

**RILEM TC 167-COM: 'Characterisation of Old Mortars with Respect to their Repair'**

## Investigative methods for the characterisation of historic mortars - Part 2: Chemical characterisation

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### ABSTRACT

In addition to the mineralogical characterisation of components of binder and aggregate in historic mortars, it is sometimes necessary to perform a chemical analysis on the materials in historic mortars. Acid dissolution/separation of binder from aggregate is the simplest method, and allows the determination of the chemical composition of the acid-soluble binder and, after separation, information on the mortar's aggregate. It is limited, when aggregate is acid-soluble. A range of significant analysis can be made including for soluble silica that relates to hydrated calcium silicates in the binder, and thus the hydraulicity of the binder. Other wet chemical analyses can be performed on the acid filtrate for soluble oxides of Fe, Al, Ca, Mg, S, Na and K. There may also be a requirement for the identification of organic substances, pigments and salts within a historic mortar. Chemical analysis forms a 2<sup>nd</sup> part of a possible scheme of characterisation of historic mortars that is presented as a flowchart. Chemical analysis also satisfies requirements for information input to conservation, repair and restoration works on historic buildings for the choice of compatible replacement materials. Corroboration of evidence of identification and quantification for chemical composition is best supported by a combination of methods, including mineralogical analysis methods. All methods of characterisation require qualified and experienced people to carry out the analyses.

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### RÉSUMÉ

*En plus de la caractérisation des composants de liants et granulats de mortiers historiques, il est parfois nécessaire de faire des analyses chimiques sur les matériaux de ces mortiers. La méthode la plus simple est la dissolution ou séparation par acides du liant attaché aux granulats ; cette méthode permet de déterminer la composition chimique du liant soluble dans l'acide et, après séparation, fournit des informations sur le granulats du mortier. La méthode n'est pas applicable aux granulats solubles dans l'acide. Il est possible d'établir toute une gamme d'analyses significatives, parmi lesquelles la détermination de la silice soluble, qui fait partie des silicates hydratés de calcium du liant, et par conséquent, sur l'hydraulicité du liant. D'autres analyses chimiques peuvent être faites sur le filtrate acide par rapport aux oxydes solubles de Fe, Ca, S, Na et K. Une identification des substances organiques, des pigments et des sels dans un mortier historique peut être exigée. L'analyse chimique figure dans la seconde partie d'un schéma possible de caractérisation des mortiers historiques, qui est présenté sous forme d'organigramme. L'analyse chimique peut répondre à des besoins d'information pour le choix des matériaux de remplacement compatibles pour des travaux de conservation, de réparation et de restauration relatives aux constructions historiques. La corroboration des preuves d'identification et de quantification par rapport à la composition chimique est mieux soutenue par une combinaison de méthodes, incluant les méthodes d'analyses minéralogiques. Toutes les méthodes de caractérisation nécessitent du personnel qualifié et expérimenté pour exécuter les analyses.*

## 1. INTRODUCTION

In this paper methods for the chemical characterisation of historic mortars are presented. The reader is referred to the discussion in the introduction of Part 1 [1] for the wider context for the analysis of historic mortars. At the end of this paper flowcharts are presented that outline a procedure for the chemical analysis of historic mortars. This should be considered together with the flowchart for mineralogical and petrographical characterisation in Part 1 [1], to constitute a complete scheme for mortar analysis.

## 2. CHEMICAL CHARACTERISATION

### 2.1 Wet chemical separation (acid dissolution) to determine aggregate and binder contents

In this section, methods for disaggregating or separating a mortar sample by dissolving the binder using dilute acids, and the subsequent chemical analysis that can be applied to the dissolved binder will be described. It is worth restating that such "wet" chemical analysis methods used for the characterisation of mortars, when used alone, cannot furnish all the information needed for a complete interpretation of a problem or issue connected to a mortar. For that reason, a mineralogical and petrographical analysis [1] should always be carried out before the chemical, and the results of the two analyses should be in agreement.

The determination of the binder to aggregate ratio requires information on the binder and aggregate types that were used. There are commonly problems of interpretation, even after chemical analysis. As the original components (aggregates and different kinds of lime as binder) are no longer available or easily separable in the mortar, one has to distinguish clearly which parts belong to the aggregate and which to the binder. This is especially the case if the aggregate used is completely or partly soluble in acid. If the individual components of mortar are not easily separated, the mixture calculations resulting from chemical analysis have to be made using assumptions. These assumptions can be supported by investigations of mortar samples with X-ray diffraction analysis and thin sections.

The most important assumption for determination of the binder to aggregate ratio derived from acid dissolution is that the binder is dissolved by the acid while the siliceous aggregate remains intact and unaffected by the acid (for details see Table 1). As binders change while hardening (due to carbonation, hydration, etc.), the method is based on the calculation of the composition of mortar samples after determination of their loss on ignition. The sample can be considered to be the same as fresh burnt materials just before being worked, before the addition of substances

due to environmental actions (penetration of salt, washing out, etc) and normal hydration and carbonation. In this way, the real initial binder and aggregate content can be calculated respectively as well as their proportions.

This rough description already highlights the limitations of the wet chemical analysis. In different geographical regions there are natural variations in the composition of binders, aggregates or even materials whose function within the mortar is not recognizable. If some acid soluble silica is present in a mortar, it does not mean that a hydraulic binder has been used. Therefore, when acid soluble silica is found, a mineralogical-petrographical analysis should be carried out. This will clarify if the silica originates from hydraulic binders, brick dust, trass, flint or clay minerals. In these cases, special knowledge of regional construction materials and practices is required, in order to make an estimation/approximation of the mixing ratio.

