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Investigative methods for the characterisation of historic mortars – Part 1: Mineralogical characterisation

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ABSTRACT

The mineralogical characterisation of historic mortars is performed for a number of reasons related to the conservation of traditional structures. The reasons for analysis and the questions posed during the conservation, repair or restoration of an old building determine the analysis methods that will be chosen. A range of mineralogical characterisation methods is available for the study of historic masonry mortars. These include X-ray Diffraction (XRD), Optical Microscopy, Scanning Electron Microscopy (SEM), Thermal and Infra-Red methods. Sample preparation is important; adequate separation of binder from aggregate is required for instrumental as opposed to microscopic investigation methods. An ordered scheme of analysis can be developed and is presented in flowchart form. It is difficult, and perhaps unwise, to analyse a mortar with only one method of characterisation. Corroboration of evidence of identification and quantification for mineralogical composition is best supported by a combination of methods, including chemical analysis methods. All methods of characterisation require qualified and experienced people to carry out the analyses.

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RÉSUMÉ

La caractérisation minéralogique des mortiers historiques est exécutée pour des raisons différentes qui sont liées à la conservation des constructions traditionnelles. Les raisons de l'analyse et les questions posées lors de la conservation, la réparation ou la restauration d'une construction historique déterminent les méthodes d'analyse choisies. Une gamme de méthodes de caractérisation minéralogique est disponible pour l'étude des mortiers historiques de maçonnerie. Celles-ci comprennent la diffractométrie par rayon X (DRX), la microscopie optique, la microscopie électronique de balayage (MEB), les méthodes thermiques et infrarouge. La préparation de l'échantillon est importante : la séparation adéquate du liant et du granulat est obligatoire pour des méthodes instrumentales (comme les analyses chimiques), ce qui n'est pas le cas pour les méthodes d'investigation microscopiques. Il est difficile, et peut-être peu judicieux, d'analyser un mortier avec une seule méthode de caractérisation. Un schéma systématique relatif aux analyses à exécuter peut être développé et est présenté sous forme d'organigramme. Toutes les méthodes de caractérisation exigent du personnel qualifié et expérimenté pour exécuter les analyses.

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1. INTRODUCTION

Analysts and test laboratories are often asked to answer questions about the material properties of mortar samples taken from historic buildings. These questions are often, for example, about causes of damage to the mortars or building, or about aesthetic factors. The definition of the mineralogical and chemical parameters of historic mortars is mostly directed towards establishing the facts surrounding these questions. However, the analytical methods that are used are not fixed or proscribed in advance in a way that considers every possible query. This paper is the first of a pair that present the methods that are available for the mineralogical and chemical characterisation of historic mortars, and places them within a context relevant to the preservation of historic monuments. This first part deals with the mineralogical characterisation of historic mortars while the second part deals with their chemical characterisation. The methods presented are not only a means for dealing with routine information requirements and problems, but also provide a fundamental knowledge base for further interpretation and discussion among all those working in the field of preservation.

Table 1 presents a non-exhaustive list of "keywords" relating to issues or requirements for factual information that can arise when dealing with mortars and the preservation of historic buildings. The mineralogical, analytical approaches that relate to these keywords, are summarised at the end of Part 2 of this paper, by way of examples to illustrate approaches to the mineralogical and analysis of historic mortars.

This list does not consider *regional* conditions or the *specific* properties of mortar but is meant to be an overview of the possible analyses which can be made. The important point to be made is that mineralogical and chemical analysis should never be used in isolation. It is not a substitute for creativity in the field of building preservation or for the dialogue between materials analysts and the curators of historic buildings.

Mineralogical and chemical characterisation of historic mortars must be performed in a systematic manner [1]. Examples of flow charts that outline a scheme for the analysis of mortars are presented in the appendix. Before analysis, the sampling of mortar must be done with due physical care and with a full understanding of the context of the desired results.

