

1 **A REVIEW ON THE APPLICATION OF NEAR-INFRARED SPECTROSCOPY**
2 **FOR THE ANALYSIS OF POTATOES**

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6 **ABSTRACT**

7 Potato (*Solanum tuberosum* L.) is one of the most important crops in the world being
8 considered as a staple food in many developing countries. Potato industry likewise other
9 vegetable and fruit industry is subject to the current demand of quality products. In
10 order to meet this challenge, food industry is relying on the adoption of non-destructive
11 and environmentally friendly techniques to determine quality of products. Near-infrared
12 spectroscopy (NIRS) is currently one of the most advanced non-destructive technology
13 regarding instrumentation and application and it also complies with the environment
14 requirements as it does not generate emissions or waste. This paper reviews research
15 progress on the analysis of potatoes by NIRS both in terms of determination of
16 constituents and classification according to the different constituents of the tubers. A
17 brief description on the fundamentals of NIRS technology and its advantages over other
18 quality assessment techniques is included. Finally, future prospects of the development
19 of NIRS technology at the industrial level are explored.

20 **KEYWORDS:** NIRS, *Solanum Tuberosum* L., chemometrics, non-destructive, calibration,
21 validation, qualitative, quantitative.

22 INTRODUCTION

23 Potato is considered as one of the main food products worldwide and occupies the
24 fourth position in terms of production after rice, wheat and maize in most of the
25 developing countries. According to the Food and Agriculture Organization of the United
26 Nations (FAOSTAT)¹ potato production in 2011 exceeded 374 million tonnes (MT)
27 followed by maize (883 MT) , rice (722 MT), and wheat (704 MT). The United Nations
28 General Assembly declared 2008 the International Year of the Potato (IYP)². This
29 declaration was based on the importance of this crop and supported by the need of
30 ensuring food security and reduce poverty in order to achieve the Millennium
31 Development Goals (MDG). The importance of this crop also derives from the fact that
32 potatoes can be used in many ways such as a staple food, cash crop, animal feed, and as
33 a source of starch for many industrial uses.

34 Despite that potato production has declined by 1% in the last 20 years in developed
35 countries, in developing nations has increased about 5% over the same period.

36 Nowadays, there are still many technical issues that affect its production and
37 development. Thus, a progress of the potato industry towards a sustainable production
38 is essential in order to assure a long-term food security and a human supply².

39 Potato is also a highly productive crop, generating more food per unit area and per unit
40 time than maize, rice and wheat.² Its production reached 19 tons hectare⁻¹ (t ha⁻¹) in
41 2011 followed by maize (5.1 t ha⁻¹), rice (4.4 t ha⁻¹) and wheat (3.1 t ha⁻¹)¹.

42 These tubers are rich in protein, calcium, potassium, and vitamin C, and have an
43 especially good amino acid balance. Moreover, they supply high levels of energy due to
44 their starch content³. Raw tubers contain about 80% of water and 20% of dry matter.
45 About 60 to 80 percent of the dry matter is starch⁴.

46 The starch in raw potato cannot be digested by humans, for this reason, its consumption
47 without any preparation is not a common practice, and normally potatoes are prepared
48 for consumption by boiling (with or without the skin), baking or frying. The preparation
49 method employed affects potato composition in a different way, but in general terms
50 they all reduce fiber and protein content. This is due to leaching into cooking water and
51 oil, destruction by heat treatment or chemical changes such as oxidation⁴.

52 Boiling is the most common method of potato preparation worldwide and this practice
53 causes a significant loss of vitamin C, especially in peeled potatoes. When potatoes are
54 fried, either for French fries and chips preparation, they absorb high content of fat and
55 reduce their mineral and ascorbic acid content. Losses of vitamin C are generally higher
56 when baking rather than boiling due to the higher oven temperatures, but losses of
57 other vitamins and minerals are lower⁴. Table 1 shows the main components of potato
58 in its most common consumption preparations⁵.

59 Quality of potatoes and potato products is determined by its constituents. The
60 commonly methods employed to determine main constituents of potatoes are chemical
61 analysis such as high-performance liquid chromatography (HPLC). These methods are
62 time-consuming, expensive and involve the destruction of the sample subjected to
63 study⁶. These reasons together with the increased consumer demands have raised the
64 interest of the potato industry in high-technology systems able to secure high-quality
65 products⁷. Near-infrared spectroscopy (NIRS) is one of the most advanced technologies
66 regarding non-destructive quality assessment techniques⁸. Since its first application in
67 the sixties NIRS technique has been successfully used for the rapid analysis of moisture,
68 protein and fat content in many agricultural and food products⁹⁻¹¹.

69 The objective of this review is to highlight the applications of NIRS for the quantitative
70 and qualitative analysis of potato and potato products.

71 **NIRS TECHNOLOGY**

72 Near-infrared spectroscopy (NIRS) studies the interaction between electromagnetic
73 radiation and matter. Near-infrared is the region of the electromagnetic spectrum that
74 extends between 780 and 2500 nanometers (nm), lying between visible light with
75 shorter wavelengths and the mid infrared (MIR) with longer wavelengths. This region is
76 characterized by overtone and combination bands of the fundamental vibration
77 occurring in the MIR¹². NIRS technique consists in the radiation of a sample with one or
78 more wavelength bands between 780-2500 nm. This radiation penetrates into the
79 sample and light is absorbed selectively according to the specific vibration frequencies
80 of the molecules present producing a spectrum that depends on the composition of the
81 sample. The interaction between energy and matter follows the Beer-Lambert's Law.
82 According to it, absorbance at any wavelength is proportional to the number or
83 concentration of absorbing molecules present in the path of the radiation^{13,14}.

84 Normally, in samples of heterogeneous chemical nature, the spectrum obtained in the
85 near infrared region is shown as a combination of overlapping spectral bands, which are
86 sometimes confused in a smooth line in which there are peaks, valleys and
87 curvatures^{15,16}. There is a need of a specific data analysis to interpret these absorption
88 bands. It must be capable of relating the electromagnetic information (spectrum) with
89 the information of the physical and chemical composition (reference method), using
90 mathematical algorithms through the application of different statistical models¹⁷. This
91 process is known as development of NIRS calibrations. To create a calibration, a
92 mathematical relationship should be established between the two sets of data, spectra

93 data and reference data including physical or chemical information of the product. This
94 can be performed via several chemometric techniques. The most commonly used
95 statistical techniques for this process are the multiple linear regression, principal
96 component regression and Partial Least Squares (PLS) regression. These chemometric
97 techniques establish a mathematical relationship between variations in the NIR spectra
98 of samples with the variation in the parameter measured. This relationship can then be
99 used to predict the parameter value in unknown samples.

