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A chemometric approach to the characterisation of historical mortars

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Abstract

The compositional knowledge of historical mortars is of great concern in case of provenance and dating investigations and of conservation works since the nature of the raw materials suggests the most compatible conservation products. The classic characterisation usually goes through various analytical determinations, while conservation laboratories call for simple and quick analyses able to enlighten the nature of mortars, usually in terms of the binder fraction. A chemometric approach to the matter is here undertaken. Specimens of mortars were prepared with calcitic and dolomitic binders and analysed by Atomic Spectroscopy. Principal Components Analysis (PCA) was used to investigate the features of specimens and samples. A Partial Least Square (PLS1) regression was done in order to predict the binder/aggregate ratio. The model was applied to historical mortars from the churches of St. Lorenzo (Milan) and St. Abbondio (Como). The accordance between the predictive model and the real samples is discussed.

Keywords: Historical mortars; Principal Components Analysis; Partial Least Square; Characterisation

1. Introduction

The production of mortars is among the oldest building techniques experimented with by human beings. Due to the relative simplicity of the preparation, to the availability of raw materials and to the important aesthetic and structural functions, mortars have always played an important role in architecture since prehistory, when rudimentary mud was used as protective of wooden huts [1]. Technological knowledge increased until the well-known examples of Roman architectures, described by Vitruvius and Pliny [2,3]. Uses ranged from plasters to bedding for brick masonry, mosaics, from wall paintings preparation layers to fine decorative elements, from integration of decayed elements of stone monuments to civil buildings such as cisterns and wells [4]. Mortars have been frequently seen as disposable materials applied to better protect masonry exposed to environment and pollution, i.e. materials to be recurrently renewed, but they have been recently re-evaluated as artistic elements, during the 19th century, especially with the discovery of modern cements and concretes.

Traditionally, mortars are composite materials whose structural properties are due to the mixture of silica or carbonate sand (*aggregate*) with a *binder* fraction [1,5–7]. Binders are mainly of two kinds: aerial or hydraulic, depending on the mechanism of hardening. The formers derive from limestones, calcined and hydrated to produce calcium and magnesium hydroxides, which set upon reaction with carbon dioxide in air. On the other hand, when limestone contains high percentages of clay in addition to calcium and magnesium carbonates, the binder is defined as hydraulic, as it hardens in presence of water. In both cases the binder contributes to workability and elasticity of mortars, while the aggregate contributes to mechanical properties, acts as filler and controls problems arising from shrinkage.

The characterisation of historic mortars, produced until the last century, is of main concern in the field of Cultural Heritage in order to evaluate production technologies, the conservation state of materials and plan an appropriate conservation work. Investigation of binder and aggregate composition has an historical value as it may suggest the provenance of raw materials and increase the knowledge of the technology skill of a specific period. From the conservation point of view, binder/aggregate ratio (referred to as B/A in the text) is of high interest, as it can guide the planning of conservation works. Together

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with some other properties, e.g. the porosity, it allows to prepare a mortar as much compatible as possible with the masonry structure, which could be used for integration in case of degraded materials [8]. Nowadays negative interactions may occur between the original materials and the ones used during remedial interventions.

As far as mortars are complex systems, different approaches can be used for their characterisation, as widely reported in literature. Actually the reconstruction of the original composition is quite complex and requires the application of various and complementary techniques [1,9–12]. X-ray Diffraction (XRD) clarifies the nature of the mineralogical phases present in the sample [13–15]. Fourier Transform Infrared Spectroscopy (FTIR) points out the nature of the binder fraction [1,5] and of salts and decay products eventually present in the mortars (nitrates, nitrites, sulphates, carbonates). Electronic Microscopy equipped with X-ray microprobe allows morphological and elemental investigation [1,9,16], while Thermal Analysis estimates the amounts of the binder fraction previously identified [1,6,7,17]. Through Ionic Chromatography analyses it is possible to obtain quantitative data on the soluble salts in the samples. Major and trace ions are commonly investigated by complexometric titration and Atomic Spectroscopy [9], while structural information may come from porosimetric analyses. In most of the cases, the two main fractions present in the mortars must be separated and dissolved by complex acid attacks [18–21], although an effective and quick procedure has recently been proposed [22]. It must be kept in mind that the measured value of B/A depends on the type of acid attack chosen for the characterisation [23]. As far as the analyses of metals are concerned, investigations are usually focused on calcium and magnesium, as representative elements of aerial binders, and on silicon, iron and aluminium, as characteristic of both hydraulic fraction and aggregate. Trace elements are investigated in case of provenance studies.

