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Machine learning tools for the classification of visible reflectance spectra of inorganic pigments historically used in wall paintings

Jordi Cruz, Roberto Sáez-Hernández

Abstract: Three different classification methods applied to the field of Cultural Heritage are compared. Focusing on the non-invasive and *in situ* identification of historical inorganic pigments using visible reflectance spectroscopy, linear and non-linear classifiers are trained and evaluated (Partial Least Squares – Discriminant Analysis (PLS-DA), Support Vector Machine (SVM-DA), and Artificial Neural Networks (ANN-DA)). Three hues (yellow, blue and green) are considered with three pigments per hue: lead-tin yellow, yellow ochre, orpiment (yellow); celadonite, green malachite, Verona green (green); and Egyptian blue, azurite, and lapis lazuli (blue). All three classification methods yielded high prediction capabilities (above 94.2 % in the external validation sets), with high sensitivity and specificity (above 88 %). In cases where spectral features are more similar, PLS-DA performed slightly worse. However, SVM-DA and ANN-DA models were comparable in all instances, with global accuracies above 98.8 %, sensitivity above 88 %, and specificity above 98 %, respectively.

Keywords: artificial neural networks, classification, chemometrics, identification, partial least squares discriminant analysis, pigments, support vector machines, visible reflectance spectroscopy

Herramientas de Machine Learning para la clasificación de espectros visibles de reflectancia de pigmentos inorgánicos usados en pintura mural

Resumen: Centrándose en la identificación no invasiva e in situ de pigmentos históricos mediante espectroscopía de reflectancia visible, se entrenan y evalúan clasificadores lineales y no lineales (*Partial Least Squares – Discriminant Analysis* (PLS-DA), *Support Vector Machine* (SVM-DA), y *Artificial Neural Networks* (ANN-DA)) aplicados al Patrimonio Cultural. Se consideran tres tonalidades (amarillo, azul y verde), con tres pigmentos por tonalidad: amarillo plomo-estaño, ocre amarillo, oropimente (amarillo); celadonita, malaquita verde, verde Verona (verde); y azul egipcio, azurita y lapislázuli (azul). Los tres métodos arrojaron alta capacidad predictiva (> 94,2 % en validación), con sensibilidades y especificidades por encima del 88 %. En casos en los que las características espectrales son más similares, PLS-DA se comportó ligeramente peor. Sin embargo, los modelos SVM-DA y ANN-DA fueron en todos los casos comparables con precisiones globales superiores al 98,8 %, sensibilidad superior al 88 % y especificidad superior al 98 %, respectivamente.

Palabras clave: clasificación, espectroscopía de reflectancia visible, identificación, máquinas de vector soporte, mínimos cuadrados parciales, pigmentos, quimiometría, redes neuronales artificiales

Introduction

Studying inorganic pigments in Cultural Heritage is a well-established field (Melo et al. 2022). Pigment analysis serves multiple purposes: it supports conservation efforts by identifying degradation processes and guiding restoration strategies; it contributes to art historical research by revealing materials and techniques used by artists; and it plays a key role in authentication, helping to verify the origin and dating of artworks (Popelka-Filcoff 2020). In particular, applying analytical methodologies to their investigation has been one of the most prolific research areas regarding chemistry and Cultural Heritage. During the development of these methodologies, the intrinsic characteristics of ancient samples have imposed some restrictions and conditions. For example, techniques need to be non-destructive (or, at least, minimally destructive) (Sáez-Hernández *et al.* 2022). Also, they must be portable, as some cases will not allow the sample to be taken to the laboratory, and must allow for *in situ* analysis (Muñoz 2023).

In this regard, some of the most commonly employed analytical techniques that have been applied are Fourier Transform Infrared Spectroscopy (FTIR), Raman spectroscopy, portable Energy Dispersive X-ray Fluorescence (XRF), or reflectance spectroscopy (Ricciardi

2012; Ricciardi 2013; Aceto 2014; Delaney 2014; Liu *et al.* 2024; Muñoz 2023). In the latter case, different techniques can be applied throughout the electromagnetic spectrum. For example, Short-Wave Infrared (SWIR), Near Infrared (NIR) or visible reflectance spectroscopy represent different alternatives that are able to characterise a sample according to its chemical composition. For the particular case of pigment studies, the visible range becomes particularly interesting, as it represents the pigments' behaviour for their main purpose: to show different colours. Consequently, these techniques have been applied in different case studies for investigating historical pigments, both using spot-wise techniques and hyperspectral or multispectral instrumentation (Cséfalvayová 2011; Wu 2016; Liu 2024).

