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Prediction of Phytochemical Constituents in Cayenne Pepper Using MIR and NIR Spectroscopy

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Abstract: The aim of the present study was to evaluate the potential of handheld near-infrared (NIR) and benchtop mid-infrared (MIR) spectroscopy for the rapid prediction of antioxidant capacity, dry matter, and total phenolic contents in cayenne pepper (*Capsicum annuum* 'Cayenne'). Using NIR spectroscopy, the best-performing model for dry matter had an R^2_{pred} = 0.74, RMSEP = 0.38%, and RPD of 2.02, exceeding the best results previously reported in the literature. This was also the first study to predict dry matter content from the mid-infrared spectra, although with lower accuracy (R^2_{pred} = 0.54; RMSEP = 0.51%, RPD 1.51). The models for antioxidant capacity and total phenolic content did not perform well using NIR or MIR spectroscopy (RPD values < 1.5), indicating that further optimization is required in this area. Application of support vector regression (SVR) generally gave poorer results compared to partial least squares regression (PLSR). NIR spectroscopy may be useful for in-field measurement of dry matter in the chili crop as a proxy measure for fruit maturity. However, the lower accuracy of MIR spectroscopy is likely to limit its use in this crop.

Keywords: FTIR spectroscopy; dry matter; antioxidant; phenolics; near-infrared (NIR) spectroscopy; NIRS; PLSR; SVR

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1. Introduction

Chilies (*Capsicum* spp.), also known as peppers, are well known for their pungent flavor and are used to season a wide variety of foods. In addition, chilies contain high levels of ascorbic acid (vitamin C), vitamin A and other micronutrients including zinc, iodine and iron [1]. More details are shown in Table 1. The principal pungent compound present—capsaicin—is an activator of the transient receptor potential ion channel of the vanilloid type (TRPV1) and hence has been investigated for treating pain and other neurological conditions [2]. In addition, the capsaicinoids, phenolics and flavonoids found in the fruit provide antioxidant activity with further potential health benefits [3–5].

Table 1. The typical content of key beneficial nutrients found in chilies.

Parameter	Typical Content	% RDI in 1 Serve (75 g)	Reference
Total phenolic content	919–1803 mg GAE/100 g	n/a	[6]
Vitamin C	80.6 mg/100 g	67%	[1]
Niacin (Vit B3)	0.48 mg/100 g	2%	[1]
Vitamin E (α-tocopherol)	0.37 mg/100 g	2%	[1]
Vitamin B6	0.224 mg/100 g	13%	[1]
Pantothenic acid (Vit B5)	0.099 mg/100 g	1%	[1]

Table 1. *Cont.*

Parameter	Typical Content	% RDI in 1 Serve (75 g)	Reference
Thiamin (Vit B1)	0.057 mg/100 g	4%	[1]
Riboflavin (Vit B2)	0.028 mg/100 g	2%	[1]
Vitamin A	18 μg RAE/100 g	2%	[1]
Folate	10 μg/100 g	2%	[1]
Vitamin K	7.4 μg/100 g	5%	[1]

GAE = gallic acid equivalents; n/a = not applicable; RAE = retinoic acid equivalents; RDI = recommended dietary intake (calculated for an adult male).

In 2014, the worldwide production of chili pepper (*Capsicum annuum*) was estimated at 409,000 tons, with the majority grown in Asian countries [1]. In Australia, the chili industry is a relatively minor player, with around 2500 tons produced in the 2013–2014 season [7]. However, the industry is worth over $21 million p.a. (2013–2014 figures) and is rapidly expanding [7]. Farmgate prices average approximately $9.50 per kg, with a 244% increase in value over the preceding five years [7]. Research and development efforts continue in the Australian chili sector, with interest in improving yield, developing high-capsaicin varieties, and developing new processing methods.

In this study, we investigate the potential use of rapidly assessing quality parameters associated with chili fruit—specifically dry matter and total phenolic content—in the Australian Cayenne pepper crop. Dry matter (DM) content is often linked to maturity and eating quality across many crops [8,9] and has also been used as an index of fruit maturity in chilies [10]. Indeed, Niklis et al. [11] and Kasampalis et al. [12] found that the DM content of *C. annuum* consistently increased during maturation, although the exact trends were dependent on the variety. Hence if calibrated for a specific chili variety, the rapid estimation of DM content could be used to inform optimum harvest times.

As previously mentioned, the phenolic content and antioxidant capacity of chilies are also of interest due to the potential health benefits associated with these compounds [13,14]. Rapid estimation of phenolic content in chilies could be used for grading fruit quality or finding applications in breeding programs attempting to develop high phenolic content chili varieties.

Near-infrared (NIR) and mid-infrared (MIR) spectroscopy have been used for the assessment of a wide range of quality parameters in dried chili powder [15–19], principally the capsaicinoid content. The main difference between these two instrument types is the wavelength used: NIR operates between wavelengths of 750–2500 nm, while MIR spectroscopy uses wavelengths of 2500–25,000 nm (4000–400 cm^{-1}). NIR spectroscopy has benefits, including cheaper cost, portability, and greater penetration depth into the sample—but at the expense of lower resolution and sensitivity for chemical moieties. A number of studies have used NIR spectroscopy for the prediction of dry matter and soluble solids [20,21], as well as vitamin C, total chlorophyll, and/or carotenoid contents in fresh fruit [10,12,20,22]. These studies have highlighted the benefits of rapid NIR spectroscopy as an in situ preliminary screening technique but noted that further work is required to develop robust models which can be applied to external populations.

The prediction of antioxidant capacity appears to have only been considered by one previous author [23], and there are very few studies outside of our laboratory attempting the prediction of total phenolic content [6,12]. In addition, many of these studies have been performed on bell peppers rather than cayenne peppers, which are more widely grown in Australia. Hence the aim of this study was to compare the use of NIR and MIR spectroscopy for the analysis of cayenne pepper (*Capsicum annuum* 'Cayenne') quality, including the prediction of DM content, total phenolic content, and antioxidant capacity.

2. Materials and Methods

2.1. Chilli Samples

One hundred samples (individual chilies) of green cayenne pepper ("Blade" variety) were provided by Austchili (Bundaberg, Queensland), the largest supplier of fresh chili in Australia. These were hand-selected from plants across two field sites to ensure that a wide range of environmental variability was incorporated into the samples chosen. The majority of samples selected were at the mature stage, and all were a uniform dark green color. Across all of the samples, the average length was 117 ± 7 mm (range 92–133 mm), while the average fresh weight was 12.4 ± 1.9 g (range 7.5–16.2 g). The dry matter ranged from 8.4–12.6% *w*/*w* (mean of 10.5 ± 0.9% *w*/*w*).