Particular difficulties will arise in analysis if several binders or aggregates have been used for the preparation of a mortar mix, for example lime with cement or different sands of different material composition. The following procedures, therefore, concern mortars with a relatively simple composition. Otherwise, the results of the chemical analysis of mortar have to be interpreted with the help of the analyst's experience and expertise. This emphasises the importance of experience and the dexterity of the analyst in recognising deviations from simple mortar compositions.

There are no international standards concerning the type of acid and its concentration for the analysis of mortar using dissolution methods. Different laboratories in different countries use different types of acids according to local practice. Therefore, it is often difficult to compare and interpret results from different laboratories [2-4]. However, in Italy an experimental programme was carried out by different laboratories on the same mortar sample over several years. The analyses were performed at the same temperature,

**Table 1 - Solvents for mineral binder in mortar**

Aggregate	Binder	Solvent / separating agent	Comments
non-carbonate or non-sulphate-bound aggregate (e.g. quartz, feldspar, mica, sandstone, basalt, pumice)	all	HCl (diluted) HCl salicylic acid/ methanol mix EN 196, part 4	concentrations and type of acids are not yet standardised, and may differ from country to country, and from laboratory to laboratory
carbonate-bound aggregate	non-hydraulic lime	water as solvent EDTA (diluted)	mechanical separation (rubber wiper), coarse particles owing to recrystallisation with grain growth have to be watched; attacks finest calcium carbonate of aggregate
carbonate-bound aggregate	hydraulic binders	water as separating agent	mechanical separation, if possible phase counting on cross section
carbonate-bound aggregate	sulphate-based binders	water as solvent	mechanical separation phase counting on polished section phase counting on thin section
sulphate-bound aggregate	non hydraulic lime	Not applicable	phase counting on polished section point counting on thin section

using the same acid at the same concentration (HCl 1N) and for the same duration. The results obtained were very close, and for this reason a code was drawn up [5].

Sampling of the mortar must be done carefully to ensure that the sample is representative of the structure. The nature of the analysis and the information required will determine the type of sample required. The mortar analysis can be carried out on the whole sample, the binder plus aggregate, or separately on the binder and the aggregate. It is recommended that the analyses of a mortar should begin with a mineralogical-petrographical analysis before carrying out the chemical analysis. This will clarify whether the aggregate may be soluble in acid, or if the binder is suspected of being hydraulic. This information will determine the nature of the separation of the mortar that is attempted and the final conclusions of the study.

If the binder is to be analysed separately from the aggregate, and this may be so especially with an acid soluble aggregate, then the sample should be carefully disaggregated to separate the binder from the aggregate. This is done by gentle crushing of the sample and ensuring, as far as possible, that the aggregate has not been crushed. Between 5-15 g (depending on the amount and size of aggregate) of sample should be prepared. This sample is dried at 40°C until mass constancy is reached and the moisture content determined. If it is suspected that the mortar contains water soluble salts, then a part of the sample can be immersed in distilled water to flush out the salts. Then the sample can be dried and the content of water soluble salts can be determined by the difference in weight.

After this, the sample can be sieved to pass 63 µm. The fraction passing through the sieve is called the binder enriched fraction, and the retaining fraction is the aggregate. Both binder and aggregate will be analysed separately, according to the sections below. An optical observation using a binocular microscope (or similar, even a hand lens) should always be performed, in order to assess the separation. This procedure can be followed for mortars with aggregate that is insoluble, partly soluble or completely soluble in acid in order to establish the binder aggregate ratio.

### 2.1.1 Acid treatment

#### 2.1.1.1 Lime mortars with aggregate insoluble in acid

Before analysing historic mortar of unknown components, as said above, one has to be sure that the aggregate is insoluble in hydrochloric acid. XRD-analysis and a mineralogical-petrographic investigation can be used to obtain this information. If salts are evident from XRD-analysis or other preliminary analyses which could falsify the results, (in the original aggregate, or in the original binder, or even in the mortar after mixing and putting in place) their content should also be determined (see 4, below).

Put 10 g of the prepared mortar sample into a 400 ml beaker. Add 200 ml of distilled water, stirring the solution in order to avoid the formation of clots. Add 30 ml of HCl (1N) continually stirring for 60 min [6]. It is important to maintain the solution in a temperature range between 20 and 23°C. Filter with glass micro fibre filter (*e.g.* at pressure of 40-93 KPa). The contact time with acid and the filtration time should not exceed 15 min in total in order to avoid the sample being over

attacked by the acid. Wash the residue 4 times with distilled water and transfer the insoluble residue from the beaker into the filter. After filtering and intensive washing of the filter with distilled water, the residue on the filter must be dried and weighed to give the amount of aggregate. From the filtrate the content of calcium and magnesium can be determined, for example by using an atomic absorption spectrometer (AAS) or by using further wet chemical analysis (see below).

The amount of carbon dioxide (CO<sub>2</sub>-content) can also be determined volumetrically or gravimetrically (according to EN 196 part 1, [7]) using another 5 g of the mortar sample. If an air hardening lime mortar and an aggregate without carbonate are present, the amount of CO<sub>2</sub> will correspond roughly to the amount of calcium and magnesium, which have been converted into calcium and magnesium carbonate, that is present in the binder. If quantities of hydraulic binders are expected the separation has to be done according to the section below that deals with hydraulic binders.