All these techniques have in common being portable and non-invasive, thus being an adequate solution to the problem (Muñoz 2023; Liu 2024). The common approach to analytically investigate Cultural Heritage samples in general, and pigments in particular, involves a multianalytical approach. Combining all the aforementioned techniques enriches the result and adds robustness (Delaney 2014; Romani 2020).

For the specific case of ancient pigments, visible reflectance spectroscopy is of particular interest, given the fact that pigments do have distinct patterns in this region (Ricciardi 2013; Aceto 2014, Liu *et al.* 2024). As a consequence of electronic transitions, absorption bands are present in the range comprised between 400 and 720 nm. By characterizing these bands, it is possible to identify the chemical species behind them (Ricciardi 2012; Ricciardi 2013). Consequently, visible reflectance spectroscopy is commonly employed in the field of Cultural Heritage to identify pigments (Ricciardi 2013; Aceto 2014; Liu *et al.* 2024). To that end, the common approach is to compare the measured spectrum with a reference one, either measured by the researchers or present in the literature (Ricciardi 2012; Delaney 2014).

Implementing chemometrics in the analytical process can help make decisions by applying adequate data treatment and modelling (Musumarra and Fichera 1998; Pouyet *et al.* 2021; Yogurtcu *et al.* 2024). In particular, for the case of pigment identification, there exist diverse kinds of classifiers that permit the synthesis of the spectral information and provide an objective identification (Muehlethaler *et al.* 2016; Mandal *et al.* 2023; Yogurtcu *et al.* 2024). These methods require a prior training step often relying on mock up samples with known compositions, or the implementation of reference analytical techniques. These techniques allow to identify the chemical component in the pigment, so that the classifier algorithms can then model their characteristic features. Among others, Partial Least Squares – Discriminant Analysis (PLS-DA) linearly decomposes the original X matrix (corresponding to the spectra), into a set of new factors (called latent variables), which are then used to predict the class to which a sample belongs, depending on its spectral features (Muehlethaler *et al.* 2016; Fan *et al.* 2018; Romani *et al.* 2020). In a more complex manner, non-linear methods like Support Vector Machines (SVM) and Artificial Neural Networks (ANN) arise as potential alternatives (Pouyet *et al.* 2021; Kastenholz *et al.* 2024; Yogurtcu *et al.* 2024). SVMs create boundaries among classes that separate them, which can be linear or non-linear by applying kernels such as the Radial Basis Function (Fan *et al.* 2018, Kastenholz *et al.* 2024). When it comes to Artificial Neural Networks (Mao *et al.* 2002), they arrange the spectral information as inputs to their architecture, transferring information among nodes by different transfer functions, and can be arranged in layers, increasing the sophistication of the model (Yogurtcu et al. 2024). In the case of ANN–Discriminant Analysis, the final output of the model is a class to which a sample belongs (Yogurtcu *et al.* 2024).

The goal of this article is to investigate the potential of adequate chemometric tools to objectively identify different inorganic pigments in the field of Cultural Heritage. A set of relevant historical pigments were applied in wall painting replicas, and subsequently measured using visible reflectance spectroscopy. The visible reflectance spectra were then treated and used to build qualitative identification models through different modelling strategies: PLS-DA, SVM-DA, and ANN-DA. The selection of these methods is further justified because PLS-DA offers robust linear discrimination in spectroscopic datasets, SVM effectively separates pigment classes with both linear and non-linear kernels, while ANN provides flexible modelling capable of capturing complex spectral relationships.

Materials and methods

— *Mock-up preparation*

Three different colour hues were selected for this investigation: yellow, blue, and green. Each of those hues was represented by three different inorganic pigments, selected based on their relevance in Cultural Heritage. All of these pigments were purchased from Kremer, and are summarised in Table 1.

