

## Potato cultivars as a source of starch in Brazil: physicochemical characteristics of the starches and their correlations

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### Abstract

As a source of starch, potato remains unexploited in Brazilian industries, where they typically utilize corn and cassava. Considering the emerging need for using potato as a source of commercial starch, this study evaluated starches extracted from seven cultivars of potatoes with limited commercial usage in Brazil. Potatoes were grown under the same environmental conditions and cultural practices. After harvesting, the potato tubers were processed for the extraction of starch. The proximate composition, amylose content, resistant starch, minerals, as well as pasting and thermal properties of extracted starch samples were analyzed. Starch characteristics varied with the cultivar. Using correlation analysis, we demonstrated that minerals have a robust effect on starch characteristics. Moreover, positive correlations were observed between phosphorus, potassium, magnesium, resistant starch, viscosity peak, breakdown, and gelatinization enthalpy. Calcium had a positive correlation with the amylose content and the percentage of starch retrogradation. Starch samples showed important differences in their physicochemical properties, which are advantageous for industrial applications allowing a larger diversification and incentive to the production of potato for industry in Brazil.

**Keywords:** *Solanum tuberosum*; starch; minerals, viscosity.

**Abbreviations:** K, potassium; Mg, magnesium; P, phosphorus; RS, resistant starch;  $\Delta T$ , variation of temperature;  $\Delta H$ , variation of enthalpy.

### Introduction

Agribusiness in the major industry in Brazil as a result of environmental characteristics, such as favorable climate, soil, water, and light conditions. Potato is a horticultural crop, which occupies the largest cultivation area in the country. The potato agribusiness involves approximately 5,000 producers in 30 regions of seven Brazilian states, and the majority of the national production is commercialized *in natura*, with only 10% being used for industrial processing, in the form of frozen potato and potato chips (Santos et al. 2016; Faostat, 2017). Potato contains approximately 18% dry matter, of which 80% is starch (Braun et al. 2011; Evangelista et al. 2011). Starch is an excellent source of carbohydrates, used by all countries with increasing consumption rates, as the country develops. In Brazil, approximately 1 million ton of starch is produced from maize and cassava, which accounts for a turnover of approximately 500 million dollars. This industrial turnover can be further increased, significantly, if the unexploited potential of other starch sources is considered.

Starch, a source of renewable energy, has been extracted with high purity from several plants for commercial purposes via

relatively simple industrial processes; widely used by-products can be obtained from starch using chemical, physical, and enzymatic processes. Thus, there have been intensive advances in the knowledge about this polymer in recent years, signifying the great potential of technological innovations in the agroindustry starch sector (Mesquita et al. 2016).

Due to the high demand of starch, for varied uses, the potential unmodified starches for industrial production are selected using two important criteria: agricultural availability and productivity; and the unique characteristics of each starch—physical and chemical properties (Matsuguma et al. 2009).

This study was designed based on the following considerations: 1) Brazil has the agroindustrial potential to produce starch from different sources and supply it to the world market; 2) despite agriculturally producing considerable amounts of potatoes, Brazil imports starch; 3) currently, the majority of potato cultivars in Brazil are primarily from Europe, making studies with potatoes of various origins very important for increasing the industrialization of this tuber;

and4) the availability of industrial infrastructure in Brazil to extract starch from corn and cassava.

Thus, this study aimed at processing seven potato cultivars that are still commercially unexploited, to evaluate the physicochemical parameters of their starches, such as proximate composition, amylose mineral content, and thermal and pasting properties and to provide useful information to the Brazilian agroindustrial industry.

## Results and Discussion

### Chemical composition

Purity is an important quality parameter for the industrial production of starch. Results of the characterization of the starches extracted from the potato cultivars were in compliance with the requirements for commercialization as native starch. In addition, the sum of the non-starch components does not exceed 1.2%, indicating high purity (Table 2).

In comparison to the starches isolated from other plants, potato starch contains high amount of starch-bound phosphates (Blennow et al., 2002; Noda et al., 2007; Leonel et al., 2016). Furthermore, potato starch naturally contains metal cations that are bound to the phosphate ester groups through ionic forces (Zaidul et al., 2007; Noda et al., 2014).

