Journal of Applied Spectroscopy, Vol. 72, No. 3, 2005

LAYER-BY-LAYER LASER SPECTRUM MICROANALYSIS OF EASEL-PAINTING MATERIALS

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UDC 535.33

A technique of layer-by-layer laser microanalysis of the materials of easel-painting works employing a two-pulse scheme of substance excitation and registration of the spectrum from one double pulse is suggested. With paintings from the Nesvizh Portrait Gallery as examples, the effectiveness of the method in identification and attribution of paintings is shown.

Keywords: *pigments, layer-by-layer laser spectrum microanalysis, double pulse.*

Introduction. At the present time, in studying paintings, methods of art expertise are more often supplemented with methods of natural sciences. Comprehensive technical–technological investigation of a work of art that encompasses each structural element of the picture (base, primer, drawing, paint layer, protective coating) includes overall examination of the work by luminescent methods on exposure to UV and IR irradiation and by the x-ray graphical method as well as studying the paint materials used. The materials used in painting a picture are very diverse and are determined by the time of creation of a picture, the tradition of the artistic school, and also by the artistic individuality of a painter — his style and technique. Accumulation of information on the materials that were used at different times by various painters and the creation of a database are essential for the success of the investigations carried out.

The most difficult problem in studying a work of art is determination of the pigments and binders that enter into the primer and paint layers. Pigments are identified by methods of microchemical analysis, petrography, and various physical methods, for example, x-ray structural analysis, as well as different kinds of spectral analysis (IR Fourier spectroscopy to identify the binder and an emission analysis to identify pigments). The x-ray structural analysis has some limitations because the intensity of a spectrum depends on substance absorption, which, in turn, influences the sensitivity of the method. Therefore, registration of even a relatively high content of pigment with low absorptivity is difficult when this pigment is mixed with a highly absorptive component [1]. The spectral electric-discharge emission method allows one to rather exactly determine the chemical composition of a sample but needs a great amount of it. Moreover, it is extremely difficult to perform a layer-by-layer analysis by this method.

In the present work, we suggest a method of two-pulse laser spectrum microanalysis of the chemical composition of easel-painting materials. Its advantage over the electric-discharge method of spectral analysis lies in the fact that it needs no special preparation and it is local and provides the possibility of layer-by-layer examination of the chemical composition of the materials of the work studied.

Experimental Technique. Model samples have a multilayer structure with known chemical composition of each layer. As the base for the two samples prepared by us, a linen canvas was used primed by titanium white on an oil binder. The paint layer of the first sample contains cadmium red CdSe and zinc white ZnO; the paint layer of the second sample contains cadmium yellow CdS and lead whiting $2PbCO_3{\cdot}Pb(OH)_2$. These samples were used to verify experimentally the method of layer-by-layer analysis in order to select an optimum generation energy and a regime of focusing that, with each exposure to a laser (double pulse), it could be possible to fix a spectrum with minimum det-

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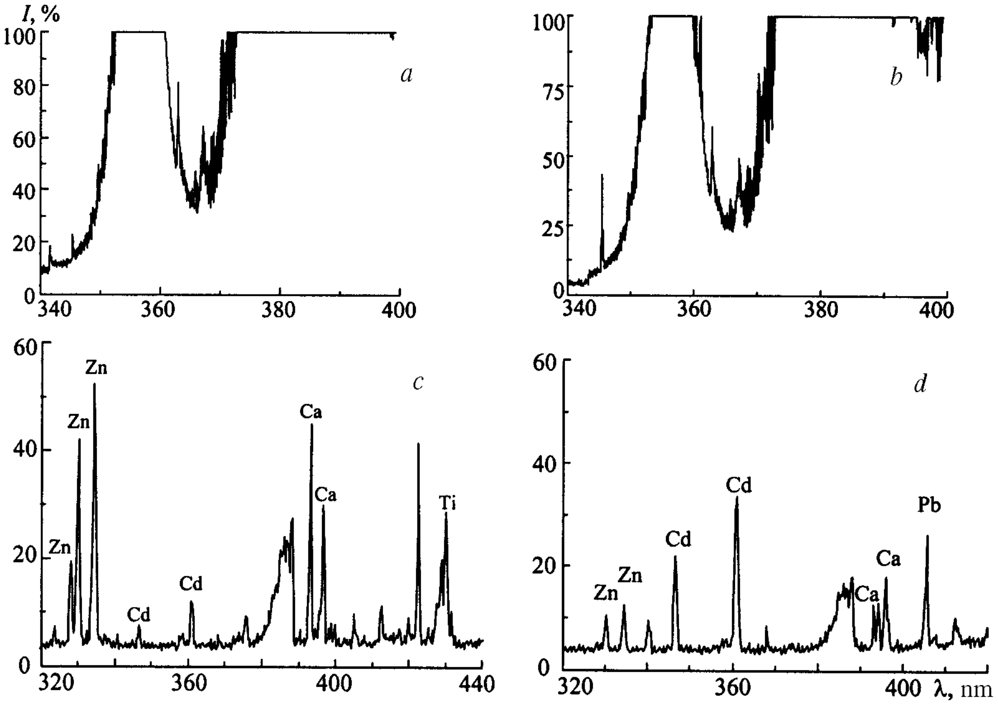

