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THE APPLICATION OF AN IMPROVED LASER MICROPROBE IN ART ANALYSIS

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Abstract

The laser microprobe has many features which would seem to make it an ideal tool for analysis of art objects. These include high spatial resolution, extremely small sample requirements, a wide variety of possible elements for analysis over a large dynamic range of concentrations and capability of sampling a variety of sizes and shapes. Problems of surface damage, spectral insensitivity, and poor accuracy and precision had limited the applicability of this technique in the past. Following a systematic study of these limitations, improved performance has been achieved. In addition, a mathematical model of the sampling process has been developed in an effort towards generating elemental depth profiles.

Introduction

The laser microprobe has been used in qualitative elemental analyses for over twenty years. Originally developed by Fred Brech and others at Jarrell-Ash in Boston, it has now been widely used in a variety of fields, i.e., in the technical examination of art objects (1,3,7) as well as in geology (4), forensics (2), and biological research (5).

The basic instrument uses a short intense pulse of focused laser light to probe the object, followed by excitation of this sampled material by a pulsed electrical arc. Some of the radiation from the excited atoms and ions is collected optically and admitted to the entrance slit of a spectrograph. Through the use of standard reference material, the resultant dispersed light can be measured to identify the sample components, and in some cases, to determine their concentrations. The instrument combines the excellent sampling properties of a high power pulsed laser (such as high spatial resolutions and controlled penetration through adjustable laser power) with arc-like cross excitations to enhance the normally weak spectral luminosity of the laser plume.

For all the early enthusiasm associated with the introduction of the laser microprobe, its applicability has been surprisingly limited. There are a number of important factors which contribute to this situation. This paper describes research which examines both advantages and limitations of the instrument (as used heretofore) and explores several new approaches in its use in art analysis.

Advantages and Limitations

For the study of art objects, utilization of a non-destructive method is generally called for--the laser microprobe approaches this restriction. Sample "spots" on the order of tens of microns in diameter are possible. Unfortunately, small diameter sampling sites (small amounts of sampled material) have usually implied limited detection limits. Thus, cross-excitation is essential to improve signal to noise ratio and to minimize self-absorption and spectral line broadening. However, the electric pulsed arc generally causes discoloration or surface damage unless several factors are carefully controlled; spectroscopic contamination from auxiliary arc impurities in the electrodes is also possible. Furthermore, to fully solve some problems, quantitative analyses are needed which have the ability to detect trace, minor, and major constituents

Key Words: Laser microprobe, fine art examination, elemental analysis, oriental lacquer, spectroscopy, micro-sampling, multi-layered material, painting cross-section.

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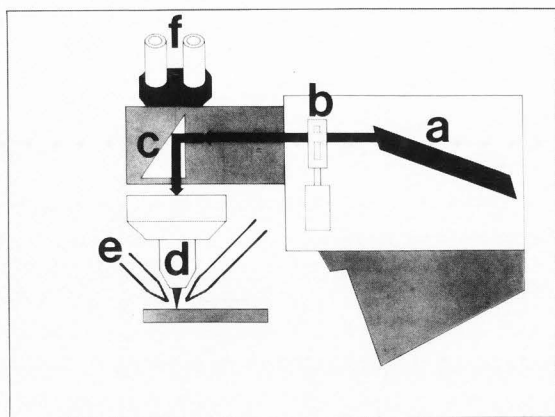


Figure 1: Representation of laser microprobe elements. a) flashlamp pumped neodymium glass laser rod, b) rotating q-switch, c) deflecting prism, d) microscope focussing objective, e) re-excitation carbon electrodes, f) viewing eyepiece.

in a variety of sample matrices.

An excellent assessment of the laser microprobe's utility as tool for quantitative analyses was reported by van Deijck et al. (6). The authors expressed concern that both precision and accuracy will always suffer as a direct consequence of utilizing independent sampling and excitation methods. Their conclusions suggest that problems were so severe that further development of the laser microprobe is not warranted. All significant literature citations dealing with the microprobe (through 1979) are included in reference 6 and are not repeated here.

Nonetheless, the many intrinsic advantages of the laser microprobe encouraged us to systematically study its utility and to make modifications to enhance its use in the technical examination of art.

Instrumental Developments

The laser microprobe in use is located in the Emission Spectroscopy Laboratories at Wayne State University. The instrument is a Jarrell-Ash Mark II, Model 45-604 unit with a Q-switched, flashlamp-pumped neodymium glass rod laser. Energy output of the laser is adjustable from about 0.1 to 1.0 joules. Depending on experimental conditions such as laser energy, degree of focus, nature of the sample, and quality and condition of the microscope lens, craters are created with diameters ranging from about 20 to over 200 microns.

Laser output (which has a pulse duration of a few nanoseconds) is manually initiated by the operator causing rotation of the laser Q-switch. Upon breakdown, laser energy is directed through the instrument head via a prism. The collimated light is focused by the microscope optics to the sample surface. The optical depth of field resulting from this arrangement is very shallow so "critical" focussing (i.e., within a few microns) is essential for efficient energy transfer.

Two ultra pure carbon electrodes are positioned close to the sample surface. These electrodes are capacitively charged and maintained at 1500-2000

Figure 2: Laser microprobe sampling of a surface accompanied by pulsed arc re-excitation of the sampled plume.