The different replicas were prepared following the information described by Vitruvius in the *Ten Books of Architecture*, as well as prior research (Piovesan 2012). The replicas were prepared using ceramic tiles as supports. The ceramic surface was first soaked with water, and different layers of sand:lime were applied. First, a rough layer consisting of a 3:1 mixture of coarse sand:lime (weight proportion) was applied and left to dry. Subsequently, a second layer was applied using the same proportion, but in this case with fine sand. After being left to dry, lime layers were applied to the surface and mechanically flattened to obtain a white, homogeneous, flat surface. When it comes to the pigment application, they were implemented as

Hue	Pigment	Chemical formula	Kremer ref.
Yellow	Lead-tin yellow (Hradil 2007)	$Pb2SnO_4$	#10120
	Yellow ochre (Montagner 2012)	FeO(OH)	#40301
	Orpiment (García-Bucio 2009)	As_2S_3	#10700
Green	Celadonite (Orsega 2011)	$K(Mg,Fe^{2+})Fe^{3+}(Si_4O_{10})(OH)_2$	#11250
	Green malachite (Cheilakou 2009)	$Cu2(CO_3)(OH)_2$	#10344
	Verona green (Orsega 2011) (celadonite + glauconite)	$KMgFe^{3+}Si_4O_{10}(OH)_2$ + $(K,Na)(Fe,Al,Mg)2(Si,Al)_4O_{10}(OH)_2$	#11010
Blue	Egyptian blue (Bianchetti 2000)	$CaCuSi_4O_{10}$	#10060
	Azurite (Barbu 2021)	$Cu_3(CO_3)_2(OH)_2$	#10210
	Lapis lazuli (Fioretti 2023)	$Na_2O \cdot 3Al \cdot 6SiO_2 \cdot 2Na_2S$	#10510

Table 1.- Description of the pigments used in the study.

previously described in the literature (Sáez-Hernández *et al.* 2024): briefly, pigments were suspended in water and applied on the wet surface. Different pigments-to-water proportions were prepared to obtain a diverse colour palette. Then, the pigments and the surface were left to dry to obtain the result observed in Figure 1.

Figure 1.- Some of the samples obtained for the different pigments under investigation.

— *Visible reflectance spectroscopy analysis*

The pigments' colour was registered using a portable spectrophotometer from Konica Minolta (CM-26d), using the D65 reference illuminant, the Specular Component Excluded mode, and the 10º standard observer. Before the measurements, the reference white and black of the instrument were measured, and it was ensured that the CIELAB values were (100, 0, 0) and (0, 0, 0), respectively. The visible reflectance spectra were acquired in the 400 – 740 nm range, with 5 nm steps. To represent the colour across the whole area of the sample, each one of them was measured at three different spots (spot size: 8 mm), and the global spectrum for each sample was obtained as the average spectrum of the three replicates.

— *Data treatment and analysis*

The modelling and data treatment were carried out using PLS Toolbox and Solo. The visible reflectance spectral signals were used to build three different classification methods: Partial Least Squares – Discriminant Analysis (PLS-DA), Support Vector Machine – Discriminant Analysis (SVM-DA), and Artificial Neural Network – Discriminant Analysis (ANN-DA). There are many classification techniques available for spectral data analysis, including decision trees, random forests, k-nearest neighbours, soft independent modelling of class analogies (SIMCA), and various forms of clustering and deep learning models. While some of these methods have shown promising results in certain contexts, PLS-DA, SVM-DA, and ANN-DA were chosen for this study because they offer a good balance between interpretability, robustness, and the ability to handle complex data. The global dataset, composed of 507 individuals, or samples, was split into calibration and validation sets (CAL and VAL, subsequently), in a 66:33 proportion using the Duplex algorithm (Daszykowski *et al.* 2002). The models were then trained using the CAL set and internally cross-validated using Venetian Blinds (10 total splits, blind thickness of 1 sample). After finding the most adequate conditions in each case, the models were then tested and externally validated using the external VAL set. By means of this external validation, the models' robustness is assessed by predicting new samples, which helps diminish the presence of overfitting.

