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ANALYTICAL TECHNIQUES. The traditional archaeological methods of classification and seriation were developed on the basis of the physical appearance of archaeological artifacts, but it is increasingly acknowledged that the material of the artifact also carries information. There is usually no difficulty, for example, describing pottery by its color and texture; it is, however, more difficult to describe artifacts made of rock or metal in this way without being inaccurate (e.g., "green stone") or even wrong. The possibility of identifying the nature of certain materials only by scientific analysis inevitably arises. To extract the maximum information locked in the material of archaeological remains it is often necessary to proceed one step farther to employ a variety of scientific techniques to establish, for example, the identity and geographic sources of the raw materials used or the techniques of manufacture. Thus, applying scientific methods to archaeological objects can simply be regarded as an extension to the sort of visual examination the magnifying lens or binocular microscope do.

Determining chemical components (or elemental analysis) is nowadays rarely accomplished by the classical wet chemical methods (i.e., gravimetric or volumetric quantification by chemical reactions in aqueous solution); it is carried out rather by applying physical techniques based on the properties of molecules, atoms, and atomic nuclei. The common principle of these analytical techniques is the exposure of the sample to some form of energy input (thermal or by irradiation with photons or particles). Exposure results in the excitation of molecules and atoms that either emit, scatter, absorb, or reemit various forms of radiation analyzable with spectroscopic methods.

The choice of any method usually depends on a variety of factors such as sensitivity, selectivity, precision, accuracy, speed, availability, or cost of analysis. Their applicability may depend on the sample matrix, sample size, or on another specific component being absent. Even more important is the sampling step. It has to be ascertained that the sample is truly representative of the whole that it represents. With archaeological objects it is often not possible to remove a sample, so that the application of nondestructive techniques becomes necessary. Sometimes it may not be possible to obtain a pure sample from a heterogeneous object. In this case, it is better to apply a microanalytical method with high lateral resolution. On the other hand, if knowing the average composition of a heterogeneous sample will suffice, the bulk analysis of a relatively large sample may provide more reliable results than any microanalytical method.

Optical Methods. The range of colors to which the human eye is sensitive is only a very narrow range of the electromagnetic spectrum of radiation. Of progressively decreasing wavelength and, hence, increasing energy are the ultraviolet, X-ray, and γ-ray regions of the spectrum, while the infrared and microwave regions have longer wavelengths than visible light. All these regions are used in chemical analysis.

UV-VIS spectroscopy (also called colorimetry) involves measuring the intensity of absorption of visible light. It is therefore restricted to colored substances, usually in solution. Often, not the substance itself but a colored derivative is measured by comparison with standard solutions. Concentrations of elements can be determined in the parts per million range in solutions (1 ppm = 1 $\mu g/g$ = 0.0001%) as well as their valency states and complex species (speciation). This method is regaining importance because it is rather inexpensive and can be applied in the field (e.g., for environmental monitoring and phosphate analysis).

In optical emission spectrometry (OES) the sample to be analyzed is vaporized at high temperatures by means of combustion flames, an electric discharge between electrodes, a laser beam, or a plasma torch. Such a treatment breaks most chemical bonds and excites the outer electrons of some atoms to higher energy levels that emit light in the visible and near ultraviolet region on their return to the ground state. This light consists of a number of sharply defined wavelengths or spectral lines that are characteristic of the particular element excited. Consequently, the determination of the constituent wavelengths in the light emitted by the sample provides the basis for identifying the elements present in the sample while the intensity of the light, at a particular wavelength, provides an estimate of the concentration of the associated element. By comparison with standards of known composition it allows, in principle, the simultaneous determination of up to seventy elements in the range of between 1 ppm and 10 percent with detection limits varying between 1 and 100 ppm in the solid sample.

Although some materials, like metals, can be used directly as electrodes, the method cannot be regarded as nondestructive. For analysis, a small sample, typically 10 mg, has to be removed from the object. The sample is either dissolved or mixed directly with pure graphite powder and placed in a graphite cup, which forms the lower electrode. An electric arc or a spark discharge is struck between this and an upper graphite electrode, thus completely volatilizing the sample and exciting its constituent atoms. A more elegant method of direct analysis is the excitation with an intense laser beam of about 100 μm in diameter. A brief burst of intense light is sufficient to vaporize a few micrograms of material and leaves behind only a very small and hardly visible crater on the surface of the object. The small cloud of sample vapor needs an auxiliary spark discharge to excite the emission spectrum used for analysis. Although this laser-induced OES may appear to be a much better technique than the first one, it has the decisive disadvantage that its reproducibility is much lower and that it can only be used for qualitative or semiquantitative analyses.