Figure 3: Improved precision mechanical support system designed for use with Jarrell Ash laser microprobe. This arrangement also allows study of larger objects than permitted by the original sampling system.

volts DC. Material which is ablated from the sample surface is in part ionized due to the tremendous energy imparted to the gaseous plume during the sampling process. These charged species travel from the sample surface and "short out" the electrode gap resulting in the pumping of electrical energy into the laser plume and subsequent re-excitation of that material. The luminosity of re-excited material is often several orders of magnitude more intense than emission resulting directly from laser sampling only. Figure 1 schematically details the arrangement of the microprobe. Figure 2 shows the actual breakdown process.

Because our work involves art applications, attention was placed on achieving maximum spectral luminosity while sampling minimum laser energy to minimize visible ablation from the surface. To this end, the standard electrode configuration was significantly altered. The angle between the electrodes was increased from approximately 90 to 150 degrees and the distance from the sampling site to the electrodes was reduced to about 1mm. This arrangement, coupled with careful optical matching to the 1.5 meter Wadsworth grating spectrograph increased spectral luminosity by one order of magnitude over standard conditions. The microscope lens was protected by a thin replaceable microscope slide cover to protect the optical surfaces from ablated material. Special airpath (non-cemented) objectives are essential; cemented lenses will fracture due to laser energy absorption.

The mechanical stability of the commercial instrument was not adequate in meeting our stringent requirements of directing energy to specific sample sites. Since a major portion of our work has been to explore "depth profiling" a surface with the microprobe, it was essential that critical alignment be maintained in order to focus on the bottom of a crater left by a previous sampling event. Figure 3 shows the added mechanical support stages designed to accomplish this requirement. Also added was an ultra fine adjustment microscope sample stage so that critical focus could be achieved. As a result, we have been able to "tunnel through" 1 to 2 mm thick surfaces with 30 to 50 successive laser shots all following the same trajectory.

Improvements in Sampling Conditions

Figures 4a and 4b illustrate the effect of one laser sampling event on a gold-plated (28 micron thickness) silver/copper alloy coin. It is obvious that "normal operation" is accompanied by severe surface discoloration and damage; the sampled area (crater) is easily detected (inside the letter U).

A simple solution to this problem was the application of a thin organic coating (diluted rubber cement is one example) as a protective medium prior

