

## Chapter IX

# Analysis of supports, grounds and pigments

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### 1. INTRODUCTION

In works of art naturally occurring and synthetic inorganic and organic compounds are used as pigments. The material upon which a painting is carried out consists mainly of two components, the actual surface or ground and the support (Fig. 1). Only in a few cases the paint layers are directly applied to the support. The chemical character, properties, and periods of application of the pigments, the ground materials and various supports are well known. The investigation of an object of art by means of scientific methods may therefore serve to characterize the material style of artistic landscapes, schools or even individual workshops. It is also possible to clarify the process of production and the technology of the painting<sup>1-7</sup>. Scientific methods are not only a valuable tool for the art historian but may also provide a good starting point for the proposal of techniques for restoration and conservation<sup>8,9</sup>.

Two complementary sources of information are to be used for the scientific investigation of works of art. The first one is based on the application of radiation with wavelengths ranging from  $\gamma$ -rays to the near infrared (Fig. 1) making possible the visualization of states of the whole object normally invisible to the naked eye. These methods — in a strict sense non destructive — have found early and widespread acceptance for a stylistic approach and determination of the state of preservation because they are relatively simple to use and, furthermore, they fit best the way an art historian or conservator would look at works of art. Examinations of this kind should always be the first step and precede the use of the second source of information, namely the determination of the chemical composition of small areas by means of analytical methods. In a wider sense these

procedures might be designated as point analysis which can be done in a nondestructive or destructive manner which makes the taking of samples necessary. A word should be given about the conception 'nondestructive'. For the conservator this term is identical with 'no sampling', whereas for the analyst it has the connotation that the sample is preserved during the analytical procedure. For different reasons sampling is very often necessary (e.g. limited dimensions of the sample chamber of the analytical instrument used).

## 2. STRUCTURE OF PAINTINGS

A discussion about the structure of paintings seems very appropriate before reviewing the possibilities of chemical, microchemical and instrumental analytical methods used for the investigation of works of art. Though the paint layer represents indeed a small portion of the whole object its structure is too complex to be exactly described in a figure. So Fig. 1 gives only a schematic survey of the components of an easel painting on wood and canvas, respectively, as it was usually realized by artists from the Middle Ages up to the 19th century. Four main elements can be distinguished<sup>10</sup>: support, ground, paint layers, varnish layers.

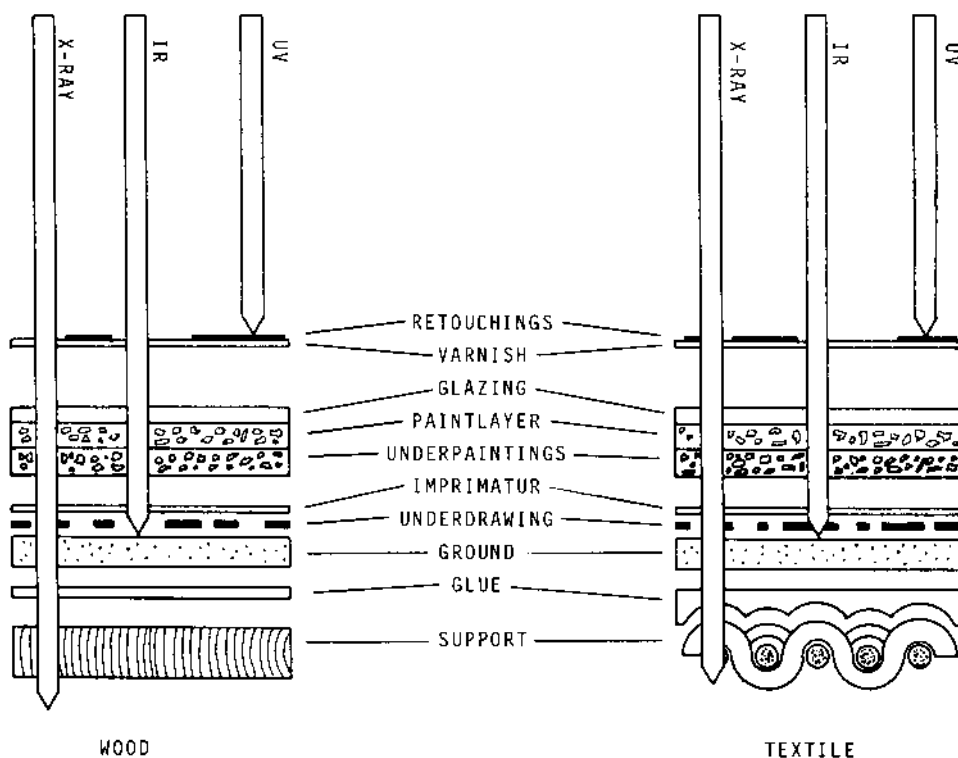


Fig. 1. Structure of Paintings and Penetration Depth of Radiations.