The amount of calcium determined can then be converted to Ca(OH)<sub>2</sub> and the amount of magnesium determined to Mg(OH)<sub>2</sub>. The sum of Ca(OH)<sub>2</sub> and Mg(OH)<sub>2</sub> is the amount of binder which is compared with the amount of aggregate (dried residue after acid treatment). The binder to aggregate ratio will be given as the equivalent being normalised, based on the amount of binder (*e.g.* hydrated lime : sand = 1 : 3 in parts of mass). The type of binder (calcitic lime, dolomitic lime) can be deduced from the ratio of calcium and magnesium.

#### 2.1.1.2 Lime mortars with aggregate completely or partly soluble in acid

When the mortar aggregate is partially or totally calcareous it is possible to make an estimation of composition of the binder, the aggregate and other components of the mortar using petrographic analysis [8] on polished or conventional thin sections, or by X-ray diffraction analysis. Acid dissolution will not give suitable results to determine the binder to aggregate ratio when the aggregate is soluble in acid

One way to disaggregate binder from calcareous aggregate is by using the mechanical separation method. It is also possible to apply a disaggregation method that uses ultrasonic equipment. The sample is placed in water and is subjected to ultrasonic waves. An optical assessment using a binocular microscope should always be performed afterwards, to check the quality of the disaggregation. After disaggregation a separation of the binder from the aggregate can be performed by sieving using a 63µm sieve. The fraction that passes through the sieve will be more enriched with binder, the fraction retained on the sieve is more enriched in aggregate. A chemical analysis of both fractions can then be carried out according to the flow charts shown in the appendix.

#### 2.1.1.3 Mortars with hydraulic binders (hydraulic lime, cement)

If preliminary examinations have shown that the mortar contains hydraulic parts of binder and acid-insoluble aggregate, the sample should be prepared as described in the chapter before, as always being careful if calcareous aggregate is detected.

#### Determination of the insoluble residue after acid treatment

The following procedure will allow the determination of the content of insoluble residue in the mortar.

Put 1 g of the prepared mortar in a 400 ml beaker. Add 200 ml of distilled water, stirring the solution in order to avoid the formation of clots. Add 30 ml of HCl (1N), continually stirring for 60 min. It is very important to maintain the solution in a temperature range between 20 and 23°C. Filter with glass micro fibre filter at pressure of 40-93 KPa. The filtration time should not exceed 15 min in order to avoid strong etching of the sample. Wash the residue many times and transfer the insoluble residue from the beaker to the filter.

The content of insoluble residue represents the percentage of siliceous aggregate content in the mortar.

Instrumental analysis (e.g. DSC, DTA, TG, XRD) can be performed on this residue. On the filtrated solution, soluble silica, sulphates and other salts soluble to acid can be determined, by different procedures, for example; wet chemistry, gravimetry, colorimetry, turbidimetry, UV/VIS, AAS.

The method used must be indicated in the analytical report.

#### Determination of acid soluble components

The solution from the determination of insoluble residue can be dried and the components of the soluble part of the mortar can be determined from the dry residue.

However, the results of this determination are not very reliable, because the presence of soluble silica can disturb the analysis. For this reason it is better to determine the acid soluble component after soluble silica determination.

#### Determination of soluble silica (CSH-phases) in the binder (Method 1 acc. U 84000150 [5])

Cool the insoluble residue to room temperature. Wet with concentrated HCl at 105°C for 1h. Cool and digest the residue with 10 ml of concentrated HCl and after few minutes dilute with hot distilled water (70-80 ml). Heat the covered mixture rapidly near boiling. Filter the hot solution through a medium texture paper into a china cup (200 ml), wash with hot water three times, allowing each portion to drain completely. Evaporate to dryness the filtrate at 105±5°C then digest with 10 ml of concentrated HCl and dilute with 70-80 ml of the hot water. Heat the mixture near boiling and filter the solution through the same filtrate into a flask (500 ml). Wash the residue and reserve the filtrate for the preparation of filtrate solution.

Wash the residue with distilled water. Put the filtration paper with the residue into a previously weighed Pt-crucible ( $m_t$ ). Ignite the Pt-crucible content at 1000±20°C for 30 minutes. Weigh and record the weight of the Pt-crucible and its ignited content ( $m_{t+s}$ ) when cooled to ambient temperature in a dessicator.

The percentage of soluble silica ( $S_s$ ) coming from binder to:

$$S_s = (m_{t+s} - m_t) / m_c \cdot 100A$$

$m_{t+s}$  = mass of Pt-crucible with the silica (g)

$m_t$  = mass of Pt-crucible weighed (g)

$m_c$  = mass of the sample (g)

It is better to transform the impure SiO<sub>2</sub> in pure SiO<sub>2</sub> according to European Standard EN 196-2 [9].

The analysis of soluble silica (SiO<sub>2</sub>) is still not standardised internationally, and care should be taken when interpreting the results. This analysis can be carried out only after mineralogical-petrographic investigation in order to assert that there is no soluble silica in the aggregates.

