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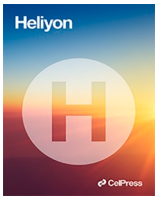

Research article

Physicochemical properties of starch of four varieties of native potatoes

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ABSTRACT

The limited industrial use of indigenous varieties of native potatoes has caused a decrease in its cultivation, restricting it to the self-consumption of the Andean population. The present study analyzed the physicochemical, thermal, and structural properties of the starches extracted from four of these varieties Aq'hu Pukucho, Yurakk Kkachun Wakkachi, Yurac Anca, and Huarmi Mallco, as a potential source of be used in industries such as food, pharmaceutical and, bioplastics. The percentage yield in wet extraction ranged between 14.53 and 20.26 %. The luminosity L* and whiteness index (WI) values were observed in ranges of 90.75–92.71 and 90.05–91.50, respectively. The Finding revealed various techno-functional properties, since the level of amylose varied between 36.29 and 43.97 %, an average zeta potential of −22 mV, and a maximum viscosity between 19,450–14,583 cP. The starches showed consistent thermal behavior since the TGA curves showed three stages with gelatinization temperatures that ranged between 54.9 and 59.75 °C, an enthalpy of 3.60–6.62 J/g, and various shapes of particles such as circular, elliptical, and oval. In conclusion, the relationships between variables such as water absorption index, swelling power, viscosity, crystallinity, enthalpy, and gelatinization temperature reveal different characteristics of each type of starch, which can influence its use.

1. Introduction

Native potatoes have great historical, social, food, genetic, and nutritional importance, contributing significantly to food security by complementing the family diet [1–3]. The potato (Solanum tuberosum L) is one of the most important crops globally in production and consumption [4]. It originated in South America, specifically in the southern region of Peru and the northwest of Bolivia [5]. The Andigenum group is cultivated in the Andean countries, namely Venezuela, Colombia, Ecuador, Peru, Bolivia, and the southern coast of Chile [6]. These regions are considered centers of wealth and diversity for potato varieties [7].

The four potato varieties selected for this study: Aq'hu Pukucho (APE) and Yurakk Kkachun Wakkachi (YKW) of the sweet variety, and Yurac Anca (YA) and Huarmi Mallco (HM) of the bitter variety, have been chosen for their significance to the high Andean

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inhabitants of the Cusco region, Peru, who primarily cultivate them for self-consumption. These crops are considered underutilized, highlighting the need to investigate their specific properties and potential. The variability in the chemical composition, particularly between sweet and bitter potatoes, influences their physicochemical and functional properties. Research on these properties enhances understanding and appreciation of the biological diversity within this crop. The selection of these varieties contributes to the scientific knowledge of the starch composition of native potatoes, thereby emphasizing their importance in promoting sustainable and resilient food systems.

Potato starch, a naturally occurring polysaccharide extracted from the tubers of the Solanum tuberosum plant, has garnered significant attention owing to its exceptional functional properties and extensive industrial applications, including food, pharmaceutical, and bioplastics industries [8–10]. Its widespread use as a thickening, gelling, and stabilizing agent in the food industry has been long acknowledged [11–13]. However, comprehensive characterization of potato starch remains a complex task, as its properties are influenced by many factors, such as genetic variations, growth conditions, and processing methodologies [14,15].

Hence, a thorough investigation encompassing the structural, physicochemical, morphological, and thermal aspects [16] of native potato starch varieties [15] is imperative to assess their suitability for application in the food industry [17,18]. Moreover, recent developments have extended the utilization of potato starch into novel domains, such as nanotechnology and bioengineering [19], as well as its use as a renewable energy source [20].

Starch derived from vegetable sources primarily comprises amylopectin and amylose. Amylopectin consists of linear chains of glucose units linked by α-1,4-glucosidic bonds and exhibits a highly branched structure with α-1,6 positions containing small glucose chains along the molecule's axis. On the other hand, amylose is essentially a linear chain of α-1,4-glucans with limited branching at the α-1,6 positions [20]. Consequently, numerous functional properties of starch are contingent on the ratio of amylose to amylopectin [15,21–23].

The quality indicators of starch for industrial applications vary based on their specific use. Higher amylose content contributes to firmer gels and films, desirable in bioplastics [24], while lower amylose content is preferred for clear gels. Transparency and clarity are crucial for food products [25] and transparent bioplastic films for packaging [26]. Reducing the tendency for retrogradation enhances the shelf life and quality of starch-based products [27]. Increased granule size, solubility, swelling power, and water absorption capacity are essential for thickeners and binders in food and pharmaceuticals [28]. Lower gelatinization temperatures are favored for energy-efficient processing, while higher temperatures may be beneficial for bioplastic applications [29].

The evaluation of starch's physicochemical and techno functional characteristics could stimulate the cultivation of native potato varieties and prevent their genetic loss [8]. Understanding the structure and composition of native potato starch should be prioritized [30]. However, research on its characteristics and potential use in the industry is limited, and a complete exploration of the properties of native potato starch from different varieties originating in Peru is still missing. The objective was to provide valuable information on the unique properties of starch from various potato varieties to improve its application as a versatile and sustainable biomaterial. In this study, starch extracted from four native potato varieties was analyzed, providing a detailed view of its morphological, physicochemical, and thermal properties through amylose content, thermal behavior, structural characteristics, particle size, color, and techno-functional properties such as swelling power (SP) and water absorption index (WAI).

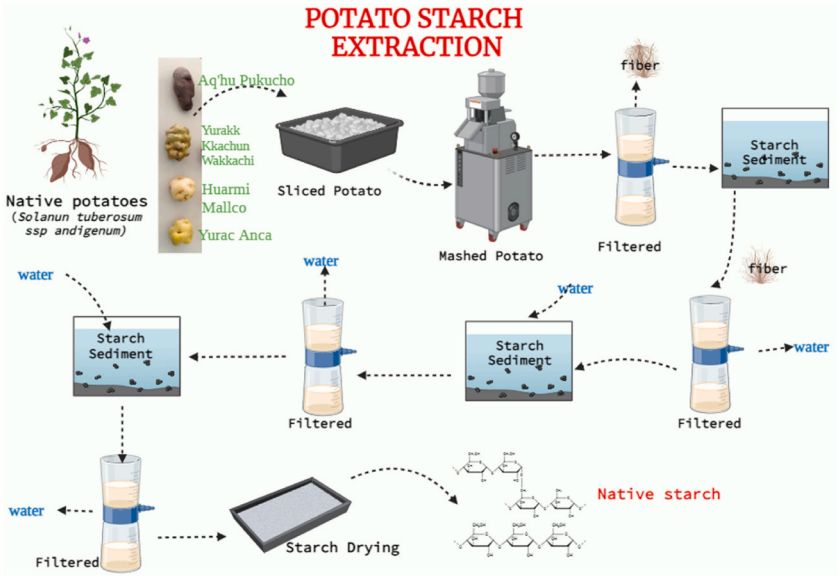

Fig. 1. Scheme of wet extraction of potato starch used to obtain the samples.

2. Materials and methods

2.1. Raw materials

Native potato (Solanum tuberosum ssp andigena.) of four varieties: Aq'hu Pukucho (APE), Yurakk Kkachun Wakkachi (YKW), Yurac Anca (YA), and Huarmi Mallco (HM) (Figs. 1 and 8), were collected in July 2021 in Espinar and Canchis Province, Cusco, Peru (Table 1).