Preliminary information

If no information is available about the original materials used for the preparation of the mortar that is to be analysed, from documentary sources or similar, or if the kind of mortar that was used cannot be assessed based on arguments by analogy (*e.g.* by the style and age of construction), then the determination of its composition is a primary aim. There are many analytical procedures for doing this. In addition to X-ray diffraction analysis, that is described below, other methods such as microscopic, chemical and thermo-analytical techniques can also be used. Following a qualitative assessment using visual analysis, the binder (lime, gypsum, cement and other hydraulic components etc.) and the aggregate (siliceous, calcareous and other natural or artificial aggregates) can be identified with X-ray diffraction analysis (XRD). Alternatively this initial assessment can be performed using thin sections with a petrographic microscope or by a combination of XRD and petrography. For a more detailed characterisation of the mortar, that depends on the questions posed in the beginning (*e.g.* in Table 1), different types of analyses can be performed. These will be described in the following pages.

By using the methods that have been already mentioned above, certain limitations and changes of the phase conditions of the components of the mortar have to be considered. For example, hydrated lime (Ca(OH)₂) reacts with air containing CO₂ forming calcium carbonate (CaCO₃), which results in the build up of mechanical strength. An example of a limitation is that XRD cannot distinguish between carbonate in the aggregate and in the lime paste formed from the binder. XRD is also only successful if the phases that result from carbonation and hardening are crystalline. Other, amorphous combinations such as calcium silica gel produced during the setting processes of hydraulic binders, for example, cannot be clearly identified in this way. In addition, XRD can only clearly identify phases when they are present in sufficient quantities for the equipment to detect, usually a few wt.-%.

Using thin sections with a petrographic microscope allows the analysis of the structure and texture of the mortar (meaning the spatial distribution of components). This can provide information about the current bonding, the kind of binder and aggregate and even partly about the hardening process and how the mortar was applied. It is also possible to get preliminary information about the use of additives and admixtures in the mortar. The microscopic analysis, that permits the identification and even quantification of proportions of components, stands between the physical and chemical methods of investigation, and compliments them both. In addition, a qualitative and quantitative distinction between binder and aggregate is possible. The content and shape of air voids and cracks qualitatively indicate something about the mechanical properties of the mortar and about the moisture content at the time when it was applied. The analysis of structure is best displayed pictorially with an explaining interpretation, which perhaps should be made after having talked to the curators of the building involved.

The different types of analysis that can be used for mortar characterisation will be treated in more detail below. We then draw a general conclusion, as to what analysis can be used to solve the types of questions asked in Table 1.

2. MINERALOGICAL - PETROGRAPHICAL CHARACTERISATION

2.1 X-ray diffraction (XRD)

In addition to chemical and microscopical analyses, X-ray diffraction (XRD) analysis is suitable for the identification and differentiation of binders and kinds of aggregate within a mortar, if they are crystalline. For example, the differentiation of cement and natural hydraulic lime is only possible by mineralogical analyses [2-4]. The same is correct for other mineralogical phases if their content within a mortar is sufficiently high (approx. 3 wt.-%). Here, normally, a powder X-ray diffractometer is used. Sample carriers made of quartz

Table 1 - List of keywords and phrases relating to
important issues often defining requirements for
technical/factual information about historic mortars
that can arise in the conservation of historic buildingsConservation (safeguarding, consolidation)compatibility (physical and compositional)

salts cohesion adhesion changes due to earlier conservation measures as well as proof of materials used aggregates, binders, admixtures and additives

- mixing ratio of mortar
- physical properties
- filling and adhesive mortars

Restoration, reconstruction (formulation of restoration mortar)

compatibility (and everything else above) previously used repair mortars (employment on small and large spaces)

Identification and documentation	
contrasting functions of mortars	
binder, aggregate, admixtures, additives	
provenance of raw materials	
traditional building practice	
mortar's position in building history- phase or stratigraphy	

or silicon have proven to be best for working with small quantities of sample because these sample holders create no diffraction peaks between $2 - 90^{\circ} 29$.

2.1.1 Investigation of binders

Approx. 5-10 g (depending on the amount and size of aggregate) of sample are disaggregated by careful crushing without destroying the aggregate particles. During this an attempt is made as far as possible to reduce the binder fraction of the mortar to a powder, whilst preserving the aggregate intact. The sample is dried afterwards at 40°C until mass constancy is reached. During the drying process the moisture content can be determined. After this the sample has to be sieved to pass 63 μ m. The fine fraction passing the sieve is called the binder enriched fraction and the retained fraction is the aggregate. The binder enriched fraction has to be made finer still for X-ray diffraction analysis, to pass a 40 μ m sieve. The binder enriched fraction in principle contains a majority of material from the binder in the mortar, though cannot be said to be pure, with no contamination from the aggregate.

