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The Laser Microspectral Analysis of Paint

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Introduction

The identification of pigments and other inorganic substances which make up the materials of painting represents a problem frequently encountered in the study of the technical aspects of art history, as well as providing fundamental information required for certain problems related to the conservation and restoration of pictures. Well-established procedures of optical microscopy of paint cross-sections [1], and transmitted light studies with the polarizing microscope of dispersed pigment mounts [2], provide sufficient evidence for many pigments to be reliably identified from their particle characteristics and optical properties alone.

Certain pigments, however, do not possess sufficiently distinctive particle properties to be recognized with certainty under the microscope, especially when present in a complex mixture or as a minor component of the paint layer. In these cases reliance must be placed on the chemical identity of the material for its characterization. Traditional microchemical tests designed to detect a characteristic cation can sometimes be used successfully in a confirmatory way, but suffer from the major disadvantages of poor sensitivity, the inevitable destruction of the sample, and the need for a separate chemical test for each element to be detected. Moreover, many pigments by their nature are relatively intractable materials, yielding only low concentrations in solution of the characteristic cation on which the test depends. In consequence, metals such as Hg, Sn, Co, Cr, Sb, Mn, Cd, Ag and Au may be detected only with difficulty and require relatively large samples. The most serious drawback of any chemical test, however, is that it is conducted in order to show the presence or absence of a single element in the sample and unexpected constituents or significant minor or trace elements will probably go unrecorded [3]. Lastly, samples of multi-layered paint systems usually require separation into discrete layers or even the extraction of the particles of interest before chemical tests may be usefully performed.

Rather stringent requirements must be met by any instrumental method of qualitative analysis if it is to be of major value to the conservation laboratory dealing with microscopic samples of paint from old master pictures. It should be capable of detecting in microgram-scale samples all the metallic and metalloid elements characteristic of the range of inorganic pigments used throughout the history of painting, and should preferably be compatible with sample preparation techniques for optical microscopy and photomicrography.

The first criterion is partially met by classical emission spectrographic analysis using the carbon arc as the spectrochemical source. However, non-conducting samples such as paint must be loaded into hollow electrodes and completely vaporized in the arc, leading not only to loss of the sample, but also limiting the analytical capability of the technique to average analyses. Although relative detection limits of the method are very good for most metallic elements, samples of the order of 10^{-2} g are required leading to relatively poor absolute limits of detection (10^{-6} g at best). Despite these limitations, spectrography with arc excitation has found numerous applications to inorganic analysis in the arts [4]. In general, samples of paint which may be taken from easel paintings are too small to permit conventional spectrographic analysis (of the order of 10^{-5} g in total) of which a minor component pigment (10^{-6}—10^{-7}g) may be of analytical interest.

Laser microspectral analysis

The invention of the laser microprobe in the early 1960s brought about a decisive advance in the spectrochemical analysis of microscopic specimens, enabling for the first time truly localized analyses to be carried out on non-conducting microsamples, whilst at the same time substantially preserving the integrity of the sample [5]. This advance, embodied in the laser microspectral analyser (LMA), represents a technique particularly well-suited to the qualitative analysis of multi-layered paint fragments where compositional information about one or more layers is required individually [6], as well as finding more general applications in the museum laboratory [7]. Spectrochemical analysis with a photographic recording system is uniquely capable of the simultaneous detection of over sixty elements, and since pigment materials are chemically a very diverse group, the LMA technique has been chosen by this laboratory as the principal tool for qualitative inorganic analysis.

The outfit for laser microspectral analysis is essentially a hybrid instrument comprising a laser-head, a specialized binocular microscope designed to focus laser radiation onto a selected region of a sample, an adjustable spark-gap (the spectrochemical light source) located just above the sample surface, and a spectrograph to disperse and record the light produced by excitation of the sample vapour. Power supply and control circuits complete the arrangement.

The function of the laser microscope is to generate from the chosen site for analysis a minute plume of plasma which rapidly expands into the region of the

spark-gap; a microscopic crater representing removed material remains in the sample surface providing a visual record of the precise area analysed. A large potential difference is maintained across the electrodes of the spark-gap, preset to just below the level required for a spontaneous discharge in air. When the ionized plasma reaches the electrode space, the electrical resistance of the gap is lowered and a spark discharge results. The high temperature inside the spark further excites the plasma (vaporization and preliminary excitation having been achieved by the laser pulse) and the resulting emission spectrum is recorded by the spectrograph [8]. The principle of operation of the laser microscope is shown schematically in Fig.1.

The instrument

The practical form of the laser microspectral analyser in the National Gallery laboratory is type LMA 1 of Carl Zeiss (Jena) and is used in conjunction with a Zeiss Q24 UV spectrograph (Fig.2). Its location in a separate room of the Scientific Department and provisions made for the stability of the bench on which the instruments rests have been described in the first issue of this *Bulletin* [9]. The individual elements of the instrument are described below.