2.2. Starch extraction

Starch extraction was carried out using the wet method (Fig. 1). The potato was washed with plenty of water and cut into uniform cubes of approximately 2 cm. Subsequently, it was ground in an industrial blender (Surco, L-20, USA) for 3 min in a proportion of potato: water 1:3. It was then filtered through a polyethylene cloth with a pore size of approximately 0.05 mm, separating the wet puree from the fibers. The obtained starch solution was allowed to settle at room temperature for 2 h. It was washed and filtered three times, and finally, the solution was allowed to stand for 3 h to precipitate and decant the starch. The wet starch is spread on a tray and dried at 20–25 °C for 72 h. For the percentage yield (Y %), use Equation (1).

$$\mathbf{Y}\ (\%) = \frac{\textbf{Mass of dried starch}}{\textbf{Total mass of potatoes}}\ \text{x}100 \tag{1}$$

2.3. Color

Color analysis of native starch samples used a Konica Minolta colorimeter, model CR-5 (Tokyo, Japan). Colorimetric measurements of lightness (L*, where 0 represents black and 100 represents white), hue angle (h*, Equation (2)), calculated as the arctangent of (b*/a*), and chroma color intensity (C*, Equation (3)), following the standard conditions established by the International Commission on Illumination (CIE).

Furthermore, they determined the yellowness index (YI, equation (4)) and the whiteness index (WI, equation (5)) [31].

$$h* = \arctan\frac{b*}{a*} \tag{2}$$

$$C* = \sqrt{a*^2 + b*^2} \tag{3}$$

$$YI = \frac{142.86\ \text{x}\ b^*}{L} \tag{4}$$

$$WI = 100 - \sqrt{(100 - L)^2 + (a^*)^2 + (b^*)^2} \tag{5}$$

2.4. Apparent amylose content

The determination of amylose content in starch samples followed the modified methodology proposed by Galicia et al. [32]. Initially, 20 mg of starch was accurately weighed and placed in a 50 mL screw cap tube. Then, he added 0.2 mL of 95 % ethanol and 1.8 mL of 1 M sodium hydroxide to the tube and let the mixture stand for 24 h at room temperature. After the incubation period, the solution was adjusted to a final volume of 20 mL using deionized water and then shaken vigorously for 30 min.

Then, a 1 mL aliquot of the resulting solution was separated, adding 2 mL of 1 M acetic acid with continuous stirring plus 0.4 mL of Lugol's solution and adjusting the volume to 20 mL with deionized water. The solution was kept in the dark for 20 min without stirring. Subsequently, an aliquot of the solution was carefully removed and transferred to cuvettes for absorbance measurement using a UV–Vis spectrophotometer at 620 nm.

The standard curve used an amylose solution at a concentration of 1 mg/mL in deionized water to accurately quantify the amylose content in the samples.

Table 1
Provenance of native potato varieties used in the present study.

Location	Sweet varieties		Bitter varieties	
	Aq'hu Pukucho	Yurakk Kkachun Wakkachi	Yurac Anca	Huarmi Mallco
Community	Tarkuyoq,	Tiruma	Apachaco	Tiruma
District	Espinar	Combapata	Coporaque	Combapata
Province	Espinar	Canchis	Espinar	Canchis
Geographic coordinate (S)	14°44′36.5	14°05′19.8	14°52′19.8	14°05′19.8
Geographic coordinate (W)	71°26′22.9	71°17′55.8	71°31′48.4	71°17′55.8
Altitude (m)	3925	3475	4001	3475

Fit the absorbance data into a linear equation and the amount of amylose (%) expressed according to Equation (6).

$$\%\ AM = \frac{M \times d}{f \times 100} \tag{6}$$

where M is the amylose (mg) obtained from the adjusted equation, d is the dilution factor, and f is the mass of starch.

Calculating amylopectin by the difference between total starch and amylose [33,34].

2.5. X-ray diffraction

X-ray diffraction measurements of the starch samples used an X'Pert Pro X-ray diffractometer (PANalytical, Almelo, The Netherlands) equipped with CuKα^{-1} radiation at 40 mA and 40 kV. The data scan was in a 2 θ range between 5 and 50 °C. Before analysis, 2 g of starch from each potato variety were weighed and conditioned to a moisture level of 4 %. Then, he placed the starch samples in a PANalytical universal powder sample holder.

Origin Pro 2019 software determined the crystalline and amorphous regions of the starches. The crystalline peak area and undeveloped area were separated using this software. Subsequently, the relative crystallinity is calculated as the ratio of the crystalline peak area to the total diffraction area.

2.6. Zeta potential (ζ)

0.10 g aliquot of starch was dispersed in 100 mL of ultrapure water and subjected to continuous agitation at 200 rpm for 24 h. The Nicomp device model ZLS, Z3000 (Massachusetts, MA, USA) was used to estimate the zeta potential, introducing 2 mL of the aqueous starch dispersion into a polystyrene cell. The reading was at a laser wavelength of 632.8 nm, with a scattering angle of −14.14° and an electric field intensity of 5 V/cm.

2.7. Swelling power (SP), water solubility index (WSI), and water absorption index (WAI)

With some modifications, SP, WSI, and WAI were determined as described by Gani et al. [35]. They weighed a sample of 0.2 g of starch (M_0) in 10 mL of distilled water. The swelling capacity, water solubility, and absorption were experimented with at 60, 70, and 80 °C. After stirring manually for 30 min, the mixture was centrifuged in a Tom's-USA Science-Tech Group centrifuge (model 033R-2) at 900×*g* for 30 min at room temperature. Gelatinized starch (M_1) and the supernatant were obtained, which was dried at 90 °C for 4 h until obtaining a constant weight (M_2). SP, WSI and WAI using equations (7)–(9).

$$SP\left(\frac{g_{swollen}}{g_{starch} - g_{soluble}}\right) = \frac{M_1}{M_0 - M_2} \tag{7}$$

$$WSI\left(\frac{g_{soluble}}{100g}\right) = \frac{M_2}{M_0} \tag{8}$$

$$WAI\left(\frac{g_{swollen}}{100g}\right) = \frac{M_1}{M_0} \tag{9}$$

2.8. Pasting properties (RVA)

Pasting properties were assessed utilizing an Anton Paar rotational rheometer (Model MCR 702e, Austria) equipped with a starch cell accessory. The water content of the starch was calculated, and a 10 % w/w suspension (approximately 12.3 g of starch) was prepared and allowed to stand for 60 min. For each test, they weighed 20 g of the suspension and quickly loaded it into the starch cell of the rheometer. The experimental procedure followed a predetermined heating and cooling regimen, which included an initial 20 s stirring period at 600 rpm, followed by a consistent 160 rpm throughout the test. This regimen began with an 8 min stabilization phase at 50 °C, followed by a heating phase at 6 °C/min until 95 °C, a 5 min isothermal hold at 95 °C, a cooling phase at 6 °C/min down to 50 °C, and a final 2 min isothermal hold at 50 °C. Key parameters, including pasting temperature, peak viscosity, trough viscosity, final viscosity, breakdown viscosity, and setback viscosity, were recorded using the Reocompass© software. For data reliability, all measurements were performed in triplicate.