The results obtained from the analysis of phosphorus, potassium, calcium, and magnesium contents in the starches showed significant differences among the potato cultivars (Table 2). The starches obtained from Harley Blackhell, Marcy, and Snowden cultivars showed high levels of these minerals. The phosphorous content in potato starches was found to be the highest, of all analyzed minerals, also in agreement with the observation by Zaidul et al. (2007).

During its biosynthesis, starch is enzymatically phosphorylated. The enzyme glucan water dikinase, using ATP, catalyzes starch phosphorylation at the C-6 position, and phosphoglucan water dikinase catalyzes the phosphorylation at C-3 (Haebel et al., 2008). Blennow et al. (2002) showed that the C-6-bound phosphate aligns well with the surface grooves of the double-helix and has a milder effect on helix packing than the C-3-bound phosphate.

Phosphorus content in the potato starches ranged from 420 to 750 mg Kg<sup>-1</sup> (Table 2). The range of the phosphorus content was similar to that reported by other researchers (Wiesenborn et al., 1994; Noda et al., 2004; Noda et al., 2006). Calcium and magnesium contents ranged from 40 to 135 mg Kg<sup>-1</sup> and 30 to 70 mg Kg<sup>-1</sup>, respectively (Table 2). Potassium content was high (485 to 875 mg Kg<sup>-1</sup>), as previously reported by Noda et al. (2014). All these prior studies have reported 663 ppm of potassium, 113 ppm of sodium, 89 ppm of magnesium, and 99 ppm of calcium in industrial potato starch. Starch is a polysaccharide containing a mixture of two biopolymers: amylose, a linear fraction; and amylopectin, a highly branched fraction. Amylose and amylopectin contents affect the starch granule architectures, pasting properties, textural attributes, and the applications for processed food. The amylose content of the potato starches ranged from 28.51% to 36.1%, with the lowest value observed in starch from the Beacon Chipper cultivar (Table 2).

Amylose content is an important characteristic for unmodified starches. Amylose is characterized by high structural stability and ability to form films, which allows various industrial uses for high-amylose starches. Moreover, starches with high levels of amylose present low digestibility issues, thereby promoting health benefits (Hu et al., 2016).

The amylose content values are consistent with those reported by several researchers (Wiesenborn et al., 1994; Kaur et al., 2002; Singh and Kaur 2004; Kaur et al., 2007; Liu et al., 2007; Santos et al., 2016). The difference in the amylose content among starches from different potato cultivars may be due to different factors, such as the genotype, environmental conditions, and cultural practices during cultivation.

Starch that is not hydrolyzed by amylolytic enzymes in the small intestine and passes into the large intestine for fermentation is defined as resistant starch, and its content is related to the rate of digestion by amylolytic enzymes. Several factors contribute to this process, such as starch source, its composition, amylose and amylopectin ratios, amylopectin chain size distribution, phosphorus content, as well as processing and storage conditions (Shu et al., 2007; Noda et al., 2008; Absar et al., 2009; Lu et al., 2011).

Data analysis showed a range of resistant starch content, 10.91% to 18.69%, with the lowest and highest contents observed in starches from BRS Ana cultivar and Harley Blackhell cultivar, respectively (Table 3). This result can be related to the phosphorus content of the starches from these cultivars. As amylolytic enzymes are incapable of bypassing the phosphorylated glucosyl residue, it is likely that high phosphorus content in starch might reduce the enzymatic digestibility of raw starch (Noda et al., 2008).

The mineral composition of starches may be decisive for their industrial applicability, as the degree of phosphorylation determines the starch's physicochemical properties and is, therefore, relevant for its industrial use (Blennow et al., 2002; Singh et al., 2003; Karim et al., 2007; Carpenter et al., 2012). In addition, the level of divalent cations, such as calcium and magnesium, appear to have a substantial impact on the pasting properties of starch, presumably by ionically cross-linking starch phosphate esters (Zaidul et al., 2007; Noda et al., 2014; Noda et al., 2015).

### Pasting properties

Pasting and thermal stability are the most important functional aspects of starch. The pasting properties of the potato starches tested here are presented in Table 3.

