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Multiariate characterization, using the SIMCA method, of mortars from two frescoes in Chiaravalle Abbey ☆

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Abstract

The percentage of acid-soluble components (ASC) and the aggregate granulometric distribution in mortars from two frescoes (Gothic and Flemish wall paintings) from Chiaravalle Abbey were determined. Principal component analysis (PCA) of these data provided a "scores" plot where Gothic plaster samples were clearly grouped, and separate from Flemish plaster samples. Classification into the above two classes was achieved by the residual standard deviation values of all samples fitted into disjoint principal components (PC) models according to the SIMCA method. Furthermore the PCA scores for the "Flemish" class pointed out differences between painted and internal plasters, indicating the use of layers with different composition and function, while those for the "Gothic" class showed no grouping indicating either the use of a single mortar or inhomogeneous layers. The above findings confirm and extend previous results on the classification of mortars into groups with similar architectural function, pointing out the generality of the SIMCA classification for both historical attribution and conservation studies.

Keywords: Flemish art; Gothic art; Mortar; Principal component analysis (PCA); Plaster; Soft independent modelling of class analogy (SIMCA); Wall paintings

1. Introduction

The characterization of mortars used with different functions in artistic, architectural and archaeological hand work, generally involves quantitative determination of the mineral binder and of the sand aggregate by means of different parameters.

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A simple analytical procedure for characterization of mortars is based on the determination of a compositional parameter (the acid-soluble percentage) and of the aggregate granulometric fractions, after chemical separation from the binder [1]. The above procedure may be applied using small quantities of sample and is therefore particularly useful for the study of painted plasters (frescoes and other wall paintings). It minimizes sampling damage and is generally sufficient to provide significant data for the characterization of such non homogeneous materials.

As the chemical methods used for the quantitative separation of the aggregate from the mortar are generally based on acid attack, this procedure, providing multivariate data, can be safely adopted only for acid-resistant aggregates (e.g. basically with a silicate composition and, at the same time, when the binder is without hydraulic components). Both conditions were satisfactorily fulfilled in the two frescoes examined.

Previous studies [2] achieved multivariate characterization of mortars from painting decorations of the Cupola of Florence Cathedral by processing the analytical data through PCA classification according to the SIMCA (soft independent modelling of class analogy) method [3, 4]. This statistical procedure has been already applied in archaeometry for the classification of ancient Mesopotamian ceramics and clay [5] and of Roman pottery [6].

The previous work [2] pointed out the possibility of obtaining a satisfactory classification of mortars into groups of similar architectural function, such as mortars between the bricks, mortars for covering plasters, and mortars used for painted plasters, evidencing differences among areas painted by different artists. Furthermore in the above case no doubt could exist on the functional role of the mortar, the sampling being performed in large lacunas of the plasters where each sample could certainly be assigned a given function. The analytical procedure was the same as that described above, consisting in the determination of the percent acid-soluble component (%ASC) and of the aggregate granulometric distribution.

In the present study we report the multivariate characterization and SIMCA classification of mortars from two different wall paintings in a side chapel of the Chiaravalle Abbey (Milano). Analysis and characterization have been carried out on samples both from the external painted plasters and from the internal preparatory layers with the aim of reciprocal comparison between the two paintings in order to obtain a better understanding of plaster layering in the chapel.

2. Materials studied

The front wall of the chapel was painted in different periods. On the left part of the Chapel there is a Flemish fresco painting, representing Christ in front of Pilato, while the right side includes two scenes of a Gothic fresco (the nativity and a group of saints).

Samples (100–200 mg) of mortar were taken from areas with paint lacunas in order to cause minimum damage. The sample distribution was as follows: 14 samples at different depth from the Gothic area; 11 samples at different depth from the Flemish area.

A stratigraphic sampling was performed. Only the externally observable painted layer can be safely attributed to the corresponding (Gothic or Flemish) plaster, while the internal layer may belong to the same plaster or to different ones. Moreover, samples taken at the same depth may contain different plasters due to the inhomogeneous thickness of man-made layers.