2.9. Thermal analysis

The thermal stability of the starch samples was assessed using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). For TGA, the sample (2 water/1 starch) was loaded into alumina crucibles (Al_2O_3) and analyzed using a Thermogravimetric Analyzer (TA Instruments, TGA550, Delaware, USA). The spectrum reading was carried out with Trios V software, and the temperature range was set from 20 to 600 °C, with a heating rate of 10 °C/min and a nitrogen flow rate of 50 mL/min.

The determination of the thermal transition parameters was performed using a differential scanning calorimeter (DSC) from TA Instruments (DSC2500, Waters TM, New Castle, USA) in a nitrogen atmosphere (50 mL/min). The starch samples were securely sealed

in aluminum pans and subjected to scanning from 20 to 200 °C at a heating rate of 5 °C/min. DSC baseline measurement was performed using an empty pan as a reference, and the sample was measured under the same conditions.

2.10. FTIR spectra

Pressed tablets containing 0.1 % native starch in KBr (IR Grade, Darmstadt, Germany) were prepared and placed in the transmittance module of the FTIR spectrometer (Fourier-transform IR spectroscopy), Thermo Fisher model Nicolet IS50 (Waltham, MA, USA), in a wavenumber range of 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}.

2.11. SEM morphology

A Quanta model 200 scanning electron microscope (SEM, Thermo Fisher, Waltham, MA, USA) was used. The sample was placed directly on the carbon tape in a vacuum chamber and measured at an accelerating voltage of 25 kV and 1000× magnification to recognize the biopolymer surface and graphically reproduce it using the instrument software.

2.12. Statistical analysis

The results were carried out using one-way Analysis of Variance (ANOVA) and LSD multiple comparison tests with a significance of 5 %, and Principal Component Analysis (PCA) using the statistical software Origin Pro 2019. The analyses were carried out with three repetitions.

3. Results and discussions

3.1. Yield

The starch recovery yield exhibited a significant difference (p-value <0.05) among the studied varieties, ranging from 14.53 % to 20.26 % (Table 2). This variation was influenced by variety, genotype, habitat, and environmental factors [22,30,36,37]. Previous studies have reported starch yields in various native potato varieties, such as 12.30 %–13.03 % for Puka viruntus, Phusi k'achun waqachi, Waka waqra, and Alq' a wayruru [38], 11.36 %–13.55 % for Puma maqui, Cuchi pelo, Yana palta, and Qayma marcela [39], and 10.42 %–9.3 % for Capiro, Huayro moro, and Amarilis-INIA varieties grown in the province of Jauja [40]. Similarly, Ruckii, Locka, Ocucuri Morado, Ccompis, Yana Imilla, and Yana Lomo varieties demonstrated yields ranging from 10.23 % to 17.60 % [41,42].

Yield is influenced by several factors, including the extraction method [43] and the degree of hydrolysis or ripening during extraction [44]. These factors contribute to the observed variability in starch recovery among different varieties and studies.

3.2. Color

The colorimetric parameters of starch vary depending on the source [45] and are influenced by the specific cultivation method used [46]. Amylose content showed a negative correlation with L*, a*, and b* values, and higher concentrations of amylopectin result in lower L* values [47]. On the contrary, we found a positive correlation in this research between amylose and the luminosity and whiteness index, with greater intensity for the bitter varieties HM and YA. Furthermore, starch granules inherently possess white and opaque characteristics. During extraction, the absence of oxidizing reagents or enzyme inhibitors can cause pigmentation by imparting a yellow-to-green hue to the starch [48].

Table 2 presents the color attribute results, indicating that all starch samples fall within the white spectrum, with luminosity values (L*) ranging from 90.72 to 92.71 and Whiteness Index (WI) values between 90.05 and 91.50. The attributes Chroma (C*) Yellow Index (YI) exhibit low values, suggesting no macroscopically observable differences between the samples. However, the hue (h*) values fall within the first quadrant of the red and yellow color space. Statistical analysis revealed significant differences in these hue attributes (p-value <0.05).

Table 2
Color coordinates by CIEL*a*b* system for starch extracted from four potato varieties.

Attribute	Aq'hu Pukucho	Yurakk Kkachun Wakkachi	Yurac Anca	Huarmi Mallco
	$\bar{x} \pm SD$	$\bar{x} \pm SD$	$\bar{x} \pm SD$	$\bar{x} \pm SD$
L*	92.68 ± 0.00^{a}	92.71 ± 0.01^{a}	90.73 ± 0.09^{c}	91.23 ± 0.07^{b}
a*	0.35 ± 0.03^{a}	0.20 ± 0.00^{b}	0.23 ± 0.02^{b}	-0.08 ± 0.03^{c}
b*	4.31 ± 0.04^{b}	4.94 ± 0.01^{a}	3.60 ± 0.03^{d}	4.09 ± 0.08^{c}
C*	4.32 ± 0.04^{b}	4.95 ± 0.01^{a}	3.61 ± 0.03^{d}	4.09 ± 0.08^{c}
h*	85.40 ± 0.30^{d}	87.68 ± 0.00^{b}	86.35 ± 0.28^{c}	91.16 ± 0.34^{a}
WI	91.50 ± 0.02^{a}	91.19 ± 0.01^{b}	90.05 ± 0.08^{d}	90.32 ± 0.08^{c}
YI	6.64 ± 0.07^{b}	7.62 ± 0.01^{a}	5.67 ± 0.04^{d}	6.41 ± 0.12^{c}
Yield (%) ± SD	16.31 ± 0.64^{b}	20.26 ± 0.82^{a}	14.53 ± 1.53^{b}	15.39 ± 0.51^{b}

Different letters in the lines indicate a significant difference, evaluated with least significant difference (LSD) test at 5 % of significance.

The Whiteness Index (WI) is a critical perceptual characteristic of color appearance. Rożnowski et al. [49] quantified the whiteness index (WI) of native potato starch as 92.98, lightness (L*) higher than 92.5, and hue (h*) ranging from 92.28 to 96.18. Additionally, he found lower chromaticity (C*) values below 2.32, and the yellowness index (YI) ranged between 3.82 and 4.36. These observations align closely with the findings of the present study.

3.3. Amylose/amylopectin ratio

As presented in Table 3, the amylose/amylopectin ratio between the different varieties was significantly different. Starch granules comprise two macromolecules, namely amylose and amylopectin [50]. A higher proportion of amylose is considered beneficial from a nutritional perspective [51]. Potatoes can produce starches with an elevated amylose ratio [10] while maintaining a similar morphology to regular starch granules [52]. In aqueous dispersions, smaller and more linear than amylopectin, amylose tends to dissociate from the granules and dissolve in water [53]. In contrast, amylopectin exhibits near-insolubility, with amylose readily dissolving in hot water [54], and is also responsible for increasing viscosity in aqueous solutions [55]. Additionally, the starch content differs according to its source [37] and correlates with the dry matter content, leading to fluctuations in amylose and amylopectin levels [22].

