

## Adsorption isotherms of flours from pre-cooked clones of Criolla potato (*Solanum tuberosum* Group Phureja) South American tuber

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### Abstract

Agricultural Research Colombian Corporation (CORPOICA) carries out researches for developing new potato varieties addressed to industrial applications as production of flours. Therefore, the objective of this research consisted in establishing adsorption isotherms of flours from 7 pre-cooked promising clones and 4 pre-cooked candidate clones for registration of Criolla potato, a Colombian native tuber, harvested in two planting zones (Sibate and Granada Towns, Colombia-South America). Flour samples characterized physicochemical (reducing sugars, starch, moisture content, and water activity) got their moisture equilibrium into 5 hygroscopic saturated salt solutions by isopiestic or static gravimetric method. Moisture and water activity ( $a_w$ ) of flours were determined as beginning as ending of the testing. The  $a_w$  covered a range from 0.200 to 0.843. Data were adjusted by GAB model for plotting the adsorption isotherm ( $0.96 < r^2 < 0.99$ ). Moreover, data obtained were examined statistically on descriptive, one-way analysis of variance completely randomized ( $p < 0.05$ ), and Tukey's HSD test ( $p < 0.05$ ). Flours showed Type II and Type III adsorption isotherms due to the alteration into internal structure of some clones because of pre-cooking effect, soil properties, and cultivar. The flours obtained from promising clone 3 and candidate clone 8 for registration showed better stability for storage conditions. The isotherms predicted hygroscopic properties of these flours for contributing with information to industries which store and apply in food processes as dehydrated soups, arepas (typical Colombian food), omelette mixes, and extrude products.

### Keywords

Water activity

GAB model

Food storage

Tubers

Equilibrium moisture

content

Monolayer

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### Introduction

Criolla potato (*Solanum tuberosum* Group Phureja) is a native crop in Colombia (South America) which has technological development last years as new varieties, quality seeds, control of sickness and plagues (Herrera and Rodriguez, 2011). Agricultural Research Colombian Corporation named CORPOICA carries out studies for developing promising clones and candidate clones for registration as new varieties addressed to industrial applications. Criolla potato possesses better nutritional characteristics than other tubers due to high content of protein (2.5% w/w) and carbohydrates (21.6% w/w). Else, it has vitamin C (15 mg/100 g), iron (1 mg/100 g), and lower fat contain (0.1% w/w) (Piñeros, 2009). Once these tubers are harvested should be consumed or conserved without rest period.

Nowadays, people around the world eat products with low fat and carbohydrates and Criolla potato offers benefits and opportunities for processing new products or foods with desired characteristics

regarding tendency. This potato can be processed industrially such as flours, according to studies of Prieto *et al.* (2013), and the precooking operation keeps its characteristic colour and avoids enzymatic browning reactions in processed products.

On the other hand, dehydrating operation conserves foods because the available water is removed for preventing microbiological growth, toxin production, enzymatic and non-enzymatic reactions with small amount of water activity ( $a_w$ ) (Barbosa-Canovas, 1996). For seizing the mentioned benefits of dehydrated foods, as flours, these should be stored at appropriate conditions of temperature and relative humidity. Maximum moisture permitted in a food is determined by adsorption isotherms which help to predict the variations during drying or dehydrating, storage, packaging, and mixing of ingredients for food formulation (Ruiz-Lopez and Herman-Lara, 2009; Madigan *et al.*, 2004).

Around 200 different mathematical models for isotherms modelling have been reported (Basu *et al.*, 2006). Some of them are based on adsorption models

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from BET equation (Brunauer-Emmett-Teller) whose models are empirical with 3 adjustable parameters. These models are useful for water adsorption in foods but propose little information about water interactions with other components. The important equations for foods are: Langmuir  $a_w$  range 0-0.3, BET  $a_w$  range 0.05-0.35, Halsey  $a_w$  range 0.05-0.8, Oswin  $a_w$  range 0.05-0.9, Smith  $a_w$  range 0.3-0.9, Henderson  $a_w$  range 0.05-0.8, and GAB (Guggenheim-Anderson-De Boer)  $a_w$  range 0.05-0.95. The last equation is most applied due to major covering of  $a_w$  in foods (Kiranoudis *et al.*, 1993; Al-Muhtaseb *et al.*, 2002; Barbosa-Canovas and Juliano, 2007).