During preparation a preferred orientation of the fine grains in the sample has to be prevented. Sometimes the nature of the material requires special preparation for analysis, for example in the characterisation of clay minerals.

The peripheral conditions fixed for X-ray diffraction have to be noted, in addition to general details of the samples. These include:

- the type of X-ray tube (Cu, Co etc.)
- current intensity of X-ray tube [mA]
- voltage of X-ray tube [kV]



Fig. 1 - X-ray diffraction phase diagram of a bulk sample of historic lime mortar [2].

- rotation speed of the goniometer in degrees per unit of time
 [° min⁻¹]
- area of angle $[2 \theta]$
- type of sample carrier

The resulting X-ray phase diffraction diagram (see Fig. 1) can then be evaluated with the help of an X-ray database (*e.g.* JCPDS-Powder Diffraction files), literature or reference samples. The phases identified here can be marked as follows according to the relative height of non-superimposed suitable reflexes:

- +++ dominantly present ++ present + traces
- ? possibly present
- not detected

If information is required only about the presence or not of mineral phases in the binder, and not the relative proportions of phases, then the phases that are present can simply be marked on the diffraction diagram.

2.1.2 Investigation of aggregates

The aggregate fraction that has been obtained in 2.1.1 from the disagregation and separation of the mortar can also be analysed using XRD. This will provide information on the mineralogy of the aggregate, but not necessarily about the lithologies of the grains present in the aggregate. This is best investigated using thin sections. However, XRD analysis may highlight unusual mineralogies that may indicate particular additives such as pozzolana, either natural or artificial and confirm identifications performed using petrography. The aggregate fraction must be further ground to pass 40 μ m for the X-ray diffraction analysis. The analysis is carried out in the same way as for the binder fraction (see 2.1.1), as is the evaluation of the diffraction diagram to identify the phases present. Phases which can be related to aggregates can be specially marked.

2.1.3 Investigation of admixtures and additives

For most cases it will be necessary to specially enrich the concentration of admixtures and additives in a sample in order to analyse them at all using XRD (the detection limit of this procedure is about 1 wt.-%). Generally, organic additives cannot be identified using X-ray diffraction. Their identification can be done by using wet chemical methods, gas chromatography, by thermal analysis (DSC, DTA, TG, see 2.3.1) or Fourier-Transform-Infrared spectroscopy (FTIR, see 2.3.2). An investigation by XRD is carried out as described in 2.1.1.

2.1.4 Evaluation of X-ray diffraction analysis

A final look at the phases detected often allows for the determination of the relationship between the binders, aggregates and admixtures, as well as hints at possible interaction with the environment (*e.g.* efflorescence). An example is given in Fig. 1. Many examples of XRD-analyses on mortar samples can be found in the literature [2, 5-12].

2.2 Microscopic methods

2.2.1 Optical microscopy

Optical microscopic methods are commonly applied using a polarising petrographic microscope to study thin sections of material. Thin sections are very thin slices of material, that are essentially two dimensional cross sections through the sample, that are mounted on clear, flat glass slides. The reduction of thickness of the material (commonly to $20-30\mu$ m) permits light to pass through crystalline or amorphous materials and for the detailed analysis and recognition, by an experienced operator, of the mortar's components.

A piece of mortar with dimensions of between 7 to 20 cm^2 is removed (sawn without using water if necessary to avoid dissolution of soluble material) from a part of a characteristic mortar sample. It is then dried at 40°C (to avoid dehydration of components, especially Gypsum if present, and physical damage due to thermal shock), until mass constancy is reached. After this it has to be impregnated with warmed low viscosity epoxy resin. To aid in the visualisation of pores, cracks and air voids, the use of a colour dyed epoxy resin is helpful.