3.4. Principal Component Analysis (PCA)

The principal components PC1 and PC2 (Fig. 2) influenced the loading of variables. PC1 (86.32 %) was associated with properties such as gelatinization temperature, chroma, amylose, luminosity, and whiteness index for the YKW variety, and yellow index, particle size, amylopectin, crystallinity, and yield for the YA and HM varieties. PC2 (13.68 %) considered different factors for each variety of starch. The APE variety took the Z potential, the water absorption rate, and the swelling. In the case of HM and YA varieties, the viscosity. Finally, for the YKW variety, the solubility index. We found different correlations between the characteristics of the varieties studied amylopectin, content, crystallinity, yellowness index, and particle size presented a direct relationship in starches of the HM and YA varieties. Furthermore, the APE variety correlated with ζ, WAI, and SP. Also, the YKW variety found a direct correlation between the enthalpy of gelatinization and the amylose content. However, there was no correlation between crystallinity and viscosity. Viscosity has an inverse relationship with WAI and SP in the APE variety. On the other hand, the particle size of the YA variety has an inverse relationship with the whiteness index.

PCA was used to deepen the correlation analysis between the results of various authors. According to Alvani et al. [56], an inverse relationship between particle size and gelatinization temperature would have been observed in the Mayan Gold variety. We confirmed the same in this study for the YKW, HM, and YA varieties (Fig. 2). Conversely, Martínez et al. [57] observed a correlation between particle size and crystallinity, a relationship further supported by the results obtained for the HM and YA varieties. For the starches of the YKW and APE varieties, correlations were found between gelatinization temperature, enthalpy, whiteness index, and luminosity, similar to that reported by Martínez et al. [57] in the white and black Imilla varieties. Sánchez-González et al. [58] would have observed the opposite and found a direct relationship between viscosity and crystallinity in the Yungay variety. However, this study found that viscosity was independent of crystallinity in HM and YA varieties. Alvani et al. [56] found a direct relationship between amylose content in Brodick and Maris Piper varieties and particle size, which was not observed in this study. Finally, a direct relationship between the amylose content and the water solubility index would have been found in the Badshah variety [59], the same in the YKW variety. Furthermore, there would be an inverse relationship between viscosity and swelling power in the Jyoti and Badshah varieties, coinciding with the APE, YA, and HM varieties in this study (Fig. 2).

3.5. X-ray diffraction

Native potato starch exhibits discernible peaks in a C-type X-ray diffraction (XRD) pattern. This particular XRD pattern is elucidated as a combination of type A and type B configurations (Fig. 3), as substantiated by previous research [60,61]. This conclusion is rooted in the presence of peaks occurring at 2 θ, approximately measured at 15.01°, 17.11°, 19.51°, and 24.08°.

Notably, the principal diffraction peak at 17.11° corresponds predominantly to the type B starch variety. This type of starch is characterized by extended branched amylopectin side chains with well-spaced branch points. In light of this observation, we deduce that the examined potato starch aligns most closely with type CB, which is close to the XRD pattern of type B [61]. A significant increase in the peak at 5.65° can also noted, attributed to type B starch, which is reinforced by the presence of phosphoric acid [62].

Table 3
Physicochemical and structural characteristics of starches from four native potato varieties.

Feature	Aq'hu Pukucho	Yurakk Kkachun Wakkachi	Yurac Anca	Huarmi Mallco
	$\bar{x} \pm$ SD	$\bar{x} \pm$ SD	$\bar{x} \pm$ SD	$\bar{x} \pm$ SD
Amylose (%)	38.92 ± 0.07^{b}	43.96 ± 0.07^{a}	37.62 ± 0.04^{c}	36.29 ± 0.12^{d}
Amylopectin (%)	61.08 ± 0.07^{c}	56.04 ± 0.07^{d}	62.38 ± 0.04^{b}	63.71 ± 0.12^{a}
ζ (mV)	-25.27 ± 3.68^{a}	-17.28 ± 3.87^{a}	-20.61 ± 1.29^{a}	-18.95 ± 2.03^{a}
Crystallinity (%)	22.4 ± 1.7	20.2 ± 0.2	21.7 ± 0.2	22.7 ± 0.7

Different letters in the lines indicate a significant difference, evaluated with least significant difference (LSD) test at 5 % of significance.

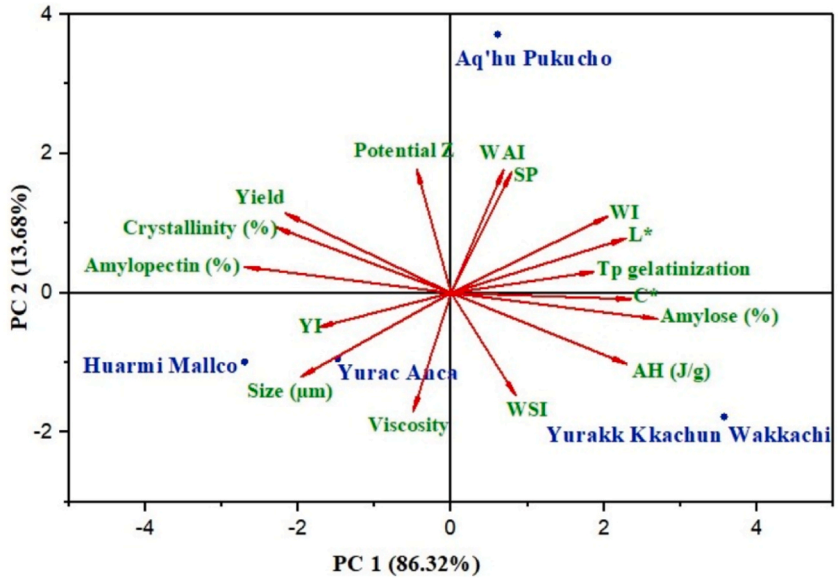

Fig. 2. Principal Component Analysis of the studied variables of starches extracted from four native potato varieties. Where: Aq'hu Pukucho (APE), Yurakk Kkachun Wakkachi (YKW), Yurac Anca (YA) y Huarmi Mallco (HM).

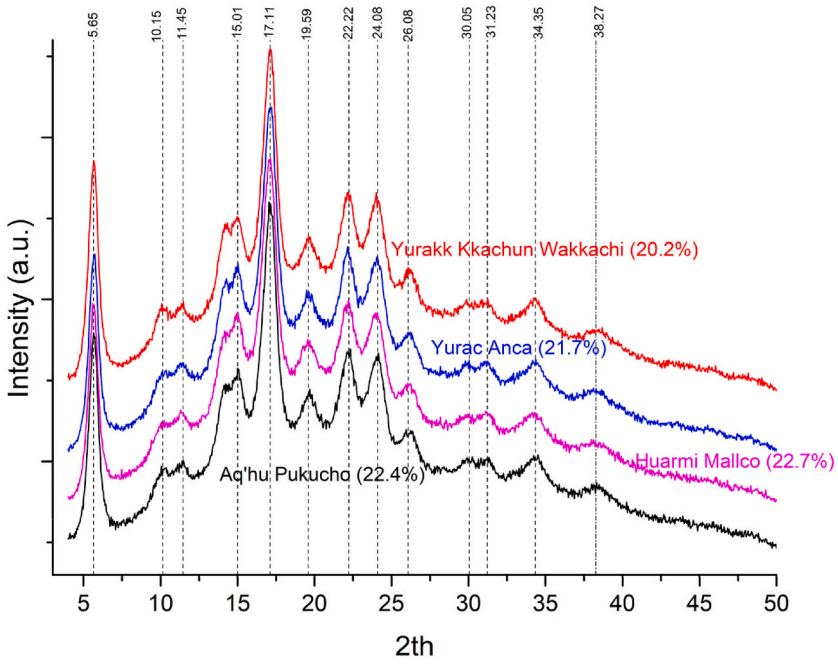

Fig. 3. X-Ray Diffraction (XRD) patterns of potato starches from four distinct varieties.