100 It should be noted that the main limitation of NIRS in the analysis of food products is
101 that the initial phase of development of the calibrations depends on reference methods
102 based on chemical analysis¹⁸.

103 The use of NIRS for the analysis of food products began in the 60's and later in the 70's
104 started to be introduced in various industries as alternative to chemical and biological
105 traditional methods¹⁹⁻²³. NIRS is considered a technology with a huge potential to obtain
106 accurate and fast predictions of the chemical composition and nutritional value of many
107 agricultural products^{24,25}.

108 The main advantages of NIRS technique over reference methods are its quickness, its
109 both non-destructive as no contaminant nature and its great accuracy^{13,26,27}. However,
110 it is worth mentioning that there are certain problems common to both the chemical
111 analysis and the NIRS. These difficulties are derived from the preparation or
112 presentation of wet samples when working with fresh products²⁸.

113 On the one hand, the preparation of wet samples is complex to obtain accurate results
114 in the chemical analysis. On the other hand, the presence of high water content in the
115 samples may limit the use of NIRS, since there are strong absorption bands in the

116 spectrum caused by water in certain spectral regions. Despite this, NIRS has been
117 successfully used on a wide variety of products with high moisture content²⁸.

118 As stated above, the application of NIRS in food products commenced in the decade of
119 the sixties. The first application of NIR in the analysis of foods was the determination of
120 moisture and still is the most widely used application¹⁸. One of the first publications of
121 NIR applications in food products was about the NIR reflectance spectra of a variety of
122 grains. The study was carried out in 1965 by Massie and Norris²⁹ under the title *Spectral*
123 *reflectance and transmittance properties of grain in the visible and near infrared*. This
124 study was a request from the U.S. Department of Agriculture (USDA) and the main
125 objective was the determination of the spectral reflectance and transmittance
126 properties of grain in order to design infrared grain driers. The former authors studied
127 the spectral reflectance of corn, oats, wheat, soybeans, rice, alfalfa seed and milled rice
128 and the results obtained showed that reflectance of the sample was the most important
129 variable for infrared drying of grain.

130 Although literature concerning NIR applications in potato is not as extended as in other
131 type of vegetables³⁰, NIR applications in this industry were initiated in the 80's. For this
132 reason, it is important to compile the information that has been published relating NIRS
133 applications to the quality determination of potato and potato products since its
134 beginning.

135 **MAJOR COMPONENTS DETERMINATION**

136 Water, dry matter and starch. One of the first applications of NIR in the potato industry
137 was to measure the moisture content of chips. In 1988, McDermott reported good
138 results with a correlation coefficient (R) of 0.95 and a standard error of estimation of
139 0.15³¹.

140 Similar studies have been conducted since then on different commercial potato chips
141 samples. The results obtained correspond to the previous report with standard errors of
142 validation (SEV) between 0.20 and 0.26 and correlation coefficients between 0.95 and
143 0.98 when PLS regression statistic method was applied^{32,33}.

144 Nevertheless, Ni *et al.* (2011)³³ obtained better results for moisture prediction using
145 Least Squares-Support Vector Machines (LS-SVM) and Kernel Partial Least Squares
146 (KPLS) methods. The coefficients of correlations were 0.99 and 0.98 with a root mean
147 square standard error of validation (RMSEV) of 0.07 and 0.10 for LS-SVM and KPLS
148 respectively. Based on the results obtained, the authors concluded that it was possible
149 to determine moisture content of chips in a fast and accurate way.

150 Some authors have used NIRS as the unique method for the estimation of moisture
151 content of potatoes in their on-line routine analyses. In 2007, Broothaerts *et al.*³⁴ used
152 NIRS technique to determine the water content of freeze-dried samples of potatoes.
153 The investigation was focused in the development of a certified reference material for
154 Genetically Modified (GM) potatoes with altered starch composition and the water
155 content of both non-GM and GM potato samples was determined by using an acousto-
156 optical tunable near-infrared spectrometer (AOTF-NIR) integrated on-line into their
157 instrumentation. NIR data were evaluated by a PLS1 regression model based on meat
158 calibrations previously evaluated by Kestens *et al.*³⁵ and able to predict water content
159 of the samples.

160 Other authors have focused on the determination of dry matter and starch in potatoes.
161 Dry matter concentration is a useful index for potato quality as it contains information
162 on both water and starch concentration³⁶. As stated before, a great percentage of dry
163 matter in potato is in form of starch and it is considered as very important constituent

164 of this food since final quality of potato products is directly related to this component.
165 Moreover, the European Potato Starch Industry bases its payments to the farmers on
166 the starch concentrations of tubers³⁷.
167 In the decade of the 80's specific gravity measurement was the best practical and non-
168 destructive method for estimating dry matter content of potatoes. Although dry matter
169 and specific gravity were known to be highly correlated³⁸, there was a need for a much
170 more rapid and accurate non-destructive technique. Therefore, from this decade
171 through the 90's and until nowadays some authors such as Haase, Hartmann, Brunt and
172 Drost^{37,39,40} studied the correlation between spectral and both dry matter and starch
173 content of these tubers. The most common method used to establish the correlation
174 was to combine NIR data with PLS regression statistic method.
175 Table 2 shows the determination coefficients as well as the standard errors of prediction
176 (SEP) obtained for dry matter and starch content in potatoes reported by several
177 authors. A wide range of potato varieties have been studied in diverse sample
178 presentations: intact, mashed, freeze-dried, etc. Also, different wavelength regions have
179 been used to develop the calibration models ranging from 734 to 931, 750 to 950, 800
180 to 1000, 1100 to 2500, 770 to 2500, 850 to 2500, 1000 to 2500 nm, or including the
181 visible range 400 to 2500 and 460 to 1040 nm. It is known that starch have bands at
182 1200, 1700, 1720 and 1780 nm⁴¹. Due to these facts a wide range of SEP values have
183 been obtained and consequently, it is difficult to establish either the type of sample
184 presentation or a specific wavelength to predict the content of dry matter and starch.
185 However, it seems that the lower SEP values for both components occurred when the
186 sample is mashed and homogenized and the range between 1100 and 2500 nm is
187 used^{30,39,40,42,43}.