Laser-head

The laser-head (Fig.3) contains the optical components of the laser which consists of a synthetic ruby resonator rod (100 mm long by 8 mm in diameter) with accurately parallel, polished faces, and the
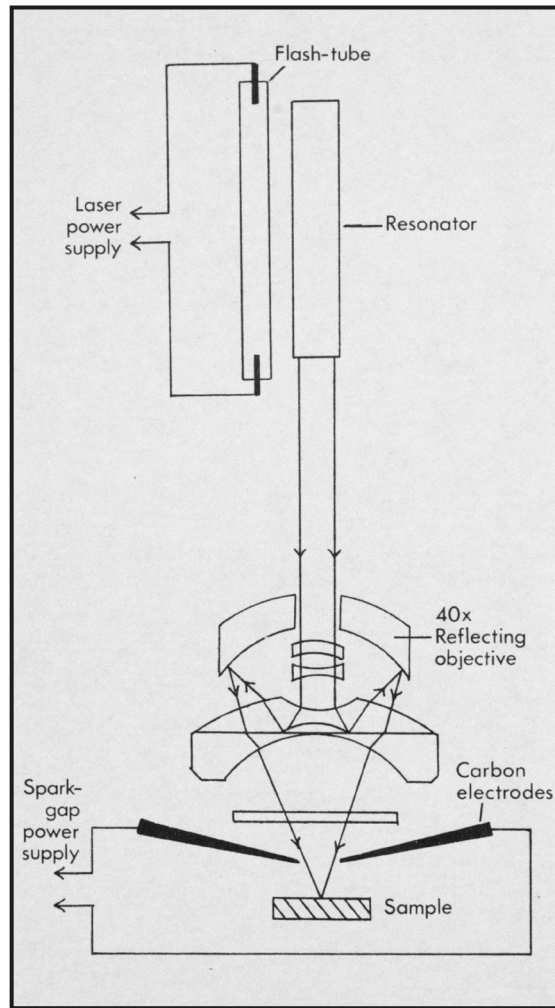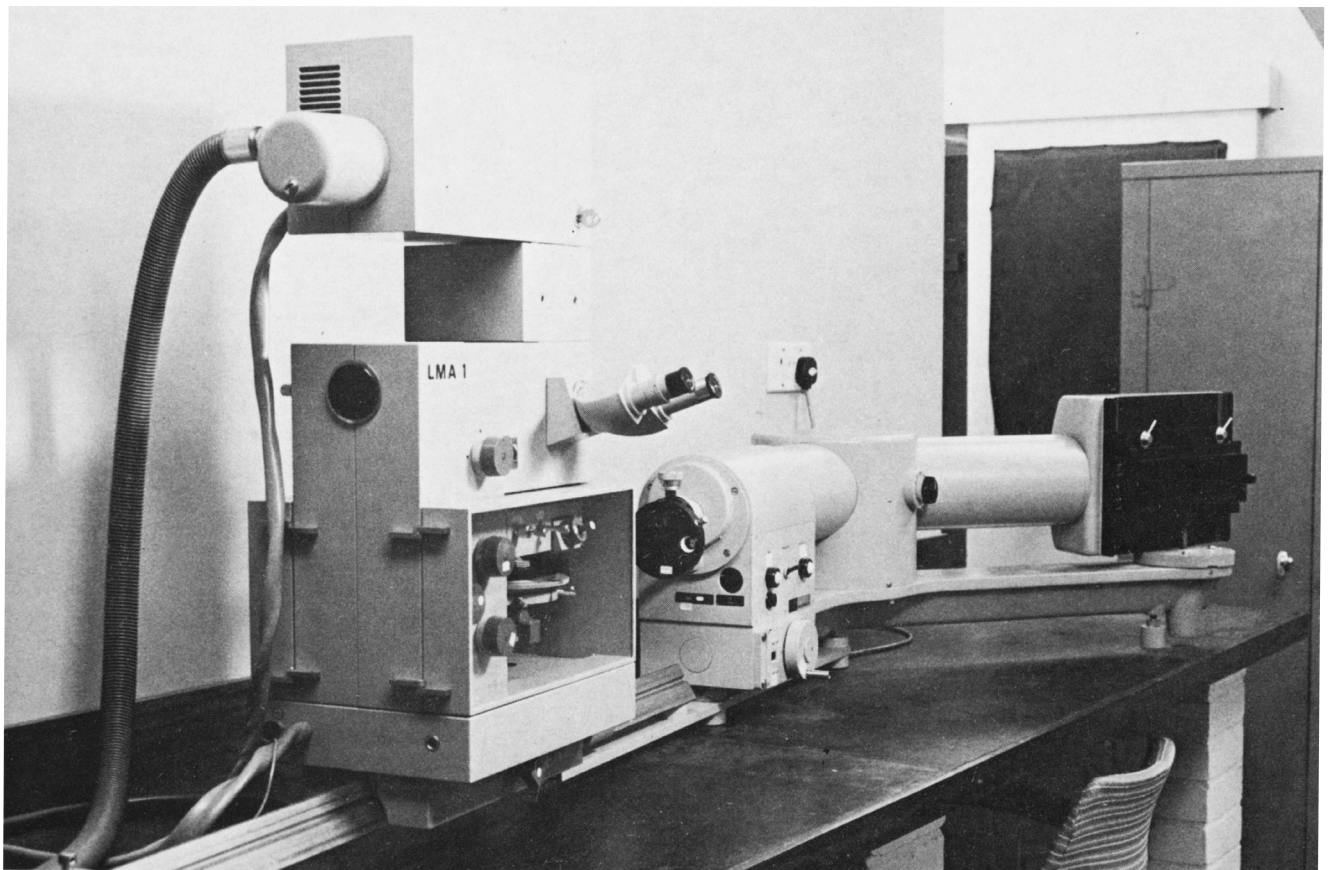

Figure 1
(Left)
Principle of operation of the laser microprobe.