### 2.1. *Supports*

Wooden panels or canvas stretched on wooden frames are predominantly used as supports for easel paintings. The kind of wood or the textile fibres are often characteristic of the date of origin and the artistic landscape. In the Middle Ages paintings were carried out on textiles made from flax and hemp fibres. Cotton can be distinguished since the 19th century. Fibre structure, weight and way of weaving may serve as a hint for the provenance of the painting. It should be mentioned, furthermore, that a great number of other materials can be found as supports for paintings, such as parchment, paper, metal foils, ceramic materials, stone, and glass. Their composition as revealed by analytical methods is of high importance for proving the authenticity of an object of art.

### 2.2. *Grounds*

In most cases untreated supports don't do well with any kind of paint. Wood, for example, cannot be made perfectly smooth or even and different parts take the paint differently. The surface has therefore to be coated with various materials to get the support smooth and even or to create special structural effects. The ground materials exert also prominent effects on the optical properties of the paint layers. Bright and mostly white grounds were used during the Gothic period, whereas yellow and brown grounds (warm colours) were preferred during the Baroque. In some cases two or more layers were applied. In Italian objects of art gesso can be detected as white ground material. Chalk and fine milled marble are typical for transalpine objects of art. White lead with oil as binding medium and various yellow and red ochre pigments are known to be used during the Baroque whereas zinc white has been used since 1850 (see also tab. 1). Usually the ground was painted with oil or resin (*imprimatur*) in order to reduce the absorption degree of the paint layer.

### 2.3. *Paint layers*

On a well prepared ground the painting can now be carried out. Coloured substances imparting their colouring effect to another material are called pigments or dyes. A pigment is mixed and ground in a liquid vehicle or carrier of the colour, remaining dispersed therein. Dyes are dissolved by the binding medium. Table 1 gives a survey on the pigments mostly used in paintings. In the Middle Ages the sources for coloured substances were the natural deposits of salts (metal oxides, carbonates, etc.). Some minerals are found in a condition ready for use in paints (coloured earths, ochres). Others are found in form of rocky material and have to be ground to powder. The grain size but especially the impurities are of high importance for estimating the provenance of pigments. In order to protect the paintlayers against dust and air pollutions as well as UV-radiation or mechanical damaging, paintings are usually coated by varnishes.

TABLE I. — SYNOPSIS OF THE MOST IMPORTANT PIGMENTS AND DYES, THEIR CHEMICAL COMPOSITION, PERIOD OF APPLICATION AND IDENTIFICATIONS (for detailed informations see notes 16-23).

