



UNIVERSITÀ POLITECNICA DELLE MARCHE  
Repository ISTITUZIONALE

## Feasibility of Two MEMS-NIR Spectrophotometers for Characterizing Different Biofuel Origin

This is the peer reviewed version of the following article:

*Original*

Feasibility of Two MEMS-NIR Spectrophotometers for Characterizing Different Biofuel Origin / Leoni, Elena; Mancini, Manuela; Assirelli, Alberto; di Stefano, Sara; Toscano, Giuseppe. - 337:(2023), pp. 667-675. (Intervento presentato al convegno 12th International Conference of the Italian Association of Agricultural Engineering, AIIA 2022 tenutosi a Palermo nel 19 - 22 September 2022) [10.1007/978-3-031-30329-6\_68].

*Availability:*

This version is available at: 11566/330713 since: 2024-05-30T07:53:16Z

*Publisher:*

Springer Science and Business Media Deutschland GmbH

*Published*

DOI:10.1007/978-3-031-30329-6\_68

*Terms of use:*

The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. The use of copyrighted works requires the consent of the rights' holder (author or publisher). Works made available under a Creative Commons license or a Publisher's custom-made license can be used according to the terms and conditions contained therein. See editor's website for further information and terms and conditions.

This item was downloaded from IRIS Università Politecnica delle Marche (<https://iris.univpm.it>). When citing, please refer to the published version.

*Publisher copyright:*

Springer (conference paper) - Postprint/Author's accepted Manuscript

This version of the conference paper has been accepted for publication, after peer review (when applicable) and is subject to Springer Nature's AM terms of use <https://www.springernature.com/gp/open-research/policies/accepted-manuscript-terms>, but is not the Version of Record and does not reflect post-acceptance improvements, or any corrections. The Version of Record is available online at: 10.1007/978-3-031-30329-6\_68.

(Article begins on next page)

# Feasibility of two MEMS-NIR spectrophotometers for characterizing different biofuel origin

Elena Leoni<sup>1\*</sup>, Manuela Mancini<sup>1</sup>, Alberto Assirelli<sup>2</sup>, Sara di Stefano<sup>1</sup> and Giuseppe Toscano<sup>1</sup>.

<sup>1</sup> Department of Agricultural, Food and Environmental Science, Università Politecnica delle Marche, 60131 Ancona (Italy)

<sup>2</sup> CREA-IT, Via delle Pascolare 16, 00016 Monterotondo, Roma (Italy)

\*e.leoni@pm.univpm.it

**Abstract.** The EU common effort to reduce fossil fuel consumption paves the way to enhancing interest towards renewable resources, as solid biofuel. Its properties and origin are fundamental issues affecting energy conversion efficiency and supply chain sustainability. Laboratory conventional analyses are time consuming and require huge economic efforts, so it is essential to obtain rapid and real-time quality information along all the supply chain. Near Infrared Spectroscopy (NIRS) is able to satisfy these requirements, minimizing the time delay and promoting on site analysis along the whole process. The aim of the present work is to evaluate the performance of two different portable MEMS (Micro Electro Mechanical System) NIR spectrophotometers for identifying the raw biomass of which pellet is made. Thus, samples of different categories have been collected, particularly Italian softwood and hardwood species, wood processing industry residues and bioenergy crops. Ten replicates for each sample have been performed and different spectral pretreatments have been tested to reduce noise and scattering effects. Principal Component Analysis (PCA) has been used to investigate the spectral variability and look for groupings among the categories. According to the spectral range, the C12 and C13 spectrophotometers revealed different performance in groups separation due to the detection of different chemical bonds, for example glue presence. More interesting results could be obtained by widening the biomass samples to manage stronger dataset for chemometrics analysis. Nevertheless, results of the research aim at introducing NIR sensor, coupled with chemometrics, onboard pellet combustion devices to improve process efficiency and environmental performance.

**Keywords:** Precision bioenergy, NIRS, PCA, quality, pellet.

## 1 Introduction

The current economic and political situation and the EU effort to reduce fossil fuel consumption paves the way to enhancing interest towards renewable resources. Solid biofuels play a key role, but their physical properties and origin are fundamental issues affecting energy conversion efficiency and supply chain sustainability [1]. But laboratory conventional analyses are time consuming and require important economic

efforts, therefore it is crucial to obtain rapid and real-time quality control method along all the supply chain [2]. Near Infrared Spectroscopy (NIRS), coupled with chemometrics, proves to be able to satisfy these requirements, minimizing the time delay of the laboratory analyses and promoting on-site monitoring along the whole process [3]. The main aim of the present work is to evaluate the performance of two different portable MEMS (Micro Electro- Mechanical System) NIR spectrophotometers for identifying and detecting the raw inner components of different pellet source. In this way, three categories are investigated to evaluate three groups separation: i) softwood and hardwood species, ii) wood processing industry residues and iii) bioenergy crops.