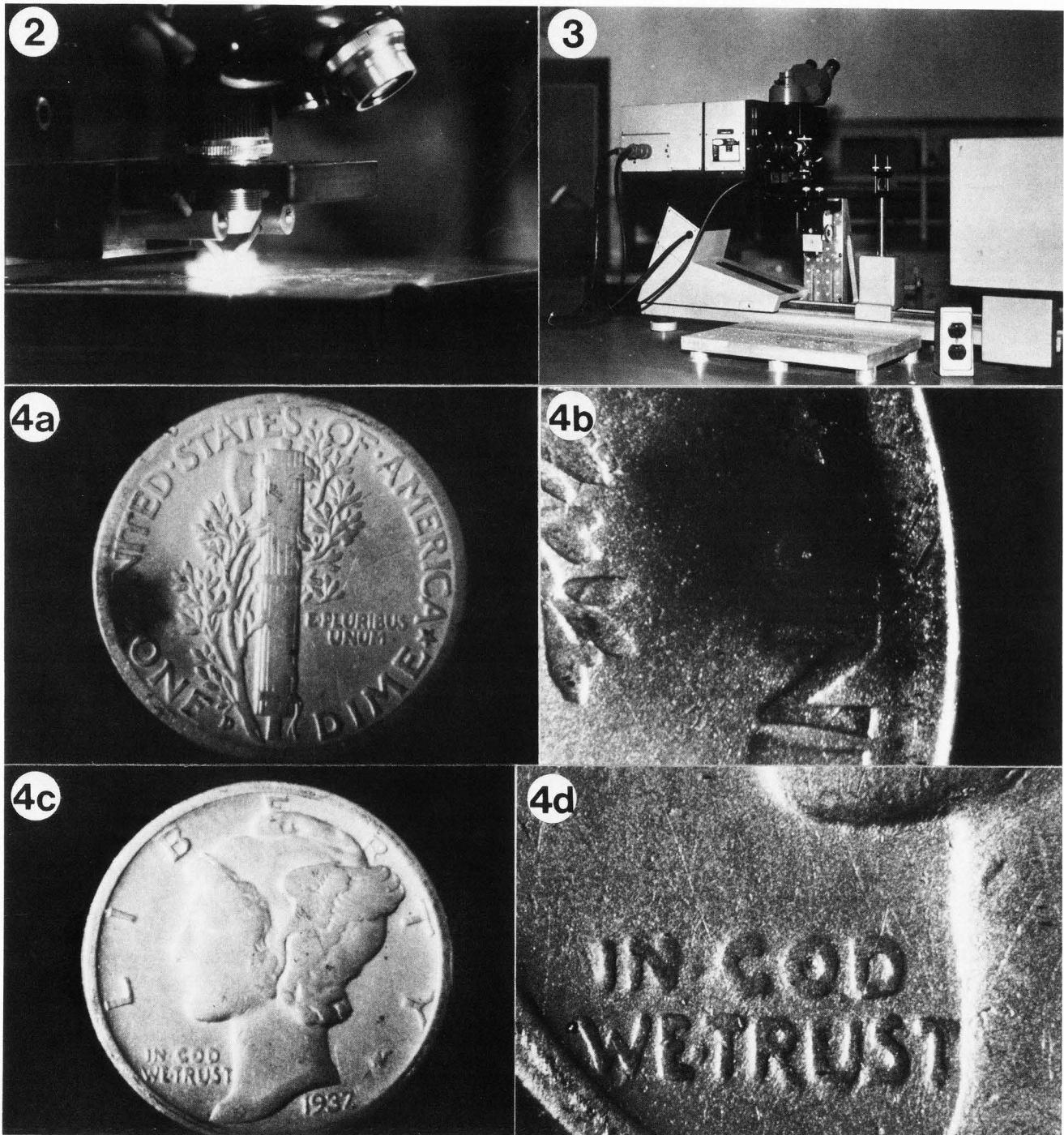


Figure 4 (a-d): a and b: laser microprobe sampling of a gold-plated coin without an organic protective coating. c and d: same, except the coin was protected by a coating during the sampling process.

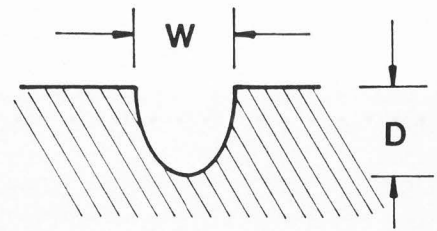
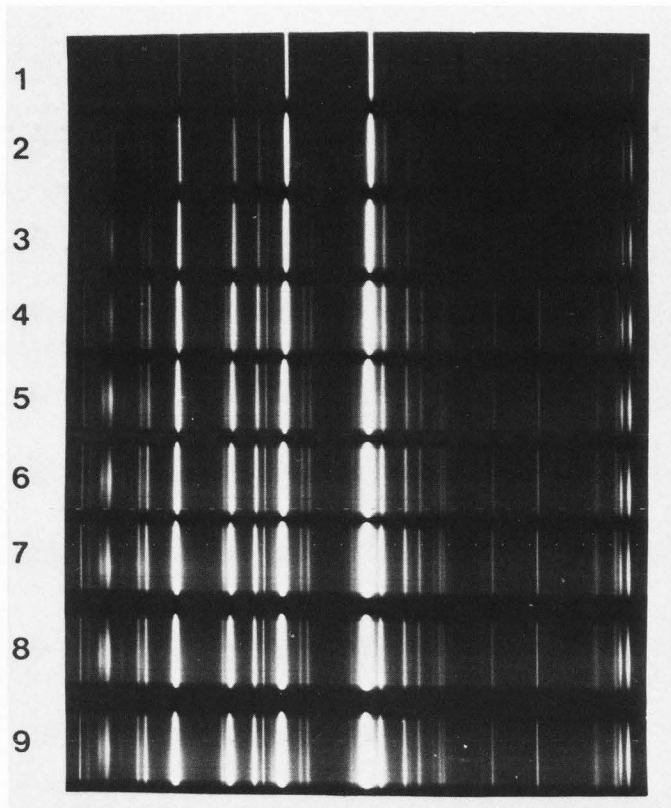
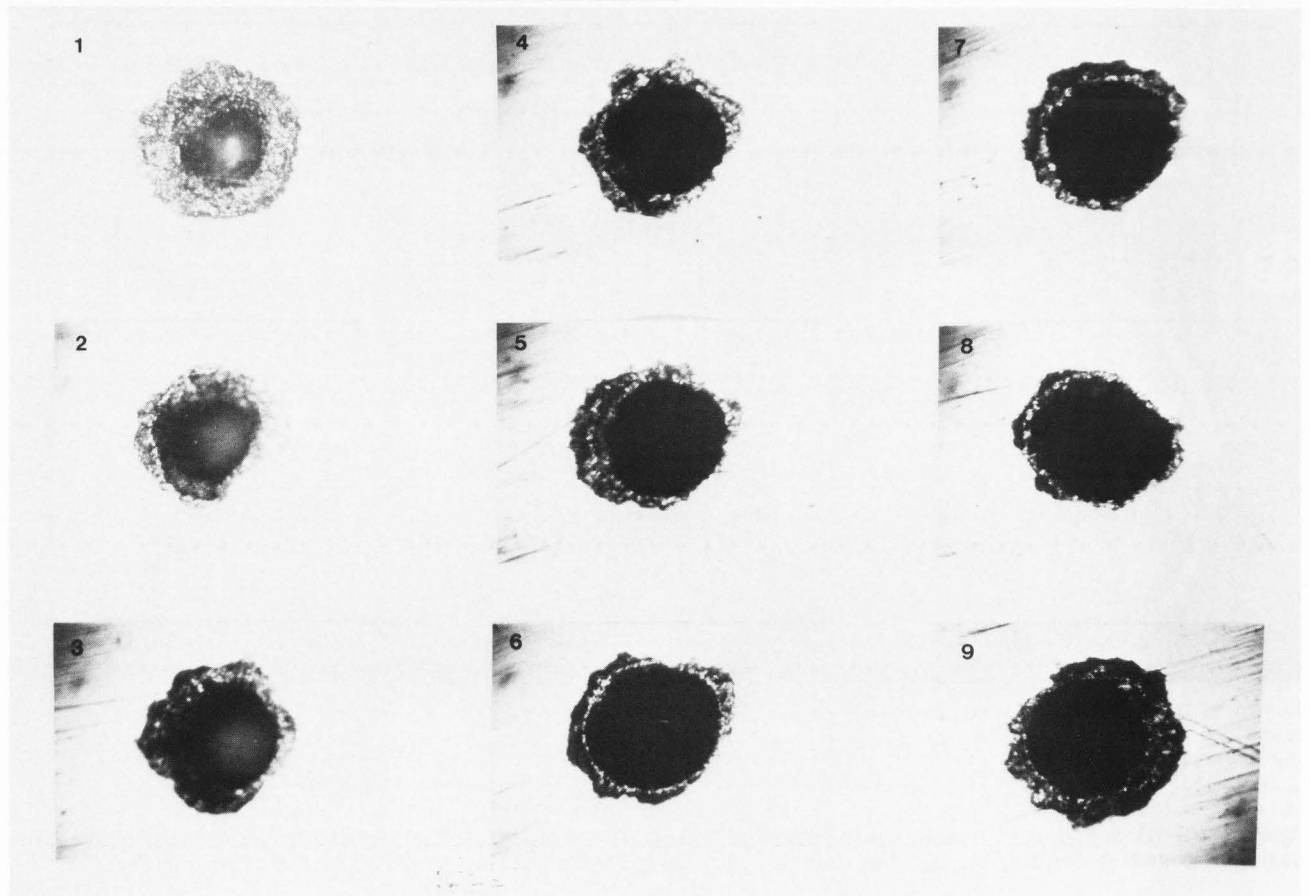