The samples were shipped to the laboratory overnight on ice before the NIR spectra were collected and the samples subsequently dried. The MIR spectra were collected after the drying process.

2.2. Collection of NIR Spectra

Near-infrared (NIR) spectra were collected from the samples using a MicroNIR OnSite handheld spectrometer (Viavi; Santa Rosa, CA, USA), operating between 908–1676 nm (6 nm resolution). This instrument uses a linear variable filter as the dispersing element coupled to a linear detector array (128-pixel uncooled InGaAs photodiode array) [24]. The spectra integration time of the instrument was set to 100 ms.

Two spectra were collected from two opposing sides of each individual chili, for a total of four spectra per chili sample (n = 400 spectra in total). In order to ensure consistency in the spectral acquisition location and minimize the prospect of background interference, chili samples were laid on a ceramic plate, and all spectra were collected approximately 3 cm down from the stem of the chili. In addition, reference black and white spectra were obtained to calibrate the instrument for every 10 samples. Spectra were exported in ASCII (*.csv) format.

2.3. Dry Matter Content and Total Phenolic Content

Following the collection of the NIR spectra, the dry matter content of the chili samples was determined gravimetrically by drying the whole chilies (approx. 5–10 g) in a forced air oven (Sunbean Food Lab Dehydrator) at 50 °C until reaching a constant mass. The DM content was expressed on a % fresh weight basis.

The dried chili samples were subsequently ground using a Retsch ZM1000 centrifugal grinding mill (Sydney, Australia) with a 1.0 mm mesh size. Polar phenolic compounds were extracted from this dried powder using 90% methanol, following previously described protocols [25]. The total phenolic content (TPC) and antioxidant activity—measured as ferric-reducing antioxidant power (FRAP) and cupric-reducing antioxidant capacity (CUPRAC)—of the extracts were determined as previously reported [26], with the results expressed in terms of gallic acid equivalents (GAE) per 100 g and Trolox equivalents (TE) per 100 g, respectively. All three (TPC, FRAP, and CUPRAC) were expressed on a dry weight basis.

2.4. Collection of MIR Spectra

Mid-infrared spectra were collected from the dried, ground chili powder using a Bruker Alpha Fourier transform infrared (FTIR) spectrophotometer (Ettlingen, Germany). A single-reflection diamond crystal attenuated total reflectance (ATR) module was used to ensure firm contact between the sample and the infrared beam. The spectra were recorded between 4000–400 cm^{-1} in triplicate for each sample (n = 300 spectra), with each spectra being the average of 24 scans at 4 cm^{-1} resolution. Spectra were exported in Opus (*.0) format.

2.5. Data Processing and Analysis

Chemometric analysis of the NIR and MIR spectra was conducted using the Unscrambler X software (Camo Analytics; Oslo, Norway). Figures were drawn in the Unscrambler X and in R Studio running R 4.0.2 [27].

For the development of the predictive chemometric models, the data set was split into a calibration set and a validation set, comprising 80% and 20% of the sample set, respectively. Two regression methods were trialed—partial least squares regression (PLS-R) and support vector regression (SVR). PLS-R is a linear quantitative modeling algorithm that has been extensively used in spectral analysis and particularly in the infrared wavelength range (NIR and MIR). It is always used to avoid multiple collinearities by reducing a large number of independent variables into a new set of unrelated variables called latent variables (LVs). In our case, the X matrix containing the MIR and NIR spectra was used to build the PLS2 models. The response matrix Y contains four variables to be predicted, namely DM, TPC, FRAP, and CUPRAC. The number of latent variables chosen in this study is based on cross-validation using the leave-one-out cross-validation procedure [28]. Support vector analysis (SVR) is oriented from SVM (support vector machine). This method is very interesting because it can solve practical problems such as a small sample, nonlinearity, and high dimension. In this study, the SVM method was applied using linear kernel algorithms applied using nu-SVM.

Before calculating regression models, the NIR and MIR spectra were subjected to different methods of pre-processing, including standard normal variate (SNV), multiplicate scatter correction (MSC), and the 1st and 2nd derivatives using a Savitzky-Golay algorithm (10 pts/side). Both SNV and MSC are generally applied to spectral data to decrease the influence of light scattering and the baseline shift. The purpose of the derivatives was to reduce the influence of random noise, highlight the subtle frequency band shape, maintain relative frequency band intensity information, and improve the resolution of overlapping frequency bands (Jie et al. [29]). The Savitzky-Golay derivative uses a smoothing procedure that is useful to decrease random noise and increase the signal-to-noise ratio.

The accuracy of the models was evaluated by root mean square error of prediction (RMSEP), cross-validation (RMSECV), calibration (RMSEC), determination coefficients calibration (R^2_{cal}), cross-validation (R^2_{CV}) and prediction (R^2_{pred}) and the ratio of prediction to deviation (RPD). RPD was calculated by dividing the standard deviation of the sample set by the RMSEP. Nicolaï et al. [30] considered that an RPD of 3 indicated an excellent model; between 2.5–3 indicated a good model; between 2–2.5 indicated that coarse quantitative predictions are possible; while an RPD of 1.5–2 suggested that the model could discriminate between low and high values of the analyte.

3. Results

3.1. Dry Matter, TPC, and FRAP Content

The mean, SD (standard deviation), minimum, maximum, and CV (coefficient of variation) of the DM, TPC, FRAP, and CUPRAC of the pepper fruit are presented in Table 2. As shown in Table 2, the DM content of the chili samples ranged from 8.39–12.64%, with a mean DM content of 10.52%. As shown by the CV of 4.8%, the range of DM contents was not as wide as that reported by previous researchers [20,21]; however, it represented the typical range of DM content found in pepper fruits around the point of harvest [11].

The TPC ranged from 898–2617 mg GAE/100 g, a slightly larger range than that obtained by Toledo-Martín et al. [6] (919–1803 mg GAE/100 g), with a much higher CV (20.5%). The FRAP and CUPRAC showed a similarly wide variation, with CVs of 23.7 and 19.8%, respectively. The mean FRAP (296 mg TE/100 g) was slightly higher than that previously found in green pepper pulp by Sora et al. [31] (107 mg TE/100 g), although lower than the value of ~425 mg TE/100 g found by Qiao et al. [32]. The mean CUPRAC (1917 mg TE/100 g) was also higher than the range of CUPRAC values (882–1280 mg TE/100 g) found by Parnea et al. [33] in a range of pepper varieties.

