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Review

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A Review of the Application of Near-Infrared Spectroscopy for the Analysis of Potatoes

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

KEYWORDS: *NIRS, Solanum tuberosum L., chemometrics, nondestructive, calibration, validation, qualitative, quantitative*

INTRODUCTION

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

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

Nowadays, there are still many technical issues that affect its production and development. Thus, progress of the potato industry toward a sustainable production is essential in order to ensure long-term food security and a human supply.[2]

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

These tubers are rich in protein, calcium, potassium, and vitamin C, and have an especially good amino acid balance. Moreover, they supply high levels of energy due to their starch content.[3] Raw tubers contain about 80% of water and 20% of dry matter. About 60−80% of the dry matter is starch.[4]

The starch in raw potato cannot be digested by humans; for this reason, its consumption without any preparation is not a common practice, and normally potatoes are prepared for consumption by boiling (with or without the skin), baking, or frying. The preparation method employed affects potato composition in a different way, but in general terms they all reduce fiber and protein content. This is due to leaching into cooking water and oil, destruction by heat treatment, or chemical changes such as oxidation.[4]

Boiling is the most common method of potato preparation worldwide, and this practice causes a significant loss of vitamin C, especially in peeled potatoes. When potatoes are fried, either for French fries and chips preparation, they absorb a high content of fat and their mineral and ascorbic acid content decreases. Losses of vitamin C are generally higher when baking rather than boiling due to the higher oven temperatures, but losses of other vitamins and minerals are lower.[4] Table 1 shows the main components of potato in its most common consumption preparations.[5]

Quality of potatoes and potato products is determined by its constituents. The common methods employed to determine the main constituents of potatoes are chemical analysis such as high-performance liquid chromatography (HPLC). These methods are time-consuming, expensive, and involve the destruction of the sample subjected to study.[6] These reasons together with increased consumer demands have raised the interest of the potato industry in high-technology systems able to secure high-quality products.[7] Near-infrared spectroscopy (NIRS) is one of the most advanced technologies regarding nondestructive quality assessment techniques.[8] Since its first application in the 1960s, the NIRS technique has been successfully used for the rapid analysis of moisture, protein, and fat content in many agricultural and food products.[9−11]

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

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Table 1. Composition[a] of Raw and Cooked Potatoes[5]

	composition of potatoes per 100 g					
	raw	skin (38 g)	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 B6 (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

[a]g grams, kcal kilocalories, mg milligrams, IU international units.

NIRS TECHNOLOGY

Near-infrared spectroscopy (NIRS) studies the interaction between electromagnetic radiation and matter. Near-infrared is the region of the electromagnetic spectrum that extends between 780 and 2500 nm (nm), lying between visible light with shorter wavelengths and the mid infrared (MIR) with longer wavelengths. This region is characterized by overtone and combination bands of the fundamental vibration occurring in the MIR.[12] NIRS technique consists of the radiation of a sample with one or more wavelength bands between 780 and 2500 nm. This radiation penetrates into the sample, and light is absorbed selectively according to the specific vibration frequencies of the molecules present producing a spectrum that depends on the composition of the sample. The interaction between energy and matter follows the Beer–Lambert's Law. According to it, absorbance at any wavelength is proportional to the number or concentration of absorbing molecules present in the path of the radiation.[13,14]

Normally, in samples of heterogeneous chemical nature, the spectrum obtained in the near-infrared region is shown as a combination of overlapping spectral bands, which are sometimes confused in a smooth line in which there are peaks, valleys, and curvatures.[15,16] There is a need of a specific data analysis to interpret these absorption bands. It must be capable of relating the electromagnetic information (spectrum) with the information of the physical and chemical composition (reference method), using mathematical algorithms through the application of different statistical models.[17] This process is known as development of NIRS calibrations. To create a calibration, a mathematical relationship should be established between the two sets of data, spectra data and reference data including physical or chemical information of the product. This can be performed via several chemometric techniques. The most commonly used statistical techniques for this process are the multiple linear regression, principal component regression, and partial least squares (PLS) regression. These chemometric techniques establish a mathematical relationship between variations in the NIR spectra of samples with the variation in the parameter measured. This relationship can then be used to predict the parameter value in unknown samples.

