https://doi.org/10.17221/57/2019-CJFS

The application of NIR spectroscopy in moisture determining of vegetable seeds

Jonna Szulc, Grażyna Gozdecka, Wojciech Poćwiardowski*

Faculty of Chemical Technology and Engineering, UTP University of Science and Technology, Bydgoszcz, Poland

**Corresponding author: wojciech.pocwiardowski@utp.edu.pl*

Citation: Szulc J., Gozdecka G., Poćwiardowski W. (2020): The application of NIR spectroscopy in moisture determining of vegetable seeds. Czech J. Food Sci., 38: 131–136.

Abstract: The aim of the study was to elaborate a universal calibration for the near infrared (NIR) spectrophotometer to determine the moisture of various kinds of vegetable seeds. The research was conducted on the seeds of 5 types of vegetables – carrot, parsley, lettuce, radish and beetroot. For the spectra correlation with moisture values, the method of partial least squares regression (PLS) was used. The resulting qualitative indicators of a calibration model (R = 0.9968, Q = 0.8904) confirmed an excellent fit of the obtained calibration to the experimental data. As a result of the study, the possibilities of creating a calibration model for NIR spectrophotometer for non-destructive moisture analysis of various kinds of vegetable seeds was confirmed.

Keywords: moisture content; seeds; non-destructive method; analysis of water; method development

Seeds vary in terms of shape, size and colour. The size of seed material is not dependent on the size of a plant; however, there is a dependence between the size of seeds and their quantity produced by a plant (Bochenek et al. 2000). The chemical composition of the seed material depends on genetic factors, as well as climatic conditions and soil (Bewley & Black 1994). The dry matter of seeds is from 70% to 94% and consists of carbohydrates, proteins, lipids, nucleic acids, minerals and other active substances (plant hormones, alkaloids, vitamins) among others (Bewley & Black 1994; Taylor 1997).

The quality of the seed material determines significantly the efficiency of its germination. Among the features which determine the quality of seeds are germination rate and moisture. The size of seeds also determines plants growth and yield. It is assumed that bigger and heavier seeds provide larger yields (Gozdecka & Gęsiński 2011). The moisture of the seed material also plays a significant role regarding quality. It determines the conditions of storage and the shelf life of seeds (Font et al. 2007; Tomkiewicz 2009). The higher the content of water inside the seeds, the more intensive is the occurrence of biochemical transformations, and the greater the likelihood of microbiological infections (Bonner et al. 1992; Domoradzki et al. 2005; Kaleta & Górnicki 2008). Low moisture allows extending the storage period. In the case of seeds of water content in the range from 5% to 14%, lowering their moisture by 1% provides twice longer storage (Strelec et al. 2010). However, personal experiences, as well as the authors' observations, indicate that the seeds with reduced water content are more susceptible to mechanical damage, and they germinate slowly.

At harvest time, in the course refining seed treatments as well as during storage, the moisture of the seed material should be monitored (Makarski 2008; Kaniewska et al. 2013). Currently, the bases to determine the water content in seed weight are the methods developed and recommended by ISTA (International Seed Testing Associations) (Bonner et al. 1992; Sivritepe et al. 2008). To measure a water content in seeds, the most commonly applied methods are resistive and capacitive ones

Supported by the European Regional Development Fund within the Regional Operational Programme of Kuyavian-Pomeranian Province for the years 2007–2013.

https://doi.org/10.17221/57/2019-CJFS

(Lazzari 1994; Makarski 2008). Laboratories frequently examining the quality of the seed material apply drying methods. Besides them the ISTA list of recommended methods also includes moisture determination using near infrared (NIR) spectroscopy.

NIR spectroscopy (10 000–4 000 cm^{-1}) has an advantage over traditional methods of determining individual features mainly due to the speed of analysis as well as the lack of need to use chemical reagents (Büning-Pfaue 2003; Cornish et al. 2004; Rahman & Cho 2016). The technique very often does not require sample treatment, and thus it is regarded as a non-invasive and non-destructive method (Fassio & Cozzolino 2004; Font et al. 2007). NIR spectroscopy is increasingly applicable to on-line control, e.g. fruit and vegetable industry (Nicolaï et al. 2007; Siger et al. 2010; Collell et al. 2012; Plans et al. 2013, Csorba et al. 2019).