3. Analytical methods

Following previously tested procedures [1] 100–200 mg of dry mortar were treated with 7 ml of 1.4 M HCl for 60 min at room temperature. The insoluble residue was centrifuged and washed with distilled water until neutrality of the solution. Percent quantities were calculated as follows:

$$\%ASC = 100(W_m - W_a)/W_m$$

where W_m is the weight of the dry mortar sample and W_a the weight of residue after acid attack and wash.

Such residue, dried to constant weight, was separated into seven granulometric fractions using seven 38 mm diameter sieves. The chosen series (Endecotts series DIN 4188 part 2) gives granulometric fractions which are significant for the characterization of the mortars from painted plasters.

Each of the seven granulometric fractions ($f_1 > 630$ μm; 630 μm $> f_2 >$ 400 μm; 400 μm $> f_3 >$ 250 μm; 250 μm $> f_4 >$ 160 μm; 160 μm $> f_5 >$ 100 μm; 100 μm $> f_6 >$ 63 μm; 63 μm $> f_7 >$ 50 μm; $f_8 <$ 50 μm) was dried, weighed and calculated as:

$$\%t_i = w_i/w_a \times 100$$

where t_i = weight percent of fraction i, w_i = weight of fraction i, and w_a = weight of the dried aggregate.

4. Statistical methods

The results of PCA depend on the scaling of the data; in SIMCA the variables are generally autoscaled by multiplying the variables by appropriate weights in order to give them the same importance. Alternatively, block weighting can be used in order to give the same importance to group of variables. In the present work block weighting was in order to give 50% importance to the only chemically derived variable (% *ASC*) and 50% to the group of granulometric measurements.

PCA using the SIMCA method and its applications have been presented in detail [7, 8], also in relation to mortar classification [2]. Consequently the statistical procedure will only be summarized here. The SIMCA method carries out PCA on a data matrix containing elements x_{ik}, where index k is used for the experimental measurements (variables) and index i for the samples (objects). Each element is described by Eq. (1), where the number A of significant cross terms (components), and the parameters p_{ak}, t_{ia} are calculated by minimizing the squared residuals e_{ik}, after subtracting $\bar{x}_k$ (the mean value of the i experimental quantities x_k).

$$x_{ik} = \bar{x}_k + \sum_{a=1}^{a=A} t_{ia} p_{ak} + e_{ik} \tag{1}$$

In this model, parameters $\bar{x}_k$ and p_{ak} (the loadings) depend only on the experimentally measured variables and t_{ia} (the scores) only on the compounds. The deviations from the model are expressed by the residual e_{ik}. The number of significant components (A) is determined using the cross-validation technique [3]. The relevance of each variable in describing the mathematical model is given by its modelling power $MPOW$, where S_k is the residual standard deviation for each variable after A dimension and after dimension zero.

$$\mathrm{MPOW}_k = 1 - \left[\frac{S_k^{(A=A)}}{S_k^{(A=0)}}\right] \tag{2}$$

5. Results and discussion

Mortar and plaster samples were characterized by nine variables: the % acid soluble component (ASC) and the granulometric distribution of the aggregate into eight different portions. The % granulometric distribution does not sum to 100% due to sample loss during the analysis, ranging from 1% to 9%. The latter loss might appear to be high from an analytical point of view. However, this is not relevant to the following statistical treatment, which fitting the data by a "soft" model, will anyway discard information from the analytical data matrix. Moreover variable sample loss overcomes the limitations due to the closure problem in the application of PCA to percentage data [9–11].

The %ASC and the granulometric distributions are recorded in Table 1, together with additional information useful for classification. In order to carry out the PCA, the data were arranged into a matrix with the 25 mortar samples as "objects" and the physicochemical measurements (%ASC and 8 granulometric percentages) as "variables". Each of the 225 elements of the matrix is indicated in Eq. (1) as x_{ik}

The SIMCA classification was achieved in two steps:

(i) Pattern recognition by PCA on the whole data set

This procedure provided a simplified picture of the multivariate data structure, by means of the loadings plot (related to the variable information content) and of the scores plot (an idea of the samples grouping).

