content critical for spray-dried Banana Passion Fruit pulp was 43.8 - 68.0% and 0.1072 and 0.1401 g / g dry base, respectively. The glass transition is a crucial phenomenon in the conservation of the antioxidant activity of spray-dried Banana Passion Fruit pulp.

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Figure 1. Experimental sorption isotherms for spray-dried Banana Passion Fruit pulp at 25, 35, 45 and 55 °C.

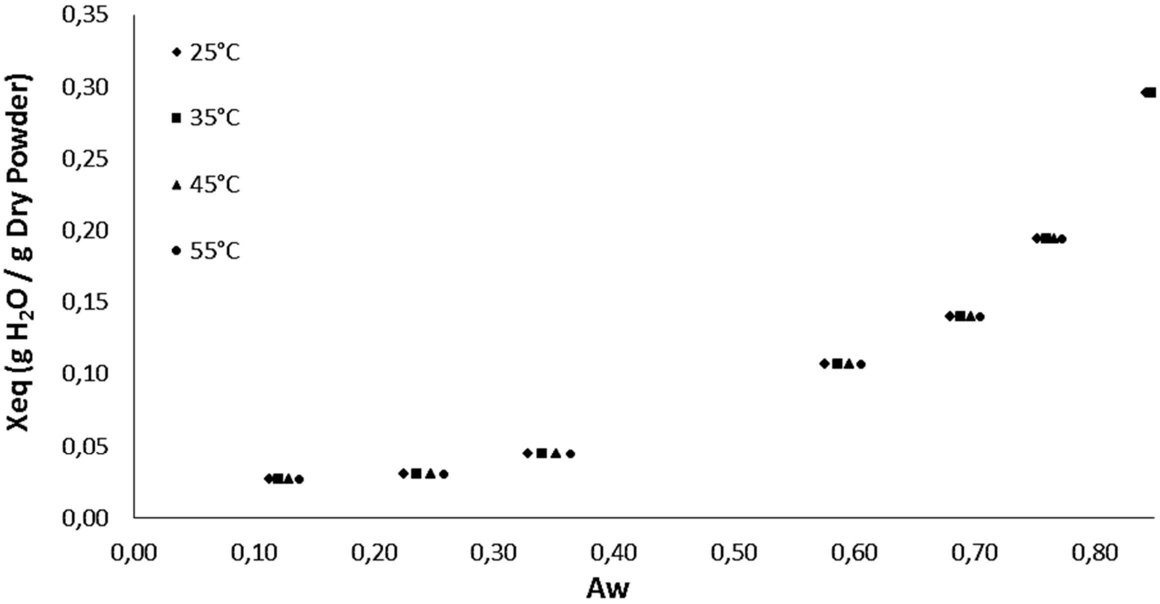

Figure 2. Comparison of the experimental data and the computed sorption isotherms from the BET and GAB models at 25, 35, 45 and 55 °C.

