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Microanalysis of Painted Manuscripts and of Colored Archeological Materials by Raman Laser Microprobe

ABSTRACT: In the field of historical analysis of works of art, specialists may have at their disposal only tiny fragments or even just traces of an object. In recent years, several microinvestigative techniques (electronic microprobes, photoelectron spectroscopy, ion, and nuclear or Raman laser microprobes) have been perfected. These techniques can afford, henceforth, precious data to experts involved in the analysis of very small fragments of matter. The Raman laser microprobe (RLMP), which can theoretically identify or characterize any chemical substances (inorganic or organic), is thus suited to the examination of many archeological materials. As for the small samples required by RLMP (their size may be as small as a few micrometres), this technique can greatly aid authentification with no major damage to the historic art object being examined. In the few case studies presented here, we show that ancient inorganic pigments have been easily identified by this technique. These preliminary studies describe also the possibility of an analysis in situ, in which no sample taking is necessary. Such a nondestructive microinvestigation is therefore particularly suited to the identification of any precious or fragile materials with pigments. This possibility has been and is being explored successfully in various fields such as gemology (for authentification), biology, and criminology.

KEYWORDS: questioned documents, archeology, spectroscopic analysis, pigments

Raman laser microprobe (RLMP) assembles on the same instrument a conventional optical microscope, an optical filter possessing a very low stray light level (built with two concave holographic gratings), and a detection system (a photomultiplier followed by an amplifier and a chart recorder). Applications of the instrument and developments of first generation Raman Laser microprobe have been reviewed in several recent communications [1-4].

In discussing the Raman effect, we shall recall briefly how a molecule under the action of a quantum of energy $h\nu$ emitted by a source of monochromatic light of frequency ν_o might pass from a vibrational state to another one so that a molecule diffuses a photon whose energy is different from the primitive energy of the photon which has excited the molecule.

When analyzed by spectroscopic means, this reemitted light shows, at the frequency ν_o, a line of strong intensity caused by the Raleigh diffusion effect and several lines of very weak intensity whose frequency $\nu_o \pm \nu_i$ is different from ν_o; that set of lines constitutes the Raman spectra.

Raman effect measurements allow us to study the vibrational spectra of any polyatomic

structure and its observation is complementary to the infrared spectroscopic measurements. One difference is that in the infrared field, local analysis cannot be reduced to about 30 or 20 μm.

As a matter of fact, a laser beam can be focused on a very small fraction of matter (up to about a fraction of micrometre), limits of this being imposed by the diffraction of the light.

In view of a possible local analysis, various laser microprobes using Raman effect have been built [4] and RLMP has allowed many developments in microanalysis on the basis of the study of the molecular properties of matter.

In recent years, the high analytical potential of RLMP has been observed in many applications as various as physico-chemical and industrial studies, works in biology, and mineralogy or geology [5-6].

We have found that RLMP was also a very convenient tool for analyzing painting materials and could greatly help, in some cases, to identify and characterize these materials [7].

The analyst involved in archeological or in art historical studies (or in the field as an expert-reporter) has to identify the nature, and sometimes the possible origin of pigments encountered in colored materials. He has to identify also their related environments: binders, fillers, or other additional substances and even artifacts or contaminations.

In this respect, the analyst must overcome two major difficulties:

1. Historical materials or works of art are unique and cannot be replaced. No injury or risk of damage proceeding from the analysis can be tolerated. When sampling is allowed (and necessary), the samples are most often limited to a tiny fraction of the materials and nevertheless have to be significant, that is, representative of the whole. Thus, RLMP is suitable to the analysis of samples as small as some cubic micrometres. Furthermore, the samples are preserved (RLMP being a nondestructive method), and complementary methods of analysis can be used successively. Moreover, RLMP can be frequently performed on the object in situ for a local analysis, which then requires, as it will be shown, no sampling at all.

2. In regard to the heterogeneous materials most frequently encountered, it is particularly interesting to locate accurately each substance detected. Operating RLMP in a multichannel mode, it is possible to map out the distribution of one chemical substance in such heterogeneous materials. That possibility can greatly help to detect local traces of substances that could not be seen otherwise. At last, this technique can be very sensitive if the wavelengths of the source coincides or is close to an electronic absorption band. In these particular conditions, we can observe, with colored substances, a Raman resonance effect that allows the identification of some pigments whereas other methods could not afford any significant finding. The limitation is that the colored component absorbs light which then increases the risks of degradation of the materials when they are excited by a high power source.

Analysis of Blue Painted Letters

Specialists working on ancient manuscripts, historians, paleographists, and codicologists have achieved significant progress in their studies of painted ornamentation of handwritten books, for instance, through stylistic research or the analysis of different kinds of decoration and their comparative investigations.

Specialists already have only a few accurate data on painting materials used by medieval painters for the illustration of their books, and their own knowledge is mostly based on their interpretations of the very rare ancient recipes that have come down to us.