Figure 5: Laser microprobe sampling of a pure copper surface tunneling into the sample. Crater diameters range from 61 microns (inset 1) to 142 microns (inset 9). Crater depths are 46 and 356 microns, respectively, for the same insets. Surface coated with diluted rubber cement during laser sampling.



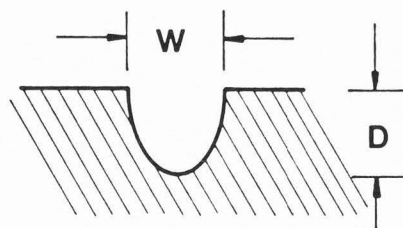
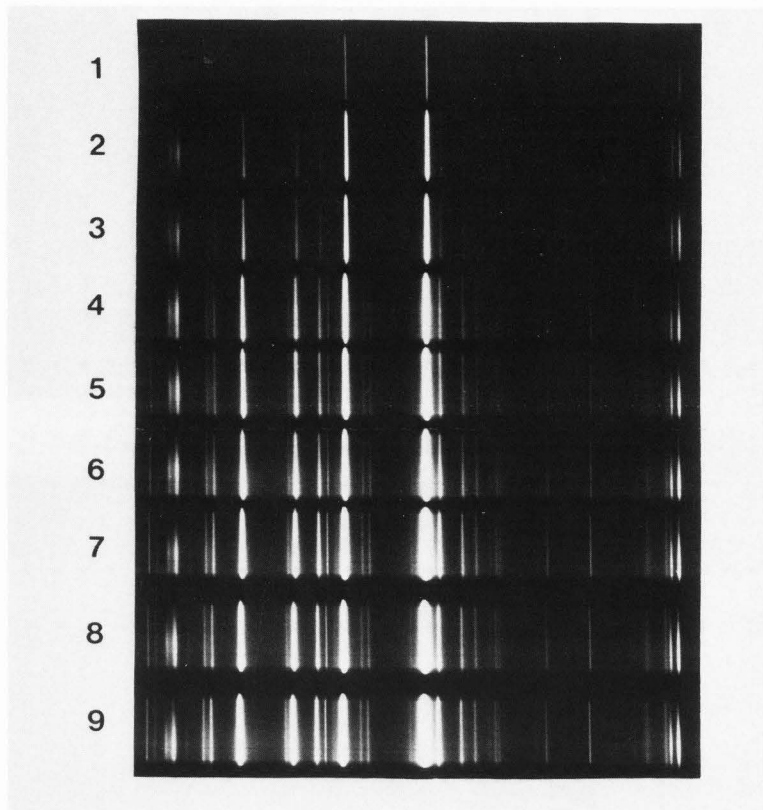
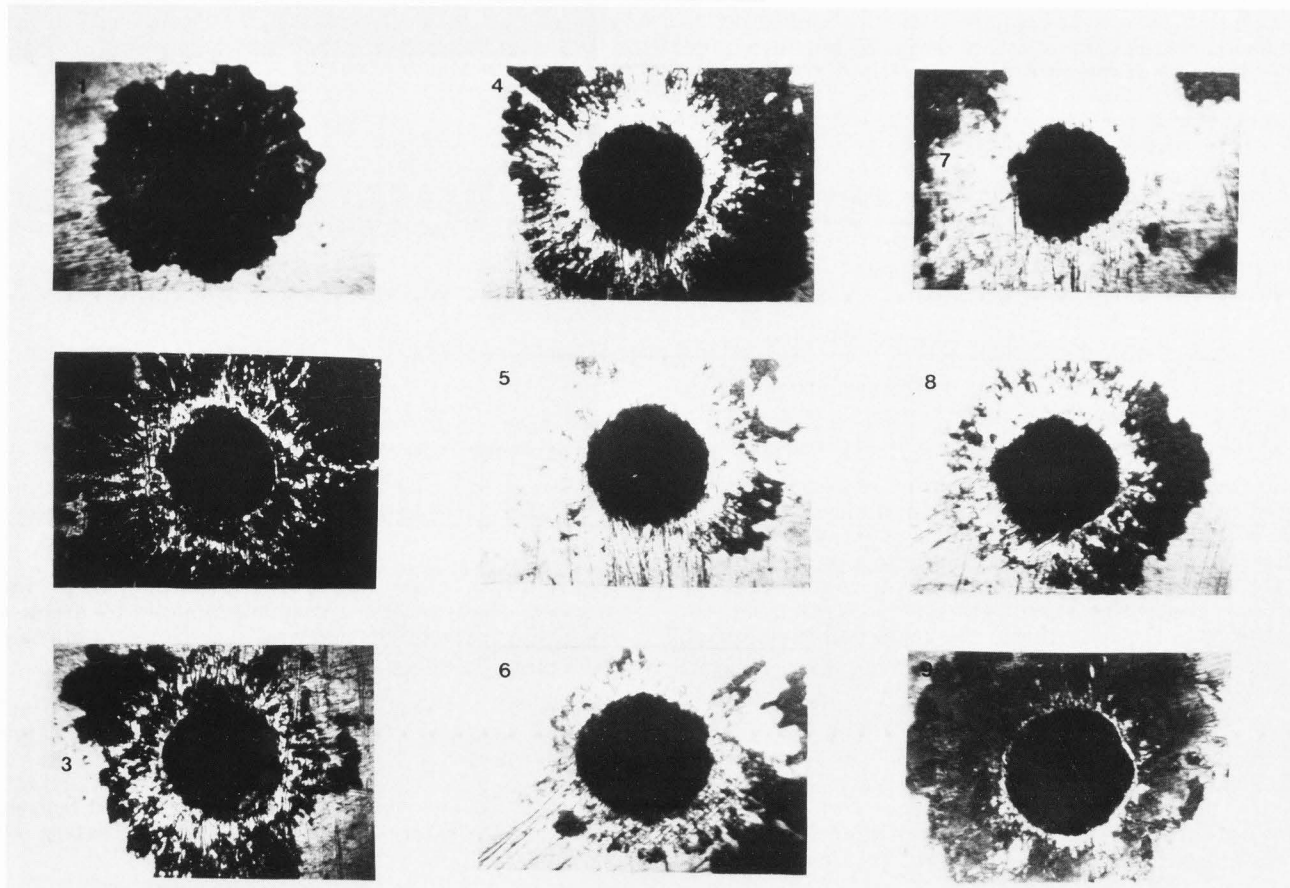