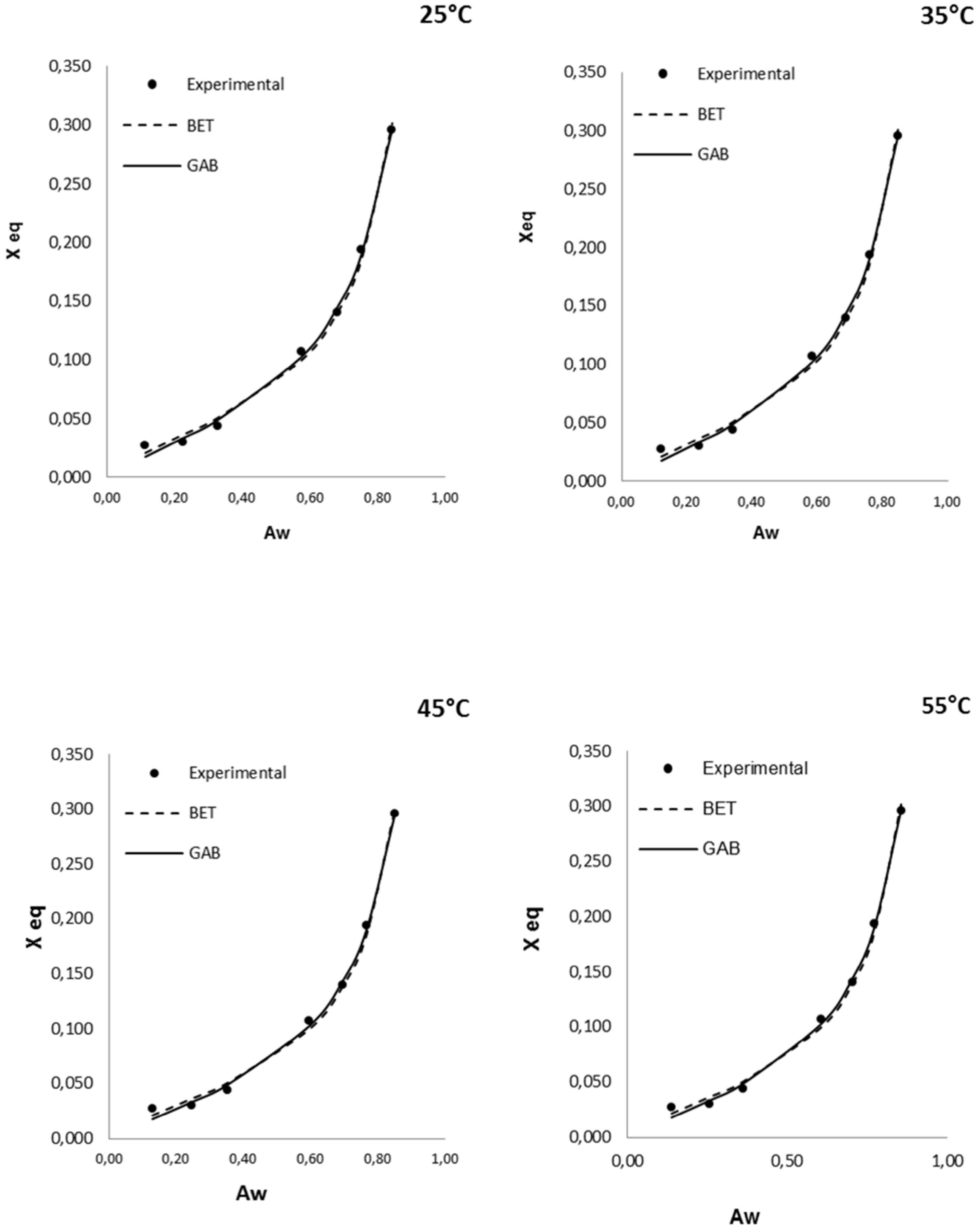

Figure 3. Isosteric heat of sorption for spray-dried Banana Passion Fruit pulp.

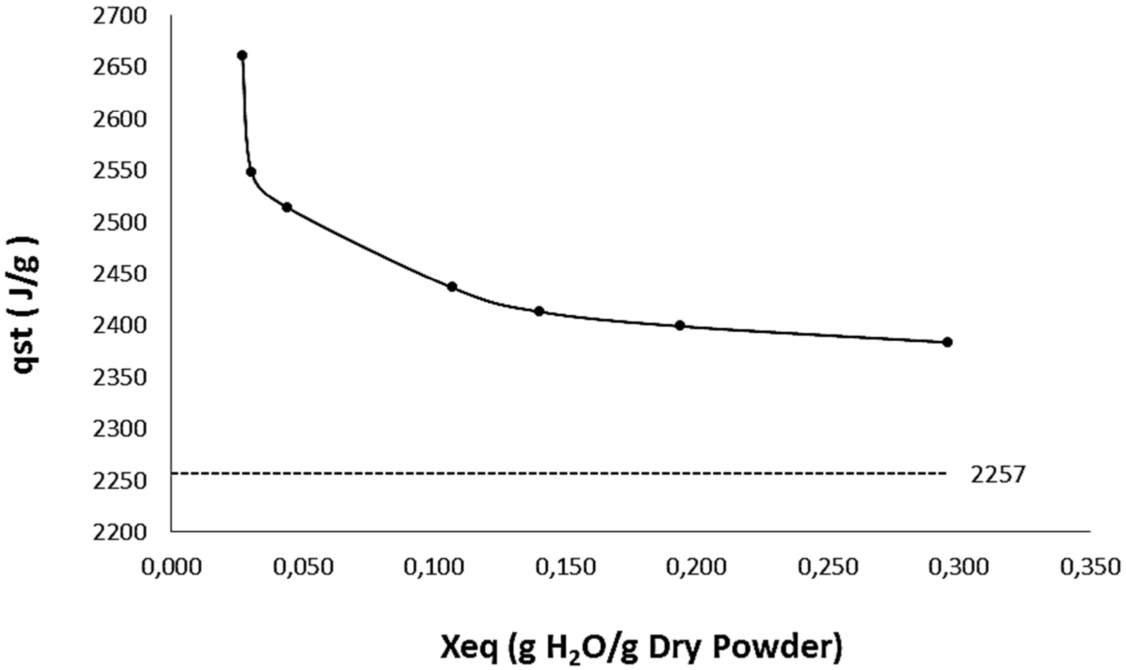

Figure 4. Gibbs free energy for spray-dried Banana Passion Fruit pulp.