## 2 Material and Method

### 2.1 Biomass material

To start the investigation, a total of 178 sample have been considered. According to the different classification analyses, different biomass typologies have been collected for each category, as shown in Table 1.

**Table 1.** Class division of considered biomass samples.

Aim	Biomass origin	Number of samples
<i>Softwood/Hardwood</i>	Pine tree	15
	Fir wood	19
	Oak	9
	Chestnut	4
	Beech	25
<i>Treated wood</i>	Oriented Strand Board (OSB)	12
	Chipboard (CB)	29
	Plywood (PW)	2
	Multilayer (MLT)	3
<i>Herbaceous</i>	Straw	15
	Sorghum	15
	Sorghum stalk	15
	Corn stalk	15

Each sample, after stabilization process, has been milled to 1 mm of particle size using a cutting mill (mod.SM 2000, RETSCH), then each sample has been stored in hermetically closed plastic vial to maintain physical characteristics unaltered.

### 2.2 NIRS analysis

NIR spectral acquisitions were performed using two compact and portable spectrophotometers MEMS (Micro Electro-Mechanical System, HAMAMATSU) operating

on different spectral range: i) C15712 model (C12): 1350-1650 nm (7407-6061  $\text{cm}^{-1}$ ), spectral resolution of 18 nm, and ii) C15713 model (C13): 1550-1850 nm (6452-5405  $\text{cm}^{-1}$ ), spectral resolution of 20 nm. These modules have built-in light source (tungsten lamp) and MEMS-FPI spectrum sensor (InGaAs photodiode), using Fabry-Perot Interferometer. Their compact size and weight (32x74x16 and 80 gr) make them handy and suitable for on-field application.

The acquisitions were carried out in reflectance mode. The reference, shading (light on) and background spectrum (light off) were acquired every hour during the analysis. Ten replicates were performed for each sample, following pyramidal scheme around the little heap poured from the plastic vial on a flat surface.

### **2.3 Chemometric elaboration**

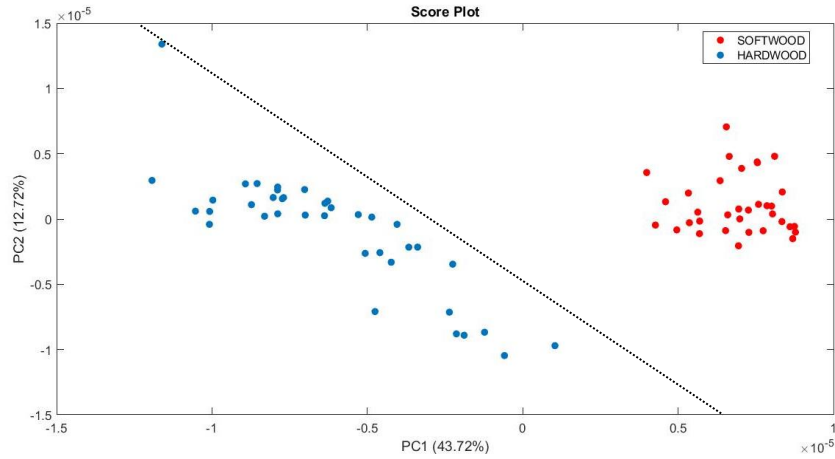
Chemometrics turned out to be fundamental to multivariate analyses performances to extract relevant information from spectral data about the material origin, according to chemical differences between biomass sources. PCA method was computed for each material classification using Matlab (ver. 9.7.0, 2019) to group sample among different categories. Spectra were pretreated to reduce noise and scattering effect, coming from external lights interference. PCA analysis were developed on mean-centered data of the replicates and performances have been checked using score plot. Then spectra interpretation has been carried out in the loading plot to main relevant peaks assessment, considering Principal Components (PCs) investigation to identify main discriminative chemical components.