(ii) SIMCA classification

Disjoint PCA models were calculated on each homogeneous data subset evidenced by the whole set scores plot and samples classified according to their distance from the appropriate PCA model.

Table 1
Classification of mortars

Sample	Painter [a]	Depth [b]	Function [c]	PCA variables 1 %ASC	2 > 630 µm	3 630 µm–400 µm	4 400 µm–250 µm	5 250 µm–160 µm	6 160 µm–100 µm	7 100 µm–63 µm	8 50 µm	9 < 50 µm
1	Gothic	0–4 mm	PP	50.1	13.2	7.9	7.2	5.3	2.9	3.0	1.5	9.8
2	Gothic	4–10 mm	IP	47.0	5.2	14.8	9.7	5.1	3.0	3.0	1.2	11.0
3	Gothic	0–4 mm	PP	46.2	5.3	13.9	8.0	6.4	3.7	4.0	1.6	10.9
4	Gothic	4–11 mm	IP	62.7	8.6	7.5	6.1	3.8	1.7	2.5	0.6	6.5
5	Gothic	0–6 mm	PP	61.2	9.1	8.3	6.2	4.2	2.0	3.6	0.7	4.7
6	Gothic	6–15 mm	IP	68.1	3.3	8.1	6.7	3.9	1.8	2.2	0.6	5.2
7	Gothic	0–10 mm	PP	69.5	4.1	8.2	5.7	3.4	1.7	2.3	0.7	4.5
8	Gothic	0–4 mm	PP	46.4	13.7	11.2	8.8	5.0	2.4	3.3	0.9	8.3
9	Gothic	4–10 mm	IP	70.2	5.4	6.9	5.4	3.2	1.4	1.8	0.8	4.9
10	Gothic	4–15 mm	IP	59.8	6.7	10.2	7.3	4.1	2.2	2.5	0.9	6.3
11	Gothic	0–10 mm	PP	68.6	8.2	5.4	5.0	3.7	1.9	2.5	0.8	3.9
12	Gothic	10–13 mm	IP	61.0	6.1	9.0	6.6	4.4	2.4	4.0	0.9	5.6
13	Gothic	0–10 mm	PP	60.3	7.7	7.3	7.4	4.8	2.3	3.1	1.1	6.0
14	Gothic	10–15 mm	IP	63.9	9.4	7.6	5.2	3.4	1.9	2.9	0.6	5.1
15	Flemish	0–6 mm	PP	33.7	2.5	9.1	14.0	14.2	7.2	7.8	1.9	9.6
16	Flemish	6–9 mm	IP	31.5	5.1	19.5	13.1	8.6	4.5	4.7	1.6	11.4
17	Flemish	9–12 mm	IP	28.9	12.8	15.1	9.0	7.4	3.5	5.5	2.8	15.0
18	Flemish	0–2 mm	PP	28.5	2.4	12.3	14.2	12.8	8.1	8.3	2.7	10.7
19	Flemish	4–8 mm	IP	41.1	1.3	14.0	9.3	6.4	3.5	5.5	1.9	17.0
20	Flemish	4–10 mm	IP	37.8	13.6	10.8	9.3	6.4	4.0	4.2	1.5	12.5
21	Flemish	0–2 mm	PP	35.5	1.7	10.8	13.1	12.6	6.6	7.9	2.1	9.7
22	Flemish	2–4 mm	IP	30.7	20.6	12.7	10.8	7.0	3.2	4.0	1.9	9.1
23	Flemish	0–2 mm	PP	31.2	2.6	10.5	14.5	13.9	7.1	7.2	1.9	11.1
24	Flemish	2–6 mm	IP	31.1	8.8	20.3	16.0	8.5	3.2	3.9	0.8	7.4
25	Flemish	6–10 mm	IP	29.9	23.5	14.8	9.9	4.4	2.7	3.0	1.5	10.3

[a] Gothic: from the Gothic areas; Flemish: from the Flemish area; [b] Sampling depth; [c] PP: painted plasters; IP: internal plasters.