As previously shown, the traditional characterisation of mortars involves various techniques and takes usually a lot of time, while conservation laboratories deal commonly with high numbers of samples and must plan proper conservation works in the shortest time possible. Conservators call for quick screening tests able to distinguish different types of mortars, e.g. to discriminate between calcitic and dolomitic or hydraulic mortars thanks to few data, e.g. the B/A value.

In this work a chemometric approach to this discrimination is discussed. The peculiarity of chemometric methods lies in the recognition of few parameters able to describe and characterise multivariate complex systems whose complete knowledge usually requires a large number of analyses. Moreover, they provide an easy-to-see way to analyze and understand rationally the great amount of data that conservation of cultural heritage requires. Chemometric elaboration of compositional data is well known in conservation field, with its contribution for instance in the determination of organic binder in wall paintings [24], in provenance studies and dating in archaeological objects [25–27]. An overview of application of chemometrics for the characterization and conservation of cultural heritage has been proposed [28]. Recently multivariate methods have been applied to historical mortars. Physicochemical data such as aggregate granulometric distribution and percent acid-soluble component were used by Giuffrida et al. [29] for discriminating mortars for plasters from mortars used for painted plasters and by Musumarra et al. [30] to distinguish between mortars used in Gothic painting and those used in Flemish painting in Chiaravalle Abbey. In both cases a SIMCA (Soft Independent Modelling of Class Analogy) approach was used. While in SIMCA method classes of samples have to be known, PCA method allows investigation of data sets in order to find out samples with similar features, i.e. samples grouping. Principal Component Analysis was carried out by Moropoulou [1,31] in order to classify historical mortars by some physicochemical characteristics, such as thermal and thermogravimetric data, mercury intrusion porosimetry and mechanical strength test results.

In this work a PCA was used to investigate features of specimens and historical samples and a PLS1 (Partial Least Squares regression for one y-variable) approach was undertaken for the elaboration of compositional data of mortar specimens previously prepared and analysed by Atomic Spectroscopy [22]. PCA [32] allows reduction of the number of variables used for the description of the system into a set of new variables (Principal Components—PC) that contains all the relevant information. The principal components are linear combinations of the original variables and they are orthogonal, i.e. uncorrelated. The first principal component accounts for as much of the variability in the data as possible, and each succeeding component accounts for as much of the remaining variability as possible. PCA provides an intuitive graphical representation of the data, making the evaluation of results easier. PLS regression [33,34] combines features from principal component analysis and multiple regression. It attempts to fit a model to observed data in order to quantify a relationship between the same data and any interesting property (in this case the B/A ratio). PLS can be used initially to suggest if relationships might or might not exist. If a linear relationship exists, the fitted model may then be used to predict values of the property in new samples, as in this case. To check how well the model will perform on new data, a validation step is fundamental.

Specimens were prepared with calcitic, dolomitic and hydraulic binders in order to simulate historical and modern types and analysed by an analytical procedure previously optimised [22]. The same method was applied on historical samples coming from two important monuments of Northern Italy. The results were arranged by chemometric methods in order to find distinct groups of samples depending on the nature of the binder fraction. The methodology distinguishes historical mortars, which are aerial and those which are hydraulic and allows characterisation of the calcitic or dolomitic nature of the binder fraction. Thus, the data were used to build a predictive model that was applied on the historical mortars, in order to find out the properties of high interest in the screening step and foresee the nature of the binder. Predictive model is able to characterise mortars in term of binder fraction with a minimum number of analyses.

2. Experimental

2.1. Mortar specimens

Two sets of mortar specimens were prepared [22] with two different types of binder and the same quartz sand as aggregate (fine granulometry: 0.125–0.9 mm). The composition, representative of historical mortars normally recovered in Northern Italy, is shown in Table 1, while the preparation of the specimens is described in details elsewhere [22]. The first group of specimens was prepared employing an aerial binder, i.e. hydrated calcitic (CaO 99.00%, MgO 1.00%) and dolomitic (CaO 47.42%, MgO 31.62%) lime, while the second set was prepared with a commercial hydraulic binder with both organic and inorganic additives. Four specimens composed respectively by three chosen kinds of lime (7a, 8a, 4 h) and the sand alone (labelled as S) were also analysed as a reference.