Thus, a physico-chemical analysis of painted manuscripts might complete their knowledge, allowing them, also, to continue by other means the comparative studies of workshops already attained by the classic methods, regardless or whether the present assumption is verified or not.

In this respect, we started several analytical works and undertook preliminary experiments on a fragment of a Twelfth Century manuscript. Yet, parts of that fragment had formerly been analyzed by classic microchemical methods [8].

Our purpose was to identify by a nondestructive method some of the pigments we found and to test the complementarity of RLMP with other methods such as X-ray fluorescence spectroscopy (XRF), X-ray diffractometry (XRD), or infrared sepctroscopy (IRS).

The manuscript fragment analyzed is a page of a French missal book dating from about the second part of the Twelfth Century (Fig. 1). It is probably one of the first pages of the missal since it shows the Latin prayers for the services of the second and third Sundays of Advent.

On the left side of it, several ornamented letters are painted in blue, red, green, or pale ochre colors. Two of them are in red filigree.

On the top of the page, there is a black painted musical notation under a pale ochre line. Several red rubrics separate the main text which is handwritten in black.

We first started studying the blue found in three illustrated letters.

Using a control sample, we obtained the Raman spectra from a small fragment of lazurite of general formula silicon dioride, aluminum oxide, sodium monoxide, sulfur, and sulfur trioxide.

With the argon laser source and with $\lambda = 514.5$ nm, the spectra show a strong and narrow band at 548 cm^{-1} and a weak and less narrow one at 1097 cm^{-1} (Fig. 2). These two observed bands have been interpreted as the vibrational Raman bands of the ion S_3^- so detected by these means in the crystal [9]. High observed intensities come from a Raman resonance effect caused by the frequency of the excitation close to the absorption band of the blue lazurite. The fundamental band is 548 cm^{-1} and 1097 cm^{-1} is one of the overtones.
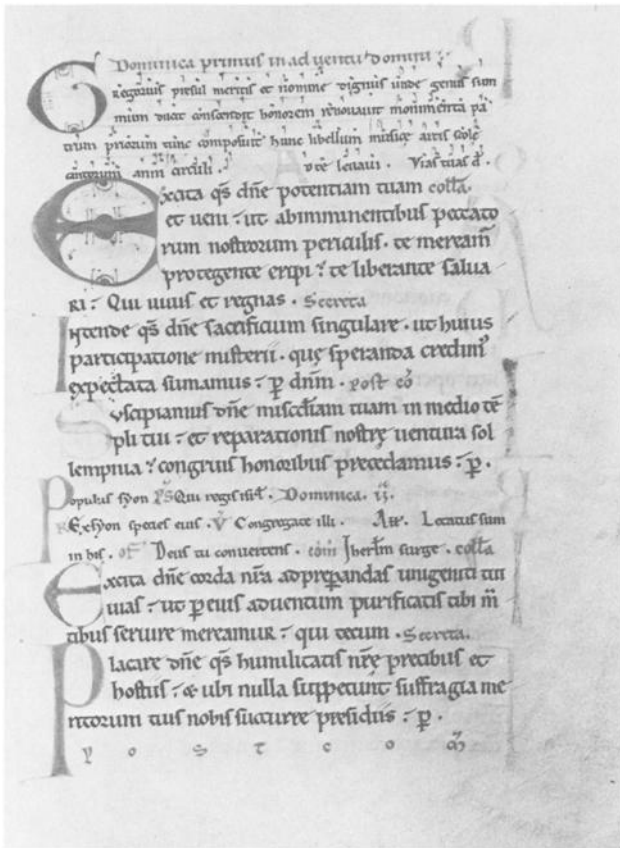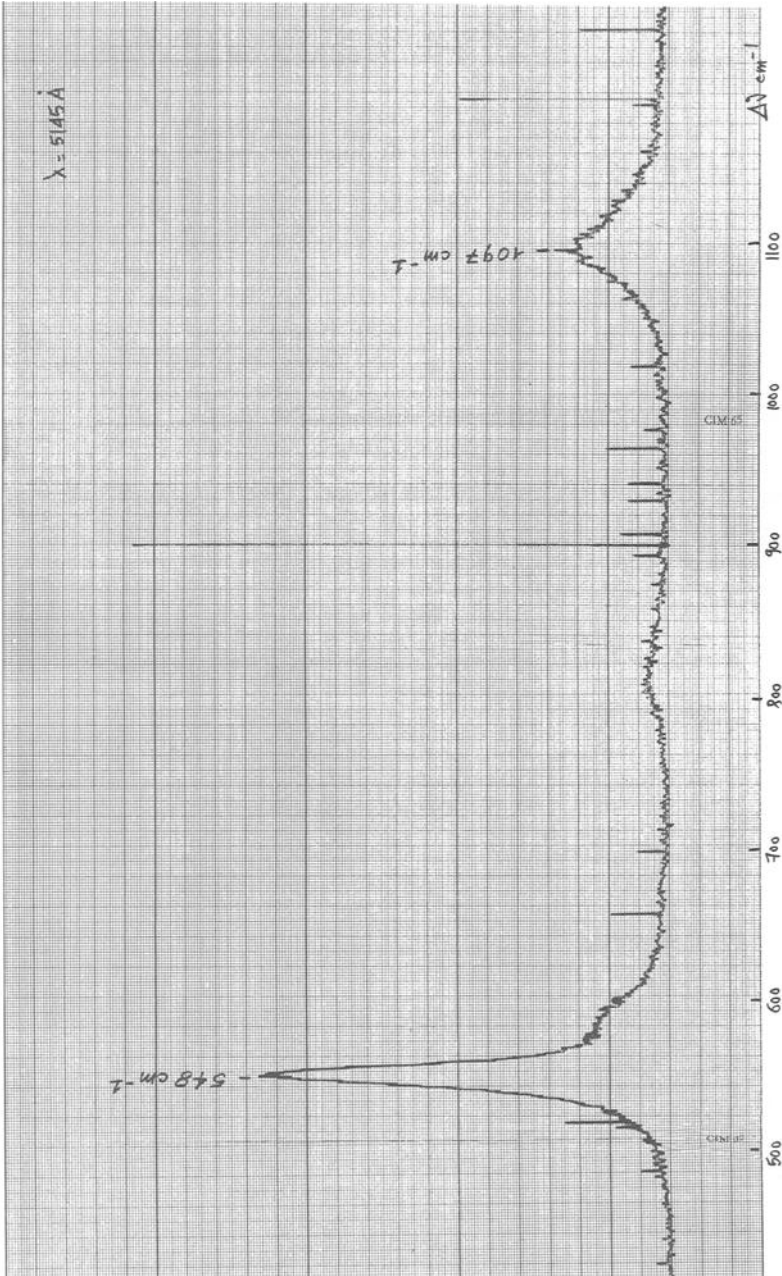