Figure 6: Same as Figure 5 except no protective surface coating employed.



to laser microprobe sampling. Figures 4c and 4d illustrate corresponding results on the other side of the same coin after application of an organic coating. It is clear that damage and discoloration have been reduced; further the crater is not visible to the unaided eyes (inside the letter O). While improvements may provide aesthetically acceptable results, changes in sampling or in spectral intensities must also be taken into account.

Figures 5 and 6 demonstrate typical performance. Shown are two sampling conditions with (Figure 5) and without (Figure 6) incorporation of a thin organic coating on an ultra pure (99.995%) copper surface. Both data sets were taken on the modified instrument and thus involve all improvements in electrode geometry, reduced laser ablation energy, critical focussing, and careful matching of the discharge emission to the spectrometer.

The inset microphotographs and corresponding spectral features show surface damage, crater characteristics, and integrated light intensity for both cases. The data result from a series of nine laser sampling events. In each case the laser was refocused at the bottom of the crater created by previous individual sampling events. Spectrum 8, for example, is emission from the eight laser ablation only. The corresponding laser crater (8) is also shown. (Exact location and subsequent refocussing was not possible with the instrument prior to the described mechanical modification.) The magnification of each photograph is approximately 1000X as observed. Note that crater damage is greater for the uncoated case and increases with the number of pulses. The two intense lines in the illustrated spectrum are the copper 3247 Å and 3247 Å resonance transitions. Furthermore, the integrated intensity of wavelength dispersed light, recorded on film in the focal plane of the spectrograph, demonstrates that application of an organic surface coating results in enhanced line intensity and ultimately improved limits of detection. This enhancement may be due to improved arcing condition brought about by the introduction of additional charged species in the ejected plume. Definitive experiments are underway to study the mechanism of this phenomena.

Examination of Multilayered Material

To explore the use of the laser microprobe on art objects composed of many layers we selected test examples from paintings and oriental lacquer (urushi).

Figure 7 shows a photomicrograph of a test painting cross section, consisting of a white ground composed of calcium carbonate and titanium dioxide in a rabbit skin glue medium, approximately 200 microns thick and an upper pigmented layer, approximately 40 microns thick. The pigment layers are lamina containing cerulean blue, ultramarine and ochre in an oil medium. A representative sample crater is located in the right ground area indicated by an arrow, approximately 70 microns in diameter.

