Chapter 1
Application of Instrumental Methods in the Analysis of Historic, Artistic and Archaeological Objects

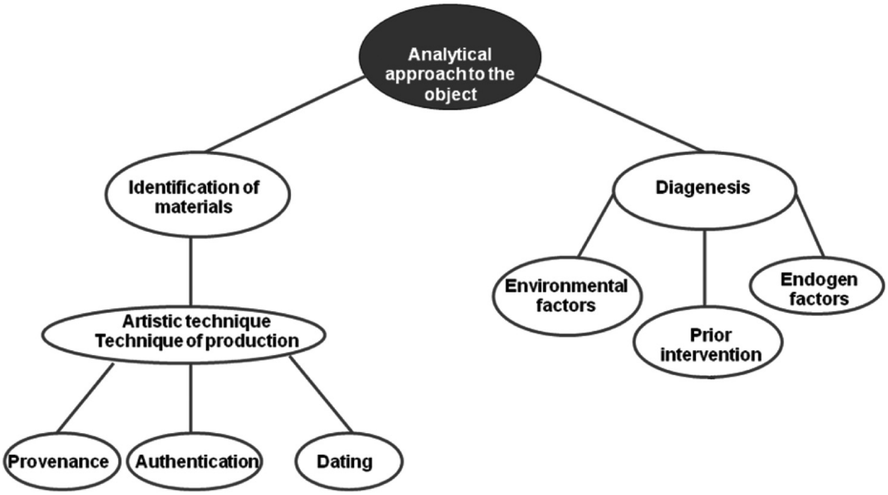
1.1 Importance of Scientific Examination for Archaeometry, Conservation and Restoration

Preservation of cultural goods is an important and rewarding task of modern societies. They are a vital source of inspiration and reflect the culture and history of the past and present. This valuable asset is the basis for future cultures and therefore, is one of the main legacies to be passed on to future generations. For this purpose, conservators, curators, art historians, and scientists combine their efforts, making it now a pluridisciplinary activity.

Cultural goods are particularly rich and diverse, as they are comprised of a great variety of materials (and often made from combinations thereof), and they are of vastly different sizes ranging from archaeological or historical sites, to monuments, and to objects of fine craft or art. Although their significance stems from the transmitted historical, cultural, or figurative messages, their conservation and perpetuation in time depends on their materials. The *Science of Conservation* has been developed for this reason, and is devoted to the scientific study of the objects and the procedures that assure the safeguarding of cultural goods.

Application of the physical and chemical sciences to tackle the problems and questions of archaeology, history, and the conservation of heritage dates back to the 18th century. The first specialized laboratory dedicated to this type of work was established in 1888: the *Chemisches Labor der Königlichen Museen zu Berlin* (Chemical Laboratory of the Royal Museums of Berlin, now the *Rathgen-Forschungslabor*). This laboratory was set up based on the idea that the scientific approach to cultural goods is always ancillary to the approach made by the art historian and the conservator. Currently, scientific disciplines play an essential role in the material characterization of art objects (Scheme 1.1). For example, the dating of archaeological remains is based on instrumental techniques. Characterization of the artistic techniques and technologies of production from the analytical data related to the chemical composition and morphology of the object often allows a clear ascription of the studied object to a geographical region, as well as an elucidation of the date of manufacture. Authentication is sometimes carried out based on analytical data (i.e., identification of a pigment used in a certain historic period or recognition

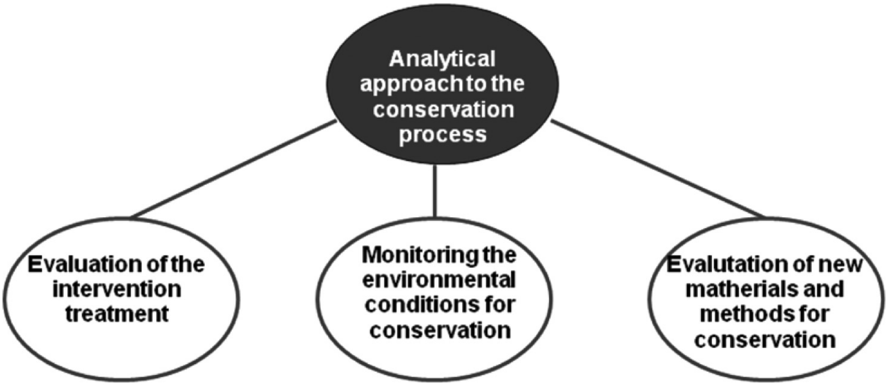
A. Doménech-Carbó et al., *Electrochemical Methods in Archaeometry, Conservation and Restoration*, Monographs in Electrochemistry,
DOI 10.1007/978-3-540-92868-3_1, © Springer-Verlag Berlin Heidelberg 2009



Scheme 1.1 Specific issues related to the materials composing the object and its state of preservation directly derived from analytical data

of a specific artistic technique). Analytical data are essential for determining the state of conservation of the object, as well as the causes and mechanisms of its deterioration. Three principal sources of deterioration are investigated: environmental factors resulting in mechanical, chemical, or biological alterations; endogen causes due to incompatibility of materials present in the object; and the ability of the object to undergo autodegradation or alterations due to old restorations. Scientific examination of the object provides a complete picture of the type of damage it exhibits: occurrence of changes in morphology and/or composition, formation of corrosion products, lixiviation of materials, etc.

Subsequently, based on this fundamental knowledge, it is further helpful to define, develop, and evaluate conservation concepts, materials, measures, methods, and techniques of intervention (Scheme 1.2). Analytical control of the intervention



Scheme 1.2 Specific issues related to the conservation and preservation treatments directly derived from analytical data

treatment is essential for assuring that the operations included in the conservation treatment are performed correctly. Monitoring of the environment is another fundamental task for guaranteeing the future conservation of the object under optimal conditions. Control of temperature, relative humidity, and pollutants in museums (exhibition and storage rooms), monuments, and buildings of interest, as well as at archaeological sites, are indispensable activities carried out during the intervention of the object and beyond. These are good examples of infield applications of analytical techniques. In parallel, research in the science of conservation is carried out in the laboratory, which is focused on the development of new, more selective and sensitive analytical methods, as well as new materials and methods for conservation.

1.2 Information Provided by the Analytical Research

Analytical techniques offer a great deal of information that is relevant to cultural goods and their preservation conditions. Analytical data provide connections among causes and effects, and they are the basis for establishing theoretical models that describe the alteration processes exhibited by the object. In this section, let us consider the analytical information according to its source: the object, the environment, and the conservation process.

1.2.1 Analytical Information Obtained from the Object

Analytical data from the object can be grouped as follows:

(a) Morphological information. Technical examination of the object provides information concerning the size, shape, and method of manufacture, as well as the presence of damage. The examination of the object can be performed with respect to the bulk, to a specific part of its surface, or with respect to a microsample prepared as a thin section or a cross section.

Morphological changes observed in the bulk or on the surface of the object are associated with the damages inflicted upon the object: debris, dust, superficial deposits, crusts, cracks, pores, fissures, fractures, laminations, lixiviations, spots, efflorescences, etc. (Figs. 1.1 and 1.2).

Examination of thin sections prepared from microsamples of organic materials such as wood, parchment, textile, paper, ivory, horn, or leather enables the recognition of anatomical and histological features characteristic of the type of organic material or botanical specie.

Examination of cross sections (in particular) of samples extracted from polychrome objects provides the complete sequence of pictorial strata present in the object, as well as the possible infiltrations or corrosion crusts formed as consequence of the alteration processes (Fig. 1.3). The distribution of pictorial layers is also essential for establishing the artistic technique used by the artist.

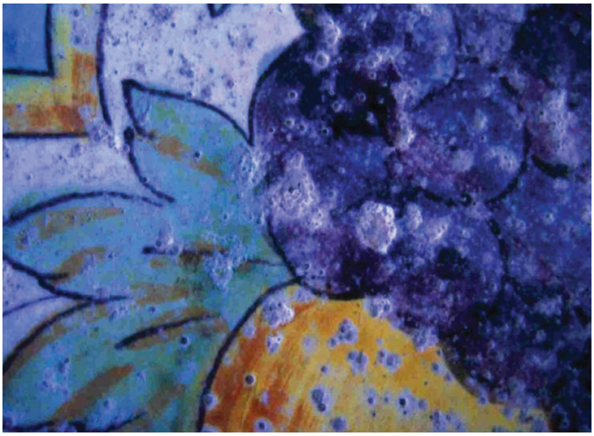


Fig. 1.1 Cracks and pores formed on the surface of a glazed tile (Manises, 18th century) from the floor of the balconies of the Basílica de la Virgen de los Desamparados de Valencia, Spain

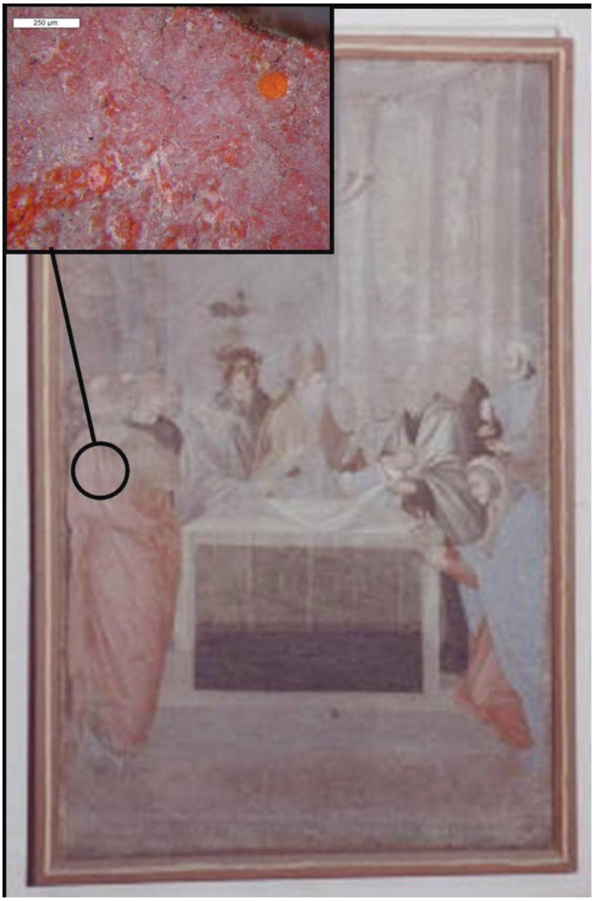


Fig. 1.2 Detail of the bleaching formed on the surface of an oil painting. Examination with stereomicroscope denotes the formation of microcrystals on the surface of the paint layer, which are responsible for the noticeable change of the visual appearance of the painting

