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Expanding the possibilities
of ATR-FT-IR spectroscopy
in determination of inorganic pigments



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LIST OF ORIGINAL PUBLICATIONS

This thesis consists of four articles listed below and a review. The articles are referred in the text by Roman numerals I–IV. The review summarizes and supplements the articles.

- I **Vahur, S.**; Knuutinen, U.; Leito, I. ATR-FT-IR spectroscopy in the region of 500–230 cm^{-1} for identification of inorganic red pigments. *Spectrochimica Acta Part A*, **2009**, 73, 764–771.
In Web: <http://dx.doi.org/10.1016/j.saa.2009.03.027>
- II **Vahur, S.**; Teearu, A.; Leito, I. ATR-FT-IR spectroscopy in the region of 550–230 cm^{-1} for identification of inorganic pigments. *Spectrochimica Acta Part A*, **2010**, 75, 1061–1072.
In Web: <http://dx.doi.org/10.1016/j.saa.2009.12.056>
- III **Vahur, S.**; Sibul, K.; Ehasalu, P.; Sammelselg, V.; Leito, I. Paint investigations of altar and pulpit in the church of St Mary, Vigala, Estonia. *e-Preservation Science*, **2009**, 6, 43–52.
In Web: <http://www.morana-rtd.com/e-preservation-science/>.
- IV **Vahur, S.**; Virro, K.; Leito, I. Web-based Infrared Spectral Databases Relevant to Conservation, *J. CAC*, **2005**, 30, 10–17.

Author's contribution

PAPER I: Main person responsible for planning and writing the manuscript. Performed all the experimental work.

PAPER II: Main person responsible for planning and writing the manuscript. Performed majority of the experimental work.

PAPER III: Main person responsible for planning and writing the manuscript. Performed all experimental work.

PAPER IV: Main person responsible for planning and writing the manuscript.

ABBREVIATIONS

ATR	Attenuated Total Reflectance
C.I.	Colour Index
DRIFTS	Diffuse reflectance spectroscopy
DTGS	Deuterated triglycine sulphate
ED	Energy dispersive
EDS	Energy Dispersive X-ray Spectroscopy
FT	Fourier' Transform
IR	Infrared
IRE	Internal reflection element
IRUG	Infrared and Raman Users Group
LM	Light Microscopy
MCT	Mercury cadmium telluride
NIST	The National Institute of Standards and Technology
n_D	Refractive index
PIXE	Particle/Proton Induced X-ray Emission
PLM	Polarized Light Microscopy
SDBS	Spectral Data Base System
SEM	Scanning Electron Microscopy
WD	Wavelength dispersive
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

I. INTRODUCTION

Analysis of materials usage of historic artefacts, such as paintings, polychrome objects, etc, is very common in conservation and art history practice. Among the components of paint layers of such objects pigments occupy an important place. Knowing the identity of the pigment is important for conservation, dating and author assignment.

Some of the old artefacts (especially polychrome objects, such as coats of arms, sculptures, altars etc) can be often over painted, either to change the colour tone or to improve the appearance (restoration). Pigment analysis may give information, when a certain paint layer was applied. For example if the paint layer contains zinc white, chrome yellow or chromium oxide then it can be said that this paint layer cannot be older than from the 19th century, because all these mentioned pigments were discovered during 19th century. Also sometimes, knowing the identity of the pigment can assist in verifying attribution and identifying forgeries as there are known dates for the introduction of certain pigments.

Knowledge of the composition of the original materials and pigments is very helpful in choosing suitable materials and colour tones for restoration work. Also that information is useful for art historians – it helps them to better understand materials handling by the artist. Many artists have their favourite painting materials, pigments and painting techniques that they most often use, and sometimes is possible to recognize some of the artist works by the materials usage.

FT-IR spectroscopy is an established technique for analysis of different materials, among them objects of cultural heritage, such as paintings, polychrome objects, etc. The method is applicable to almost any sample and is relatively inexpensive. Micro-ATR or microscope accessories allow analysis of very small samples, this is important because principally all the paint samples that are taken from an art object are very small. At the same time, the spectra are not always easy to interpret, especially in complex samples, where the absorption bands of different components overlap.

Traditionally the main strength of FT-IR lies in analysis of organic constituents. These have numerous absorbance lines in the convenient mid-infrared ($4000\text{--}400\text{ cm}^{-1}$)¹ region. Most of the pigments used historically in paintings and other artefacts are inorganic compounds. FT-IR has found limited use for determination of inorganic pigments, because the mid-IR part of the IR

¹ The lower wavenumber limit of the IR spectral region is quoted differently by different authors, ranging from 500 cm^{-1} to 200 cm^{-1} . The value 400 cm^{-1} is the most common. From practical viewpoint, IR spectra in databases are often given down to 500 cm^{-1} and ATR IR spectroscopy below 500 cm^{-1} tends to find little use. Therefore in this work is considered the spectral range below 500 cm^{-1} as the “low wavenumber range” and most of the spectra are discussed starting from 550 cm^{-1} .

spectrum of many of them is not characteristic enough and a number of important pigments (cadmium red, cinnabar, etc) do not absorb in the mid-IR region. Therefore pigment identification has traditionally been performed using Raman spectroscopy and also some elemental analysis techniques, such as SEM-EDS, XRF, etc.

It is known that many pigment materials absorb IR radiation in the far-IR region (below 500 cm^{-1}). In contrast to the mid-IR region the far IR region has traditionally been significantly less accessible for routine IR spectroscopic measurements. However, recent advances in instrument design have brought the wavenumber range below 500 cm^{-1} well within reach of commercial FT-IR equipment. Nevertheless, this wavenumber region has up to now found almost no use in investigation of historic artefacts.