FIG. 1—*Page of a Twelfth Century French missal.*

FIG. 2—*Raman spectrum of lazurite (control sample).* 1 Å = 0.1 nm.

We were able to observe throughout the experiment the perfect stability of the sample under the laser beam excitation.

Then we placed under the laser beam the whole manuscript and at 548 cm^{-1}, we scanned a small part of a blue ornamented letter, using reduced power and with the laser beam slightly unfocused. At some fixed places, we observed a very intense response on the photon counter output. At several places, we recorded the spectra with the same conditions (Fig. 3). These spectra showed bands at 548 cm^{-1} quite similar to the bands observed previously with the control sample, but the background noise was more intense.

These findings reveal that the blue ornamented letters are composed of lazurite.

During the experiment we observed the constant stability of the material under laser beam excitation and this confirms that the method used in completely nondestructive.

Analysis of the Red Pigment

Using RLMP again, we attempted to identify the red pigment found on the painted letters and red rubrics of the manuscript (Fig. 4).

As before, we placed the whole page directly on the platen of the microscope under the laser beam to get the Raman spectra of the red painted materials without sampling.

We first used the green line of the argon laser ($\lambda = 514.5$ nm), with a reduced power, keeping in mind that we had to restrict all possible risks.

Several spectra were obtained at various parts painted red but none showed any significant band despite the fact we modified amplifications, scanning time, and integration constant time. At higher amplifications, we could observe a slight drift of the spectra. This drift was caused by the fluorescence of the materials, probably revealing a local presence of organic binder.

Starting then from the hypothesis [8] that the red was a mercury sulfide vermilion, we chose to start by testing a control sample of French vermilion (maker, Sennelier). We checked it first by XRF and XRD analysis. The rays observed (Fig. 5) on the diffraction pattern (at 0.335, 0.31867, 0.236 nm and so forth) identify mercury sulfide.

In the same conditions as before, we got the Raman spectra for the control sample (Fig. 6). Again, it does not show any significant bands apart from a small one at 255 cm^{-1} with a poor signal to noise ratio. However, no background fluorescence was observed.

We then used a different laser source, a krypton laser whose higher wavelength excitation line was better suited to the absorption of the red pigment in the visible field (Fig. 7).

Using the line $\lambda = 647.1$ nm, the new spectra that we got from the control sample shows a very intense narrow band at 344 cm^{-1}, another one less intense at 255 cm^{-1}, and several weaker bands at 87, 95, 125, 235, and 285 cm^{-1} (Fig. 8).

In similar conditions, the spectra of different red painted letters of the manuscript show more or less the same bands (Fig. 9). The main difference was a lower signal to noise ratio.