The crystallinity values obtained (APE 22.4 ± 1.7 %, YKW 20.2 ± 0.2 %, HM 22.7 ± 0.7 %, YA 21.7 ± 0.2 %) are within the range of values reported by other authors for native potato starch which is in a wide range between 21 and 30 % [62–64].

3.6. Zeta potential (ζ)

The dispersibility of starch in aqueous media and its interaction with other ingredients can attributed to the surface properties of starch granules [65]. To evaluate the repulsion or attraction forces between starch granules, the value of the zeta potential ζ is often used, which is related to the stability of colloidal dispersions [66,67]. Colloids with high zeta potential charges tend to remain in suspension, while those with lower charges tend to aggregate and sediment [68].

Zeta potential measurements of commercially produced Farina potato starch [65] and waxy potato starch from WPS AVEBE company [67] reported −11 mV and −13.8 mV, respectively. These values are lower than the zeta potential obtained in our current study (Table 3). Zeta potential values within the −30 to +30 mV range are critical as they indicate an unstable system, which could lead to aggregation or flocculation processes [69].

3.7. Water absorption index (WAI), swelling power (SP) and water solubility index (WSI)

The native potato varieties studied influenced the techno-functional characteristics of native potato starch. Starches of superior quality typically exhibit high water absorption, low solubility, and significant swelling power [22]. The capacity to swell and form a thick paste when subjected to water and heat is particularly crucial for commercial applications. In contrast, solubility plays a vital role in the ability of starch to disperse effectively in an aqueous solution [17].

Significant differences (p-value <0.05) were observed between different varieties of starch in the water solubility index (WSI) at temperatures of 60, 70, and 80 °C. The APE variety exhibited no increase in solubility with temperature, unlike the other varieties under study, which demonstrated an increase in solubility with rising temperature (p-value <0.05).

The WSI values obtained in this study ranged from 3.48 ± 0.34 % to 7.39 ± 0.18 % (Table 4) and were lower than those reported by Ligarda et al. [22] for starches obtained from native potato clones (*Solanum tuberosum*), which ranged from 13.03 ± 0.32 % to 17.69 ± 0.85 %, and for potato variety Van Rosa, which was reported as 27.3 ± 1.2 % by Zhu & Cui [70]. Conversely, our results showed similar values to those written by Martinez et al. [23] for native potato starches from Sanchez Carrion province, La Libertad region, Peru, ranging from 3.86 to 6.35 %, and those reported by Karim et al. [71] for potato starch from six cultivars at the National Agricultural Research Center of Hokkaido-Japan, ranging from 3.3 ± 0.8 to 8.9 ± 0.5.

The Water Absorption Index (WAI) exhibits significant variations among different starch varieties (p-value <0.05) and displays an increasing trend with rising temperature. For instance, at 60 °C, the APE variety demonstrates a WAI of 19.72 ± 0.22 g/g sample, while the YA variety exhibits a WAI of 11.14 ± 0.28 g/g sample (Table 4). These values surpass the water absorption capacity of the Hausa potato variety, which was reported as 2.42 ± 0.14 g/g starch [17], the native potato clones [22] with a WAI of 6.71 g/g sample, and the commercial native CDH potato starch with a WAI of 10.44 g/g [72]. However, these values are lower than the water absorption capacity of starches from the native potato variety Pitikiña (PI), ranging from 21.7 ± 0.65 to 17.0 ± 0.32 g/g starch, as reported by Martinez et al. [73].

The swelling power of starch granules can be influenced by the relative proportions of amylose and amylopectin, with a higher amylopectin content resulting in increased granule swelling [74]. This study demonstrated that amylopectin content is unrelated to swelling power because it acts independently. A significant difference (p-value <0.05) in starch varieties is observed at 60 °C, and the swelling power increases with temperature. The APE variety exhibits the highest average swelling power of 47.45 ± 1.17 g/g starch, while the YA variety shows 33.21 ± 0.42 g/g starch at 80 °C (Table 4). These values surpass the swelling power reported for commercial potatoes from Palakkad, Kerala, India [17] at 5.15 g/g and 7.82 g/g, the native potato colons in Andahuaylas, Peru [22] at 17.91 g/g, the native potato starches from Sanchez Carrion province, the Libertad region, Peru [73] ranging from 22.94 to 29.79 g/g starch, and the native potatoes at 80 °C for starches in Pampacorral community of Lares district, Calca province, Cusco region, Peru [73] with a range of 25.7 ± 0.65 to 19.6 ± 0.29 g/g starch. Comparable values to those reported in this study were found by Zhu & Cui [70] with a swelling power of 45.5 ± 1.4 g water/g starch for starches extracted from potatoes of the commercial variety Van Rosa.

3.8. Pasting properties

RVA provides information on the physicochemical properties, particularly the pasty properties of starches. The steepness of the initial increase in viscosity in the curves reflects the swelling and rupture of the starch granules with increasing temperature (Fig. 4). The RVA analysis found that each variety of potato starch showed different behavior in Peak, Breakdown, and Setback Viscosity, as shown in Table 5. According to Fonseca et al. [75], when the carboxyl and carbonyl radicals are larger than the hydroxyl groups, the amylose chains tend to separate further; this prevents the molecules from approaching each other and prevents the retrogradation process. The results of this study indicated that the YKW variety experienced a smaller decrease in viscosity during the retrogradation

Table 4
Functional properties of starches from four native potato varieties.

Techno-functional property	T (°C)	Aq'hu Pukucho	Yurakk Kkachun Wakkachi	Yurac Anca	Huarmi Mallco
		$\bar{x}$ ± SD	$\bar{x}$ ± SD	$\bar{x}$ ± SD	$\bar{x}$ ± SD
WSI (%)	60 °C	5.50 ± 0.29^{a}	4.54 ± 0.41^{b}	3.48 ± 0.34^{c}	4.89 ± 0.28^{ab}
	70 °C	5.50 ± 0.54^{bc}	6.7 ± 0.58^{a}	4.97 ± 0.43^{c}	6.19 ± 0.42^{ab}
	80 °C	4.59 ± 0.33^{b}	7.39 ± 0.18^{a}	5.26 ± 0.33^{b}	6.72 ± 0.62^{a}
WAI (g/g)	60 °C	19.72 ± 0.22^{a}	14.64 ± 0.20^{b}	11.14 ± 0.28^{d}	13.25 ± 0.38^{c}
	70 °C	24.88 ± 0.28^{a}	24.77 ± 0.49^{a}	22.11 ± 0.29^{b}	22.44 ± 0.18^{b}
	80 °C	45.27 ± 1.24^{a}	33.96 ± 0.14^{b}	31.47 ± 0.33^{c}	33.09 ± 0.73^{b}
SP (g/g)	60 °C	20.87 ± 0.19^{a}	15.33 ± 0.15^{b}	11.55 ± 0.32^{d}	13.93 ± 0.44^{c}
	70 °C	26.33 ± 0.39^{a}	26.55 ± 0.37^{a}	23.27 ± 0.41^{c}	23.92 ± 0.10^{b}
	80 °C	47.45 ± 1.17^{a}	36.67 ± 0.22^{b}	33.21 ± 0.42^{c}	35.48 ± 0.57^{b}

Different letters in the lines indicate a significant difference, evaluated with least significant difference (LSD) test at 5 % of significance.