The sample is then ground flat with a lapping or polishing machine. For this an abrasive paste, suspended in water, petroleum or oil, with hardness adequate for the removal of binder and aggregate is used. Next, the sample is placed in an ultrasonic bath of an appropriate liquid to clean away remains of the abrasive. The sample has to be dried carefully and is fixed using more epoxy resin, with pressure, onto a flattened ground glass slide having been ground in advance. The sample fixed to the slide must be reduced to a thickness of about 20 - 30 µm plane-parallel to the microscope slide through successive sawing, milling and lapping. For this, the abrasive and abrasive aggregate have to be carefully matched to the phase composition and physical properties, especially hardness, of binder and aggregate. After another ultrasonic cleaning and drying, the finished thin section can be covered with a thin glass plate or the surface polished using up 0.25 µm sized abrasives.

The thin section is now examined with a petrographic microscope using polarised transmitted light. (Note: If the RED I compensation plate is used, the pores are also visible without dyed epoxy.) Although the binder fraction is mostly very fine, identification of the type of binder (gypsum, lime, natural hydraulic lime, cement) is mostly possible [10, 12-15]. Owing to their form and/or their interference colours, aggregate particles can also be viewed and identified by using polarised light. The structure of aggregate particles can be described as a textural feature (Fig. 2). If organic fibres (*e.g.* hair, straw) or pozzolanic reactive materials, such as trass, brick dust etc. are in the mortar, they can often be detected using the petrographic microscope (Fig. 3).

The mortar structure should be investigated first at a low magnification. In most cases the binder phases are very finely divided and/or amorphous, which causes difficulties for identification. The spatial resolution of optical petrography is 1 μ m at best, and the interference of many layers in a thickness of 20-30 μ m in the path of the light is problematical. Nevertheless, one can assess the quality of binding in the mortar and if recrystallisation or transformations due to, for example, penetrating salt



Fig. 2 - Thin section of lime mortar with quartz (Q), limestone (L) and feldspar (F) aggregates. Crossed nicols (XPL) were used.



Fig. 3 - Thin section of lime mortar with a piece of brick. A pozzolanic reaction border (identified by the arrow) can be seen. XPL.

solutions etc. have occurred (*e.g.* Fig. 4). Indications for traditional building practice and the provenance of raw materials can also be obtained [10, 15]. Fig. 5 shows a mortar prepared with dry slaked lime. Unmixed areas of lime, lime "lumps" or inclusions can easily be identified [16]. Methods for quantitative analysis of mortar mix proportions are given in separate publications [17-19].

The result of petrographic and textural investigations has



Fig. 4 - Thin section of leached lime mortar. Pores with recrystallisation layers on the surface (arrow) of the joint can be seen. XPL.



Fig. 5 - Thin section of lime mortar prepared by using dry slaked lime. A typical lime lump can easily identified (centre left).



Fig. 6 - Polished section of a hydraulic mortar. Non- hydrated hydraulic phases (C_2S) can be identified more in detail.

to be presented in a report with regard to features relevant for building preservation. Illustration of features, using photography if possible, or with annotated drawings is desirable.

Using reflected light microscopy combined with surface etching by acid of polished sections of hydraulic mortars, non-hydrated hydraulic phases (*e.g.* C₂S, C₃S, C₃A, etc) can be identified in more detail (Fig. 6). This way, different types of cements or hydraulic limes can be identified. More details are given in [13, 14].

When the samples are impregnated with a fluorescent resin, fluorescent light microscopy (using ultraviolet light) can be used to visualise in more detail the structure of pores and cracks. Estimation of porosity, outlining porous areas and very fine micro-cracks, which may not be otherwise observable, can be performed [14]. With image-analysis, porosity can also be estimated [17, 19, 20].

2.2.2 Scanning electron microscopy (SEM)

Using SEM the structure of a mortar can be analysed at high magnifications and in three dimensions on rough, broken surfaces to directly visualise the structural components of the mortar. If the SEM is equipped with an X-ray detector (EDX, WDX) a qualitative determination of the chemical elements within the components of the sample is possible. The samples which are analysed with SEM should be small and need to be covered with a conductive layer of gold and/or carbon, that facilitates the removal of electrical charge from the sample, which otherwise interferes with image formation. However, by using an Environmental-SEM (ESEM) with low vacuum system the sample can be analysed without covering. Fig. 7 shows as an example of the microstructure of a historic gypsum mortar that can be confirmed by an experienced analyst from the shape and habit of the crystals present as well as chemistry using EDX or WDX. SEM-analysis is important for the characterisation of very fine-grained hydraulic mortars. The hydrated hydraulic phases in cement or hydraulic lime mortars are mostly too fine to identify with conventional petrographic microscopy and can not be identified by XRD since most of these phases are less crystalline or amorphous. Analyses at higher magnifications allows the recognition of the microstructure of such hydrated hydraulic phases (e.g. needle-