These findings clearly show the presence of vermilion mercury sulfide in the red painted letters and red rubrics of the manuscript [10].

As before with lazurite, this identification was made directly on the whole fragment without sampling and without any damage to the manuscript. Besides this, the time needed for the measurement alone was very short for it did not exceed 15 min.

RLMP Analysis of a Yellow Painted Fragment

The mask fragment we studied (Reference No. T 117) came from the MX necropolis of Mirgissa, dating back to the 13th Dynasty (about 1780 to 1680 B.C.) (Fig. 10).

It was discovered in the excavations carried out in Sudanese Nubia by the French Archeological Mission [11] before the completion of the Aswan Dam submerged the Mirgissa site.

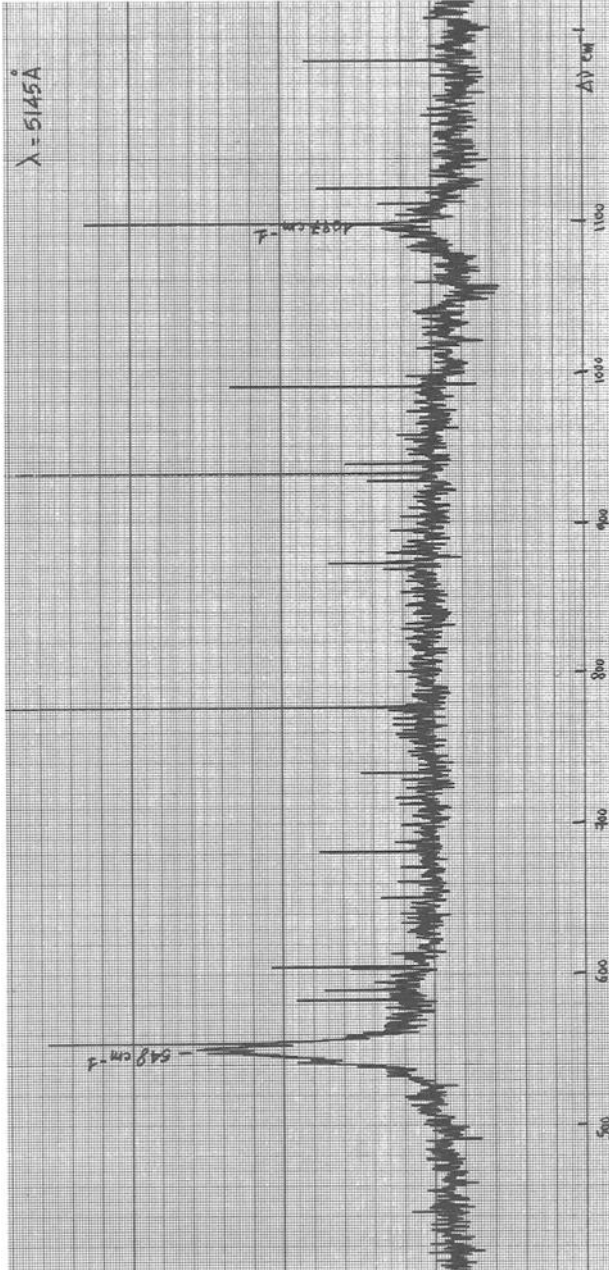The general shape of the fragment resembles a slightly curved equilateral triangle 15 mm

FIG. 3—*Raman spectrum of a blue painted letter.* 1 Å = 0.1 nm.

FIG. 4—*Twelfth Century French missal; example of a red ornamented letter analyzed.*

long and about 2 mm thick. Its front surface is smooth and painted bright yellow. The reverse side, white-grayish in color has a rather rough surface and shows regular square reliefs similar to a canvas print.

Archeologists have observed, indeed, that these masks, tightly fitting the head of the dead and exactly suited to the shape of the skull, were probably made, for the most part, by casting plaster directly on the fabric of the swathing.

Multi-element analysis of the fragment with XRF spectrometry showed the presence of:

(1) major elements of calcium and arsenic;

(2) minor elements of iron, titanium, potassium, and strontium; and

(3) traces of sulfur, chlorine, antimony, copper, gold, and silicon.

The high concentration of calcium observed in the painted stucco fragment was expected but we also observed an abundance of arsenic, which might reveal the presence of yellow arsenic sulfide orpiment (As_2S_3).

Nevertheless, because of the presence of iron detected by XRF in the fragment, the yellow pigment could also be composed of yellow iron oxides. Thus we are not certain what the yellow pigment is composed of.

However, orpiment has been frequently identified in the past in Egyptian painting materials. [12].