Isotherms present five typical Van Der Waals curves (Shyam *et al.*, 2001) according  $a_w$  in foods, physical states of components, porous structure, temperature, and surface tension (Rahman, 1995). One is Langmuir isotherm or Type I which is typical for porous solids. Other isotherm is sigmoid or Type II for foods with solutes of high molecular weight. The third isotherm Type III which shows concave curve for food compounds with water-soluble substances. The last isotherms of Type IV and V are for foods with capillary phenomenon. The majority of foods are represented by isotherms Types II and IV (Mathlouthi and Roge, 2003).

Therefore, this research carried out the objective of establishing the adsorption isotherms of flours obtained from pre-cooked promising clones and pre-cooked candidate clones for registration of Criolla potato (*S. tuberosum* Group Phureja) harvested in two Colombian Towns for recommending the isotherm-curves to food industry.

## Materials and Methods

### Materials

Criolla potato tubers: CORPOICA supplied 7 promising clones (PC) and 4 candidate clones for registration (CCR) of Criolla potato (*S. tuberosum* Group Phureja) harvested in Sibate Town (SB) to 2,700 m.a.s.l. (04°30'N 74°17'W) and Granada Town (GR) to 2,450 m.a.s.l. (04°31'N 74°21'W) at average temperatures of 14°C and 16°C respectively.

Saturated salts: potassium acetate with initial 0.2  $a_w$  ( $K_2H_3O_2$ , Mallinckrodt, Chemical Works, St. Louis, MO, Canada), magnesium chloride with initial 0.32  $a_w$  ( $MgCl_2$ , Sigma-Aldrich Chemie, Steinheim, Germany), sodium chloride with initial 0.75  $a_w$  ( $NaCl$ , Scharlau Chemie SA, Barcelona, Spain), ammonium sulphate with initial 0.81  $a_w$  ( $[NH_4]_2SO_4$ , Panreac, Barcelona, Spain), and potassium chloride with initial 0.84  $a_w$  ( $KCl$ , Merck, Darmstadt, Germany). Saturated salt solutions were put in close sealed Petri

dishes for maintaining equilibrium relative humidity.

### Process of obtaining flours

Flours from harvested tubers were obtained at Pilot Plant of Universidad de La Salle (Bogota, Colombia) from  $200 \pm 0.01$  g of each clone. The process proposed by Prieto *et al.* (2013) consisted in washed, disinfected, pre-cooked in one steam jacketed boiling pan (Manufacturas Metalicas RAE Ltda, RMVA 50-304, Bogota, Colombia) to 92°C by 10 min, and dehydrated in a tray-dehydrator at 60°C (JJ Industrial, M89, Bogota, Colombia) by 6 h. Product was reduced of size in laboratory disk mill (Fundicion Corona, Medellin, Colombia) and milled again until getting a fine powder with a basic analytical mill (IKA, A10, IKA Works, Inc; Wilmington, NC). Flours were sieved by 60 mesh of ASTM E 11/09 ( $\Phi=250\mu m$ ) (Pinzuar Ltda, Bogota, Colombia) and stored in Zip-lock® bags of high density polyethylene during 2 months at 18°C. The final weights of each obtained flour (FW) were related with initial weights of each clone tubers (IW) for determining the obtaining yield of flour (Y) regarding the following equation:

$$Y = \left( \frac{FW}{IW} \right) \times 100$$

### Reducing sugars content

It was estimated by spectrophotometric method with 3,5-dinitrosalicylic acid (DNS) (Miller, 1959). The reading of absorbance was done at a wavelength of 540 nm by a spectrophotometer (Genesys 20 UV Spectrophotometer, Thermo Electron Corporation, Madison WI, USA).

