International Scientific Conference 20 UNITECH 26

INTERNATIONAL SCIENTIFIC CONFERENCE
19-21 November 2026
GABROVO

СПЕКТРОФОТОМЕТРИЧНИ МЕТОДИ ЗА ХАРАКТЕРИЗИРАНЕ И КЛАСИФИКАЦИЯ НА ЧЕРВЕН ПИПЕР

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SPECTROPHOTOMETRIC METHODS FOR CHARACTERIZATION AND CLASSIFICATION OF RED PAPRIKA

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Abstract
Red paprika is an important spice and natural food colorant whose commercial quality is closely related to color intensity, carotenoid composition and pigment stability. Because the major paprika pigments absorb strongly in the visible spectral region, spectrophotometric methods provide a convenient approach for rapid quality assessment. The present review summarizes the main principles used for spectrophotometric characterization of red paprika, with emphasis on extractable color, ASTA units, red and yellow carotenoid fractions and the use of UV–Vis and Vis–NIR spectra as analytical fingerprints. Particular attention is paid to the combination of spectral data with chemometric methods for classification according to geographical origin, technological treatment and authenticity. The advantages and limitations of spectrophotometric methods are also discussed in relation to chromatographic techniques.

Keywords: red paprika, Capsicum annuum, spectrophotometry, carotenoids, ASTA color, chemometrics, classification

INTRODUCTION

Paprika is a powdered spice obtained mainly from dried fruits of selected varieties of Capsicum annuum L. In addition to its flavoring role, paprika is valued for its intense red color and is widely used as a natural colorant in meat products, sauces, soups, snacks and other processed foods. Color is therefore not only a sensory characteristic but also an important commercial quality parameter. Its intensity depends on the plant genotype, maturity of the fruit, cultivation conditions, drying technology and storage history [1, 2] The characteristic color of red paprika originates mainly from carotenoid pigments. Capsanthin is usually the predominant red pigment, while capsorubin, β-carotene, zeaxanthin, β-cryptoxanthin and several other xanthophylls and carotenes contribute to the final color profile. During ripening, chlorophylls decrease and carotenoid biosynthesis becomes dominant. identified

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Print ISSN: 1313-230X, Online ISSN: 3033-1404

34 carotenoids in ripe red paprika and reported capsanthin as the largest individual fraction. This complex pigment composition explains why paprika may show similar overall redness while differing in hue, color stability and nutritional characteristics. [3]

Instrumental evaluation is preferable to visual grading because the latter is strongly affected by illumination, observer perception and sample heterogeneity. Spectrophotometry offers a relatively simple and reproducible means of measuring the optical properties of paprika extracts or powders. Classical methods quantify extractable color at selected wavelengths, whereas contemporary approaches use complete UV–Vis or visible-near infrared spectra as chemical fingerprints. These data can then be combined with multivariate statistics for classification and authentication.

EXPOSITION

Spectrophotometric characterization of red paprika

The analytical basis of UV–Vis spectrophotometry is the absorption of electromagnetic radiation by molecules containing chromophores. Carotenoids possess an extended system of conjugated double bonds that absorbs strongly in the visible region, mainly between about 400 and 550 nm. The resulting spectra contain broad, partly overlapping bands that reflect the combined contribution of the carotenoid mixture. For routine analysis, the pigments are commonly extracted with acetone, producing a colored solution suitable for absorbance measurement.

A widely accepted quality parameter is the extractable colour expressed in ASTA units. According to ISO 7541:2020, extractable colour in paprika is determined spectrophotometrically by measuring the absorbance of an acetone extract. The method is applicable to ground paprika, including sweet, hot and smoked products. In practice, higher ASTA values indicate greater extractable colour intensity and usually a higher concentration of colouring pigments. This makes the ASTA scale useful for comparing raw materials, commercial products and samples subjected to different storage conditions [4]

However, a single absorbance value cannot fully describe paprika colour because different carotenoids contribute differently to the red, orange and yellow regions. A rapid spectrophotometric method based on absorbance measurements at 472 and 508 nm has been proposed for this purpose. Using the Lambert–Beer law for multicomponent mixtures, the method estimates red and yellow isochromic carotenoid fractions, total pigment content and the ratio between the two fractions. Compared with HPLC results, the reported error was below 5%, showing that the method can provide useful compositional information without requiring chromatographic separation.[5]

The red/yellow pigment ratio can be particularly informative. Mature fruits contain larger proportions of red keto-carotenoids such as capsanthin and capsorubin, whereas yellow and orange carotenoids contribute more strongly at earlier stages of maturation. Consequently, spectral changes can reflect fruit maturity and subsequent pigment degradation. Nevertheless, the interpretation should be cautious because processing can alter carotenoid stability and may change the ratio independently of maturity.