Table 2. Range, mean standard deviation, and coefficient of variation for the DM, TP, FRAP, and CUPRAC datasets.

	DM Content (%)	TPC (mg GAE/100 g)	FRAP (mg TE/100 g)	CUPRAC (mg TE/100 g)
Minimum	8.39	898	168	1256
Maximum	12.64	2617	615	3138
Mean	10.52	1300	296	1917
SD	0.86	267	70	379
CV (%)	4.82	20.54	23.65	19.77

SD = Standard deviation; CV = coefficient of variation.

3.2. NIR and MIR Spectra

Figure 1 shows the unprocessed NIR spectra of the chili samples. Peaks were located at approximately 1450, 1190, and 970 nm, similar to that reported by Penchaiya et al. [20]. These absorption bands can be attributed primarily to the OH 1st overtone, CH 2nd overtone stretch, and OH 2nd overtone, respectively [34,35].

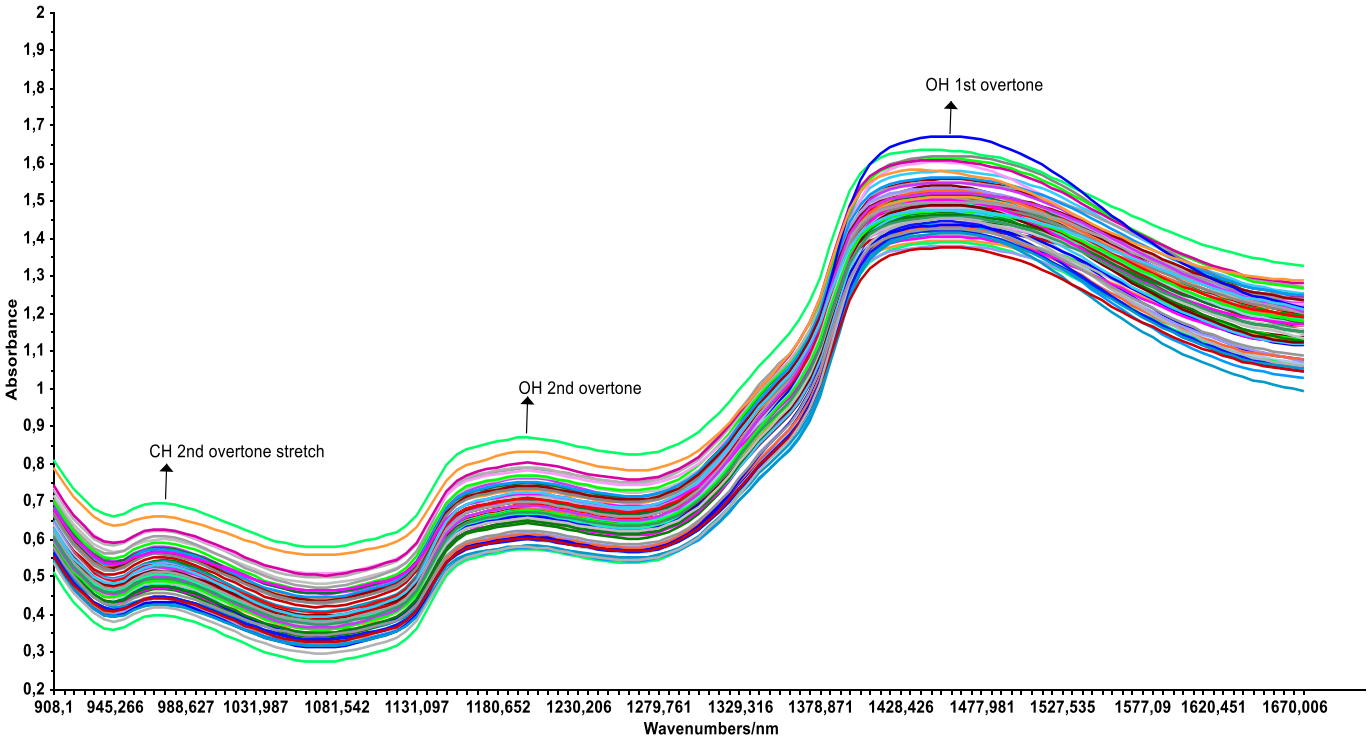


Figure 1. The NIR spectra of the chili samples, between 908–1676 nm were obtained using the handheld microNIR probe.

The MIR spectra of the dried chili powder showed a greater number of peaks (Figure 2), with major peaks corresponding to OH from moisture (approx. 3300 cm^{-1}), CH_3, and CH_2 groups such as those found in fatty acids (3000–2800 cm^{-1}), C=O (1750 cm^{-1}), amide and cellulose groups (1000 cm^{-1}) [36,37].