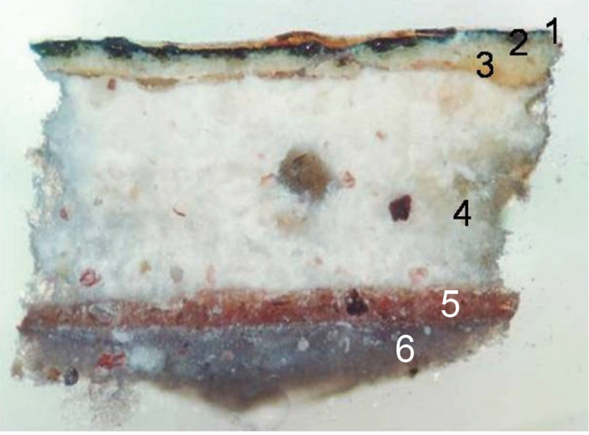


Fig. 1.3 Cross section of an ancient wall painting illustrating the strata distribution: on the top a thin translucent protective coating can be recognized, (1); green paint layer, (2); white paint layer, (3); and thick layer of ground, (4). Underneath all that an original clayey paint layer (5) and its corresponding ground (6) can be recognized

(b) Physical information. Physical, mechanical, and optical properties of the object characterize the material behavior. Consequently, the changes in their original values indicate that some alteration process took place. Among the properties commonly determining the mechanical behavior of the object include density, Young's modulus, ultimate tensile strength, ultimate compressive strength, and ultimate flexion strength. Other physical properties that determine the behavior of the solid object are those related to the porous structure of the material that conforms the object—namely, saturation coefficient, water vapor conductivity coefficient, water absorption coefficient, and permeability.

Optical properties such as color, pleochroism, refractive index, and birefringence, among others, discovered on thin sections when they are examined by means of a petrographic microscope, are essential for characterizing rocks (sculpture and architectural materials). They also provide useful information for characterizing pigments, ceramics, glass and glazes, plasters, metals, and slags, as well as for recognizing alteration processes.

(c) Chemical information. A wealth of qualitative and quantitative chemical information can be obtained from the materials and alteration products formed on the object. Depending on the analytical technique used, that information can be very diverse. Elemental composition is a usual type of data. Structural information can also be available, including recognition of functional groups or of the complete molecular structure, mineralogical distribution, degree of crystallinity, and cell parameters. Presence of isomeric species is frequently detected in organic materials. Electrochemical techniques enable identification of electroactive species, and make speciation studies of the examined materials possible. Calorimetric data are available from thermoanalytical techniques.

In chromatographic techniques, qualitative identification of organic binders requires quantification of species obtained from the original polymeric materials: amino acids from proteins, fatty acids from drying oils, or monosaccharides in plant gums.

Occasionally, determination of properties of the aqueous solution in equilibrium with the solid, such as pH, conductivity, or concentration of ionic species is also of interest—in particular, in the monitoring of cleaning and consolidation of archaeological artifacts.

Chemical and morphological information can be combined by scanning lines or areas of the sample with the appropriate detection system. Compositional mapping of the studied region of the sample is then obtained.

Aging studies, performed in the laboratory, are useful for confirming theoretical models describing the behavior of the object at short-, medium-, and long-term intervals. Formed alteration products, (e.g., by oxidation, reduction, polymerization, scission, hydration, dehydration, dehydrogenation, etc.) are the target compounds in such studies. Three-dimensional (3D) diagrams can be built from the spectra or other characteristic curves obtained at different times.

(d) Biological information. Biological studies focus on the identification of the attacking species (fungi, algae, or bacterial microorganisms, as well as insects, plants, etc. . . .), the products resulting from their metabolic activity, and the alteration products resulting from their interaction with the object. Identification of microorganisms and quantification of species are the tasks of primary studies. Following that, reaction pathways, as result of metabolic activity, are established from data provided through instrumental techniques. Morphological and chemical changes of the object due to biological activity are determined according to that described earlier.

1.2.2 Analytical Information Obtained from the Environment

The term “environment” includes both general and local conditions surrounding the object. According to that definition, three main types of environment can be established: aerial, terrestrial, and underwater. Most of the cultural goods are exposed to the atmosphere, and therefore, determination of physical and chemical parameter characteristics of this environment is of interest when attempting to accurately establish the causes of the damage exhibited on the object. In outdoor conditions, water in the atmosphere (precipitation, humidity, condensation) is an important data for characterizing the effect of the environment on the object. Determination of the content of pollutants in the air (CO_2, NO_x, SO_2, O_3, organic compounds, marine aerosols, suspended matter, etc.), along with the determination of temperature, are also commonly required for characterizing the aerial environment to which the object is exposed. In indoor conditions, emanations from furniture and exhibition cases are investigated, together with most of the above-mentioned parameters. Other environmental factors to be considered are solarization, microorganisms, wind and rain regime, and vibrations caused by road, rail, and traffic.

A large number of archaeological artifacts are found in burial conditions. Water acting as a solvent, as well as a carrier of ionic species coming from the soil, is responsible for the migration of the latter—the acid/alkaline attack on the object material and further lixiviation of materials and ionic species from the object. Thus, determination of physical and chemical properties of the soil (pH, conductivity, chemical composition, etc.) is of great importance.

Finally, underwater and waterlogged environments require a complete chemical analysis of the water (pH, content of ionic species, etc.), as well as the determination of its physical properties (temperature, density, conductivity).

1.2.3 Analytical Information Obtained from the Conservation Process

Analytical control of restoration, conservation, and preservation processes is increasingly demanded by personnel in charge of these protective tasks who attempt to carry them out in the most appropriate mode. Analytical information involving these activities varies widely depending on the methodology employed in the intervention, the chemical products used, and the class of material treated. Cleaning operations on ceramics and (less frequently) on stone or plasters require successive measurement of conductivity in the cleaning bath until the content of soluble salts in the object is reduced to a specific low value. Loss of material from the object and, in general, changes in morphology and chemical composition are controlled by a comparison of the analytical data obtained during the intervention by using a number of microscopic, spectroscopic, spectrometric, chromatographic and electrochemical techniques, among others. Changes in the visual appearance of the object (in particular, color) are controlled by spectrophotometric data obtained from the surface of the object. Sometimes lixiviated and extracted materials are determined during cleaning. In parallel, the chemical and physical properties of the products used for cleaning are controlled. Mechanical cleaning, or cleaning by means of laser ablation systems, can also be analytically controlled.

Similar to cleaning operations, consolidation and adhesion treatments are usually under analytical control. Measurements of the chemical, morphological, and physical properties of the consolidated material are indispensable to assure the efficiency of the operation. Changes in mechanical strength, color, and gloss, as well as chemical composition are assessed. Studies of stability of consolidants are frequently performed by means of natural and accelerated aging trials.

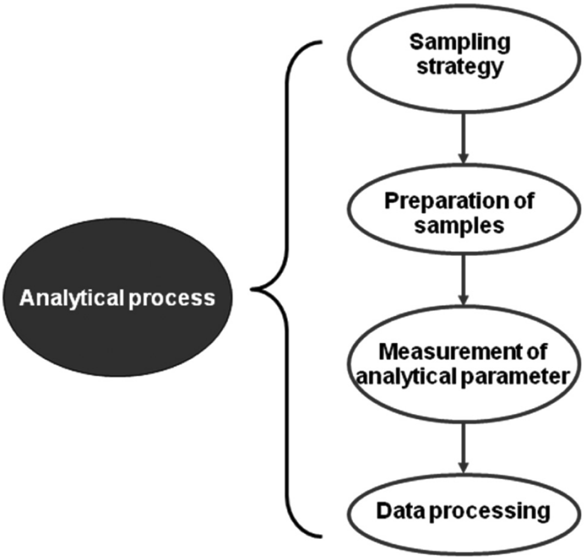
Application of finishes or protective coatings and products for casting and filling missing parts is also surveyed analytically. Compatibility among the products applied and the original materials is assessed from a chemical and physical point of view. Likewise with the consolidants and adhesives, accelerated aging trials are applied to check the stability of the products proposed as coatings and fillers. Experimental conditions for their application—in particular, temperature and humidity—are considered as they determine the final results of the treatment.

Resistance to biodeterioration is another factor to be considered when a new material is proposed for conservation purposes. Accelerated aging trials on inoculated specimens are developed in an attempt to characterize the behavior of this product from the point of view of its resistance to the biological attacks.

Physical conditions of transport and storage of works of art require analytical controls in order to guarantee the preservation of the object. Temperature, humidity, and vibrations, among other parameters, are considered in such instances.

1.3 Requirements of Analytical Methodology Applied to Archaeometric and Conservation Research

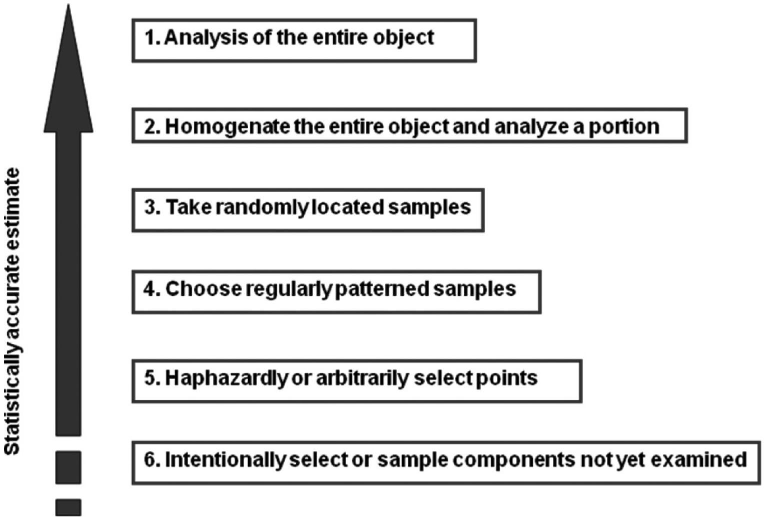
The premise establishing that each cultural good is unique and irreplaceable, and as consequence must be preserved as intact as possible, restricts the conditions for applying analytical procedures. Thus, the four steps comprised in the complete process of analysis, as shown in Scheme 1.3, are conditioned by this singular character inherent to monuments, art, and archaeological objects.



