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Laboratory Experiment

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Simple Analysis of Historical Lime Mortars

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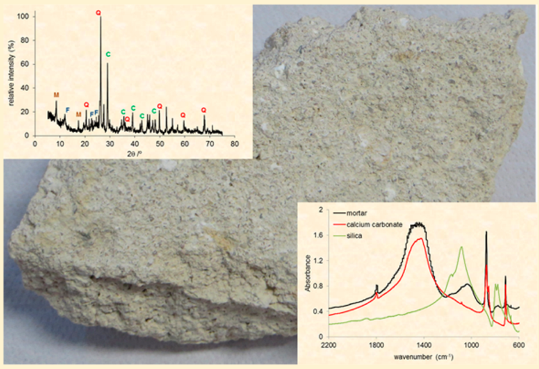
Supporting Information

ABSTRACT: A laboratory experiment is described in which a simple characterization of a historical lime mortar is made by the determination of its approximate composition by a gravimetric method. Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD) are also used for the qualitative characterization of the lime mortar components. These types of experiments are particularly suitable to teach aspects of general chemistry and to present techniques such as FTIR or XRD at an introductory laboratory level to students who have their major in courses that are related to cultural heritage but also have science disciplines, such as chemistry.



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The interest of students in science courses has declined in the last years; this is a known fact and a matter of concern and debate in various countries.[1−3] Within sciences, chemistry has been particularly hit; the causes for this are multiple and complex,[3] and solutions are not easily found. Contributions for a broader and correct public perception of chemistry are important in this context. A route for this, although not new, is the relation of chemistry with conservation science and the thematic of cultural heritage, for instance, through instrumental applications[4] or courses where schools of sciences and schools of fine arts collaborate. The latter allows teaching chemistry at university level but to students that may have limited backgrounds in science disciplines; therefore, because chemistry is an experimental science, the choice of simple and motivating laboratory experiments to teach basic chemistry aspects is mandatory. Various proposals of lab experiments that are related to the arts and cultural heritage exist, but the majority is related to pigments and colorants.[5] Curiously, little attention has been paid to lab experiments related to historical mortars, particularly lime mortars. The main reason for this is most probably because samples of historical mortars to study may not be easily available. This apparent limitation is also a major opportunity for a given school or chemistry department to interact with the community and, therefore, to contribute to the perception of chemistry by the community external to the university. Depending on the specific situation in a given country or region, various types of pathways can be followed to obtain samples of historical mortars. For instance, a specific protocol can be established either with a museum or an institute related with conservation. The analysis of historical mortars is an interesting theme since its composition, among other aspects that can be studied, can give information for archeological or conservation purposes.[6] A list of published works, where the analysis of historical mortars was made for archeological and conservation objectives, is presented in the Supporting Information. In this text, an example of a simple analysis of historical lime mortars, for students with a low backgrounds in chemistry, is presented, and the potentialities to expand this laboratory activity are discussed.

EXPERIMENTAL OVERVIEW

Historical lime mortars are composed by three main components. Two are the major fractions: the binder (essentially calcium carbonate, chemical reactions for its formation in Supporting Information, Scheme S1) and the aggregates (or sand), which is essentially silica. The third component is a minor fraction, the fines, and is formed for instance by clays. Various experimental procedures were proposed for the characterization of lime mortars,[7] and a comparison of results from different procedures were discussed.[8] The most commonly used method is hydrochloric acid dissolution of the binder, which can be used to determine its weight percentage in the overall mortar composition as well as the aggregates and fines weight percentages. The experimental techniques used for this objective were simple but important (rigorous weighing, filtration, eventual preparation of an acid solution by dilution) and could be handled by students of fine arts with low backgrounds in experimental chemistry.

In a more advanced stage of the course, or in a close relation to a discipline more focused on instrumentation, historical lime mortars were used again. For instance, applications of Fourier

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transform infrared (FTIR) spectroscopy or X-ray diffraction (XRD) were exemplified through the identification of the IR absorption bands or XRD peaks of the binder and aggregates.[7,8]

■ EXPERIMENTAL PROCEDURES

Chemical Analysis

An aqueous solution of HCl, approximately 4 M, was needed (about 25 cm^3 per analysis). Depending on the objectives of the course, in the case that students have limited laboratory backgrounds, this solution could be already prepared. Alternatively, the opportunity could be given to the students to prepare it from concentrated HCl, which illustrates all of the precautions that are necessary. The concentration itself was not very critical, so a dilution of one volume of concentrated (usually 37%) HCl in three volumes of water (~4 M) worked well.

Before the analysis, students observed the mortar sample and took note of the shape, color, and degree of homogeneity. When the sample was not disaggregated, it was crushed eventually with a hammer and then in a porcelain mortar to obtain a powder as finely divided as possible. Once disaggregated, the sample was placed in an oven at 100 °C and brought to ambient temperature in a desiccator. About 1 g of sample was then rigorously weighed (w1) in a 25 cm^3 beaker whose weight was registered also (w2). A volume of 3 cm^3 of distilled water was added to the beaker, together with a magnetic bar, and the beaker was then placed on a magnetic stirrer unit. While it was stirred, the prepared HCl was added dropwise until effervescence stopped (stirring was interrupted for a correct observation of the end of effervescence). Then 2–3 cm^3 more of HCl solution were added.