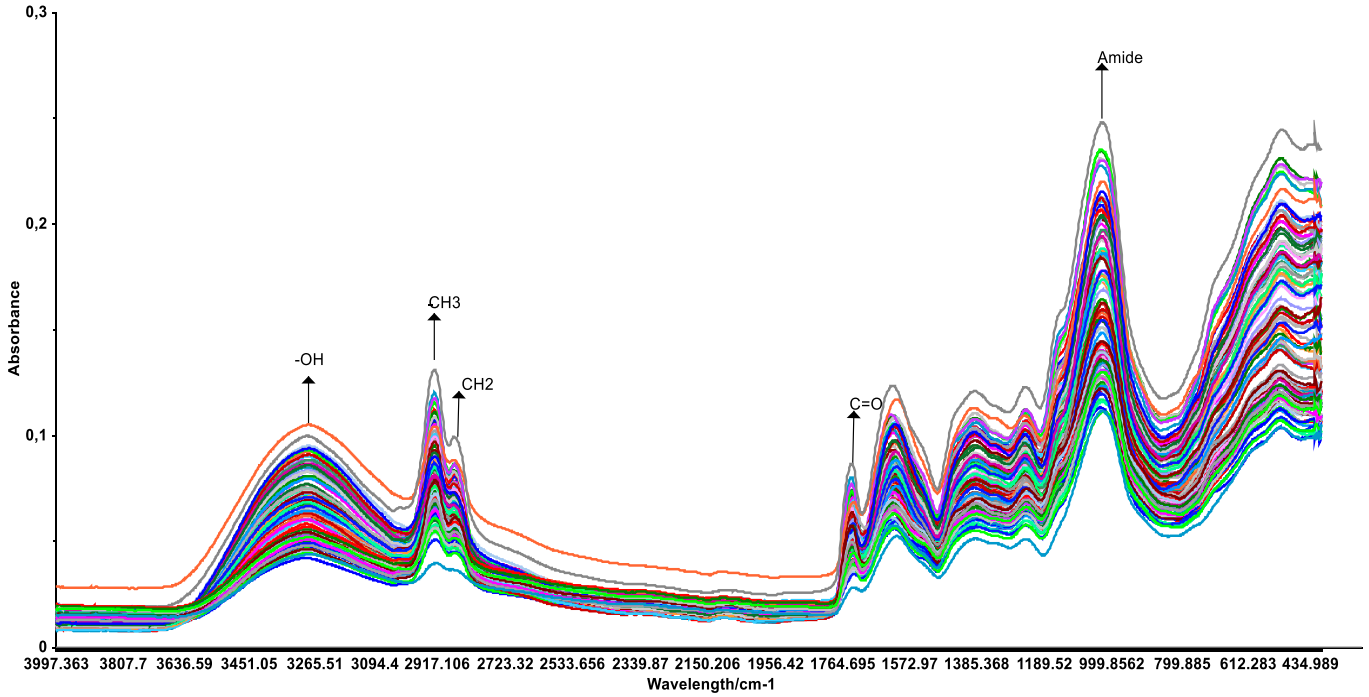


Figure 2. The MIR spectra of the chili samples are between 4000–400 cm^{-1}.

3.3. Prediction of DM, TPC, FRAP, and CUPRAC Using NIR Spectroscopy

Table 3 summarizes the results obtained for the prediction of the four parameters of interest using NIR spectroscopy combined with PLS-R or SVR. As can be seen in this table, the pre-processing methods used had a significant impact on the quality of the PLS-R and SVR models.

Using the PLSR algorithm, NIR spectroscopy showed good results for the prediction of dry matter content, with most of the R^2 values ranging between 0.67–0.79 and 0.27–0.74 (0.60–0.74 excluding the SG1 pre-processing) respectively for the calibration and prediction datasets, respectively. The relative error obtained varied between 0.40–0.51% and 0.38–0.48% for calibration and validation, respectively. The pre-processing method had a strong influence on the model quality, with the best model constructed using no pre-processing. In contrast, quite poor results were found using PLS regression for the prediction of TPC, FRAP, and CUPRAC contents, with RPD values <1.5 for all of these analytes.

On the other hand, the application of the SVR algorithm showed satisfactory results for the prediction of the four analytes of interest. The best predictive results for TPC exhibited an R^2_{pred} of 0.65 and an RMSEP of 464 mg/100 g, using the first derivative Savitsky-Golay pre-processing. For FRAP, the best model presented an R^2_{pred} of 0.71 and an RMSEP of 70 mg/100 g. For CUPRAC, the best predictive model gave an R^2_{pred} of 0.73 and RMSEP of 512 mg/100 g, while the best model for DM showed an R^2_{pred} of 0.96 and RMSEP of 0.63% (Figure 3). Those models were calculated after applying the second derivative with the Savitsky-Golay algorithm to the spectral data (Table 3).

As has been noted for PLSR, the application of spectral pre-processing had a significant effect on the prediction results obtained by SVR. Furthermore, the optimal pre-processing method differed depending on the targeted analyte.

Table 3. Statistical parameters were obtained from the application of the PLSR and SVR algorithms on the NIR spectra dataset using different pre-processing methods.

Pre-Processing	Analyte	LVs (PLS)	R^2_{cal}		RMSEC		R^2_{pred}		RMSEP		RPD	
			PLS	SVR	PLS	SVR	PLS	SVR	PLS	SVR	PLS	SVR
None	DM	16	0.79	0.26	0.403	0.77	0.74	0.00	0.384	0.748	2.020	1.037
	TPC	14	0.33	0.17	134.704	150.012	0.00	0.00	466.55	478.457	0.974	0.950
	FRAP	9	0.47	0.44	47.095	48.219	0.00	0.58	65.669	68.365	0.825	0.793
	CUPRAC	12	0.51	0.3	227.701	272.766	0.11	0.00	397.912	408.715	1.088	1.059
SG1	DM	16	0.67	0.84	0.506	0.356	0.27	0.00	0.646	0.407	1.200	1.905
	TPC	16	0.57	0.53	107.029	116.674	0.00	0.65	451.12	463.816	1.008	0.980
	FRAP	7	0.48	0.58	46.485	41.599	0.00	0.62	66.396	72.911	0.816	0.743
	CUPRAC	8	0.52	0.64	225.74	196.814	0.1	0.00	410.437	421.314	1.055	1.028
SG2	DM	14	0.74	0.96	0.451	0.178	0.70	0.53	0.411	0.737	1.887	1.052
	TPC	14	0.33	0.85	133.998	64.145	0.00	0.00	458.849	498.795	0.991	0.911
	FRAP	14	0.54	0.78	43.612	30.317	0.00	0.18	69.897	109.985	0.775	0.493
	CUPRAC	16	0.55	0.94	217.4	81.961	0.16	0.73	387.086	512.456	1.118	0.845
SNV	DM	14	0.74	0.57	0.45	0.592	0.60	0.00	0.477	0.695	1.626	1.116
	TPC	13	0.33	0.29	134.351	142.789	0.00	0.00	463.32	483.741	0.981	0.940
	FRAP	12	0.52	0.46	44.619	47.303	0.00	0.00	66.706	68.768	1.064	1.065
	CUPRAC	11	0.51	0.42	227.34	247.69	0.1	0.68	406.903	406.541	0.812	0.133
SNV Detrend 1	DM	13	0.73	0.65	0.453	0.548	0.68	0.86	0.428	0.618	1.812	1.255
	TPC	12	0.31	0.27	136.107	141.195	0.00	0.00	467.973	480.962	0.971	0.945
	FRAP	12	0.53	0.5	44.401	37.4	0.00	0.19	68.356	137.117	0.793	0.395
	CUPRAC	11	0.51	0.45	226.828	241.311	0.1	0.00	403.157	398.094	1.074	1.087
SNV Detrend 2	DM	15	0.77	0.56	0.42	0.606	0.65	0.96	0.449	0.627	1.727	1.237
	TPC	11	0.35	0.28	131.832	142.285	0.00	0.00	456.291	478.666	0.996	0.950
	FRAP	10	0.52	0.47	44.591	46.796	0.00	0.71	66.036	69.674	0.821	0.778
	CUPRAC	5	0.44	0.41	48.316	250.391	0.1	0.00	410.62	401.767	1.054	1.078
MSC	DM	14	0.76	0.58	0.433	0.586	0.69	0.92	0.421	0.603	1.842	1.286
	TPC	10	0.31	0.26	136.506	142.963	0.00	0.00	466.013	478.457	0.975	0.950
	FRAP	11	0.51	0.46	45.229	47.476	0.00	0.59	66.642	71.41	0.813	0.759
	CUPRAC	11	0.52	0.4	226.31	251.503	0.1	0.00	403.342	400.865	1.073	1.080