#### Determination of soluble silica (CSH-phases) in the binder (Method 2)

Dry some grams of crushed mortar (depending on aggregate size) at 40°C until mass constancy is reached. Weigh the dried mortar (1<sup>st</sup> weight). Put the dried mortar in a 1000 ml beaker and add 400 ml HCl (1:3). Stir it for about 5 min. After gas evolution has decayed the sample has to be heated quickly until weak boiling, heating on constant weak boiling should take about 5 min. Filter the hot solution to a medium texture paper into a ceramic container. Save the filtrate for further investigations. Wash the residue with distilled hot water (at least three times). Dry the residue and weigh it again (2<sup>nd</sup> weight). The insoluble content represents the acid-insoluble aggregate; the soluble content is the binder. For the calculation of the binder to aggregate ratio of the mortar the following equation can be used:

$$b/a = (1^{\text{st}} \text{ weight} - 2^{\text{nd}} \text{ weight}) / 2^{\text{nd}} \text{ weight}$$

In the next step the insoluble part (aggregate) should be boiled with 200 ml of saturated Na<sub>2</sub>CO<sub>3</sub>-solution for about 4 min., filter and wash the residue by using HCl (1:4), afterwards wash it at least three times with distilled water. Dry the insoluble content again at 40°C until mass constancy is reached (3<sup>rd</sup> weight). Because of the fact that by using saturated Na<sub>2</sub>CO<sub>3</sub> solution the CSH-phases will be cracked, the insoluble lost weight, which reflects the content of hydraulic components, can be calculated by using the following equation:

$$\text{soluble SiO}_2 [\text{vol.-%}] = ((2^{\text{nd}} \text{ weight} - 3^{\text{rd}} \text{ weight}) * 100) / 1^{\text{st}} \text{ weight}$$

#### 2.1.2 Determination of the soluble Fe<sub>2</sub>O<sub>3</sub>

Transfer 100 ml of filtrate from the determination of soluble silica into a 400 ml beaker. Bring the solution to a pH = 2 ± 0.1 (use diluted HCl). Heat to 50-55°C and add 1 ml of the indicator (dissolve 5g of sulphursalicilic acid in 100 ml of distilled water). Titrate with 0.025 m EDTA until colour changes from pink violet to yellow.

Preserve this same solution for the subsequent determination of Al<sub>2</sub>O<sub>3</sub>.

The quantity of soluble iron  $F_s = 0.998 \cdot V_{\text{EDTA}}$  is expressed in % (mass/mass) of Fe<sub>2</sub>O<sub>3</sub>.

$V_{\text{EDTA}}$  = volume in mol of EDTA solution used for the titration

#### 2.1.3 Determination of the soluble Al<sub>2</sub>O<sub>3</sub>

Add to the solution previously used for the soluble iron oxide determination, 30 ml of 0.025 m EDTA. Bring to pH = 5 ± 0.1 by using a solution of hydrated potassium

hydroxide (4 N KOH). Heat the solution near boiling point for about 3 minutes. The beaker should be covered. Cool the solution to a temperature of 25-30°C and add 3 to 5 drops of an indicator (orange of xilenol). Titrate over a magnetic stirrer with a 0.025 m zinc sulphate solution until colour changes from yellow to pale pink.

The amount of Al<sub>2</sub>O<sub>3</sub> (%) can be determined by using the following equation:

$$\text{Al}_2\text{O}_3 = (30 - V_{\text{ZnSO}_4} \cdot f_{\text{ZnSO}_4}) \cdot 0.632$$

$V_{\text{ZnSO}_4}$  = volume of ZnSO<sub>4</sub> solution used for the titration of EDTA excess in the soluble Al<sub>2</sub>O<sub>3</sub> determination;

$f_{\text{ZnSO}_4}$  = molarity factor of the ZnSO<sub>4</sub> solution 0.025m

#### 2.1.4 Determination of soluble CaO

Take 50 ml of solution from the flask containing the filtrate of the determination of unreactive silica and put them into a beaker (400 ml). Dilute with 150 ml of distilled water, add 5.0 ml of TEA (triethanolamine) and bring to pH 12.5 ± 0.2 by using a KOH solution (4 N). Add the reagent methylene blue and titrate by using a magnetic stirrer with 0.025 m EDTA until the colour changes from blue to yellow.

The amount of CaO can be determined by using the following equation:

$$\text{CaO} = 1.402 \cdot V_{\text{EDTA} \cdot \text{Ca}}$$

$V_{\text{EDTA} \cdot \text{Ca}}$  = volume of EDTA 0.025 m solution used for titration of soluble calcium

#### 2.1.5 Titration and calculation of soluble CaO and MgO

Transfer 5.0 ml of the solution from the determination of the unreactive silica into a 400 ml beaker. Dilute with 150 ml of distilled water and add 5.0ml of TEA (triethanolamine). Bring the pH to 10.1±0.1 (NH<sub>3</sub>-solution), add the indicator and titrate by using a magnetic stirrer and a 0.025 m EDTA solution until colour changes from blue to yellow.

The percentage of soluble magnesium ( $M_{\text{Mg}}$ ) is given by:

$$M_{\text{Mg}} = 1.008 (V_{\text{EDTA Ca+Mg}} - V_{\text{EDTA Ca}})$$

$V_{\text{EDTA Ca+Mg}}$ : volume of 0.025 m EDTA used to titrate the soluble Ca and Mg

$V_{\text{EDTA Ca}}$ : volume of 0.025 m EDTA used to titrate only Ca

#### 2.1.6 Determination of the soluble SO<sub>3</sub>

Transfer 200 ml of solution from the determination of the soluble silica into a 400 ml beaker. Reduce the pH to 1.5±1 by using HCl and boil 5 minutes after covering the beaker. Put the beaker with the boiling solution over a magnetic stirrer and add drop by drop 20 ml of a hot barium chloride solution. Heat for 15 minutes near boiling. Barium sulphate will precipitate. Keep the solution in the covered beaker at 70 - 90°C for 24 h.

Filter the precipitated barium sulphate through a retentive paper. Wash the precipitate accurately by using

hot water. Place the paper and the contents in a weighed Pt crucible and char and consume the paper slowly without inflaming. Ignite at 800 to 900°C, cool in a desiccator and weigh the residue (SO<sub>3</sub>).