188 Dry matter content was also highly predicted in potato chips (Root mean square error
189 of cross validation RMSECV: 0.84) where the percentage of this component is
190 significantly higher than in intact and mashed potatoes⁴⁴.

191 Other authors have focused on the study of the optimum region in potato tubers to be
192 scanned by NIRS in order to predict dry matter content of the whole tuber. As a result,
193 Peiris *et al.* (1999)⁴⁵ stated that the dry matter content of potatoes was greater toward
194 the surface of the tuber than at the center. This result matched with that obtained by
195 Scanlon *et al.* (1997)⁴⁶ where the most closely correlated values were those of the center
196 outside section of the tuber.

197 Helgerud *et al.* (2012)⁴⁷ also obtained better results for the measurements taken at the
198 center of the longest axis in a recently published paper about the ability of NIR to rapidly
199 estimate dry matter content of intact potatoes. They compared the performance of two
200 different NIR instruments to the performance of the traditional specific gravity
201 measurement method. Firstly, they used a 1D NIR interactance for stationary analysis
202 and secondly, a commercially available 2D NIR interactance system to provide on-line
203 estimation. The specific gravity (SG) was calculated based on equation 1.

$$204 \quad SG = \frac{\text{Weight in air}}{\text{Weight in air} - \text{Weight in water}} \quad (1)$$

205 And then following an equation provided by Lunden (1956)⁴⁸, they calculated the dry
206 matter content (DM).

$$207 \quad DM = 215.73(SG - 0.9825) \quad (2)$$

208 A standard normal variate (SNV) pretreatment was applied only to the data obtained by
209 the 1D NIR interactance equipment. Table 2 shows that the lowest RMSECV and highest
210 R² were obtained when specific gravity method was employed. However, this can only

211 be used with small sample volumes and takes much more time than the other two
212 systems able to record multiple spectra per second.

213 Nevertheless, a direct relationship exists between specific gravity and cooking quality of
214 these tubers. Some investigators have reported that specific gravity could be used as a
215 direct measure of quality characteristics of potatoes⁴⁹⁻⁵². In 2005, Chen *et al.*⁵³ examined
216 the correlation between NIR spectroscopy and specific gravity of intact potatoes. 250
217 samples of potatoes from three different varieties were used for this study. Samples
218 were scanned by NIR in interactance mode in the 700 to 1100 nm wavelength range,
219 and the specific gravity of each sample was measured by using specific gravity
220 measurement equipment based on the principle of liquid displacement. For the
221 development of the calibration equation samples were divided into two groups: 150 for
222 calibration model and 100 to validate it. PLS regression method was applied in order to
223 obtain the prediction models. The results obtained showed high correlation coefficients
224 between NIR spectra data and specific gravity. The correlation coefficients achieved for
225 the calibration set of samples ranged from 0.94 to 0.95 for different pretreatments
226 employed with SEC values between 0.0041 and 0.0043 g/cm³. The highest correlation
227 coefficients and lowest SEC values obtained were for raw spectra, normalization and
228 second derivative all with the same values (R: 0.95 and SEC: 0.0041g/ cm³). For
229 prediction set of samples, R values ranged from 0.93 to 0.94 with SEP values between
230 0.0044 and 0.0047g/cm³. The highest R values and lower SEPs were those obtained for
231 raw spectra and normalization.

232 Based on the results of this study, authors concluded that NIR spectroscopy was able to
233 accurately measure the specific gravity of intact potatoes.

234 The estimation of the components of potato starch by NIRS has also been a matter of
235 research. Accordingly, in 2001, Thygesen *et al.*⁵⁴ carried out a study for the
236 determination of phosphate content and viscosity behavior of potato starch by NIRS
237 combined with PLS regression method. The viscosity behavior of the starch is one of the
238 most important quality parameter for potato starch. Since this parameter is normally
239 measured by viscograms that are time and sample consuming, the aim of that project
240 was to evaluate the feasibility of NIR to predict viscosity behavior in a faster way. 97
241 samples of potato were used for this study prepared from a set of 100 potato samples.
242 They were measure by NIR and by a viscoqram for viscosity determination. Phosphate
243 content of samples was determined by wet oxidation with sulphuric acid and
244 colorimetric determination of the formed inorganic phosphate according to Stuffins
245 (1967)⁵⁵. Phosphate content of the samples was between 0.029 and 0.11%. The results
246 obtained showed that NIR combined with PLS for the prediction of phosphate content
247 was possible with a RMSECV value of 0.006% on a basis of standardized sample
248 preparation. Moreover, prediction of viscosity was also possible as this parameter was
249 highly related to phosphate content in the data set.

250 Protein. As shown before, protein content of potatoes is considerably smaller than dry
251 matter and starch content (0.5-2%), therefore, it seems difficult the prediction of this
252 component by NIRS.

253 Table 3 shows several studies carried out in order to predict protein content of potatoes.
254 Best results were obtained for the estimation of coagulating protein with a root mean
255 square standard error of prediction (RMSEP) values ranging from 0.06 to 0.16 whereas
256 crude and recoverable protein were harder to predict achieving higher SEP values and
257 lower coefficients of determination^{30,40,42,56,57}.

258 Some authors attributed these lower values to the reduced range of these constituents
259 and the high values of the reference method errors³⁰.

260 Furthermore, the ability of NIRS to qualitative classify samples according to their protein
261 content has been assessed. In a research developed by Fernández-Ahumada *et al.*³⁰
262 (2006), a discriminant analysis was performed in order to classify samples in two
263 categories regarding to their protein content. Samples were split into two groups: one
264 including the samples with low recoverable protein content ($<14\text{mg g}^{-1}$) and the second
265 with the samples that presented high values ($\geq 14\text{mg g}^{-1}$) for that parameter. A total of
266 184 samples were used for the study and an overall of 161 (87.5%) were correctly
267 classified. The results obtained demonstrated that, in spite of the low protein content,
268 it was possible to classify potato samples by NIRS regarding that parameter (Table 3).