It should be noted that the main limitation of NIRS in the analysis of food products is that the initial phase of development of the calibrations depends on reference methods based on chemical analysis.[18]

The use of NIRS for the analysis of food products began in the 1960s and later in the 1970s it started to be introduced in various industries as an alternative to chemical and biological traditional methods.[19−23] NIRS is considered a technology with a huge potential to obtain accurate and fast predictions of the chemical composition and nutritional value of many agricultural products.[24,25]

The main advantages of NIRS technique over reference methods are its quickness, its both nondestructive and no contaminant nature, and its great accuracy.[13,26,27] However, it is worth mentioning that there are certain problems common to both the chemical analysis and the NIRS. These difficulties are derived from the preparation or presentation of wet samples when working with fresh products.[28]

On the one hand, the preparation of wet samples is complex to obtain accurate results in the chemical analysis. On the other hand, the presence of a high water content in the samples may limit the use of NIRS, since there are strong absorption bands in the spectrum caused by water in certain spectral regions. Despite this, NIRS has been successfully used on a wide variety of products with high moisture content.[28]

As stated above, the application of NIRS in food products commenced in the decade of the 1960s. The first application of NIR in the analysis of foods was the determination of moisture and still is the most widely used application.[18] One of the first publications of NIR applications in food products was about the NIR reflectance spectra of a variety of grains. The study was carried out in 1965 by Massie and Norris[29] under the title *Spectral reflectance and transmittance properties of grain in the visible and near-infrared*. This study was a request from the U.S. Department of Agriculture (USDA), and the main objective was the determination of the spectral reflectance and transmittance properties of grain in order to design infrared grain driers. The former authors studied the spectral reflectance of corn, oats, wheat, soybeans, rice, alfalfa seed, and milled rice, and the results obtained showed that reflectance of the sample was the most important variable for infrared drying of grain.

Although the literature concerning NIR applications in potato is not as extended as in other types of vegetables,[30] NIR applications in this industry were initiated in the 1980s. For this reason, it is important to compile the information that has been published relating NIRS applications to the quality determination of potato and potato products since its beginning.

MAJOR COMPONENTS DETERMINATION

Water, Dry Matter, and Starch. One of the first applications of NIR in the potato industry was to measure the moisture content of chips. In 1988, McDermott reported good results with a correlation coefficient (R) of 0.95 and a standard error of estimation of 0.15.[31]

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

Nevertheless, Ni et al. (2011)[33] obtained better results for moisture prediction using least squares-support vector machines (LS-SVM) and kernel partial least squares (KPLS) methods. The coefficients of correlations were 0.99 and 0.98 with a root-mean-square standard error of validation (RMSEV) of 0.07 and 0.10 for LS-SVM and KPLS, respectively. On the basis of the results obtained, the authors concluded that it was possible to determine moisture content of chips in a fast and accurate way.

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

Other authors have focused on the determination of dry matter and starch in potatoes. Dry matter concentration is a useful index for potato quality as it contains information on both water and starch concentration.[36] As stated before, a great percentage of dry matter in potato is in the form of starch, and it is considered as a very important constituent of this food since the final quality of potato products is directly related to this component. Moreover, the European Potato Starch Industry bases its payments to the farmers on the starch concentrations of tubers.[37]

In the decade of the 1980s specific gravity measurement was the best practical and nondestructive method for estimating the dry matter content of potatoes. Although dry matter and specific gravity were known to be highly correlated,[38] there was a need for a much more rapid and accurate nondestructive technique. Therefore, from this decade through the 1990s and until nowadays some authors such as Haase, Hartmann, Brunt and Drost[37,39,40] studied the correlation between spectral and both dry matter and starch content of these tubers. The most common method used to establish the correlation was to combine NIR data with the PLS regression statistic method.

