

*Technical  
glossary*

**Energy dispersive X-ray (EDX) fluorescence analysis.** Whereas X-ray diffraction (XRD) separates the characteristic X-rays of a material by their wavelengths, EDX does so by their energies. The data can be displayed as peaks on a graph, where energy is on the horizontal axis and intensity is on the vertical axis. Elements are identified from their characteristic patterns of peaks. Energy dispersive X-ray apparatus is compact, and can be linked to a scanning electron microscope (SEM) – hence SEM-EDX. Extremely small samples can be studied. Also, SEM-EDX can show not only which elements are present but also their relative amounts. From this and evidence from optical microscopy, particular pigments can be identified. SEM-EDX, unlike XRD, is a primary analytical tool – and an important first-choice method of analysis, see page 20. X-ray fluorescence is used by many museums and galleries as a non-destructive technique – without a paint sample being taken. It can be used directly on the painting or object, and gives the overall pattern of elements present in the area examined. What it cannot do is pin-point where in the paint layer structure – from the surface to the ground – a particular element is.

**Fourier transform infrared spectroscopy (FTIR).** Every pair of atoms joined by a bond in a molecule is vibrating. The frequency of the vibration in a particular bond depends on which atoms are joined by the bond, and also to some extent on what other bond vibrations are happening nearby in the molecule. If infrared (IR) radiation is shone through a sample of a substance, the frequencies of radiation which are absorbed usually can tell us which kinds of bonds are in those molecules. A conventional IR machine gradually changes the frequency of the radiation passing through the sample – only one frequency goes through at a time. Over a period of several minutes the machine produces a plot of absorption against frequency. The peaks on the plot give information about which kinds of bond are in the molecule.

In FTIR all the IR frequencies go through the sample simultaneously. The same frequencies are absorbed as with the ordinary IR, but in FTIR a computer interprets the information carried by the radiation which passes through the sample. The mathematics involved is complicated, and is called a Fourier transformation after the early 19th century French mathematician who developed the mathematical theory. The spectrum plot looks the same as for ordinary IR. Fourier infrared spectroscopy is much faster and more sensitive than conventional IR. Also, a spectrum can be obtained from a very small (pinprick size – about 1 mm<sup>2</sup>) sample by adding together the information obtained from several scans of the sample, if the equipment is linked to a microscope. This is obviously useful when analysing tiny flakes from paintings. Fourier transform infrared spectroscopy has often been used to find which medium was used for the paint, but although it can identify an oil, it cannot identify what kind of oil – *eg* linseed, walnut, poppy – is present, because they have the same types of bonds, but arranged differently. Fourier transform infrared spectroscopy leaves the sample intact. It is non-destructive, although it could be argued that taking a sample from a painting is in itself a destructive process.

**Gas chromatography (GC).** You may be familiar with paper chromatography, and the basic principle here is the same. In paper chromatography, the paper is the stationary phase and water or some other liquid is the solvent or mobile phase. As the mobile phase flows past the stationary phase, the different solutes carried by the mobile phase are held back to different extents by the stationary phase. In GC, a non-reactive carrier gas is the mobile phase, and the stationary phase is a solid, or a non-volatile liquid coated on inert solid particles, held in a long, coiled narrow column in an oven. A small sample is injected into a heated chamber. The sample is swept slowly through the column by a carrier gas, such as helium or nitrogen. The column can be held at the same temperature or gradually heated. The different solutes emerge from the column into the detector at different times. The detectors used are quite complicated, and usually work through changes in thermal conductivity or by flame ionisation. Sample sizes can be very small. Gas chromatography can be particularly useful in deciding which medium has been used in making the paint, or what is in the varnish which protects the surface of the painting. The sample has to be treated chemically to release the different components in the medium, and also to make them sufficiently volatile. Once that is done, egg tempera gives a gas chromatogram which is very different from those of the drying oils. Further, it is easy to distinguish linseed oil, walnut oil and poppy seed oil by the relative areas of certain peaks in their chromatograms. If the peaks are very sharp, the peak heights can be used. Because of the chemical reactions involved and the separation of components, GC destroys the sample – it is a destructive analytical technique. In gas chromatography – mass spectrometry (GC-MS), the output from the GC is put into a mass spectrometer. This very powerful (and very expensive) method is used to detect traces of minor constituents of the paint medium that are too small to be detected by GC. It has also been used to detect traces of drugs in athletes and racehorses.