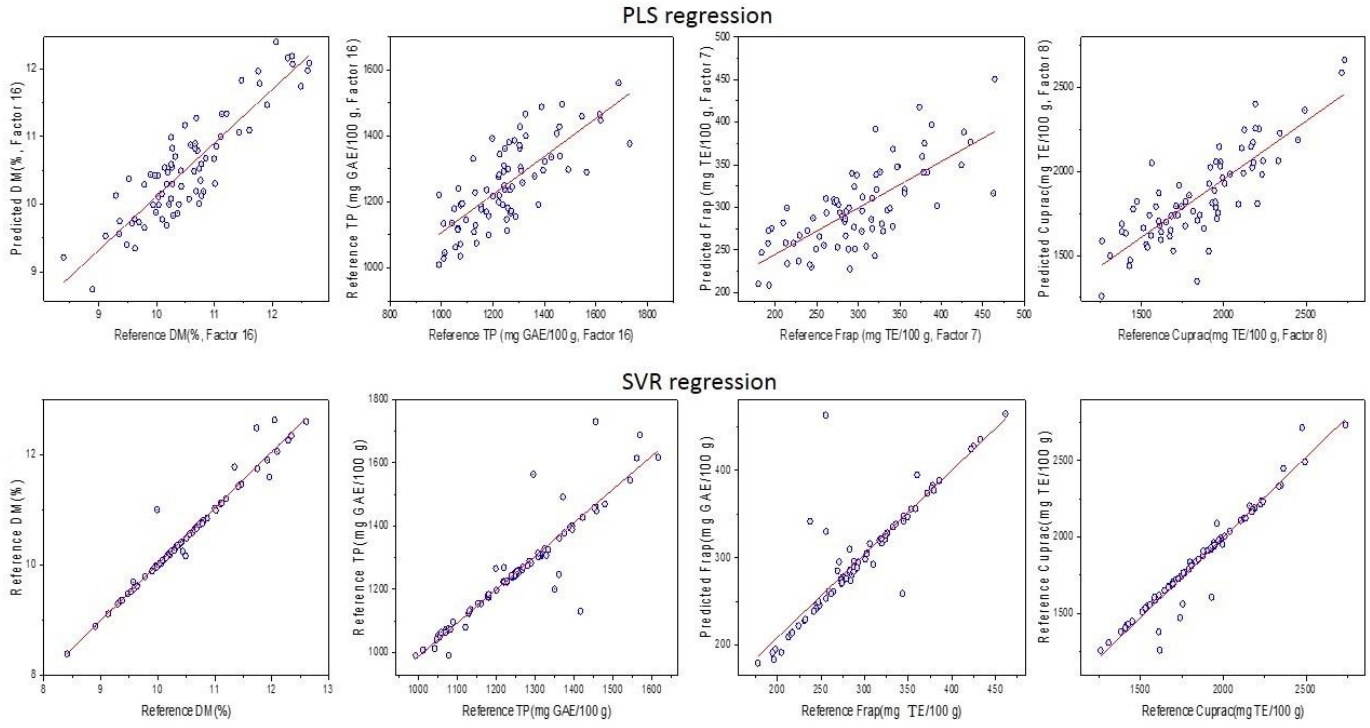


Figure 3. Predicted vs. reference results for the application of NIR spectroscopy for the prediction of dry matter, TPC, FRAP, and CUPRAC contents.

3.4. Prediction of DM, TPC, FRAP, and CUPRAC Using MIR Spectroscopy

The investigation of the MIR spectral data by PLS regression revealed good calibration results for the four parameters of interest but poor predictive ability when applied to the validation dataset (Figure 4; Table 4). The best-performing model was for DM content, with an R^2_{pred} of 0.54, RMSEP of 0.51%, and RPD of 1.51. The other models showed R^2_{pred} of $\leq$0.2 and RPD values below 1.5. Again, the pre-processing method had a moderate impact on model accuracy.

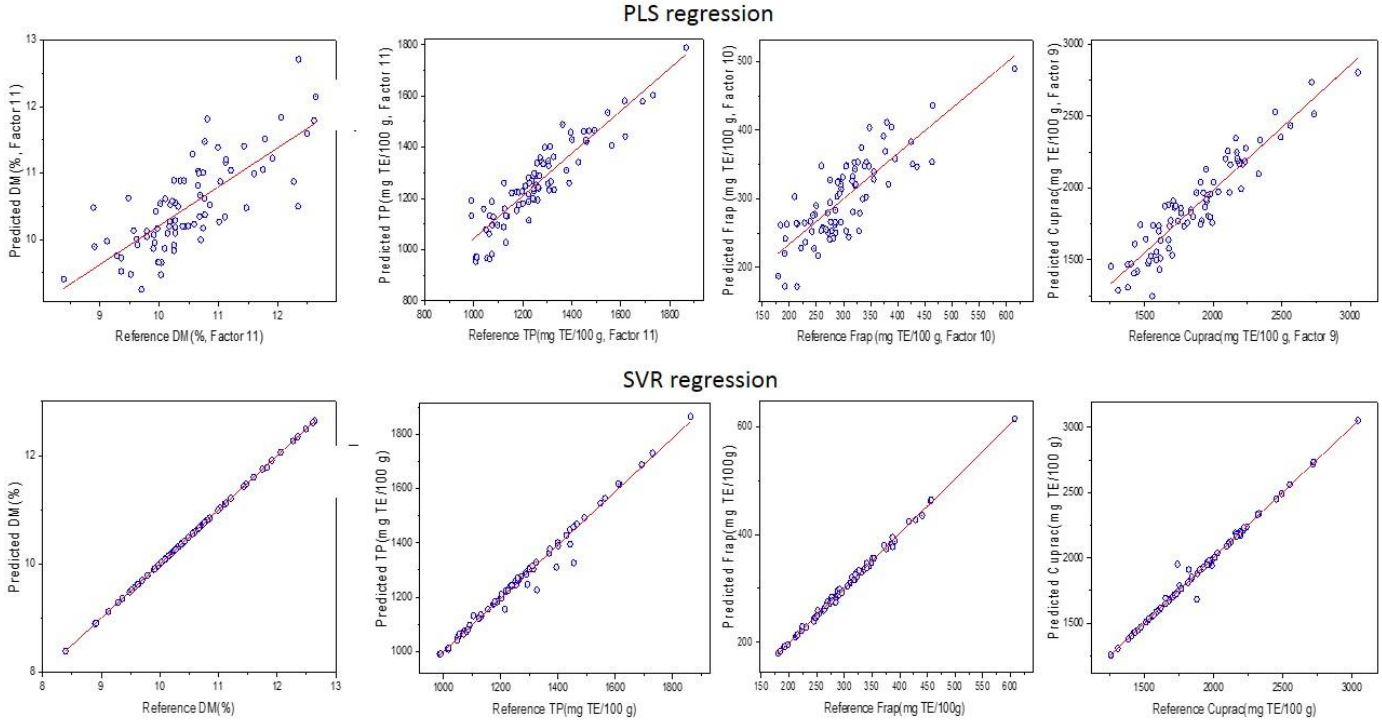


Figure 4. Predicted vs. reference results for the application of MIR spectroscopy for the prediction of dry matter, TPC, FRAP, and CUPRAC contents.