Further improvement of the technique has been made by the introduction of a plasma torch for the vaporization and excitation of the sample instead of the electric discharge. It has only relatively recently been possible to obtain a stable plasma (a completely ionized gas) under laboratory conditions. The most widely employed plasma for analytical purposes consists of argon flowing through a quartz tube placed with its upper end into a high-frequency (about 30 MHz) magnetic field. Once ignited to plant a "seed" of electrons in the gas, the electron are accelerated by the oscillating field and obtain enough energy to ionize all other argon atoms within a very short time. The result is a very high-temperature flame (up to 10,000°C) through which the solution of the dissolved sample is transported as an aerosol. This technique is called inductively coupled plasma-OES (ICP-OES) and is a highly reliable method for the analysis of many elements in the parts per billion (ppb) range in solutions (1 ppb=1 ng/g=0.0000001%). Because solids have to be dissolved for analysis, elemental concentrations in the ppm range can be determined in the solid sample. A disadvantage is that the dissolution step is very critical for the accuracy of the method and the sample is lost on analysis.

In atomic absorption spectrometry (AAS) the sample, usually in the form of a solution, is also volatilized and atomized with combustion flames or by electrothermal heating in a small graphite tube. This method utilizes the fact that free atoms can absorb radiation at the same wavelength that they would emit on excitation. If copper is being determined, a copper-containing light source is used to pass a beam through the atomized sample. The amount of light absorbed can be detected electronically and is directly proportional to the number of atoms present. Comparison with standard solutions yields elemental concentrations. The instrumentation of AAS is cheaper than that of OES and the method is less sensitive to interelement interferences. Detection limits are roughly comparable. However, only one element can be determined with one measurement, whereas with OES all detectable elements are measured simultaneously. Only elemental concentrations can be determined with both methods.

The methods discussed so far are based on the fact that electrons of the outer shells of atoms can be excited, which results in absorption and emission of light in the visible and UV range of the electromagnetic spectrum. The energy of infrared radiation is too low for such processes, but it can excite oscillations and vibrations in molecules. Certain specific wavelengths that depend on the structure of the compound being tested are absorbed when a beam of infrared radiation is passed through a suitably prepared specimen of almost any inorganic or organic compound. The greatest use of this technique (IRS) is in the qualitative identification of organic compounds. Structural information on the presence or absence of certain functional groups is obtained. It is thus a typical method for species analysis. Many compounds exhibit typical infrared spectra that can be used as a "fingerprint." Resonance raman spectroscopy (RRS) is a complementary technique to IRS in that the radiation scattered and partly reemitted in a direction perpendicular to that of the incident beam is measured.

X-Ray Methods. When an element is irradiated with X-rays of appropriate wavelength, X-rays of different but smaller wavelength, characteristic of the element, are emitted. The underlying process is the displacement of an electron of one of the inner shells of the atom followed by filling of the vacancy by one of the outer electrons combined with simultaneous emission of a photon. Complex mixtures can usually be analyzed without prior separation of the components by the spectroscopy of the secondary radiation with diffracting crystals or semiconductor detectors and—most important—the method is virtually nondestructive (only some glasses and gemstones may change color on irradiation with X-rays, but this can be reverted by gentle heating). However, the depth of analysis is only in the range of 0.1 mm in silicates and even less in metals, so that the surface of an object has to be representative of the bulk composition, which is not always the case. Therefore, it may often be better to take a representative sample and perform the analysis on that.

The sensitivity of the method depends on the matrix and the element to be analyzed, but typical detection limits are around 10–100 ppm. XRF is the standard method for rock analysis in geology, and it is also widely employed for analyzing metals and alloys. The analyzed area is usually about 1 cm in diameter but can be reduced with appropriate slits; however, these also reduce the intensity of the primary beam and accordingly extend the necessary measurement time.

X-rays can also be excited by energetic electrons that can be focused with magnetic lenses. In the electron probe microanalyzer, a fine electron beam is focused on the surface of the sample (approximately 1 μm in diameter); the position of the beam can be changed systematically. Thus, it is possible to obtain information on the concentrations and distribution of the elements within a small area of the sample. For quantitative analysis the sample is mounted in a resin and the surface polished. Accordingly, strictly nondestructive analysis is not possible, but small objects like coins can be investigated with little damage. Electrons induce more background radiation in the sample. Therefore, detection limits are somewhat higher ($>$ 100 ppm) than with XRF.

Protons produce much less background and can also be focused so that proton-induced X-ray analysis (PIXE) combines lower detection levels and high lateral resolution. However, the instrumental effort to produce a proton beam is much larger than for electrons. Accordingly, this method is rarely available and comparatively expensive.

With X-ray diffraction analysis (XRD), crystal structures (and thus mineral compounds) can be identified. This method is very useful to complement chemical analysis when different materials have similar chemical composition.