### Starch content

First, other carbohydrates minus starch were separated by dilution with ethanol 80% v/v at 85°C during 5 min and centrifuged (Dynac centrifuge model 420102, Clay Adams, USA) (Vasanthan, 2001). To the precipitated was done an acid hydrolysis by perchloric acid ( $HClO_4$ , Sigma-Aldrich Chemie, Steinheim, Germany), acetic acid ( $CH_3COOH$ , Sigma-Aldrich Chemie, Steinheim, Germany), and distilled water in relation 3:2:5 respectively (NTC 4566, 2009) for simplifying the chains of polysaccharide. After, it was determined sugars as equivalents of starch content (Miller, 1959).

### Moisture content and water activity

Moisture was measured as beginning as ending of the experiment by 44-15.02 method (AACC, 2010) with hot air oven (Mettler Universal Oven, Model EX-969, Mettler GmbH + Co.KG, Schwabach, Germany). Water activity by 978.18 method (AOAC,

2000) with a water activity detector (Novasina ms1-a<sub>w</sub>, Axair Ltd, PFAF-fikon, Switzerland) calibrated with standard salts according to Greenspan (1977).

#### Determination of adsorption isotherms

Adsorption isotherms were determined by isopiestic or static gravimetric method (Shyam *et al.*, 2001). The flours were put on aluminium dishes and weighed 2±0.2g in electronic analytical balance (Mettler Toledo, Inc., Model No. AB204-S, Greifensee, Switzerland). Aluminium dishes with samples were positioned on supports to avoid contact with saturated salts which were placed in Petri dishes for maintaining equilibrium relative humidity with a<sub>w</sub> from 0.225 to 0.843 (Greenspan, 1977). For a<sub>w</sub> > 0.81 was used sodium azide (NaN<sub>3</sub>, Merck, Darmstadt, Germany) to prevent microbial spoilage of flour. The Petri dishes were sealed hermetically for allowing osmotic interchange between the sample and saturated salt solution according Prieto *et al.*, (2006) in an incubator (Binder BD 53I, Tuttlingen, Germany) with air to 25±1°C and 42±1% of relative humidity. Temperature and relative humidity were measured by a thermo-hygrometer (HMP35D, Vaisala, Helsinki, Finland). The samples of flours were weighed day by day until constant weight (±0.001 g) indicating the equilibrium with their respective salts.

#### Modelling mathematical

GAB model was chosen due to some authors recommend this model for describing precisely the behaviour of potato products (Nurtama and Jenshinn, 2010). The isotherms were plotted on Cartesian coordinates thus x axis for a<sub>w</sub> and y axis for moisture (g of water / 100 g of dry solid). The mathematical setting of each isotherm was established by following GAB model (Bell & Labuza, 2000; Van den Berg, 1984):

$$\frac{X}{X_m} = \frac{C \cdot k \cdot a_w}{[(1-k \cdot a_w) \cdot (1-k \cdot a_w + C \cdot k \cdot a_w)]}$$

With these parameters:

$$k = \frac{2\alpha}{-\beta \pm \sqrt{\beta^2 - 4\alpha\alpha}}; \quad C = \frac{\beta}{k \cdot \gamma} + 2 = 1 - \frac{\alpha}{k^2 \cdot \gamma}; \quad X_m = \frac{1}{C \cdot k \cdot \gamma} = \frac{(C-2)}{C \cdot \beta} = \frac{(1-C)k}{C \cdot \alpha}$$

And these constants:

$$\alpha = \frac{k}{X_m \left( \frac{1}{C-1} \right)}; \quad \beta = \frac{1}{X_m \left( 1 - \frac{2}{C} \right)}; \quad \gamma = \frac{1}{X_m \cdot C \cdot k}$$

The X<sub>m</sub> moisture obtained represented the adsorption capacity of monolayer; the C was energy constant or Guggenheim's constant; the k correction factor was standard chemical potential difference among molecules. Those constants were obtained by least-squares no-linear regression of the direct

equation (Microsoft® Office Excel® 2007, Microsoft Corporation, Redmond, WA, USA) (Timmermann *et al.*, 2000). The form of each isotherm and its adjust was determined from each equation. Constants and coefficient of determination (r<sup>2</sup>) were got since polynomial of third order regression (Kablan *et al.*, 2008). Additionally the mean relative error (MRE) was determined for each isotherm with this equation (Ruiz-Lopez and Herman-Lara, 2009):

$$\%MRE = \frac{100}{N} \sum_{n=1}^n \frac{|M_{exp} - M_{pr}|}{M_{exp}}$$

Where M<sub>exp</sub> is the experimental value, M<sub>pr</sub> is predictable value and N is the number of data.