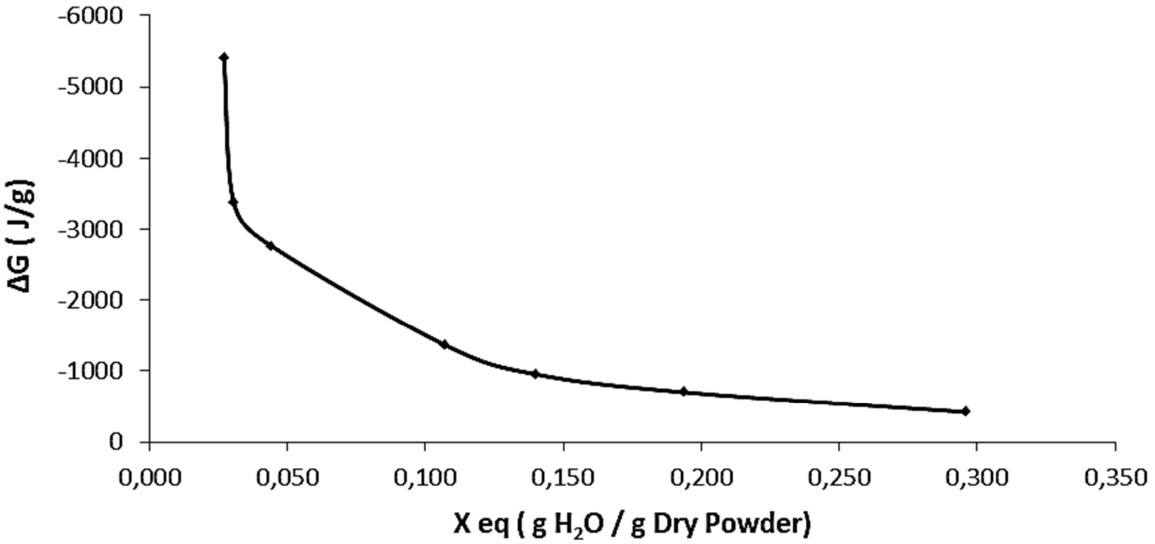

Figure 5. The antioxidant activity of spray-dried Banana Passion Fruit pulp at different water activities determined by the FRAP assay

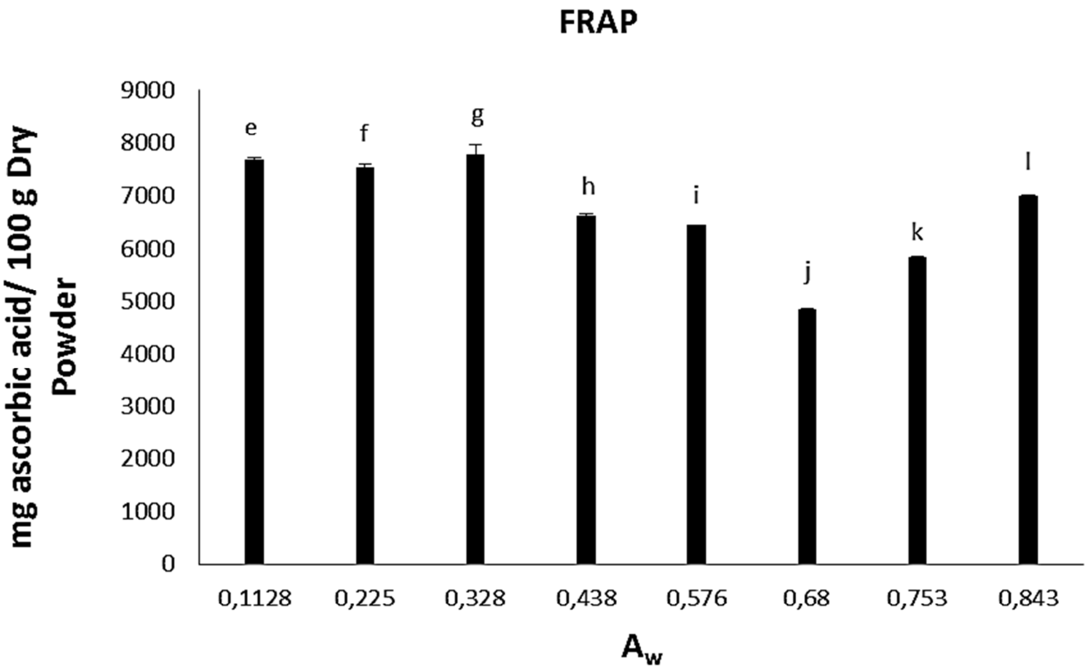

Figure 6. The antioxidant activity of spray-dried Banana Passion Fruit pulp at different water activities determined by the total phenol content