Nuclear Methods. While the preceding methods make use of physical processes taking place in the molecules or in the electron shells of atoms, nuclear methods are based on reactions that occur between nuclei and neutrons or charged particles. Such reactions are usually accompanied or followed by the emission of radiation that is phenomenologically largely identical with the radiation emitted by the electron shells—with the difference that it originates from the nucleus. The most important of these techniques is neutron activation analysis (NAA), in which a sample is irradiated with thermal neutrons to interact with the atomic nuclei of the constituent elements, transforming them into unstable radioactive isotopes. The decay of these isotopes is often accompanied by the emission of γ-rays, which can be used for identifying and quantifying the elements in question. The spectroscopic techniques for γ-rays are similar to the ones used for X-rays. Because radioactivity can be measured very sensitively, this method offers an unparalleled combination of selectivity and sensitivity for simultaneously determining many elements. Typically, about 40 elements can be determined in rock samples from major components to the ppb range. For several elements this is the most sensitive method of analysis altogether. Depending on their major compositions, small objects can be analyzed nondestructively, if no long-lived isotopes are produced. In any case, the sample is preserved and can be used for other investigations after the decay of the radioactivity. The major disadvantage of this method is the low and diminishing availability of strong neutron sources—that is, nuclear research reactors.

Analogous to AAS, Mössbauer effect spectroscopy (MES) involves the absorption of γ-rays of characteristic energies within a very narrow energy range by specific nuclei in the sample. This method is mainly used for the speciation of iron in various matrices or, more generally, provides information on the immediate crystallographic environment of the isotope under investigation. Typically, it is the ratio of Fe^{2+}/Fe^{3+} in minerals that is of interest because it bears on the ambient conditions during the formation of iron-containing minerals.

A mass spectrometer is an instrument that will sort out charged gas molecules (ions) according to their masses by accelerating them electrically to form a beam that is deflected magnetically into separate beams according to the mass-to-charge ratio of the ions involved. These beams can be made to pass through a series of slits to reach separate detectors where they are individually counted. In thermal-ionization mass spectrometry (TIMS) the element sought has to be separated from the sample and is then evaporated and ionized from an array of hot filaments. Quantification is achieved by adding known amounts of different isotopes of the same element (isotope dilution). For many elements this is the most sensitive technique available, but it is rather time consuming and usually only one element can be measured at a time. The major advantage is that not only the concentration of an element can be determined, but also its isotopic composition—which is especially important for elements with varying abundances of their constituent stable isotopes. Most elements on Earth have a uniform isotopic composition regardless of their location or chemical form. Variations can be induced in light elements (from hydrogen to sulfur) by physical processes such as diffusion that are sensitive to isotopic differences (e.g., "heavy" water, D_2O can be enriched by repeated evaporation of ordinary water) or by the decay of radioactive elements occurring in nature. A typical example is the decay of uranium and thorium to lead, so that the isotopic composition of lead varies according to which geochemical environment it derives.

There are also alternative ways to produce ions from the sample: One is the direct atomization and ionization by an electric spark similar to OES (spark-source mass spectrometry, or SSMS) or the introduction of a sample solution into a plasma torch (ICP-MS). Both combine the high sensitivity of MS with multielement detection. However, especially SSMS can only be regarded as a semiquantitative method unless a tedious multielement isotope dilution technique is applied. If a sample is directly evaporated by a narrow laser beam and then introduced into an ICP-MS, high lateral resolution is also possible. Even better resolution is achieved by ionization with a primary beam of ions (secondary-ion mass spectrometry, or SIMS), so that the features of the EMPA are combined with high sensitivity and isotopic analysis. Unfortunately, precision and accuracy of all these methods is not yet competitive with conventional instrumental methods (e.g., XRF or NAA) because of interelement effects that are as yet difficult to correct. However, with their increased use, these new techniques will certainly become powerful and reliable analytical tools.

The main field of application of MS in analytical chemistry is actually the analysis of complex organic molecules. To increase its selectivity, it is now common practice to separate the individual components first in a gas chromatograph (GC) by differential adsorption on a solid stationary phase (GC-MS). Because of these differences, each component diffuses at a different speed through a narrow column packed with, for example, silica gel, so that at the end of the column the components are completely separated and introduced into a MS one after the other.

Selected Archaeological Applications. OES was the first widely employed physical method of chemical analysis; thus, most of the analytical data published since 1930 was, until recently, derived from this technique. Most noteworthy are the many thousands of analyses of prehistoric metal objects from Europe, the eastern Mediterranean, and the Near East carried out at the Württembergisches Landesmuseum in Stuttgart, Germany. These data are still the primary source for studying the development of alloying techniques in various regions and have frequently been discussed in terms of the provenance of raw materials. The method is still in use but XRF, AAS, NAA, and ICP-OES are replacing it increasingly in determining major and trace elements. A significant methodical extension has been the introduction of TIMS for determining lead isotope ratios not affected by production processes.