Table 4. Statistical parameters were obtained from the application of the PLSR and SVR algorithms on the MIR spectra dataset using different pre-processing methods.

Pre-Processing	Analyte	LVs (PLS)	R^2_{cal}		RMSEC		R^2_{pred}		RMSEP		RPD	
			PLS	SVR	PLS	SVR	PLS	SVR	PLS	SVR	PLS	SVR
None	DM	12	0.51	0.56	0.613	0.863	0.54	0.08	0.513	1.232	1.512	0.629
	TPC	12	0.58	0.84	113.289	75.956	0.00	0.77	482.832	499.78	0.942	0.910
	FRAP	12	0.65	0.89	42.962	26.14	0.00	0.17	128.45	180.553	0.422	0.300
	CUPRAC	12	0.88	0.84	120.36	148.391	0.00	0.37	519.759	618.733	0.833	0.700
SG1	DM	12	0.52	0.99	0.613	16.043	0.40	0.84	0.585	0.815	1.326	0.952
	TPC	12	0.71	0.99	93.607	3.431	0.00	0.80	471.339	533.946	0.964	0.851
	FRAP	12	0.59	0.99	46.706	9.691	0.00	0.68	65.721	70.712	0.824	0.766
	CUPRAC	12	0.82	0.99	116.077	0.006	0.00	0.79	491.5	671.999	0.881	0.644
SG2	DM	11	0.58	0.99	0.569	0.001	0.38	0.67	0.595	1.048	1.303	0.740
	TPC	11	0.83	0.99	72.582	0.204	0.00	0.79	474.649	483.197	0.958	0.941
	FRAP	10	0.66	0.99	42.248	0.078	0.20	0.96	46.323	95.737	1.170	0.566
	CUPRAC	4	0.87	0.99	126.191	0.372	0.10	0.99	404.672	477.769	1.070	0.906
SNV	DM	3	0.49	0.99	0.631	0.102	0.32	0.88	0.624	0.685	1.243	1.132
	TPC	14	0.86	0.98	66.217	23.542	0.01	0.86	440.574	433.142	1.032	1.050
	FRAP	9	0.43	0.99	54.637	4.162	0.00	0.57	56.479	77.343	0.959	0.701
	CUPRAC	5	0.57	0.99	232.55	35.394	0.10	0.52	405.221	505.185	1.068	0.857
SNV Detrend 1	DM	12	0.5	0.98	0.623	0.126	0.30	0.87	0.633	0.742	1.225	1.045
	TPC	15	0.86	0.98	65.913	42.887	0.02	0.85	438.021	458.281	1.038	0.992
	FRAP	3	0.17	0.99	70.496	8.293	0.00	0.59	54.036	82.396	1.003	0.658
	CUPRAC	5	0.55	0.98	241.938	44.334	0.10	0.50	401.332	503.293	1.079	0.860

Table 4. *Cont.*

Pre-Processing	Analyte	LVs (PLS)	R^2_{cal}		RMSEC		R^2_{pred}		RMSEP		RPD	
			PLS	SVR	PLS	SVR	PLS	SVR	PLS	SVR	PLS	SVR
SNV Detrend 2	DM	12	0.49	0.98	0.629	0.127	0.29	0.87	0.635	0.718	1.221	1.080
	TPC	15	0.88	0.99	61.821	18.8	0.04	0.86	435.235	446.348	1.044	1.018
	FRAP	6	0.25	0.99	62.869	6.942	0.00	0.66	55.665	70.199	0.973	0.772
	CUPRAC	5	0.57	0.98	233.641	48.374	0.10	0.88	406.149	522.235	1.066	0.829
MSC	DM	12	0.52	0.99	0.613	0.062	0.37	0.88	0.601	0.664	1.290	1.168
	TPC	14	0.85	0.99	85.685	13.029	0.00	0.85	449.565	446.884	1.011	1.017
	FRAP	6	0.25	0.99	63.098	4.671	0.00	0.58	54.328	76.234	0.997	0.711
	CUPRAC	5	0.57	0.97	233.596	63.031	0.10	0.42	407.824	504.007	1.062	0.859

The use of the SVR method showed strong potential for the estimation of the four parameters of interest, as shown by the high R^2 values ranging from 0.86 to 0.99 for both calibration and validation. The best prediction for CUPRAC and FRAP was obtained by applying the second derivative Savitzky-Golay pre-processing method, with an R^2_{pred} of 0.99 and 0.96 and RMSEP of 478 and 96 mg/100 g, respectively. For TPC and DM, the best prediction results were obtained using SNV and MSC pre-processing, respectively. The R^2_{pred} was >0.86 for both analytes, with an RMSEP of 433 mg TE/100 g and 0.66%, respectively.

3.5. Prediction of DM, TPC, FRAP, and CUPRAC Contents Using Data Fusion of NIR and MIR Spectroscopy

Finally, data fusion of MIR and NIR spectra was investigated for the prediction of the four parameters of interest (Figure 5). The application of PLS regression showed a good ability for the prediction of DM, with an R^2_{pred} of 0.66 and RMSEP of just 0.47% (Table 5). This was found using no pre-processing, similar to the results previously observed for both the NIR and MIR models for this analyte. For the other parameters, the application of PLS regression did not allow the prediction of TPC, FRAP, and CUPRAC with suitable accuracy (RPD < 1.5 for all).