This (and other) test cross sections showed that, while the crater is larger than some thin pigment layers (sometimes layers are less than 10 microns thick), major and minor constituent elements could be detected in the ground and in pigment layers. In many cases this information is extremely helpful as qualitative results are sufficient to

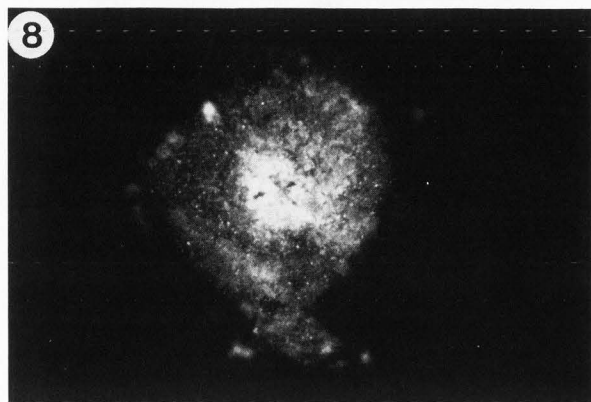
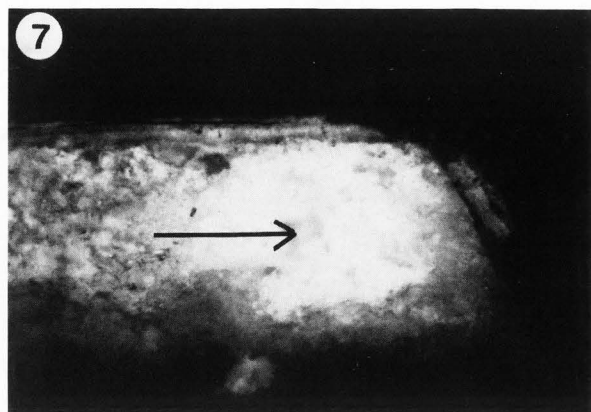


Figure 7: Laser microprobe sampling of a test painting cross section. Crater indicated by arrow at right, approximate diameter is 70 microns. Details of structure in text.

Figure 8: Laser microprobe sampling of black lacquer surface. Crater diameter is approximately 300 microns.

Figure 9: Laser microprobe sampling of red lacquer surface. Crater diameter is approximately 70 microns.

Laser Microprobe in Art Analysis

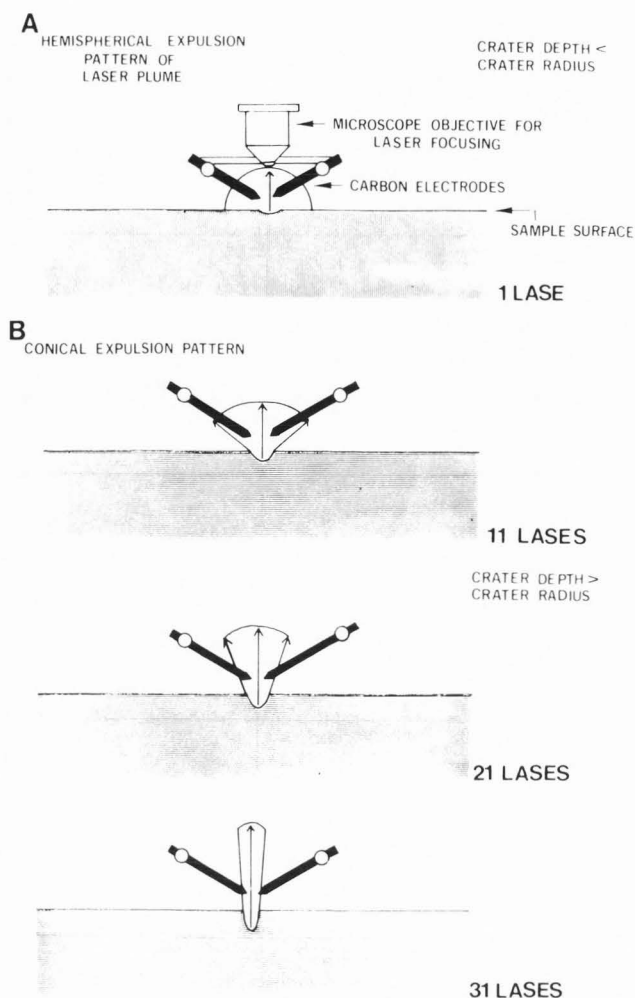


Figure 10: Model of changing sample trajectories as a function of laser induced crater depth.

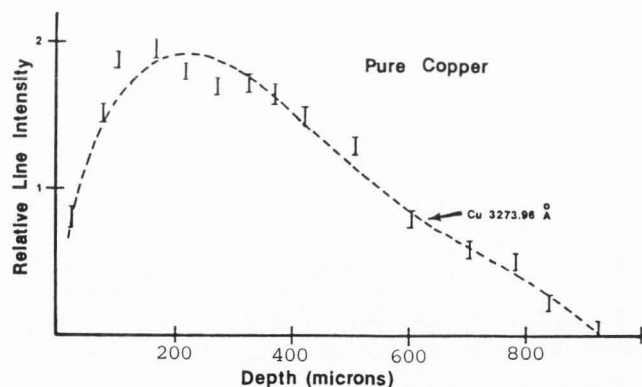


Figure 11: Relative copper emission intensity as a function of crater depth. Error bars indicate the range of experimental data for five individual experiments.