Spectrophotometric data can also be related to instrumental colour coordinates. The CIELAB system describes lightness (L*) and the chromatic axes a* and b*, corresponding broadly to green-red and blue-yellow variation. ASTA and CIELAB parameters calculated from UV–Vis spectra of acetone extracts have been successfully used for geographical differentiation of Spanish paprika. Such an approach links conventional colour measurement with spectral information and facilitates objective comparison among samples. [6]

Influence of processing and storage

Drying is one of the technological stages with the strongest influence on paprika colour. Carotenoids are sensitive to heat, light and oxygen and may undergo oxidation, isomerization and other degradation reactions. Comparative studies of smoked, oven-dried and sun-dried commercial paprikas have shown clear differences in ASTA values, pigment concentrations and colour stability. Smoked paprika showed the highest ASTA units and pigment concentrations, whereas other drying procedures produced different red/yellow ratios and different rates of colour loss during ultraviolet exposure. [2]

Storage may continue these changes. A progressive decrease in visible absorbance usually indicates deterioration of the carotenoid system. Temperature, oxygen availability, light exposure, moisture and packaging conditions all influence the rate of degradation. For this reason, spectrophotometric monitoring can be useful in shelf-life studies, where repeated measurements provide a direct indication of color retention. At the same time, a low ASTA value should not automatically be interpreted as poor initial raw material, because it may also result from inappropriate processing or prolonged storage.

Classification and authentication using spectral data

Modern spectroscopic analysis increasingly uses the complete spectrum rather than one or two wavelengths. A full spectrum contains many correlated variables and can be regarded as a fingerprint of the sample. Because direct interpretation of hundreds of spectral variables is difficult, chemometric techniques are used to reduce dimensionality, identify patterns and construct classification models. Principal component analysis (PCA) is often applied first to visualize natural groupings and detect atypical samples. Supervised methods such as linear discriminant analysis (LDA), partial least-squares discriminant analysis (PLS-DA), support vector machines (SVM) and artificial neural networks (ANN) may then be used when reference classes are known.

The potential of this strategy has been demonstrated using paprika samples from the Spanish Protected Designations of Origin Murcia and Extremadura, analyzed by UV–Vis spectrophotometry. Models based on color parameters or PCA scores obtained from absorbance spectra were developed using LDA, SVM and ANN. The best ANN models reached classification efficiencies of approximately 92–95%. These results show that relatively inexpensive UV–Vis measurements can provide information not only about color strength but also about geographical origin [6].

Visible-near infrared spectroscopy further expands this possibility because measurements can often be made directly on powders with little or no sample preparation. Vis–NIR spectra have been successfully used for authentication of paprika belonging to the Protected Designation of Origin “Pimentón de La Vera”. Multivariate classification models successfully differentiated PDO from non-PDO samples, with particularly good performance in the NIR region. The approach is attractive for industrial screening because it is fast and non-destructive [7].

Spectroscopy combined with chemometrics is also useful for detecting adulteration. A portable NIR spectrometer has been applied to paprika adulterated with potato starch, acacia gum and annatto. PLS-DA models distinguished authentic and adulterated samples with specificity above 90% and very low classification error [8]. NIR and FTIR spectroscopy have also been successfully used to detect substitution of paprika with spent paprika when the spectral data were treated chemometrically [9]. Such methods are particularly valuable for rapid screening, although suspicious samples should be confirmed by more

specific analytical techniques.

Advantages and limitations

The main advantages of spectrophotometric methods are speed, relatively low cost and straightforward instrumentation. UV–Vis spectrophotometers are common in analytical laboratories, while portable Vis–NIR instruments make on-site screening increasingly realistic. Spectral measurements can support several levels of analysis: a single wavelength for routine color control, selected wavelengths for estimation of pigment fractions, or the complete spectrum for chemometric classification.

The principal limitation is the overlap of absorption bands. A paprika spectrum represents the combined response of numerous carotenoids and other constituents, so it is usually not possible to quantify individual pigments with the same selectivity as HPLC. Sample preparation, solvent composition, particle size, moisture and extraction time can also affect reproducibility. In classification studies, an additional limitation is model dependence: a model performs well only when the calibration set adequately represents the variability of future samples. External validation and periodic model updating are therefore essential.

For these reasons, spectrophotometry and chromatography should be regarded as complementary rather than competing approaches. Spectrophotometry is well suited to rapid quality control and screening, whereas HPLC is preferable when individual carotenoids must be identified and quantified with high specificity. A practical analytical strategy may therefore use spectral methods for routine classification and reserve chromatographic analysis for confirmation or detailed compositional studies.