NIR spectroscopy is based on the use of the examined material spectrum which is different for each molecule (Sinelli et al. 2011). This allows determining absorption bands with a specific wavelength for individual functional groups typical for a given molecule, e.g. C-H, N-H, O-H (Osborne et al. 1993; Font et al. 2007). However, for sample qualitative and quantitative analysis, it is necessary to develop calibration. The calibration in the case of NIR spectroscopy is a mathematical model describing the relationship between typical points of the spectrum and the results achieved by means of the reference method used to determine a given feature. The commonly used methods for linear constructions of calibration models are Principal Component Regression methods (PCR) and Partial Least Squares (PLS) (Jin & Chen 2007; Stanimirova et al. 2008; Plans et al. 2013). PLS model was used among others by Fassio & Cozzolino (2004), Huang et al. (2013), Montes et al. (2013), while predicting a chemical composition of seeds.

In seed production the method using NIR spectroscopy to determine water content inseeds is becoming increasingly common. The first paper describing determination of the moisture content of seeds by NIR spectrophotometry of their methanol extracts was published in 1962 by Hart et al. This technique was intensively developed and widely used; however, it is based most often on a calibration model for a given seed type (Norris & Hart 1965; Robertson & Barton 1984; Gergely & Salgó 2003; Lestander & Geladi 2003; Fassio & Cozzolino 2004; Baiannu et al. 2011). It is mainly determined by a large morphological and chemical variety of various types of plant seeds. However, as far as the requirements for water content are concerned, these are similar for all types. The possibility of rapid measurement of water content in seeds is useful in the control of a refining operation including seeds drying. Thus the NIR spectroscopy due to a short period of analysis should be appropriate at each stage of technology improving the seed material quality as well as during its storage. An improvement in the use of this technique to control the quality of seeds would be the possibility to use a universal calibration for determining water content that works well with a number of seeds and currently there is none.

The aim of this study was to develop a universal calibration for NIR spectroscopy to determine moisture of various kinds of vegetable seeds.

MATERIAL AND METHODS

Samples and spectra collection. The seeds of the following species of vegetables were the research material: carrot, parsley, lettuce, radish and beetroot. The spectra were achieved using NIR spectrophotometer NIRFlex N-500 equipped with a module to examine fixed specimen NIRFlex Solids by Büchi (Büchi AG, Switzerland). The samples (~25g) were placed in a Petri dish of 10 cm diameter and located in a measuring cell of NIR spectrophotometer NIRFlex N-500. The settings of the parameters in the experiment were as follows: the spectrum range was 10 000–4 000 cm^{-1}, the number of scans was 32, and the resolution was 4 cm^{-1}. Nine spectra were collected for each seed species.

Reference method for moisture determination of seed. The same samples which were used to spectra collection were then used to determine their moisture. The content of water of the seed material of 5 types of seeds was obtained with low temperature drying method (105 °C) in drier with a forced air circulation POL-EKO model SLW 115 (Pol-Eko Aparatura, Poland), repeated three times and accurate to 0.001% (ISTA 2006).

Calibration of NIR method. The mathematical model of calibration was created by means of NIRCal 5 Chemometric Software (Büchi, Switzerland) attached to the spectrophotometer. All collected NIR spectra were matched with moisture values determined by the drying method. The data (45 spectra) needed the initial processing. In order to remove as much noise as possible from spectra in wavelength space without losing spectral data a Savitzky-Golay procedure of a nine-point spectra smoothing was used. Key frequency ranges were selected to create calibration within which significant shifts between the spectra were observed. These were the frequencies 10 000–7 800, 6 600–5 400 as well as 4 800–4 400 cm^{-1} (Figure 1).