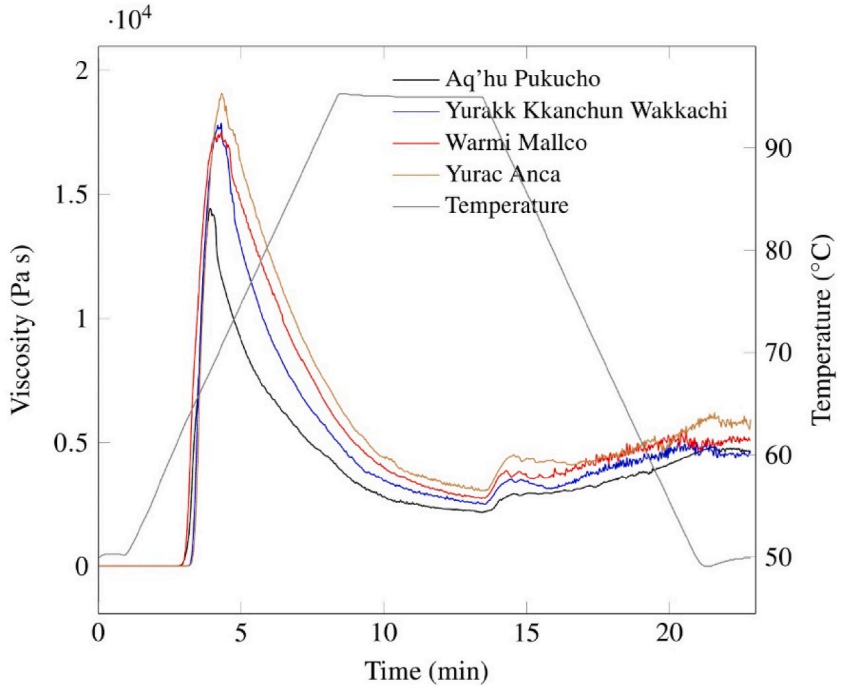

Fig. 4. Pasting profiles analyzed by RVA for starch from four native potato varieties.

Table 5
Pasting parameters analyzed by RVA for starch from four native potato varieties.

Parameters	Aq'hu Pukucho	Yurakk Kkachun Wakkachi	Yurac Anca	Huarmi Mallco
	$\bar{x} \pm$ SD	$\bar{x} \pm$ SD	$\bar{x} \pm$ SD	$\bar{x} \pm$ SD
Pasting Temperature (°C)	60.3 ± 0.1^{c}	62.67 ± 0.12^{a}	62.8 ± 0.20^{a}	60.9 ± 0.26^{b}
Peak Viscosity (cP)	14583 ± 113.7^{b}	17930 ± 1210.5^{a}	19450 ± 1772.1^{a}	17853 ± 1584.4^{a}
Breakdown Viscosity (cP)	12413 ± 120.9^{b}	15433 ± 1221.4^{a}	16447 ± 1721.9^{a}	15137 ± 1346.5^{a}
Setback Viscosity (cP)	9928 ± 161.2^{b}	13356 ± 980.3^{a}	13536 ± 1483.8^{a}	12770 ± 1593.8^{a}
Final Viscosity (cP)	4656 ± 98.8^{c}	4573 ± 224.6^{c}	5912 ± 320.9^{a}	5086 ± 320.9^{b}

Different letters in the lines indicate a significant difference, evaluated with least significant difference (LSD) test at 5 % of significance.

stage, while the APE variety experienced a more significant reduction. In addition, it was observed that the YA variety presented a more significant decrease in breakdown viscosity, suggesting a greater decomposition of starch, while the YKW variety showed a more minor reduction. The YKW variety demonstrated more excellent resistance to decomposition and retrogradation than the other varieties analyzed.

Analysis of the RVA spectrum reveals that the viscosity peak decreases with increasing zeta potential (negative) magnitude. This effect was also noticed by Desam et al. [76] for corn starch, attributing it to increased cross-linking at the higher z-potential (negative). As shown in Table 3, the YKW, HM, and YA varieties with the lowest zeta potential had a higher maximum viscosity peak than the APE variety (Fig. 4), providing information on the starch's water absorption capacity during processing. This study showed no discernible relationship between amylose content and peak viscosity.

Previous research found the maximum viscosity for native potatoes from Hunan Xiang Feng Potato Industry, China, of 5227 cP at 79 °C [68]. [77]. [69] studied 87 potato varieties produced in the Hokkaido region, finding peak viscosity values between 2520 and

Table 6
Gelatinization temperatures and transition enthalpies for starches extracted from four potato varieties.

Variety	T_0	T_p	T_c	AH(J/g)
Aq'hu Pukucho	53.5	59.17	64.68	3.6305
Yurakk Kkachun Wakkachi	54.17	59.75	65.77	6.6211
Yurac Anca	53.86	59.6	66.28	4.2982
Huarmi Mallco	49.31	54.69	60.76	3.6032

Where T_0 is initial temperature, T_p peak temperature and T_c final temperature.

5328 cP. The maximum viscosity of 9166 cP was determined for commercial potato starch [78]. While in India, the maximum viscosity of different varieties of potato starch varies from 4350 cP to 6800 cP [79].

The paste temperature (PT) indicates the beginning of the increase in starch viscosity, and considering that viscosity only begins to increase when the starch granules are completely gelatinized, the paste temperature will be higher than the gelatinization temperature [80], which is consistent with the gelatinization data reported in Table 6.

3.9. TGA thermogravimetric analysis

The thermal behavior of native potato starches (Fig. 5) varies according to the specific potato variety. The initial stage of decomposition involves releasing both free and bonded water and takes place within the temperature range of 25–100 °C. This stage continues until approximately 239 °C, with the YA variety experiencing this initial decomposition at a slightly lower temperature of 232.5 °C. The HM variety exhibits the most minor water loss among the tested varieties, approximately 17.046 ± 0.619 %. The APE, YA, and YKW varieties demonstrate water losses of 17.56 ± 0.32 %, 17.86 ± 0.020 %, and 19.059 ± 0.11 %, respectively.

The thermal characteristics of unmodified starches are illustrated in Fig. 5, displaying thermogravimetric analysis (TGA) profiles for APE, YKW, YA, and HM. These starch varieties manifest strikingly similar decomposition patterns across the three distinct stages of decomposition. The TGA profiles reveal a biphasic degradation process marked by the liberation of moisture and the subsequent thermal degradation of the polymer matrix, as expounded upon by Martinez et al. [23]. Notably, the residual mass observed at 592 °C, conventionally associated with the inorganic remnants post-polymer degradation, exhibits a marginally higher magnitude for the sweet cultivars APE and YKW when compared to the bitter variety YA, as well as for HM.

The TGA derivative analyses (Fig. 5) reveal a convergence of the peak thermal degradation rates among the examined potato starch varieties. Specifically, the APE variety exhibits a maximal thermal degradation rate at 298.3 °C, while the YKW variety peaks at 301.79 °C. The HM and YA varieties also showcase thermal degradation peaks at 303.32 °C.

3.10. Thermal properties

Differential scanning calorimetry (DSC) is a valuable tool for elucidating the intricate thermal responses of starch in the presence of water, as previously explored by Jagadeesan et al. [19]. The thermal perturbations evidenced by the weight loss of potato starch and the concomitant reduction in enthalpy requisite for the gelatinization process signify a notable augmentation in thermal resilience, as Chou et al. [13].

