X

X-RAY DIFFRACTION ANALYSIS. The first step in identifying an unknown piece of matter is normally chemical analysis. However, this will mainly provide information on the elements present and not on how they are combined. If the material is crystalline (and almost all solids are, with the exception of glass), X-ray diffraction can supplement the information given by chemical analysis and indicate which compounds are present.

For X-ray diffraction measurements, the specimen is exposed to a beam of monochromatic X-rays (i.e., X-rays with a narrowly defined wavelength) and the intensity of the scattered radiation is monitored at various angles. Because the interatomic spacings in crystals are of the same order of magnitude as the wavelengths of X-rays, crystal structures behave as three-dimensional diffraction gratings for X-rays. A special property of such gratings is that the scattered radiation is reinforced at certain angles while it is extinguished at all others. Therefore, for a given wavelength (λ), appreciable scattered (or diffraction) intensities are only observed when the angle (Θ) satisfies the so-called Bragg condition, which is given by $n\lambda = 2d \sin\Theta$, where d is the spacing between the crystal lattice planes and n is an integer (i.e., 1, 2, 3, etc.).

The simplest technique for obtaining X-ray diffraction patterns is the powder method, which is the one most useful for archaeological specimens. A small sample, which can be less than 1 mg, is pulverized and inserted into a thin-walled glass capillary or deposited on a glass fiber. It is then mounted on the axis, which can be rotated, of a cylindrical X-ray camera, around whose interior a photographic film is wrapped. Because in a finely powdered and rotating sample the respective lattice planes exist at all orientations with respect to the incident beam, the Bragg condition is satisfied along the surface of a cone with a semiangle of 2Θ.

The spacings between crystal planes in a certain crystal system are characteristic parameters of each crystalline substance; it therefore follows that the diffraction pattern (i.e., the observed X-ray intensities at various angles) is also characteristic and can be used as a fingerprint to identify mineral phases by comparing them with cataloged patterns of pure substances. Mineral mixtures, of course, give mixed patterns, but mineral components of less than 10 percent are usually not detected. Thus, minerals can be identified even in mixtures; moreover, their relative amounts in the mixture can be estimated from the X-ray intensities. Only glass does not give any refraction pattern.

The major fields of application for X-ray diffraction analysis in archaeology are pottery analysis, to determine constituent minerals (clay, temper, decoration)—information often required to determine production techniques and provenance; identifying pigments in wall paintings and pottery decoration after firing; identifying corrosion products on the surface of metal objects for purposes of authentication; and identifying the microcrystalline structure of worked metals, which may reveal their mechanical and thermal pretreatment (e.g., if a wire has been drawn or rolled and hammered) as well as information concerning the development of metallurgy in ancient societies.

BIBLIOGRAPHY

Lipson, Henry S. *Crystals and X-Rays*. London and Winchester, 1970. Well-written and accessible introduction to the application of X-rays to the investigation of crystalline phases.

Noll, Walter. *Alte Keramiken und ihre Pigmente: Studien zu Material und Technologie*. Stuttgart, 1991. The most comprehensive text to date on the scientific investigation of archaeological pottery and pigments.

Zussman, J. "X-Ray Diffraction." In *Physical Methods in Determinative Mineralogy*, edited by J. Zussman, pp. 391–473. 2d ed. London, 1977. An authoritative review of the subject.

ERNST PERNICKA