#### Statistical analysis

Descriptive statistic was applied for the constants of GAB model. Data of moisture and a<sub>w</sub> were evaluated on one-way analysis of variance (p<0.05) completely randomized, and Tukey's HSD test (p < 0.05) by Statistix® 9.0 (Analytical Software, Tallahassee FL, USA). Additionally, physicochemical characteristics were analysed by correlation statistic (-1<r<1) respect to isotherms obtained of clone flours.

## Results and Discussions

#### Flour yields

The processes of obtained flours had average yields of 25.55±2.66% w/w and 21.47± 2.35% w/w for clones from SB and GR respectively. Each flour yield had a direct relation with dry solids contain into the tubers which are affected for soil properties of two planting zones (Santos *et al.*, 2010; Estevez *et al.*, 2000). Also, the high yields were got because tubers were processed with skin, whereas Castiblanco (2004) reported 16.89% w/w for a commercial variety of Criolla potato without skin. This last value confirms the relation between amounts of solids with flour yields.

#### Physicochemical characteristics of flours

Initial moisture, a<sub>w</sub>, reducing sugars, and starch content of clones flours of Criolla potato are exhibit in Table 1. The average moisture of flours were 9.5% w/w and 13.5% w/w for clone flours from SB and GR respectively. The maximum value of moisture contain in Colombian legislation is 15.5% (NTC 267, 2007) for avoiding enzymatic reactions, spoilage, and alteration due to mycotoxins presence in flours. Obtained flours showed acceptable moisture content and low a<sub>w</sub> in order to be utilized in processing and stored by long time.

Higher reducing sugars of clone flours 7PC and

Table 1. Initial physicochemical characteristics of clone Criolla potato flours

Clone	Sibate Town				Granada Town			
	Moisture <sup>2</sup> (% w/w)	a <sub>w</sub>	Reducing Sugars <sup>1</sup> (% w/w)	Starch <sup>1</sup> (% w/w)	Moisture <sup>2</sup> (% w/w)	a <sub>w</sub>	Reducing Sugars <sup>1</sup> (% w/w)	Starch <sup>1</sup> (% w/w)
1PC	10.3	0.499	8.43	73.12	10.5	0.601	13.60	67.11
2PC	2.3	0.495	4.78	77.72	13.3	0.610	7.60	72.51
3PC	8.9	0.510	9.95	73.98	12.5	0.585	17.81	78.29
4PC	9.7	0.480	7.04	81.78	11.5	0.610	14.50	67.51
5PC	7.7	0.503	4.45	88.83	16.0	0.608	4.38	87.22
6PC	11.5	0.486	6.88	73.81	15.8	0.580	9.41	72.22
7PC	9.0	0.529	10.08	78.15	13.6	0.591	5.75	81.77
8CCR	8.7	0.547	7.26	73.56	20.0	0.625	5.95	81.73
9CCR	11.1	0.371	6.37	81.42	10.5	0.596	22.52	65.85
10CCR	10.0	0.553	6.73	93.51	15.0	0.639	14.60	80.84
11CCR	9.1	0.572	2.89	86.76	12.5	0.627	7.40	78.69

<sup>1</sup> Dry Basis<sup>2</sup> Wet basis

PC: promising clone; CCR: candidate clone for registration

9CCR from SB and GR respectively developed browning or Maillard reaction generated by high temperature during pre-cooking of tubers. But low reducing sugars content favored that yellow characteristic colour of tubers was remained in some flours (Vega-Galvez *et al.*, 2006).