The pasting temperatures of isolated starch ranged from 66.33°C (Beacon Chipper cultivar) to 69.95°C (Marlen cultivar). Chung et al. (2014) previously analyzed the characteristics of starches from different potato cultivars grown in different locations in Canada and reported that the pasting temperature of isolated starch ranged from 62.2 °C to 65.8°C, which are lower than those observed in our study. This could be due to the amylose content of the analyzed starches, as high amounts of amylose cause delayed starch swelling, thereby increasing the pasting temperature.

Upon measuring the temperature and time taken to reach the melting point of the crystals, we observed that the starches from the Marcy, Beacon Chipper, and Snowden cultivars showed characteristics that indicate weak granular organization, easy cooking, and production of weak gels, which may be of interest for industrial applications, for example, in instant foods.

The analyzed potato starches showed a marked peak viscosity ranging from 771.21 to 1209.22 RVU (Table 3). The starch from the BRS Ana cultivar had the lowest peak viscosity, which may be related to its low phosphorus and high amylose content.

Lu et al. (2011) report that starches with high phosphorus content tend to exhibit high viscosity peaks and low breakdowns, but an increase in phosphorus content does not

produce a significant impact on the setback. Phosphorus, when covalently bound to the starch granule, because of their ionic organization, can assist in the incorporation of water molecules, and thereby alter the functional properties of starch. The amorphous fraction of the starch granules consists mainly of amylose; therefore, several physicochemical properties of starch can be changed by varying the content of this polymer (Mesquita et al., 2016).

Starches from the Beacon Chipper and Marcy cultivars presented high peak viscosity but showed low resistance to heating and agitation, that is, high breakdown (Table 3). Peak viscosity demonstrates the ability of the starch granules to swell during heating. Starches with high peak viscosity have low resistance to heat and agitation and exhibit high breakage of viscosity during cooking (Singh *et al.*, 2008). It must be noted that calcium may have a possible effect on these properties. Noda *et al.* (2015) reported that starches with high calcium content exhibit low peak viscosity and breakdown, and a decreased swelling ability. We observed similar results in the starch from the Beacon Chipper cultivar, which had the lowest calcium content and highest peak viscosity and breakdown.

Final viscosity is an important parameter in the definition of potential applications of unmodified potato starches. For example, in food products such as dehydrated soups, starches with low final viscosity are desirable; on the other hand, a high final viscosity is desirable in products such as frozen pie fillings. Our analysis showed a final viscosity variation ranging from 322 to 448.1 RVU for the analyzed potato starches (Table 3), with the highest value observed in the starch from the BRS Ana cultivar, potentially, due to its low phosphorus content (Table 2).

### Thermal properties

The molecular disorder in starch during heating in the presence of water promotes the decomposition of the crystalline region; this molecular disorder can be analyzed through differential scanning calorimetry (DSC) (Leonel *et al.*, 2016).

The gelatinization temperatures [onset ( $T_o$ ), peak ( $T_p$ ), and conclusion ( $T_c$ )] and the enthalpy of gelatinization ( $\Delta H$ ) of potato starches are shown in Table 4.  $T_o$ ,  $T_p$ , and  $T_c$  ranged from 63.42°C to 65.88°C, 66.38°C to 68.85°C, and 70.27°C to 73.56°C, respectively.

The gelatinization temperatures ( $\Delta T$ ) of the potato starches ranged from 6.85°C to 8.12°C. The enthalpy of gelatinization ranged from 14.59 to 17.81 J g<sup>-1</sup> (Table 4).  $\Delta T$  indicates the degree of heterogeneity of the crystals within the granules. The gelatinization temperatures (initial and peak) can be used as a measure of stability or completeness of the crystalline regions.  $\Delta H$  reflects the number of double helices that are broken during the gelatinization process (Mesquita et al., 2016). Thus, starch from the Colorado cultivar showed the lowest homogeneity of crystalline area amongst all analyzed cultivars.

The behavior of gelatinized starches during cooling and storage is of great interest to food scientists and technologists as it profoundly affects quality, acceptability, and shelf-life of starch-containing foods (Karim et al., 2000).

During cold storage, gelatinized starch undergoes a process of molecular re-association, resulting in the formation of an ordered structure: a process called retrogradation. The thermal transition temperatures and enthalpy of retrograded potato starch from DSC thermograms are presented in Table 4.