Scheme 1.3 Steps involved in the analysis process

1.3.1 Sampling Strategy

Sampling strategy is the first step in the analysis process, in which the analyst must make a number of decisions about location of sampling points, method of sampling, and the number and size of the samples. Concerning the former and, according to



Scheme 1.4 Sampling strategies for the analysis of a single object

Reedy and Reedy [1], there are six possible sampling strategies for the analysis of a single art or archaeological object, as summarized in Scheme 1.4:

1. *Analysis of the entire object*. Sampling the entire object is usually impossible in archaeometric and art conservation studies, despite the fact that this is the best method for obtaining an accurate result. Nevertheless, some instrumental techniques that do not require sampling, such as photography or x-ray radiography of the entire artifact, are good examples of application of this strategy.
2. *Homogenate the entire object and analyze a portion*. Similar to the prior strategy, this method of sampling is usually impossible in archaeometric and art conservation studies.
3. *Take randomly located samples*. This strategy is equivalent to Strategy 2, since it provides an estimate of the composition of the entire object from a portion of the object. In contrast to Strategy 2, this method of sampling is applicable to cultural goods.
4. *Choose regularly patterned samples*. This strategy consists of taking samples at regular intervals across an object. The accuracy of the estimate is satisfactory for this strategy. Nevertheless, the risk of obtaining a biased result is comported in this strategy when a spatial pattern is present in the object at the same scale as the sampling interval.
5. *Haphazardly or arbitrarily select points*. This strategy imposes restrictions in sampling—in particular, positions for aesthetic or preservation reasons. Thus, there is the risk of obtaining a biased estimate when this strategy is applied on an object.
6. *Intentionally select or sample components not yet examined*. This strategy is frequently applied in art conservation research aimed at the identification of specific alterations or the characterization of the artist's palette.

The number of samples to take depends upon the type of object analyzed and the level of accuracy required for the estimate. In general, the larger the number of samples, the higher the level of accuracy is reached in the analysis; however, the number of samples is restricted by the constraints within the field of art conservation research, so a compromise between these requisites must be achieved.

The size of sample is also restricted in the field of art conservation research. Nevertheless, the degree of heterogeneity of the object imposes an inferior limit to the sample's size, so a compromise between size of sample and size of the confidence interval acceptable should be achieved in each particular case study.

Finally, the sampling method is also conditioned by the singular character of cultural goods. Analytical techniques not requiring sampling are preferred in art conservation research, but they do not always provide the necessary information on the composition of the object so therefore sampling must be carried out. The method of sampling depends on the analytical technique chosen for performing the analysis. Mechanical excision of samples in micro to nano scale is frequently carried out. Restrictions in the size of samples impose the use of scalpels, lancets, needles and, less frequently, instruments specially designed for this purposes. Sampling is, sometimes, performed by abrasively transferring a few grains of the solid material from the object onto a small SiC disk, which does not interfere when techniques such as attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) are used for analysis. Samples of soluble materials can be taken by dissolving them with an appropriate solvent. In such instances, a cottons swab is impregnated with solvent, and then is rolled on the surface of the object until complete extraction of the soluble materials (which are retained in the swab) is complete. The materials retained in the swab are redissolved and then the solution obtained is analyzed. Less frequently, they are directly analyzed in the swab (i.e., by means of pyrolysis gas chromatography mass spectrometry, Py-GC-MS).

1.3.2 Preparation of Samples

Most of the analytical techniques applied in art conservation research require the preparation of the sample prior to the analysis step. Although the sample preparation procedures vary in a wide range, five basic types of procedures can be established: grinding, dissolving, derivatizing, melting and embedding.

Powdering, or grinding, of samples is a simple preparation method required in a number of spectrometric and spectroscopic techniques, such as x-ray diffraction (XRD), nuclear magnetic resonance (NMR), differential thermal analysis (DTA), thermogravimetric analysis (TG), or ATR-FTIR spectroscopy. Control of the particle size during grinding must be taken into account in attempting to obtain reliable results.

Dissolution of the sample is the method required in a number of spectroscopic and chromatographic techniques (e.g., UV-Vis spectrophotometry, atomic absorption spectroscopy (AAS), high performance liquid chromatography (HPLC), and thin-layer chromatography (TLC)). Selection of the suitable solvent is essential when this preparation methodology is used. Occasionally, it is necessary to perform an acid or alkaline attack for dissolving the sample.

Application of gas chromatographic techniques is restricted by the necessary volatility that the analyzed compounds should exhibit. A derivatization reagent is added, in a prior step, to render volatile the components of the analyzed organic materials. In some cases, a prior step consisting of an acid or alkaline hydrolysis of the organic material is necessary for releasing the molecular constituents of the polymeric structure. Inclusion of a prior step in the preparation procedure devoted to the suppression of interfering species is sometimes included.

Melting of samples is necessary for performing the analysis of ceramics and glass materials by means of x-ray fluorescence (XRF). Lithium tetraborate is added as flux for lowering the melting temperature. The homogeneous disks that form can be considered a solid solution of the sample compounds in the binder.

Finally, microscopic examination of samples often requires their preparation as cross sections or thin sections, or by mounting the sample on a glass slide by means of a mounting medium. For preparing thin and cross sections, samples are embedded in a polymer solution. After curing of the polymer, the thin or cross section is obtained by polishing the embedded sample with SiC abrasive disks. Aluminum suspensions or diamond paste are occasionally employed in a final polishing step.

1.3.3 Measurement of Analytical Parameters

At the beginning of the analytical process the analyst has to select the method of analysis. That at least partly determines the sampling strategy, and it completely determines the preparation of the sample.

Two basic requirements must be met for the instrumental technique when it is applied in art conservation research: sensitivity, for obtaining relevant data from small samples on the nano, micro or mili (-gram, -meter) scale; and specificity, for unambiguously identifying compounds and quantifying the analytes from the complex mixtures of substances that form the materials present in the monument or artwork. Other requirements are also desirable for an analytical method when it is applied to objects of artistic, historic, and archaeological nature: according to Lahanier et al. [2], these are:

- nonintrusiveness of the analytical method so that physical integrity of the object is safeguarded
- nondestructiveness of the analytical method so that the bulk of the sample is recoverable after analysis
- fastness, allowing the analysis of single objects as well as large assemblages of them
- universality, enabling the analysis of materials and objects of various shapes, sizes, and compositions with minimum sampling amounts and a minimum of pretreatment

- versatility, to provide information on both average or bulk composition of the object and the specific composition of local areas
- multielement analysis capability, allowing qualitative information on multiple elements or compounds present in the object by means of a single measurement

1.3.4 Data Processing

Chemometric techniques are, nowadays, a valuable tool for achieving a more accurate characterization of the materials composing the art object. Whereas descriptive statistics are commonly used in conservation research, estimation methods are less frequently used. Among them, linear regression methods are mainly used in specific case studies. Multivariate techniques such as cluster analysis and discriminant analysis have been increasingly applied to case studies in archaeometric and conservation research over the last few decades. T-test and analysis of variance are the two hypothesis-testing methods most commonly used in art conservation research. An increasing number of papers have appeared in specialized literature in which fuzzy logic and data-fusion techniques have been applied to archaeometric studies [3].

1.4 An Overview on Analytical Methods Applied in Archaeometry and Conservation of Cultural Goods

As a result of the progressive practical application of the ideas of art historians like Johann Wincklemann (1717–1768) on art and technical history, a scientific approach to art and archaeological objects commenced around 1780 in parallel to that based on a text-based methodology [4]. At the beginning of the 20th century, analytical techniques were restricted to spot tests, optical microscopy, and some spectroscopy techniques. Nevertheless, the number of analytical techniques has significantly increased in the last few decades, extending the scope of classical chemical and physical analysis. Nowadays, there are a wide variety of scientific methodologies providing information on morphology, chemical composition, and structure of the materials present in the monument, archaeological artifact, or art object.

Application of scientific methods to archaeometry and the conservation of cultural heritage is carefully carried out to ensure that the methods chosen are in line with the purposes of the research. According to Lahanier [5], methods currently available are classified into three categories:

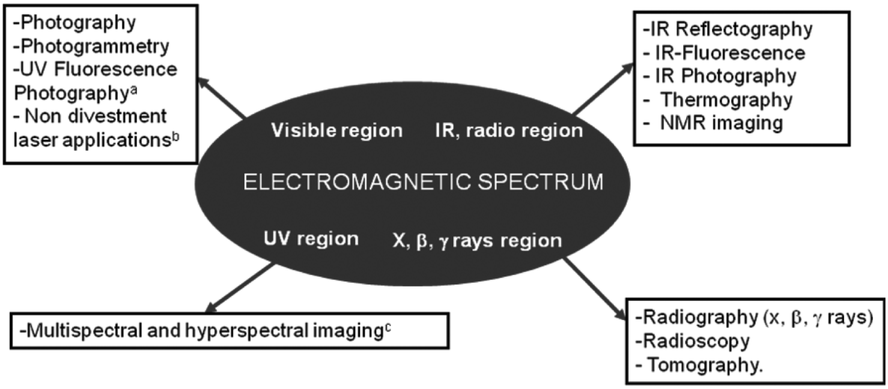
- Examinations based on recording images seen by electromagnetic radiations or electrons
- Analytical methods
- Dating methods

1.4.1 Examination Based on Recording Images: The Holistic Approach

This approach includes images of the object as a whole, visible to the naked eye, acquired in the range of visible, ultraviolet, and infrared light, x-rays, beta rays, and gamma rays, as summarized in Scheme 1.5. These methods work well with the manner in which art historians or conservators approach their work. As there is no sample extraction requirement, these methods can be considered nondestructive. Although, in a strict sense, they can be destructive—i.e., radiation could damage an object. In general, these technologies have been applied to the study of materials of archaeological, cultural, and historic value, monitoring and evaluation of conservation treatments, and digital imaging for documentation and archiving.