Using RLMP, we attempted to analyze the fragment by Raman spectroscopy. As before, the
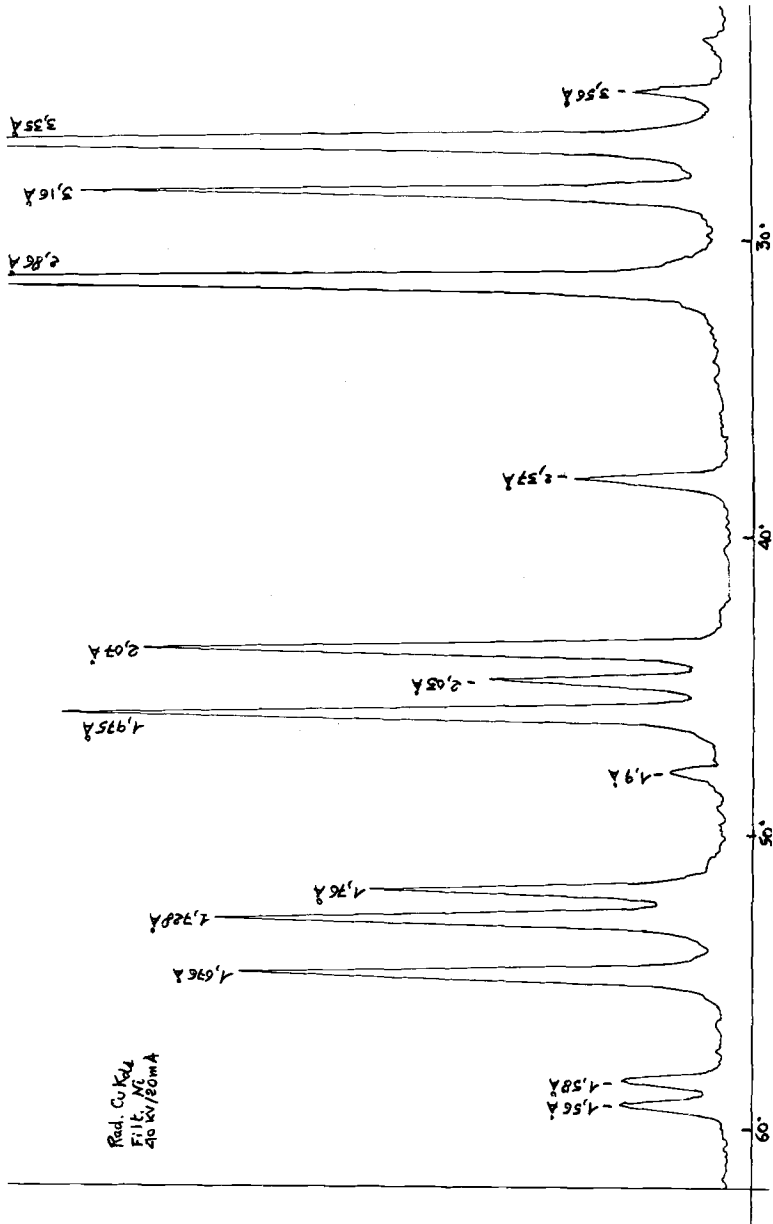
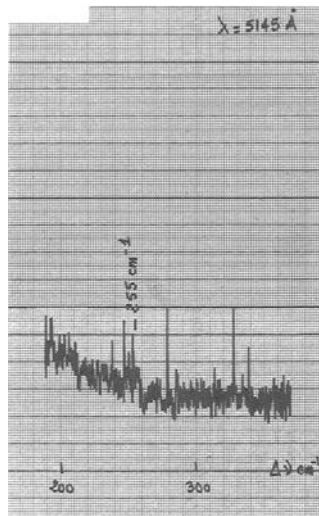FIG. 5—X-ray powder diffraction pattern of French vermilion Sennelier (control sample). 1 Å = 0.1 nm.

FIG. 6—*Raman spectrum of French vermilion Sennelier observed with the argon laser green line* λ = *514.5 nm (5145 Å).*