Fig. 1. Emission spectra of model samples obtained with the aid of electric discharge atomization (a, b) and laser atomization (c, d): a, c) CdSe + ZnO; b, d) CdS + $PbCO_3 \cdot Pb(OH)_2$.

riment to the object over its depth (Fig. 1). A region is shown which in the spectra obtained with the aid of electric-discharge atomization with application of carbon electrodes is "entirely light-struck" by the molecular bands of CN, as a result of which it is noninformative, whereas the same region in the spectra registered with the aid of laser atomization gives the necessary information on the composition of the substance.

The emission spectra were registered by two techniques. In one of these, electric-discharge atomization was used [2]. From the studied portion of a picture (model) some paint was scraped, which was then put into the crater of a carbon electrode and covered from above by coal powder, which was packed down. With the aid of an IVS-28 a.c. arc generator (U = 220 V, I = 7.5 A) the sample was vaporized from the crater for 40 sec. The other electrode was also a carbon one. The emission spectrum was registered with the aid of a PGS-2 diffraction spectrograph (Carl Zeiss, Germany) with a 600 lines/mm grating and reciprocal linear dispersion of 0.7 nm/mm. The spectrum was registered photoelectrically by four CCD-registers. This made it possible to obtain the spectra of all the paint layers scraped.

To obtain emission spectra by the other technique, laser atomization was used, which made it possible to employ the layer-by-layer method of analysis directly on objects (see Fig. 1) and on samples of scraped paint. Investigations were carried out on a laser spectrum analyzer [3]. A two-pulse laser with a radiation wavelength of 1064 nm and repetition rate of 10 Hz was used. The energy of each pulse was 0.04–0.05 J, length 10 nsec, with the time interval between the pulses being 7 μsec. Plasma was ejected by the first pulse into a relatively dense air medium at a temperature of 300 K, whereas the plasma of the second pulse was developed in a cloud of the vapor heated to a higher temperature. As a result, a considerably greater portion of the energy of the second pulse is supplied to the sample surface than in the case of one pulse at atmospheric pressure. Here, the quantity of the substance vaporized from the sample by the second pulse and the radiation intensity of the cloud are increased. The time of the glow of plasma and correspondingly of the spectral lines is increased and the intensity of the background is decreased [4]. We applied defocusing of the laser beam; the size of the light spot was ≈900 μm. The spectrum was registered photoelectrically in the entire visible spectral range with the aid of an S-100 spectrometer (Solar LS, Belarus). The use of this spectrometer made it possible to register spectra from one double pulse.