These techniques are usually classified according to the type of radiation or spectral region in which data are provided, namely, electromagnetic radiation (x-ray, UV, visible, IR, radio, etc.), acoustic radiation, etc.

(a) Electromagnetic radiation in the visible region. Digital cameras and high-resolution digital scans have progressively replaced more conventional photographic equipment as new documentation and recording techniques. Photogrammetric techniques are based on obtaining orthophotographic images and clouds of 2D or 3D scanned points (matrix-oriented or scattered) by means of digital cameras or laser scanners, which use different digitizing strategies. While photogrammetry and metric surveying techniques can be suitable for archaeological sites and buildings, they present certain disadvantages for smaller and more complex objects. These techniques, together with the development of image processing and image analysis approaches, combined with classification strategies based on fuzzy logic, have extended the scope of application of photographic techniques to a variety of fields, such as authentication of artwork or 3D virtual restoration [6].



[a] Fluorescence in the visible region induced by UV radiation
[b] Laser emitting in the visible and UV region
[c] Imaging in visible, IR and UV region

Scheme 1.5 Main analytical methods based on recording images seen by electromagnetic radiation

Ultraviolet light and fluorescence is a common diagnostic tool for the examination of painted surfaces and for monitoring cleaning processes used since 1925 when UV lamps were commercially available. This method provides information on the composition and specific characteristics of the paint surface, such as retouching and overpainting. Fluorescence lifetime imaging (FLIM) provides images of the fluorescence induced by two lasers emitting in the visible and UV ranges and recovered by a nanosecond time-gated intensified charge coupled device (CCD) camera [7].

Other real and potential uses for lasers in art conservation analyses and practice have been investigated over the last few decades. They are so-called nondivestment laser applications, and are being increasingly used in artwork conservation. [8] These include holographic interferometry nondestructive testing (HINDT), speckle pattern interferometry (SPI), and speckle pattern shearography (SPS), also called grazing-incidence laser scattering.

(b) Electromagnetic radiation in other spectral regions. Infrared photography has been routinely used to examine paintings with films sensitive in the spectral range of 700–900 nm since the 1930s. The obtained images provide interesting information on the working procedures and presence of retouching and overpainting, and enable the identification of underdrawing and the detection of changes in the composition of the materials used by the artist. In 1960s reflectography, using radiation in the wave-length range of 1000–2000 nm was introduced, providing greater penetration through the object strata, and thus enabling a better study of underdrawings. Reflectographic equipment is currently coupled to TV monitors, digitized video cameras, solid-state cameras based on either PtSi and InGaAS sensors, and high-resolution infrared cameras [9].

Computer controllable spectral-imaging techniques measure optical reflectance spectra at many points on a target simultaneously, producing a digital stack of information on defined areas of an object exposed to many different wavelengths of light. Originally described as "multispectral" imaging, the continuous increase in the number of spectral bands resolved by the new generations of imaging spectrometers resulted in the appearance of the term "hyperspectral." The system records light intensity as a function of both wavelength and location, so that a full image at each individual wavelength is included in the data set and thus extends the capabilities for diagnostic imaging [10].

X-rays discovered by Röntgen in 1895 are the foundation of noninvasive radiological techniques. The image formed by the x-ray emitted from a x-ray source, and transmitted through an object, is observed on a fluorescent screen using radioscopic techniques, registered on radiographic films using radiographic techniques (Fig. 1.4), or registered as digital images. The voltage applied in the x-ray tube depends on the characteristics of the studied object. Gammagraphy techniques use radioactive isotopes as a source of more energetic gamma rays [11].

Computed X-ray tomography (CT) was developed as a radiological imaging technique in the 1970s. Three-dimensional CT images in any plane can be reconstructed from a set of sequential cross-sectional slices with resolution of 0.1 mm. Main applications of this technique involve monitoring of the deterioration of natural building stones. More recently, x-ray computed microtomographs (μCT) achieve higher resolution so that mineral grains, micropores, or cracks in the range

Fig. 1.4 Radiograph of a polychromed sculpture. Internal nails used for assembling the different parts of the sculpture are clearly viewed. Courtesy of J.A. Madrid, Instituto de Restauración del Patrimonio, Universidad Politécnica de Valencia, Spain

of 10–100 μm can be detected. This technique has been successfully applied to the examination of paintings and to the characterization of buried archaeological glasses [12].

Magnetic resonance imaging (MRI) has been applied to the study of the distribution of fluid components (i.e., water or a polymer used as consolidant) in a porous material such as stone or waterlogged wood by a direct visualization of the water or fluid confined in the opaque porous medium [13].

(c) Other radiations. Acoustic emission (AE) based on the energy released due to microdisplacements in a structure undergoing deformation, which is detected on the surface using a piezoelectric transducer, has been used for studying the alterations and damage on wooden objects [14].

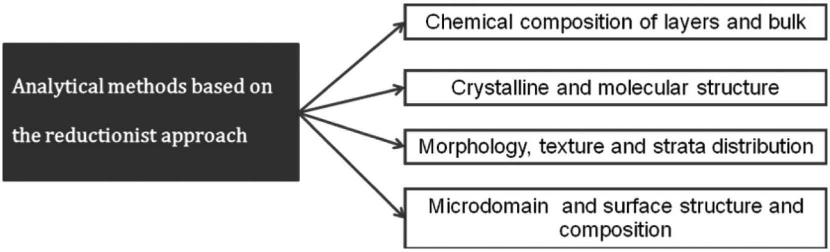
Laser-induced ultrasonic imaging is used quite widely to study the interiors of opaque objects such as sculptures and paintings from the exploitation of laser-induced stress waves [8].

In laser Doppler vibrometry (SLDV), surfaces are slightly vibrated by mechanical activation while the vibrometer scans the object producing 2- or 3D maps of velocity, amplitude, and phase, which allow the detection and mapping of structural defects [15].

Thermography using heat radiation enables the observation of temperature differences, thermal emissivity, or thermal conduction of the studied object. This technique is mainly used in the examination of monuments [16].

1.4.2 Analytical Methods: The Reductionist Approach

Characterization of the objects based on the holistic approach is often combined with point analysis, in which the material composition of a minute portion of the object is determined by classical analytical procedures or instrumental methods. Since the samples under examination are unique and irreplaceable, the specimens should be submitted to nondestructive or at least microdestructive analysis. Nevertheless, a number of instrumental techniques require the total or partial destruction of the



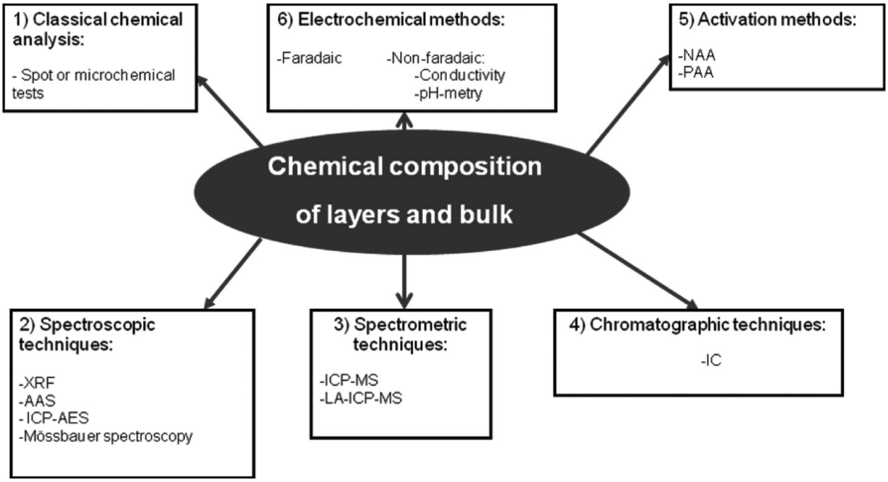
Scheme 1.6 Classification of point analysis methods according to the information yielded

sample. Thus, depending on the procedure involved, the analysis can be considered destructive or nondestructive, and is carried out on the bulk or the object surface. Moreover, and depending on the instrumental technique used, the obtained data can be panoramic or sequential and the measurements can be directly performed on the work itself or on a sample.

According to Mairinger and Schreiner [17], chemical and physical methods can be classified in four categories, as illustrated in Scheme 1.6.

1.4.3 Point analysis providing chemical composition of layers and bulk

Chemical methods and instrumental techniques included in this group provide elemental composition and characterization of ionic species present in the bulk or layers of the object. According to the physical or chemical principia in which the method is based, it can be classified as illustrated in Scheme 1.7:



Scheme 1.7 Main analytical methods for characterizing chemical composition in layers and bulk

(a) Classical chemical analysis The first chemical investigations on the components of historical materials, carried out in the late 18th century, were based on the classical analytical procedures. At that early time, microchemical tests were applied to identify pigments and inorganic materials. During the 20th century, microchemical tests based on classical analytical procedures have been frequently used in specialized laboratories. They not only can serve to calibrate instrumental methods but also they provide a quick and sensitive method of identifying ionic species in materials. In addition, they have, as another advantage, the feasibility of identifying the efflorescence crusts or the pigment within the paint layer, as these tests can be directly performed on cross sections, and the reaction can be observed with the help of a stereomicroscope [18].

(b) Spectroscopic techniques. Spectroscopic techniques have been widely used in the identification and determination of artist's materials of both organic and inorganic types [19]. The provided information and the application of each specific technique depends on the range of electromagnetic radiation and the phenomenon involved in its interaction with the materials present in the analyzed object.

X-ray spectrometric techniques involve radiation in the wavelength range from about 10^{-4} to about 10 nm. These techniques are based on the identification of the characteristic x-rays emitted by the atoms of a sample irradiated by a sufficiently high energy source. Portable instruments enabling in situ investigations, as well as alternative techniques such as micro-XRF, polychromatic synchrotron micro-XRF, total reflection XRF or x-ray absorption have been proposed in an attempt to improve the obtained results [20]. The main advantages of XRF techniques are their rapidily enabling multicomponent analysis, and providing simple spectra, accuracy, and reproducibility. Applications of this technique to the analysis of artwork have been related to the identification and determination of major, minor, and trace elements composing inorganic materials such as pigments, metal, stone, ceramics, glass, surface coatings, and deposits of adventitious materials on the surface, etc. [21].