In all instances, the visible reflectance spectra were pre-processed using a first derivative (using the Savitzky-Golay filter: polynomial order 2, window width of 3 points). This technique, which has been successfully applied in the literature in reflectance spectroscopy studies (Radpour *et al.* 2022), allows to remove slight differences in the baselines among different spectra, and converts the typical S-shaped visible reflectance spectra into peaks. Subsequently, spectra were mean centred in the wavelengths' direction.

Results and discussion

The three different classification methods were applied to the dataset and compared in terms of their predictive capacity. The results show an increasing degree of complexity, from a linear method to a non-linear one.

— *Partial Least Squares – Discriminant Analysis (PLS-DA)*

The models' number of LVs was selected so that it minimized the cross-validation error during the internal validation. Figure 2 shows the evolution of calibration and cross-validation classification error.

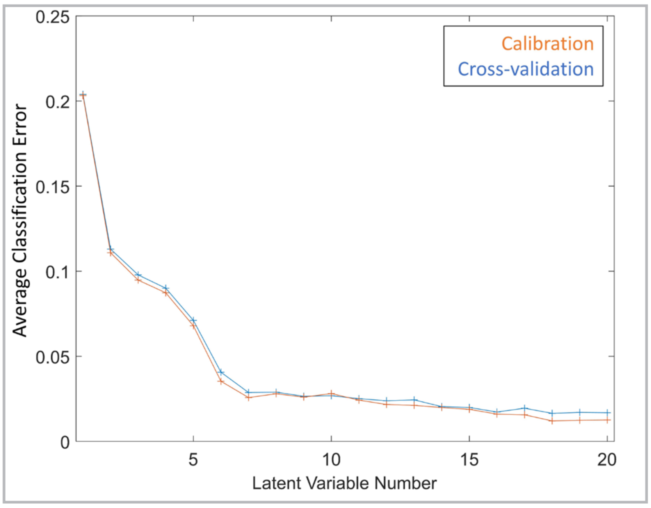

Figure 2.- Evolution of the average classification error during calibration (in orange) and cross-validation (in blue), as a function of the number of Latent Variables.

As can be seen, the model performance significantly increases as the number of Latent Variables increases. This improvement is more important when going from 6 to 7 factors. From this point, even though the error still decreases, that improvement is marginal and would come at the expense of unnecessary model complexity. Thus, seven factors were selected to build the PLS-DA model. Using these many factors, 99.4 % of the X matrix (spectra) variance was successfully explained.

Subsequently, the model was evaluated using the confusion matrix for the CAL and VAL sets. Results are summarised in Table 2. As observed, the models yielded satisfactory classifications for the nine investigated pigments. Overall, the accuracy of the model (the total correct classifications divided by the total possible cases) was 94.3 % for the CAL set and 94.2 % for the VAL set. This first result demonstrates how the approach works well for any of the classes and shows that no overfitting occurred (a model that is very well trained to predict itself but falls short when predicting new samples).

Analysing the VAL results in detail, the sensitivity (that is, the model's ability to correctly identify samples belonging to that class (Ballabio *et al.* 2013) was above 88 % in all instances, and the specificity (that is, the model's ability to reject samples from each class (Ballabio *et al.* 2013) was above 92 %.

— *Support Vector Machines – Discriminant Analysis (SVM-DA)*

Next, SVM-DA was tested for classification purposes. In this case, the model was built with a Radial Basis Function as a kernel, and the cost and gamma parameters were set at 100 and 3.16, respectively. Results are synthesized in Table 3.

In this case, the global accuracy of the model was 98.5 % for the CAL set and 98.8 % for the VAL set. Regarding sensitivity and specificity, they were above 88 % and 99 % in all classes.

— *Artificial Neural Network – Discriminant Analysis (ANN-DA)*

Last, an ANN-DA was built using only one hidden layer containing four nodes, and trained using the backpropagation algorithm. Table 4 summarises the results for this model. Results for the ANN-DA yielded an overall classification success of 97.9 % for CAL and 98.8 % for VAL. When it comes to the sensitivity and specificity, they were 88% and 98 %, respectively.

