site during an excavation, or on unmoveable objects such as wall paintings, cave paintings, mosaics *etc.* When compared to a bench-top microscope, the drawbacks of a probe include reduced signal intensity, spatial and spectral resolution, a

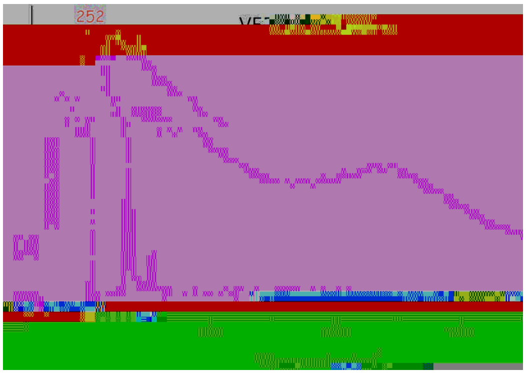

Fig. 2 (A) Raman spectrum of the red pigment vermilion on plaster, showing no fluorescence (note the flat baseline) and clearly de

critical to a successful outcome of the Raman analysis that the single particle under observation is kept in focus at all times. To avoid vibrations, or at least reduce them as much as possible, a variety of aids can be used. These include padded snake weights and glass weights, which can be positioned on the page under analysis as close as possible to the microscope objective in order to keep the area under observation flat and still.

Size restrictions

If only a traditional microscope set up is available for the analysis, then only relatively small objects can be analysed because large ones simply cannot fit under the microscope. This problem is more easily overcome if an open architecture system is available or if a fibre optic probe or hand-held Raman instrument can be used, as discussed at the beginning of this brief.

Interference

As mentioned above, if an oil binding medium is present in the pigment mixture, it can cause fluorescence which may mask the Raman signal of the pigment. It is much easier to analyse pigments mixed with a water-based binding medium (gum Arabic or animal glue for example).

Miscellaneous limitations

A Raman microscope using visible excitation is not particularly suitable for the analysis of binding media, whose spectrum is usually very weak and is swamped by that of the pigments or dyes. It is also of limited usefulness with many very dark materials that absorb most of the incident light, as they are prone to local overheating and laser-induced degradation.

Analysis of spectra

Identifying compounds on the basis of their Raman bands can be a complex operation, which requires a detailed knowledge of group theory and involves lengthy calculation. Realistically, this is rarely done and usually artists' materials are identified with the help of already existing spectral databases. Many of these are available in the published domain and can be used as a reference (see list at the end of this brief). Fig. 3 shows an example of a Raman spectrum from an unknown material matched with the Raman spectra of relevant reference materials.

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This Technical Brief was prepared by the Heritage Science Subcommittee and approved by the AMC on 24/04/15.

Further reading

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