Fig. 7 - SEM figure of the microstructure of a historic gypsum mortar. Crystals can be identified. Width of the figure: 145 µm.

shaped calcium silicate-hydrates (CSH), hexagonal portlanditeplates, etc) and with EDX or WDX analysis, the chemical composition of the phases can be determined [4, 21-23]. However, due to the complexity of the analysis the measurements should only be carried out by experienced analysts.

2.3 Additional techniques

To analyse or to identify binders, aggregates and admixtures, additional techniques can be used, for example thermal methods like Differential Scanning Calorimetry (DSC), Differential Thermal Analysis (DTA) or Thermogravimetric methods (TG) [24, 25]. The main advantage of these methods is the need of very small sample quantities. However, the analyses are complex to perform, requiring detailed training and experience. Due to the complexity of the analyses it is recommended that the measurements should only be executed by qualified analysts.

2.3.1 Thermal analysis

Thermal analysis can be applied to mortars using three basic techniques, Thermogravimetry (TG), Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC). Each method, though having its distinct features, gives approximately the same information, being based on the physical transformations that compounds experience on being heated in controlled conditions.

Thermogravimetry (TG) measures the weight loss in a sample as it is heated. Weight loss during heating can be related to specific physical decompositions in the materials that are due to the effects of increasing temperature. For example gypsum can be recognised by weight loss of approximately 26.5 wt.-% as a result of the transformation to anhydrite.

Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC) are the most useful, and most used methods. With DTA, a graph is continuously plotted during heating that shows the temperature difference between the sample and an inert standard (usually Al₂O₃), which is heated at the same rate and at the same time. Endothermic peaks are recorded when the standard continues to increase in temperature and the sample does not. At these times the sample is absorbing heat energy and using it to drive decomposition or a mineralogical transformation. This is usually the loss of chemically bound components, for example water from gypsum or carbon dioxide from calcite and dolomite. The endothermic or exothermic transitions are characteristic of particular minerals, which can be identified and quantified using DTA. Fig. 8 shows as an example a DTA-TG analysis of a mortar taken from a historic building in Thessaloniki, Greece.

Differential Scanning Calorimetry (DSC) follows the same basic principle as DTA. Whereas temperature differences are measured in DTA, during heating using DSC, energy is added to maintain the sample and the reference material (Al_2O_3) at the same temperature. This energy use is recorded and used as a measure of the calorific value of the thermal transitions that the sample



Fig. 8 - DTA-TG analysis of old mortar taken from a historic building in Thessaloniki, Greece [9].

experiences [26]. DTA and DSC pose another advantage over TG in the identification of minerals in mortars in that they are capable of resolving polymorphic transformations in compounds that do not involve weight loss. An example of this is given by [27] where quartz aggregate in plasters undergoes the transition from α -quartz to β -quartz at 573°C, something they suggest could be usefully employed as an internal temperature calibration.

The identification of mineral phases in mortars, be they non-hydraulic, hydraulic or magnesian is mostly straightforward. However, some ambiguity can arise when some phases decompose or experience phase changes at similar temperatures. Water loss from calcium-silicatehydrates-phases (CSH) takes place at a similar temperature to some clays [28]. It is also possible to confuse the identification of portlandite (Ca(OH₂)) and magnesite (MgCO₃) as both can decompose at around 520°C [27, 29]. In these cases it is important to perform additional analyses using complimentary methods to confirm identifications.

The identification of hydrated hydraulic components in historic mortars using thermal analysis has not yet been convincingly demonstrated. The analysis of the hydraulic components of Portland Cement is however well understood [30]. The main hydraulic clinker phases of Portland Cement C₃S and C₂S undergo phase transitions at a range of discrete temperatures from 500°C to 1425°C. This in principle permits the identification of unhydrated C₃S and C₂S in hydraulic mortars. However, C₂S, which is likely to be more common in natural hydraulic lime and mortars found in historic buildings due to the lower temperatures required for its formation, undergoes its phase transitions at temperatures in excess of 693°C [30]. It is at approximately this temperature that calcite begins to disassociate. As calcite is generally a dominant phase in historic mortars it may mask the identification of C₂S.