At this point, the binder ($CaCO_3$) reacted completely with the HCl, which liberated CO_2 and left the calcium ions in solution. Therefore, the solid phase was then composed by the aggregates and the fine fraction. At that time, a decantation was made, so the aggregates remained in the beaker, but the fines went along with the liquid, from which they were separated by filtration. The magnetic stirrer was removed. A filter paper was weighed (w3), placed in a funnel (which should be in a holder), and moistened with water. The mixture in the beaker was stirred with a glass rod and decanted. This step was repeated several times; some cm^3 of water was added in each step. Because the dimensions of the aggregate particles and the fines were so different, decanting in this way allowed their separation. The filter paper with the fine fraction was dried and weighed (w4). The aggregates in the beaker were also dried and weighed (w5).

Extension of the Work to Characterization by FTIR and XRD

For the collection of FTIR spectra, the pellet method, by mixing with KBr, was preferred (example in Figure 1). The X-ray diffractogram was obtained by the powder method (example in Figure 2).

When the FTIR and XRD analyses were made, some difficulties were found for some historical mortar samples due to the heterogeneity in their grain sizes, particularly of the aggregates. Therefore, some extra grinding of the sample was needed in these cases before the pellets for FTIR and the mounts for XRD were made. Additionally, for XRD, if the sizes of the silica aggregates were too large, the sample could not be studied in powder, but a pellet and use of an IR pellet presser without any dilution worked well.

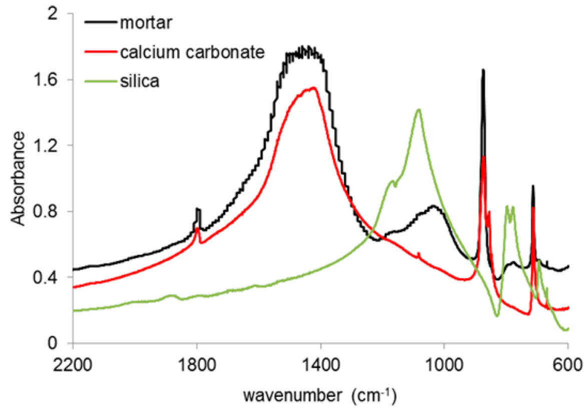

Figure 1. FTIR spectra of a historical mortar, silica, and calcium carbonate.

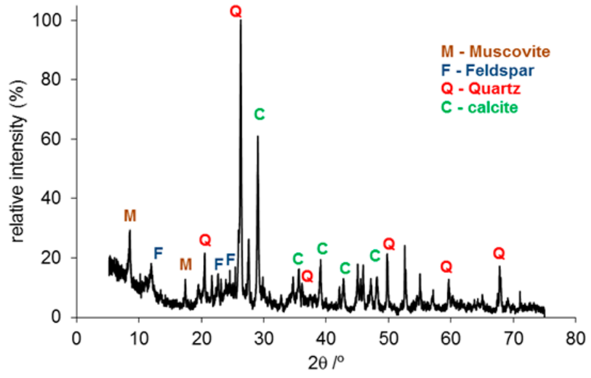

Figure 2. XRD spectra of a historical mortar with the identification of some major components.

■ HAZARDS

Hydrochloric acid fumes or mist can cause severe irritation of the respiratory tract; therefore, it must be used in a well-ventilated area. Contact with HCl can cause burns and irritation to the skin and eyes.

■ RESULTS AND DISCUSSION

The students started to chemically interpret what happened in the experimental section by writing the chemical equation for the reaction of the binder with the HCl solution. With the values of the weights w1–w5, the registry sheet, similar to the one presented in the Supporting Information, was filled out, and the mortar composition in percentage of aggregates, binder, and fines was determined. Depending on the number of students (or groups) and the amount of sample available, each group of students could make replicates of the analysis. In any case, the comparison of results among students, for the analysis of the same mortar, was important. In fact, some variation in the results obtained by different groups was expected for the majority of cases of historical mortars analysis, and the results obtained by different groups of students normally varied within 10% or even more. This point was emphasized in the discussion of results because it was clearly related to the expected heterogeneity of a historical sample and, additionally, helped to clarify for the students the relevance of the steps that are previous to the analysis itself, such as the sampling.

Figure 1 displays an example of a FTIR spectrum of a historical mortar. It was also instructive to obtain the spectra of pure silica and pure calcium carbonate, which are the main constituents of the mortar, so the students could compare the respective main absorptions. For calcium carbonate, the bands near 1500 and 875 cm^{-1} are attributed to the carbonate ion stretching band and the O−C−O bending band, respectively. The most intense bands of the silica are near 1080 and 780 cm^{-1} and are due to the asymmetric and symmetric stretching modes, respectively, of Si−O−Si. As expected, the most intense bands of silica and calcium carbonate also appeared in the mortar spectra.

Figure 2 gives an example of a XRD pattern of a historical mortar where the peaks of major components were attributed accordingly to the Power Diffraction File Alphabetical Index of the International Center for Diffraction Data (ICDD). A summary of diffraction peaks from ICDD files of some relevant components that can be found in mortars is given in the Supporting Information.

As noticed in Figure 2, the peaks for quartz (silica) and calcite are displayed along with some other minor components, such as clay (muscovite) and feldspar.

■ CONCLUSIONS

The experiment described illustrates aspects of an abbreviated characterization of a historical mortar. It is particularly suitable to teach various aspects of chemistry to students that have their major in disciplines related to fine arts or cultural heritage but that also have a component of chemistry in their courses, since it also shows the close relation between different aspects of their courses. Both sections of the work, that is, the chemical analysis and the FTIR and XRD characterization, have been successfully performed by second-year undergraduate students of courses that do not have chemistry as their major disciplines.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Chemical scheme for the formation of lime, detailed experimental procedures, registry sheet for the chemical analyses, and resume of the main diffraction data for substances usually found in historical mortars. This material is available via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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