The percentage of soluble sulphate ( $M_{\text{SO}_3}$ ) is given by:

$$M_{\text{SO}_3} = (34.3 \cdot m_{\text{BaSO}_4}) / m$$

$m_{\text{BaSO}_4}$ : mass of barium sulphate (g),

$m$ : mass of sample (g)

34.3: molecular value of SO<sub>3</sub>/BaSO<sub>4</sub> (0.343 multiplied by 100)

#### 2.1.7 Determination of sulphides

The sample is decomposed by hydrochloric acid under reducing conditions. The sulphides are transformed into hydrogen sulphide, which is carried over by a gaseous stream into ammoniac solution of zinc sulphate. The precipitate zinc sulphide is determined by iodometry [10].

#### 2.1.8 Determination of soluble Na<sub>2</sub>O and K<sub>2</sub>O

This method is based on spectrophotometry, with the elimination of the influence of calcium (eventually present) with phosphoric acid. First standard solutions and standard curves for the photometrical work have to be determined.

Transfer 50 ml of the solution from the determination of the unreactive silica into a volumetric flask of 100 ml (use a 60 ml pipette). Add 10 ml of diluted phosphoric acid 1:19 into the flask. By using distilled water make up the volume to 100 ml and shake. Atomise the solution by using a spectrometer and measure the obtained intensity at 589 nm for sodium and at 768 nm for potassium. Use the standard curves in order to obtain by interpolation the concentrations of sodium oxide ( $C_{\text{Na}_2\text{O}}$ ) and of potassium oxide ( $C_{\text{K}_2\text{O}}$ ) in the solution.

The amount of Na<sub>2</sub>O and K<sub>2</sub>O can be determined by using the following equations:

$$C_{\text{Na}_2\text{O}} = C_{\text{Bn}} + (C_{\text{Bh}} - C_{\text{Bn}}) \frac{I_{\text{Na}_2\text{O}} - I_{\text{Bn}}}{I_{\text{Bh}} - I_{\text{hn}}}$$

$$C_{\text{K}_2\text{O}} = C_{\text{Bn}} + (C_{\text{Bh}} - C_{\text{Bn}}) \frac{I_{\text{K}_2\text{O}} - I_{\text{Bn}}}{I_{\text{Bh}} - I_{\text{hn}}}$$

$C_{\text{Na}_2\text{O}}, C_{\text{K}_2\text{O}}$ : concentrations of Na<sub>2</sub>O and K<sub>2</sub>O of the examined solution obtained by interpolation;

$C_{\text{Bn}}$ : concentration of Na<sub>2</sub>O and K<sub>2</sub>O of the standard solutions which has a concentration lower than the examined solution (the value is expressed in mg/l or ppm);

$C_{\text{Bh}}$ : concentration of Na<sub>2</sub>O and K<sub>2</sub>O in the standard solution with a higher concentration than the examined on (mg/l);

$I_{\text{Bn}}$ : intensity of the standard solution with lower concentration;

$I_{\text{Bh}}$ : intensity of the standard solution with higher concentration.

The percentage of soluble Na<sub>2</sub>O and K<sub>2</sub>O can be examined on the basis of the concentrations as shown below:

$$\text{Na}_2\text{O} = 0.1 C_{\text{Na}_2\text{O}} / m_c;$$

$$\text{K}_2\text{O} = 0.1 C_{\text{K}_2\text{O}} / m_c;$$

$m_c$ : mass of examined mortar sample (g).

### 2.1.9 Determination of ignition loss

From another part of the original sample, the ignition loss at 1000°C has to be determined. If this sample contains lime or hydraulic lime as binder, one should determine CO<sub>2</sub> volumetrically or gravimetrically from the original substance.

The content of siliceous aggregate will be related to the sample being free of ignition loss and thus gives the aggregate content within the original mortar. The difference from 100% gives the binder content without ignition loss which depending on the type of binder (e.g. cement 5 wt.-%, eminently hydraulic lime 3-20 wt.-%, hydraulic lime 18-21 wt.-% ignition loss) has to be converted to the composition of the original binder with ignition loss. The binder-aggregate ratio will be given as the equivalent normalised to the binder content (e.g. OPC / sand = 1 / 6 in mass proportions). For determination of the mixing ratio see the calculation with examples in the literature [11].

Regarding the characterisation of the binder and the determination of its content in the mortar, it is assumed that the acid-soluble parts of the examined building material sample result solely from the binder. As “leading oxides” for the determination of binder or, if necessary, also of a two-component mix, the contents of calcium oxide (CaO), magnesium oxide (MgO), silicon dioxide (SiO<sub>2</sub>) and sulphate (SO<sub>3</sub>), after ignition, can be used.

## 2.2 Gypsum mortars

If the results of microscopic analyses and/or the X-ray phase analysis have shown that the mortar is a gypsum or gypsum/anhydrite-mortar with an acid-insoluble aggregate such as quartz or feldspar, the quantitative determination of binder and aggregate can be done according Middendorf [11] and Middendorf and Knöfel [12]. In order to prepare a part of the mortar sample, 20g is crushed carefully and dried at 40°C until mass constancy is reached.

About 5 g of the pre-treated sample are solved in 80 ml of boiling diluted hydrochloric acid (1:3) for about 2 min. Adding 200 ml of boiling distilled water will prevent precipitation of sulphates during cooling. After this the sample is filtered and the residue dried and weighed. The residue is the aggregate within the mortar.

For the determination of the binder composition, the filtrate is put into a 500 ml volumetric flask and the latter is filled up to the calibration mark (to 500 ml) with double-distilled water. The complete binder content of the mortar sample is now in this 500 ml solution. From aliquot parts, the determination of the calcium and magnesium content [8] is determined titrimetrically, photometrically, flame-photometrically or by using atomic absorption spectrometry (AAS). From another aliquot the sulphate content of the sample is determined gravimetrically, nephelometrically or by using indirect procedures.