Emission spectroscopic techniques, using spark source or continuous direct current (DC) arc to excite the emission lines of the elements, and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) together with AAS, have been widely applied in the detection and determination of the chemical composition of inorganic materials. They are especially good at detecting trace elements so they were employed for many of the major analytical studies of glass, glazes, and alloys among other antiquities and archaeological materials in earlier decades [22]. In contrast to other spectroscopic techniques, these are intrinsically destructive and require specific analytical procedures and calibration standards for each analyte.

Mössbauer spectroscopy is a selective tool for the quantitative analysis and speciation of a very limited number of elements. It has been mainly used to study iron compounds—e.g., ceramics, as it gives valuable information about iron-bearing oxide and silicate minerals. This technique has been applied to the identification of the provenance of clay and used raw materials—the manufacturing method employed in pottery and, to a lesser extent, to the characterization of pigments and weathering crusts formed on stone monuments [23].

(c) Spectrometric techniques. Inductively coupled plasma-mass spectrometry (ICP-MS) is a relatively new analytical technique developed during the 1980s and increasingly used in earth sciences and archaeometry fields. Its recent combination with laser ablation to create inductively coupled plasma-mass spectrometry (LA-ICPMS) has increased the capabilities of this technique. A large number of analyzed elements (10–30 typically), a minimal amount of material (tens of mg or less), and the rather simple pretreatment required, as well as the feasibility of performing isotope ratio measurements are the main advantages of this technique. This technique has been applied to the trace element characterization and source tracing of obsidian (*vide infra*), compositional analysis of metallic artifacts, and lead isotope ratio analysis [24].

(d) Chromatographic techniques. Ion chromatography (IC) is a convenient technique for identifying and determining the content of soluble salts on metals, stone and ceramics materials used in monuments—in particular, the anions—and to monitor the ionic species removed during water immersion treatments of archaeological ceramic remains [25].

(e) Activation methods. Activation analysis (AA) has become a popular analytical technique in archaeology, which has provided interesting data enabling the elucidation of the major, minor, and trace element composition of art and archaeological artifacts, which, in turn, can be used to establish their provenance and temporal origin. Detection limits and the range of elements analyzed depends on the type of activation—namely, neutron, fast neutron, charged particle, or gamma photon.

Neutron activation analysis (NAA), based on the interaction of the object material with fast neutrons, has been used in the identification and determination of the content of elements present in pigments, coins and alloys, stone, glass, and pottery [26]. Multi-elemental analysis (about 20 elements) can be performed on small samples off less than 5 mg, with sensitivities in the ppm range. The requirement of a nuclear reactor, the handling of radioactive materials, and the time-consuming procedures required for preparing the samples are the main drawbacks of this technique.

Proton activation analysis (PAA) provides chemical composition of the materials at a depth of 300–500 μm under the irradiated surface. This technique has been used in the study of metallic objects such as ancient coins [27].

(f) Electrochemical methods.

(I) Faradaic electrochemical methods. From a general analytical point of view, electrochemical techniques are very sensitive methods for identifying and determining the electroactive species present in the sample and, in addition, they also are able to carry out speciation studies, providing a complete description of the states of oxidation in which the ionic species are present in the object. Other applications and improvements obtained by their hyphenation with other instrumental techniques, such as atomic force microscopy (AFM), will be described in the following chapters.

(II) Non-Faradaic electrochemical methods. Conductometric methods have been extensively used by scientists and conservators for monitoring the content of salts removed during water immersion treatments of ancient tiles and archaeological ceramic remains. In a different manner to IC, this technique provides the total ionic

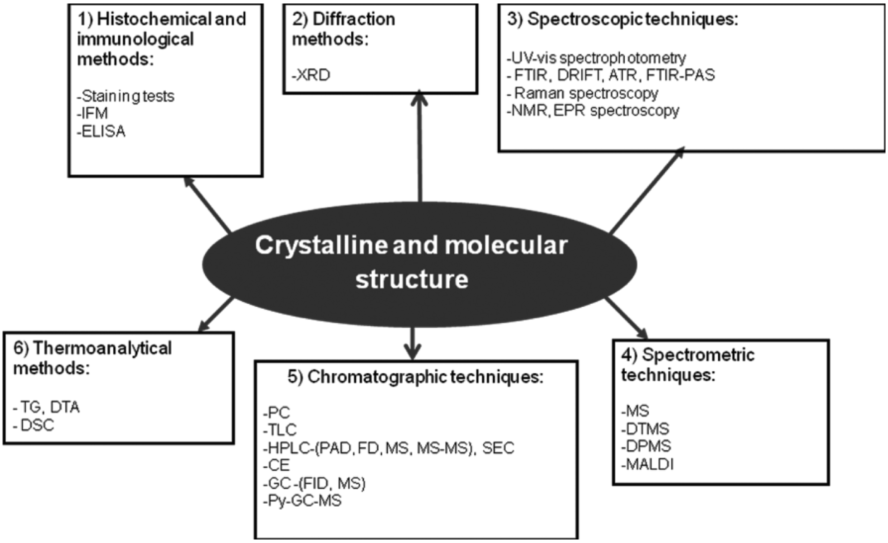
content of ionic species present in the cleaning bath. Its main advantage is the simplicity of the instruments [28].

Measurement of pH is a potentiometric technique frequently used for measuring the degree of the deterioration of materials that are subjected to natural aging. The determination of pH levels is commonly carried out on ethnographic objects manufactured with parchment or leather, and it is especially relevant in altered paper due to the formation of acidic compounds from the decomposition of the woodpulps and other raw materials, which can induce the hydrolysis of the cellulose and then decrease the resistance and mechanical properties of the document [29].

1.4.4 Point analysis providing molecular and crystalline structure

An overview of the analytical techniques most frequently used that provide molecular and crystalline structure is illustrated in Scheme 1.8. Basically, they can be grouped into histochemical and immunological methods, diffraction, spectroscopic, spectrometric, chromatographic, and thermoanalytical techniques.

(a) Histochemical and immunological analysis. As for spot tests applied to pigments, the first investigations of the organic components of historical materials were carried out in the late 18th century and consisted of solubility tests, tests for determining some characteristic physical property of the medium (such as the melting point), and, preferably, histochemical tests [4]. Application of histochemical tests to binding media identification is limited, however, because of its low specificity (i.e., discrimination between albuminoids, casein, or gelatin within proteinaceous materials is hardly obtained). Despite that, a noticeable number of methods have been proposed in the literature [30].



Scheme 1.8 Main analytical methods for characterizing crystalline and molecular structure

Further improvement of microchemical methods for proteinaceous media was based on immunological techniques. The high specificity of the antigen-antibody reaction enables the discrimination of the same protein coming from different species, or the detection of multiple antigens in the same sample. Application to the analysis of artwork has been reported in two types of immunological techniques: immunofluorescence microscopy (IFM), and enzyme-linked immunosorbent assays (ELISA) [31].

(b) Diffraction techniques. X-ray diffraction has been an excellent tool in the service of art and art conservation, as it provides essential information on mineralogical composition and the crystalline structure of materials. Thus, a number of monographs can be found devoted to the description of historic pigments, which include data concerning the x-ray diffraction patterns of many minerals and pigments from historic collections [32]. In addition to pigments, a wide variety of materials can be identified by means of this instrumental technique: stone, clays and ceramic bodies, glazes, efflorescences, and corrosion products formed on metallic objects.

New portable spectrometers have been used for in situ analyses. Powder x-ray microdiffraction instruments or those with highly collimated and parallel x-ray beams have also been used for characterizing cultural goods.

(c) Spectroscopic techniques. Application of the UV-Vis spectrophotometry solution to the study of dyes dates back to 1889 and has been further used in the identification of these substances [33]. Use of this technique for analyzing organic binders is notably restricted because of the nonspecific spectra provided by these materials. In parallel, instrumentation providing visible region reflectance spectra and color specification using colorimetry according to the Comission Internacional de l'Eclairage (CIE) and hand-held spectrophotometers has been a common tool in the field of art and art conservation for in situ characterization of materials such as wall painting pigments or glazed ceramics [34].

Photoluminescence spectroscopy provides information on the composition of the painting surface and the presence of retouchings and overpainting. This technique has progressively evolved using laser sources, giving rise to laser-induced fluorescence (LIF) spectroscopy [35].

Infrared spectroscopy is a widely used technique in the field of art and art conservation due to its versatility and ability to provide structural information on both inorganic and organic materials, the small amount of sample required, and minimum pretreatment.

Since its introduction in the field of conservation science in the 1950s, an increasing number of studies have been reported in the technical literature, as illustrated in some reviews [19, 36]. The noticeable improvements in the instrumentation—in particular, the incorporation of IR Fourier transform spectroscopy—have significantly contributed to extending the scope of this technique so that nowadays it is routinely used for analyzing art and archaeological objects, monitoring conservation treatments, and assessing new conservation products and methods. A wide range of FTIR methods are currently in use: diffuse reflection Fourier-transform infrared spectroscopy (DRIFT), ATR (Fig. 1.5), FTIR photoacoustic spectroscopy (FTIR-PAS), and FTIR microspectroscopy (*vide infra*), either in the transmission or reflection mode [37].