Pigment	Chemical Composition	Period of Application from until	Chemical Tests for Identification
<b>White Pigments</b>			
Barytes	BaSO <sub>4</sub>	a.p.	+ soluble in HNO <sub>3</sub> or by fusing with Na <sub>2</sub> CO <sub>3</sub> , yellow green flame test
Chalk	CaCO <sub>3</sub>	a.p.	+ bubbling in mineral acids, forms typical needles of gypsum in H <sub>2</sub> SO <sub>4</sub>
Gypsum	CaSO <sub>4</sub> × 2H <sub>2</sub> O	a.p.	+ soluble in HCl, crystallization of needles
White lead	2PbCO <sub>3</sub> × Pb(OH) <sub>2</sub>	a.p.	+ bubbling in HNO <sub>3</sub> , Pb-test as minimum
Zinc white	ZnO	1834	+ fluorescence in UV, spot test with dithizone
Lithopone	~ 30% ZnS + 70% BaSO <sub>4</sub>	1874	+ black colour with AgNO <sub>3</sub> + H <sub>2</sub> O, test as zinc white and barytes
<b>Red and Orange Pigments</b>			
Red lead (minimum)	Pb <sub>3</sub> O <sub>4</sub>	a.p.	+ HNO <sub>3</sub> -sln + K <sub>2</sub> CrO <sub>7</sub> → yellow pptt of PbCrO <sub>4</sub>
Iron oxide red	Fe <sub>2</sub> O <sub>3</sub>	a.p.	+ HCl-sln + KSCN → red coloration
Sienna (Red earth)	Fe <sub>2</sub> O <sub>3</sub> + clay	a.p.	+ blue pptt of Prussian blue with K <sub>4</sub> (Fe(CN) <sub>6</sub> )
Umber	Fe <sub>2</sub> O <sub>3</sub> + MnO <sub>2</sub> + clay	16th	+ Cl <sub>2</sub> -gas with HCl under heating; Fe-test as iron oxide red
Vermilion	HgS	a.p.	+ thermal reduction with Fe → formation of Hg-droplets
Realgar	As <sub>2</sub> S <sub>2</sub>	a.p.	+ as orpiment
Dragon blood	org. resin	m.a.	+ red sln in alcohol, benzene and chloroform
<b>Yellow Pigments</b>			
Ochre	Fe <sub>2</sub> O <sub>3</sub> × nH <sub>2</sub> O	a.p.	+ as iron oxide red
Orpiment	As <sub>2</sub> S <sub>3</sub>	a.p.	+ 19th As : sublimation and formation of octahedral crystals of As <sub>2</sub> O <sub>3</sub> by heating S : sodium azide/iodine test
Cadmium yellow	CdS (+ BaSO <sub>4</sub> )	1829	+ thermal reduction with Fe-powder → metallic Cd
Massicot	PbO	a.p.	+ as minimum
Chrome yellow	2PbSO <sub>4</sub> × PbCrO <sub>4</sub>	1818	+ typical Pb(NO <sub>3</sub> ) <sub>2</sub> -crystals in HNO <sub>3</sub> -sln
Naples yellow	Pb <sub>3</sub> (SbO <sub>4</sub> ) <sub>2</sub>	17th	+ for Sb as orpiment
Gamboge	organ. resin	1640	+ yellow aqueous sln turns red with alkali
Indian yellow	Mg, Ca-salt of euxanthic acid	1620	+ discoloured in HCl and pptt of crystalline euxanthic acid

<b>Green Pigments</b>						
Green earth	Fe-Mg-Al-K-hydrosilicate	a.p.	+	typical grain shape ; Fe-test as iron oxide red after fusion in $\text{NH}_4\text{HSO}_4$		
Malachite	$\text{CuCO}_3 \times \text{Cu}(\text{OH})_2$	a.p.	18th	bubbling in HCl ; spot test with rubeanic acid → greenish black		
Verdigris	basic or neutral Cu-acetate	a.p.	19th	spot over $\text{NH}_3$		
Emerald green (Paris green)	$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \times 3\text{Cu}(\text{AsO}_2)_2$	1814	20th	for As as orpiment		
		1780	1919	Co : orange red spot with $\alpha$ -nitroso- $\beta$ -naphthole Zn : violet pptt with $\text{K}_3(\text{Fe}(\text{CN})_6)$ and p-phenetidine after fusing with $\text{KHSO}_4$		
Cobalt green	$\text{CoO} \times \text{nZnO}$	1809	+	red pptt with $\text{AgNO}_3$ after fusing with $\text{Na}_2\text{CO}_3/\text{Na}_2\text{O}_2$		
Chromium oxide green	$\text{Cr}_2\text{O}_3$	1859	+	yellow pptt of $\text{PbCrO}_4$ with Pb-acetate		
Veridian	$\text{Cr}_2\text{O}(\text{OH})_2$					
<b>Blue Pigments</b>						
Ultramarine blue :						
— natural	$(\text{Na}_{8-10}\text{Al}_6\text{Si}_6\text{O}_{24}) \text{S}_{2-4}$	11th	19th	Al : alizarin-S forms red brown pptt		
— artificial	id.	1826	+	S : sodium azide/iodine test		
Azurite	$2\text{CuCO}_3 \times \text{Cu}(\text{OH})_2$	a.p.	19th	as malachite		
Cobalt blue	$\text{CoO} \times \text{Al}_2\text{O}_3$	1804	+	as cobalt green		
Smalt	K-Co-Al-silicate	1584	19th	as cobalt green		
Prussian blue	$\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$	1704	+	as iron oxide red		
Indigo		1880	+	deep blue sin in chloroform, bleached by Na-hypochlorite		
<b>Brown Pigments</b>						
Umber	Fe-Mn-Al-oxide	16th	+	$\text{Cl}_2$ -gas with HCl, Fe-test as iron oxide red		
Brown ochre	$\text{Fe}_2\text{O}_3 \times \text{nH}_2\text{O} \times \text{SiO}_2 + \text{clay}$	a.p.	+	as iron oxide red		
Van Dyck brown	bituminous earth + Fe, Mn	16th	+	partly soluble in benzene, petroleum, etc.		
Asphaltum	bitumen	17th	+	incombustible residue can be tested for Fe		
<b>Black Pigments</b>						
Bone black	C + $\text{Ca}_3(\text{PO}_4)_2$	a.p.	+	incombustible residue gives a red flame test (Ca), phosphate test with ammonium molybdate		
Lamp black	C	a.p.	+			
Charcoal black	C	a.p.	+			
Graphite	C	a.p.	+			
Gold powder	Au	a.p.	+	only soluble in aqua regia, pptt with $\text{SnCl}_2$		
Silver powder	Ag	a.p.	+	soluble in $\text{HNO}_3$ , white pptt with HCl (see also veridian)		
a.p. : Ancient Period    m.a. : Middle Ages    + : Pigment is still used    sin : solution    pptt : precipitation						