Figure 2
(Below)
Overall view of the Zeiss Laser Microspectral Analyser and Q24 spectrograph.
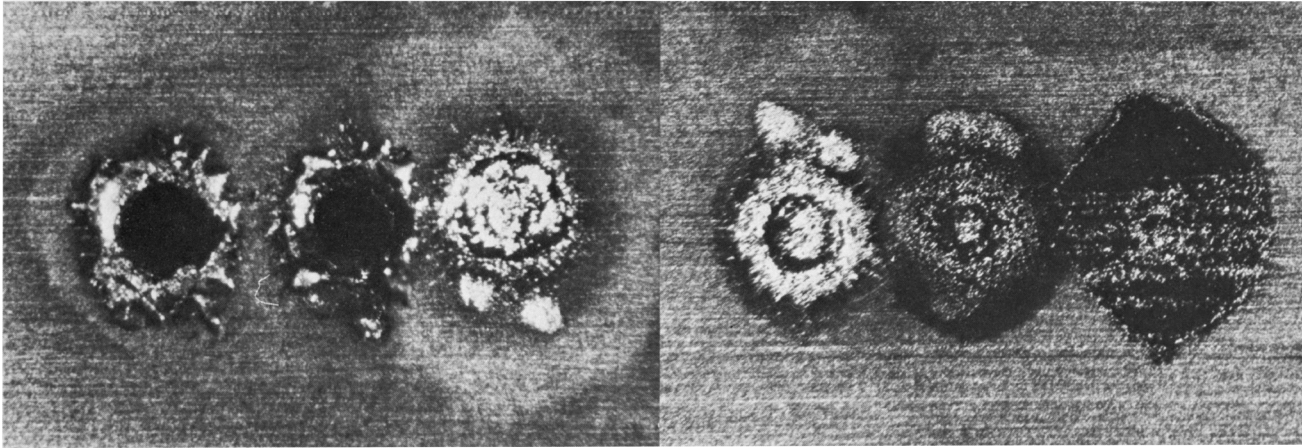
Figure 4 Laser craters in steel showing effect of Q-switch position on crater geometry. Far left: crater produced by uncontrolled, multi-spike laser operation; depth c.150 μm, diameter c.200 μm. Far right: crater produced by single giant pulse output; depth c.3 μm, diameter c.650 μm. Intermediate craters produced by semi-switched operation, with laser supply parameters in all six cases: $C = 381\ \mu F$, $L = 127\ \mu H$, $V = 2\ kV$, 16 × focusing objective.
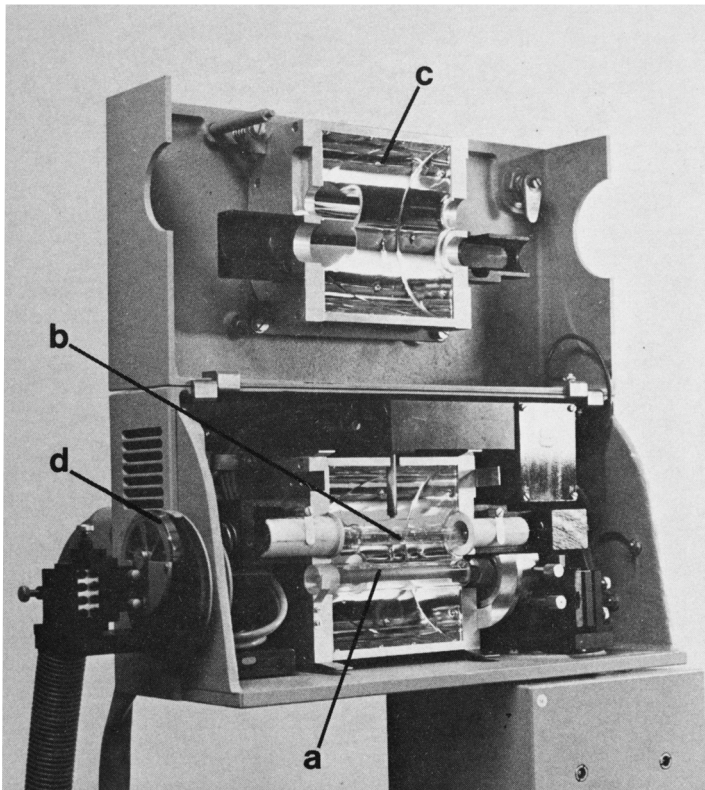

Figure 3
Interior of laser-head showing
(a) ruby resonator inside glass protective sleeve
(b) xenon flash-tube
(c) polished reflector
(d) Q-switch cell.

pumping source for the resonator — a coaxial xenon flash-tube [10]. The resonator rod and flash-tube are mounted along the two focal lines of an enclosing elliptical reflector, ensuring optimum use of the pumping light energy. The resonator is cooled by filtered air drawn into the housing of the unit by an electric fan and when in operation a flash repetition rate of two pulses per minute may be obtained.