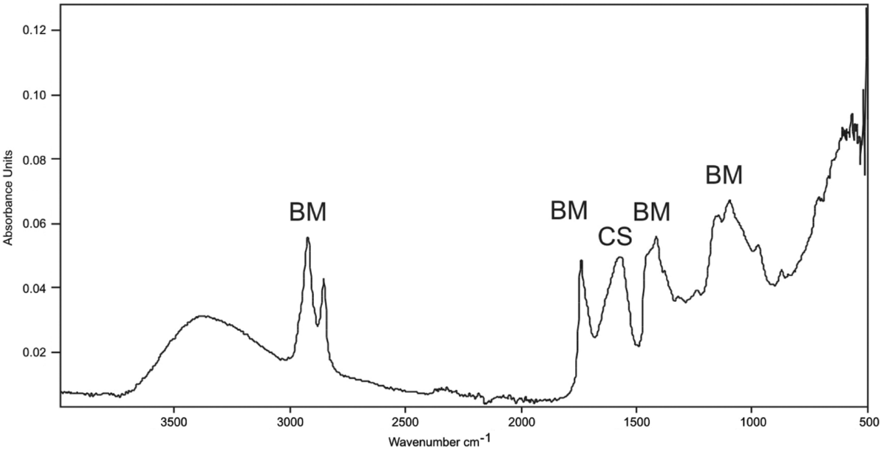


Fig. 1.5 IR spectrum, obtained in ATR mode, of a sample of yellow pigment from José Benlliure's palette (1937). (BM) IR bands ascribed to the drying oil used as a binding medium. Interestingly, and (CS) appearing at 1569 cm^{-1} is associated with carboxylate groups from cadmium soaps formed as a consequence of natural aging

Similarly to FTIR spectroscopy, Raman spectroscopy is a versatile technique of analyzing both organic and inorganic materials that has experienced noticeable growth in the field of art and art conservation, in parallel to the improvement of the instrumentation [38]. In particular, the introduction of fiber optic devices has made feasible the development of mobile Raman equipments, enabling nondestructive in situ analyses [39]. On the other hand, the coupling of Raman spectroscopes with optical microscopes has given rise to Raman microscopy (*vide infra*).

NMR has been primarily applied in archaeometric studies [40]. In contrast, NMR has had a restricted application in the art conservation field due to the complexity of the paint samples. This technique has been chiefly used for identifying highly polymeric materials, such as triterpenoid varnishes, oil, oleoresinous media, and synthetic media [41].

Electron paramagnetic resonance spectroscopy (EPR) (also called electron spin resonance spectroscopy, ESR) has been scarcely applied in the field of art and art conservation. Some work can be found in which EPR is used as complementary technique to SEM-EDX, NMR, and mass spectrometry (MS) for studying free radicals occurring in polymerization, pyrolytic, oxidative, and other radical degradative processes in artwork, as well as in the characterization of varnishes and oleoresinous media [42].

(d) Spectrometric techniques. Mass spectrometry (MS) is an excellent tool at the service of the art and art conservation field due to its great potential to resolve molecular structures without sample pretreatments. Nevertheless, application of this technique in conservation practice is limited by the complexity of art materials. This drawback can be resolved by hyphenation of MS with a chromatographic method. Despite this, a noticeable number of works can be found in literature using, preferably, three different MS techniques. Direct infusion MS has been applied in the analysis of proteinaceous and oil media [43]. Direct pyrolysis MS (DPMS) has been

applied to the identification of natural gums, resins, and waxes in ancient Egyptian mummy cases, as well as in the study of thermally degraded products formed from traditional binding media [44]. Direct temperature-resolved MS (DTMS) has been applied to the analysis of traditional binding media and synthetic varnishes [45].

The introduction of matrices to assist the laser desorption ionization (LDI) process has lead to the development of the so-called matrix-assisted LDI (MALDI). This technique has been applied to identify terpenoid varnishes and their oxidized products [46]. Combined with enzymatic cleavage, MALDI has also been used in the identification of animal glue.

(e) Chromatographic techniques. Chromatographic techniques are commonly used in the analysis of artwork due to their ability to separate the organic components of the complex mixtures present in objects of historic, artistic, and archaeological nature. In general, they not only achieve a higher discrimination of the type of material present in the object, but they also identify the alteration products of these materials. Technological advances have determined the evolution of these techniques in the field of art and art conservation. Thus, gas chromatography (GC) or liquid chromatography (LC) have progressively replaced other simpler techniques, such as paper chromatography (PC) or TLC. Hyphenation of GC and LC to a MS detector, as well as use of pyrolysis devices coupled to the GC, have significantly improved and extended the scope of applying these techniques. Complex and time-consuming sample preparation [47] is the main drawback of these techniques, sometimes limiting their application—in particular, when a large number of measurements must be periodically performed on large assemblages of specimens (i.e., laboratory experiments on monitoring alteration processes of artists' materials or conservation products). Despite that, these techniques are abundantly used in specialized laboratories for analyzing organic materials such as organic pigments, binding media, and coatings.

Reverse-phase columns with a gradient elution in combination with UV-Vis spectrophotometers using photodiode-array (PDA) (Fig. 1.6) and spectrofluorimeters are common devices employed in this technique. In a lesser extent, MS, tandem mass spectrometry (MS-MS), and nano liquid chromatography-electrospray ionization-quadrupole time-of-flight tandem mass spectrometry (nanoLC-nanoESI-Q-qTOF-MS-MS) has been used as detection system. This instrumentation has been mainly used in the analysis of dyes and proteinaceous media, and in some extent, in the analysis of drying oils and terpenoid varnishes [47, 48].

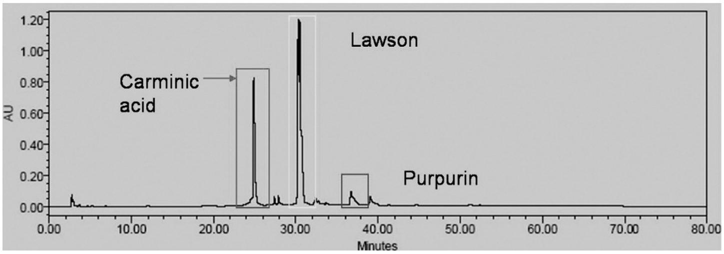


Fig. 1.6 Liquid chromatogram from a mixture of compounds responsible for the color of cochineal henna, and madder. Courtesy by DJ Yusá, Instituto de Restauración del Patrimonio, Universidad Politécnica de Valencia, Spain

Size-exclusion chromatography (SEC) has been also used as complementary technique for characterizing changes in the composition of synthetic resins due to aging. In particular, it enables the determination of molecular weight distributions and the glass transition temperatures of resins.

In recent years, capillary electrophoresis (CE) has been introduced as an alternative method for performing a chromatographic analysis of art objects, and thus, a number of methods for analysis of waxes, resins, drying oils, animal glues, and plant gums have been proposed [49].

GC has been extensively applied in the identification of organic media and varnishes given its versatility. In the first analytical studies of artworks, flame ionization detectors (FID) were used. The higher capacity of MS detectors—coupled with the GC for identifying compounds—and their high sensitivity are the reasons for the extended use of GC-MS instruments, preferably quadrupole mass spectrometers and ion-trap mass spectrometers. Specific derivatization methods have been proposed according to the type of target compound: polysacchraides, oils and waxes, terpenoid resins, or proteinaceous media [47]. Additionally, a number of papers can be found in the literature in which more sophisticated pretreatments are proposed to identify more than one class of compounds in the same paint sample [50].

The combination of pyrolysis, gas chromatography (Py-GC) and MS (Py-GC-MS) has notably improved the identification of organic artists' materials and, in particular, has extended the scope of GC to the identification of synthetic materials. Thus, this technique has become a powerful tool for scientists involved in art and art conservation. Py-GC-MS offers a number of advantages: minimum sample preparation—it can be directly analyzed in a solid or liquid state with no hydrolysis or derivatization pretreatment and high sensitivity and LOD (below the μg). In contrast, the obtained pyrograms are more complex than the chromatograms obtained with conventional GC-MS due to the new compounds appearing in the pyrogram as a result of the pyrolytic fragmentation. Recent progress in Py-GC-MS relies on the development of online derivatization methods. This technique has been mainly applied to the analysis of lipids, natural di- and triterpenoid resins, and synthetic resins [51].

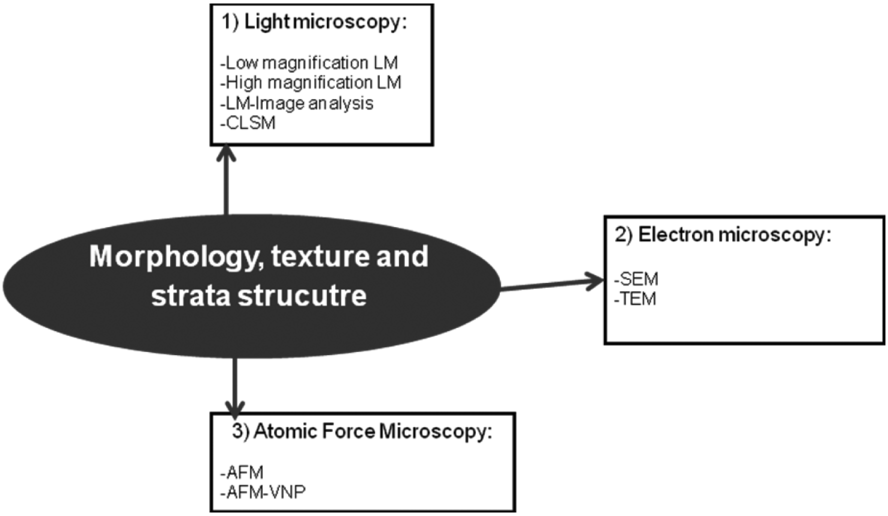
(f) Thermoanalytical methods. TG and DTA have frequently been applied in the field of art and art conservation as complementary techniques together with chromatographic, spectroscopic, or spectrometric techniques. They provide interesting information concerning the crystalline structure of the target compound and the degree of hydration of inorganic salts. More occasionally, these techniques and differential scanning calorimetry (DSC) have been applied to the analysis of binding media because a number of works have developed methods for ascribing exothermal reactions to specific organic compounds [52].

1.4.5 Point Analysis Providing Morphology, Texture and Strata Distribution

Many of the instrumental methods yielding morphological, topological, and textural information of objects are based on microscopy techniques. Although light microscopy (LM) has pioneered the technical examination of art objects and antiquities, other microscopy techniques, such as electron microscopy or atomic force microscopy, have been further developed, which overcomes the magnification limitations of LM or the extremely shallow depth of field at high magnifications (Scheme 1.9).