Out of another part of the original sample (about 10 g) the content of fixed water is determined with the help of drying in an oven at 380°C on condition that the mortar does not contain any additives that can be oxidised. If non-hydraulic lime may be present within the binder, one should do an additional volumetric or gravimetric analysis of the carbon dioxide content (CO<sub>2</sub>) in the original sample.

The gypsum content (CaSO<sub>4</sub>\*2H<sub>2</sub>O), being the expected calcium sulphate phase in the mortar, will be calculated on the basis of the measured content of hydrate and sulphate. Any surplus content of calcium that might remain, should be considered to be anhydrite (CaSO<sub>4</sub>). The measured content of calcium must correlate with the calculated content of calcium, which is generally possible if the work has been done accurately. Surplus calcium should only be there if CO<sub>2</sub> was found. This will be converted to calcite (CaCO<sub>3</sub>).

The following steps have to be taken for determination of binder to aggregate ratio. Firstly, the gypsum content is converted to the hemi hydrate (CaSO<sub>4</sub> \* 0.5 H<sub>2</sub>O) which was in general originally the composition of the dry unmixed binder. The calculated content of anhydrite (CaSO<sub>4</sub>) remains unchanged and the content of calcite (CaCO<sub>3</sub>) will be converted to calcium hydroxide. These different degrees of content are added to each other, in proportion, and compared to the insoluble aggregate content. The binder to aggregate ratio will be given as the equivalent normalised to the binder content (e.g. hemi hydrate : lime : sand = 1 : 0.1 : 2 as mass proportions).

## 3. DETERMINATION OF THE AGGREGATE GRADING CURVE

The size grading curve of the aggregate, and the binder to aggregate ratio are interesting for the characterisation and “reproduction” of the mortar. For determination of the aggregate grading curve one has to consider that a decreasing mass of sample with a constant maximum grain size results in a less precise measurement. Therefore, it does not make sense to determine a grading curve for 15 g of sample with a maximum grain size of 8 mm. Nevertheless, one can answer the question regarding the maximum grain size, even based on small samples taken specifically [13].

Besides the fact that the precision of statements depends on the sample mass, further problems come up when binder and aggregate are separated. Very often errors can occur during separation, especially if the aggregate is very fine. Solvents or careful mechanical procedures should be chosen. Certain combinations of binder and aggregate cannot, in practice, be separated (see Table 1).

The samples must be crushed carefully, normally by hand. For friable samples, a thermal pre-treatment at 400°C can be performed to disaggregate the mortar and, depending on the particle size of aggregate, up to about 200 g of sample carefully crushed in a mortar. Depending on the sort of binder that has been determined through other analysis, a suitable solvent/separation agent is chosen which will only dissolve the binder and not the aggregate. Table 1 gives advice regarding possible solvents or separation agents.

The solvents/separation agents must react with the mortar until the binder is dissolved and separated from the aggregate particles. If larger amounts of silicates are to be expected in the binder, the aggregate can be boiled with saturated  $\text{Na}_2\text{CO}_3$  solution for about 4 min. If water is used as the separation agent by mechanical separation, the mortar must be kept in motion in the water in order to avoid mechanical abrasion. If necessary, it can be crushed mechanically by hand. Using ultrasonic methods of separation, one should consider that the aggregate particles might be crushed. As a next step, either the aggregate must be filtered and washed with water or for mechanical separation the water must be decanted carefully. The decanted suspension can be taken as a basis for further investigations. The aggregate is dried at  $105^\circ\text{C}$  (for aggregates containing gypsum dry at  $40^\circ\text{C}$ ) until mass constancy is reached.

The dry aggregate is then weighed and sieved (with apertures of 0.063, 0.125, 0.250, 0.5, 1, 2, 4, 8, 16 mm, or whatever dimension is required). The weights of the fractions retained on the sieves are recorded. The results of weighing the fractions must be displayed in a cumulative semi-logarithmic diagram (see Fig. 1) of weight percentages passing through the sieves. It may also be necessary to integrate particle size distribution curves.

#### 4. WATER SOLUBLE COMPONENTS

Owing to a building's position or the influences of environment, substances such as salt, can penetrate the mortar or can be developed there which result in a transition or change of physical and chemical properties [14]. The formation of gypsum or other salts results from the absorption of sulphur dioxides or from the migration of salt-containing solutions. If parts of the building are damaged by salt, very often a gradient exists from the buildings surface inwards as well as from the pedestal up into the masonry. Therefore, harmful salts can

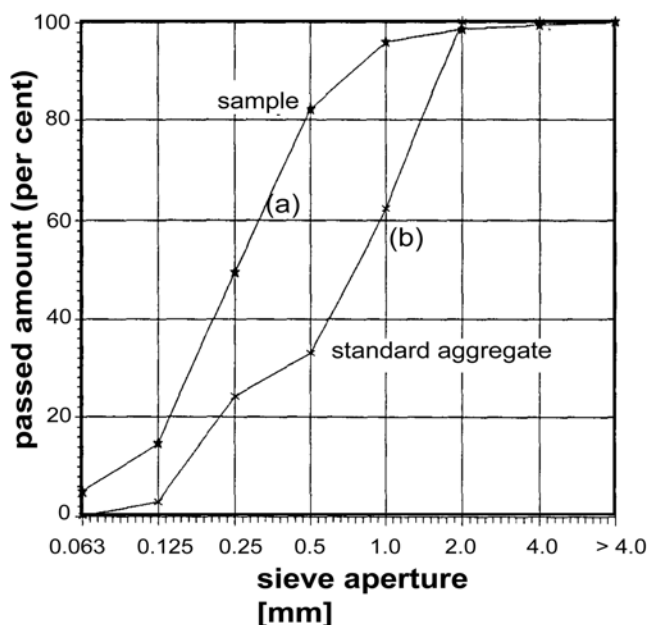


Fig. 1 - Cumulative aggregate grading curves (a) aggregate from a historic mortar, (b) standard aggregate acc. EN 196-1.