**High performance liquid chromatography (HPLC).** In ordinary liquid chromatography, the mobile phase (the solvent, plus solutes) runs by gravity through a vertical column which contains the stationary phase. This could be particles of silica gel, alumina, or cellulose. The different solutes move down the column at different rates. If they are coloured, bands of colour separate as they move down. In HPLC the stationary phase consists of uniform very small porous silica particles (typical diameter  $10^{-6}$  m). This results in a very high surface area, which gives much better separation of the solutes. But small particle size means that liquid would only run very slowly through the column, so a constant high pressure (up to 100 atm) is applied, to push the liquid through. The column is normally 10–30 cm and is made of metal to resist the pressure. Once more, small sample sizes can be used. The sample is destroyed in the process. The method can be used for analysing the medium in paint, and for examining large and delicate molecules which would be destroyed in GC or by heating. In the National Gallery it has been used to study dyestuffs used in lake pigments.

**Infrared (IR) reflectography.** Some wavelengths of visible light are absorbed when it passes through a transparent coloured material – *eg* stained glass. What you see is what gets through. The wavelengths which are absorbed give information about the substances in the material which the light passes through. But visible light cannot get through the pigment on the surface of a painting. So, instead, light is shone on to the surface at right angles to it. The wavelength of the light is changed gradually across the spectrum. The surface of the painting is rough and reflects light in all directions. Light reflected at, say, 450 nm is collected and examined. The light which is reflected is the light which is not absorbed by the pigment. (If a paint looks green, it is because it reflects green and absorbs the other colours). A reflectance spectrum is therefore a kind of opposite to the absorption spectrum, and gives much the same information. Infrared radiation is at wavelengths which are longer, and therefore at frequencies which are lower, than visible light. Infrared reflectography is particularly good for detecting the underdrawing in a painting – *ie* where the artist has used charcoal, graphite pencil or black ink (all involving carbon) to mark out the design. Carbon absorbs IR strongly, and IR can penetrate surface layers of pigment better than visible light can, if the paint is not too thick and does not contain a pigment – *eg* carbon black or azurite – which absorbs IR. This technique is non-destructive and provides information about the whole painting at once.

**Laser microspectral analysis (LMA).** This is definitely a destructive analytical technique! A high-energy pulse of laser light vaporises the sample. Laser light is monochromatic – *ie* all the light has the same frequency. The energy is enough to vaporise even the crystalline compounds of metals which most of the old pigments are made of. The tiny plume of vapour from the sample rises to the gap between two electrodes. A high voltage spark between the electrodes then excites the atoms and ions in the vapour – *ie* some of their electrons are given extra energy, and move into higher energy levels. As they return to their original energy levels, light is given out – an emission spectrum is produced. The frequencies of the emitted light depend on the element or elements involved, and so can be used to identify pigments. This technique is very sensitive and can be used with pigment samples as small as  $10^{-7}$  g; but it was never widely used and has mostly been replaced by SEM-EDX (p14).

**Microscopic analysis.** Before modern analytical machines were invented, this was virtually the only technique available for scientific analysis of paint layers. Skilled and experienced workers could gain a great deal of information by using it. It is still widely used. Usually, a paint sample is embedded edgewise in a resin and cut and polished to expose its layer structure. A good sample shows the gesso ground, possibly the glue which seals the ground and the material used for underdrawing, the underpaint, and the surface paint layers. An experienced operator can tell from the colour, shape and size of the particles which pigments are present, and even whether hydrated or anhydrous calcium sulfate (gypsum or anhydrite) has been used for the ground. The use of polarised light, which interacts strongly with crystals – on a dispersed sample, not a cross-section – provides further information. Inspection of particles in the top layers can show whether a pigment has faded. The electron microscope and its variations – such as the scanning electron microscope (SEM) – can reach far higher magnifications than can optical microscopes, and can give direct information about elements present.