— *Method comparison*

All three methods yielded successful classification results. Next, a comparison of the three models in terms of analytical results is presented. Figure 3 summarises the most relevant information for comparison purposes.

Based on these results, PLS-DA can be seen to generally perform worse than the other two methods (SVM-DA and ANN-DA). Generally, classification errors are higher for this technique both in cross-validation and external validation. This is probably due to its linear nature, which generates limitations in class modelling for cases with greater spectral similarities. For example, in the case of green pigments, it can be observed that more confusion exists among classes [Tables 2 – 4]. This generally results in higher prediction errors, but is more marked for PLS-DA. An in-depth analysis of the 1st-derivative spectra used for prediction [Figure 4] suggests that the spectral features of green malachite may not be as distinctive as for the other pigments. This could justify why this is the hue in which less global accuracy was found.

Addressing SMV-DA and ANN-DA, they performed better than PLS-DA in most cases, yielding lower prediction errors. This improvement can be attributed to the fact that both approaches include non-linearity, which allows them to model more subtle spectral differences. Comparing them, it can be seen that they have similar performances: in some instances, ANN-DA performs better (for example, for

		Real class (pigment)								
		Lead-tin yellow	Yellow ochre	Orpiment	Egyptian blue	Azurite	Lapis lazuli	Celadonite	Green malachite	Verona green
Predicted class (pigment)	Lead-tin yellow	18	0	0	0	0	0	0	0	0
		18	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
	Yellow ochre	0	28	0	0	0	0	0	0	0
		0	**13**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
	Orpiment	1	0	26	0	0	0	0	0	0
		1	**0**	**17**	**0**	**0**	**0**	**0**	**0**	**1**
	Egyptian blue	0	0	0	46	0	0	0	0	0
		0	**0**	**0**	**44**	**0**	**0**	**0**	**1**	**0**
	Azurite	1	0	0	0	61	0	0	0	0
		0	**0**	**0**	**0**	**19**	**0**	**0**	**0**	**0**
	Lapis lazuli	0	0	0	0	0	58	0	0	0
		0	**0**	**0**	**0**	**0**	**33**	**0**	**0**	**0**
	Celadonite	0	0	0	0	0	0	21	2	0
		0	**0**	**0**	**0**	**0**	**0**	**7**	**3**	**0**
	Green malachite	0	0	0	0	9	0	5	27	0
		0	**0**	**0**	**0**	**1**	**0**	**1**	**4**	**0**
	Verona green	0	0	0	0	0	0	0	1	31
		0	**0**	**0**	**0**	**0**	**0**	**0**	**2**	**7**
	Sensitivity	0,90	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00
		1,00	**1,00**	**1,00**	**1,00**	**1,00**	**1,00**	**1,00**	**1,00**	**0,88**
	Specificity	0,95	1,00	0,96	1,00	0,93	1,00	0,98	0,81	0,95
		0,93	**1,00**	**0,92**	**1,00**	**0,97**	**1,00**	**0,96**	**0,92**	**0,95**

Table 2.- Confusion matrix and classification parameters for the PLS-DA model during cross validation. In bold, the prediction results for the external validation.

		Real class (pigment)								
		Lead-tin yellow	Yellow ochre	Orpiment	Egyptian blue	Azurite	Lapis lazuli	Celadonite	Green malachite	Verona green
Predicted class (pigment)	Lead-tin yellow	19	0	0	0	0	0	0	0	0
		18	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
	Yellow ochre	0	28	0	0	0	0	0	0	0
		0	**13**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
	Orpiment	0	0	26	0	0	0	0	0	0
		0	**0**	**17**	**0**	**0**	**0**	**0**	**0**	**1**
	Egyptian blue	0	0	0	46	0	0	0	0	0
		0	**0**	**0**	**44**	**0**	**0**	**0**	**0**	**0**
	Azurite	0	0	0	0	69	0	0	0	0
		0	**0**	**0**	**0**	**20**	**0**	**0**	**0**	**0**
	Lapis lazuli	0	0	0	0	0	58	0	0	0
		0	**0**	**0**	**0**	**0**	**33**	**0**	**0**	**0**
	Celadonite	0	0	0	0	0	0	25	0	0
		0	**0**	**0**	**0**	**0**	**0**	**8**	**0**	**0**
	Green malachite	0	0	0	0	2	0	1	29	0
		0	**0**	**0**	**0**	**0**	**0**	**0**	**10**	**0**
	Verona green	1	0	0	0	0	0	0	1	31
		1	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**7**
	Sensitivity	0,95	1,00	1,00	1,00	0,97	1,00	0,96	0,97	1,00
		0,95	**1,00**	**1,00**	**1,00**	**1,00**	**1,00**	**1,00**	**1,00**	**0,88**
	Specificity	1,00	1,00	1,00	1,00	1,00	1,00	1,00	0,81	0,95
		1,00	**1,00**	**1,00**	**1,00**	**1,00**	**1,00**	**1,00**	**1,00**	**0,99**