## **3 Results**

### **3.1 Softwood/Hardwood**

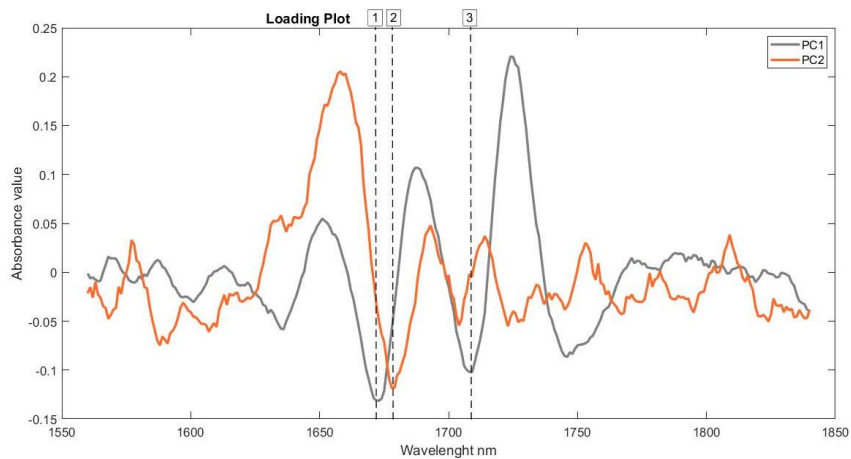
A total of 72 virgin wood samples have been considered to discriminate softwood from hardwood. According to the spectral range, C13 spectrophotometer has shown to provide a better separation between hardwood and softwood species than C12 due to C-H bonds detection related to wood components. The best performance has been obtained with second derivative pre-treatment (second polynomial order, 21 smoothing points with Savitzky-Golay) on the entire spectral range and each sample was averaged across its ten replicates.

The spatial distribution for the first and second PC has been provided in the score plot (Fig.1). The clear separation between groups and the higher scattering distribution of hardwood samples could be due to their higher inner variability [4].



**Fig. 1.** Score plot of the two PCs for the virgin wood separation (softwood/hardwood). The dash line shows the evident separation between groups.

The most relevant wavenumbers, related to the negative peaks according to the derivative pretreatment (second derivative), have been provided in the loading plot (Fig.2). Dash line and corresponding number have been used to identify the main negative peaks both related to the first and second PCs. In particular: 1) peak at 1672 nm is related to aromatic groups of lignin, while 2) peak at 1679 nm and 3) peak at 1709 nm are related to hemicellulose (C-H stretching bonds) [5].

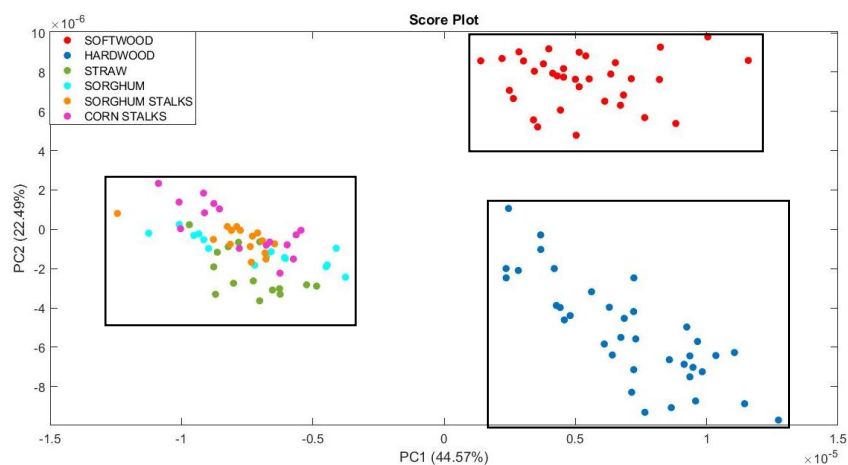


**Fig. 2.** Loading plot of spectra with second derivative (second polynomial order, 21 smoothing points with Savitzky Golay) related to softwood/hardwood separation. Dash lines and respective number refer to the main negative peaks revealed.