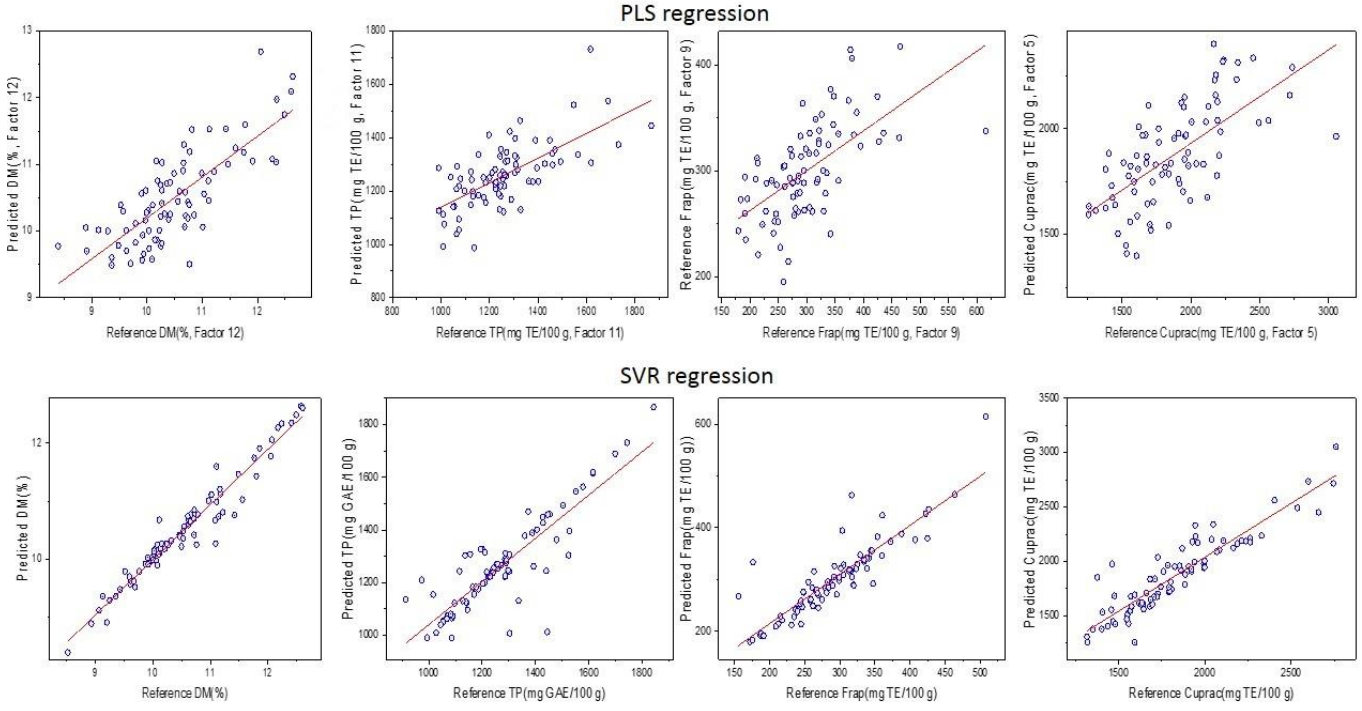


Figure 5. Predicted vs. reference results for the fusion of NIR and MIR spectroscopy datasets for the prediction of dry matter, TPC, FRAP, and CUPRAC contents.

Table 5. Statistical parameters were obtained from the application of the PLSR and SVR algorithms on the combined NIR and MIR spectra datasets, using different pre-processing methods.

Pre-Processing	Analyte	LVs (PLS)	R^2_{cal}		RMSEC		R^2_{pred}		RMSEP		RPD	
			PLS	SVR	PLS	SVR	PLS	SVR	PLS	SVR	PLS	SVR
None	DM	16	0.69	0.93	0.492	0.245	0.60	0.12	0.467	0.734	1.661	1.057
	TPC	9	0.38	0.8	138.715	89.122	0.00	0.00	444.826	504.43	1.022	0.901
	FRAP	8	0.46	0.72	53.613	48.173	0.00	0.10	72.669	155	0.746	0.350
	CUPRAC	4	0.44	0.94	264.692	93.514	0.20	0.10	377.131	463.964	1.148	0.933
SG1	DM	12	0.63	0.99	0.54	0.005	0.40	0.46	0.58	0.806	1.337	0.962
	TPC	10	0.38	0.99	138.302	0.638	0.02	0.00	442.631	519.086	1.027	0.876
	FRAP	11	0.45	0.99	53.811	3.966	0.00	0.02	68.738	71.269	0.788	0.760
	CUPRAC	2	0.49	0.99	253.393	9.41	0.10	0.35	378.035	576.296	1.145	0.751
SG2	DM	12	0.61	0.98	0.549	0.138	0.49	0.22	0.539	0.96	1.439	0.808
	TPC	11	0.46	0.98	128.641	23.998	0.03	0.00	437.273	482.028	1.040	0.943
	FRAP	9	0.38	0.96	216.228	14.408	0.00	0.10	65.005	79.026	0.834	0.686
	CUPRAC	5	0.63	0.94	0.576	85.739	0.10	0.51	400.408	517.878	1.081	0.836
SNV	DM	11	0.57	0.82	131.945	0.467	0.48	0.23	0.546	1.173	1.420	0.661
	TPC	10	0.44	0.57	60.258	138.805	0.02	0.00	437.747	451.948	1.038	1.006
	FRAP	7	0.31	0.77	202.685	36.318	0.00	0.77	69.791	67.445	0.776	0.803
	CUPRAC	10	0.67	0.84	0.521	147.952	0.10	0.55	404.968	466.772	1.069	0.927
SNV Detrend 1	DM	12	0.65	0.92	132.309	0.267	0.55	0.27	0.505	0.949	1.536	0.817
	TPC	10	0.43	0.74	46.033	95.437	0.03	0.69	436.035	424.868	1.043	1.070
	FRAP	14	0.6	0.86	204.903	29.065	0.00	0.35	68.737	73.335	0.788	0.739
	CUPRAC	10	0.67	0.84	0.514	164.865	0.10	0.14	406.269	379.48	1.141	1.066
SNV Detrend 2	DM	12	0.66	0.94	131.038	0.215	0.61	0.36	0.471	0.835	1.646	0.929
	TPC	10	0.44	0.74	60.769	95.629	0.04	0.52	433.938	433.212	1.048	1.049
	FRAP	7	0.44	0.81	203.345	35.055	0.00	0.1	69.287	66.516	0.782	0.815
	CUPRAC	10	0.67	0.86	0.574	138.588	0.10	0.22	400.107	435.655	1.082	0.994
MSC	DM	10	0.58	0.82	132.535	0.452	0.48	0.21	0.544	1.098	1.426	0.706
	TPC	10	0.43	0.81	60.288	79.788	0.02	0.00	438.065	440.913	1.038	1.031
	FRAP	7	0.31	0.74	203.178	39.967	0.00	0.56	69.613	65.96	0.778	0.821
	CUPRAC	10	0.67	0.86	203.178	142.06	0.10	0.00	406.983	453.391	1.064	0.955

Application of SVR showed good results for all calibration models and moderately high R^2_{pred} values for the validation models, although interestingly poorer results for the prediction of DM content. Again, SNV pre-processing showed optimal results for the prediction of FRAP and CUPRAC, with R^2_{pred} of 0.77 and 0.55 and an RMSEP of 67 & 467 mg/100 g, respectively. The best model for TPC prediction gave an R^2_{pred} of 0.69 and RMSEP of 425 mg/100 g. However, the RPD values remained low for the application of SVR to the prediction set.