The laser-head also incorporates a six-position passive optical switch (Q-switch) which allows control over the energy distribution contained in the laser pulse, permitting a range of outputs from uncontrolled, multi-spike operation to a single giant pulse mode to be selected [11]. This in turn ensures that samples of widely differing reflectivity, transparency, thermal conductivity and volatility may be efficiently and reproducibly evaporated by the laser beam. The number and amplitude of the spikes contained within the laser pulse envelope also

determines the profile of the crater produced in the sample, and the laser output may be switched to give the range from deep penetration to selective vaporization of a surface layer a few microns thick (Fig.4). Power densities of the focused radiation at the sample surface lie typically in the range $100 - 30,000\ MW/cm^2$; the highest figure representing a fully-switched, giant pulse laser oscillation [12]. Available rates of energy delivery are sufficiently high to vaporize refractory materials, metals and substances which are nominally transparent to the wavelength of the laser radiation (694 nm), for example, certain silicate minerals and glasses.

The laser light pulse is directed into the microscope section by a deflecting prism fixed directly above the telescope system of an optical adaptor. The latter encloses at its focus a set of diaphragms of varying diameter offering one means of restricting the sample area exposed to laser radiation; alternatively, if a bulk sample is to be evaporated, the apertures may be swung out of the light path.

Laser microscope

The microscope section of the LMA is designed to fulfil the dual functions of an optical microscope for sample examination and analytical site selection, and as the microprobe for focusing laser light onto the fraction of a specimen to be vaporized. Interchange between the two functions is achieved by a lever-operated shutter which protects the operator's eyes from accidental exposure to reflected laser light when the microscope is set for visual observation (Fig.5).

The microscope has built-in illumination for both transmitted and reflected light observations and has facilities for sample examination in polarized light, with a fixed polarizer and rotatable analyser on a sliding mount. A slide containing λ and $\lambda/4$ compensators enables low contrast features on the specimen surface to be enhanced; a particularly

valuable feature for layer analysis with paint micro-cross-sections.

The microscope objectives are required to have especially long working distances in order that the spark-gap may be interposed between the sample surface and objective. They must also be designed to cope with the very high radiant flux of repeated laser pulses without damage to the optical components of the system [13]. Two objectives posessing the required characteristics are supplied with the equipment and are carried on a sliding mount which allows them to be rapidly exchanged. One, a 16 × refracting achromat is suitable for both reflected and transmitted light use; the second, a 40 × catadioptric arrangement [14] is suitable only for high-power reflected light observations and laser spot focusing down to 10 μm diameter. The fragile internal optical components of the latter are protected from spark damage and electrode spattering during analysis by a flat quartz plate screwed into the lower part of the body of the objective. In combination with eye-pieces of 12.5 ×, the sample surface may be viewed at up to 500 × in reflected light. A third, low-power refracting objective, not suitable for laser focusing, is provided for accurate setting of the spark-gap distance. An eye-piece graticule with cross-hairs enables the diameter of laser craters to be measured as well as indicating the focal point of laser impact on the sample surface. Crater depths may be estimated using a vernier fine-focus control.

Spark-gap

The auxiliary spark-gap is physically part of the laser microscope and forms the actual source of the emission spectrum (Fig.5). In general, spectrally pure carbon electrodes (50 mm long by 5 mm diameter) are used, although pure metal electrodes may be substituted for carbon if an analysis requires carbon lines and cyanogen bands to be absent from the spectrum. Fine adjustments may be made to the electrode holders to set the gap in the range 0.8 – 1.2 mm and to align the sharpened electrodes relative to one another.

The use of a two-stage excitation process — so-called cross-excitation — where energy for sample excitation is derived both from the vaporizing laser light and from the electrical spark, optimizes spectrum intensity for a given volume of sample.

The operator is protected from accidental contact with the electrodes when they are under high tension by hinged glass doors which enclose the microscope stage and spark-gap. These doors are fitted with microswitches which release the high tension from the electrodes as soon as they are opened.

Power supplies and control console

The high voltage supplies for the laser flash-tube and spark-gap are housed in a console separate from the microprobe. This provides the controls for setting the most appropriate electrical parameters for particular types of analytical problem.