Table 2 shows the determination coefficients as well as the standard errors of prediction (SEP) obtained for dry matter and starch content in potatoes reported by several authors. A wide range of potato varieties have been studied in diverse sample presentations: intact, mashed, freeze-dried, etc. Also, different wavelength regions have been used to develop the calibration models ranging from 734 to 931, 750 to 950, 800 to 1000, 1100 to 2500, 770 to 2500, 850 to 2500, 1000 to 2500 nm, or including the visible range 400 to 2500 and 460 to 1040 nm. It is known that starch has bands at 1200, 1700, 1720, and 1780 nm.[41] Because of these facts, a wide range of SEP values have been obtained, and consequently, it is difficult to establish either the type of sample presentation or a specific wavelength to predict the content of dry matter and starch. However, it seems that the lower SEP values for both components occurred when the sample is mashed and homogenized, and the range between 1100 and 2500 nm is used.[30,39,40,42,43]

Dry matter content was also highly predicted in potato chips (root mean square error of cross validation RMSECV: 0.84) where the percentage of this component is significantly higher than in intact and mashed potatoes.[44]

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

Helgerud et al. (2012)[47] also obtained better results for the measurements taken at the center of the longest axis in a recently published paper about the ability of NIR to rapidly estimate dry matter content of intact potatoes. They compared the performance of two different NIR instruments to the performance of the traditional specific gravity measurement method. First, they used a 1D NIR interactance for stationary analysis and second, a commercially available 2D NIR interactance system to provide online estimation. The specific gravity (SG) was calculated based on eq 1.

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

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

$$\mathrm{DM} = 215.73(\mathrm{SG} - 0.9825) \quad (2)$$

A standard normal variate (SNV) pretreatment was applied only to the data obtained by the 1D NIR interactance equipment. Table 2 shows that the lowest RMSECV and highest R^2 were obtained when specific gravity method was employed. However, this can only be used with small sample volumes and takes much more time than the other two systems able to record multiple spectra per second.

Nevertheless, a direct relationship exists between specific gravity and cooking quality of these tubers. Some investigators have reported that specific gravity could be used as a direct measure of quality characteristics of potatoes.[49−52] In 2005, Chen et al.[53] examined the correlation between NIR spectroscopy and specific gravity of intact potatoes. 250 samples of potatoes from three different varieties were used for this study. Samples were scanned by NIR in interactance mode in the 700−1100 nm wavelength range, and the specific gravity of

Table 2. Overview of Applications of NIR Spectroscopy To Measure Dry Matter and Starch Content of Potatoes[a]

type of sample	number of samples	variety	wavelength range (nm)	preprocess	validation	analysis	mode	range %	R^2	SEP	refs
				DM & Starch							
mashed	275	n/a	1000−2500	first der. & MSC	cross & external	PLS	interactance-reflectance	19.5−29.8	0.92	0.45	30
								13.4−21.9	0.81	0.50	
freeze-dried	628	n/a	850−2500	none	external	n/a	reflectance	16.7−33.4	0.98	0.518	37
				first der.					0.98	0.514	
				second der.					0.97	0.568	
				none				12.1−27.3	0.96	0.638	
				first der.					0.96	0.622	
				second der.					0.95	0.678	
mashed & homogenized	116	Granola & Nicola	1100−2500	first der.	cross & external	MPLS & PCA	reflectance	15.6−21.0	0.97	0.19	39
	116							10.0−14.8	0.93	0.28	
mashed & homogenized	504	n/a	1100−2500	smoothing & MSC	external	PLS	n/a	19.5−29.2	0.93	0.22	40
								14.2−23.4	0.84	0.39	
mashed & homogenized	219	18 different	1100−2500	smoothing	external	PLS	reflectance	19.8−34.0	0.93	0.47	42
									0.84	0.63	
mashed, homogenized and freeze-dried	2517	n/a	850−2500	SNV & DT	cross & external	MPLS	n/a	14.1−35.4	0.99	0.39	43
								12.8−27.2	0.96	0.47	
mashed & homogenized	81	Nicola	1100−2500	none	full cross-validation	PLS & PCA	reflectance	16.9−30.2	0.86	1.66	77
		Irene						10.8−21.8	0.90	0.96	
		Bintje									
				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	910	Russet	800−1000	second der.	external	linear regression	transmittance	14.1−32.5	0.84	1.52	83
sliced	907	Burbank							0.90	1.69	
flesh	200	Shepody & Russet Burbank	770−2500	second der.	external	MLR	reflectance	n/a	0.77−0.58	1.3−1.5	58
intact	49	n/a	734−931	none	cross validation	PLS & MLR	n/a	n/a	1.04	0.62	84
				second der.					1.09	0.58	
intact	114	Asterix, Bruse, Celine, Folva, Saturna	760−1040	SNV (1D)	cross validation	PLS	interactance	14.4−30.5	0.95	0.91	47
				none (2D)					0.83	1.68	
				none (SG)					0.97	0.65	
intact	100	Nicola, Spunta	750−950	second der.	cross validation	PLS	n/a	17.6−25.5	0.85	1.52	36
clean	100	Golden Delight							0.81	1.64	
peeled	100	Sebago							0.90	1.13	
sliced	100	Russet Burbank							0.86	1.08	