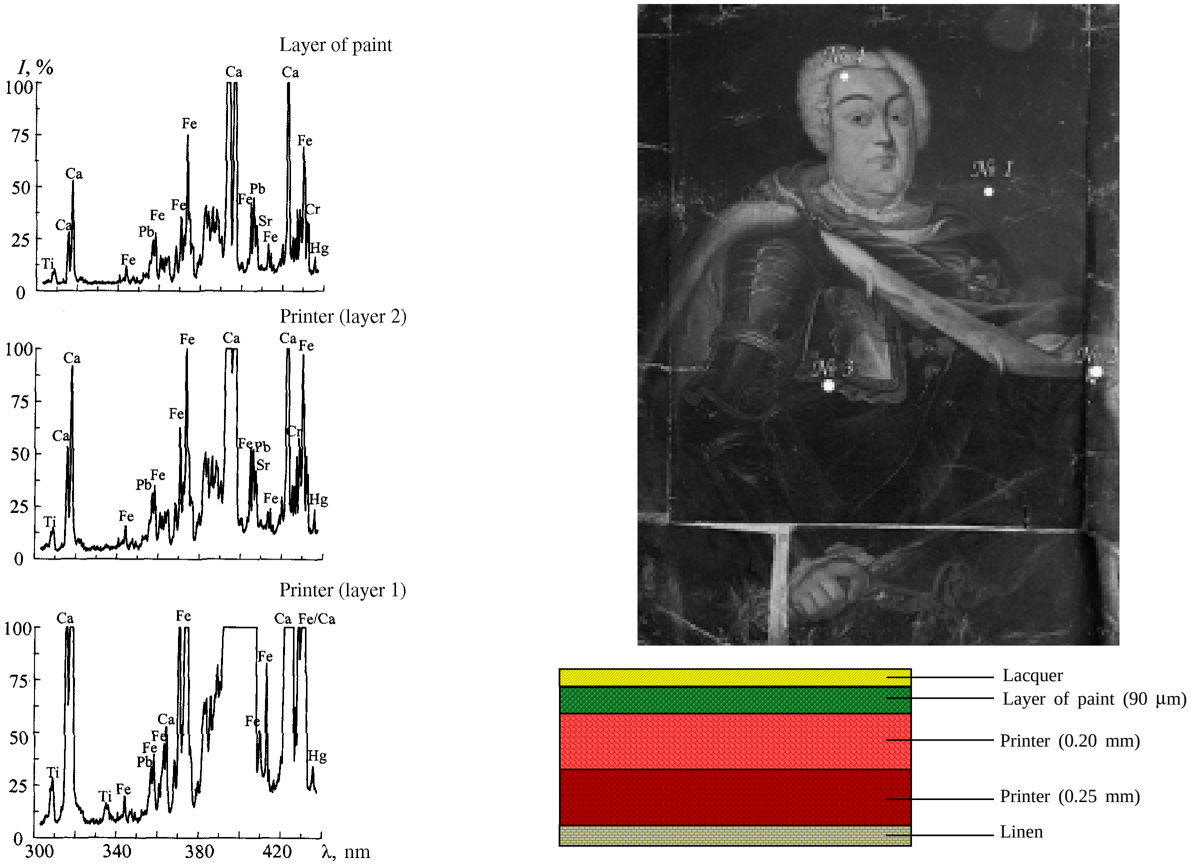

Fig. 2. "Portrait of a Stranger" (linen, oil), schematic of the transverse cut of the work and emission spectra of sample No. 1.

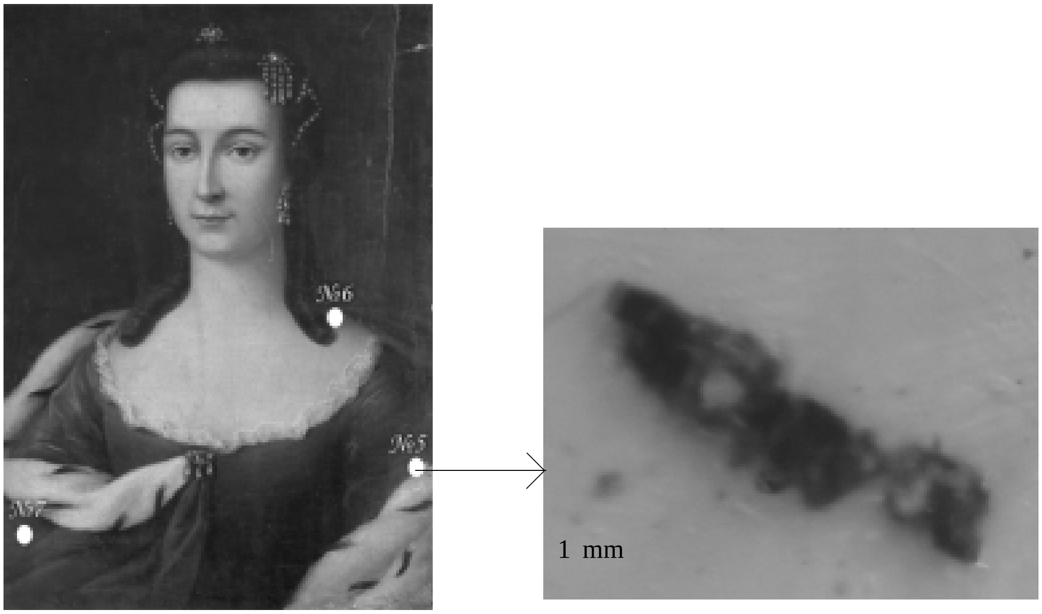

Fig. 3. "Portrait of a Woman" (linen, oil) (a); photograph of sample No. 5 with the laser trace left on it (b).