Starch content were between 73.12-93.51% d.b. w/w for flours with clones from SB, and 65.87-87.22% d.b. w/w for flours with clones from GR. Fonseca *et al.* (2013) reported maximum starch content of 85.3% d.b. w/w for obtained flours from pre-cooked promising clones of Criolla potato harvested in SB. These authors recommended these potential flours due to starch content for processing of bread, spaghetti, extruded, cookies, and soups.

#### Adsorption isotherms of flours

The flours had a different behaviour depending on initial moisture, type of clone and salt employed. For potassium acetate, the flours increased their moisture from 13.53 to 18.68% w/w and a<sub>w</sub> from 0.6 to 0.37 during 10 days. For magnesium chloride, the moisture was between 13.53 – 18.54% w/w and a<sub>w</sub> between 0.6 – 0.65 during 25 days. For sodium chloride, the moisture increased between 13.53 – 15.75% w/w and a<sub>w</sub> between 0.6 – 0.67 during 15 days. For potassium chloride, the moisture was between 13.53 - 31.56% w/w and a<sub>w</sub> between 0.6 - 0.8 during 10 days. For ammonium sulphate, the moisture increased from 13.53 to 27.47% w/w and a<sub>w</sub> from 0.6 to 0.82 during 16 days. Each isotherm did not show a definite pattern due to each flour depended of class of clone with its particular characteristic and moisture.

Some authors have reported isotherms of potato flours as S shape or Type II and J shape or Type III

(Shyam *et al.*, 2001). Similarly, clone flours of this research showed the same two typical Van Der Waals curves of isotherms (Table 2). Clone flours 7PC and 9CCR had a tendency to absorb quickly water in the first phase of their curves Type III (Table 2) due to more hydroxyl groups content or more hydro-solubility according to the pre-cooking grade of their tubers. The sorption in flours was affected during their heat treatment in pre-cooking (> 45°C), since such a treatment is responsible for phase transitions in starch and denaturation in proteins as reported in the literature (Thomas and Atwell, 1999). This can be related to the higher absorptive capacity of the hydrophilic starch possessing more active sites (groups) than the less hydrophilic protein (Riganakos *et al.*, 1992).

Thus, the form of isotherms varied because of gelatinized and no-gelatinized starch into clone flours as result of the pre-cooked during the obtainment of flours. Further, data of reducing sugars and starch content did not present correlation statistic with coefficients between 0<r<0.4 for their isotherms, due to all flours showed variability into values, and there was a direct influence with the form of obtained isotherms depending of own characteristics of tuber.

#### Modelling mathematical

Guggenheim's constant C<1 of some clones showed isotherm Type II obtained polynomic tendency of third grade and r<sup>2</sup> = 0.998 (Table 3a). Likewise, this shape was similar to adsorption isotherms of pre-cooked cassava flour with r<sup>2</sup> between 0.9916 – 0.9997 (Rodriguez, 2009). This isotherm presented an asymptotic trend when a<sub>w</sub> was close to 1, and it showed an inflection point for low values of

Table 2. Isotherms of clone Criolla potato flours

Isotherms		Granada Town	Sibate Town
Type II	experimental		
	modelled by GAB		
Type III	experimental		
	modelled by GAB		

$a_w$  (Ayala-Aponte, 2011). The results coincided with Kaymak-Ertekin and Gedik (2004), who reported isotherms for potato products with similar trend as a result of their high content of starch. For Type II isotherms,  $k$  values were found in a range of 0.705-1.128 (Table 3a). Ayala-Aponte (2011) reported a value of 0.851 for cassava flour which was into range mentioned.

Moisture content in monolayer ( $X_m$ ) demonstrated a range of 2.248 to 6.369 g of water/100 g of dry solid (Table 3a) which agreed with the range of 3.2-16 g of water/100 g of dry solid reported for starchy foods (Dominguez-Dominguez *et al.*, 2007). This value indicated the maximum amount of water that could be adsorbed on a single layer on the surface of flour and it was considered as the value more stable for storage (Ayala-Aponte, 2011; Kulchan *et al.*, 2010). Whereby, the flours of clones 3PC and 8CCR showed the best characteristic of stability with  $X_m$  of 5.847 and 6.369 g of water/100 g of dry solid respectively. Thus, the clone flours evaluated showed similar properties of water adsorption respect to cassava flour but with a wide range of values of monolayer (Bell and Labuza, 2000).