269 Other carbohydrates. Carbohydrate compounds, commonly referred to as sugars, are
270 presented in narrow concentrations in potatoes; therefore, their estimation based on
271 NIRS might not be as accurately as in other compounds such as dry matter and starch³⁹.
272 Results obtained for the NIR estimation of carbohydrates reported by several authors
273 are summarized in table 4. It can be extracted from the table that a robust NIR
274 calibration model to predict sugar content in potatoes has not yet been developed.
275 However, Mehrübeoglu and Coté (1997)⁶ while investigating the on-line application of
276 NIR to estimate total reducing sugars (TRS) of potatoes achieved a RMSECV and RMSEP
277 values that complied with the specifications of less than 0.15% of TRS. Thus, the authors
278 concluded that NIR spectroscopy met the requirements to be used for the on-line real-
279 time measurements of these compounds. On the other hand, Scanlon *et al.* (1999)⁵⁸
280 reported poor ability of NIRS to predict fructose content, results (not shown) that
281 differed from those reported by the former authors.

282 Other authors have studied NIRS prediction of individual sugars components such as
283 glucose, fructose and sucrose along with the estimation of TRS content. The results
284 obtained showed that the prediction of these individual components had to be
285 improved³⁹.

286 It seems that the estimation of TRS gave lower SEP values than the prediction of glucose
287 and fructose separately. This fact might be useful since TRS content seems to be
288 technologically more important than the content of the single compounds⁵⁹ (Table 4).

289 **MINOR COMPONENTS DETERMINATION**

290 Fat and acrylamide. Determination of acrylamide contents in potato chips is currently
291 necessary due to its potentially toxic attributes and the fact that very high
292 concentrations can be produced in amylaceous fried foodstuffs⁶⁰. Moreover, consumer
293 awareness of the fat content in potato products is increasing worldwide as do so the
294 seeking for low fat products. Some studies have been developed for the determination
295 of both fat and acrylamide content in potato processed products.

296 Segtnan *et al.* (2006)⁶¹ investigated the determination of acrylamide contents in potato
297 chips using process variable settings and NIRS. Acrylamide is normally present at
298 elevated concentrations in different types of heat treated foods and is considered a
299 carcinogen constituent. For this study potato samples were sliced, fried and ground
300 before NIR analysis. Then PLS regression method was applied to build the spectral
301 prediction models. A correlation coefficient between predicted acrylamide values and
302 reference values was 0.952 with a RMSECV of 246.8µg/kg. The high correlation
303 coefficient along with the low RMSECV suggested that NIR spectroscopy could be
304 accurate enough for determining the acrylamide contents in processed potato chips.

305 Another related study was accomplished by Pedreschi *et al.* (2010)⁴⁴ for the on-line
306 monitoring of different constituents in potato chips using near infrared interactance and
307 visual reflectance imaging. The objective of the study was to determine dry matter, fat
308 and acrylamide contents in potato chips by NIR in routine analysis. Raw potatoes were
309 hydrogenated with palm oil, cut into slices and fried at different durations resulting in
310 60 samples analyzed by NIR, visible spectroscopy (VIS), combination of both and
311 reference methods. The corresponding correlation between predicted values by NIR and
312 reference values was 0.99 for fat with a SEP value of 0.99. Therefore, on-line NIR
313 interactance technology was found to predict fat content of potato chips with high
314 accuracy. For acrylamide content the best model resulted from the use of NIR and VIS
315 (both spectral regions) with a correlation coefficient of 0.83 and a SEP value of 266
316 $\mu\text{g}/\text{kg}$. Pedreschi *et al.* (2010)⁴⁴ concluded that the acrylamide estimation error was a
317 little high and thus, they suggested that the system should be used for classification of
318 samples with high and low acrylamide contents rather than prediction.

319 Shiroma and Rodriguez-Saona (2009)³² investigated the potential of NIR combined with
320 chemometric to determine fat and moisture content in potato chips and its capacity to
321 classify samples based on their composition. A total of 15 commercial potato chips fried
322 from different sources according to their label were used in this study. PLS regression
323 method was used for the prediction models and a Soft Independent Modeling of Class
324 Analogy (SIMCA) was used for qualitative analysis. The correlation coefficient of cross-
325 validation obtained was 0.97 for fat with a SECV value of 1.54. The classification model
326 based on SIMCA was able to differentiate potato chips by source of frying oil. Based on
327 these results authors concluded that it was possible to determine fat content in potato

328 chips as well as classify them according to their composition by a fast, simple and
329 accurate method.

330 Ni *et al.*³³ (2011), investigated NIR application in potato chips for prediction of the
331 following quality parameters: fat, moisture, acid and peroxide values. The aim of the
332 investigation was to compare the performance of calibration models developed using
333 NIR spectra and PLS method with non-linear KPLS and LS-SVM models for the
334 determination of the parameters above. For this purpose samples of four commercial
335 brands were analyzed both by chemical methods and NIR. The results showed that both
336 KPLS and LS-SVM methods performed well for the four parameters with correlation
337 coefficients for cross-validation ranging from 0.930 to 0.996 with RMSEP values between
338 0.076 and 0.518. The highest correlation coefficient for independent validation was
339 obtained for fat content by LS-SVM with a RMSEP of 0.211. However, PLS calibrations
340 performed well for three parameters but the results for peroxide value were poor with
341 the lowest correlation coefficient (0.762) and highest RMSEP (0.772). Authors
342 summarized that NIR spectroscopy combined with the use of chemometric was able to
343 accurately predict quality parameters in potato chips.

344 According to these studies, it may be assumed that NIR spectroscopy performs well for
345 the parameter fat whereas for acrylamide content more robust models need to be built.

346 In the meantime, NIR spectroscopy is a useful tool for classifying samples according to
347 this last constituent.

348 Carotenoids. Benefits of carotenoids have been reported by several authors.
349 Carotenoids are well known for their health promoting functions to the immune system
350 and reduction of the risk of degenerative diseases⁶²⁻⁶⁴. Due to these advantages
351 consumer concern for products with high carotenoids concentration is growing in the

352 same way as the industry interest for the screening and development of food crops with
353 increased concentrations of those components^{65,66}.