TABLE 1. Qualitative Analysis of the Material of Easel Painting

Layers	Pigments	Chemical formula of the pigment
Portrait of a Woman		
Primer	Brown earths, white lead, chalk	Oxides **Fe** and **Al**, clay $2\mathbf{Pb}CO_3\cdot(OH)_2$ **Ca**
Layer of paint	Berlin blue	$\mathbf{Fe}_4[\mathbf{Fe}(CH)_6]_3$
Portrait of a Stranger		
Primer, lower layer	Red ocher, chalk, white lead, titanium oxides, quartzite	**Ca** $2\mathbf{Pb}CO_3\cdot(OH)_2$ $\mathbf{Ti}O$ **Si**
Primer, upper layer	Red ocher, chalk, white lead, cinnabar, titanium oxide, quartzite	**Ca** $2\mathbf{Pb}CO_3\cdot\mathbf{Pb}(OH)_2$ $\mathbf{Hg}S$ $\mathbf{Ti}O$ **Si**
Layer of paint	Glauconite, chrome green, ultramarine yellow	**Fe**, **Al**, **Mg**, **Si** $\mathbf{Cr}_2O_3$, $\mathbf{BaCr}O_4+\mathbf{SrCr}O_4$

Note. In bold are the elements the lines of which were identified in the spectrum.

In the spectra obtained on laser excitation of a substance, in contrast to electric-discharge atomization, there are no lines of the elements of the electrode material, which can hamper interpretation of the spectrum as well as molecular bands, as a result of which the spectrum becomes more informative. The informativeness of the spectrum is also attained due to the absence of the influence of the sample composition, since in the case of laser atomization, in contrast to electrical atomization, there is no selective entry of elements into the plasma. Moreover, it is convenient to carry out investigation of paintings with the aid of laser microanalysis, because this method does not require taking samples; excitation is conducted on the spot, and the diameter of the crater left does not exceed 0.10–0.05 mm, with its depth made by one pulse being equal to about 1–2 μm. This allows examination of a specimen layer-by-layer, evaluating the inhomogeneity in the distribution of the substances contained on the surface of the work of art and not damaging the structure of the latter.

Investigation of Paintings. For the experiment we selected samples (microscrapings) from two portraits from the Nesvizh Portrait Gallery — "Portrait of a Stranger" (62.5 × 54.8; Inv-5954, Fig. 2) and "Portrait of a Woman" (59.7 × 41.7; KP-2687, Fig. 3a) — which at the present time are kept at the National Art Museum of the Republic of Belarus.

Before we carried out the spectral analysis, we had investigated the samples by the traditional method of chemical microdrop spot analysis to obtain preliminary information on each of the samples.

Based on the analysis carried out, it has been established that in both "Portrait of a Woman" and "Portrait of a Stranger" the base is made of linen. The primer in "Portrait of a Woman" is colored and consists of one layer. The thickness of the primer varies within 0.15–0.20 mm. Brown iron-containing pigment (brown earth) with a small addition of a black organic pigment was used as the filler of the primer. The binders in the primer are glue and oil.

It has been established that the primer in "Portrait of a Stranger" is colored, consists of two layers, and was put on the linen preliminarily coated with glue. The thickness of the primer in different specimens was about 0.2 mm. The filler of the primer in the lower layer was brownish red pigment (red ocher) with a small addition of a black organic pigment and lead whiting; inclusions of small quartz grains were also revealed; red pigment (red ocher) and cinnabar were used as fillers of the upper layer. Glue and oil were the binders of the primer. Both portraits were painted in oils. The painting is multilayer and smooth. The color layer consists of a denser underlayer and thin overlayers. Everything is coated with a thick layer of yellowed lacquer.

The microdrop spot microchemical method allowed us to reveal red ochers, cinnabar, ferriferous brown, green pigment, organic black, and lead whiting in "Portrait of a Stranger" and red ochers, ferriferous brown, blue pigment, organic black, white lead and chalk in "Portrait of a Woman."