Low-magnification LM is a valuable technique for the examination of art and archaeological objects, used to gather preliminary information on alterations and damages suffered by the object and its state of conservation. High-magnification LM is currently performed in the range of ×100–×1500. The depth of focus is relatively small, requiring a time-consuming preparation of samples to obtain a suitable image of the specimen. Image analysis enables point counting, and stereological and densitometric studies. In particular, characteristics of materials such as a percentage of aggregates, pores, temper or specific minerals, pore or grain size, and grain shape can be determined, which allows a better analysis and interpretation of composition, technology, provenance, deterioration, and preservation [53]. Other optical microscopy techniques, such as confocal laser scanning microscopy (CLSM) have been scarcely applied to the stratigraphic study of cross sections and the examination of canvas fibers.

Electron microscopy is an efficient microscopy technique that has been extensively used for the material characterization of artistic and archaeological objects, especially in combination with x-ray microanalysis [54]. The use of electrons instead of light in these instruments is the basis of the higher resolution ($\sim$9–0.2 nm) and has greater depth of field than LM. Thus, characterization of the finest topography of the surface objects is possible, and additional analytical information can be obtained. Different electron microscopes are currently used in art and art conservation studies: scanning electron microscopes (SEM), Cryo-SEM



Scheme 1.9 Main analytical methods for morphological, textural, and strata distribution

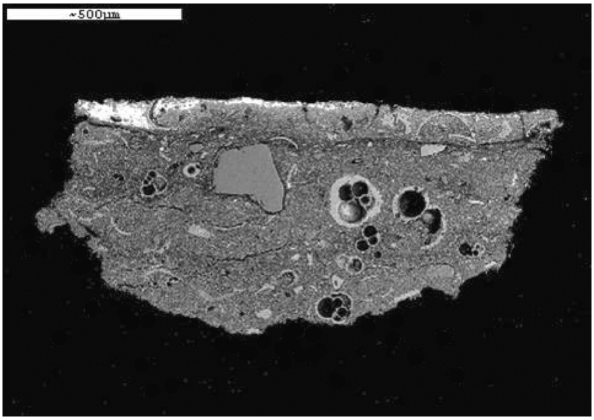


Fig. 1.7 Cross section of a painting (17th century, Taormina, Italy). Interestingly, the ground was prepared with a pigment obtained by crushing a biocalcarenite rock containing abundant microfossils (globigerine foraminifers, Sicily)

and environmental scanning electron microscopes (ESEM), and transmission electron microscope (TEM). These techniques have been widely used for studying the texture of materials (Fig. 1.7), the alteration and biodeterioration of materials, and for monitoring consolidation and cleaning treatments on stone, ceramics, paintings, sculpture, archaeological, and ethnographical objects, etc.

The AFM maps the topography of a substrate by monitoring the interaction force between the sample and a sharp tip attached to the end of a cantilever so that the morphology of the surface of the studied sample can be reproduced at nanometer resolution (Fig. 1.8). Some works can be found in literature, reporting studies in which AFM has been applied to the examination of art and archaeological objects [55].

1.4.6 Microbeam Analysis Providing Microdomain, Surface Structure, and Composition

In general, methods of surface investigation are based on the interaction of the incident energy provided by a microbeam of photons, electrons, or particles with the atoms or molecules located in the surface of the sample. Here the concept of "surface" should not be considered in a strict sense. Analytical interactions take place in the subjacent matter, achieving a depth in the range of a few micrometers. As result of the interaction between the incident beam and the sample, atoms or molecules release photons, electrons, ions, or neutral particles. These emitted corpuscles are carrying analytical information that is registered after they are conveniently detected. Moreover, the use of highly collimated microbeams for exciting the studied material results in a high spatial resolution, and therefore, low dimensions for the analyzed

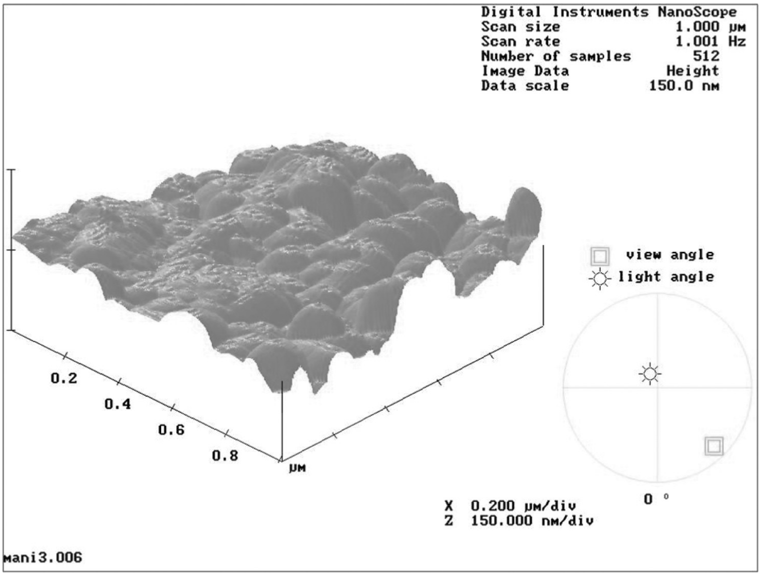


Fig. 1.8 Topographic map of the surface of an altered archaeological glass obtained by AFM

area. Table 1.1 summarizes the surface analysis techniques most frequently used in the characterization of art and archaeological objects.

Suitable high-resolution spatially resolved microspectroscopes operating in the vis region and IR region (FTIR and Raman) have been progressively applied to the analysis of art and archaeological samples providing spectral resolution for discriminating features in the different paint strata of a cross section [56–58]. In a lesser

Table 1.1 Classification of analysis surface techniques used in the study of cultural heritage according to the method of excitation and the resulting emitted corpuscles carrying analytical information

Excitation emission	Photon	Electron	Ion	Neutral particle
Photon	Vis light imaging microspectroscopy, microspectrofluorimetry, LIBS, Raman and FTIR imaging microspectroscopy, μXRF, μSRXRF, μXANES, XAS μSRXRD	SEM-EDX, EPMA		
Electron	XPS	AES, EELS		
Ion	PIXE, PIGE, LDMS, MALDI		RBS, SIMS	FAB

extent, microspectrofluorimetry and laser-induced breakdown spectroscopy (LIBS) have been applied to identify the type of binding media and the layer-by-layer pigment distribution, respectively [59].

Fast-atom bombardment mass spectrometry (FAB-MS) has been applied to the identification of diterpenoid compounds and their oxidation products. Similarly, laser-induced desorption mass spectrometric (LDMS) techniques have been applied to the identification of natural and synthetic organic pigments in microscopic paint samples prepared as cross sections [60].

Techniques of microscopic XRF (µ-XRF) developed in the last 20 years provide 2D images and elemental maps of each element present in the target material. Portable/in situ µ-XRF, µ-XRF spectrometers synchrotron-based (µ-SRXRF) and micro-x-ray absorption spectroscopy/micro-x-ray absorption near-edge structure spectroscopy (XAS/µ-XANES) have improved the mineralogical characterization, as well as the elemental and chemical imaging of samples at the submicrometer scale [61].

Synchroton-based micro-x-ray diffraction (µ-SRXRD) is being increasingly applied in the mineralogical characterization of art and archaeological objects [62].

External beam proton-induced x-ray emission (PIXE), and particle-induced gamma-ray emission (PIGE), are mainly applied to the characterization of porcelain, glass, glazes, pigments, gemstones, obsidian, bone and teeth, inks, stamps, coins, jewelry, and the imaging of faded letters on ancient papyrus, for establishing the provenance of the pieces or in authentication studies [27]. Similarly, x-ray photoelectron spectroscopy (XPS) has been applied to the analysis of archaeological glasses, pigments, metals, and their degradation products.

X-ray microanalysis techniques—in particular, electron probe x-ray microanalysis (EPXMA or EPMA) and SEM coupled with energy dispersive spectrometers (EDS, EDX) are, by far, one of the surface analysis techniques most extensively used in the field of art and art conservation, and they have actually become routine methods of analyzing art and archaeological objects and monitoring conservation treatments [34, 61, 63].

Other surface analysis techniques have been less frequently applied in the analysis of art objects. Auger electron spectroscopy (AES)/scanning Auger microscopy (SAM) in the art and art conservation field involve studies of metallurgical archaeomaterials or the microscopic deteriorated structure of archive and book collections and the effectiveness of the applied conservation methods. Electron-energy-loss spectroscopy (EELS), carried out with the help of a conventional TEM or with a scanning transmission electron microscope (STEM) or Rutherford backscattering spectrometry (RBS), have eventually been applied in the study of objects of artistic and archaeological nature—in particular, characterization of the elemental composition of the wood and protective varnish of old musical instruments, or characterization of metallic archaeological artefacts. Finally, secondary ion mass spectrometry (SIMS) has been applied to the characterization of cross sections of ancient paintings, and in the obsidian hydration dating technique (*vide infra*).

1.4.7 Dating Methods

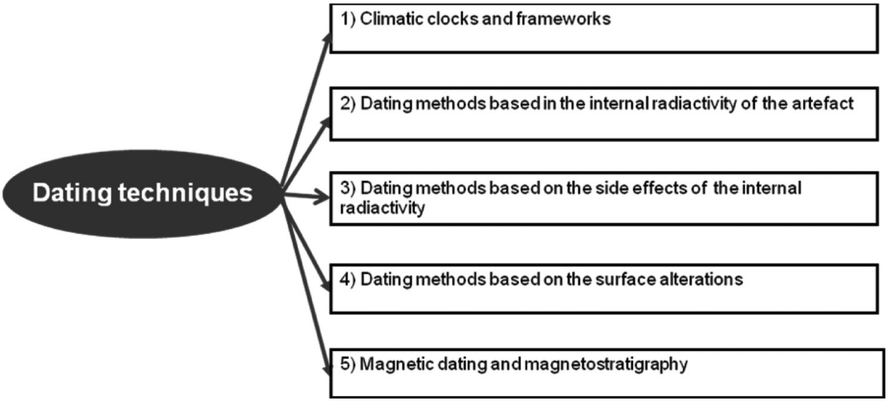
Dating methods primarily applied in archaeological and archaeometric studies are aimed, in general, at providing the basic chronological framework of a specific region or archaeological site. Despite the diversity of the basic phenomena of dating methods, all follow a general scheme based on a measurable time-dependent quantity or parameter with a well-known value associated with a determined event, which is used as “reference point” or “starting point” in a time-scale relatable to the archaeology of interest [64]. Most of the current dating techniques can be considered absolute, but not all. In general, dating techniques can be classified into different groups according to the type of phenomenon in which they are based as it is overviewed in Scheme 1.10.