The onset temperatures of the starches in retrogradation ranged from 48.90°C to 50.53°C. Peak temperatures differed between the cultivars, ranging from 54.78°C to 58.87°C. The final temperatures ranged from 62.90°C to 69.37°C. The enthalpy of the retrograde starch ranged between 4.85 and 6.37 J g<sup>-1</sup> (Table 6). These results were similar to those reported in other studies with starches obtained from different potato cultivars (Lu et al., 2011; Chung et al., 2014). The retrogradation percentages ranged from 28.46% to 39.83%, with the highest value being observed in the starch from the Colorado cultivar (Table 4).

### Pearson correlation

A correlation analysis for potato starch characteristics, independent of the cultivar, showed that minerals are correlated to important characteristics (Table 5).

Phosphorus, potassium, and magnesium had positive correlations with each other and with the resistant starch content, peak viscosity, breakdown, and enthalpy of gelatinization. These same minerals also had a negative correlation with the final viscosity. Potassium further showed a positive correlation with the retrogradation tendency and a negative correlation with amylose, variation of gelatinization temperatures ( $\Delta T$ ), and percentage of retrogradation (% R). The positive correlation between phosphorus and peak viscosity, breakdown, and enthalpy of gelatinization has been previously reported in other studies (Yoneya et al., 2003; Karim et al., 2007).

Calcium, which negatively correlated with potassium, had a positive correlation with amylose, gelatinization temperatures ( $T_o$ ,  $T_p$ , and  $T_c$ ), and percentage of retrogradation (% R). Noda *et al.* (2014), had observed in the thermal properties of control- and modified- starches that  $T_o$  and  $T_p$  were slightly but significantly higher in the calcium- and in the magnesium-fortified starches (this study focused on the preparation of potato starches fortified in calcium and magnesium). As a divalent cation, we expected magnesium levels to be correlated to the starch characteristics, similar to calcium; however, this was not observed in our study.

Some authors report that the levels of cations tend to be high in potato starches with high phosphorus content and that the presence of these cations strongly affects the rheological properties of the starches (Kainuma et al., 1978; Wiesenborn et al., 1994; Chen et al., 2003; Noda et al., 2007; Zaidul et al., 2007).

Our results on correlations of minerals with pasting properties agree with those observed by Zaidul et al. (2007) in starches from different cultivars of potato. They showed that high levels of sodium and potassium resulted in high values of peak viscosity and setback. In contrast, high amounts of calcium and magnesium in the potato starch resulted in a low peak viscosity and high breakdown and setback.

The correlation analysis of the amylose content with the other analyzed characteristics shows that amylose content was positively correlated with the final viscosity and peak temperature ( $T_p$ ) and negatively correlated with the viscosity peak, breakdown, and enthalpy of gelatinization.

Zaidul et al. (2007) showed that a high level of amylose resulted in a low peak viscosity and breakdown in potato starches, which is consistent with our results. On the other hand, Šimková et al. (2013) showed that the amylose content negatively correlated with the phosphorus content in 16 cultivars that were grown in the Czech Republic; these findings were not supported by our study.

The results of the Pearson analysis for resistant starch contents showed a positive correlation with levels of

**Table 1.** Characteristics of potato cultivars.

Cultivars	Origin	Characteristics
BRS Ana	Brazil- Potato Genetic Improvement Program of Embrapa and IAPAR	The tubers show oval shape, red and slightly rough skin, white flesh and shallow eyes. It has a deep root system, which makes it drought-resistant
Colorado	France	The tubers are elongated, oval, large and uniform. The skin of the tubers presents a dull red color with light yellow flesh.
Marlen	Netherlands	The tubers are oval and round-oval, with skin and yellow flesh, smooth bark and semi-deep eyes.
Snowden	Parentage: B5141-6 X Wischip Breeder: University of Wisconsin, Madison	Tubers have smooth and buff skin, oval shape, shallow eyes. This cultivar shows high agricultural yield with large number of small tubers.
Harley Blackhell	Parentage: B0564-8 USDA potato breeding program	The tubers have a tan to buff skin color with a netted texture, cream flesh and a rounded shape, with semi-deep eyes.
Marcy	Parentage: The cultivar was selected from a cross between 'Atlantic' and Q155-3 Cornell University Potato Breeding program	The tubers are oval, slightly flattened, with light yellow skin, shallow eyes, white pulp. It has a high agricultural yield.
Beacon Chipper	Michigan State University, Maine Seed Potato Board, and Maine Potato Board	The tubers are round with yellow skin, white flesh and shallow eyes. It shows good resistance to storage and tolerance to impact/pressure blackening.