Table 3.- Confusion matrix and classification parameters for the SVM-DA model during cross validation. In bold, the prediction results for the external validation.

Real class (pigment)

Predicted class (pigment)	Lead-tin yellow	Yellow ochre	Orpiment	Egyptian blue	Azurite	Lapis lazuli	Celadonite	Green malachite	Verona green
Lead-tin yellow	20 **19**	1 **0**	1 **0**	0 **0**	0 **0**	0 **0**	0 **0**	0 **0**	0 **1**
Yellow ochre	0 **0**	27 **12**	0 **0**	0 **0**	0 **0**	0 **0**	0 **0**	0 **0**	0 **0**
Orpiment	0 **0**	0 **1**	25 **17**	0 **0**	0 **0**	0 **0**	0 **0**	0 **0**	0 **1**
Egyptian blue	0 **0**	0 **0**	0 **0**	46 **44**	0 **0**	0 **0**	0 **0**	0 **0**	0 **0**
Azurite	0 **0**	0 **0**	0 **0**	0 **0**	69 **20**	0 **0**	0 **0**	0 **0**	0 **0**
Lapis lazuli	0 **0**	0 **0**	0 **0**	0 **0**	0 **0**	58 **33**	0 **0**	0 **0**	0 **0**
Celadonite	0 **0**	0 **0**	0 **0**	0 **0**	0 **0**	0 **0**	25 **8**	2 **0**	0 **0**
Green malachite	0 **0**	0 **0**	0 **0**	0 **0**	1 **0**	0 **0**	1 **0**	27 **10**	0 **0**
Verona green	0 **0**	0 **0**	0 **0**	0 **0**	0 **0**	0 **0**	0 **0**	1 **0**	31 **7**
Sensitivity	0,95 **1,00**	0,96 **0,92**	0.96 **1,00**	1,00 **1,00**	1,00 **1,00**	1,00 **1,00**	0,96 **1,00**	0,93 **1,00**	1,00 **0,88**
Specificity	0,99 **0,99**	1,00 **1,00**	1,00 **0,99**	1,00 **1,00**	1,00 **0,99**	1,00 **1,00**	0,98 **1,00**	0,99 **0,98**	0,99 **1,00**

Table 4.- Confusion matrix and classification parameters for the ANN-DA model during cross validation. In bold, the prediction results for the external validation.