have different effects on different parts of the building. If a profile of the damage caused by salt in building parts has to be done, several samples may have to be taken from different heights and depths. For this, the specific conditions with regard to the state of the building must be considered for the part to be sampled.

The content of salt is determined carefully according to the test rules by dissolution with water.

A part of hardened mortar sample is carefully crushed in a mortar (particle size ca. 2 mm). The sample is weighed and dried at  $40^\circ\text{C}$  until mass constancy is reached. The dried sample is weighed in a container that can be sealed, and 50 times of its content (1:50) of demineralised boiled and cooled water are added. This is shaken at room temperature for an hour and filtered.

The following is determined from the solution by using different methods [15, 16]:

pH, conducting capacity	alkalis ( $\text{Na}^+$ , $\text{K}^+$ , etc.) e.g. AAS earth alkalis ( $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ ) e.g. AAS
ammonium	e.g. wet chemistry anions ( $\text{Cl}^-$ , $\text{SO}_4^{2-}$ , $\text{NO}_3^-$ , etc.) e.g. ion chromatography.

Most salts (chloride, sulphate and nitrates of alkalis, earth alkalis and ammonia) are easily soluble in water and show high saturation concentrations. If the concentration of this salt is high or when calcium ions are present, the saturation limit for sulphates can be exceeded. As a consequence they cannot be dissolved away completely. Therefore, the method has to be repeated with a higher degree of dilution (e.g. 1:100) if the complete analysis of the eluate hints at possible reaching of sulphate saturation limit.

The measured contents are related to the dried solid matter. In addition, extraction with a Soxhlet apparatus can also be carried out. Furthermore it is possible to use indicator strips to get an overview of the salt content. The method has to be mentioned in the test report as the result can be extremely different from that of the method described here.

#### 5. DETERMINATION OF MOISTURE CONTENT IN MORTARS

##### 5.1 Determination of unbound moisture

The amount of unbound moisture is important for different reasons. For example, the taking up of moisture within a layer of plaster which has suffered from heavy rain can be determined in the same way as the moisture content of a masonry mortar in a condensation zone or affected by rising damp. If the moisture distribution in a part of the building is being investigated, this must be considered when planning sampling which must be done very carefully. The mortar sample must be quickly placed in an air-tight wrapping or containers. Mortars do dry very easily, and the state of moisture as sampled must be preserved until the sample is dried in the laboratory. Caution must be applied here if high amounts of salts containing crystal water are present in the mortar. There can be a great difference between the result of

the method suggested here compared with others methods with higher drying temperatures.

The sample is put in a dry container with known empty weight or in a transport container that is air-tight, and is subsequently dried in a warming cabinet at 40°C. The change of mass determined by weighing is compared to the amount of mass for the dried sample which corresponds to the moisture content of the sample related to its dry mass. Mass constancy is reached when controlled weighing with a difference of one day during further drying time does not differ more than 0.1 %.

## 5.2 Determination of bound water content

This method described below can be used to assess if there is water in the sample that is chemically bound in hydrated phases which normally cannot be found by using X-ray diffraction analysis. If the sample contains gypsum, hemi hydrate, calcium or magnesium hydroxide, the methods can also be used in order to determine their contents or degrees of conversion. The methods do not distinguish between mono-hydrate from binders or from salts being rich in crystal water. If volatile components, such as organics are present, the ignition loss should be determined with inert gas (*e.g.* argon) to prevent oxidation.

### Method 1

Around 20g of hardened mortar is carefully disaggregated in a mortar without destroying the aggregate. The sample is then dried at 40°C until mass constancy is reached.

About 15 g of the dried mortar is weighed to 0.01g in a suitable container. The content of mono-hydrate water is determined as ignition loss at 500°C, related to the dried mass of hardened mortar. If volatile components, such as organics are present, the ignition loss should be determined with inert gas (*e.g.* argon) to prevent oxidation. For a mortar containing dolomite, one should determine bound water with method B, owing to the low dissociation temperature of dolomite.

### Method 2

If no volatile, oxidisable components (organic substances, sulphides etc.) are present, the content of mono-hydrate (mh) can be calculated as follows from the difference between ignition loss (il 1000°C) and CO<sub>2</sub> or moisture content:

$$\text{mh} = \text{il } 1000^{\circ}\text{C} - \text{CO}_2 - \text{moisture}$$

CO<sub>2</sub> content can be determined volumetrically.

## 6. DETECTION OF ORGANIC COMPOUNDS CONTAINING PROTEINS

While ingredients such as hair, straw or charcoal can be seen macroscopically after binder dissolution, or with a microscope, substances containing proteins which hint at the use of casein, whey or blood serum can only be identified qualitatively with a specific kind of analysis. However, this detection is non specific with regard to the sort of protein and is based on the general detection of amino acids as protein elements. As organic compounds containing protein may be decomposed by bacteria, and as

a consequence cannot be shown with this method as the content is too small (below the detection limit), a negative result of analysis does not inevitably mean that the mortar was produced without organic agents. For gypsum-anhydrite mortars this method cannot be used.