### 3. CHEMICAL AND PHYSICAL ANALYTICAL METHODS FOR INVESTIGATIONS OF PIGMENTS, GROUNDS AND SUPPORTS

Methods well known in the field of material sciences can be used for the characterization of works of art. The advantage of instrumental physical analyses lies in their high yield of information with respect to elemental composition, elemental distribution, surface analysis and microdomains. Classical analytical procedures are still valuable. On one hand they can serve for calibration of instrumental methods since in most of the cases a comparison with standard substances is necessary on the other hand quick tests have gained great importance in conservation and restoration.

During the following discourse it should be kept in mind that the sampling procedure is of utmost importance since the sample has to be taken in a way that it is representative for the chosen area on the object under investigation. Preliminary investigations by means of visible and invisible radiation<sup>10</sup> and stereomicroscopic examination have proven to be very useful in selecting the appropriate area for direct analysis or taking a sample. There is a guiding principle for sampling to keep the amount and size of the sample as small as possible. The allowable size lies in the order of 0.1 to 0.5 mm<sup>2</sup>. The sampling technique used depends strongly on the object and its material composition. With respect to the posed problem eye scalpels, lancets, and dissecting needles as well as hole drills are suitable sampling tools. Taking a sample for cross sectioning the paint layers has to be done with particular care<sup>11</sup>. For this purpose an undamaged particle containing the complete sequence of all paint layers including the ground is required. Various methods have been recommended for the preparation of paint layer cross sections. Following metallographic procedures the sample is embedded in a transparent resin. After setting of the resin it is cross ground, the cross section ground with silicon carbide papers and finally polished with alumina or fine grained diamond pastes.

#### 3.1. *Microscopic investigations*

Light microscopy is an important aid for the identification of materials in the field of art<sup>3-5</sup>. Low magnifications as used in a stereomicroscope allow the visualization of the surface of the paintings, their present state and the effect of ageing, normally invisible to the naked eye. To characterize the structure of the object under investigation a cross section should be examined under the light optical microscope. Such examinations elucidate structure and thickness of paint layers, recognition of overpaintings and in some cases the determination of particle size as well as the identification of pigments by comparison with standard materials. But it is not always possible to characterize pigments on the basis of their peculiar grain size or grain form as seen in the conventional bright field microscope. The use of polarized light

may become necessary in some cases. Special techniques such as fluorescence microscopy using narrow band excitation or interference contrast microscopy have already been used for the identification of pigments.

There is certainly a great number of coloured substances having grain sizes below the working range of light optical microscopy. Indigo, zinc white, Prussian blue, carbon black, some sorts of vermilion, etc., exhibit grain sizes below 1  $\mu\text{m}$ . Also the extremely shallow depth of field at high magnifications, normally useful for examination of surface textures of fibres, has been shown to be highly disadvantageous in this case. Such problems necessitate the use of more efficient instrumental methods such as scanning electron microscopy (SEM) or transmission electron microscopy (TEM). Fig. 2 shows the limits of resolution for the various methods and the detectable particle size<sup>12</sup>.