354 In 2009, Bonierbale *et al.*⁶⁷ examined the potential of NIR to estimate total and individual
355 carotenoid concentrations in cultivated potatoes. 189 samples of potato were used for
356 the development of NIRS calibrations and external validation. Samples were freeze-
357 dried and milled prior to NIRS analysis. The individual carotenoids analyzed were
358 anteraxanthin, violaxanthin, lutein, zeaxanthin and β -Carotene. The concentration of
359 total carotenoids ranged between 440 and 8560 μ100g^{-1} dry weight and of individuals
360 from 0 to 2240 μ100g^{-1} dry weight. Coefficients of determination obtained ranged from
361 0.60 to 0.92. Best results were obtained for total carotenoids estimation (R^2 : 0.91) and
362 zeaxanthin (R^2 : 0.92) with SEP values of 610 and 410 μ100g^{-1} dry weight respectively.

363 Results demonstrated that NIR had the potential to accurately predict total carotenoids
364 and zeaxanthin and the rest of the individual carotenoids with relatively good accuracy.

365 **OTHER CHARACTERISTICS**

366 Crop's yield evaluation. NIR major application in potatoes is generally for determining
367 internal components (dry matter, starch, soluble solids, carotenoids, etc); but also,
368 sensory texture of cooked potatoes has been evaluated⁶⁸. Despite this, in general terms,
369 the scope of NIRS covers a wide range of applications nowadays such as the
370 determination of physiological indices of crops⁶⁹ or the optimal date for fruit picking⁷⁰.

371 In 2008, Jeong *et al.*⁷¹ studied the correlation between sprouting capacity in potato
372 tubers and NIRS. They used 380 potato tubers divided into four groups, two groups of
373 the same variety (Superior) harvested at two consecutive years, a group of another
374 variety (Atlantic) and the last group containing the total number of samples. The

375 sprouting capacity of the four calibration sets ranged between 0.24 and 7.70 with a
376 standard deviation between 1.03 and 1.95.

377 NIR spectra were measured in reflectance mode in the 400-2500 nm wavelength range.
378 First derivative, standard normal variate and detrend (SNV-DT) pretreatments were
379 applied to the data. Modified partial least squares (MPLS) was used as a regression
380 method to correlate spectral data and sprouting capacity. The coefficients of
381 determination (R^2) obtained for cross and external validation ranged from 0.69 to 0.93
382 with SECV and SEP values between 0.40 and 0.68. Based on the results obtained Jeong
383 *et al.*⁷¹ concluded that it was possible to predict the sprouting capacity of potato tubers
384 by NIRS with a reliable accuracy. That fact was an important discovery and could have
385 significant implications in the potato industry⁷¹.

386 Other authors have found that the relationship between the absorption of nitrogen and
387 the total fresh weight in potato crops could be used to calculate proportions of
388 supplemental nitrogen fertilizer⁷². Consequently, the correlation between NIR
389 spectroscopy and nitrogen absorption of potato plants has been investigated in order to
390 be used for this purpose.

391 As an example, Young *et al.*⁷² developed a study in 1997 for the NIR determination of
392 nitrogen in potato tissues. They used samples of two different potato varieties grown
393 under six nitrogen treatments. Samples of leaves, stems and tubers with nitrogen
394 concentrations between 0.60 to 3.65%, 0.68 to 5.88 and 2.25 to 8.00% (on a dry weight
395 basis) respectively were scanned by NIR and by reference method (Dumas combustion).
396 The coefficients of determination obtained were 0.96, 0.95 and 0.96 with SEP values of
397 0.11%, 0.03% and 0.09% for leaf; stem and tuber respectively⁷². Authors concluded that
398 the estimation of nitrogen concentration in potato crops by NIR techniques was cheaper

399 and safer than comparable chemical methods. These results were in accord with those
400 reported by Váradi *et al.*⁷³(1987), however, they studied NIR reflectance for the
401 determination of total nitrogen in ground grape leaf samples rather than in potatoes.

402 MacKerron *et al.*⁷⁴ published a report in 1997 about the influence of particle size, milling
403 speed and leaf senescence to the assessment of total nitrogen in potato tissues by
404 comparing near infrared reflectometry and Dumas combustion methods. Samples of
405 leaf stem and tubers were used for this research with nitrogen concentration levels
406 between 0.55- 1.35%. The results obtained reported the particle size as a source of error
407 in analysis by NIR whereas milling speed within the range examined did not appear to
408 be an important variable. The coefficients of determination obtained at two different
409 milling speeds were 0.79 and 0.89 with RMSEP values of 0.05 and 0.16 for tuber and leaf
410 material respectively.

411 Later in the same year, the second part of the experiment explained above was carried
412 out. At this time authors compared the influence of operator, moisture and maturity
413 class in the assessment of total nitrogen comparing the two methods explained before.
414 Once again, samples of leaf stem and tubers were analysed by Dumas combustion and
415 by NIR, and in the following two years, by a number of operators who made estimates
416 of nitrogen concentrations. Authors achieved a good correlation between NIR and
417 Dumas combustion methods in the determination of nitrogen for the different operators
418 who tested the samples⁷⁵. The coefficients of determination obtained ranged from 0.94
419 to 0.98 with SEP values between 0.02 and 0.11.

420 Texture. Texture of potatoes at the time of consumption is an important factor related
421 to products quality. Consumers associate the quality of potatoes according to the
422 texture they perceive when consuming. This sensory perceived quality is normally

423 measured using a panel of trained judges. These procedures require a considerable
424 amount of time as well as an important investment. Therefore, much research has been
425 developed to determine the texture of potatoes by instrumental technologies rather
426 than methods based on human's perception⁷⁶.

427 Some authors have studied the correlation between NIRS and texture profiling of
428 potatoes. Researches have focused on cooked potatoes as the most consumed potato
429 based food product (Table 5).