**Table 2.** Chemical composition of potato starches.

	Cultivars						
	Snowden	Harley Blackhell	Marlen	Colorado	BRS Ana	Beacon Chipper	Marcy
Moisture (g 100g <sup>-1</sup> )	13.0 <sup>a</sup>	10.0 <sup>d</sup>	11.2 <sup>bcd</sup>	11.4 <sup>bc</sup>	10.9 <sup>bcd</sup>	10.4 <sup>cd</sup>	11.8 <sup>ab</sup>
Ash (g 100g <sup>-1</sup> )	0.17 <sup>b</sup>	0.29 <sup>a</sup>	0.16 <sup>b</sup>	0.12 <sup>b</sup>	0.02 <sup>c</sup>	0.14 <sup>b</sup>	0.26 <sup>a</sup>
Protein (g 100g <sup>-1</sup> )	0.23 <sup>a</sup>	0.32 <sup>a</sup>	0.29 <sup>a</sup>	0.33 <sup>a</sup>	0.31 <sup>a</sup>	0.33 <sup>a</sup>	0.29 <sup>a</sup>
Fiber (g 100g <sup>-1</sup> )	0.32 <sup>a</sup>	0.38 <sup>a</sup>	0.45 <sup>a</sup>	0.33 <sup>a</sup>	0.06 <sup>c</sup>	0.13 <sup>bc</sup>	0.27 <sup>ab</sup>
Lipids (g 100g <sup>-1</sup> )	0.25 <sup>a</sup>	0.29 <sup>a</sup>	0.29 <sup>a</sup>	0.23 <sup>a</sup>	0.25 <sup>a</sup>	0.29 <sup>a</sup>	0.30 <sup>a</sup>
Total sugar (g 100g <sup>-1</sup> )	0.04 <sup>ab</sup>	0.04 <sup>ab</sup>	0.02 <sup>b</sup>	0.03 <sup>ab</sup>	0.05 <sup>a</sup>	0.05 <sup>a</sup>	0.04 <sup>ab</sup>
Starch	82.31 <sup>c</sup>	84.07 <sup>b</sup>	85.50 <sup>a</sup>	81.90 <sup>e</sup>	83.45 <sup>bc</sup>	84.75 <sup>ab</sup>	82.20 <sup>c</sup>
Amylose (%)	31.74 <sup>c</sup>	31.93 <sup>bc</sup>	34.08 <sup>abc</sup>	34.35 <sup>a</sup>	36.10 <sup>a</sup>	28.51 <sup>d</sup>	28.51 <sup>d</sup>
Resistant starch (%)	13.96 <sup>b</sup>	18.69 <sup>a</sup>	12.47 <sup>bc</sup>	13.52 <sup>b</sup>	10.91 <sup>c</sup>	14.60 <sup>b</sup>	14.36 <sup>b</sup>
P (mg kg <sup>-1</sup> )	687 <sup>ab</sup>	750 <sup>a</sup>	550 <sup>c</sup>	587 <sup>bc</sup>	420 <sup>d</sup>	477 <sup>cd</sup>	750 <sup>a</sup>
K (mg kg <sup>-1</sup> )	875 <sup>a</sup>	800 <sup>b</sup>	600 <sup>c</sup>	485 <sup>d</sup>	505 <sup>d</sup>	850 <sup>ab</sup>	850 <sup>ab</sup>
Ca (mg kg <sup>-1</sup> )	100 <sup>bc</sup>	100 <sup>bc</sup>	105 <sup>b</sup>	135 <sup>a</sup>	85 <sup>c</sup>	40 <sup>d</sup>	85 <sup>c</sup>
Mg (mg kg <sup>-1</sup> )	65 <sup>ab</sup>	70 <sup>a</sup>	50 <sup>d</sup>	55 <sup>cd</sup>	30 <sup>e</sup>	60 <sup>bc</sup>	70 <sup>a</sup>