2.2. Historical samples

St. Lorenzo is one of the most important Basilicas in Milan. The first nucleus dates back to the 4th century. It includes various architectural marble elements, coming from the close Roman amphitheatre. In the following centuries the building suffered many fires and underwent further modifications. The masonry of bricks is covered by plasters. As far as St. Abbondio is concerned, it was built in the Romanesque period on the site of a palaeochristian church. The church is considered a masterpiece of Romanesque style, after the demolition of the added parts carried on in the 19th century.

The samples, collected by means of a small chisel in areas representative of the building materials, were labelled as shown in Table 2.

2.3. Procedure of chemical dissolution

Specimens and samples were dissolved by a microwave-assisted acid digestion, formerly optimised [22] and summarised in Table 3. A weighed amount of dried mortar sample (1.00 g) was transferred in a sealed Teflon vessel and treated with 2.5 mL of HCl (37% Fluka TraceSelect) and 2 mL of ultrapure water in a Milestone MLS-1200 microwave system equipped with a temperature control unit. The instrument allowed the simultaneous attack of eight samples in around 30 min.

Solutions were filtered on Whatman GF/C fibre-glass round filters. The acid soluble part was then analysed by ICP-OES and ET-AAS.

In the case of analysis of historical samples, supposed to be composed with silica aggregate, the residue fraction was accurately washed, dried and weighted in order to calculate values of B/A in the traditional way (from the percentage of acid soluble and the residue fractions after acid attack of the mortars). The obtained values were compared with those calculated by the PLS model in order to verify the good working of the model.

Table 1
Composition of mortar specimens (B/A = binder/aggregate ratio; cal. = calcitic; dol = dolomitic; hydr = hydraulic)

Specimen	1a	2a	3a	4a	5a	6a	7a	8a	1 h	2 h	3 h	4 h
Binder	cal	dol	cal	dol	cal	dol	cal	dol	hydr	hydr	hydr	hydr
B/A	1:1	1:1	1:2	1:2	1:3	1:3	–	–	1:1	1:2	1:3	–

Table 2
Description of the historical samples

Site	Monument	Samples
Milano	St. Lorenzo's Basilica	SL1, SL2, SL3, SL4, SL5
Como	St. Abbondio's Basilica	SA1, SA2, SA3, SA4, SA5

2.4. Instrumentation

Fe and Al analysis was performed by ET-AAS using the analytical lines at 248.3 nm for Fe and at 309.3 nm for Al. All analyses were performed on a GBC Avanta G double beam spectrometer, equipped with a GBC GF 3000 graphite furnace system and a GBC PAL 3000 auto-sampler. The detection limits (using argon for 20 μL injection) were 0.08 ng/mL for Fe and 0.25 ng/mL for Al.

ICP-OES spectra were collected with a Jobin Yvon Jy24 spectrometer, equipped with a Meinhard nebulizer (spectral lines: 393.366 nm Ca, 279.533 nm Mg, 252.411 nm Si). The detection limits were 0.02 ng/mL for Ca, 0.05 ng/mL for Mg and 0.01 ng/mL for Si.

Relative instrumental standard deviation (RSD, $n = 3$) for all the metals were among 0.5% and 4.0%.

2.5. Data treatment

The resulting data were treated in Microsoft Excel in order to obtain the weight percentages of species and then imported to Unscrambler Version 9.1.2 (CAMO AS, Trondheim, Norway). Data pre-treatment, Principal Components Analysis (PCA) and Partial Least-Squares Regression (PLS1) were done as implemented in this software. Calibration models were constructed by cross-validation (using leave-one-out approach) and the optimum number of PLS components was evaluated by the default Unscrambler criterion and by the plot of residual variance versus number of factors. The accuracy of the calibration model was described by the root mean square error of calibration (RMSEC) and the root mean square error of prediction (RMSECV). The latter can be interpreted as the average prediction error, expressed in the same units as the original response values, in this case the B/A ratio.

Table 3
Microwave assisted digestion of mortar specimens

Step	T_{max} (°C)	Power (W)	Time (min)
Pre-heating	75	250	3
Pause	–	0	1
Mineralisation	150	500	10
Cooling down	–	0	15

3. Results and discussion

All the specimens and the historical samples were dissolved by the acid attack and the solution analysed by ICP-OES and ET-AAS. They were characterized by five variables: the weight percentages of calcium, magnesium, silicon, iron and aluminium in the soluble fraction (labelled as %Ca, %Mg, %Si, %Fe and %Al in PCA loading plot). Data are shown in Table 4.