MRE was high in spite of  $r^2$  had a good adjust to polynomic shape (Table 3a). MRE was above 10%

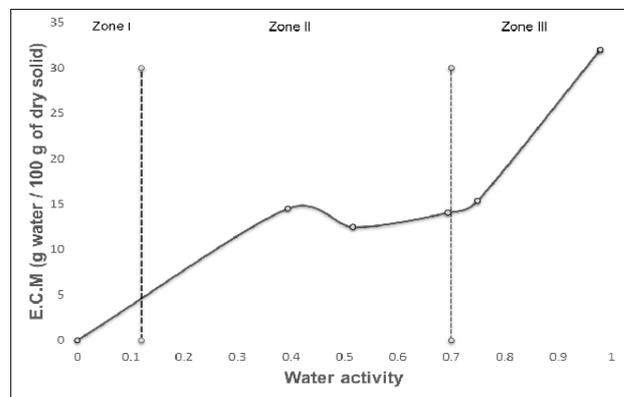


Figure 1. Regions for adsorption isotherm characteristic of Type II (Promising Clone 1)

because of GAB model was applied to wide range of  $a_w$  (0.1 – 0.9), but MRE increased drastically to  $a_w$  data above 0.9. For high  $a_w$ , GAB presented a deviation toward down due to appearance of a sorption third grade (Timmerman and Chirife, 1991). This effect determined a higher limit for application of GAB to practical purposes (Rahman, 1995).

Isotherms of Type II were divided in three zones (Figure 1 and Table 2) as Martínez *et al.* (1998) and Lagoudaki *et al.*, (1993) suggested. Zone I showed adsorption of water by monolayer with average moisture between 0.15 and 6.82 g of water/100 g of

Table 3. GAB constants for isotherms with polynomic tendency of third grade for flours from Criolla potato clones evaluated at 25°C: (a) Type II and (b) Type III

(a)

Clone	C		k		X <sub>m</sub>		r <sup>2</sup>		MRE	
	SB	GR	SB	GR	SB	GR	SB	GR	SB	GR
<b>1PC</b>	-3.714	-2.095	0.867	0.999	4.6	3.744	0.998	0.996	13.04	12.75
<b>2PC</b>	-2.987	-2.599	1.021	0.957	3.867	4.25	0.999	0.996	8.49	6.33
<b>3PC</b>	-1.559	-3.906	1.121	0.896	3.18	6.369	0.999	0.999	14.47	16.94
<b>4PC</b>	-4.153	-2.492	1.007	0.987	4.95	4.933	0.999	0.998	13.18	10.47
<b>5PC</b>	-3.015	-1.685	1.082	1.072	3.002	2.248	0.998	0.963	2.13	5.7
<b>6PC</b>	-10.374	-6.731	1.061	1.088	4.523	4.475	0.999	0.999	11.35	12.33
<b>8CCR</b>	-3.87	-3.092	0.911	0.705	5.847	6.136	0.999	0.992	16.05	11.8
<b>10CCR</b>	-3.354	-1.776	1.026	1.128	5.232	2.828	0.999	0.977	7.15	18.63
<b>11CCR</b>	-1.79	-2.674	1.044	0.922	3.664	4.732	0.999	0.999	4.86	14.32
$\bar{x}$	-3.869	-3.006	1.016	0.973	4.318	4.413	0.999	0.991	10.08	12.14
$\sigma$	2.595	1.554	0.08	0.127	0.959	1.362	0	0.013	4.697	4.308
<b>4CV%</b>	-67.07	-	7.895	13.047	22.202	30.87	0.044	1.272	0.466	0.355

(b)