430 Boeriu *et al.* (1998)⁷⁶ carried out a project determining the correlation between NIRS
431 and texture profiling of steam cooked potatoes. The texture of steam-cooked potatoes
432 samples was sensory evaluated at one, three and six months after storage and NIR
433 spectra were measured. They used 87 samples in the range between 1100 and 2500 nm.
434 A quantitative model based on PLS was developed and according to the results obtained,
435 authors determined that NIR was able to evaluate the texture of cooked potatoes with
436 good accuracy⁷⁶ as it can be extracted from table 5.

437 Another study with similar characteristics was carried out in 2000, but this time
438 measurements were made in raw and water boiled potatoes. 24 samples of six different
439 potato varieties were used. NIR measurements were made in reflectance mode in the
440 1100-2500 nm wavelength range and then, PLS regression method was applied.

441 As it is shown in table 5 the correlation coefficients for the sensory texture attributes:
442 firmness, mealiness and moistness were lower than those obtained by Boeriu *et al.*
443 (1998)⁷⁶ for the same attributes. Moreover, the range of values of the sensory attributes
444 was much smaller than in the previous work and therefore SEP values were greater⁶⁸.

445 Another research on the same topic was developed by Van Dijk *et al.* (2002)⁷⁷. They
446 studied the relationship between dry matter content, sensory-perceived texture and

447 NIRS in steam cooked potatoes. 81 potato tubers samples representing different types
448 of cooking behavior were used for this assessment. Sensory texture analysis was
449 accomplished by a panel of 16 trained judges. The results obtained were very similar to
450 those reported by Thybo *et al.*⁶⁸.

451 Damages evaluation. Damage to potato tubers either by mechanical harvesting or by
452 transport causes a great loss of quality of the final product and as a result almost two-
453 thirds of the potatoes sold in the market show external or internal damages⁷⁸. Economic
454 losses due to tuber's damages are also significant⁷⁹.

455 In spite of the fact that there have been several investigations focused on reducing the
456 degree of damage, there is still a need to continue working in this field⁸⁰.

457 Evans and Muir (1999)⁸¹ published a report with the aim to investigate the feasibility of
458 NIR spectroscopy as a method for determining the discoloration of potatoes associated
459 with bruising in a non-destructive way. Bruising is considered one of the biggest
460 problems in the potato industry since it causes very important economic losses⁸⁰.

461 Therefore, investigation in this field is always welcome.

462 For that research samples of Record variety susceptible to bruising were used. The
463 tubers were given a consistent impact and then were stored for 16 hours. NIR spectra
464 were measured in both unpeeled and peeled tubers as in bruised and unbruised sites.

465 The results showed that reflectance spectra from unpeeled bruised tubers had higher
466 reflectance in the NIR than unbruised tubers. Moreover, in peeled tubers, the
467 differences were higher in those regions. Based on these results, authors suggested that
468 bruise detection by NIRS may be possible in unpeeled tubers and almost certainly in
469 peeled tubers. Nevertheless, they stated that the method required an improvement in
470 order to be a reliable technique.

471 A different type of research was developed by Kemsley *et al.*⁸² (2008) when they studied
472 the feasibility of NIR diffuse optical tomography to monitor quality of fresh fruit and
473 vegetables. For that study a NIR tomograph built from relatively low cost components
474 was used along with potato samples as model specimens or phantoms to develop the
475 image reconstruction approach. Authors found that NIR tomography had the potential
476 to monitor internal defects in agricultural products.

477 That conclusion entails an important discovery given that the determination of internal
478 damages such as bruising in potatoes before reaching the market could save a lot of
479 money since as stated before, internal bruising is one of the main concerns in the potato
480 industry and causes many annual losses.

481 **FUTURE CHALLENGES**

482 The continuously growing demand for quality control of food products in recent years,
483 together with the concern acquired by consumers about the methods of handling and
484 processing of these products, has led to a very severe control of the nutritional contents
485 of many foodstuffs. Moreover, since potato represents a pillar in the human nutrition
486 the mechanization and optimization of tools for quality control at the delivery point are
487 essential.

488 The potato industry covers a wide range of products, from seed potatoes, raw, for deep
489 frying, baking, grilling to chips or crisps and therefore, there is a need for a rigorous
490 control of different parameters such as the starch content, dry matter, etc. as well as
491 the determination of internal damage at different points of its productive stage.

492 For that reason, it is required the development of techniques capable of determining
493 food components quickly and at a competitive price. As have been demonstrated
494 through the studies carried out by the food industry since the beginning of the

495 application of NIRS in the seventies, these technologies have the potential to predict
496 those components in an easy, fast and accurate way.

497 The principal problem confronted by this technology is to obtain a representative group
498 of samples to develop the calibration models. Sample preparation plays a key role in the
499 success of the analysis for that reason parameters such as sample size, temperature,
500 homogeneity and presentation must be standardized. Additionally, NIRS accuracy
501 depends on a large scale on the precision of reference methods used in the development
502 of calibration equations. Therefore, the accomplishment of robust and accurate
503 laboratory analysis is crucial.

504 The challenge for coming years within this field is in the direction of a wide
505 implementation and optimization of in-line NIR systems for the real time monitoring of
506 potato quality parameters at the delivery point.

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510 **ABBREVIATIONS USED**

511 AOTF-NIR; acousto-optical tunable near-infrared spectrometer; CP, Crude protein; RP,
512 recoverable protein; CGP, coagulating protein; DM, dry matter; DT, detrend; FAO, food
513 and agriculture organization; FTIR, Fourier transform infrared spectroscopy; GM,
514 genetically modified; HPLC, high-performance liquid chromatography; KPLS, kernel
515 partial least squares; LS-SVM, least squares-support vector machines; nm, nanometer;
516 MDG, millennium developments goals; MLR, multiple linear regression; MPLS, multiple
517 partial least squares; MSC, multiplicative scatter correction; MT, million tonnes; NIRS,
518 near-infrared spectroscopy; PCA, principal component analysis; PLS, partial least

519 squares; R, correlation coefficient; R², coefficient of determination; RMSECV, root mean
520 square error of cross validation; RMSEP, root mean square error of prediction; RMSEV,
521 root mean square standard error of validation; SD, standard deviation; SEP, standard
522 error of prediction; SEV, standard error of validation; SIMCA, soft independent modeling
523 of class analogy; SNV, standard normal variate; TRS, total reducing sugars; TS, total
524 sugars; USDA, U.S. Department of Agriculture; VIS, visible spectroscopy.