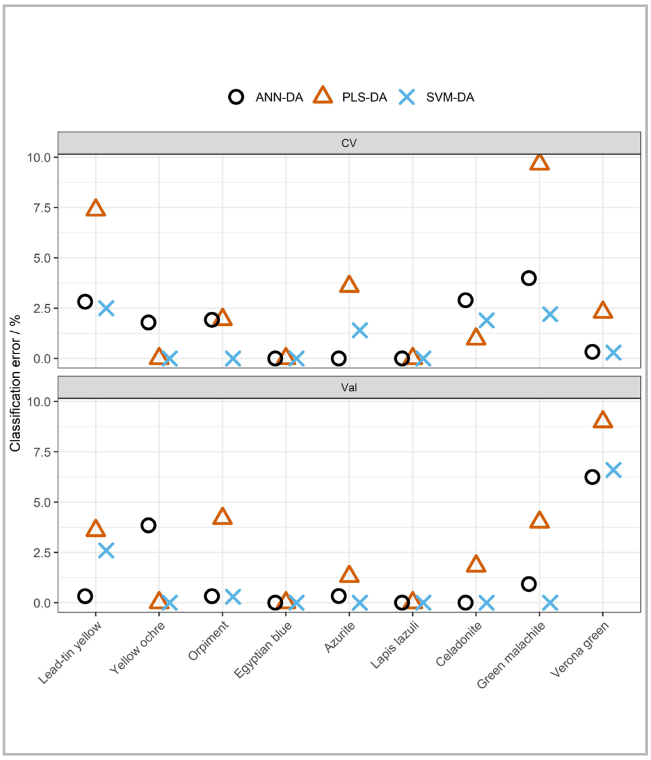

Figure 3.- Methods' comparison: classification parameters for the PLS-DA, SVM-DA, and ANN-DA. The classification errors for cross-validation (top) and external validation (bottom) for each class are shown.

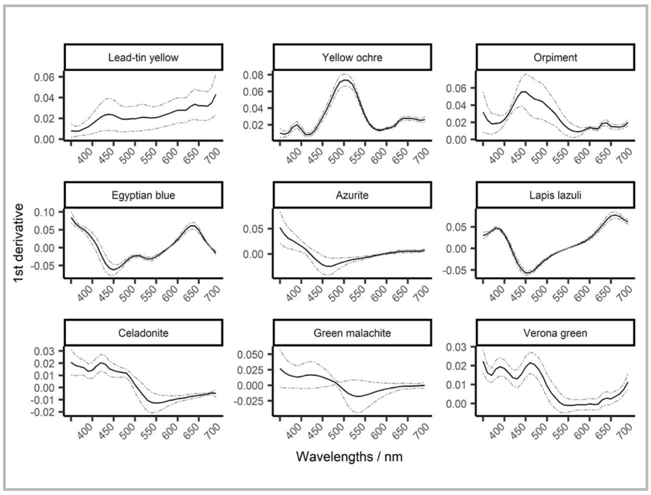

Figure 4.- First derivative average spectra for the different pigments under investigation. In grey, the standard deviation.

lead-tin-yellow), and in some others, SVM-DA yields better predictions (for example, yellow ochre). However, these differences are not significant, and it can be concluded that both methods successfully discriminate among pigments in the spectral modelling. This similarity in classification potential of both approaches is further corroborated by the global accuracy values for the VAL sets of both models (98.8 % in both instances). Additionally, sensitivity values for the VAL set were above 88 % in both cases, with specificities above 99 % and 98 % for SVM-DA and ANN-DA, respectively.

It must be considered that these two models, by their non-linear nature, require a more complex optimization process. Consequently, the computational effort required to train them is slightly higher than the one required for PLS-DA. Additionally, due to the more complex model architecture, they are also more prone to overfitting. In this regard, it becomes crucial to assess their robustness by implementing a fully external validation set to check that the results obtained during internal validation are sustained when predicting new samples.

—*Practical implications in the field of Cultural Heritage*

With the approach proposed in this manuscript, we have developed three chemometric strategies to deal with spectral information in the field of Cultural Heritage. Particularly, we have focused on inorganic pigment identification through visible reflectance spectroscopy. This approach compares three methods, both linear and non-linear, aiming to provide the analyst with an objective tool to enhance the fieldwork decision-making. Most usually, visible reflectance spectroscopy is used in the field of pigment analysis, given its highly descriptive nature of the electromagnetic spectrum range of interest. In that region, inorganic species present electronic transitions reflected in absorption bands in the visible range. The usual approach is to check the measured spectra, and sometimes visually compare them with a reference spectra database. Despite being useful and simple, this approach relies on a subjective component and can be systematised by data treatment.

In this direction, the work proposed here aims to provide a new approach that uses an already common and well-known tool (spectrophotometer) coupled to chemometric tools to make the process more robust. In this manner, we are enriching the information that can be extracted from a common instrument by creating a calibration dataset for pigment identification. By implementing this methodology, the analyst/restorer will not only have the spectra of the different points that have been measured, but also a first and tentative prediction of its nature.

