news and views

MÖSSBAUER spectroscopy has never achieved the universality of application experienced by many other spectroscopic methods, and will probably never do so. This is not due to any intrinsic difficulty in the technique itself, but rather because the number of different elements which can be studied without special facilities is small, and also because the information obtained from the spectra, although frequently crucial to the elucidation of a structure, can rarely be fully interpreted in the absence of other data about the compound concerned. But the technique possesses a number of valuable attributes which may be exploited where other analytical methods would fail, and this allows its use in systems which would otherwise pose considerable analytical problems.

The basis of Mössbauer spectroscopy is the recoilless emission and resonant absorption of gamma rays of suitable energy. The line width of this resonant process is so narrow that the effect can only be demonstrated where the emitting and absorbing atoms are isotopically similar, spectra normally being generated by the Doppler modulation of source or absorber to allow absorption measurements over a small range of photon energies.

First observed by Rudolf L. Mössbauer in 1957, the effect was rapidly found to have possibilities for the study of changes in the electronic environment of the atoms whose spectrum was measured, because the atoms' environment influenced the nuclear energy levels between which the resonant gamma ray transitions occurred. This influence was twofold, and allowed structural information regarding the atomic environment to be obtained.

First, any difference between the s-electron density as experienced by the emitting and absorbing nuclei will cause a displacement of the absorption line known as the 'isomer shift'. This allows the comparison of s-electron densities in different compounds and thus gives, among other things, information about oxidation states. Second, any electron distribution which is not spherically symmetrical may give rise to a 'quadrupole splitting' in which the single absorption line becomes a doublet centering on the original position. The separation of the doublet is proportional to the field asymmetry, and provides information on the geometry of the atom's immediate environment. In addition, the presence

of an internal or external magnetic field may lift the nuclear spin degeneracy and be exhibited as a multi-line spectrum.

The letter from Hedges in this issue of *Nature* (page 501) exemplifies the situation where Mössbauer spectro-

a simple and resolvable additive spectrum will be obtained.

The elements most suited to Mössbauer studies on archaeological material are iron and tin, although nickel, zinc and gold might be useful in certain circumstances.

Iron is not only a particularly convenient element for study, but its very wide occurrence in raw materials results in its presence in a diversity of artefacts. Iron impurities in ceramics were first investigated by Cousins and Dharmawardena (*Nature*, **223**, 732; 1969) for typing purposes, and at the recent Symposium on Archaeometry and Archaeological Prospection at Oxford (19–22 March, 1975) Longworth and Warren presented data relating to the black slip on certain samples of Etruscan pottery. Here the problem is to identify an iron compound present, with other minerals, in particles too small for conventional X-ray diffraction, but presenting no difficulty regarding the Mössbauer spectrum. Though it is not possible to arrive at an identification of an unknown compound from the Mössbauer spectrum alone, comparison with spectra of known likely compounds can readily be used to characterise such materials. Glasses and glazes are another class of substance which, having no long-range ordering, are unsuitable for X-ray diffraction, but yield valuable information about the environment of iron atoms present in the network or as microcrystalline impurities.

Mössbauer spectroscopy has also been used by Keisch (*Archaeometry*, **15**, 79; 1973) to identify iron-containing pigments on paintings where its non-destructive nature and ability to 'ignore' compounds not containing iron were used to the full. Quantitative analysis using Mössbauer spectroscopy is more difficult, at the lattice dynamics of different compounds cause the absorbing atom to vary in its efficiency, but with suitable calibration a degree of quantification can be achieved.

There is therefore a number of situations where Mössbauer spectroscopy provides information on archaeological and art materials which is otherwise difficult to obtain, and much useful work remains to be done on glazes and colouring materials. Ancient alloys have been little studied from this point of view, and it is likely that such materials as tin bronzes would repay investigation.

Mössbauer spectroscopy in archaeology

from Nigel J. Seeley

scopy has been used to gain information which would not readily be obtained by other methods. Archaeological materials and works of art present many difficulties to the analyst. They are frequently complex and unknown mixtures, and in many cases sampling cannot be allowed. Provided that the sample geometry is suitable, wholly non-destructive analysis is possible, but unless surface scattering spectra are to be obtained it is generally more convenient to take a sample unless the object is thin, as in the case of a painting.

Also, because the Mössbauer spectrum obtained is that of one specific atomic species, the presence of impurities containing other elements, even when present as a major constituent, will not complicate the spectrum, although their attenuation of the gamma rays may be inconvenient. This means that the spectrum obtained will be only that of the atomic species being studied, and if that element is present in two or more compounds or environments in the sample