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750 TABLES

751 Table 1 Composition of raw and cooked potatoes⁵

| Composition of potatoes per 100g | | | | | | |
|----------------------------------|-------|------------|-------|---------------------|--------------------|-------------|
| | Raw | Skin (38g) | Baked | Boiled without salt | Fried without salt | Chips plain |
| Water (g) | 83.29 | 31.65 | 75.42 | 76.98 | 61.51 | 2.54 |
| Energy (kcal) | 58 | 22 | 93 | 87 | 172 | 559 |
| Protein (g) | 2.57 | 0.98 | 1.96 | 1.87 | 2.66 | 4.45 |
| Fat (g) | 0.10 | 0.04 | 0.10 | 0.10 | 5.22 | 38.41 |
| Carbohydrates (g) | 12.44 | 4.73 | 21.55 | 20.13 | 28.71 | 52.02 |
| Fiber (g) | 2.5 | 1.0 | 1.5 | 1.8 | 2.6 | 3.1 |
| Potassium (mg) | 413 | 157 | 391 | 379 | 451 | 751 |
| Sodium (mg) | 10 | 4 | 5g | 4 | 32 | 388 |
| Phosphorus (mg) | 38 | 14 | 50 | 44 | 97 | 125 |
| Magnesium (mg) | 23 | 9 | 25 | 22 | 26 | 43 |
| Calcium (mg) | 30 | 11 | 5 | 5 | 12 | 27 |
| Vitamin C (mg) | 11.4 | 4.3 | 12.8 | 13 | 13.3 | 8.2 |
| Vitamin A (IU) | 0 | 0 | 0 | 3 | 0 | 0 |
| Vitamin B 6 (mg) | 0.239 | 0.091 | 0.301 | 0.299 | 0.184 | 0.407 |
| Niacin (mg) | 1.033 | 0.393 | 1.395 | 1.439 | 2.218 | 3.240 |

752 g grams, kcal kilocalories, mg milligrams, IU international units

753 **Table 2** Overview of applications of NIR spectroscopy to measure dry matter and starch content of
754 potatoes

| | Type of sample | Number of samples | Variety | Wavelength range (nm) | Pre-process | Validation | Analysis | Mode | Range % | R ² | SEP | Refs |
|-------------|------------------------------------|-------------------|--------------------------|-----------------------|--|-----------------------|-------------------|----------------------------|------------------------|--|--|------|
| DM & Starch | Mashed | 275 | n/a | 1000-2500 | 1st der. & MSC | Cross & external | PLS | Interactance - reflectance | 19.5-29.8 13.4-21.9 | 0.92 0.81 | 0.45 0.50 | 30 |
| | Freeze-dried | 628 | n/a | 850-2500 | None 1st der. 2nd der. None 1st der. 2nd der. | External | n/a | Reflectance | 16.7-33.4 12.1-27.3 | 0.98 0.98 0.97 0.96 0.96 0.95 | 0.518 0.514 0.568 0.638 0.622 0.678 | 37 |
| | Mashed & homogenized | 116 116 | Granola & Nicola | 1100-2500 | 1st der. | Cross & external | MPLS & PCA | Reflectance | 15.6-21.0 10.0-14.8 | 0.97 0.93 | 0.19 0.28 | 39 |
| | Mashed & homogenized | 504 | n/a | 1100-2500 | Smoothing & MSC | External | PLS | n/a | 19.5-29.2 14.2-23.4 | 0.93 0.84 | 0.22 0.39 | 40 |
| | Mashed & homogenized | 219 | 18 different | 1100-2500 | Smoothing | External | PLS | Reflectance | 19.8-34.0 | 0.93 0.84 | 0.47 0.63 | 42 |
| | Mashed, homogenized & freeze-dried | 2517 | n/a | 850-2500 | SNV & DT | Cross & external | MPLS | n/a | 14.1-35.4 12.8-27.2 | 0.99 0.96 | 0.39 0.47 | 43 |
| | Mashed & homogenized | 81 | Nicola Irene Bintje | 1100-2500 | None | Full cross-validation | PLS & PCA | Reflectance | 16.9-30.2 10.8-21.8 | 0.86 0.90 | 1.66 0.96 | 77 |
| DM | Chips | 60 | Saturna | 460-1040 | SNV | Full cross-validation | PLS | Interactance | 82.9-98.6 | 0.94 | 0.84 | 44 |
| | Intact | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | 0.93 | n/a | 46 |
| | Intact Sliced | 910 907 | Russet Burbank | 800-1000 | 2nd der. | External | Linear regression | Transmittance | 14.1-32.5 | 0.84 0.90 | 1.52 1.69 | 83 |
| | Flesh | 200 | Shepody & Russet Burbank | 770-2500 | 2nd der. | External | MLR | Reflectance | n/a | 0.77 - 0.58 | 1.3-1.5 | 58 |
| | Intact | 49 | n/a | 734-931 | None 2nd der. | Cross validation | PLS & MLR | n/a | n/a | 1.04 1.09 | 0.62 0.58 | 84 |
| | Intact | 114 | Asterix, Bruse, Celine, | 760-1040 | SNV (1D) None (2D) None (SG) | Cross validation | PLS | Interactance | 14.4-30.5 | 0.95 0.83 0.97 | 0.91 1.68 0.65 | 47 |

| | | | | | | | | | | | | |
|--------|-------------------------------------|--------------------------|---|----------|--|---------------------|------|-----------------|---------------|------------------------------|------------------------------|---------------|
| | | | Folva, Saturna | | | | | | | | | |
| | Intact Clean Peeled Sliced | 100 100 100 100 | Nicola, Spunta, Golden Delight, Sebago, Russet Burbank | 750-950 | 2nd der. | Cross validation | PLS | n/a | 17.6- 25.5 | 0.85 0.81 0.90 0.86 | 1.52 1.64 1.13 1.08 | ³⁶ |
| Starch | Mashed | 268 269 272 | n/a | 850-2500 | SNV & DT + None 1st der. 2nd der. | External | MPLS | Reflec tance | 9-30 | 0.90 0.89 0.88 | 0.74 0.75 0.79 | ⁸⁵ |
| | Mashed & homoge nized | 126 | Aveka, Festien, Karakter , Karniko, Mercato r, Seresta, Valiant | 400-2500 | MSC | Cross validation | PLS | Reflec tance | 18.0- 23.4 | n/a | 0.4 | ⁵⁷ |

