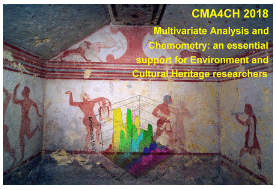
opening lecture at
CMA4CH 2018, Mediterraneum Meeting
Multivariate Analysis and Chemometry: an essential support for Environment and Cultural Heritage researchers
7th ed., 2018



DRIFTS Characterization of the "Soft Stone of the Berici Hills" and Classification of its Main Varieties Through Multivariate Analysis

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Abstract

Twenty samples of "Soft Stone of the Berici Hills" are studied through a combination of spectroscopic and chemometric tools. Their diffuse reflection infrared Fourier transform (DRIFT) spectra are analysed and the region corresponding to the non-carbonatic content subjected to a principal component analysis (PCA) showing that these features allow to discriminate among the different stone varieties. A soft independent modelling of class analogy (SIMCA) is then performed on these data allowing to characterize appropriately the four varieties.

Introduction

In this work twenty samples of "Soft Stone of the Berici Hills", aka "Vicenza Stone" or "Palladio Stone", are investigated as the starting point in the building of a model for the classification of their main varieties. The Soft Stone is a carbonatic material extracted from caves in the Berici Hills area located near Vicenza, in North-East Italy, and is widely employed in building activities since ancient times. Its name was made famous by the extensive use Andrea Palladio made of it in his villas, but architectural and decorative elements made of this material are still employed. The Soft Stone comes in different types, that can be related to external characteristics (mainly color, fossil inclusions and hardness), age origin or extraction place. Consequently, different approaches on the classification of the Soft Stones are found: in the traditional classification, aspect or provenance are privileged (e.g. "Giallo Dorato", "Bianco Avorio", "Pietra di Villabalzana", "Grigio di Grancona"); a classification proposed in 1976 based on the geological age classifies the Soft Stones in two groups: "Pietra di Vicenza" (Oligocene) and "Pietra di Nanto" (Eocene), the latter containing a subgroup made up of the stones quarried in the Nanto location, called "Pietra di Nanto p.d." (p.d. standing for "propriamente detta" that is "in strict sense") [1]; more recently a distinction based on the stone colour has been proposed ("White", "Yellow" and "Gray" groups with subgroups made up according to the stone origins) [2]. In a former study of the samples investigated here [3], a classification combining the two recent approaches has been proposed, dividing the samples in the two age-based groups "Pietra di Vicenza" and "Pietra di Nanto", with the two sub groups "White Vicenza" and "Coloured Vicenza", and "Nanto-like" and "Nanto p.d."; such classification was found to reflect the different non-carbonatic content of the Soft Stone varieties.

Materials & Methods

The twenty samples considered representative of the different Soft Stone varieties were analysed through diffuse reflection Fourier transform infrared spectroscopy (DRIFTS); the spectra, recorded by a Bruker Optik Vertex 70 spectrometer equipped with a Pike DiffusIR accessory in the 370 - 4000 cm^{-1} range with a resolution of 4 cm^{-1} and 500 scan average, were converted into Kubelka-Munk units and subjected to a 200-pts rubberband correction. To increase their representativeness, each stone specimen was sampled four times to give four independent spectra (suffixes r1, r2, r3 and r4 in the spectra labels).

A PCA was performed in the 900 – 1220 cm^{-1} range of the spectra to evaluate similarities and differences in the non-carbonatic content of the samples and to recognize the four groups mentioned above on which, finally, a SIMCA classification was run.

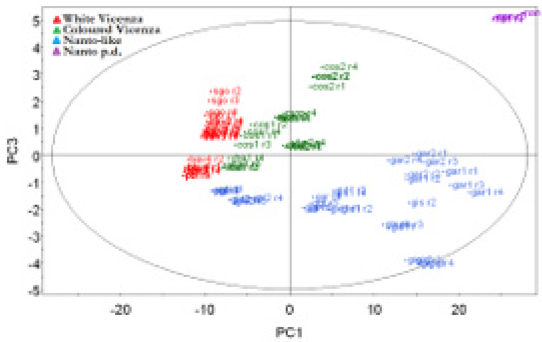

Fig.1; PC3 vs PV1 scores plot of the DRIFT spectra of the Soft Stone samples in the non-carbonatic range 900-1220 cm^{-1}

Results

The PCA analysis performed on the twenty samples of Soft Stone (each sampled four times) showed that all the variance could be explained by the first five PCs (0.759, 0.208, 0.024, 0.008, 0.001); of all the possible scores plot, the PC3 vs PC1 reported in Fig 1. allowed the best separation among the samples, as highlighted by the different colours employed in the labels adopted for the points representative of the samples.

A SIMCA was then conducted on the samples, divided in four classes corresponding to the different stone types. For each class a different number of PCs were employed in the modelling, as reported in Tab. 1 together with other results of the calibration.

Tab.1 SIMCA modelling of the twenty samples (each sampled four times) of Soft Stones of the Berici Hills divided in four classes according to their varieties.

	# of samples	# of PCs	Cumulative R^2	Cumulative Q^2
White Vi	5 x 4	3	0.998	0.998
Coloured Vi	6 x 4	4	1	0.999
Nanto-like	8 x 4	5	1	0.999
Nanto p.d.	1 x 4	2	0.991	0.978

As a final step all the samples were used in the validation procedure, which gave the results reported in Tab.2 showing that no sample was assigned to the wrong class while a few samples were not recognized as belonging to their variety.

Tab.2 Prediction results of the SIMCA analysis on the twenty samples of Soft Stone of the Berici Hills

	White Vi class	Coloured Vi class	Nanto-like class	Nanto p.d. class
White Vi samples	21/24	0/24	0/24	0/24
Coloured Vi samples	0/20	17/20	0/20	0/20
Nanto-like samples	0/32	0/32	27/32	0/32
Nanto p.d. samples	0/4	0/4	0/4	4/4

Conclusions

The DRIFT spectra of twenty samples of "Soft Stones of the Berici Hills" were investigated in the spectral range corresponding to the non-carbonatic content in order to build a model describing the four different varieties of this material. A SIMCA model on these samples proved the viability of this approach that will be the basis for a further analysis of an extended set of samples.

References

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