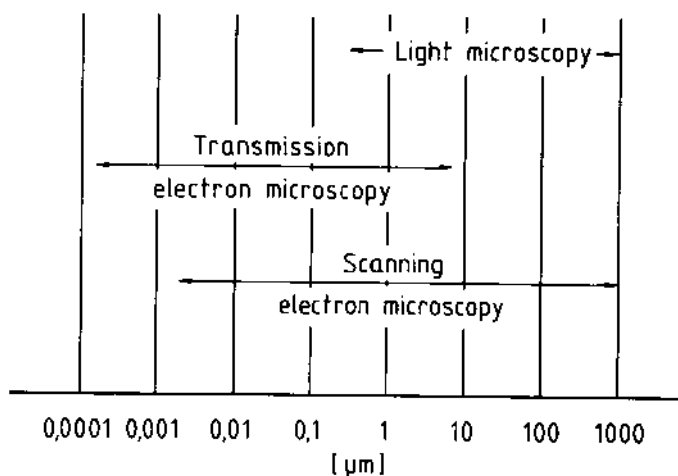


Fig. 2. Working Range of Light-optical, Scanning and Transmission Electron Microscopy.

Not only are high resolution and great depth of field the advantages of electron microscopy. Additional analytical informations can be gained. Qualitative, semiquantitative and in some cases quantitative analysis is possible. Using backscattered electrons in the SEM for image formation there is a dependence of the yield of backscattered electrons on the atomic number of the elements being present in the sample. Lighter elements (e.g. Ca) appear therefore darker than heavy elements (e.g. Pb). Furthermore the impact of electrons generates a characteristic X-ray radiation specific for the different elements. Energy and intensity of the photons can be used for qualitative and semiquantitative analysis. Usually energy dispersive systems (EDS) are applied<sup>13</sup>. Fig. 3 shows the backscattered electron images and the X-ray distribution images of Ca and Cu of the cross section of a sample taken from a polychromed sculpture from the 15th century. Fig. 3d shows the X-ray spectrum of a paint layer according to point analysis as indicated in Fig. 3a.

These results usually allow the correlation between the major detectable elements and the colour layers. A basic limitation of this technique is that only elements with atomic numbers higher than 10 and therefore no anions such as  $O^{2-}$ ,  $CO_3^{2-}$  or  $NO_3^-$  can be distinguished. Trace elements in concentrations below 0.1 % are also not detectable. Performance of analysis depends strongly on surface and particle geometry.

Quantitative analysis of pigment grains is generally carried out in an electron probe micro analyzer (EPMA) having functional features similar to those of the SEM. Wavelength dispersive analysing systems (WDS) are used here<sup>14-15</sup>. Higher signal-to-noise ratio brings about lower detection limits for the elements. Even light elements such as lithium or fluorine can be determined quantitatively. The diameter of pigment particles is a limiting factor for analysis in EPMA and SEM. Compared to SEM a larger diameter of the electron beam is used in EPMA's. For reliable results a grain size of 2-5  $\mu m$  is imperative.

### 3.2. Chemical and microchemical analysis

The chemical elements contained in pigments or compounds characteristic for a certain dye-stuff can be detected by specific chemical reactions. In the last decade simple new micro and ultramicroprocedure have been developed and especially adapted for problems the art historian or restorer is daily confronted with<sup>3-5, 16, 17</sup>. Some pigments can already be identified by their solubility in water, alkaline or acidic media. A blue pigment which for instance is soluble in hydrochloric acid and gives a positive test for copper should probably be azurite. White ground material developing gas bubbles in HCl indicates the presence of carbonate and therefore chalk may be present. A number of synthetic organic compounds also used as pigments are partially soluble in organic solvents such as trichloromethane (chloroform). The shape of their crystals can be used for identification. Tab. 1 gives a survey of the most important pigments and ground materials, their chemical composition and reactions for their identification. Some tests for inorganic substances can be carried out on a suitable porcelain plate as spot tests. This analytical method developed by Feigl<sup>18, 19</sup> permits rapid and sensitive identification of trace substances as well as testing of materials.