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Table 2. continued

type of sample	number of samples	variety	wavelength range (nm)	preprocess	validation	analysis	mode	range %	R^2	SEP	refs
				Starch							
mashed	n/a		850–2500	SNV & DT +	external	MPLS	reflectance	9–30	0.90	0.74	85
				none					0.89	0.75	
	268			first der.					0.88	0.79	
	269			second der.							
	272										
mashed & homogenized	126	Aveka, Festien, Karakter, Karniko, Mercator, Seresta, Valiant	400–2500	MSC	cross validation	PLS	reflectance	18.0–23.4	n/a	0.4	57

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

each sample was measured by using specific gravity measurement equipment based on the principle of liquid displacement. For the development of the calibration equation samples were divided into two groups: 150 for calibration model and 100 to validate it. PLS regression method was applied in order to obtain the prediction models. The results obtained showed high correlation coefficients between NIR spectra data and specific gravity. The correlation coefficients achieved for the calibration set of samples ranged from 0.94 to 0.95 for different pretreatments employed with SEC values between 0.0041 and 0.0043 g/cm^3. The highest correlation coefficients and lowest SEC values obtained were for raw spectra, normalization, and second derivative all with the same values (R: 0.95 and SEC: 0.0041 g/cm^3). For prediction set of samples, R values ranged from 0.93 to 0.94 with SEP values between 0.0044 and 0.0047 g/cm^3. The highest R values and lower SEPs were those obtained for raw spectra and normalization.

On the basis of the results of this study, authors concluded that NIR spectroscopy was able to accurately measure the specific gravity of intact potatoes.

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

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

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

Some authors attributed these lower values to the reduced range of these constituents and the high values of the reference method errors.[30]

Furthermore, the ability of NIRS to qualitative classify samples according to their protein content has been assessed. In research developed by Fernández-Ahumada et al.[30] (2006), a discriminant analysis was performed in order to classify samples in two categories regarding to their protein content. Samples were split into two groups: one including the samples with low

Table 3. Overview of Applications of NIR Spectroscopy to Measure Protein Content of Potatoes[a]

type of sample	parameter	number of samples	variety	wavelength range (nm)	preprocess	validation	analysis	mode	range	R^2	SEP	refs
mashed	CP	275	n/a	1000−2500	first der. & MSC	cross & external	PLS	interactance-reflectance	1.23−3.21	0.62	2.4	30
	RP								0.58−2.05	0.46	1.7	
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	176	n/a	850−2500	SNV & detrend +	external	MPLS	reflectance	0.85−2.91	0.61	0.20	85
		174			none					0.59	0.20	
		173			first der.					0.58	0.21	
	CP	187			second der.					0.25	0.09	
		190			none				0.85−2.91	0.22	0.08	
		188			first der.					0.13	0.10	
					second der							
mashed & homogenized	CP	126	n/a	400−2500	MSC	cross validation	PLS	reflectance	0.69−1.95	n/a	0.025	42

[a]CP, crude protein; RP, recoverable protein; CGP, coagulating protein.

recoverable protein content (<14 mg g^{-1}) and the second with the samples that presented high values (≥14 mg g^{-1}) for that parameter. A total of 184 samples were used for the study, and an overall of 161 (87.5%) were correctly classified. The results obtained demonstrated that, in spite of the low protein content, it was possible to classify potato samples by NIRS regarding that parameter (Table 3).