The laser flash-tube supply is continuously variable from 0 – 2 kV, with laser output produced at voltmeter-monitored settings above 1.5 kV. Lowering
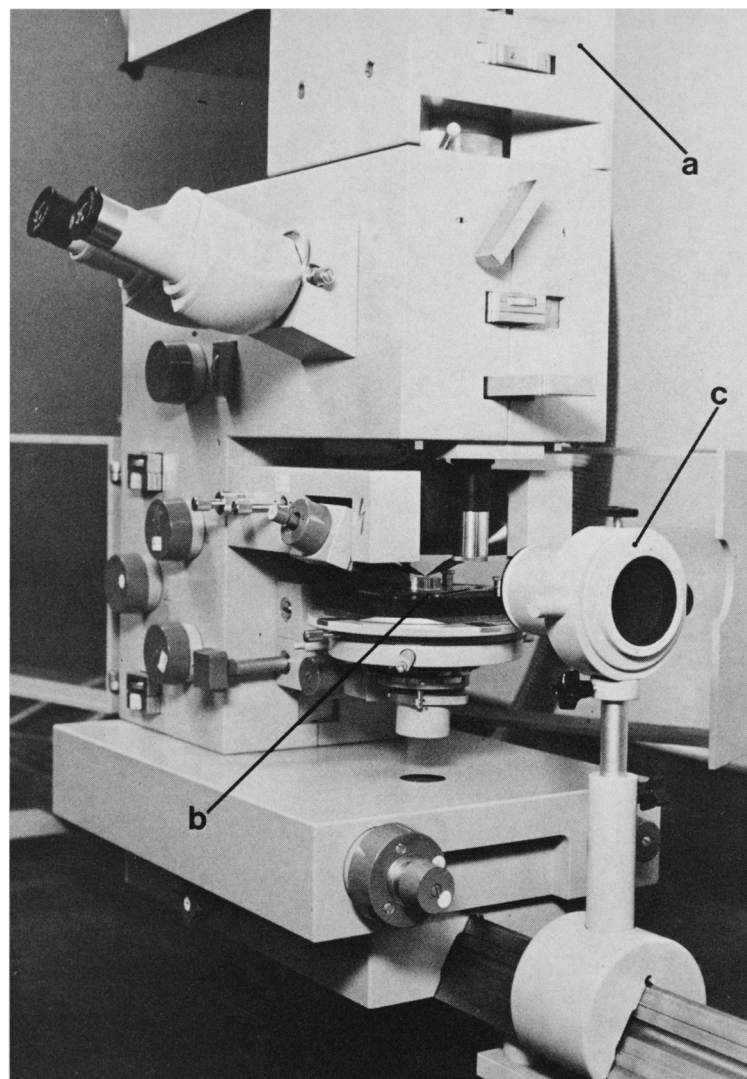
the flash-tube voltage reduces the total energy contained in the laser pulse and accordingly limits the laser-produced crater dimensions. Energization of the xenon tube is by capacitative discharge, and both the total capacitance and inductance of the pumping circuit may be varied in steps in order to shape the laser pulse characteristics. The lowest value of the charging capacitor battery is 125 μF, whilst the highest of 508 μF provides the maximum flash-tube output energy of 1016 J (at 2 kV), of which 0.3 J is available as laser radiation. Reduction of the capacitance, therefore, provides another means of reducing crater sizes.

Circuitry for the high tension supply to the electrodes is also adjustable, offering a continuously variable voltage from 0 – 5 kV, four discharge capacitance settings (1 – 2.5 μF), and six independent inductance steps (30 – 1000 μH). For qualitative paint analysis, where the aim is often to detect both principal and minor elemental constituents in a single analysis, a spark discharge of short duration and high peak current is desirable and this is achieved with a high capacitance value in combination with one of the lower inductance settings. A high voltage, spark-like discharge favours the ion spectrum resulting in the best spread of element detection in an intense, well-

Figure 5
Close-up of the laser microscope showing
(a) optical adaptor
(b) sample stage and spark-gap
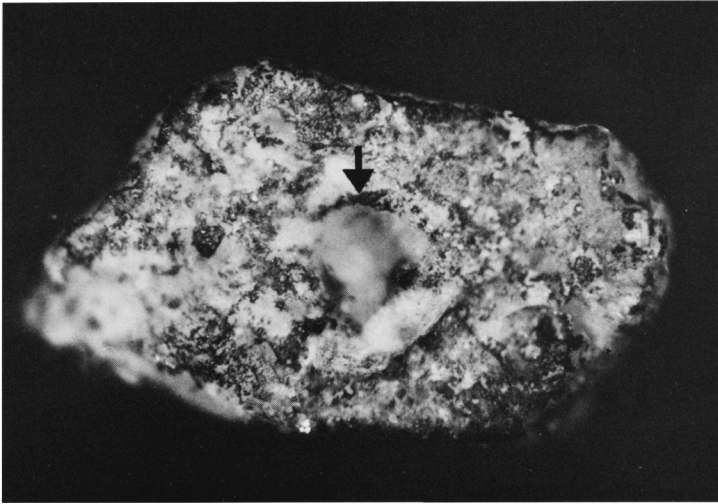**(c)** imaging quartz lens for spectrograph.

Figure 6 95 μm diameter laser crater in an unmounted fragment of paint from No.6437, van Dyck, *Lady Thimbleby and Viscountess Andover:* thick yellow paint of Lady Andover's sleeve (see Fig.8, spectrum no.2). Photographed at 110 ×, actual magnification *c*.170 ×.
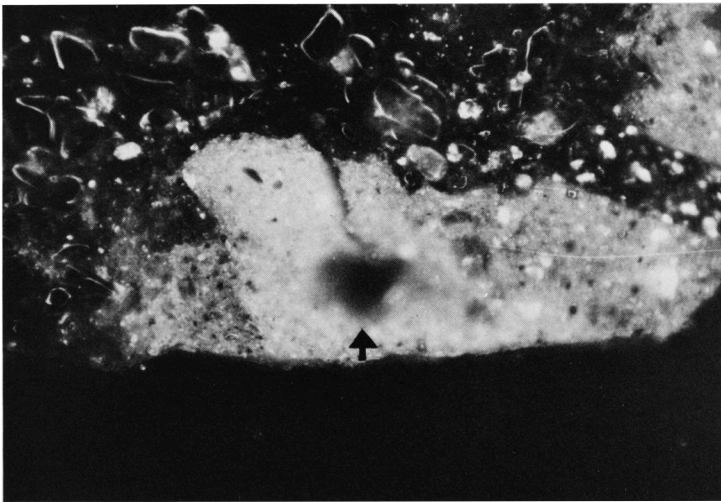