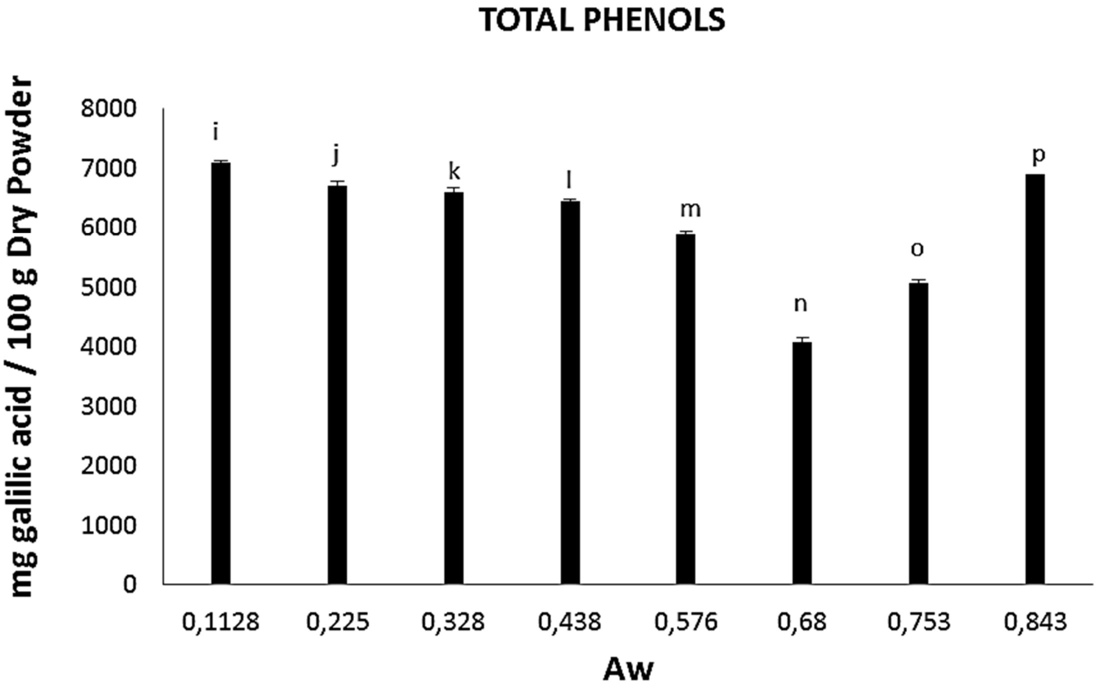

Figure 7. SEM Micrographs of spray-dried Banana Passion Fruit pulp stored at relative humidity levels of (A) 11.3%, (B) 22.5%, (C) 32.8%, (D) 43.8%, (E) 57.6%, (F) 68%, (G) 75.3%, and (H) 84.3%.