**Mass Spectrometry (MS).** This technique is used for analysing organic materials such as paint, binding media, resins, and varnishes. Modern MS machines can use nanogram ( $10^{-9}$  g) or even smaller samples. The method needs samples to be at least reasonably volatile, so is usually used for the medium rather than the pigment. The sample is vaporised (and so destroyed). Some of the molecules in the vapour are made into positive ions by bombardment with a beam of electrons – if one electron is knocked out of the molecule M, it becomes the ion  $M^+$ . Because ions are charged, they will respond to an electric field. A high voltage can therefore be used to accelerate the ions, which are focussed into a thin beam. A moving ion will be deflected by a magnetic field, but the amount of deflection will depend on the mass/charge ratio of the ion. So different ions fly through the magnetic field on different curves, and arrive at a detector. A mass spectrum of the sample is produced, with the mass number – *ie* the number of protons + neutrons in the particle – on the horizontal axis, and the peak heights giving the relative number of particles with the different masses. Under these conditions, big molecules break up into smaller pieces, and this fragmentation pattern gives a great deal of information about what is in the original molecule. For all this to happen, the inside of the mass spectrometer must be kept under vacuum so that the ions do not collide with air molecules. As stated earlier, MS can be coupled with GC to give an extraordinarily sensitive method of detecting – *eg* traces of drugs in urine or blood. A complex mixture can be separated by GC and each pure component can have its molecular structure examined by MS.

**X-ray diffraction (XRD).** This technique is used for the characterisation and identification of crystalline pigments. The structures of solid materials can be studied using X-rays – but NOT by shining the X-rays right through (as, for example, when finding out whether your ankle is broken, or whether Titian changed his mind while painting Ariadne). Instead, use is made of the fact that the wavelength of X-rays is comparable with the distance between the layers of atoms in a regular crystal lattice. If X-rays of a particular wavelength are shone on the crystal at an angle, some X-rays are absorbed but others pass straight through the crystal. The X-ray energy absorbed by the different layers of atoms is re-emitted as X-rays: it could loosely be said that some of the X-rays are reflected by the layers. As the angle at which the X-rays hit the crystal changes, the X-ray waves reflected from the different layers alternately cancel each other out (causing a dark region on a photograph) and reinforce each other (causing a bright region). What is called a diffraction pattern is produced. You can see a diffraction pattern if you look at a small bright light through a stretched piece of fine fabric such as silk. The pattern is caused by light waves interacting with the regularly-spaced threads of the fabric, just like X-rays interacting with the layers of atoms in a crystal. You can also see diffraction effects – this time splitting up white light into the colours of the spectrum – when light shines on the surface of a CD or at a shallow angle on the surface of an old LP record. Sir William Bragg and his son Sir Lawrence found an equation which linked the wavelength of the X-rays, the angle at which they hit a crystal, and the distance between the layers of atoms in a crystal. This equation provided a basis for working out simple solid structures, and the Braggs were awarded a Nobel Prize. Big molecules were a much more difficult problem, but methods were eventually found for materials such as vitamin B<sub>12</sub> (for which Dorothy Hodgkin won a Nobel Prize). However, the crystals in gesso ground or in pigments are very small indeed. Fortunately, every crystalline substance has a unique X-ray powder pattern, produced when X-rays are shone on the millions of randomly-arranged tiny crystals in the powder. These patterns are now recorded and stored internationally, and when a paint flake is examined by XRD the crystalline materials in it can easily be identified by comparing their diffraction patterns with those held in the store.