Some workers contend that it is possible to distinguish between different mortar and binder types on the basis of data derived from thermal analysis [16, 25, 31-36]. To do this they use the weight loss from a sample during thermogravimetry between 200-600°C to represent all the structurally bound water in hydraulic components. They plot this figure against the weight loss due to the decomposition of calcite, both figures transformed to percentages. They were able to define domains on the graphs for crushed brick mortars, cements and hot-lime mortars though the best distinction was between these hydraulic types and the non-hydraulic lime mortars.

Due to the complexity of the analyses it is again recommended that the measurements should only be executed by experts.

The following are the typical temperatures of disassociation of common binder forming minerals:

CaCO ₃	650 - 890°C
Ca(OH) ₂	400 - 520°C
MgCO ₃	450 - 520°C
$Mg(OH)_2$	350 - 420°C
Ca ₃ SiO ₅ (C ₃ S, Alite)	1425°C (phase
	transitions so DSC or DTA only)
Ca_2SiO_4 (C ₂ S, Belite)	phase transitions 693°C
CaSO _{4*} 2H ₂ O	45 - 120°C

2.3.2 Infra-Red analysis

By using Infra-Red spectroscopy (IR), especially Fourier Transform Infra-Red spectroscopy (FTIR), in addition to the identification of the main mineral phases in a binder, small quantities of admixtures and additives can be identified. For FTIR-measurements small sample quantities are required. As for thermal analysis, due to the complexity of the analyses it is recommended that the measurements should only be executed by experts.

This method of analysis relies on the interaction between applied infra red radiation and the molecules in compounds. Bonds between atoms have distinctive geometries and natural states of rotation and vibration. Incident infra red radiation will excite these vibrations and rotations when a critical wavelength is reached that can impart energy to the bond. At this point the atomic bond that is being excited will absorb that wavelength of infra red radiation. If the sample is placed between the source of infra red radiation and a detector these times of absorption of the infra red radiation can be recorded as reduced intensity and can be related to specific types of atomic bonds characteristic of particular functional groups in compounds, for example CO₃-group in carbonates. Infra red spectrometry is therefore suitable for the identification of materials and the study of chemical structure and the nature of inter-atomic bonds. For our purposes we are solely interested in the identification of mortar materials, primarily in the binder, and the possibilities for the quantification of their abundance.

Several experimental studies demonstrate the potential for the use of FTIR in the quantification of carbonate materials relevant to mortar studies [37, 38]. Studies of historic mortars that employ infra red spectrometry rarely use the technique in isolation. Most commonly it is used in combination with XRD, TG, DSC or DTA [29, 39]. Gypsum is easily identified as are carbonates. Silicates (as SiO₄) can also be identified, including as CSH. The potential for recognising hydraulic binders therefore also exists [40]. Furthermore, Luxan *et al.* [40] also identify the presence of organic compounds, which the infra red method is particularly suited. Varnishes, pigments and other organic based additives can be identified easily. The FTIR-technique can use very small samples of less than 0.5 mg with an area of less than 0.5mm², making it invaluable for the study of valuable objects, such as wall paintings or indeed building fabric [41].

3. CONCLUSIONS TO PART 1: MINERALOGICAL CHARACTERISATION OF OLD MORTARS

Table 2 (presented in Part 2) presents the relationship between the "keywords" or issues raised in table 1, and the types of information that are required in order to deal with each issue. Precise methods of analysis are not listed here but can be inferred from the contents of this paper and part 2, on chemical characterisation. Table 2 is presented as a general guide to deciding what information is required for adequate characterisation for whatever purposes are defined by the study that requests the analysis.

The characterisation of old mortars is, as yet, not subject to precise definition in standards or national norms, and due to the highly variable nature of the materials is unlikely ever to be so precisely. Generic approaches are available for mineralogical analysis, that demand individual laboratories to develop protocols and approaches of their own. The degree to which results can be compared must be carefully considered in this context.

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Appendix:

Flowchart to illustrate a scheme for the mineralogical and petrographical characterisation of historic mortar