An excellent treatise on the identification of pigments and on group tests for binding media is given by Schramm<sup>20-22</sup>. In some cases even specific reactions for certain substances are possible. Less than 1  $\mu g$  of sample is mostly sufficient for the detection of an element. Reactions are carried out in capillaries or in micro test tubes, on micro slides with cavities, grains of silica gel or on condenser rods. Spot test techniques are also widely used<sup>21, 22</sup>. Simple light microscopes serve for the examination of characteristic crystalline precipitates. But separation procedures for mixtures of cations as they



normally occur in paint layers have not yet been developed. Particular sampling is necessary for each cation or pigment. This difficulty can be overcome by the ringoven technique after Weisz<sup>23</sup>, a highly perfected method which is rather underestimated. Another drawback of microchemical methods must be seen in the fact that only elements which have been looked for are detected. Unexpected elements will scarcely be found by the microchemist. In such cases instrumental analytical methods are preferable but should be preceded by microscopic investigations.

### 3.3. Instrumental methods for elemental analysis

For the investigation of elemental composition of inorganic materials such as pigments, metals or ceramic materials the instrumental methods of X-ray fluorescence analysis (XRF)<sup>14</sup> and neutron activation analysis (NAA)<sup>24</sup> are often applied with great success. Identification of the radiation, generated by X-rays or bombardment of the sample with thermal neutrons in a nuclear

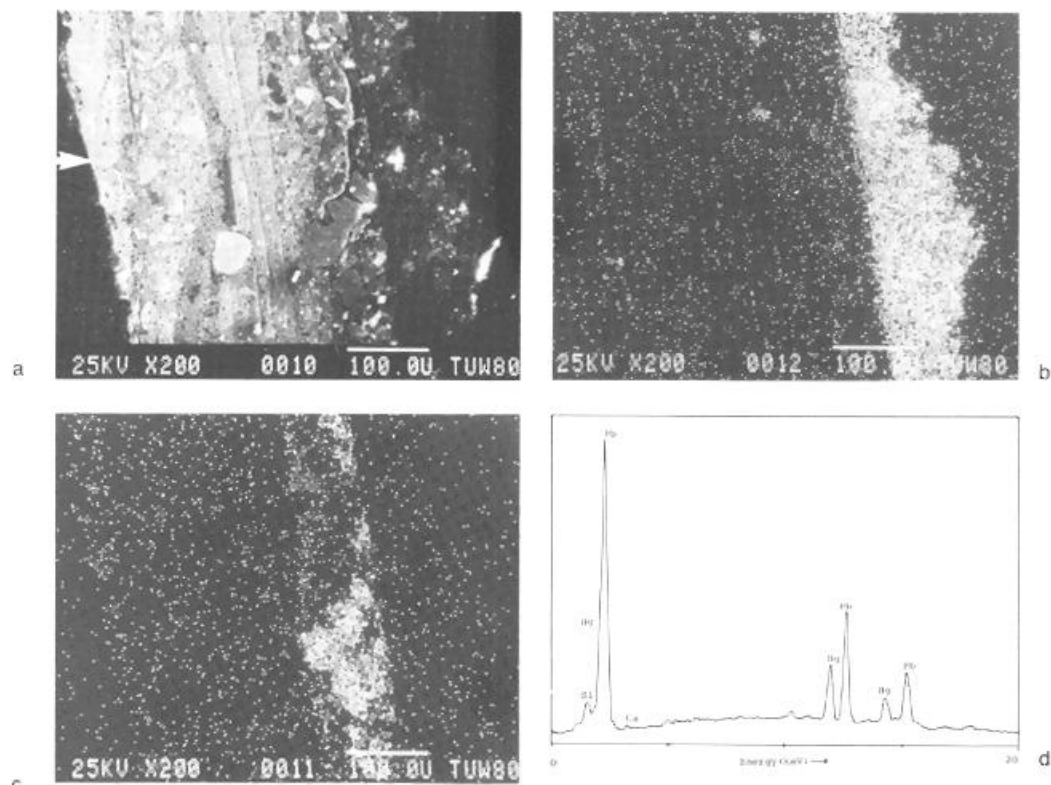


Fig. 3. Investigations of paint layer cross section with scanning electron microscopy  
 a. Backscattered electron image ;  
 b. Ca distribution ;  
 c. Cu distribution ;  
 d. Energy dispersive analysis of the paint layer indicated in Fig. 3 a.

reactor, can be achieved by wavelength dispersive (WDS)<sup>14,15</sup> or energy dispersive analysing systems (EDS)<sup>13</sup> similar to SEM discussed above. XRF and NAA proved to be useful for the analysis of the main elements in pigments and grounds as well as in supports. Neutron activation analysis is also successfully used for studies in art history through the examination of trace elements. White lead samples taken from oil paintings can be described with regard to their Ag and Sb content, different from white Pb of the 20th century<sup>25</sup>.