Elevated gelatinization temperatures indicate an augmented degree of structural organization within the crystalline lattice or an enhanced abundance of the starch double helical motif. This phenomenon, outlined by Chen et al. [81], is pivotal in facilitating the compact aggregation of amylopectin within the crystalline domain. Such structural intricacies fortify the overall thermal robustness of the starch matrix.

The maximum gelatinization temperature (Tp) exhibited comparable values among the four examined starch types (Fig. 6a), ranging from 54.69 °C to 59.75 °C. The enthalpy measurements ranged from 3.6032 J/g to 6.6211 J/g, as detailed in Table 6. These

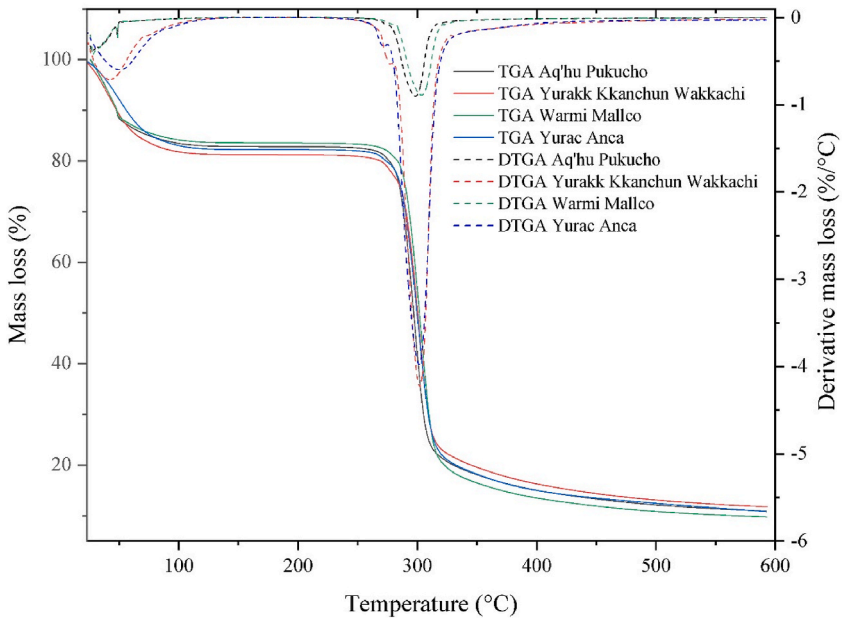

Fig. 5. TGA and DTGA thermograms of potato starch from four varieties.

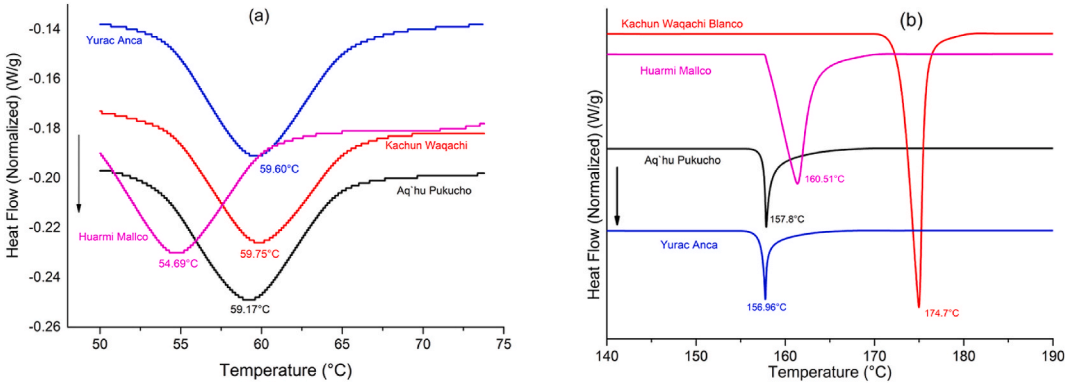

Fig. 6. DSC thermograms of potato starch from four varieties. Where: Gelanitization temperature (a), and fusion temperature (b).

results indicate a lower gelatinization behavior compared to potatoes cultivated in Kavlinge, Sweden, which exhibited Tp values ranging from 66.4 ± 70.5 °C to 69.1 ± 70.4 °C, along with enthalpy values spanning from 8.2 ± 72.0 J/g to 10.3 ± 72.0 J/g [82]. Additionally, potato starch sourced from Noukouren Hokkaido, Japan, displayed a Tp of 66.77 ± 0.16 °C with an associated enthalpy of 16.70 ± 0.39 J/g [83].

Comparable findings to the current investigation were also observed in the study by Martinez et al. [23], wherein Tp values ranged from 60.11 ± 0.11 °C to 58.17 ± 0.04 °C for bitter potatoes grown in Ilave, Puno, Peru. Notably, the enthalpy values in this case were higher, ranging from 16.56 ± 0.30 J/g to 15.08 ± 0.69 J/g. Similarly, starch from different potato varieties in India has a Tp range of 58.8–62.4 °C and an enthalpy between 3.5 and 6.8 J/g [79].

The increase in Tp value may be due to extended molecular chains, especially amylopectin. Such long chains tend to create extended double helical structures, necessitating a heightened temperature for their complete dissociation [71]. In alignment with this rationale, the bitter cultivar denoted as HM manifested the most diminished Tp value among the examined varieties. Furthermore, the enthalpy of gelatinization exhibited values ranging from approximately 3.6032 J/g to 4.2982 J/g for this variety, while a slightly augmented enthalpy magnitude was observed for the YKW variety, measuring 6.6211 J/g.

The maximum temperature (endothermic peak) associated with starch fusion differs among starch varieties, with 174.7 °C for YKW being higher than HM, APE and YA at 160.51 °C, 157.8 °C and 156.96 °C respectively (Fig. 6 b).

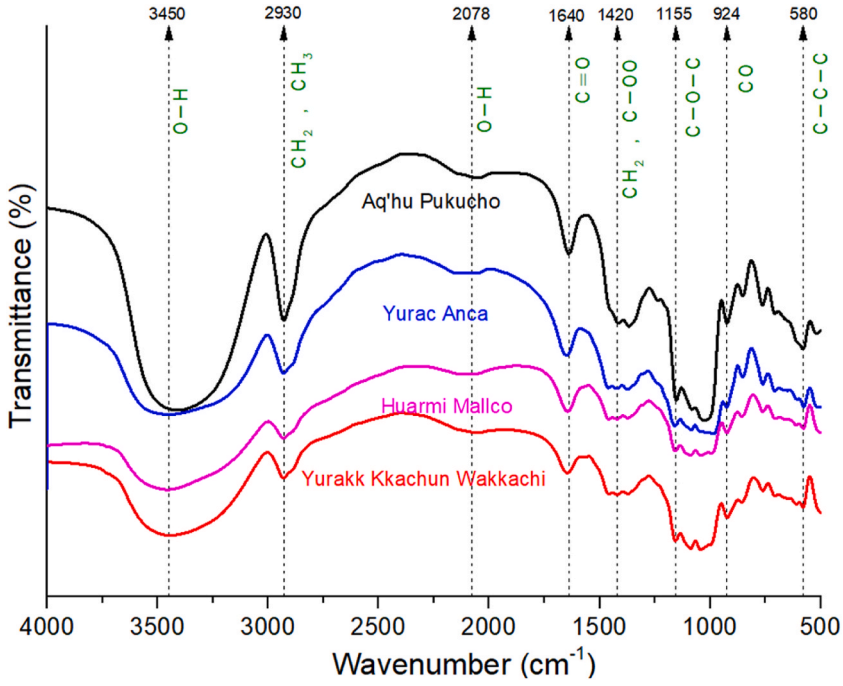

Fig. 7. FTIR Spectra comparing potato starch among four varieties.