### 3.2 Virgin wood/Herbaceous

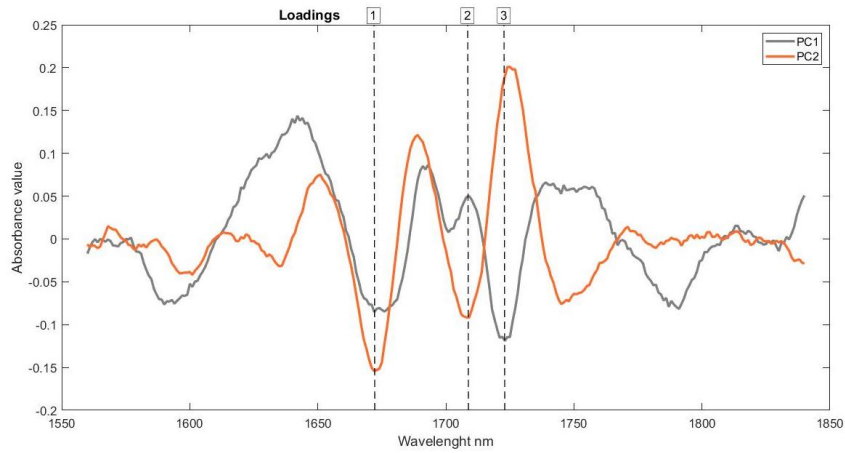
A total of 72 virgin wood and 60 herbaceous samples have been considered to discriminate between different biomaterials. According to the spectral range, C13 spectrophotometer has again shown a slight better separation between typologies than C12, related to wood components. The best performance has been obtained with second derivative pre-treatment (second polynomial order, 21 smoothing points with Savitzky-Golay) on the entire spectral range and each sample was averaged across its ten replicates.

The spatial distribution for the first and second PC has been provided in the score plot (Fig.3). The clear separation between hardwood and softwood is confirmed, as well as the separation with herbaceous material, where samples show a less scattering because of the reduced heterogeneity.



**Fig. 3.** Score plot of the two PCs for the virgin wood-herbaceous separation. The rectangular blocks help to better shaping the separation.

The most relevant wavenumbers, related to the negative peaks according to the derivative pretreatment (second derivative), have been provided in the loading plot (Fig.4). Even in this case, dash line and corresponding number have been used to identify the main negative peaks both related to the first and second PCs. Detected peaks comply with the previous detection for the virgin material separation, in particular: 1) peak at 1670 nm is related to aromatic groups of lignin, while 2) peak at 1705 nm is related to hemicellulose; 3) peak at 1725 nm corresponded to C-H stretching bonds [5].

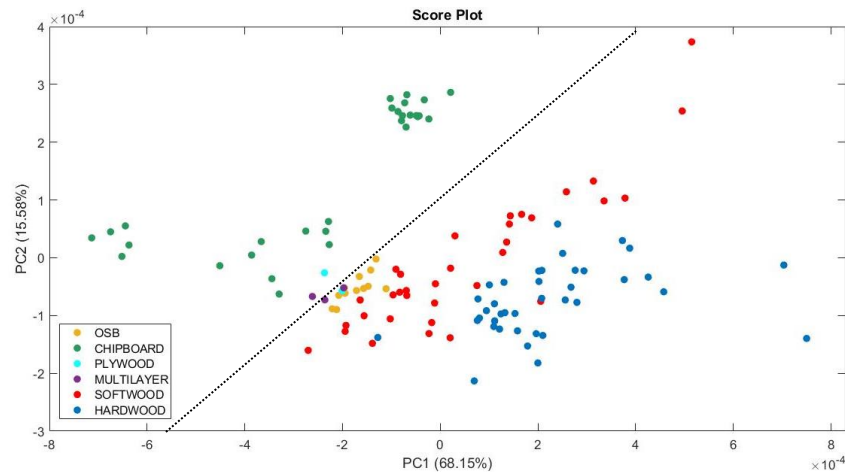


**Fig. 4.** Loading plot of spectra with second derivative (second polynomial order, 21 smoothing points with Savitzky Golay) related to virgin wood/herbaceous samples separation. Dash lines and respective number refer to the main negative peaks revealed.

### 3.3 Virgin wood/Treated wood

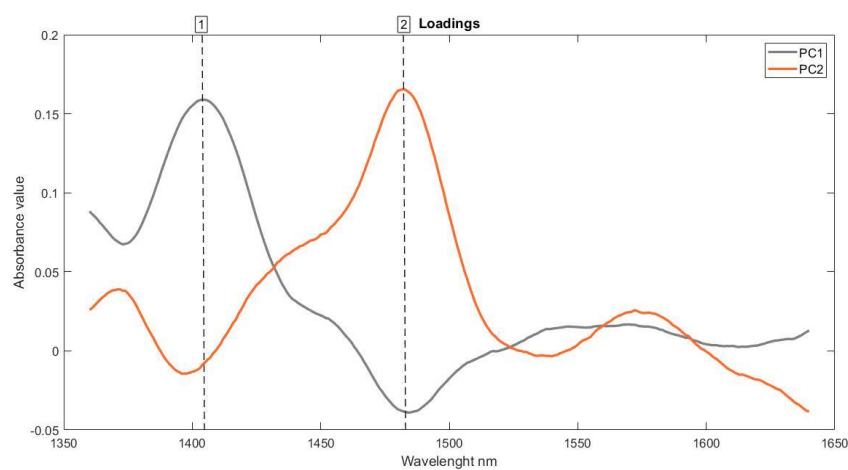
A total of 72 virgin wood and 46 treated wood samples have been considered to discriminate the treatment degree of wood. According to the spectral range, C12 spectrophotometer has shown better performance than C13 in grouping related to wood additives and components. The best performance has been obtained with first derivative pre-treatment (second polynomial order, 21 smoothing points with Savitzky-Golay) on the entire spectral range and each sample was averaged across its ten replicates.