The following section supplements the review on spectrophotometric characterization and classification of red paprika with quantitative results reported in experimental studies. The selected data illustrate the relationship between extractable color, carotenoid composition, processing conditions and spectroscopic classification. Particular attention is given to ASTA color values, because this parameter is routinely used in the paprika industry, although recent results show that it should not always be interpreted as a direct measure of the concentration of individual carotenoids.

Comparison of color parameters in paprika produced by different drying methods

Drying technology has a measurable influence on the color characteristics of paprika. A comparison of commercial sweet paprika obtained by sun drying, oven drying and smoke drying shows that the visual redness of the powder and the extractable color expressed in ASTA units do not necessarily follow the same trend. Sun-dried paprika showed the highest surface redness (a* = 33.20), whereas smoked paprika had the highest ASTA value (139.15). This indicates that a sample which appears visually redder does not necessarily contain the highest amount of extractable coloring pigments [2].

Table 1. Selected color parameters of commercial paprika produced by different drying methods [2]

Parameter	Sun-dried	Oven-dried	Smoked
L*	42.76 ± 1.15	37.96 ± 0.14	37.17 ± 4.37
a* (redness)	33.20 ± 0.77	31.07 ± 0.23	31.57 ± 0.98
b*	51.69 ± 1.35	46.34 ± 0.52	44.96 ± 5.11
ASTA colour	98.18 ± 13.37	115.10 ± 8.00	139.15 ± 18.49
Red/yellow ratio	0.93 ± 0.02	1.00 ± 0.02	0.99 ± 0.01
Browning index	0.21 ± 0.04	0.07 ± 0.00	0.25 ± 0.03

The ASTA value of smoked paprika was approximately 42% higher than that of sun-dried paprika. At the same time, the a* coordinate was slightly higher in sun-dried samples. Oven-dried paprika presented the highest red/yellow pigment ratio (1.00) and the lowest browning index (0.07). Velázquez et al. also observed that color degradation under ultraviolet exposure was much more rapid in sun-dried and oven-

dried samples, whereas smoked paprika showed a more progressive loss and retained better color stability even after prolonged exposure.

Carotenoid variability among red paprika cultivars

Variation among cultivars is another factor that can influence spectral behavior. A comparative study of 27 paprika types with different colors, fruit shapes and cultivation systems was performed using UPLC. Six carotenoids were identified in red paprika. Capsanthin was generally characteristic of red samples, but the results also demonstrated that visual color alone cannot predict the detailed carotenoid profile. The red cultivar 'Mini Goggal Red', for example, contained 121.41 ± 30.10 mg/100 g dry weight of zeaxanthin, a concentration more typical of orange paprika. Such findings support the use of spectrophotometric screening in combination with chromatographic confirmation when a detailed chemical classification is required [10].

CONCLUSION

Spectrophotometric characterization provides a useful and versatile basis for assessing the quality of red paprika. Classical UV–Vis methods allow rapid determination of extractable color and estimation of red and yellow carotenoid fractions, while complete spectral profiles provide richer information about the chemical and technological characteristics of the product. The combination of UV–Vis or Vis–NIR spectra with chemometric techniques has extended the role of spectroscopy from simple color measurement to classification according to origin, processing history and authenticity.

Spectral methods must nevertheless be carefully standardized and cannot fully replace chromatographic identification of individual carotenoids. Their speed, simplicity and relatively low cost make them highly suitable for routine control and preliminary screening, while future development will probably rely on portable instruments, larger reference databases and more robust multivariate models.

The present review aims to present and comparatively analyze published spectrophotometric data related to the characterization of red paprika and to identify the main factors that should be considered when its quality is evaluated on the basis of color measurements. The comparison of literature results shows that similar ASTA color values may correspond to different carotenoid concentrations, and that processing technology, geographical origin and cultivar can significantly influence the spectral characteristics of paprika. Therefore, the use of a single color parameter may not always provide sufficient information for a complete assessment of the product.

On this basis, the present study also provides a methodological framework for further experimental work. A subsequent stage of the research will include spectrophotometric measurements of red paprika samples available on the Bulgarian market and/or produced in Bulgaria. The aim will be to determine their spectral characteristics, extractable color and selected color-related parameters and to compare the obtained results with published data for paprika of different geographical origins. Such an approach could provide initial information about the variability of Bulgarian samples and may contribute to the development of a simple methodology for their quality assessment and preliminary classification.

ACKNOWLEDGEMENTS: *This report is published in connection with the results from the implementation of activities under Project No. NIP2026-8, "Integrated Approach for a Sustainable Industry through Smart and Innovative Technologies."*

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