4. Discussion

The best-performing results for the prediction of DM content found in this study (R^2_{pred} = 0.74; RMSEP = 0.38%; RPD = 2.02) were considerably better than the corresponding cross-validation statistics reported by Sánchez et al. [21] for the prediction of DM in fresh bell pepper fruit (R^2_{CV} = 0.62; RSECV = 0.66%; RPD = 1.64). As accurate prediction results are more difficult to obtain than accurate cross-validation results (because the samples being predicted do not comprise part of the test set, the model has not encountered these spectra before), this indicates considerably better accuracy and robustness of the model. A comparison with the results of other studies is provided in Table 6.

A lower accuracy was found for the prediction of DM content using MIR spectroscopy (R^2_{pred} = 0.54; RMSEP = 0.51%; RPD = 1.51). As the MIR spectra were collected from the dried chili powder, this method could not have been predicting the DM content directly from the water in the sample. Rather, this prediction is more likely to be an indirect correlation between the water content and other matrix constituents (e.g., cellulose) that is intrinsic to the chili samples.

The best model for total phenolic content had an R^2_{pred} of 0.69, RMSEP of 425 mg/100 g, and RPD of 1.07 (using SVR on the combined NIR and MIR dataset). This was much poorer than the cross-validation results reported by Toledo-Martín et al. [6], who found a cross-validation (DW basis) for the prediction of total phenolics in 14 different pepper types.

However, Toledo-Martín et al. [6] used a high-resolution laboratory-based NIR instrument (FOSS NIRSystems; 400–2500 nm) with the spectra collected from freeze-dried chili powder. Furthermore, an external validation set was used in the present study rather than just cross-validation against the calibration samples. This likely contributes further to the lack of predictive power for TP content and highlights the challenges of detecting phenolics in fresh chilies. It is likely that high levels of moisture content could interfere with and obscure the absorption bands of this analyte. In addition, Toledo-Martín et al. [6] found minimal loading of peaks in the short-wave NIR region in their TP content model, indicating that phenolic compounds may not show strong absorption across the range of wavelengths included in this study (908–1676 nm).

Table 6. Summary of the results for the prediction of DM, TP, FRAP, and CUPRAC content in green cayenne pepper and their comparison to previous studies on other chili varieties. Note: R^2_{pred} and RMSEP values are provided where reported; R^2_{CV} and RMSECV values are provided where a test set was not analyzed.

Study	Chili Type	DM Content	TPC	FRAP	CUPRAC
NIR spectroscopy					
Present study	Green cayenne	R^2_{pred} = 0.74, RMSEP = 0.38%	R^2_{pred} = 0.65, RMSEP = 464 mg/100 g	R^2_{pred} = 0.71 RMSEP = 70 mg/100 g	R^2_{pred} = 0.73, RMSEP = 512 mg/100 g
Sánchez, et al. [21]	Bell pepper (various)	R^2_{CV} = 0.62, RMSECV = 0.66%			
Toledo-Martín, et al. [6]	Bell pepper (various)		R^2_{CV} = 0.71, RMSECV = 104 mg/100 g		
Ignat, et al. [10]	Bell pepper (various)	R^2_{CV} = 0.93, RMSECV = 0.4			
Kasampalis, et al. [12]	Bell pepper (various)	R^2_{CV} = 0.53, RMSECV = 0.63%	R^2_{CV} = 0.67, RMSECV = 44 mg/100 g		
Johnson, et al. [38]	Habanero	R^2_{CV} = 0.65, RMSECV = 0.50%	R^2_{CV} = 0.21, RMSECV = 162 mg/100 g	R^2_{CV} = 0.27, RMSECV = 38 mg/100 g	
Kusumiyati, et al. [39]	Green cayenne	R^2_{pred} = 0.85, RMSEP = 0.61%			
MIR spectroscopy					
Present study	Green cayenne	R^2_{pred} = 0.54, RMSEP = 0.51%	R^2_{pred} = 0.86, RMSEP = 433 mg TE/100 g	R^2_{pred} = 0.96, RMSEP = 96 mg/100 g	R^2_{pred} = 0.99, RMSEP = 478 mg/100 g
Johnson, et al. [38]	Habanero	R^2_{CV} = 0.28, RMSECV = 0.86%	R^2_{CV} = 0.37, RMSECV = 145 mg/100 g	R^2_{CV} = 0.40, RMSECV = 35 mg/100 g	
Domínguez-Martínez, et al. [19] [1]	Serrano		R^2_{CV} = 0.94, SEP = 0.02 mg GAE/100 g		

[1] Study was performed on the ground, freeze-dried powder.

Similarly, the best models for FRAP and CUPRAC had an RMSEP of 46 mg/100 g (RPD = 1.17) and an RMSEP of 379 mg/100 g (RPD = 1.07), respectively. This indicated that the infrared spectroscopy methods used in this study were unable to accurately discriminate between high or low levels of antioxidant capacity of chili samples. Prediction of antioxidant capacity (as measured by either of these methods) does not appear to have

been previously attempted in this crop in the literature; however, the DPPH method has been used [23]. While these authors reported some success, the results are not directly comparable to either the FRAP or CUPRAC assays.

5. Conclusions

As demonstrated in this study, the use of rapid handheld NIR instrumentation shows promise for the prediction of dry matter content in cayenne peppers. This could potentially be useful for measuring the ripeness of fruit in the field while the fruit is still on the plant. In turn, this could guide decisions on harvesting times, staffing requirements, and irrigation requirements. The model for predicting total phenolic content did not perform well, suggesting that further research in this field is required. Furthermore, the optimal spectra pre-processing strategy differed between various analytes, suggesting that it is difficult to know beforehand which pre-processing would lead to the most accurate predictive models. On the other hand, MIR spectroscopy showed limited accuracy in this crop, which is likely to limit its use—particularly as it also is confined to benchtop operation at present.

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