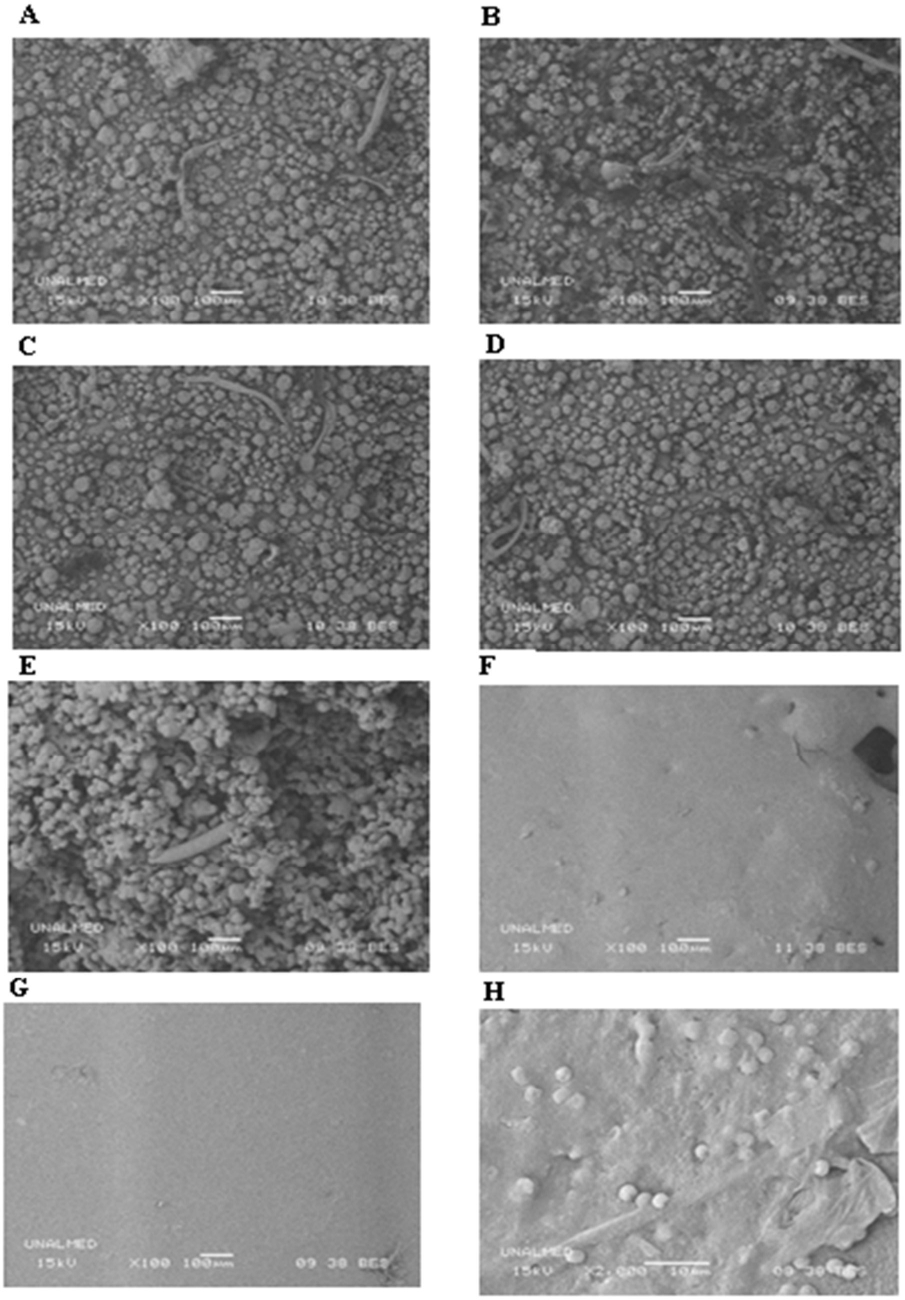

Table I. Computed parameters of the BET model at 25, 35, 45 and 55 °C.

Temperature °C	X_m	α	*MRE%*	*r*
25	0.04925	4.6442	10.45	0.9955
35	0.04768	4.6169	10.41	0.9953
45	0.04638	4.4850	10.26	0.9955
55	0.04514	4.3908	10.11	0.9955

Table II. Computed parameters of the GAB model at 25, 35, 45 and 55 °C.

Temperature °C	*Xm*	*α*	*K*	*MRE%*	*r*
25	0.05716	3.0017	0.9732	9.62	0.9970
35	0.05589	2.8825	0.9723	9.57	0.9971
45	0.05419	2.8112	0.9738	9.46	0.9972
55	0.05315	2.6820	0.9733	9.24	0.9973

Table III. Antioxidant activity expressed as FRAP and the total phenolic content of spray-dried Banana Passion Fruit

Aw	**FRAP**	**TOTAL PHENOLS**
0.114	7677.08 ± 44.27 [a]	7083.56 ± 37.09 [i]
0.225	7545.71 ± 43.99 [b]	6710.35 ± 70.05 [j]
0.328	7783.90 ± 182.82 [c]	6600.12 ± 77.08 [k]
0.438	6618.26 ± 22.77 [d]	6439.60 ± 41.00 [l]
0.576	6440.03 ± 2.95 [e]	5891.45 ± 43.68 [m]
0.680	4845.92 ± 13.08 [f]	4067.66 ± 77.81 [n]
0.753	5833.80 ± 8.00 [g]	5059.83 ± 63.50 [o]
0.843	7011.36 ± 15.65 [h]	6894.75 ± 4.29 [p]