https://doi.org/10.17221/57/2019-CJFS

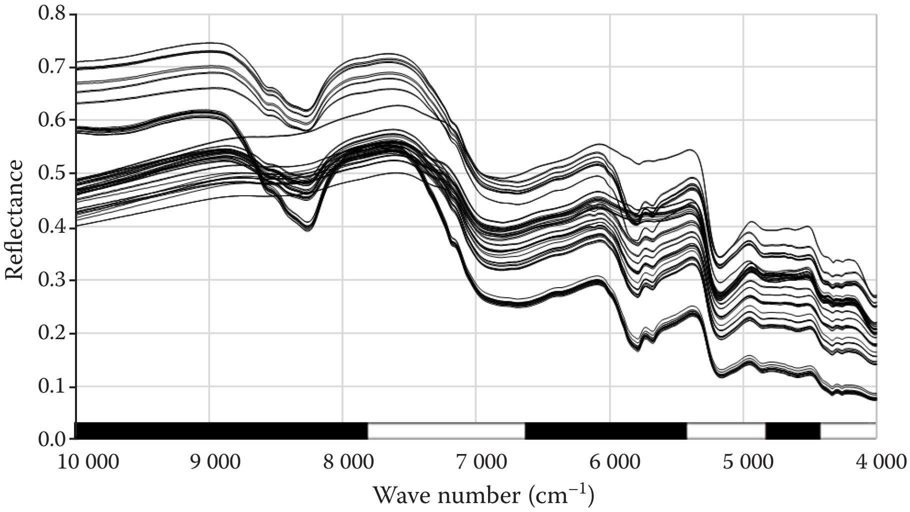

Figure 1. Seeds samples spectra

Black regions on axe X present wave number used in the calibration method: 10 000–7 800, 6 600–5 400, 4 800–4 400 cm^{-1}

The spectra were divided into two collections. The collection of 2/3 of all the spectra was the one to create the calibration (30 spectra). The remaining spectra were used to validate the mathematical model.

RESULTS AND DISCUSSION

In order to develop the calibration partial least squares method was used (PLS). The NIRCal program also calculates the Q coefficient (Q-Value) showing the calibration quality. The Q indicator takes under consideration significant statistical indicators such as SEE – Standard Error of the Equation, SEP – Standard Error of the Prediction, BIAS – the linearity deviation analysis. Q for the used calibration method was 0.8904. It is assumed that the calibration of $Q > 0.7$ is appropriately adjusted to the data (Doll & Lehwald 2009; Elfadl et al. 2010).

A very good correlation between the data obtained by the reference (drying) method and by a spectrophotometer in NIR is clearly seen in Figure 2. Statistical parameters of the calibration were presented in Table 1.

The correlation accuracy (BIAS) for the accurate calibration should equal 0 (Elfadl et al. 2010). The value was obtained for the spectra sets forming the calibration. The validation set was characterised by the correlation accuracy near 0. Similar accuracy results within calibration and validation sets while creating calibration for the quantitative oil determining in safflower were obtained by Efladl et al. (2010) and Ribeiro et al. (2013). While creating the calibration to determine a fatty acids content in flax seeds for the spectrophotometer NIR and MIR, the PLS analysis was also used. Depending on the used data processing they obtained a determination coefficient $R > 0.95$ acting on the basis of 38 seed spectra. Montes et al. (2013) examining the properties of Jatropha curcas achieved R in the range from 0.35 to 0.97, depending on the feature. The regression coefficients of the straights describing the experimental data (the moisture determined by the drying method) dependence on predicted by the calibration model ones are close to 1. Such values confirm the right choice of the calibration model.