Other Carbohydrates. Carbohydrate compounds, commonly referred to as sugars, are presented in narrow concentrations in potatoes; therefore, their estimation based on NIRS might not be as accurately as in other compounds such as dry matter and starch.[39] Results obtained for the NIR estimation of carbohydrates reported by several authors are summarized in Table 4. It can be extracted from the table that a robust NIR calibration model to predict sugar content in potatoes has not yet been developed. However, Mehrübeoglu and Coté (1997)[6] while investigating the online application of NIR to estimate total reducing sugars (TRS) of potatoes achieved RMSECV and RMSEP values that complied with the specifications of less than 0.15% of TRS. Thus, the authors concluded that NIR spectroscopy met the requirements to be used for the online real-time measurements of these compounds. On the other hand, Scanlon et al. (1999)[58] reported poor ability of NIRS to predict fructose content, results (not shown) that differed from those reported by the former authors.

Other authors have studied NIRS prediction of individual sugars components such as glucose, fructose, and sucrose along with the estimation of TRS content. The results obtained showed that the prediction of these individual components had to be improved.[39]

It seems that the estimation of TRS gave lower SEP values than the prediction of glucose and fructose separately. This fact might be useful since TRS content seems to be technologically more important than the content of the single compounds[59] (Table 4).

MINOR COMPONENTS DETERMINATION

Fat and Acrylamide. Determination of acrylamide contents in potato chips is currently necessary due to its potentially toxic attributes and the fact that very high concentrations can be produced in amylaceous fried foodstuffs.[60] Moreover, consumer awareness of the fat content in potato products is increasing worldwide as is the seeking of low fat products. Some studies have been developed for the determination of both fat and acrylamide content in potato processed products.

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

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

Shiroma and Rodriguez-Saona (2009)[32] investigated the potential of NIR combined with chemometric to determine fat

Table 4. Overview of Applications of NIR Spectroscopy to Measure Carbohydrate Content of Potatoes[a]

type of sample	parameter	number of samples	variety	wavelength range (nm)	preprocess	validation	analysis	mode	range	R^2	SEP	refs
sliced	TRS	39	Russet Chipping	n/a	n/a	cross & external	PLS	interactance	0.04−0.2	0.57	0.0009	6
mashed & homogenized	glucose	116	Granola & Nicola	1100−2500	first der.	cross & external	MPLS & PCA	reflectance	0.002−0.12	0.62	0.0001	39
	fructose	100							0.148−0.520	0.70	0.04	
	sucrose	109							0.101−0.439	0.89	0.02	
	Σ red. sugars	134							0.136−0.399	0.62	0.03	
									0.249−0.790	0.82	0.06	
mashed, homogenized and freeze-dried	red. sugars	2517	n/a	850−2500	SNV & detrend	cross & external	MPLS	n/a	$9 \times 10-5-9 \times 10^{-3}$	0.43	38.9×10^{-6}	43
	sucrose								$1 \times 10^{-3}-22 \times 10^{-2}$	0.71	96.9×10^{-6}	
	TS								$1.2 \times 10^{-3}-27 \times 10^{-2}$	0.66	$135 \times 10-6$	
intact	carbohydrate	250	n/a	700−1100	smoothing second der.	cross & external	PLS	interactance	11.1−22.6	0.86	0.98	86
										0.86	0.98	

[a]TRS, total reducing sugars; TS, total sugar.

and moisture content in potato chips and its capacity to classify samples based on their composition. A total of 15 commercial potato chips fried from different sources according to their label were used in this study. PLS regression method was used for the prediction models and a Soft Independent Modeling of Class Analogy (SIMCA) was used for qualitative analysis. The correlation coefficient of cross-validation obtained was 0.97 for fat with a SECV value of 1.54. The classification model based on SIMCA was able to differentiate potato chips by source of frying oil. On the basis of these results authors concluded that it was possible to determine fat content in potato chips as well as classify them according to their composition by a fast, simple, and accurate method.