Figure 7 Mounted cross-sectional sample from No.1432, David, *Virgin and Child with Saints and a Donor:* blue (azurite) with yellow-brown (ochre) inclusions of brocade pattern (see p.62). The ground layer and underpaint are missing from the cross-section. A 40 μm diameter laser crater can be seen in the pale (ochre) inclusion at the base of the sample (see Fig.8, spectra nos.4 and 5). Photographed at 220 ×, actual magnification *c*.250 ×.

resolved spectrum. Where the solution to an analytical problem requires the production of an arc-like spectrum, the higher inductance values are available.

Spectrograph

The Zeiss Q24 spectrograph is a quartz single prism dispersing instrument, covering the spectral range 200 – 580 nm in one photographic exposure. In practise, as the dispersing power of the prism decreases with increasing wavelength, only the spectrum up to approximately 460 nm is used for element detection. The strong UV absorption of the plate gelatin at short wavelengths imposes a lower limit of about 220 nm.

The spectrograph slit width, which may be varied on a micrometer scale from 0 – 300 μm, is set to about 15 μm providing a successful compromise between spectral line resolution and spectrum intensity for the qualitative analysis of paint [15]. Slit heights down to 1 mm may be used without loss of spectral information.

An external quartz condenser lens (f = 75.8 mm), mounted on the triangular steel rail which carries both the laser microscope and spectrograph, is used to image the spark source onto the slit, ensuring that maximum light is gathered from sample emission. This system in conjunction with a projection lamp built into the microscope also serves to adjust the tips of the electrodes symmetrically on either side of the slit immediately before an analysis is performed.

Emission spectra are recorded on 6 × 24 cm glass plates of good UV sensitivity and fast response; ORWO (DDR) ZU2 'Astro' special plates have proved to be highly suitable for the purpose. The spectral plate is held in a cassette with dark-slide and can be racked-up with a geared handwheel linked to an exposure number counter. It is usual to record about twelve to fifteen separate spectra per plate, although as many as forty exposures may be made if the spectra are unspaced and the minimum slit height is used. The spectrograph provides for a rough wavelength scale to be photographically printed onto the plate at the start of an exposure series, although the spectrum of pure iron is always recorded as an accurate wavelength calibration.

Analytical procedure

Sample preparation for laser microspectral analysis is minimal; a certain degree of short-range flatness of the specimen is desirable to ensure adequate focusing of the impinging laser radiation. For pigment identifications, the technique lends itself to paint flakes mounted in cross-section, unmounted paint fragments and extracted pigment particles (see Figs.6 and 7). Provided the layers in a paint micro-cross-section are greater than 10 μm thick, as is frequently the case, the laser spot may be focused to locally vaporize part of the layer without interfering elements from adjacent layers contributing to the recorded spectrum. Similarly, inclusions and pigment particles greater than 10 μm across may be selectively analysed. The ease with which particles *in situ* may be vaporized enables analyses to be performed on paint, ground and

metal leaf fragments adhering to microscopic bundles of wood and canvas fibres, or to any other substrate.

At the start of a series of analyses, new carbon electrodes are placed in their holders, aligned relative to one another and to the spectrograph slit and set about 1 mm apart. The breakdown voltage of the gap is then determined. The electrode tips are cleaned of surface contaminants by generating a rapid series of sparks at maximum voltage, and then realigned.

The sample for analysis is fixed to a glass microscope slide with double-sided adhesive tape and the slide placed on the microscope stage. The stage is then raised until the specimen surface is about 1 mm below the inclined tips of the electrodes and is brought to focus under the microscope. For the most localized analyses the 40 × reflecting objective is employed and the sample surface scanned for the sites of analytical interest. Where spark damage to the specimen resulting particularly from oxidation is to be avoided, the surface may be protected by a small shield of thin card with a 0.1 mm hole drilled through the centre [16].

Basing the operating mode on sample type and size of laser crater to be produced, appropriate settings for the Q-switch, laser supply and optical adaptor are selected. The spark-gap potential is set to 10% below the breakdown voltage determined previously and the spectrum generated by firing the laser. Where detection of a single component material is required, especially when present in the sample in trace amounts, multiple spectrum exposures may be 'stacked' on the photographic plate in order to improve the detection limits of the method. Increased background fogging imposes an upper limit of about five or six superimposed exposures.

Having recorded a spectrum, the microscope is re-set to the visual mode and the location and size of the laser crater checked. The electrodes are re-cleaned by several spark discharges and the equipment is then ready for the next spectrum exposure. At the end of a run, the iron calibration spectrum is recorded and the plate developed, fixed, washed and dried according to standard darkroom procedures (see, for example [17]).