Clone	C		k		X <sub>m</sub>		r <sup>2</sup>		MRE	
	SB	GR	SB	GR	SB	GR	SB	GR	SB	GR
<b>7PC</b>	11.263	10.707	0.949	0.915	6.074	6.779	0.999	0.999	12.45	13.21
<b>9CCR</b>	0.914	2.176	0.815	0.853	17.083	11.41	0.999	0.999	11.14	18.73
$\bar{x}$	6.088	6.442	0.882	0.884	11.579	9.094	0.999	0.999	11.795	15.97
$\sigma$	7.317	6.032	0.095	0.044	7.785	3.275	0	0	0.926	3.903
<b>CV (%)</b>	120.18	93.642	10.776	4.937	67.233	36.012	0	0	0.079	0.244

GAB model constants: k, C, X<sub>m</sub> = Moisture content of the monolayer (g water / 100 g dry solid)r<sup>2</sup>= correlation coefficient $\bar{x}$  = average $\sigma$ = standard deviation

CV= coefficient of variation (%)

MRE= mean relative error

SB = Sibate Town, GR= Granada Town (origin of the materials)

PC: promising clone; RCC: candidate clone for registration

dry solid. This Zone was the most stable for native potato flours. Zone II had average moisture between 4.89 and 13.62 g of water / 100 g of dry solid and these values corresponded to the adsorption of water in multilayers. In this Zone, the flours had lost their stability because the available of water interacted with the air relative humidity (%RH) and generated biochemical reactions (Al-Muhtaseb *et al.*, 2002). Moreover, this humidity affects lipid oxidation, enzymatic activity, non-enzymatic browning, flavor, and conservation (Menkov *et al.*, 2004). Zone III corresponded to the average moisture greater than 13.62 g of water / 100 g of dry solid. In this zone occurred condensation of water in the pores of flours and followed their solubility with tendency to enzymatic and microbiologic alterations (Al-Muhtaseb *et al.*, 2002; Van Den Berg and Bruin, 1981).

The isotherms of Table 2 indicated the variation of

moisture content in flours which it depended of %RH of the atmosphere where the flours were stored. When the %RH decreased, the starches into flours rejected moisture; when the %RH increased, the starches absorbed humidity (Swinkels, 1985). The shape of the curves was sigmoid, showing one inflection point which has been reported for characteristic materials with high sugar content (Maskan and Göğüs, 1997).

Likewise the isotherms Type II of clone flours showed respect  $a_w$  (Chungcharoen and Lund, 1987) the following changes: Zone I for  $a_w < 0.2$  which related to adsorption of monomolecular film of water, Zone II for  $a_w$  range of 0.22–0.7 corresponding to adsorption of additional layers over this monolayer, and Zone III for  $a_w$  range of 0.7–0.99 corresponding to condensation of water in the pores of the material followed by dissolution of soluble material (Benado and Rizvi, 1985). The equilibrium moisture content increased rapidly at low  $a_w$  (0–0.13), and it increased

Table 4. Equilibrium moisture content (EMC) critical and  $a_w$  of isotherms for two planting zones

Clone	Sibate Town		Granada Town	
	$a_w$	EMC	$a_w$	EMC
1PC	0.51	14	0.56	14
2PC	0.55	14	0.64	14
3PC	0.61	15	0.57	17
4PC	0.65	16	0.7	20
5PC	0.64	13	0.66	12
6PC	0.50	12	0.60	15
7PC	0.52	12	0.60	14
8CCR	0.60	18	0.55	20
9CCR	0.48	10	0.65	17
10CCR	0.57	16	0.70	15
11CCR	0.65	16	0.66	18

PC: promising clone; CCR: candidate clone for registration

slowly between 0.15 and 0.7, after it followed by a steep rise above 0.7 (Aboubakar *et al.*, 2008).

On the other hand, GAB constants for isotherms Type III (Table 2) with polynomic tendency of third grade are presented in Table 3b (Guggenheim's constant  $C > 1$ ). This type of isotherm has been reported in food with high sugar content (Labuza *et al.*, 1985) i.e. the starch of some clone-tubers was degraded to sugar when tubers were not processed immediately to their harvesting and tubers continued maturing (Piñeros, 2009; Hubbard *et al.*, 1990).