Emission spectroscopic analysis is a classical instrumental method. In favourable cases the detection limits are nearly equal to those of NAA. Excitation is obtained by flame or by spark. Excitation by a laser light source represents a relatively recent development<sup>26</sup>, but is already often applied for detecting the inorganic material composition of paintings<sup>27</sup>. The laser beam is focused by means of a specially designed microscope. The damages done to the painting are practically invisible (nearly 10 µm in dia and 20-100 µm in depth). So laser microanalysis (LMA) is quasi nondestructive. The method has also been used for determination of pigments in cross sections, for illuminated manuscripts and metals.

Recently mass spectroscopy has also become involved in the analysis of art and archaeological objects. By the ionization energy and by the detected ions and molecular groups, conclusions can be drawn as to the crystallographic and/or molecular structure of the substances under investigation. Solid samples such as pigments are evaporated by means of a spark or laser excitation similar to the LMA discussed above.

Certainly the importance of mass spectroscopy for works of art is not essential for the identification of the materials but for detailed information on their geological origin. The <sup>206</sup>Pb/<sup>204</sup>Pb-ratio in white lead allows a geographical and temporal localization of its manufacture<sup>4</sup>. In similar way marbles show a different <sup>13</sup>C/<sup>18</sup>O-ratio<sup>28</sup> and could be assigned to certain quarries. High energy mass spectrometers even can detect the small <sup>14</sup>C/<sup>12</sup>C-ratio in natural materials (wood, fibres). In comparison to conventional radiocarbon dating a much lesser amount of sample is needed<sup>29</sup>.

#### 3.4. *Compound specific analysis - crystal and molecular structure*

The crystal structure of inorganic and organic crystalline substances can be investigated by X-ray diffraction analysis. A few micrograms of sample are necessary, which have to be fixed on glass capillaries or filled into tiny tubes of glass. The diffraction of the incident X-rays at the crystal planes produces patterns, recorded on a photographic film, characteristic for the unit cell of the crystalline specimen. In connection with elemental analysis the distance and intensity of the diffraction lines can be compared to reference patterns of known compounds or evaluated by means of ASTM-data files<sup>30, 31</sup>.

X-ray diffraction analysis is widely used for the characterization of pigments, ceramic and metallic phases<sup>32-34</sup>. Amorphous substances such as glass, multicomponent samples and small amounts of a single phase don't lead to patterns.

The methods of thermal analysis such as differential thermal analysis (DTA) or thermogravimetry (TG) are valuable for the identification of certain inorganic and organic substances. DTA and TG are often used in the field of ceramic materials, stone conservation, building materials and also pigments. In special cases DTA also is suitable for identifying mixtures of binding media or investigating chemical changes of materials<sup>35, 36</sup>. Certainly the sample size, necessary to obtain representative results, is limiting a widespread application in the field of painting materials. Compound specific analysis of organic pigments can generally be carried out by means of chromatographic methods. The characteristic colours or fluorescence of substances or their derivatives in paper chromatography, thin layer chromatography and high performance thin layer chromatography or the retention times in gas-liquid chromatography can serve for the analytical identification. In certain cases a combination of separation steps and spectroscopic methods applicable on the microscale or at even lower levels, such as infrared spectroscopy, mass spectrometry, nuclear magnetic resonance or electron spin resonance is successfully used as well as the spectroscopic identification of evaluated substances<sup>35-38</sup>.

#### 4. NOTES

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RÉSUMÉ

La diversité des matériaux utilisés dans la réalisation d'œuvres d'art a entraîné la multiplication des méthodes d'analyse adoptées pour les étudier. Les techniques traditionnelles chimiques et microchimiques de même que les nouvelles méthodes instrumentales d'analyse bien connues dans les sciences exactes donnent d'amples informations à propos de la composition de l'objet d'art. L'avantage de l'analyse instrumentale réside dans l'abondance de l'information qu'elle procure concernant la distribution des éléments, l'analyse de surface, l'analyse des microdomaines et l'identification des composés.

Le but de la présente contribution est de donner un aperçu des méthodes les plus utilisées pour la caractérisation des composants inorganiques des peintures. Cependant, une meilleure compréhension des problèmes spécifiques à l'histoire de l'art et à la conservation des œuvres ne peut être atteinte que par une interprétation prudente et la comparaison avec d'autres résultats.