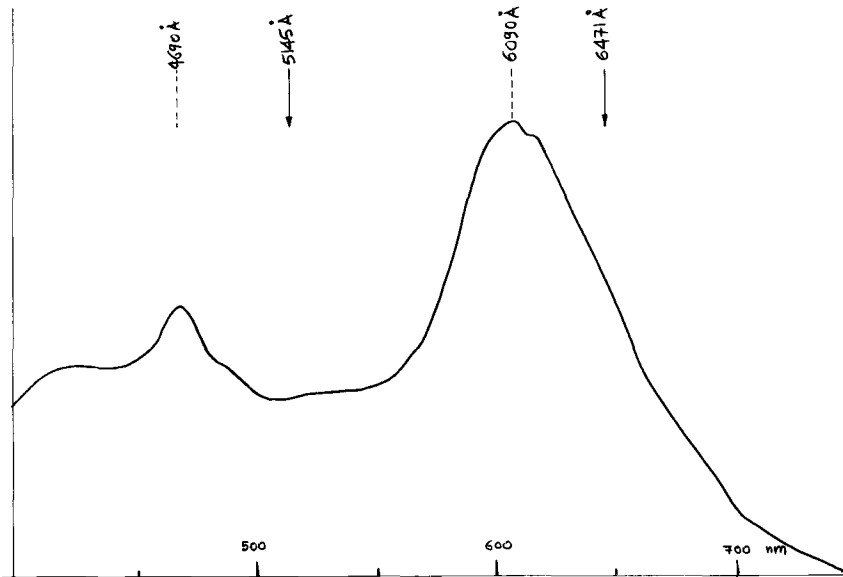FIG. 7—*Absorption spectrum of French vermilion Sennelier. Arrows show the locations of the green argon laser line (*λ = *514.5 nm [5145 Å]) and of the red krypton laser line (*λ = *647.1 nm [6471 Å]).*
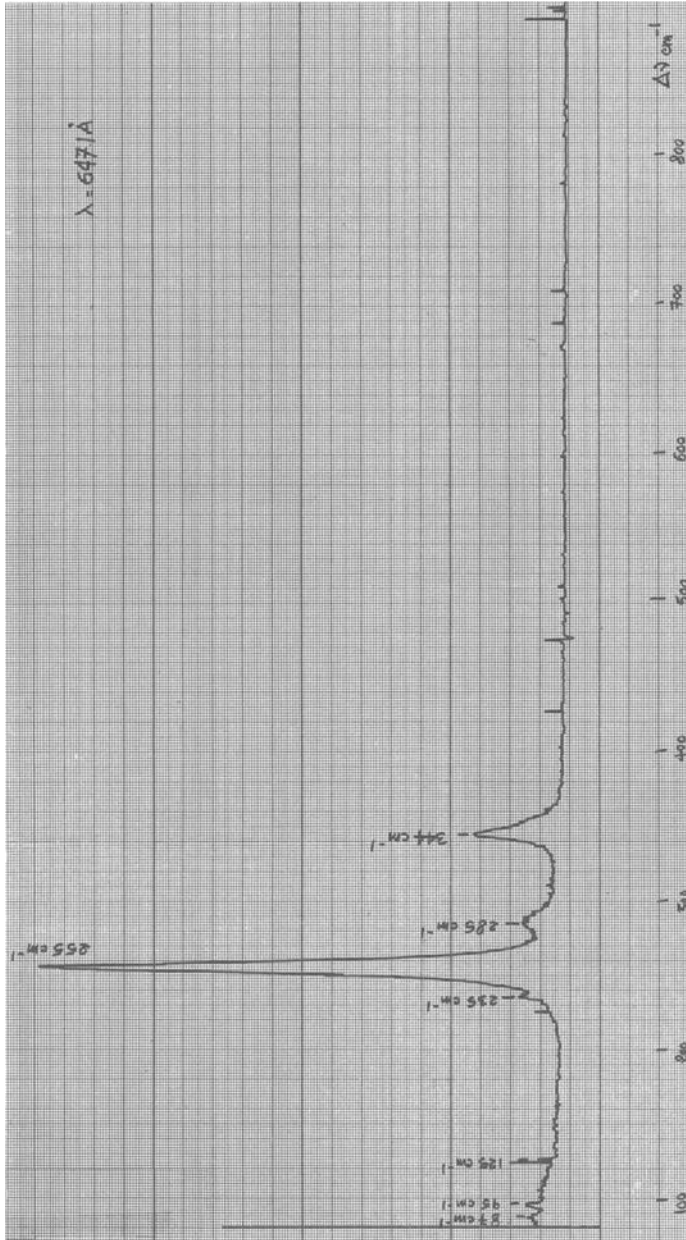
FIG. 8—*Raman spectrum of French vermilion Sennelier observed with the red krypton laser line* λ = 647.1 *nm (6471 Å).*
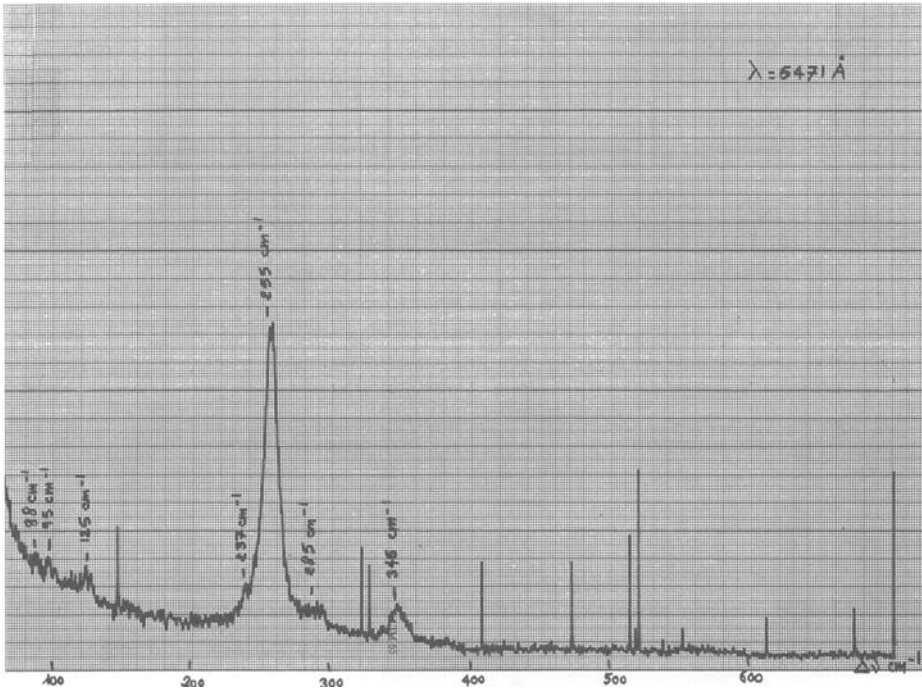
FIG. 9—*Raman spectrum of a red painted letter. 1 Å = 0.1 nm.*
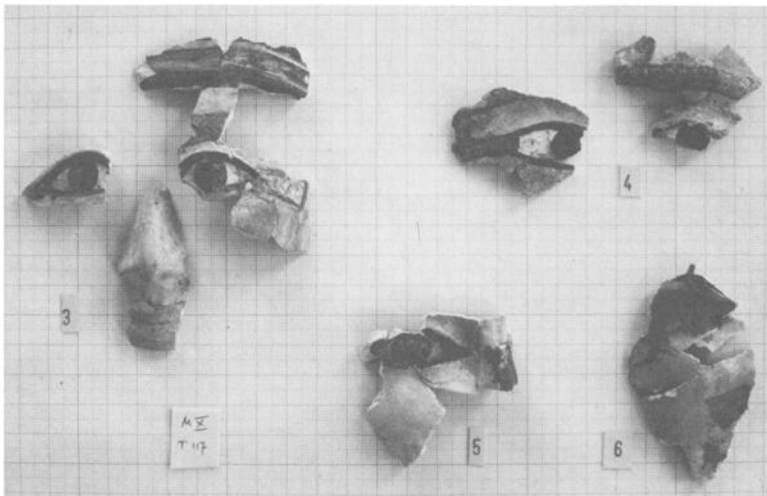
FIG. 10—*Fragments of death mask, Necropolis of Mirgissa, Nubia (1780 to 1680 B.C.).*