3.1. PCA elaboration

In order to carry out the PCA and to study the features of specimens and samples, data were arranged into a matrix characterised by samples (specimens and historical samples) as objects (rows) and chemical measurements (as weight percentages) as variables (columns). Autoscaling was applied as a pretreatment prior to the calculation. Interpretation of the results was carried out looking at the score plot, which gives information about samples, and at the loading plot, which represents the variables in the new space formed by the principal components. The investigation of both graphs allows recognizing similarities between samples and the role of the variables in the samples grouping detected. The first model (78% of the information supplied by the first two PC) was built only with data obtained by the chemical analysis of the specimens. Score plot shows that the considered chemical variables are able to find groups depending on the nature of the binder fraction (Fig. 1).

Actually specimens prepared with hydraulic binder (1 h, 2 h, 3 h and 4 h) are located at positive values of PC1, while specimens prepared with calcitic (7a) or dolomitic (8a) binder are located in the upper area of the graph (highly positive value of PC2). The sample of sand (S) is separated from the specimens coming from the mixture of hydrated lime and aggregate (1a–6a).

Table 4
%Ca, %Mg, %Al, %Fe and %Si composition of the acid soluble fraction (weight percentages in the sample) of specimens and historical samples [LOD=limit of detection]

	% Ca	% Mg	% Al	% Fe	% Si
1a	23.0	0.50	0.31	0.58	0.026
2a	14.0	8.24	0.37	0.64	0.026
3a	15.5	0.25	0.42	0.79	0.027
4a	9.7	5.99	0.39	0.76	0.028
5a	12.5	0.25	0.47	0.91	0.022
6a	6.7	3.99	0.50	0.92	0.021
7a	41.9	0.25	0.02	0.02	0.021
8a	25.7	16.5	0.09	0.05	0.012
1 h	37.6	1.89	2.64	0.98	<LOD
2 h	27.2	1.54	2.05	1.05	0.006
3 h	17.8	1.09	1.49	1.03	0.008
4 h	28.1	3.16	4.32	0.60	<LOD
S	0.6	0.61	0.80	0.80	0.032
SL1	6.2	2.59	0.57	0.44	0.037
SL2	6.1	1.98	0.60	0.55	0.028
SL3	11.1	2.20	0.46	0.37	0.013
SL4	7.6	2.61	0.36	0.37	0.038
SL5	8.5	3.85	0.41	0.42	0.016
SA1	14.9	2.25	0.19	0.70	0.028
SA2	12.5	2.04	0.26	0.48	0.026
SA4	14.4	2.09	0.29	0.41	0.013
SA5	15.0	1.96	0.25	0.50	0.016
SA3	7.5	1.22	0.32	1.03	0.020

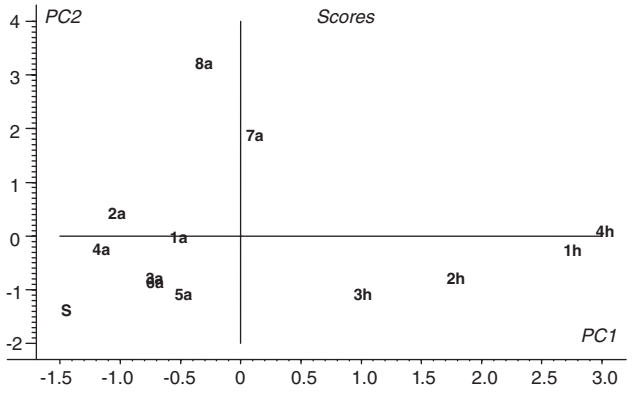

Fig. 1. PCA on specimens (score plot).

A second model was built with chemical data from specimens and historical samples in order to find out similarities or different behaviours. The score plot (70% of the variability of the system explained by the first two PC) shows that historical samples and specimens built with aerial binder are placed in the same area of the graph (Fig. 2).

As concerns the considered chemical variables, the two sets of historical samples have very similar features and both are different from specimens built with hydraulic binder.

Focusing on historical samples and specimens built with aerial binder, an interesting result comes out from a following PCA calculation: in the score plot (73% of information supplied by the first 2 PC) samples are located depending on the B/A ratio and on the composition of the binder (Fig. 3).