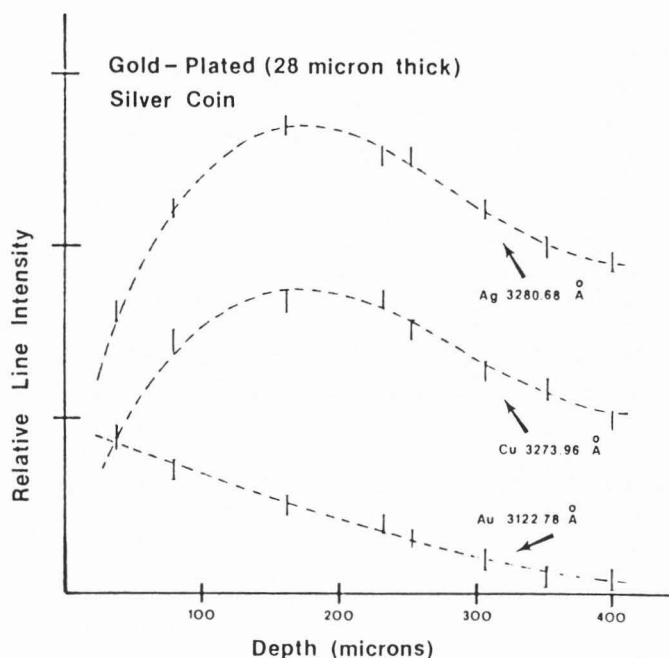


Figure 12: Depth profiling through the thin gold-plated silver-based coin shown in Figure 4.

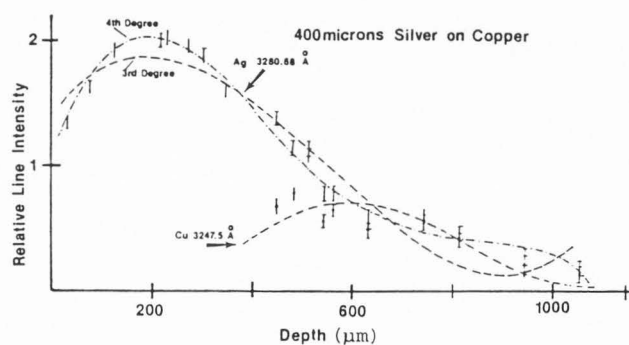


Figure 13: Depth profiling through a thick (400 micron) silver coating on a pure copper surface.

uniquely identify pigments or ground. Additionally, improved optics would allow smaller crater size; this would further improve spatial resolution in thin pigment layers.

Oriental lacquer is material composed of many individual layers. In some objects there may be over 100, sometimes containing different pigments or metal dust or flakes for decoration. Laser microprobe analysis from lacquer test objects are shown in Figures 8 and 9. A comparison was made of the sampling of two highly polished traditional types of Japanese lacquer (black and red pigmented). The black surfaces strongly absorb laser radiation. Thus one observed a larger crater (approximately 300 microns) as compared to the red lacquer (approximately 70 microns). In both cases major elements in the lacquer pigment were identified from the spectrographic dispersed light.

These test results provide very encouraging evidence that the laser microprobe can provide important information from very complex, highly structured objects.

An Empirical Model

A major thrust of this work has also been to explore the feasibility of using the laser microprobe as a tool for depth profile analysis of various surfaces. If available, this technology would be useful in applications such as analysis of plated metal surfaces or of multilayered materials; in paintings and decorated lacquerware.

The principal model which we have invoked for these studies deals with the effective trajectory of material following laser ablation from the surface. As noted in Figure 10, the laser plume resulting from the first laser sampling event is probably hemispherical in nature. After a series of consecutive laser sampling events (into the same hole), a more conical expulsion pattern is expected due to confinement by walls of the crater. Because of the change in plume density at the electrode position as a function of crater depth, this phenomenon is expected to have a major effect on observed spectral intensities.

This is seen for pure copper which was chosen as a primary test case. Experimental data points for copper resonant transition emission are shown as a function of crater depth in Figure 11. The general shape of intensity versus depth profiles are remarkably similar when going from material to material although the specific details are element and line specific. These shapes may also show a concentration dependency at trace levels. The dotted line corresponds to a third order polynomial fit of the experimental data points:

$$\text{INT} = b + mX + nX^2 + pX^3 \quad (1)$$

where INT is the observed intensity, b the intercept, and n, m, p, the higher order polynomial coefficients associated with crater depth X. With a mathematical description of depth versus intensity information at hand, we view this as a first step to eventual deconvolution of emission intensities with an appropriate function in order to extract direct concentration data in practical experiments.

Figure 12 shows results of depth profiling through the silver based gold plated (28 micron) coin which was illustrated in Figure 4. Note the experimental reproducibility for each data point collected (each point is the average of 10 different experiments) as well as the similarity of curve shapes for both the silver and copper constituted. Intensity due to gold emission is highest from the first "shot" and then falls off rapidly since the gold layer was rapidly penetrated. The diameter of the laser sampled tunnel gets slightly larger as one continues to profile through the surface. As a result, spectral intensities resulting from gold transitions continue to be observed to a depth of about 400 microns. These and similar factors complicate a simplistic conical trajectory model and will have to be configured into our experimental description and model.