As the objects for spectroscopic investigations we selected a green portion of the background in "Portrait of a Stranger" (No. 1, see Fig. 2) and the blue portion of the dress in "Portrait of a Woman" (No. 5, see Fig. 3a), because the composition of the pigments in these portions was not determined unambiguously by the microdrop stop method. The emission spectra were measured layer-by-layer with the aid of laser atomization.

As seen from Fig. 2, the emission spectra of the layers differ in their composition both qualitatively (in elements) and quantitatively (in the concentration of the elements), on the basis of which we can judge the layered structure of the work. Thus, in the first vaporized layer we can see such elements as **Ti**, Ca, Fe, Pb, **Hg**, Si, Mg, Al, and Ba, and in the second layer Ca, Fe, Pb, **Sr**, **Cr**, Si, Mg, Al, and Ba as well as Ti and Hg but in considerably smaller amounts. In the third vaporized layer there are the same lines of Ca, Fe, Pb, **Sr**, **Cr**, Si, Mg, Al, and Ba but less intense and also there is one line of Ti and one line of Hg, which is explained by the inhomogeneity of the specimen. Having carried out a qualitative analysis, we concluded that the lower layer of the primer was mainly filled with red ochers (Fe, Al), chalk (Ca), and lead whiting, corresponding to which in the spectrum are the Pb lines. The filler of the upper layer of the primer is similar to that of the lower one with the addition of cinnabar HgS. Moreover, in both layers of the primer we found titanium oxides TiO and quartzite SiO_2. For the green background in "Portrait of a Stranger" the painter used glauconite (Fe, Al, Mg, Si). The revealed green pigment based on chromium (chromium-based pigments were discovered at the end of the XVIIth century, produced industrially from the middle of the XIXth century) and ultramarine yellow [$BaCrO_4$+$SrCrO_4$] is related to the materials that were used in carrying out restorative works. In investigating specimens No. 5, we found that on the blue portion of the dress the following elements were present: Al, Ca, Fe, and Pb. After carrying out a qualitative analysis, we concluded that the dark-brown primer contains brown earths (oxides of Fe and Al, clay), chalk, to which the Ca lines correspond, and a small amount of lead whiting, to which in the emission spectrum of the test-specimen art the Pb lines correspond (see Table 1). The same lead whiting was used to dilute paints. For the garment of blue color the painter used Berlin blue [$Fe_4[Fe(CN)_6]_3$].

Conclusions. We have suggested and tested the method of laser spectrum microanalysis of the works of easel painting. Its main advantages are the high locality of substance evaporation (see Fig. 1) and the possibility of registering the spectrum from a single double pulse, which is very important in analyzing a small amount of a sample and in layer-by-layer analysis. Moreover, the method is convenient because it does not require preparation of the sample, or needs minimum preparation, and allows one to examine the specimen layer-by-layer to evaluate the inhomogeneity in the distribution of elements over the surface. Due to the two-pulse circuit of excitation and to the absence of the influence of the composition, the resulting spectra appear most informative.

Following the appearance of the lines of a new element in the emission spectrum during passage of laser radiation through a specimen, we managed to identify layer-by-layer the chemical elements entering into the composition of the specimens investigated. This allowed us to conclude what pigments had been used as fillers of primers and as components of paints.

The authors express their gratitude to S. V. Zhukovskii for fruitful discussions with E. V. K., Joris Dik (Holland) for help in preparing the samples and to the Solar LS enterprise (Belarus) for the S-100 spectroscope placed at our disposal for carrying out experiments.

REFERENCES

1. Yu. I. Grenberg (Ed.), *Technology, Study, and Storage of Masterpieces of Wall and Easel Paintings* [in Russian], Izobrazitel'noe Iskusstvo, Moscow (1987).
2. A. K. Rusanov, *Principles of Quantitative Spectral Analysis of Ores and Minerals* [in Russian], Nedra, Moscow (1978).
3. Laser spectral analyzer. Advertisement, *Zh. Prikl. Spektrosk.*, **70**, No. 1, 144–145 (2003).
4. M. L. Petukh, V. A. Rozantsev, A. D. Shirokanov, and A. A. Yankovskii, *Zh. Prikl. Spektrosk.*, **67**, No. 6, 798–801 (2000).