Type III isotherms had  $k$  values for SB and GR between 0.882 to 0.884 (Table 3b) close to the reported by Navia *et al.*, (2011) of 0.860 for cassava flour. Flours of clones 7PC and 9CCR were obtained after pre-cooking process which caused structural changes resulting in the increase of active points for adsorption of water (Navia *et al.*, 2011; Al-Muhtaseb *et al.*, 2004).

Flour of clone 7PC obtained  $X_m$  of 6.074 and 6.779 g of water/100 g of dry solid for SB and GR respectively (Table 3b), these values were less than 7.0598 g of water / 100 g of dry solid obtained by Navia *et al.*, (2011). Flour of clone 9CCR had  $X_m$  of 17.08 g of water/100 g of dry solid for SB and 11.41 g of water/100 g of dry solid for GR, which are outside the range proposed by Labuza *et al.* (1985), who mentioned that maximum  $X_m$  must not be more than 10 g of water/100 g of dry solid for foodstuff, in order to avoid deterioration caused by humidity.

Coefficients of no-linear determination were high ( $r^2 > 0.96$ ) for clones from two planting zones but better adjust for SB than GR with MRE of 10.08 and 12.14 (Table 3b). In addition, the results obtained a high variation among them and their averages showed that each clone had a particular response. Alike, one-way analysis of variance completely randomized, and Tukey's HSD test confirmed a significant difference ( $p < 0.05$ ) for all clones. Moreover, isotherms are important for characterizing each promising clone and each candidate clone of registration individually according its genotype (Gough and King, 1980), and also differences showed as a result of the pre-cooking process (Iguedjtal *et al.*, 2007).

Besides, the isotherms by mathematical modelling GAB allowed got the equilibrium moisture content (EMC) or point critic. It was determined for the pre-cooked clone flours (Table 4), thus: monolayer moisture ( $X_m$ ) and  $a_w$  were into range 10-20 g of water / 100 g of dry solid, and 0.48-0.70 for 25°C, respectively. Those data agree with the values reported by Velasquez (1995) for flours of one commercial variety of Criolla potato without pre-cooking. These critical values of EMC and  $a_w$  are maximum values for flours of different clones which they would be never overtaken during their storage in order to ensure the stability of flours without getting alterations or spoilages (Gabas *et al.*, 2009; Martinez *et al.*, 1998). These ranges were higher than critical  $a_w$  ranges of cassava flour between 0.2270 – 0.3596 reported by Rodriguez (2009).

The content of  $a_w$  is useful for knowing the optimum conditions of storage and controlled its environment as temperature and relative humidity for flours of pre-cooked Criolla potato due to there is not information nor studies about these products. Instead, other studies on isotherms for other products from different potato varieties as starch potato, dehydrated potato, or flours without pre-cooked which had different data and behaviour of their isotherms (Yanniotis and Blahovec, 2009; Kaymak-Ertekin and Gedik, 2004; Timmermann and Chirife, 1991).

## Conclusion

Soil properties of two planting zones of two Towns influenced the yield and composition of obtained flour from promising clones and candidate clones for registration of Criolla potato (*S. tuberosum* Group Phureja). Flours showed isotherms Type II and Type III. Clone flour of promising clone 7 and candidate clone of registration 9 were affected by the degradation of starch in sugars and pre-gelatinisation during the pre-cooking of the tubers with changes of

water adsorption capability. Clone flour of promising clone 3 and candidate clone of registration 8 showed the best stability; and these flours could be stored in similar conditions of cassava flour due to their similitude into adsorption isotherms. Besides, GAB model was appropriated for mathematical modelling of adsorption isotherms of potato flours because it showed a good setting ( $r^2 > 0.96$ ). Many authors recommended to applying other mathematical models for comparing and continuing these studies for food industry. On the other hand, the results of isotherms can be utilized for preparation or production of flakes, extruded, agglomerated, among others. Criolla Potato flour can be employed for substituting other kind of flours in bakery industry, formulations of spaghetti, dehydrated soups, and typical foods, due to its capacity for retaining oil and water as well as to its starch content for agglutinating and thicken.

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