A final example (Figure 13) results from depth profiling through a 400 micron thick silver layer plated onto a pure copper surface. Penetration of

the silver layer and subsequent detection of the copper layer are quite evident. In Figure 10, silver data are plotted as both 3rd and 4th order polynomials. It is clear that the fourth order polynomial gives an excellent fit to a depth of about 400 microns. As noted, neither polynomial provides a completely acceptable numerical fit at great distances. Research will continue to model surface depth intensities and will ultimately link this model in such a way as to allow one to calculate "corrected intensities" from complex surfaces.

Conclusions

The above observations indicate that we have not given up on the laser microprobe. Indeed, improved mechanical stability and optical considerations have resulted in increased spectral intensities and in more predictable sample site selection. Incorporation of surface coatings reduces observed damage. Finally, we have completed first steps which encourage us to continue in the quest for improved "quantitative results" from complex layers and/or alloys.

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Discussion with Reviewers

W.C. McCrone: I believe that the use of a laser microprobe on paintings is an entirely inappropriate application of the laser microprobe. There is

nothing wrong with the paper itself as it relates to the instrument but I have strong reservations about using a tool which:

- 1) gives only elemental analytical information,
- 2) destroys the sample, and
- 3) is applied to a matrix of small particles that could be identified molecularly by other methods (e.g. polarized light microscopy). I believe the laser microprobe is a useful instrument but only for homogeneous samples like glass or at least more nearly homogeneous samples like metals. When applied to paintings it destroys those features of the sample (individual particles of pigments etc) that would give the kind of information one needs to decide what pigments were used, when they were prepared, how they were prepared and how authentic that painting might be.

There is no substitute for removing nanogram to micrograms samples of individual paint layers and studying them microscopically in order to identify the individual particles present in those layers. No elemental analysis instrument comes close to yielding the kind of information we need for painting. Many pigments, for example, gamboge, bitumen, van dyke brown, indigo, charcoal, lamp black are organic or carbon and certainly can't be identified by any of the elemental analytical tools. Many pigments have similar elemental composition, for example, gypsum and anhydrite; bitumen, charcoal, lamp black and van dyke brown; azurite, malachite, blue verditer and verdigris; viridian and chromium oxide; alizarin and madder; red lead, litharge, massicot and lead white; prussian blue and iron earth pigments; and finally calcined bone and bone black. It is crucial in painting analysis to be able to distinguish between these various components. Furthermore, in at least one recent case we found the shapes of the microscopic pigment particles to be strongly indicative of a particular painter's pallet by comparison with shapes of the same pigments in other paintings of that artist. This could never be done unless you used the microscope.

I don't think the art world should be encouraged to use a laser microprobe when they can get so much better information by use of the polarized light microscope.

You can see that I feel very strongly on the point of using inappropriate instruments. The analytical chemical world is now so complicated in terms of the possible analytical tools that few analytical chemists are able to evaluate the capabilities and limitations of all of those methods. Often times too, they can't afford some of the more sophisticated analytical tools that might be best for the problem at hand...

Authors: In principle, we agree with the observation of Dr. McCrone. However, we feel that, when a variety of analytical techniques is available, it is unnecessary and sometimes dangerous to rely on only one method such as optical microscopy. The laser microprobe is most usually used to provide information that supplements other analytical results.

In addition, there are some instances where different pigments are very difficult to differentiate, with respect to optical properties and morphology, i.e., vermilion (HgS) and red iron oxide (Fe₂O₃). In this case, elemental information could be extremely helpful for correct identification. As a further example, in early studies of yellow pigments relying

solely on optical microscopy, samples of lead-tin yellow were incorrectly identified as massicot (PbO). Correct identification was accomplished through the detection of tin using spectroscopic methods.

R.J. Koestler: Is it possible to regulate the depth of penetration of the laser to less than 20 microns? This would help in those cases where multi-layered samples were being analyzed. Is there a theoretical / practical lower limit depth penetration?

Authors: The sampled spot size is dependent upon a large number of factors including the diffraction limit of the light source used, the diameter and focal length of the lens used, the quality of the optics employed, the nature of the surface, etc., etc. Minor improvements beyond those listed in the manuscript are probable with replacement optics.

The sampling depth is related to the above, as well as showing a particular dependence on the laser power. There is a tradeoff here. Lower laser power will reduce the crater depth at the expense of sample uptake. At some lower limit so little sample is removed that it becomes difficult to initiate the cross excitation and/or spectroscopically observe the species of interest.

R.J. Koestler: Can the laser beam be collimated smaller for each succeeding shot to reduce ablation of upper layers?

Authors: Unfortunately no. This would be a significant improvement in the laser microprobe. Since simple airpath objectives are used (to avoid destruction of normal cemented / corrected lens systems) the prospect is not good.

R.J. Koestler: What else could be used as a protective coating that is completely reversible?

Authors: For completely flat surfaces we used "Saran Wrap" with some success. For irregular surfaces this is not feasible since the trajectory of sampled species becomes unpredictable.