whole fragment was placed directly on the platen of the microscope under the laser beam, and both sides were analyzed.

We used the line $\lambda = 514.5$ nm of an argon laser at 200 mW. The spectra show a high background fluorescence for both sides of the fragment with a large drift of this fluorescence which made it quite difficult to measure. The fluorescence might be caused by various organic contaminations of the surfaces that are common in archeological samples which have been buried for a long time in the soil. Nevertheless, we did not attempt to clean the surface, keeping in mind that we had to avoid altering the fragment in any way. Despite the fluorescence, a few significant bands were identified on the spectra.

On the front side (Fig. 11) two bands of medium intensity were observed at 356 and 310 cm^{-1}, and several weaker ones at 293 and 382 cm^{-1}.

These bands were similar (Fig. 12) to the ones observed in orpiment Raman spectra reported in previous articles [13]. This fact allows us to conclude that the bright yellow pigment used for painting the Egyptian death mask is composed of orpiment.

As for the reverse side of the fragment, two significant bands were observed on the spectra, in spite of a more intense fluorescence (Fig. 13). One narrow band was visible at 1087 cm^{-1} and another one, less intense, at 280 cm^{-1} which were identified as the main Raman bands of calcite ($CaCO_3$).

The spectra did not show any other bands of significant intensity and we did not proceed with statistical accumulations for fear of overexposure of the fragment to the laser beam.

In conclusion, the painted fragment entrusted to us by archeologists for analysis has been studied without any special preparation or sampling. Most importantly, RLMP caused no damage to this unique and irreplaceable testimony of the past.

Conclusions

Using Raman laser microprobe as a nondestructive technique, a few inorganic pigments have been rapidly identified by spectroscopic measurements performed in situ on various ancient works of art.
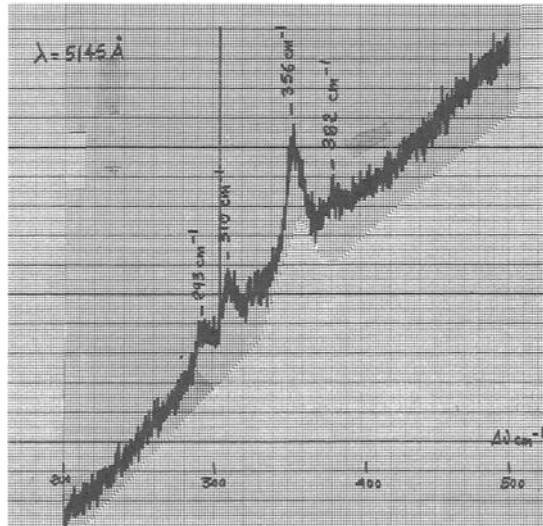