Obsidian, a naturally occurring volcanic glass that has been used widely for blades from Paleolithic periods through the Bronze Age, is a much better material for provenance studies because the production of artifacts does not alter its chemical composition in any way and it is also very resistant to chemical weathering. OES has been used to characterize many obsidian sources in the Aegean, in central and eastern Anatolia, in Armenia, and in Ethiopia, as well as obsidian artifacts from Near Eastern sites. It appears that the Levant was mainly supplied from Cappadocian sources, whereas obsidian from eastern Anatolia was dominant along the Zagros flanks. Today, the most widely applied analytical methods for this purpose are NAA and RFA, although the latter is not applicable for very small samples. So far, TIMS has offered little advantage over these methods.

In a similar approach, OES has also been used for the chemical analysis of pottery; however, characterizing clay sources presents more difficulties than obsidian. There is a very large number of potential clay sources, and the variation within a source is likely to be larger than with obsidian. On the other hand, for mineralogical reasons, the variation between sources is rather small; as a result, they can hardly be distinguished with the relatively low precision of OES. Progress, thus, came only after the introduction of NAA, which is now the standard method for pottery analysis.

Stone artifacts have also been studied extensively, particularly marble, starting with isotope analysis of carbon and oxygen. As with all studies where many sources have to be considered, various overlapping parameters prevent the unique assignment of an artifact to any source. Better resolution between sources can only be achieved by increasing the number of geochemical parameters. Hence, isotope analysis is now routinely complemented by trace element and petrographic analysis.

Of organic materials, amber has been the most extensively studied, especially by IRS, with the aim of localizing raw-material sources and establishing trade routes in the Late Bronze Age. A promising field seems to be the analysis of food residues by GC-MS.

[*See also* Dating Techniques; Microscopy; Neutron Activation Analysis; Spectroscopy; *and* X-Ray Diffraction Analysis.]

BIBLIOGRAPHY

Beck, Curt W., Constance A. Fellows, and Edith MacKennan. "Nuclear Magnetic Resonance Spectrometry in Archaeology." In *Archaeological Chemistry: A Symposium Sponsored by the Division of the History of Chemistry at the 165th Meeting of the American Chemical Society, Dallas, Texas, April 9–10, 1973*, edited by Curt W. Beck, pp. 226–235. American Chemical Society, Advances in Chemistry Series, no. 138. Washington, D.C., 1974. Good introduction to an important technique (not covered in this article) for analyzing organic materials in archaeology.

Boumans, Paul W. J. M., ed. *Inductively Coupled Plasma Emission Spectroscopy*. New York, 1987. Comprehensive overview of this relatively new analytical technique.

Ehmann, William D., and Diane E. Vance, eds. *Radiochemistry and Nuclear Methods in Analysis*. New York, 1991. The most readable modern treatment of analytical radiochemistry.

Harbottle, Garman. "Chemical Characterization in Archaeology." In *Contexts for Prehistoric Exchange: Studies in Archaeology*, edited by Jonathan E. Ericson and Timothy K. Earle, pp. 13–51. New York, 1982. Useful review of the application of chemical analyses in archaeology.

Kolthoff, I. M., and Philip J. Elving, eds. *Treatise on Analytical Chemistry*. 2d ed. New York, 1978–. Authoritative series on analytical chemistry that treats the field comprehensively.

Pollard, A. M., ed. *New Developments in Archaeological Science: A Joint Symposium of the Royal Society and the British Academy, February 1991*. Proceedings of the British Academy, 77. Oxford, 1992. The most recent collection of specific applications of scientific methods to archaeological problems.

Potts, P. J. *A Handbook of Silicate Rock Analysis*. Glasgow, 1987. Summarizes the principles and experimental techniques of all analytical methods discussed in this text with the exception of IRS, RRS, and GC-MS.

Tite, Michael S. *Methods of Physical Examination in Archaeology*. London and New York, 1972. Concise overview of physical methods applied for the location, dating, and compositional analysis of archaeological artifacts.

Wagner, U., F. E. Wagner, and J. Riederer. "The Use of Mössbauer Spectroscopy in Archaeometric Studies." In *Proceedings of the 24th International Archaeometry Symposium*, edited by Jacqueline S. Olin and M. J. Blackman, pp. 129–142. Washington, D.C., 1986. Useful introduction to the principles of the method, with an archaeological application.

Zussman, J., ed. *Physical Methods in Determinative Mineralogy*. 2d ed. New York and London, 1977. Somewhat dated but detailed and authoritative review of OES, XRF, XRD, AAS, IRS, and SSMS.

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