Although the use of the cross-excitation method yields the sharpest, most intense spectra, the very high power densities produced in the focused laser pulse enable samples to be excited to emission without additional electrical energy. Laser induced spectra show line broadening, self-absorption and tend to be less intense than those produced with auxiliary spark excitation, but can be useful where the spark would destroy the value of the sample for other purposes — for example, photomicrography or X-ray diffraction analysis. The method also eliminates the spectral lines which result from excitation of the electrode material and so allows carbon to be detected in the sample.

Interpretation of the spectrum

The LMA technique is capable of producing emission spectra containing at least two clear lines in the wavelength range of the spectrograph for over sixty elements from At. No. 3 (lithium) to At. No. 92 (uranium). Of the elements up to At. No. 83 (bismuth), with the exceptions of five of the lanthanides and technetium and ruthenium of the second transition series, all the metals and metalloids are detectable. Absolute detection limits are very good for most elements ($10^{-9} — 10^{-12}$ g); at worst about three orders of magnitude better than conventional spectrochemical analysis. Relative limits of detection are in the great majority of cases less than 1000 ppm contained in a microgram-scale sample [18].

The lines of significance in the spectra are identified by using a spectrum projector (Zeiss SP2) to produce a 20 × magnified image of the plate directly onto an atlas of emission lines of the elements recorded alongside the spark spectrum of pure iron [19]. In this way the iron calibration spectrum on the plate can be brought into coincidence with that of the atlas. Each unknown spectrum is then projected in turn and analytically meaningful lines are identified from their precise locations on the atlas. In contrast to conventional emission spectrography, lines arising from the excitation of carbon and the inevitable cyanogen bands do not interfere with the emission lines produced by the sample plasma (see Fig.8).

For paint analysis, qualitative element detection is usually enough information for conclusions to be drawn about the pigment composition of the sample. Although the spectral line intensities bear a complex relationship to the element concentrations from which they arise, visual estimates of line intensities allow certain approximate quantitative judgements to be made. More rigorous semi-quantitative analysis is possible with the LMA, particularly for metallographic problems, provided meaningful standards are available. Quantitative work requires microdensitometry of the plate or the use of direct-reading photomultiplier detectors to record line intensities.

Conclusion

In this laboratory we have found laser microspectral analysis to be a versatile and sensitive analytical tool for the qualitative detection of the characteristic and trace elements found in pigment materials. A particular asset for the conservation laboratory is that each spectrum represents a permanent unambiguous record of an analysis, in a form suitable for future comparative studies. LMA provides a valuable adjunct to the examination of the layer structure of minute paint flakes by optical microscopy, and when information gathered from these two techniques is combined with X-ray diffraction studies using the powder camera method, the majority of the inorganic materials found in paintings can be identified with certainty.
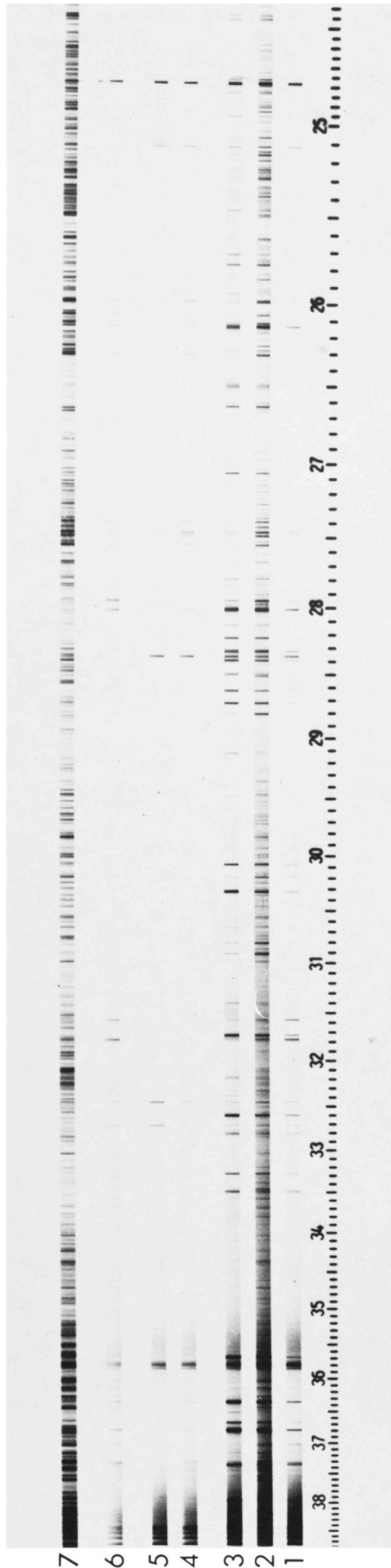
Figure 8 Portion of an LMA spectral plate in the range 385—245 nm, magnification approx. 2.5 ×.
1. No.1432, David, *Virgin and Child with Saints and a Donor*, bright yellow highlight layer of brocade shown in Plate 7d, p.59: lines for Pb (368.4, 363.8, 283.7, 280.2 nm) and Sn (326.2, 317.5, 286.3, 284.0 nm). Conclusion: lead-tin yellow.
2. No.6437, van Dyck, *Lady Thimbleby and Viscountess Andover*, thick yellow paint of Lady Andover's sleeve (see Fig.6): lines for Pb and Sn (wavelengths as for spectrum no.1), plus lines for Fe (275.6, 259.9, 259.8 nm) and Si (288.2, 252.9 nm). Conclusion: lead-tin yellow mixed with yellow ochre.
3. Reference powder sample of lead-tin yellow prepared at the Doerner Institute, 1961.
4. No.1432, brown inclusion in blue of brocade pattern (see Fig.7): lines for Fe (wavelengths as for spectrum no.2). Conclusion: ochre.
5. As spectrum no.4, blue of brocade (Fig.7): lines for Cu (327.3, 324.8 nm). Conclusion: azurite.
6. No.4004, Tintoretto, *Vincenzo Morosini* (see p.9), purple-red lake glaze on sitter's sash: lines for Al (309.3, 308.2 nm) and weak lines for Fe. Conclusion: aluminium hydroxide substrate for the lake pigment.
7. Iron calibration spectrum.
The following LMA parameters were used for all spectra: spark-gap, V = 1.6 — 1.8 kV, C = 2 μF, L = 60 μH; laser flash-tube, V = 1.7 — 1.9 kV, C = 381 μF, L = 127 μH.