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

According to these studies, it may be assumed that NIR spectroscopy performs well for the parameter fat, whereas for acrylamide content more robust models need to be built. In the meantime, NIR spectroscopy is a useful tool for classifying samples according to this last constituent.

Carotenoids. Benefits of carotenoids have been reported by several authors. Carotenoids are well-known for their health promoting functions to the immune system and reduction of the risk of degenerative diseases.[62−64] Because of these advantages, consumer concern for products with high carotenoids concentration is growing in the same way as the industry interest for the screening and development of food crops with increased concentrations of those components.[65,66]

In 2009, Bonierbale et al.[67] examined the potential of NIR to estimate total and individual carotenoid concentrations in cultivated potatoes. 189 samples of potato were used for the development of NIRS calibrations and external validation. Samples were freeze-dried and milled prior to NIRS analysis. The individual carotenoids analyzed were anteraxanthin, violaxanthin, lutein, zeaxanthin, and β-carotene. The concentration of total carotenoids ranged between 440 and 8560 μ100 g^{-1} dry weight and of individuals from 0 to 2240 μ100 g^{-1} dry weight. Coefficients of determination obtained ranged from 0.60 to 0.92. Best results were obtained for total carotenoids estimation (R^2: 0.91) and zeaxanthin (R^2: 0.92) with SEP values of 610 and 410 μg 100g^{-1} dry weight respectively.

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

Table 5. Overview of Applications of NIR Spectroscopy To Measure Texture of Potatoes

		parameter								
refs	data	hardness/ crumbliness	firmness	springiness	adhesiveness	graininess	mealiness	moistness	chewiness	waxines
Boeriu et al.[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 et al.[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 et al.[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

[a]Values are dimensionless.

OTHER CHARACTERISTICS

Crop's Yield Evaluation. NIR major application in potatoes is generally for determining internal components (dry matter, starch, soluble solids, carotenoids, etc), but also sensory texture of cooked potatoes has been evaluated.[68] Despite this, in general terms, the scope of NIRS covers a wide range of applications nowadays such as the determination of physiological indices of crops[69] or the optimal date for fruit picking.[70]

In 2008, Jeong et al.[71] studied the correlation between sprouting capacity in potato tubers and NIRS. They used 380 potato tubers divided into four groups, two groups of the same variety (Superior) harvested at two consecutive years, a group of another variety (Atlantic) and the last group containing the total number of samples. The sprouting capacity of the four calibration sets ranged between 0.24 and 7.70 with a standard deviation between 1.03 and 1.95.

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

Other authors have found that the relationship between the absorption of nitrogen and the total fresh weight in potato crops could be used to calculate proportions of supplemental nitrogen fertilizer.[72] Consequently, the correlation between NIR spectroscopy and nitrogen absorption of potato plants has been investigated in order to be used for this purpose.

As an example, Young et al.[72] developed a study in 1997 for the NIR determination of nitrogen in potato tissues. They used samples of two different potato varieties grown under six nitrogen treatments. Samples of leaves, stems, and tubers with nitrogen concentrations between 0.60 to 3.65%, 0.68 to 5.88, and 2.25 to 8.00% (on a dry weight basis) respectively were scanned by NIR and by reference method (Dumas combustion). The coefficients of determination obtained were 0.96, 0.95, and 0.96 with SEP values of 0.11%, 0.03%, and 0.09% for leaf, stem, and tuber respectively.[72] Authors concluded that the estimation of nitrogen concentration in potato crops by NIR techniques was cheaper and safer than comparable chemical methods. These results were in accord with those reported by Váradi et al.[73] (1987); however, they studied NIR reflectance for the determination of total nitrogen in ground grape leaf samples rather than in potatoes.

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

Later in the same year, the second part of the experiment explained above was carried out. At this time, authors compared the influence of operator, moisture, and maturity class in the assessment of total nitrogen comparing the two methods explained before. Once again, samples of leaf stem and tubers were analyzed by Dumas combustion and by NIR, and in the following two years, by a number of operators who made estimates of nitrogen concentrations. Authors achieved a good correlation between NIR and Dumas combustion methods in the determination of nitrogen for the different operators who tested the samples.[75] The coefficients of determination obtained ranged from 0.94 to 0.98 with SEP values between 0.02 and 0.11.