(a) Climatic clocks and frameworks. This type of dating technique has evolved from the visual observation of materials of archaeological and geological origin. They are based on the chronological framework provided by the climatic variations taking place on the Earth during the recent geological period (roughly the last two million years) [65].

A study of the loess deposits of windblown sediment that are found in large areas in the middle latitudes of the Northern hemisphere, South America, and New Zealand provide more or less continuous records of the change in the climate in these regions—in particular, the glacial stages [65].

The oxygen-isotope ratio ($^{18}O/^{16}O$) found in the calcareous tests has been used as an indicator of the amount of water locked up in glaciers, which reflects the state of the global climate. Another source of continuous records of oxygen-isotope variation, as well as dust content and acidity, is found in the long cores drilled in polar ice caps in which annual layers can be counted and seasonal variation can be established [65].

The classical work of Milankovitch, further elaborated on by other authors, focuses on the study of the correlation between climate change and the Earth’s orbital variations—in particular, the build-up and decay of glaciations [65].



Scheme 1.10 Dating techniques classified according to the type of phenomenon in which they are based

Analysis of pollen and spores preserved in acid soils and peat bogs has given rise to palynology. This approach is based on the assumption that the type of tree and plants growing in a particular terrestrial region are indicator of the climate. Morphological characteristics of the specimens are observed with the help of light and electron microscopes [64].

Varve or rhythmites chronology is another approach based on the examination of geological materials. In this model, the distribution of the laminated sediments formed in the bottom of the beds of dried-out lakes (as a consequence of the seasonal melting of glaciers and the subsequent deposition of coarse particles supplied by streams, followed by finer materials such as sand, silt, and clay) is analyzed and correlated with climate changes [64].

Finally, the dendrochronology first proposed by A. E. Douglas as a dating method has played a relevant role in the development of a general chronological framework. Dendrochronology not only has put a distortion in the prior time-scale into evidence, but also has provided a more accurate calibration establishing a specific relationship between Europe and the Near East during the Neolithic and Bronze Ages [66].

(b) Dating methods based on the internal radioactivity of the artefact. Four dating methods of great relevance in archaeological and archaeometric studies can be included in this section. They can be considered radiometric methods because they are based on the measurement of the internal radioactivity displayed by the object: (a) radiocarbon, (b) potassium-argon, (c) uranium series dating, and (d) lead isotope ratio dating.

Radiocarbon dating originated with W. F. Libby (1955, 1965) and is routinely applied in specialized laboratories of archaeology and in the environmental sciences field. Radiocarbon technique is based on the constant rate at which carbon-14 spontaneously decays. A ^{14}C/^{12}C or ^{14}C/^{13}C ratio can be determined by measuring the rate of emission of beta particles per unit mass of total carbon, which is proportional to the concentration ratio, and alternatively by measuring the ^{14}C content or the ^{14}C/^{12}C or ^{14}C/^{13}C ratios in an accelerator mass spectrometer (AMS) [67]. This equipment is not only used for measuring ^{14}C, but also other longer-lived radionuclides such as ^{26}Al, ^{10}Be, ^{36}Cl, ^{41}Ca, and ^{129}I can be determined. This technique has been applied to a wide range of artistic and archaeological objects and human remains [68].

The radioactivity of the ^{40}K isotope, with a half life of 1,250 million years, is used in potassium-argon dating. The experimental determination of the ^{40}Ar content is carried out by MS after releasing the gas via fusion of the sample. Single grains ($\sim$1 mg) can be analyzed by using a high-powered laser to fuse the grain and drive off the argon for measurement in a super-sensitive mass spectrometer. This method is called single crystal laser fusion (SCLF) [68]. Alternatively, determination can be performed by irradiating the sample with neutrons in a nuclear reactor so that a part of the K atoms are converted into ^{39}K. After this, the ^{40}Ar/^{39}Ar ratio is measured with a thermal ionization mass spectrometer (TIMS) [68].

The uranium series dating is based on the determination of the ^{234}U/^{230}Th or ^{235}U/^{231}Pa. Isotopic ratio measurements can be made by means of a mass spectrometer. Multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) or LA-ICP-MS are now used instead of TIMS due to the greatly reduced sample size, increased precision, sampling resolution, and shorter run times that these techniques provide. This technique is mainly applied on stalagmitic calcite formed from ground water where U is present on rock art fossil teeth or coral and mollusk shells [68].

Lead isotopic composition analysis has proven useful for sourcing a number of archaeological materials, including metallic leads, silver, copper, bronze, faience, glass, glazes, and pigments. Determination of lead isotope content can be performed using different methods: TIMS, quadrupole inductively coupled plasma mass spectrometry (Q-ICPMS), inductively coupled plasma sector field mass spectrometry (ICP-SMS), multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS), and inductively coupled plasma time-of-flight mass spectrometry (ICP-TOF-MS) [69].

(c) Dating methods based on the side effects of internal radioactivity. The methods included in this group are based on the cumulative effect of nuclear radiation on crystal structure. Fission track dating is based on the determination of the ratio of tracks found in a mineral sample (i.e., zircon, obsidian) due to the split of ^{238}U atoms to the tracks induced by exposure in a nuclear reactor. Identification and counting of tracks are performed under a high-magnification microscope from samples prepared as cross sections. Obsidian knife blades and flakes have been dated in the range of 400–600 years. Application to bones and teeth has also been reported [65].

Stimulated luminescence dating methodologies is the term used to refers to two techniques in which the observed signal increases with age. Both thermoluminiscence (TL) and optically stimulated luminescence (OSL) are based on the assumption that many natural samples are able to accumulate (in trap states with a long mean life) electrons that have acquired sufficient energy from α, β, and γ radiations emitted from natural radionuclides belonging to the ^{238}U, ^{232}Th, and ^{40}K decay chains, and from cosmic radiation. Mainly used for dating pottery, they have extended their use to other materials such as polymineral fine-grained fractions from sediments, zircon, calcite and stalagmitic calcite, other salts, meteorites, flint, quartz, loess, volcanic materials (obsidian, tephra), and metallurgical slags [68].

In TL, the light emission induced in the mineral or ceramics sample heated up to 500°C is measured by means of a photomultiplier detector. In addition to laboratory instrumentation, portable gamma spectrometers have been used when circumstances make sampling impractical.

Optical dating techniques, including OSL, optically stimulated phosphorescence (OSP), and phototransferred thermoluminiscence (PTTL) are applied to the dating of anthropological remains such as teeth and bones [65].

ESR has been applied to the dating of secondary carbonates precipitated as stalagtites, stalagmites, and flowstones (speleothems). Other applications include tooth enamel, bone and dentine, and mollusks and shells [64].

(d) Dating methods based on surface alterations. Three methods based on chemical treatments of samples that have undergone surface alterations or isomorphic changes in their composition are included in this category of dating methods:

(a) amino acid racemization, (b) obsidian hydration, and (c) substitution of U, N, or F in bone (FUN dating).

The amino acid racemization method is based on the measurement of the degree of racemization acquired by a material expressed as the ratio "dextro amino acid (D) enantiomeric form/levo amino acid (L) enantiomeric form," which is an indicator of the age of the object. This method has been applied in fossil shells, bones, teeth, wood, plant remains, and coral [68].

Obsidian is a volcanic glass frequently used as tool by prehistoric men. The thickness of the hydration layer that has developed on the surface of the artifact since it was made can be used to date it. Measurement of the hydration layer is carried out by a variety of instrumental techniques. Among them are nuclear resonance reactions, LM, PAS, XPS, XANES, sputter-induced optical spectrometry (SIPS), and SIMS [70].

FUN dating is applied to obtain a relative dating of bones found in the same archaeological site or deposit rather than for absolute dating.

(e) Dating methods based on changes in the direction or orientation of the Earth's magnetic field. Paleomagnetism applies to burnt geological material (volcanic lava) or unburnt sediments that record the polarity changes in the Earth's magnetic field over time. The reversal stratigraphy focuses on the study of Paleomagnetism, providing interesting data for a more accurate establishment of Paleolithic time scales. Parameters such as remanent magnetization or susceptibility are used for this purpose.

Archaeomagnetism can be considered a branch of Paleomagnetism specifically devoted to the dating of archaeological materials from the measurement of the remanent magnetization achieved by the iron oxide impurities present in clay after cooling of the ceramic artifact. This recording mechanism primarily provides information on the direction of the Earth's field at the time the artifact was fired or the kiln was last used.

The main recording mechanism considered in archaeomagnetism is the thermoremanence (TRM). Measurement of this remanent magnetism is experimentally performed by means of spinner magnetometers. This method has been applied in combination with potassium-argon dating for dating remains ascribed to homo erectus (1.64 ± 0.03 million years) or for establishing the age of early man's tools in Asia around two million years ago. Remanent magnetization dating of sunbaked bricks, the discrimination of cast coins from struck ones, or dating the firing temperature of pottery have also been other interesting applications included in archaeomagnetism [71].

1.5 Final Considerations

Electroanalytical techniques and, in particular, solid state electroanalytical techniques introduced in the field of archaeometry, art, and art conservation in recent years (as will be described in the following chapters) provide new and singular information complementary to that of the analytical techniques described in the previous sections. Thus, they not only allow identification of electroactive elements present in the sample, but they can also simultaneously discriminate their state of oxidation. When solid state electroanalytical techniques are coupled with AFM, phase identification can be performed at nanoscale levels on electroactive samples. Additionally, electroanalytical data processed by means of standard addition methods or Tafel analysis can provide, in complex samples containing several pigments, an accurate determination of the content of the different pigments—thus enabling an adequate knowledge of the dosages used by the artist and, as consequence, of its artistic technique. These capabilities situate electroanalytical techniques in a relevant position and give them a promising future as a novel and powerful analytical tool at the service of archaeometry, art, and art conservation.