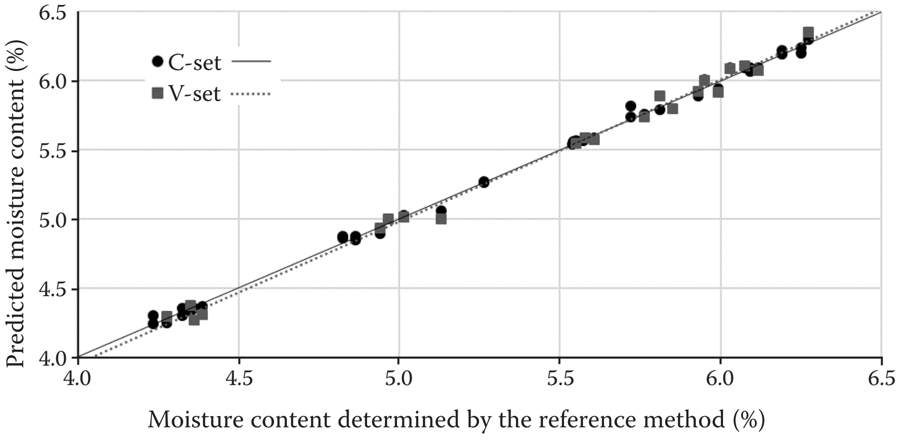

Figure 2. The seeds moisture determined by the drying method dependent on the moisture predicted by calibration

C-set: calibration data set; V-set: validation data set

https://doi.org/10.17221/57/2019-CJFS

Table 1. Selected parameters of the calibration to the quantitative analysis of the seed moisture

Parameter	C-Set	V-Set
Accuracy (BIAS)	0	0.009
Linear regression equation	$y = 0.9973x + 0.0147$	$y = 1.0261x - 0.1509$
Regression coefficient (*R*)	0.9986	0.9968
Standard deviation (SD)	0.0351	0.0567
Q-Value	0.8904	–
Calibration range	4.2 ÷ 6.2 (%)	–

C-set: calibration data set; V-set: validation data set

On that basis it can be assumed that the application created on the basis of the proposed model may be used to mark the seed moisture of the examined vegetable types.

The NIRCal software generates the verification of the selected mathematical model correctness to create the calibration. However, for comparison, an individual validation was performed and consisting of determining the moisture of new seed specimen of the 5 examined types by means of the reference method and NIR spectrophotometer. The results were presented in Table 2.

In the case of 4 out of 5 examined seed types the correlation between both methods was crucial (Table 2). It indicates a proper calibration modelling for NIR spectrophotometer. The calibration parameters calculated on the basis of the PLS method are very good. Excellent data fit to the model are confirmed by BIAS as well as the regression coefficients (Figure 2). However, it should be noted that the calibration was created on the basis of 45 spectra. In the case of the presented research the application for determining the moisture should work for 5 different species; thus such a number of spectra is an absolute minimum. Moreover, the research material was characterised by a narrow span of water content (from 4.2% to 6.2%). For the application to be a reliable method for moisture determination it is necessary to extend the calibration by measuring of spectra of seeds with higher water content.

Table 2. The comparison of the seed moisture marked by the NIR calibration and the drying method

No.	Seed type	NIR (%)	Drying method (%)	*R*
1	Carrot	5.96	6.03	0.93* ± 0.02
2	Parsley	5.65	5.58	0.81 ± 0.05
3	Lettuce	4.85	5.01	0.90* ± 0.01
4	Radish	4.28	4.22	0.95* ± 0.03
5	Beetroot	5.12	5.26	0.94* ± 0.02

NIR – near infrared spectroscopy; *R* – regression coefficient ± SD; *determination coefficient statistically crucial at $P = 0.05$

CONCLUSION

The conducted research confirmed the possibility of creating universal calibration for the selected seed species to determine moisture by means of NIR spectrophotometer. The development of the calibration for NIR spectrophotometer allows quick and precise measurement of seed moisture in real time. Moreover, the developed method allows the determination of water content of different species of seeds. It is expected that the calibration method can be expanded both in measurement range and also in the number of seed species.

REFERENCES

Baianu I., Guo J., Nelson R., You T., Costescu D. (2011): NIR calibrations for soybean seeds and soy food composition analysis: Total carbohydrates, oil, proteins and water contents. Nature Precedings: 1–40.

Bewley J.D., Black M. (1994): Seeds: Physiology of Development and Germination. 2nd Ed. Springer Science+Business Media, New York, USA: 377–420.