3.11. FTIR spectrum

In the FTIR spectrum analysis, specific wavenumbers reveal distinct molecular vibrations associated with the potato starch composition. The band at 3450 cm^{-1} is commonly linked to the O–H stretching vibrations of hydroxyl groups within polysaccharides, signifying the presence of water and/or hydrogen bonding interactions consistent with previous findings [84]. This phenomenon arises due to the ability of glucose units, which make up potato starch, to form hydrogen bonds with neighboring glucose units and water molecules. At 2930 cm^{-1}, vibrations corresponding to C–H stretching in aliphatic hydrocarbon groups are evident. In the context of potato starch, these vibrations are attributed to the presence of CH_2 and CH_3 groups within the starch structure, as reported in studies by Hong et al. [84] and Liu et al. [85]. These hydrocarbon moieties are associated with the amylase and amylopectin components of starch, including their glucose units and branching points. The peak at 2078 cm^{-1} lacks a specific assignment within potato starch samples, yet it could arise from the presence of non-bound water molecules under the studies by Dankar et al. [86] and Olsson & Salmén [87].

At 1640 cm^{-1}, the stretching vibration of C=O is due to the carbonyl group. In potato starch, this peak can attributed to water molecules absorbed within the amorphous regions of the starch structure, as suggested by Dankar et al. [86]. The peak at 1420 cm^{-1} linked to the deformation vibrations of locally symmetric groups, such as CH_2 and C-OO within carbohydrates, consistent with research by Hong et al. [84], Kizil et al. (2002), and Wiercigroch et al. [88]. Vibrations at 1155 cm^{-1} correspond to the C–O–C stretching vibration of the glycosidic linkage in carbohydrates, characteristic of starches and indicative of the presence of glycosidic bonds connecting individual glucose units within the starch molecule, as reported by Hong et al. [84]. The peak at 924 cm^{-1} is associated with C–O stretching vibrations of the glycosidic linkage in amylase and amylopectin, reflecting the α-type configuration, confirming the presence of starch in the sample, consistent with Dankar et al. [86] and Hong et al. [84]. Lastly, the peak at 580 cm^{-1} corresponds to the bending vibrations of the C–C–C linkage within the glycosidic bond of carbohydrates, reaffirming the presence of starch in the analyzed sample, as suggested by Wiercigroch et al. [88].

The four potato starch samples analyzed showed characteristic peaks approximated by specific wave numbers (Fig. 7).

3.12. SEM morphology

Starch granules possess intricate and multifaceted architectures, with their complexity arising from inherent variations in composition encompassing α-glucans, moisture, lipids, proteins, and phosphorylation levels, as well as their component arrangements that exhibit structural differences between amorphous and crystalline regions [20]. Scanning electron microscopy (SEM) facilitates examining and elucidating the inherent structural constituents constituting potato starch [19]. SEM-generated micrographs depicting starch granules reveal a repertoire of shapes encompassing round, oval, and elliptical forms within the native starch matrix [35,89]. These observations align with analogous findings illustrated in Fig. 8.

Using ImageJ v1.54f image analysis software, the particle size of starch granules in four distinct varieties was quantified from micrographs (Fig. 8), revealing statistically significant differences (p-value = 0.016). The APE variety exhibited the smallest particle size, measuring 12.7 ± 6.8 μm, followed by the YKW, HM, and YA varieties with mean particle sizes of 14.9 ± 5.3, 17.0 ± 4.3, and 20.0 ± 4.5 μm, respectively.

4. Conclusions

This study identified the unique physical, chemical, techno-functional, and thermal properties of native potato starch obtained by wet extraction. The extraction process produced starches with favorable attributes, such as high yields, notable gloss and whiteness indices, and high viscosity and amylose content. Furthermore, an average ζ potential between −19 and −25 mV confirms its excellent techno-functional performance of its characteristics, such as water absorption index, swelling power, and water solubility index. Thermogravimetric analysis of the granules showed that less energy was required for gelatinization. Regarding the structure, FTIR spectroscopy confirmed the presence of functional groups characteristic of starch. Furthermore, the starch granules of all four varieties had characteristic circular, oval, and elliptical shapes with smooth surfaces.

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Data availability statement

Data will be made available on request.

CRediT authorship contribution statement

Antonieta Mojo-Quisani: Writing – original draft, Methodology, Conceptualization. **Katiuska Licona-Pacco:** Methodology, Conceptualization. **David Choque-Quispe:** Methodology, Data curation, Conceptualization. **Miriam Calla-Florez:** Validation, Formal analysis. **Carlos A. Ligarda-Samanez:** Writing – review & editing, Validation, Formal analysis. **Raúl Mamani-Condori:** Writing –

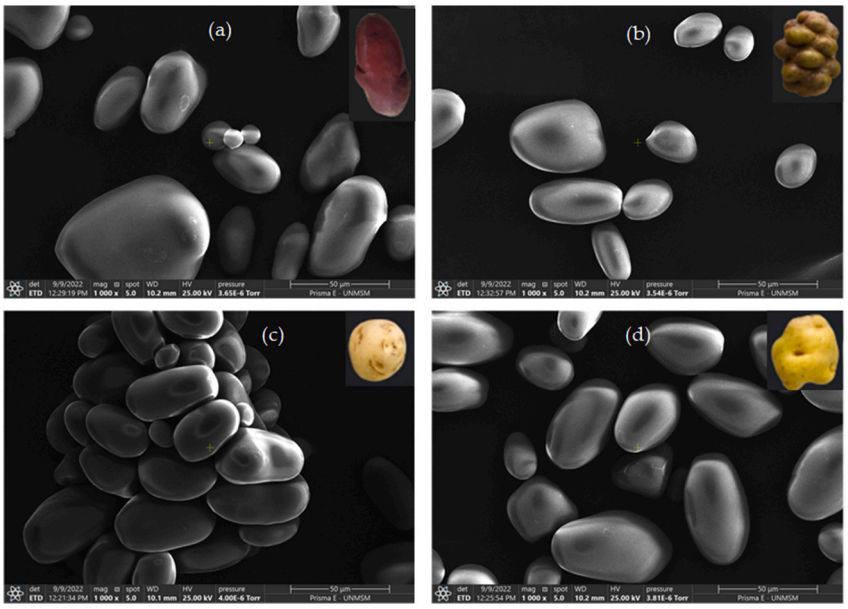

Fig. 8. SEM micrographs of potato starch granules, 1000 × magnification (a) Aq'hu Pukucho, (b) Yurakk Kkachun Wakkachi, (c) Yurac Anca (d) Huarmi Mallco.

review & editing, Formal analysis. **Karin Florez-Huaracha:** Supervision, Methodology. **Víctor J. Huamaní-Melendez:** Validation, Supervision.

Declaration of competing interest

The authors declare no conflict of interest.

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