Notes and references

1. PLESTERS, J., 'Cross-sections and Chemical Analysis of Paint Samples', *Studies in Conservation*, **2**, 3 (1956), pp.110 – 31.
2. BUTLER, M. H., 'Application of the Polarizing Microscope in the Conservation of Paintings and Other Works of Art', *Bulletin of the American Group – IIC*, **11**, 2 (1971), pp.107 – 19.
3. This point has been clearly demonstrated by Jacobi in the 1940s at the Doerner Institute, who showed by emission spectrography that the principal manufactured opaque yellow used in European easel painting before the mid-eighteenth century was a mixed oxide of lead and tin (lead-tin yellow). Before the spectrographic detection of tin in actual samples from paintings, the yellow pigment was generally assumed to be the yellow oxide of lead – massicot or litharge. See KÜHN, H., 'Lead-tin Yellow', *Studies in Conservation*, **13**, 1 (1968), p.8.
4. See, for example, STODULSKI, L. P., 'The Use of the Emission Spectrograph in the Conservation Laboratory', *Bulletin of the American Group – IIC*, **15**, 2 (1975), pp.66 – 90; and, BARKER, H., 'Spectrographic and X-ray Diffraction Methods in the Museum Laboratory', in *Application of Science in Examination of Works of Art*, Proceedings of the Seminar, 1965, Museum of Fine Arts, Boston, p.219.
5. BRECH, F. and CROSS, L., 'Optical Microemission Stimulated by a Ruby Laser', *Applied Spectroscopy*, **16** (1962), p.59. See also, BRECH, F., 'Spectrochemical Analysis Using a Laser Microprobe', *Laser Focus*, **1**, 23 (1965), p.5.
6. PETRAKIEV, A., SAMOV, A. and DIMITROV, G., 'The Application of the LMA 1 Zeiss Laser Microspectral Analyzer for the Identification of Pigments in Old Multilayer Wall Paintings', *Jena Review*, **4** (1971), pp.250 – 2.
7. BRECH, F. and YOUNG, W. J., 'The Laser Microprobe and Its Application to the Analysis of Works of Art', in *Application of Science in Examination*

of Works of Art, Proceedings of the Seminar, 1965, Museum of Fine Arts, Boston, pp.230 – 7.

8. A detailed review of the technique and instrumentation available may be found in MOENKE, H. and MOENKE-BLANKENBURG, L., *Laser Micro-Spectrochemical Analysis,* trans. R. Auerbach, Adam Hilger (London 1973).

9. *National Gallery Technical Bulletin,* **1** (1977), p.23.

10. The original LMA 1 laser-head was equipped with a neodymium-doped glass resonator rod of laser wavelength 1046 nm and maximum output of 1 J. This has recently been replaced by a Q-switched ruby resonator (laser wavelength 694 nm) which permits much greater control over laser function and reproducibility of output. Where a particular application requires, it is possible to reintroduce the neodymium-glass resonator.

11. MOHR, J., 'Laser Microspectral Analysis with Q-Switched Solid-State Laser', *Jena Review,* Special Issue Spring Fair (1971), p.93 – 6.

12. The extremely high power densities available from the focused laser pulse arise from a total energy output of less than 1 J, concentrated into a spot of the order of 10^{-3} cm across, in a pulse of approximately 10^{-7} s duration.

13. The problem of lens design for laser light focusing is discussed in RASBERRY, S. D., SCRIBNER, B. F. and MARGOSHES, M., 'Laser Probe Excitation in Spectrochemical Analysis. I: Characteristics of the Source', *Applied Optics,* **6,** 1 (1967), p.83.

14. Catadioptric objectives possess both refracting and reflecting surfaces. For spectrochemical analysis with the laser probe, the 40× objective is a lens-mirror combination designed in such a way that laser light is not brought to a focus within any of the individual optical components.

15. SLAVIN, M., *Emission Spectrochemical Analysis,* Wiley-Interscience (New York 1971), p.94.

16. RASBERRY, S. D., *et al., op. cit.,* p.84.

17. SLAVIN, M., *op. cit.,* p.124ff.

18. MOENKE, H. and MOENKE-BLANKENBURG, L., *op. cit.,* p.215ff.

19. *Q-24 Eisenspektrum,* VEB Carl Zeiss (Jena 1959).