Texture. Texture of potatoes at the time of consumption is an important factor related to product quality. Consumers associate the quality of potatoes according to the texture they perceive when consuming. This sensory perceived quality is normally measured using a panel of trained judges. These procedures require a considerable amount of time as well as an important investment. Therefore, much research has been developed to determine the texture of potatoes by instrumental

technologies rather than methods based on human's perception.[76]

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

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

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

As it is shown in Table 5, the correlation coefficients for the sensory texture attributes: firmness, mealiness, and moistness were lower than those obtained by Boeriu et al. (1998)[76] for the same attributes. Moreover, the range of values of the sensory attributes was much smaller than in the previous work, and therefore SEP values were greater.[68]

Another research study on the same topic was developed by Van Dijk et al. (2002).[77] They studied the relationship between dry matter content, sensory-perceived texture, and NIRS in steam cooked potatoes. 81 potato tubers samples representing different types of cooking behavior were used for this assessment. Sensory texture analysis was accomplished by a panel of 16 trained judges. The results obtained were very similar to those reported by Thybo et al.[68]

Damages Evaluation. Damage to potato tubers either by mechanical harvesting or by transport causes a great loss of quality of the final product, and as a result almost two-thirds of the potatoes sold in the market show external or internal damages.[78] Economic losses due to tuber's damages are also significant.[79]

In spite of the fact that there have been several investigations focused on reducing the degree of damage, there is still a need to continue working in this field.[80]

Evans and Muir (1999)[81] published a report with the aim to investigate the feasibility of NIR spectroscopy as a method for determining the discoloration of potatoes associated with bruising in a nondestructive way. Bruising is considered one of the biggest problems in the potato industry since it causes very important economic losses.[80] Therefore, investigation in this field is always welcome.

For that research, samples of Record variety susceptible to bruising were used. The tubers were given a consistent impact and then were stored for 16 h. NIR spectra were measured in both unpeeled and peeled tubers as in bruised and unbruised sites. The results showed that reflectance spectra from unpeeled bruised tubers had higher reflectance in the NIR than unbruised tubers. Moreover, in peeled tubers, the differences were higher in those regions. On the basis of these results, authors suggested that bruise detection by NIRS may be possible in unpeeled tubers and almost certainly in peeled tubers. Nevertheless, they stated that the method required improvement in order to be a reliable technique.

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

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

FUTURE CHALLENGES

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

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

For that reason, the development of techniques capable of determining food components quickly and at a competitive price is required. As have been demonstrated through the studies carried out by the food industry since the beginning of the application of NIRS in the 1970s, these technologies have the potential to predict those components in an easy, fast, and accurate way.

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

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

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Notes

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■ ABBREVIATIONS USED

AOTF-NIR, acousto-optical tunable near-infrared spectrometer; CP, crude protein; RP, recoverable protein; CGP, coagulating protein; DM, dry matter; DT, detrend; FAO, Food and Agriculture Organization; FTIR, Fourier transform infrared spectroscopy; GM, genetically modified; HPLC, high-performance liquid chromatography; KPLS, kernel partial least-squares; LS-SVM, least-squares-support vector machines; nm, nanometer; MDG, millennium developments goals; MLR, multiple linear regression; MPLS, multiple partial least-squares; MSC, multiplicative scatter correction; MT, million tonnes; NIRS, near-infrared spectroscopy; PCA, principal component analysis; PLS, partial least-squares; R, correlation coefficient; R^2, coefficient of determination; RMSECV, root-mean-square error of cross validation; RMSEP, root-mean-square error of prediction; RMSEV, root-mean-square standard error of validation; SD, standard deviation; SEP, standard error of prediction; SEV, standard error of validation; SIMCA, soft independent modeling of class analogy; SNV, standard normal variate; TRS, total reducing sugars; TS, total sugars; USDA, U.S. Department of Agriculture; VIS, visible spectroscopy

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