All data in the table are the means from triplicate experiments. Values within each column, marked with different superscript letters, are significantly different ( $p < 0.05$ )

**Table 3.** Pasting properties of potato starches.

Cultivars	Viscosity (RVU)				Pasting temperature (°C)
	Peak	Breakdown	Final	Seatback	
Snowden	1094.1 <sup>bc</sup>	947.7 <sup>b</sup>	334.8 <sup>ef</sup>	99.4 <sup>d</sup>	66.9 <sup>f</sup>
Harley Blackhell	1063.7 <sup>cd</sup>	801.8 <sup>c</sup>	348.9 <sup>de</sup>	76.1 <sup>e</sup>	67.9 <sup>d</sup>
Marlen	993.9 <sup>d</sup>	669.8 <sup>d</sup>	405.1 <sup>b</sup>	81.0 <sup>de</sup>	70.0 <sup>a</sup>
Colorado	1045.1 <sup>cd</sup>	740.5 <sup>cd</sup>	356.2 <sup>d</sup>	51.6 <sup>f</sup>	69.2 <sup>b</sup>
BRS Ana	771.2 <sup>e</sup>	459.7 <sup>e</sup>	448.1 <sup>a</sup>	127.5 <sup>c</sup>	67.5 <sup>e</sup>
Beacon Chipper	1167.7 <sup>ab</sup>	999.7 <sup>ab</sup>	322.0 <sup>f</sup>	201.9 <sup>b</sup>	66.4 <sup>e</sup>
Marcy	1209.2 <sup>a</sup>	1098.9 <sup>a</sup>	374.0 <sup>c</sup>	225.3 <sup>a</sup>	68.9 <sup>c</sup>

All data in the table are the means from triplicate experiments. Values within each column, marked with different superscript letters, are significantly different ( $p < 0.05$ )

**Table 4.** Thermal properties of potato starches.

Cultivars	Gelatinization				$\Delta H$ (J g <sup>-1</sup> )	
	T <sub>0</sub> (°C)	T <sub>p</sub> (°C)	T <sub>c</sub> (°C)			
Snowden	63.4 <sup>d</sup>	66.4 <sup>c</sup>	70.3 <sup>d</sup>		17.81 <sup>a</sup>	
Harley Blackhell	64.1 <sup>c</sup>	67.2 <sup>b</sup>	71.5 <sup>bc</sup>		17.32 <sup>a</sup>	
Marlen	65.3 <sup>b</sup>	68.7 <sup>a</sup>	72.1 <sup>b</sup>		14.96 <sup>c</sup>	
Colorado	65.4 <sup>ab</sup>	60.6 <sup>d</sup>	73.6 <sup>a</sup>		15.99 <sup>b</sup>	
BRS Ana	63.4 <sup>d</sup>	66.6 <sup>bc</sup>	70.5 <sup>d</sup>		14.58 <sup>c</sup>	
Beacon Chipper	63.8 <sup>cd</sup>	66.7 <sup>bc</sup>	70.9 <sup>cd</sup>		16.25 <sup>b</sup>	
Marcy	65.9 <sup>a</sup>	68.8 <sup>a</sup>	73.2 <sup>a</sup>		17.33 <sup>a</sup>	
Cultivars	Retrogradation				$\Delta H$ (J g <sup>-1</sup> )	%R
	T <sub>0</sub> (°C)	T <sub>p</sub> (°C)	T <sub>c</sub> (°C)			
Snowden	49.1 <sup>b</sup>	55.6 <sup>b</sup>	63.9 <sup>b</sup>		6.14 <sup>a</sup>	34.50 <sup>bc</sup>
Harley Blackhell	48.9 <sup>b</sup>	54.8 <sup>b</sup>	62.9 <sup>b</sup>		4.93 <sup>cd</sup>	28.45 <sup>f</sup>
Marlen	49.2 <sup>b</sup>	56.2 <sup>b</sup>	68.8 <sup>a</sup>		5.43 <sup>b</sup>	36.30 <sup>b</sup>
Colorado	48.9 <sup>b</sup>	55.8 <sup>b</sup>	69.4 <sup>a</sup>		6.37 <sup>a</sup>	39.83 <sup>a</sup>
BRS Ana	50.5 <sup>a</sup>	55.4 <sup>b</sup>	63.6 <sup>b</sup>		4.85 <sup>d</sup>	33.30 <sup>cd</sup>
Beacon Chipper	50.5 <sup>a</sup>	58.9 <sup>a</sup>	68.4 <sup>a</sup>		5.15 <sup>c</sup>	31.73 <sup>de</sup>
Marcy	50.5 <sup>a</sup>	58.9 <sup>a</sup>	68.4 <sup>a</sup>		5.15 <sup>c</sup>	29.73 <sup>ef</sup>