The specimen constituted of sand only is located at high positive values of PC1, while those of calcitic and dolomitic binder at high negative values. So, along this axis specimens and samples are located according to their B/A ratio, which increases from right to left. Actually, values of PC1 are quite similar for couples of specimens that have the same B/A value as 6a and 5a (1:3), 4a and 3a (1:2) and 2a and 1a (1:1). Interpretation of loading plot together with score plot confirms these results (Fig. 4). As shown in the plot, at positive values of

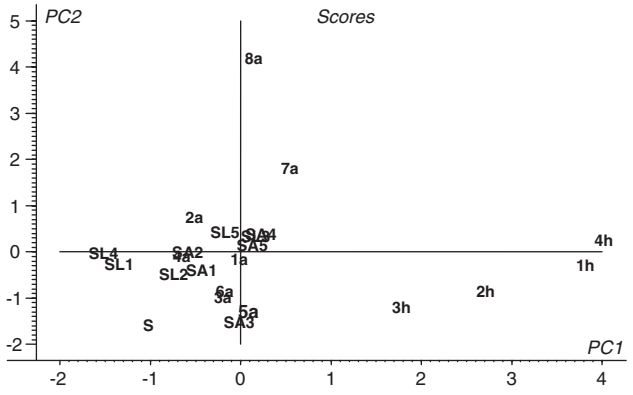

Fig. 2. PCA on specimens and historical samples (score plot).

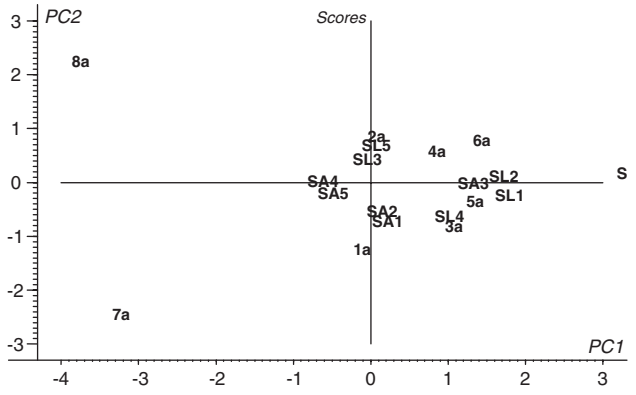

Fig. 3. PCA on specimens (aerial binder) and historical samples (score plot).

PC1 variables related to chemical composition of sand are placed, while at negative values of the same axis variables that characterize binder fraction are located.

Score plot gives another interesting result. Along PC2 specimens and samples are located according to the nature of lime used in the aerial binder preparation. Specimens and samples built with dolomitic and calcitic binder take place respectively at positive and negatives PC2 values. Looking at the loading plot again, percentage of magnesium is found at positive PC2 value whilst at negative value of the same axis percentage of calcium is located.

The models previously discussed seem to be able to study the properties of historical mortars from specimens' features. The determination of five analytes in the solution obtained by a quick acid attack of samples can suggest the kind of binder used for the preparation of mortars, i.e. hydraulic or aerial, in a simple graphical way with a PCA model. Furthermore PCA score plot allows to distinguish in an easy-to-see way dolomitic or calcitic binder in specimens and samples. This is particularly convenient in case of plenty of samples to investigate, when to handle with a lot of chemical data is necessary.

3.2. PLS elaboration

Historical samples and specimens could be correlated by PCA in a qualitative way. The following goal was to clarify the correlation by a quantitative point of view. In particular, the

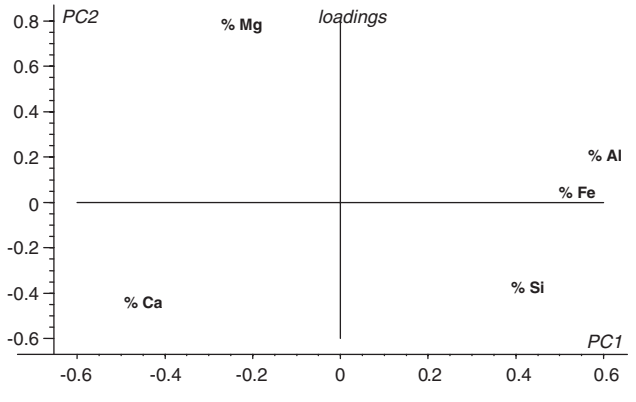

Fig. 4. PCA on specimens (aerial binder) and historical samples (loading plot).

Table 5
Specimens B/A value (expressed as weight percentage of binder): true values and values predicted by PLS1 model

Specimens	B/A (true value)	B/A (predicted)
1a	50.00	51.82
2a	50.00	42.62
3a	33.00	32.95
4a	33.00	33.39
5a	25.00	31.13
6a	25.00	26.80
7a	100.00	97.74
8a	100.00	104.16
S	0.00	2.37

work was focused on the determination of an important property of mortar, i.e. the B/A ratio.