FIG. 11—*Raman spectrum of the Fragment T 117 of the death mask, bright yellow painted (front side). 1 Å = 0.1 nm.*

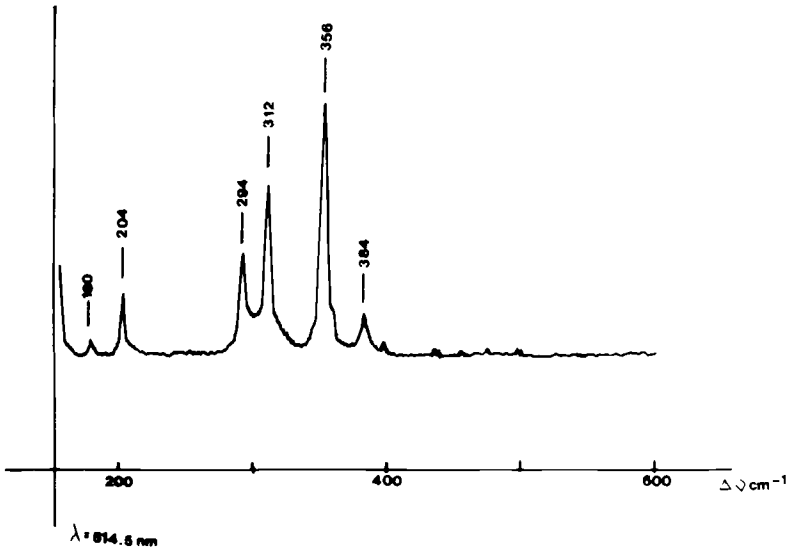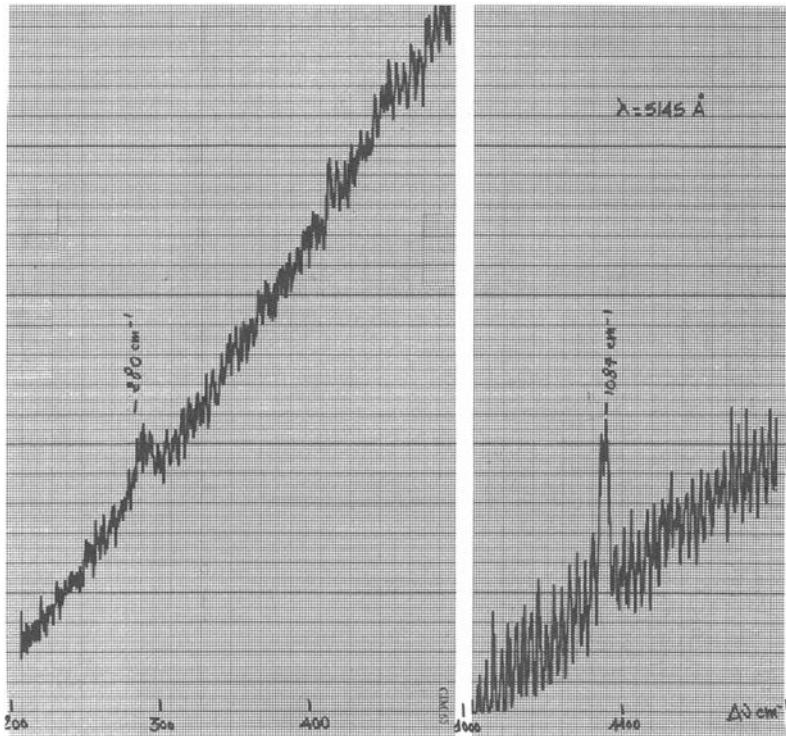FIG. 12—*Raman spectrum of yellow orpiment. 1 Å = 0.1 nm.*

FIG. 13—*Raman spectrum of the reverse side of the Fragment T 117 of the death mask. 1 Å = 0.1 nm.*

Every vibrational spectrum observed can be regarded as the unique "fingerprint" of one of these ancient pigments.

In the same manner, azurite, verdigris, and white lead were also identified. For each of them, the fingerprint was characteristic.

As for the detection of possible fraud, we have never yet observed the signs of modern pigments such as varieties of chrome yellow or chrome red (whose spectra show characteristic resonant bands).

Nevertheless, lazurite, vermilion, and orpiment have been in use for a long time and their identification in only one archeological work cannot be related to a particular period of time.

For this, it would be necessary to take into account associations of several pigments and to point out by constant observations the most frequent occurrences of the latter. This could be the subject of a later paper.

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