The spatial distribution for the first and second PC has been provided in the score plot (Fig.5). The limited separation between virgin and treated wood is more evident along both PC1 and PC2 directions. In particular, virgin wood main fitting the positive PC1 and negative PC2, whereas the opposite has been confirmed for treated wood. The closeness between softwood and treated wood reflects the use of fir wood residues in industrial wood treatment, in particular for OSB and plywood [6], while hardwood is confirmed more heterogenous than other groups [4].



**Fig. 5.** Score plot of the two PCs for the virgin wood-treated wood separation. The dash line shows the slight and not marked separation between groups.

The most relevant wavenumbers, related to the positive peaks according to the first derivative pre-treatment, have been provide in the loading plot (Fig.6). Even in this case, dash line and corresponding number have been used to identify the main positive peaks both related to the first and second PCs. Although detected peaks shown to be less significant, they are more concentrated in different wavenumbers than previous separations, in particular: 1) peak at 1405 nm, related to lignin and extractives and 2) peak at 1480 nm, related to cellulose and to O-H stretching bonds This shifting is probably related to specific glue bonds detection [7].



**Fig. 6.** Loading plot of spectra with first derivative related to virgin wood/treated wood samples separation. Dash lines and respective number refer to the main positive peaks revealed.



## 4 Conclusion

Results demonstrate the reliability of the performances of NIR application to discriminate origin and biomass chemical components. More useful results could be obtained by widening the biomass samples to manage stronger dataset for chemometrics analysis. Nevertheless, NIRS can be considered a smart, rapid and cost-effective tool to characterize biofuel quality and to improve the effectiveness of biomass placing and utilization as a renewable resource. Furthermore, the use of portable NIRS instruments, coupled with chemometrics, could enhance the monitoring performance, onboard combustion devices and along conveyor belts, to control environmental impact.

## References

- [1] G. Toscano, E. Leoni, G. Feliciangeli, D. Duca, and M. Mancini, "Application of ISO standards on sampling and effects on the quality assessment of solid biofuel employed in a real power plant," *Fuel*, vol. 278, no. October 2019, p. 118142, 2020, doi: 10.1016/j.fuel.2020.118142.
- [2] M. Mancini, D. Duca, and G. Toscano, "Laboratory customized online measurements for the prediction of the key-parameters of biomass quality control," *J. Near Infrared Spectrosc.*, vol. 27, no. 1, pp. 15–25, 2019, doi: 10.1177/0967033518825341.
- [3] C. Pasquini, "Near infrared spectroscopy: A mature analytical technique with new perspectives – A review," *Anal. Chim. Acta*, vol. 1026, pp. 8–36, 2018, doi: 10.1016/j.aca.2018.04.004.
- [4] D. Duca *et al.*, *Soft Independent Modelling of Class Analogy applied to infrared spectroscopy for rapid discrimination between hardwood and softwood*, vol. 117. 2016. doi: 10.1016/j.energy.2016.10.092.
- [5] M. Schwanninger, J. C. Rodrigues, and K. Fackler, "A review of band assignments in near infrared spectra of wood and wood components," *J. Near Infrared Spectrosc.*, vol. 19, no. November, pp. 287–308, 2011, doi: 10.1255/jnirs.955.
- [6] M. Mancini *et al.*, "Near infrared spectroscopy for the discrimination between different residues of the wood processing industry in the pellet sector," *Fuel*, vol. 217, no. November 2017, pp. 650–655, 2018, doi: 10.1016/j.fuel.2018.01.008.
- [7] M. Mancini, Á. Rinnan, A. Pizzi, and G. Toscano, "Use of Fourier transform near infrared spectroscopy for the detection of residues from wood processing industry in the pellet sector," *Proc. 18th Int. Conf. Near Infrared Spectrosc.*, pp. 77–84, 2019, doi: 10.1255/nir2017.077.