5.1. Pattern recognition

The PCA of the entire data matrix gave a model comprising two significant principal components (Table 2). The first component explained 48.1% of the total variance and the second one a further 19.2%; the planar model thus accounted for 67.3% of the total variance. A third component was not significant according to cross validation [3].

Table 3 reports the variable parameters, i.e. the weights (w), the averages ($\bar{x}$), the loading values (p_1 and p_2) and the modelling powers after two PCs for variable 1 (%*ASC*) and for variables 2–9, the granulometric variables.

The modelling powers, giving an estimate of how much each single variable contributes to the two PC model, show that variables 3, 8, and 9 are not relevant in describing the mathematical model. Moreover, the second PC is required to describe the granulometric variables, mainly 5, 6 and 7. The PCA loadings plots (Fig. 1) shows that the information provided by the chemical variable 1 (direction *a*) lies in a direction orthogonal with respect to that (b) of granulometric variables 2–8; variable 9, very close to zero, has little systematic variation.

The t_1 and t_2 values (the "scores" for samples 1–25) are listed in Table 4.

The plot of t_1 vs t_2 for all 25 examined samples ("scores plot", Fig. 2) shows a clear

Table 2
PCA for classes A–C [a]

Class	Objects in the reference set [b]	% Variance [c]
A	1–25	67.3(48.1 + 19.2)
B	1, 2, 4–7, 9–14	56.2(41.9 + 14.3)
C	15–19, 21–25	70.1(44.1 + 26.0)

[a] Variables 1–9 were included in all classes; weights for each class are recorded in Table 3; [b] For numbering see Table 1; [c] Total variance explained; % variances for 1st and 2nd PC reported in parentheses.

Table 3
Weight (w), PC loadings (p) and modelling power (MPOW) for variables 1–9 in class A, and weights for classes B and C

Var [a]	Class A					Class B	Class C
	w	p_1	p_2	$MPOW_1$	$MPOW_2 - MPOW_1$	w	w
1	0.065	0.920	0.359	0.759	0.198	0.137	0.266
2	0.038	0.145	−0.372	0.080	0.303	0.061	0.030
3	0.079	0.098	−0.179	0.023	0.038	0.091	0.066
4	0.132	−0.073	0.299	0.003	0.152	0.184	0.101
5	0.096	−0.184	0.435	0.148	0.586	0.413	0.068
6	0.168	−0.196	0.420	0.172	0.561	0.723	0.117
7	0.168	−0.115	0.455	0.040	0.504	0.257	0.123
8	0.519	−0.152	0.186	0.091	0.050	0.720	0.435
9	0.126	0.092	0.068	0.000	0.000	0.346	0.085

[a] For variable numbering see Table 1; modelling powers calculated by use of Eq. (2).

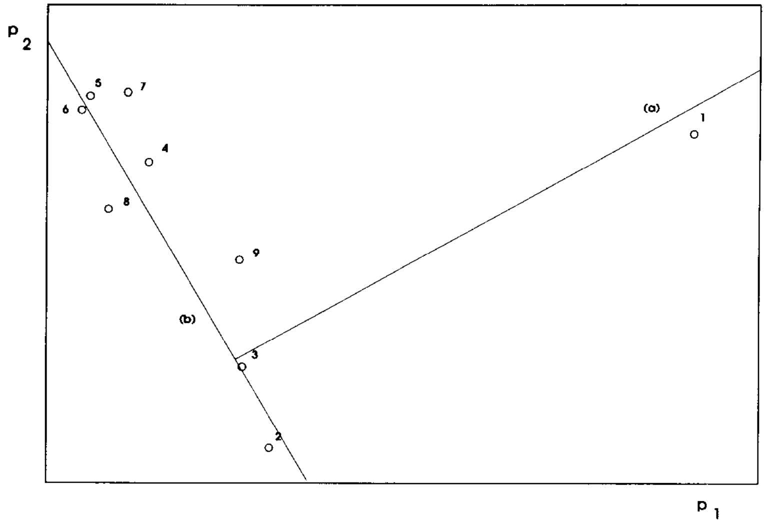

Fig. 1. p_1–p_2 "Loadings" plot for class A.