Bochenek A., Górecki R., Grzesiuk S. (2000): Overall biological properties of seeds. In: Duczmal K., Tucholska H. (eds): Nasiennictwo. Powszechne Wydawnictwo Rolnicze i Leśne (PWRiL), Poland: 116–170. (in Polish)

Bonner F.T., Hooda M.S., Singht D.P. (1992): Moisture determination of seeds honeylocust and mimosa. Tree Plants' Notes, 43: 72–75.

Büning-Pfaue H. (2003): Analysis of water in food by near infrared spectroscopy. Food Chemistry, 82: 107–115.

Collell C., Gou P., Anrau J., Muñoz I., Comaposada J. (2012): NIR technology for on-line determination of superficial a_w and moisture content during the drying process of fermented sausages. Food Chemistry, 135: 1750–1755.

Cornish K., Myers M.D., Kelley S.S. (2004): Latex quantification in homogenate and purified latex samples from various plant species using near infrared spectroscopy. Industrial Crops and Products, 19: 283–296.

Csorba V., Fodor M., Kovács S., Tóth M. (2019): Potential of fourier transformed near-infrared (FT-NIR) spectroscopy for rapid analysis of elderberry (*Sambucus nigra* L.) fruits. Czech Journal of Food Sciences, 37: 21–28.

Doll N., Lehwald L. (2009): Creation of a calibration for the determination of the active ingredient content of tablets by NIR-Spectroscopy. Büchi Information Bulletin, 53: 2–4.

https://doi.org/10.17221/57/2019-CJFS

Domoradzki M., Korpal W., Weiner W. (2005): Evaluation of seed size distribution on laboratory screens. Inżynieria Rolnicza, 11: 87–94.

Elfadl E., Reinbrechta C., Claupein W. (2010): Development of near infrared reflectance spectroscopy (NIRS) calibration model for estimation of oil content in a worldwide safflower germplasm collection. International Journal of Plant Production, 4: 259–270.

Fassio A., Cozzolino D. (2004): Non-destructive prediction of chemical composition in sunflower seeds by near infrared spectroscopy. Industrial Crops and Products, 20: 321–329.

Font R., del Río-Celestino M., de Haro-Bailón A. (2007): Near-infrared reflectance spectroscopy. Methodology and potential for predicting trace elements in plants. In: Wiley N. (ed.): Phytoremediation. Methods in Biotechnology. Humana Press, Totowa, USA: 23: 205–217.

Gergely S., Salgó A. (2003): Changes in moisture content during wheat maturation: What is measured by near infrared spectroscopy? Journal of Near Infrared Spectroscopy, 11: 17–26.

Gozdecka G., Gęsiński K. (2011): Characteristics of quinoa seed weight after harvest. Inżynieria i Aparatura Chemiczna, 3: 27–28. (in Polish)

Hart J. R., Norris K. H., Golumbic C. (1962): Determination of the moisture content of seeds by near-infrared spectrophotometry of their methanol extracts. Cereal Chemistry, 39: 94–99.

Huang Z., Sha S., Rong Z., Chen J., He Q., Khan D.M., Zhu S. (2013): Feasibility study of near infrared spectroscopy with variable selection for non-destructive determination of quality parameters in shell-intact cottonseed. Industrial Crops and Products, 43: 654–660.

ISTA (International Seed Testing Association) (2006): International Rules for Seed Testing – Polish Edition. IHAR – PIB, i: 5–56.

Jin S., Chen H. (2007): Near-infrared analysis of chemical composition of rice straw. Industrial Crops and Products, 26: 207–211.

Kaleta A., Górnicki K. (2008): Safe grain storage – The study of the issue. Inżynieria Rolnicza, 1: 137–144. (in Polish)

Kaniewska J., Żórawski D., Domoradzki M. (2013): Resistance of air flow through the bed of carrot seeds in the vibrating drier. Inżynieria Rolnicza, 3: 113–122. (in Polish)

Lazzari F.A. (1994): Comparison of methods for moisture content determination on soybeans. Proceedings of the 6th International Working Conference on Stored-product Protection, Canberra, Australia. 17–23 April 1994, 2: 701–703.