Conclusions

In this article, we have developed a chemometric investigation into historical pigment identification by combining visible reflectance spectroscopy to classification chemometric tools. Visible reflectance spectroscopy was selected as the analytical technique given its intrinsic advantages, like portability, low cost, easiness to use, and wide availability in the Cultural Heritage field. However, this technique does not usually provide unambiguous identification based exclusively on the visible reflectance spectra. Thus, this contribution delved into the development of chemometric classification methodologies that, combined with the information provided by the analytical instrumentation, enhances the amount of information provided to the analyst.

In this context, three different methodologies have been developed and assessed, comparing their qualitative identification capabilities: a linear one based on Partial Least Squares – Discriminant Analysis, and two non-linear ones (Support Vector Machines – Discriminant Analysis and Artificial Neural Networks – Discriminant Analysis). The models have been developed and analysed for three colour hues (yellow, green, and blue), each one of them being represented by three inorganic pigments. All the implemented models yielded satisfactory prediction capabilities, with global accuracy values (for the external validation set) above 94.2 %. A comparison among the three methods demonstrated how PLS-DA yielded slightly worse results when compared to the two non-linear approaches. While the PLS-DA worked well for cases with clear spectral differences, it found some pitfalls in cases with similar spectral features. Both SVM-DA and ANN-DA provided better classification potential in those cases, thanks to the non-linearity included in those models. In both instances, classification errors and parameters were similar, with neither having clear advantages over the other. However, these models require more computational power to be trained, and must be optimized with caution to avoid overfitting.

This work provides a new alternative combining traditional chemometric techniques, like PLS-DA, with machine learning tools, like SVM-DA and ANN-DA, in the field of Cultural Heritage. The overall results of the in-situ investigations are enhanced by implementing adequate data treatment procedures for common instrumentation and data. This method aims to help and enhance fieldwork decision-making for professionals who may get a fast, objective, and tentative in situ identification for a sample.

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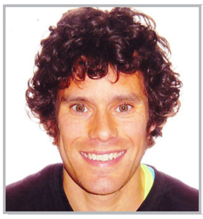
Autor/es



Jordi Cruz
jcruz@euss.cat
EUSS School of Engineering, Barcelona
https://orcid.org/0000-0001-8191-8689

Jordi Cruz is a University Associate Professor and lecturer at the EUSS School of Engineering in Barcelona since 2011. He holds an h-index of 11 and has authored over 30 scientific publications. He has supervised two PhD theses and one master's student. His research focuses on multivariate analysis applied to rapid analytical techniques such as NIR, Raman, FTIR, and NIR chemical imaging spectroscopy. These methods are used to develop fast, reliable analytical tools across various industrial sectors, including pharmaceuticals, phytotherapy, petrochemicals, cultural heritage, and forensics. Dr. Cruz conducts most of his research at the Agri-Food Technology Research Institute (IRTA) in Monells (Girona) and Forensics and Cultural Heritage at SmartChem Lab at the University of Valencia. He also maintains active collaborations with several international institutions: the Department of Pharmaceutical Chemistry at Mahidol University (Bangkok, Thailand), the Institute of Chemical Engineering at the Bulgarian Academy of Sciences (Sofia, Bulgaria), the University of the Basque Country, Teagasc in Ireland, and the Department of Forensic Chemistry at Florida International University (USA).

Roberto Sáez-Hernández
roberto.saez@uv.es
University of Valencia
https://orcid.org/0000-0001-9010-9445

Roberto Sáez-Hernández is an Assistant Professor at the Analytical Chemistry department of the University of Valencia. His research focuses on the analytical treatment and interpretation of spectroscopic and imaging signals through chemometric exploratory and supervised methods. Particularly, he has focused his research on the fields of food science – delving into the investigation of food contamination and food fraud –, Cultural Heritage – investigating construction materials of relevant historical sites or ancient gold coinage –, and more recently Forensics. In this regard, he has carried out research stays in national and international universities and research facilities, like the Institute of Food Science and Technology (IATA – CSIC), and the Universities of Bologna, Autonomous of Barcelona, and Copenhagen

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