grouping of the Gothic samples on the right of the plot. Therefore the first score t_1 differentiates Gothic mortars from Flemish ones, regardless of their function (i.e. covering or painted plasters). Moreover Flemish mortars, located on the left in Fig. 2, exhibit a clear grouping of surface Flemish samples (15, 18, 21, 23) in the upper left located on the left in Fig 2 of the plot, indicating that the second score differentiates Flemish painted plasters (FPP), characterized by high t_2 values, from Flemish covering plasters (FIP). Fig. 2, giving a clear insight into the total data set structure, provides the basis for SIMCA classification.

5.2. *SIMCA classification*

SIMCA classification implies calculation of PCA models for two separate classes (Gothic and Flemish samples, classes B and C, respectively), fitting of new samples (objects) into each model, and classification of unknown samples by means of their residual standard deviation (RSD). Table 2 reports the samples used as training set for classes B and C (Gothic and Flemish samples respectively). Three objects, (3, 8 and 20), whose appurtenance to a given class is not evident from Fig. 2, were kept out of the training set to be used as a test set for both models.

Table 2 reports the results of the PCA for class B containing 108 elements (12 objects, 9 variables) and for class C containing 90 elements (10 objects, 9 variables). The explained variances are similar to those found for class A. The weights adopted in PCA, calculated by block weighting (see section 4), are recorded in Table 3.

Fig. 3, the scores plot for class B, shows no clear grouping of the samples according to sampling depth (painting plaster, internal plaster), which might be due to the use of similar mortars for internal and external layers or to an inhomogeneous layer thickness.

Table 4
PC "Scores" (class A), and residual standard deviations (classes B and C) for mortar and plaster samples 1–25

Sample[a]	Class A		Class B	Class C
	t_1	t_2	*RSD*[b]	*RSD*[c]
1	0.188	−0.263	0.09	[0.44]
2	0.114	−0.316	0.04	[0.26]
3	−0.070	−0.047	[0.29]	[0.23]
4	1.146	−0.142	0.22	[0.61]
5	0.935	0.047	0.16	[0.58]
6	1.281	0.485	0.13	[0.68]
7	1.374	0.370	0.16	[0.71]
8	0.184	−0.639	0.22	[0.32]
9	1.470	0.231	0.13	[0.75]
10	0.866	−0.026	0.07	[0.54]
11	1.271	0.350	0.06	[0.78]
12	0.783	0.348	0.20	[0.58]
13	0.759	0.398	0.15	[0.49]
14	1.193	−0.114	0.20	[0.64]
15	−1.445	1.147	[1.20]	0.07
16	−1.001	−0.349	[0.55]	0.11
17	−1.077	−0.671	0.22	0.16
18	−1.770	0.873	[1.15]	0.10
19	−0.399	0.115	[0.52]	0.06
20	−0.520	−0.511	0.12	0.18
21	−1.295	1.071	[1.08]	0.06
22	−0.911	−1.012	[0.61]	0.12
23	−1.504	0.856	[1.10]	0.06
24	−0.882	−0.691	[0.41]	0.15
25	−0.688	−1.521	[0.98]	0.09

[a] For additional information on samples see Table 1; [b] Samples with *RSD* smaller than $1.5 \times 0.17 = 0.26$ belong to class B, other samples in parentheses; [c] Samples with *RSD* smaller than $1.5 \times 0.12 = 0.18$ belong to class C, other samples in parentheses.

Grouping of superficial samples characterized by low t_2 values (15, 18, 21, 23) in the lower left part of Fig. 4 (the scores plot for class C) suggests the interpretation of t_2 as an index for sampling depth in Flemish mortars (see Table 1).

The statistical classification procedure of the SIMCA program implies fitting of all samples (learning + test sets) to subset classes B and C. In order to assign samples (objects) to a given class, each sample should be fitted into the class PCA model and its residual standard deviation (RSD) calculated [7]. The object belongs to a given class if its RSD is smaller than 1.5 times the class RSD (in the present case $1.5 \times 0.17 = 0.26$ for class B and $1.5 \times 0.12 = 0.18$ for class C).