All data in the table are the means from triplicate experiments. Values within each column, marked with different superscript letters, are significantly different ( $p < 0.05$ ).

phosphorus, potassium, and magnesium, as well as with the viscosity peak, breakdown, and enthalpy of gelatinization, providing evidence for the effect of phosphorus. In the potato starch, the phosphate groups are attached to C6 and C3 of the B chains of amylopectin. Thus, phosphoryl-oligosaccharides are released instead of glucose, as amylolytic enzymes are incapable of hydrolyzing the phosphorylated glucosyl residue. This could explain why the phosphorus content also affects starch digestibility (Haebel et al., 2008; Lu et al., 2012; Carpenter et al., 2012).

Another point to be highlighted is the negative correlation between the amylose content and the percentage of retrogradation, suggesting a close relationship between phosphorus and amylose content on this parameter.

It is reported that, among the potato starches, starches with high phosphorus levels show higher RS content than those with medium phosphorus levels, in comparison to other tuber and root starches, and that the amylose content alone in potato starch did not greatly affect digestibility (Absar et al., 2009).

Analysis of pasting and thermal properties showed positive correlations between peak viscosity and viscosity breakage; the tendency for retrogradation and enthalpy of gelatinization, and a negative correlation with final viscosity. Moreover, the enthalpy of gelatinization had a positive correlation with mineral content (phosphorus, potassium, and magnesium) and the percentage of retrogradation of the starches; a negative correlation with amylose, highlighting the close relationship between minerals bound to starch molecules; and amylose content on these determining properties for the applicability of starches.

Low amylose starches require high energy for the rupture of the double helices of amylopectin, which is reflected by the enthalpy of gelatinization.

## Materials and Methods

### Cultivation of potatoes

Seven potato cultivars were studied: BRS Ana, Colorado, Marlen, Snowden, Harley Blackhell, Beacon Chipper, and Marcy. Table 1 shows the main characteristics of the cultivars. The cultivation of potato cultivars was conducted in Pouso Alegre, State of Minas Gerais, Brazil (latitude -22.2341, longitude -45.9332, 22°14'3"S, 45°55'60" W, altitude 822m,

humid subtropical climate with hot humid summer and mild winter). The soil of the area is classified as Red-Yellow Dystrophic Latosol. The experimental design was a randomized block design with five replicates and seven treatments, represented by potato cultivars. Before planting, fertilization was performed using NPK (04-16-08) 300 kg ha<sup>-1</sup> and applied to the furrow. After 30 days of planting, fertilization of the cover with ammonium sulfate (300 kg ha<sup>-1</sup>) was carried out. Irrigation was performed by spraying when necessary and interrupted 30 days prior to the harvest. For preventive control of pests and diseases, application of insecticides was carried out in the furrow and after planting. Desiccation was done 95 DAP (days after planting) with the herbicide Diquat (396 g of i.a. ha<sup>-1</sup>), and the harvest was performed 114 DAP.

### Starch extraction

After harvesting the tubers, the extraction of the starch was performed by a physical method, with three repetitions per cultivar. Peeled tubers were disintegrated in an industrial liquefier, and starch extraction was performed using rotary sieves with different aperture sizes (0.25 to 0.088mm). The "starch milk" was purified in a centrifuge, and the pre-drying and drying steps performed using a vacuum filter and flash dryer, respectively.