The qualitative detection of proteins can be done with an alcoholic ninhydrin-solution up to a certain limiting concentration of the organic substances. Using this test a blue-violet colour appears if they are present. A statement about the origin of the proteins (*e.g.* agents or micro-biological attack) cannot be made with this method.

An amount of about 100-200 mg of crushed mortar is briskly boiled with about 10 drops of 1% proof alcoholic ninhydrin-solution. While boiling a positive result is shown by a blue-violet colour. Blank tests should also be made for control reasons. The decision about the presence of proteins should be made directly after boiling, as later on the sample solution will turn red-violet even if no proteins are present.

## 7. CHARACTERISATION OF PIGMENTS

Inorganic pigments will mostly be finely distributed in low concentrations in the mortar. They can only be found with an analysis if they are materially and structurally different from the binder or aggregate. As the detection of pigment enrichment and also the characterisation of its spatial distribution in the mortar are required, the use of SEM is recommended, which combined with electron beam micro analysis can characterise the chemical composition of pigment particles or pigment agglomerates. In this way one can also visually present the distribution of pigments in the mortar.

If binders (*e.g.* lime or gypsum, partly also cement) can easily be dissolved from the mortar and if the pigments used are not soluble in the solvent employed, investigations of the insoluble part can reveal something about what pigment was chosen. The methods necessary for this (XRD analysis, microscopy, dyeing methods and other micro-chemical methods) and the interpretation of analytical results require an analyst with sufficient expert knowledge.

## 8. DEALING WITH STANDARD QUESTIONS

Finally a list of questions and different problems is listed in Table 2, which relate directly to the "keywords" in Table 1 of part 1. For answering the standard questions in this table the methods used, or the type of information needed are listed. The relative sample mass and the level of technical requirements are also estimated in the right hand columns in Table 2.

Precise methods of analysis are not listed here but can be inferred from the contents of this and the previous chapter. 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.



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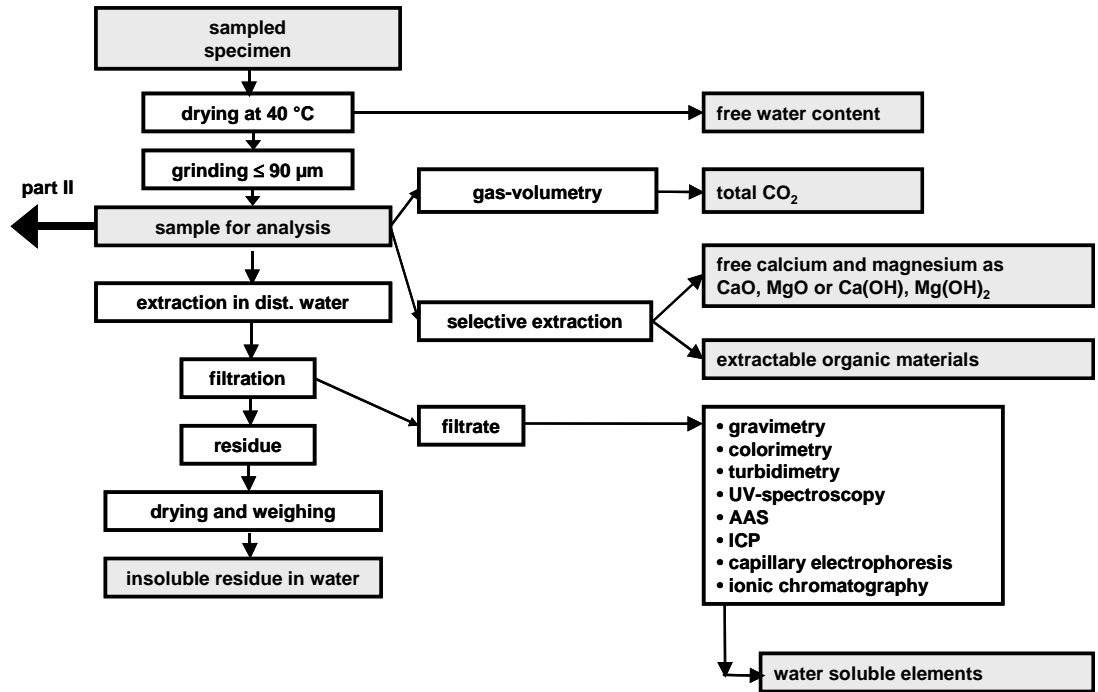
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**Table 2 - Chemical-mineralogical treatment of questions**

Methods and information required	Questions concerning keywords listed in Table 1 (Part 1)															Sample mass	Tech. requirements
	Compatibility	Salts	Cohesion	Adhesion	Changes due to earlier measures	Components	Mixing ratio	Physical properties	Filling and adhesive	Compatibility for restoration	Previous repairs	Functions	Components	Provenance	Building practice		
Types of mortar constituent	X		X	X	X	X	(X)	(X)	X	X	X	X	X	X	X	+	++
b/a ratio	X		X	X	X		X	X	(X)	X		X			X	++	+++
Moisture	X	(X)	(X)	(X)		X			X			X	X			+	+
Bound water		(X)		(X)					X	X		(X)				+	+
Salt content	X	X			(X)	X	(X)			X		X	X			+	++
Proteins						X				X		(X)	X			+	+
Pigments	(X)				(X)	X				X		(X)	X	X	(X)	+	+++
Aggregate grading curve	X		(X)	(X)	X	X		(X)	(X)	X	X	X	X	X		+++	++

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

Part I:



Part II:

