

Through a Lens Clearly: Instrumental Analysis as Applied to Architectural Materials

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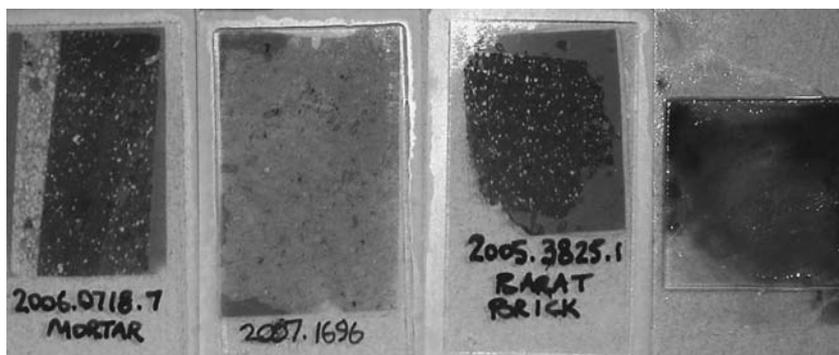
Instrumental analysis is defined as the identification of simpler components from more complex materials and may include techniques ranging from optical microscopy (magnification of an object using visible light) to advanced spectroscopic techniques. In preservation, instrumental analysis may be used to identify a historic material, to date a building or element, to characterize decay mechanisms, or to evaluate materials for treatment. Most modern techniques have been used for decades. However, recent advancements have allowed for analysis of smaller samples and for quicker and more accurate interpretation.

While the equipment and theories of analysis may be complex, most techniques rely on a simple premise: an energy source is directed at a material; that material interacts with the energy source; and a detector identifies changes to the energy source. These changes are interpreted and provide information regarding the material. A simple illustration of this process is visual analysis, in which visible light is directed at a material and our eyes detect the reflection of that light. From this process we observe color, texture, and gloss.

Analytical techniques may identify elements, molecules, or crystals. Depending on the material being analyzed, elemental, molecular, and/or crystalline identification will provide the desired compositional information. For example, dolomite (calcium magnesium carbonate) and calcite (calcium carbonate) have similar molecular and crystalline characteristics but different elemental compositions. Therefore, elemental analysis would be most helpful in distinguishing between these two minerals.

Analysis may also be qualitative or quantitative. Qualitative analysis identifies what materials are present and may be adequate for many studies. Quantitative analysis identifies how much of a specific material is present. Standards such as those developed and published by ASTM International may identify the specific analytical techniques used for a particular study, or the scientist or conservator may select the appropriate techniques based on conditions observed in the field, previous studies, and prior experience.

The following discussion of analytical methods includes a basic summary and brief case studies of several techniques commonly used for analysis of building materials, including optical microscopy, polarized-light



microscopy, scanning electron microscopy, energy-dispersive X-ray spectroscopy, X-ray diffraction, and Fourier-transform infrared spectroscopy. Some or all of these techniques may be useful to study coatings or mortars.

Optical Microscopy

Optical microscopy should be the starting point for nearly all analysis. Typical light sources in optical microscopy include visible, polarized, or ultraviolet light. The light may be either reflected by the sample or transmitted through the sample. The image generated is magnified through lenses. Optical microscopy is used to analyze coatings, stones, and mortar and to identify constituents such as minerals (crystals). Microscopy is typically qualitative but may be semiquantitative.

The most basic type of laboratory microscope is a stereomicroscope, which is a compound microscope (a microscope consisting of multiple lenses) that uses reflected light and provides magnifications of up to 200x. Samples need very little preparation. Stereomicroscopes have an excellent depth of field but limited magnifications. Textural features are often enhanced when samples are illuminated with low-angle light.

Polarized Light Microscopy

The polarized-light microscope (PLM), sometimes referred to as a petrographic microscope, is used to identify minerals (crystals) and evaluate the microstructure of building materials, including stones, mortars, and concrete. A PLM is a type of compound microscope. A

Fig. 1. Samples prepared for examination using a polarized-light microscope. From left to right: mortar-and-brick-masonry thin section, stone thin section, brick thin section, and grain mount of black pigment. All images by the authors.

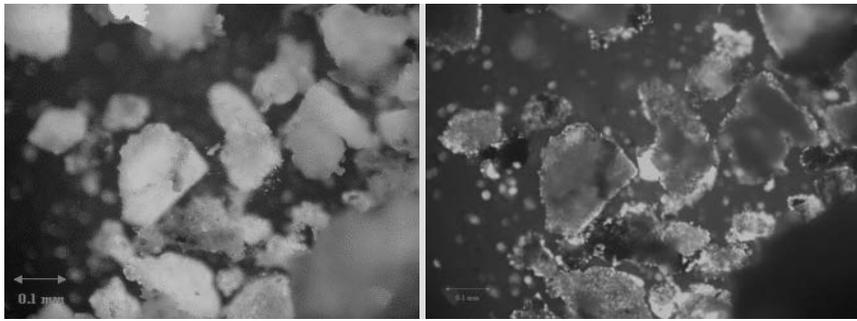


Fig. 2. Grain mount of angular sand grains with white coating viewed using reflected light. Observing the coating with reflected light helps to identify the particles with the stain when observed using cross-polarized light.

Fig. 3. Grain mount of same area of the same grain mount shown in Fig. 2 viewed using cross-polarized light. The coating on the grains can be clearly seen under this lighting condition.

compound microscope uses multiple ocular lenses (the lens nearest the viewer's eyes) and objective lenses (the lens nearest the sample). Magnifications of up to 800x are used with a PLM. Typically, a PLM uses transmitted light: the light source originates under the sample, travels first through the polarizer (a filter that converts light to a plane-polarized condition), and then is transmitted through the sample. Ordinary light vibrates in all directions; when the light passes through a polarizer, the polarizer cancels the light that is not vibrating in a specific direction. Microscopic examination using plane-polarized light of mineral grains immersed in a medium of known refractive index can be used to assist in identification of specific minerals. Light entering into a mineral specimen is refracted at different angles that are related to the crystal structure. This condition results in a phenomenon called birefringence, or double refraction. The amount of birefringence can be measured for a mineral fragment of known thickness when another polarizing filter called an analyzer is inserted above the sample with its vibration direction oriented at 90 degrees to the polarizer located beneath the specimen. This technique is referred to as cross-polarized light. If the analyzer and polarizer are at right angles to each other, all light is canceled. Consequently, the field of view appears black, unless the specimen is capable of double refraction. At a given thickness the birefringence color of a mineral can be used as an aid in its identification.

Typically samples are prepared in two different ways for examination using a PLM: grain mounts, sometimes called powder mounts, and thin sections (Fig. 1). For grain mounts, a few grams of material are crushed to produce a fine powder. The powder is sieved, and a fraction of the sample (typically between 0.105 and 0.074 mm in diameter) is placed on a glass microscope slide and immersed in a liquid of known refractive index. For thin sections, a small block of material (typically 27 by 46 mm) is embedded in epoxy resin. The embedded sample is bonded to a glass slide. The bulk of the sample is removed using a low-speed saw and ground to a thickness of 15 to 25 μm .

Other accessories, such as retarders or wave plates, shift the phase of light, allowing for the further identification of specific minerals. Chemical stains and spot tests may also be used during analysis or slide preparation to assist in identifying specific constituents.

A PLM Case Study

A poor bond between the brick and mortar was observed in a masonry wall constructed in the 1960s. The brick had a weak sand coating, which had been exposed to the environment for about 40 years. The coating was analyzed to determine whether any fea-

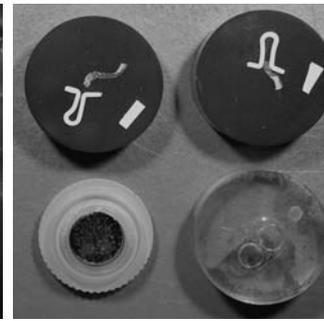


Fig. 4. Samples prepared for scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). The two top samples are fragments of architectural metal. The bottom-left sample is a grain mount of a stain observed on a piece of limestone. The bottom-right sample is the cross section of a coating.

tures could have contributed to the weak bond to the mortar. Optical microscopy techniques were used for the analysis. Fragments of sand removed from the brick surface were prepared as a grain mount and immersed in a liquid with a refractive index of 1.524, which is nearly equal to the refractive index of the mineral gypsum (calcium sulfate dehydrate). Figure 2 shows the grain mount viewed with reflected light, and Figure 3 shows the same location of the grain mount viewed with cross-polarized transmitted light. A white crystalline material was observed to be coating the sand fragments removed from the brick surface. The coating material had low birefringence (the difference between the refractive indexes). The intermediate refractive index was very near 1.524. These features are consistent with the mineral (crystal) gypsum. A subsequent microchemical spot test for sulfate was positive, confirming that the white coating was gypsum, which likely contributed to the poor bond between the mortar and the brick.

Scanning Electron Microscopy

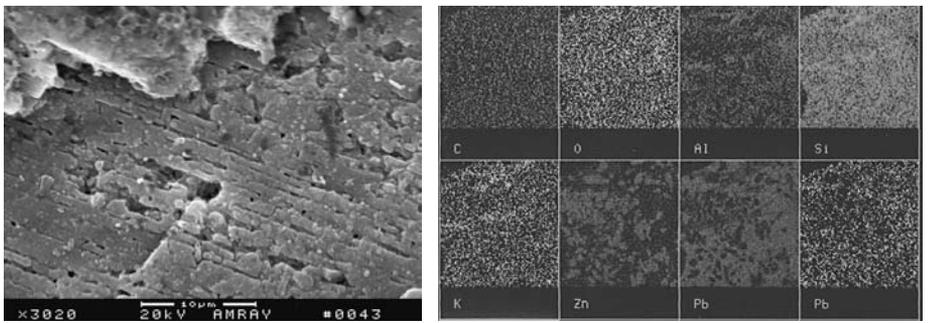
A scanning electron microscope (SEM) is used to identify morphology (shape) and minerals. In SEM a cathode creates an electron beam. A series of magnetic lenses focuses the beam of electrons and directs it at the sample. The result is high-resolution, black-and-white images of small areas. Lighter areas correspond to a greater concentration of electrons, and darker areas correspond to a lesser concentration of electrons.

SEM uses two different imaging modes: secondary electrons (SE) and backscattered electrons (BSE). During secondary-electron imaging, the electrons are emitted from the sample and generate high-resolution topographic images useful in identifying crystals. During backscattered-electron imaging, the electron beam bombards the sample, and some electrons are backscattered or elastically scattered from the sample based on its atomic number. Heavier atoms in the sample scatter the beam electrons more than lighter atoms; hence, heavier atoms (such as iron) appear brighter in the resulting image than lighter ones (such as carbon). Backscattered images provide compositional information about the sample.

Samples for SEM may be very small powdered samples, exposed surfaces, or samples embedded in epoxy and polished (Fig. 4). Samples are typically limited in size by the sample holder, which can hold a sample up to a few square centimeters. The sample is often coated with carbon or gold to dissipate the electrical charge.

Application of SEM

SEM was used to characterize the surface texture of a granite dimension stone that had been exposed to



weathering in an urban environment for about 100 years. Exposed feldspar in granite is normally thought to weather to hydrated aluminosilicates (kaolinite clay). However, in this case, examination at high magnification revealed a selective loss of material, probably along cleavage planes of exposed feldspar crystals. The texture of the stone suggests that the weathering channels may have resulted from hydrofluoric acid exposure rather than natural weathering (Fig. 5). Hydrofluoric acid is a chemical contained in some chemical cleaners used on building facades. SEM was used to examine the sample at higher magnification than is typically used in optical microscopy.

Energy-Dispersive X-ray Spectroscopy

Energy-dispersive X-ray spectroscopy (EDS or EDX) identifies concentrations of elements of less than 0.1 percent. Today, most SEMs are equipped with EDS. The interaction of the SEM electrons with sample material produces X-rays that are characteristic of specific elements. As a result, EDS provides elemental composition of materials and may be performed on any sample used for SEM. It can typically identify elements with an atomic number greater than 5 (boron), but it is more routinely used for elements with an atomic number greater than 11 (sodium). The higher the atomic number the clearer the identification of the material, because heavier elements typically have more characteristic X-ray emission peaks than lighter elements. EDS is usually qualitative, but may be semiquantitative.

EDS is typically used in conjunction with SEM to generate spectra. It may also be used to generate images known as dot maps. These images are compositional maps of the sample. The figure is divided into different boxes, with one element assigned to each box (Fig. 6). Dot maps indicate the location of each element analyzed. The brightness of the dots is related to the concentration of that element in the sample.

X-ray Diffraction

X-ray diffraction (XRD) is used to identify inorganic, crystalline components. In XRD energy is generated from an X-ray source, directed through a slit at a sample, and diffracted off of crystalline components through a range of angles. The intensity of the diffracted energy is measured by a detector. The distance between atoms in the crystals is measured, and this information is used to identify the crystals. A spectrum is then generated.

Powder diffraction is the most common method of XRD used in the analysis of architectural materials. In this technique samples are crushed and sieved, and the resulting powder is adhered to a glass slide using double-sided tape. Analysis is conducted of the fine,

randomly oriented crystals. Typically a 10-gram sample is adequate for analysis, and a mineral must be available in concentrations of at least 5 to 10 percent for identification. X-ray diffraction is qualitative but may be semiquantitative.

Application of XRD

Very hard fragments of extremely fine-grained calcium carbonate were detected in a concrete sample from a nineteenth-century building. Based on textural features observed using optical microscopy, it was not possible to determine whether the particles represented limestone fragments or large lumps of an incompletely mixed (and subsequently carbonated) hydrated-lime binder. X-ray diffraction was conducted on a powdered fragment. The XRD pattern indicated the presence of the minerals calcite and aragonite (Fig. 7). In nature these two minerals are almost never detected together, making it unlikely that the lumps are naturally occurring limestone aggregate. Therefore, it can be surmised that the sample consists of hydrated lime.

Fourier-Transform Infrared Spectroscopy

Fourier-transform infrared (FTIR) spectroscopy identifies molecular bonds and is most often used to identify organic compounds. In FTIR spectroscopy infrared energy is absorbed by the sample and produces vibrational motion in molecules. The most common vibrations involve the stretching and bending of bonds between atoms in a molecule. As a result of the vibrations, the sample displays a series of absorption zones related to molecular bonds within the material. Typically, an IR instrument uses the mid-infrared spectral region (4000 to 400 cm^{-1}). The absorption of infrared energy is based on the specific bond strength and the mass of the molecules. When analyzing a sample, an IR spectrometer produces a spectral pattern of absorption peaks, plotted as percent transmission on the y-axis and wave

Fig. 5. SEM image of weathered granite at 3020x magnification. Note the channels in the surface of a feldspar grain exposed on the surface.

Fig. 6. Dot map of ceramic-tile glaze identifying elemental composition.

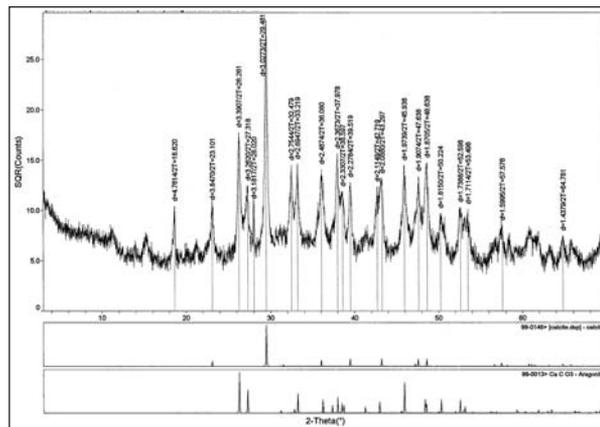


Fig. 7. XRD spectrum of a powdered fragment. The top spectrum is the unknown sample; the middle spectrum is a standard for calcite; and the lowest spectrum is the standard for aragonite. Note that the characteristic peaks observed in the lower two spectra are also present in the spectrum of unknown sample.

number (cm^{-1}) on the x-axis. IR spectra are often referred to as molecular fingerprints. FTIR spectroscopy is a very sensitive analytical technique that allows analysis of samples of less than 0.1 gram. FTIR spectroscopy is qualitative but may be semiquantitative.

Solvent extraction may be used to isolate materials and improve interpretation of spectra. The sample is placed on a potassium bromide salt plate (a small, flat, optically clear plate that will not interfere with the IR energy). Interpretation can often be complicated if the sample contains different materials, as in the case of architectural coatings. While computer databases have facilitated identification, computer software is typically not able to interpret the spectra as well as a trained chemist, especially if the material is composed of many different components. Analysis using FTIR may identify some crystalline materials, such as gypsum, depending on the specific locations of the peaks in the spectra.

Conclusion

This article provides a basic overview of some of the analytical techniques commonly used in the identification of architectural materials. Other techniques that may be used include Raman spectroscopy, atomic absorption, X-ray fluorescence, mass spectrometry, differential thermal analysis, and many others. Like microscopy, SEM, XRD, and FTIR spectroscopy, each requires a specific energy source and a range of detectors. Accurate interpretation of findings depends on the skill of the individual performing the analysis, as well as on the analyst's knowledge of historic architectural materials.

The cost of analysis is typically based on the length of time required to conduct the analysis and the cost of the equipment. Costs may range from a few hundred dollars to tens of thousands of dollars, depending upon the scope and extent of analysis required.

The role of analysis in preservation is indispensable, but there is no single method that can identify all materials. Knowledge of the history, chronology, and context of the sample helps to identify an appropriate first step in analysis. The vast array of analytical techniques that can be used suggests the irony of analysis: it is necessary to have some idea of what the material is to select the appropriate analytical technique. When developing an analytical program, it is important that the process remains dynamic, as the results of any analysis may indicate that the rest of the analytical process should be altered.

While analysis provides an invaluable tool, it answers only some questions. Analysis must be directed in such a way that the results obtained will lead to a better understanding of the historic materials used,

decay mechanisms present, or appropriate conservation treatments. For example, using PLM may help to identify the decay mechanisms of a stone but does not in itself provide the answer to what conservation treatments may be appropriate. Treatment decisions must be based on a variety of parameters and on questions that analysis may assist in answering.

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Equipment Manufacturers

- Nikon Instruments. www.nikon-instruments.com (optical microscopes)
- Meiji Techno. www.meiji-microscopes.com (optical microscopes)
- Thermo Scientific. www.thermo.com (FTIR, Raman spectroscopy, UV-visible spectrophotometers, mass spectrometry)
- Jeol. www.jeol.com (SEM/EDS)
- Bruker. www.bruker.com (FTIR, Raman spectroscopy, XRF, XRD, mass spectrometry)

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