### Chemical composition

The starches of potato cultivars were analyzed to assess moisture, ash, lipid, protein (calculated from the nitrogen content through the factor 6.25), total sugars, and starch content, according to the AOAC methodologies (AOAC, 2007). The content of phosphorus, potassium, calcium, and magnesium was analyzed as described by Malavolta *et al.* (1997). Samples of 250 mg were placed in digestion tubes, and 7mL of a 6:1 (v/v) solution of HNO<sub>3</sub> and HClO<sub>4</sub> was added. The tubes were placed in digestion blocks with temperatures ranging from 50°C to 250°C until a clear extract was obtained. Subsequently, samples were cooled, and the volume was adjusted to 25 mL with deionized water.

The phosphorus content was determined based on the formation of the yellow complex vanado-molybdo-phosphoric acid. Four milliliters of deionized water and 2 mL of the mixture ammonium metavanate 0.25% (w/v) and ammonium molybdate 5% (w/v) were added to a 1mL aliquot of extract.

After resting for 5 min, the absorbance was measured at 420 nm using a spectrophotometer (FEMTO 600S).

For the quantification of potassium, calcium, and magnesium, 0.2 mL aliquots of the extract were added to 19.8 mL of lanthanum oxide 0.25% (w/v), and the content of potassium, calcium, and magnesium was analyzed at 766.5, 422.7, and 285.2 nm, respectively, using an atomic absorption spectrophotometer (Analyst 800, Perkin Elmer-USA).

The amylose content of the starches was determined according to the ISO-6674 method (ISO, 1987). The amylose content was calculated from the standard curve of amylose, and the results were expressed as percentage of amylose. The resistant starch content was determined by the method described by Goñi et al. (1996).

### Pasting properties

Pasting properties of potato starches were determined using a Rapid Visco Analyzer (Model RVA 4, Newport Scientific Pty. Ltd., Warriewood, Australia), using starch suspensions (2.5 g of starch in 25 mL of water), corrected for the basis of 14% of moisture. The program used was Standard 1. Peak viscosity (PV), breakdown (BD), setback (SB), and final viscosity (FV) were measured from the pasting curve using Thermocline for Windows software (Newport Scientific Pvt., Ltd., Australia) (Santos et al. 2016).

### Thermal properties

Starch samples (2.0 mg, dry basis) were weighed into aluminum pans, mixed with deionized water (6  $\mu$ L) and sealed. The sealed pans were kept at 25°C for 2 h, for balance, and heated at a rate of 10°C min<sup>-1</sup> from 25°C to 100°C. An empty aluminum pan was used as reference. After running the samples in a differential scanning calorimeter (DSC; Pyris 1, Perkin Elmer, USA), they were refrigerated at 5°C for 14 days and analyzed again under the same conditions to determine the thermal properties of retrograded starches. The instrument was calibrated using indium, and an empty pan was used as a reference. Onset ( $T_o$ ), peak ( $T_p$ ), and conclusion ( $T_c$ ) temperatures and enthalpy ( $\Delta H$ ) were determined from the DSC thermograms using the Pyris 1 software (Perkin Elmer, USA) (Santos et al. 2016).

### Data analysis

All samples were tested in triplicates, in each analytical technique. Analysis of variance (ANOVA) was used to conduct the statistical analysis of the results with SAS (Version 9.2 for Windows, SAS Institute Inc., Cary, NC, USA). When appropriate, the difference among the means was determined using Tukey's multiple comparisons. Statistical significance was set at 5% level of probability. Pearson correlation coefficients were determined to evaluate the relationship between variables.

### Conclusion

In a constantly evolving and competitive market, a major factor that differentiates an industry involves the creation of new products and/or the production of products with improved characteristics. Thus, the search for native starches with properties that meet the different demands of the consumer market is of great significance. The results of this study show that the starches of the seven potato cultivars have a high degree of purity, with different characteristics regarding the content of minerals, amylose, and resistant

starch, and thermal and pasting properties. Phosphorus, potassium, and magnesium contents are closely related to the higher viscosity peak, tendency to retrogradation, percentage of resistant starch, and enthalpy of gelatinization; calcium and amylose contents have an opposite effect on these properties. The information obtained from this study can be useful for food-related industries in Brazil that use potato starch.

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