RSD values, reported in the Table 4 and plotted in Fig. 5, correspond to the orthogonal distances between each sample (object) and class B. Assuming as belonging

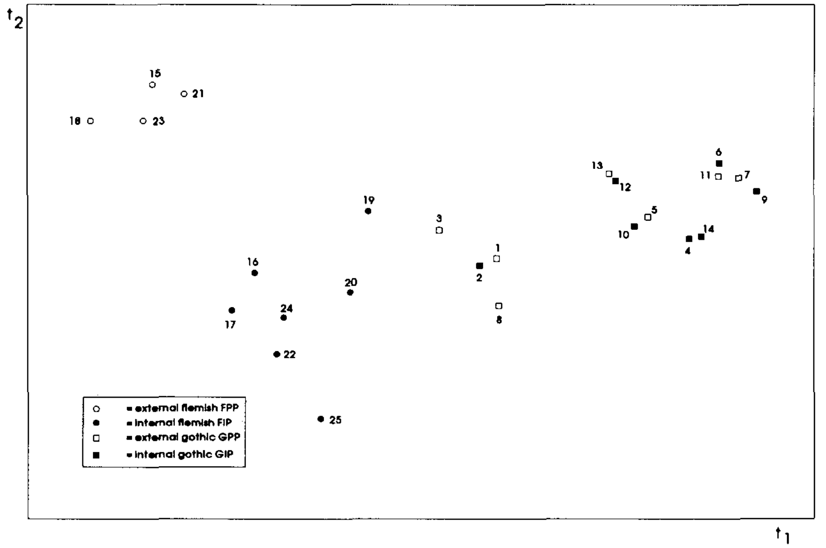

Fig. 2. t_1–t_2 "Scores" plot for class A.

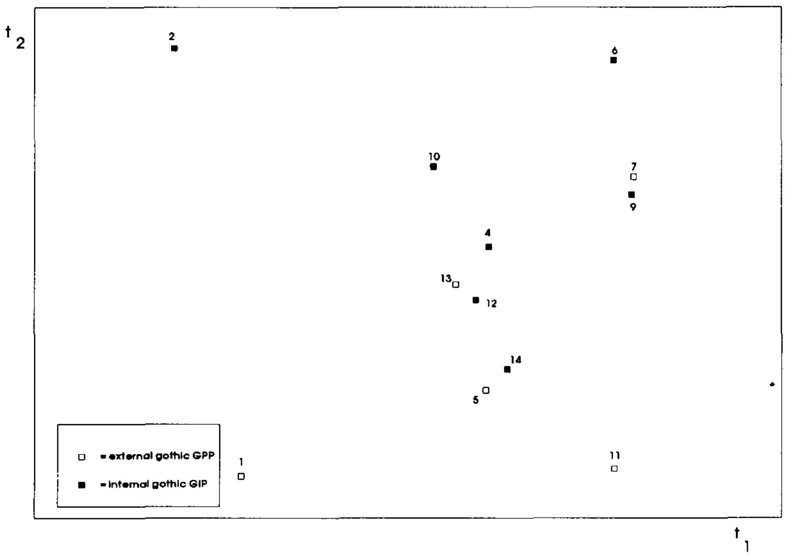

Fig. 3. t_1–t_2 "Scores" plot for class B.

to class B all samples with RSD < 0.26 and to class C those with RSD < 0.18, the SIMCA method correctly classifies all samples in the reference set of both classes apart from 17, which could be attributed to either class. As regards test set samples, 8 is correctly assigned to class B, while 3 and 20 remain with uncertain assignment.