Lestander T. A., Geladi P. (2003): NIR spectroscopic measurement of moisture content in Scots pine seeds. Analyst, 128: 389–396.

Makarski P. (2008): Using virtual instruments in seeds humidity measurements. Inżynieria Rolnicza, 11: 179–184. (in Polish)

Montes J.M., Technow F., Bohlinger B., Becker K. (2013): Grain quality determination by means of near infrared spectroscopy in *Jatropha curcas* L. Industrial Crops and Products, 43: 301–305.

Nicolaï B.M., Beullens K., Bobelyn E., Peirs A., Saeys W., Theron K.I., Lammertynet J. (2007): Nondestructive measurement of fruit and vegetable quality by means of NIR spectroscopy: A review. Postharvest Biology and Technology, 46: 99–118.

Norris K.H., Hart J.R. (1965): Direct spectrophotometric determination of moisture content of grain and seeds. In: Principles and Methods of Measuring Moisture in Liquids and Solids, Reinhold, New York, 4: 19–25.

Osborne B.G., Hindle P.T., Fearn T. (1993): Practical NIR spectroscopy with applications in food and beverage analysis. 2nd Ed. Harlow UK Addison-Wesley Longman Ltd., Harlow, United Kingdom: 190–193.

Plans M., Simó J., Casañas F., Sabaté J., Rodriguez-Saona L. (2013): Characterization of common beans (*Phaseolus vulgaris* L.) by infrared spectroscopy: Comparison of MIR, FT-NIR and dispersive NIR using portable and benchtop instruments. Food Research International, 54: 1643–1651.

Rahman A., Cho B.K. (2016): Assessment of seed quality using non-destructive measurement techniques: A review. Seed Science Research, 26: 285–305.

Ribeiro L.F., Peralta-Zamora P.G., Maia B.H.L.N.S., Ramos L.P., Pereira-Netto A.B. (2012): Prediction of linolenic and linoleic fatty acids content in flax seeds and flax seeds flours through the use of infrared reflectance spectroscopy and multivariate calibration. Food Research International, 51: 848–854.

Robertson J. A., Barton F. E. (1984): Oil and water analysis of sunflower seed by near-infrared reflectance spectroscopy. Journal of the American Oil Chemists' Society, 61: 543–547.

Siger A., Świecki K., Czubiński J. (2010): On-line analytical techniques in the food production proces. Przemysł Spożywczy, 2: 12–18. (in Polish)

Sinelli N., Casiraghi E., Barzaghi S., Brambilla A., Giovanelli G. (2011): Near infrared (NIR) spectroscopy as a tool for monitoring blueberry osmo-air dehydratation process. Food Research International, 44: 1427–1433.

Stanimirova I., Daszkowski M., Walczak B. (2008): Supervised learning methods – calibration, discrimination and classification. In: Zuba D., Parczewski A. (eds): Chemometry in Analytics. Selected Issues. IES, Kraków, Poland: 1–60. (in Polish)

Sivritepe N., Sivritepe H.Ö., Türkben C. (2008): Determination of moisture content in grape seeds. Seed Science and Technology, 36: 198–200.

Strelec I., Popović R., Ivanišić I., Jurković V., Jurković Z., Ugarčić-Hardi Ž., Sabo M. (2010): Influence of temperature

https://doi.org/10.17221/57/2019-CJFS

and relative humidity on grain moisture, germination and vigour of three wheat cultivars during one year storage. Poljoprivreda, 16: 20–24.

Taylor A.G. (1997): Seed storage, germination and quality. In: Wien H.C. (ed.): The Physiology of Vegetable Crops. CAB International, United Kingdom: 1–36.

Tomkiewicz D. (2009): Construction and operation of corn seed humidity sensor using near-infrared radiation. Inżynieria Rolnicza, 6: 309–314. (in Polish)

Received: March 19, 2019
Accepted: January 2, 2020