755 DM dry matter, PLS partial least squares, n/a no available data, MPLS multiple partial least squares, PCA principal
756 component analysis, MSC multiplicative scatter correction; SN, standard normal variate, DT detrend, MLR multiple
757 linear regression

758 **Table 3** Overview of applications of NIR spectroscopy to measure protein content of potatoes

| Type of sample | Parameter | Number of samples | Variety | Wavelength range (nm) | Preprocess | Validation | Analysis | Mode | Range | R ² | SEP | Refs |
|----------------------|-------------|--|--------------|-----------------------|--|------------------|----------|--------------------------|----------------------------|--|--|---------------|
| Mashed | CP RP | 275 | n/a | 1000-2500 | 1st der. & MSC | Cross & external | PLS | Interactance-reflectance | 1.23-3.21 0.58-2.05 | 0.62 0.46 | 2.4 1.7 | ³⁰ |
| Mashed & homogenized | CGP | 504 | n/a | 1100-2500 | Smoothing & MSC | External | PLS | n/a | 0.65-1.58 | 0.84 | 0.0036 | ⁴⁰ |
| Mashed & homogenized | CGP | 219 | 18 different | 1100-2500 | Smoothing | External | PLS | Reflectance | 0.87-1.53 | 0.84 | 0.0036 | ⁴² |
| Mashed | P CP | 176 174 173 187 190 188 | n/a | 850-2500 | SNV & detrend + None 1st der. 2nd der. None 1st der. 2nd der | External | MPLS | Reflectance | 0.85-2.91 0.85-2.91 | 0.61 0.59 0.58 0.25 0.22 0.13 | 0.20 0.20 0.21 0.09 0.08 0.10 | ⁸⁵ |
| Mashed & homogenized | CP | 126 | n/a | 400-2500 | MSC | Cross validation | PLS | Reflectance | 0.69-1.95 | n/a | 0.025 | ⁴² |

759 *CP Crude protein, RP recoverable protein, CGP coagulating protein*

760 **Table 4** Overview of applications of NIR spectroscopy to measure carbohydrate content of potatoes

| Type of sample | Parameter | Number of samples | Variety | Wavelength range (nm) | Preprocess | Validation | Analyses | Mode | Range | R ² | SEP | Refs |
|------------------------------------|---|--------------------------|------------------|-----------------------|--------------------|------------------|------------|--------------|--|------------------------------|--|---------------|
| Sliced | TRS | 39 | Russet Chipping | n/a | n/a | Cross & external | PLS | Interactance | 0.04-0.2 0.002-0.12 | 0.57 0.62 | 0.0009 0.0001 | ⁶ |
| Mashed & homogenized | Glucose Fructose Sucrose Σ red. sugars | 116 100 109 134 | Granola & Nicola | 1100-2500 | 1st der. | Cross & external | MPLS & PCA | Reflectance | 0.148-0.520 0.101-0.439 0.136-0.399 0.249-0.790 | 0.70 0.89 0.62 0.82 | 0.04 0.02 0.03 0.06 | ³⁹ |
| Mashed, homogenized & freeze-dried | Red. sugars Sucrose TS | 2517 | n/a | 850-2500 | SNV & detrend | Cross & external | MPLS | n/a | 9*10 ⁻⁵ - 9*10 ⁻³ 1*10 ⁻³ - 22*10 ⁻² 1.2*10 ⁻³ - 27*10 ⁻² | 0.43 0.71 0.66 | 38.9* 10 ⁻⁶ 96.9*1 0 ⁻⁶ 135*10 ⁻⁶ | ⁴³ |
| Intact | Carbohydrate | 250 | n/a | 700-1100 | Smoothing 2nd der. | Cross & external | PLS | Interactance | 11.1-22.6 | 0.86 0.86 | 0.98 0.98 | ⁸⁶ |

761 TRS Total reducing sugars, TS Total sugar

762 **Table 5** Overview of applications of NIR spectroscopy to measure texture of potatoes

| Refs | Data | Parameter | | | | | | | | |
|--------------------------------------|-------------------------|--------------------------|----------|-------------|--------------|------------|-----------|-----------|-----------|-----------|
| | | Hardness/ crumbliness | Firmness | Springiness | Adhesiveness | Graininess | Mealiness | Moistness | Chewiness | Waxines |
| Boeriu <i>et al.</i> ⁷⁶ | Range ^a | n/a | 11-70 | n/a | n/a | n/a | 7.9-79.4 | 9.5-70.1 | n/a | 12.3-79.1 |
| | R _{prediction} | n/a | 0.82 | n/a | n/a | n/a | 0.89 | 0.91 | n/a | 0.79 |
| | SEP | n/a | 8.64 | n/a | n/a | n/a | 11.28 | 8.72 | n/a | 14.64 |
| Thybo <i>et al.</i> ⁶⁸ | Range ^a | 2.9-5.9 | 2.1-5.9 | 1.4-4.4 | 2.7-5.0 | 2.3-6.9 | 1.7-7.4 | 1.7-7.4 | 2.9-5.8 | n/a |
| | R _{raw} | 0.69 | 0.71 | 0.62 | 0.25 | 0.66 | 0.73 | 0.67 | 0.63 | n/a |
| | R _{cooked} | 0.50 | 0.67 | 0.67 | 0.54 | 0.77 | 0.83 | 0.82 | 0.67 | n/a |
| | SEP _{raw} | 0.28 | 0.38 | 0.36 | 0.36 | 0.70 | 1.12 | 0.56 | 0.34 | n/a |
| | SEP _{cooked} | 0.40 | 0.43 | 0.32 | 0.26 | 0.51 | 0.75 | 0.33 | 0.32 | n/a |
| Van Dijk <i>et al.</i> ⁷⁷ | Range ^a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a |
| | R | 0.88 | 0.82 | n/a | n/a | 0.85 | 0.88 | 0.92 | n/a | 0.87 |
| | SEP | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a |

763 ^aValues are dimensionless

764 TOC GRAPHIC