Traditionally B/A estimation requires determination of the residue weight after acid attack. The accurate weight of the residue (in most of the cases tenths of milligrams) of the original sample, and the following transfer with probable loss of material, are important sources of errors, which lead to a wrong estimation of the B/A ratio. The chemometric approach, here undertaken, takes into account only the acid soluble fraction avoiding errors ascribable to the weight procedure.

Partial Least Squares regression for one *y*-variable (PLS1) was used in order to determine the B/A ratio. Specimens built with aerial binder and samples of sand and binder (calcitic and dolomitic) were used to build the model. Variables used were weight percentages of calcium, magnesium, silicon, iron and aluminium in the soluble fraction. Vector *y* of response, which contains the true values of the B/A ratio for the specimens, was built from data showed in Table 1 and conveniently transformed. In particular, B/A ratio was expressed as weight percentage of binder in the specimens (e.g. for sand specimen was used 0% and for specimens 7a and 8a was used 100%). Autoscaling was applied to the original data prior to calculation. Full cross validation was used to validate the model: it consists of a systematic removal of one of the training samples and use only of the remaining ones for the construction of latent factors and regression [35].

PLS1 calibration gives good results. Two factors explain 100% of *y* vector, with an RMSECV of 3.75% and a RMSEC of

Table 6
Comparison between B/A values of historical samples obtained by the PLS1 model and by the classical method: the calculated weight percentages of binder fraction and related prediction error are shown

Sample	% of binder calculated	Prediction error (% of binder)	B/A ratio PLS1 model	B/A ratio classical method
SL1	23.04	5.12	1:3	1:3
SL2	24.61	2.77	1:3	1:3
SL3	52.63	5.15	1:1	1:2
SL4	34.86	5.80	1:2	1:2
SL5	49.56	3.74	1:1	1:1
SA1	46.29	2.84	1:1	1:1
SA2	48.52	2.42	1:1	1:2
SA3	29.33	3.96	1:2	1:2
SA4	61.11	4.48	1:1	1:1
SA5	58.54	3.63	1:1	1:1

2.38%. As concerns the considered specimens, a good agreement is observed, as shown in Table 5.

3.3. Prediction of B/A ratio in historical samples

PLS1 model was applied for the determination of the B/A ratio in historical samples. The model calculated a prediction error for each sample. Prediction was carried on 10 samples, 5 from St. Abbondio Basilica and 5 from St. Lorenzo Basilica. Values of the B/A ratio calculated by PLS model were compared with results obtained with the classical approach previously described. The results (Table 6) show that the B/A ratio is correctly calculated for 8 of the historical samples considered.

4. Conclusions

In this work a chemometric approach is taken into account in order to study chemical features of historical mortars and to provide an effective alternative method to estimate their binder to aggregate ratio (B/A). The aim was in fact to study ancient mortars using information obtained from modern mortars (specimens) with simple analytical measures and an easy-to-see graphic of the results.

Analysing five main components, in a few specimens and historical samples, PCA models were able to distinguish hydraulic from aerial binder and to evaluate the chemical properties of the aerial binder itself, i.e. if calcitic or dolomitic, respect to the straightforward interpretation of score plot and loading plot. Moreover, PLS1 model allowed to correctly predict the B/A ratio both in specimens and in historical samples, according to the results obtained applying the traditional gravimetric method. It is evident that the results in terms of B/A ratio reflect the present composition, not the original one, because of curing process and well known decay phenomena. As already indicated by the authors (Section 2.3), the method is working in case of mortars characterised by silica aggregate. It must be taken into account that in many historical mortars the aggregate may contain a carbonate fraction, which is dissolved together with the binder during the acid attack. In these cases the chemical approach to the mortar characterization is not reliable.

The method proposed in this survey is set up with a small amount of data but would acquire much more validity analysing a large set of samples. That often occurs in conservation works of large buildings, where useful information can only be obtained spending a lot of resources in evaluating a great amount of chemical data. The proposed method allows analysing just a few metals and obtain a reliable estimate of the essential parameters: the B/A ratio in the PLS1 calculation and the similarity among samples, just observing the score plot coming from PCA calculation.

The method, which already provides good results, could be furthermore improved considering a larger number of specimens, possibly with different compositional features as, for example, the MgO content (magnesian limes).

Coming to a new culture of ancient plasters' conservation, the proposed approach allows to easily investigate historical buildings from the compositional point of view, indicating some of the main features necessary to correctly prepare compatible repair mortars.

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