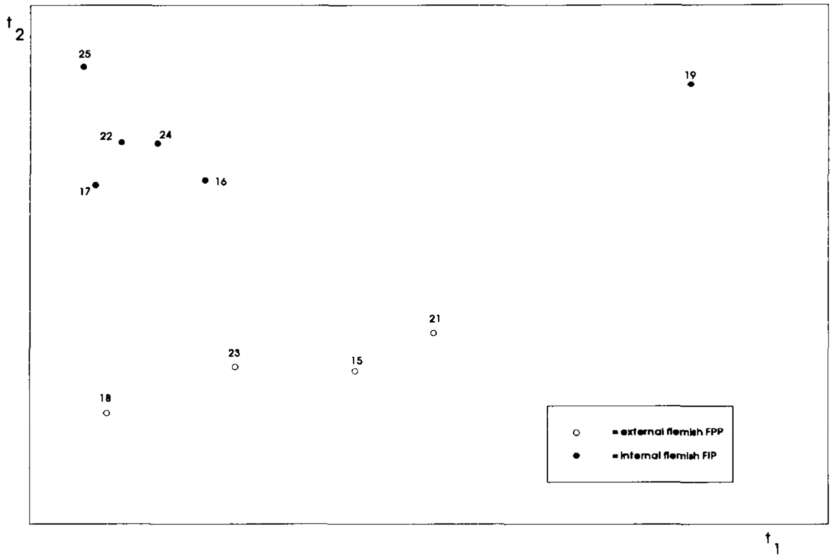

Fig. 4. t_1–t_2 "Scores" plot for class C.

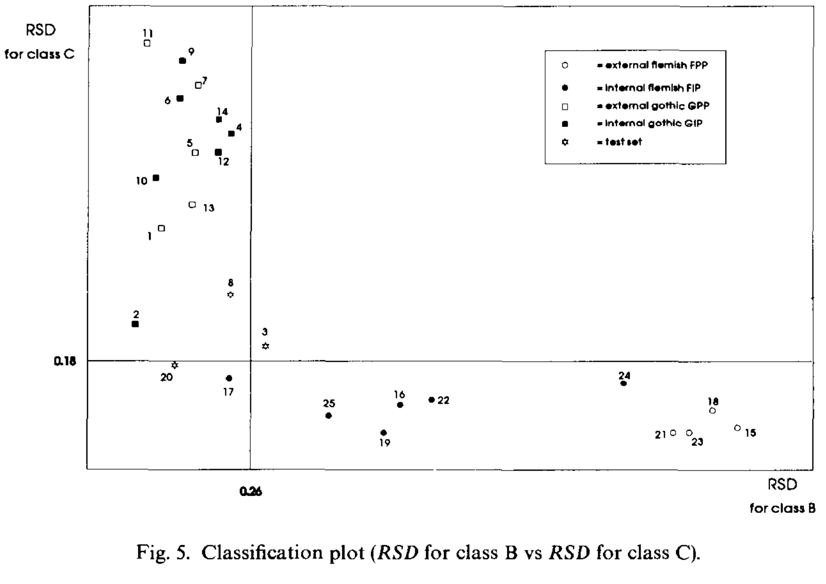

Fig. 5. Classification plot (*RSD* for class B vs *RSD* for class C).

6. Conclusions

PCA of 25 mortar samples from the Chiaravalle Abbey wall paintings, characterized by the acid soluble component percentage and by eight granulometric fractions provided the following information:

(a) actual analytical classification into two different groups of mortars belonging, respectively, to the Gothic painting and to the Flemish one, regardless of their function (painting or internal plasters), by means of the first PC scores in the overall model;

(b) differentiation of Flemish mortars into painted plasters and internal plasters by means of the second PC scores both in the overall model and in the Flemish class model; and

(c) no clear indication of mortar function in the Gothic area.

These results can be given in the following interpretation:

(a) Gothic and Flemish artists actually used different mortars both internally and for painting;

(b) Flemish artists used different mortars as the internal plaster and as the painted plaster;

(c) Gothic artists either used the same mortar for the internal and the external plasters or applied the internal plaster in such an inhomogeneous thickness that it is not possible to distinguish it from the painted plaster because samples taken at definite depth are unavoidable mixtures of the two plaster layers.

The above findings confirm and extend previous results on the classification of mortars into groups with similar architectural function pointing out the generality of the SIMCA classification for both historical attribution and conservation studies.

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