The main hypothesis of this dissertation is the following: the usefulness of ATR-FT-IR for identification of inorganic pigments will increase significantly if the low wavenumber region ($550\text{--}230\text{ cm}^{-1}$) will be used thus making ATR-FT-IR a useful tool in identification of inorganic pigments.

The main goals of this dissertation are the following:

1. To develop an analytical method for analysis of paint layers for inorganic pigment by micro-ATR-FT-IR using the wavenumber region $550\text{--}230\text{ cm}^{-1}$ (*publications I, II*).
2. To explore the usability of this method for 47 most widespread inorganic pigments historically used in art objects (paintings, coats of arms etc) and to compile a collection of ATR-FT-IR spectra of these pigments in the low wavenumber region and to map potential interferences from other sample components (*publications I, II, IV*).
3. To demonstrate the application of this method on 5 case studies of analysis of different art objects of which some are important in Estonian history (*publications I – III*).

An added value of this work is a collection of ATR-IR spectra of 47 widespread inorganic pigments in the low wavenumber region that can be used by material scientists and also art conservators.

2. GENERAL ASPECTS

2.1. Paints and their components

For centuries artists have used different painting materials to compose their masterpieces. Paint's purpose may be to be the medium for creating art, to provide decoration and also to protect the surface to which it is applied (for example canvas, wood, metal, paper, stone etc). The protective role is that of shielding the surface (substrate) from ultraviolet radiation, moisture and oxygen [1].

Two most important components of paints are colouring matter (pigment or dye) and binder (medium). Often different additives and fillers (extenders) are added to paint to enhance some properties of the paint or to make it cheaper. There are many different paints by chemical composition of the binder: oil paints, tempera paints, acrylic paints, alkyd paints, gouache, watercolour, etc.

To thin the paint to the best consistency for the work, diluents (solvents) must be used. A diluent may be a solvent used to decrease the concentration or viscosity of paint. It can be added to the mixture only to a limited extent without causing precipitation of the solid pigment. [2] The best known diluents (solvents) are turpentine, mineral spirits (or white spirits – hydrocarbon petroleum distillate), different organic solvents (aromatic, esters, ketones, etc.), water [1, 3].

Colouring matters

As early as in remote prehistoric times colouring matters – pigments and dyes – from animal, plant and mineral sources have been used for personal adornment, for decorating tools, weapons, utensils, and for making pictures. Early pigments were simply ground earth or clay, and were made into paint with spittle or fat [4]. These naturally coloured minerals have been widely used because of their high colouring capacity and stability under different weather conditions, light, oxidation and corrosion [5]. There are also different synthetic (or artificial pigments), which may be inorganic compounds of metals or organic compounds (for example Indigo).

Pigments are composed of finely divided particles which do not dissolve in binders. Pigments are derived from wide variety of substances, mostly inorganic, but also organic, natural and artificial. They may be classified according to colour, chemical composition or source [2]. In chapters 2.2 and 2.3 is a short overview of common inorganic pigments and their properties.

Dyes are mostly complex organic compounds. Dyes dissolve in the binder to form coloured liquids. Dyes are mostly used to colour textiles. [2, 3]

Fillers (or extenders)

Filler (also called extender and inert) is an inert, colourless or white powdered material used to diffuse or to dilute pigments [2]. Filler is used to modify the properties or increase the bulk (volume) of a material [6].

Fillers can be also such inactive white pigment which has little or no hiding power or tinting strength when it is used in a binder. Good examples are chalk (CaCO_3), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), barium sulphate (BaSO_4) etc [2, 3]. They usually have a refractive index below 1.70. These compounds are used in priming materials and also they may be used as fillers for pigments. For example barium sulphate is used as filler with titanium white (titanium dioxide), the cost of the mixture is less than that of pure titanium white, but there is not lessening in hiding and covering power. Calcium sulphate is often present in artificial iron oxide reds [2].

Also some silicates, for example kaolin, silica may be used as extenders for pigments [3].

In principle fillers are additives that are added into paints to decrease the quantity of pigments and thereby lower the price of the paint, but also in some cases these are added to improve the properties of the paint.

Binders (Binding media)

Binder is a liquid or semi-liquid substance in which the pigment is suspended and which form a strong film of paint when it's dry. Binder provides the adhesion and cohesion, keeps the pigment within the coating and ensures that the paint remains attached to the substrate [1]. Binders also protect pigments from deterioration due to passage of time and ambient conditions. [4]

Binders can be divided as follows: oils, waxes, resins, proteins and carbohydrates (gums, polysaccharides). A short description about two most common binders – oils and proteins – is presented in Appendix 1.

2.2. Inorganic pigments, general remarks

In this dissertation the main attention is on the inorganic pigments and in this chapter these are shortly described.

Inorganic pigments are natural pigments prepared from minerals, earth deposits or are made synthetically (artificially) [2, 3]. Synthetic pigments are made by processes of chemical synthesis. Some synthetic pigments, like Egyptian blue, white lead, verdigris, have been known since ancient time or earlier.

Pigments differ widely by their properties. When choosing a pigment several points have to be considered. The following properties are very important [2, 3, 6, 7]:

- *General chemical and physical properties*: chemical composition, moisture and salt content, particle size and shape, density;

- *Colouring properties*: colour, refractive index and hiding power, tinting strength² or lightening power³;
- *Stability properties*: resistance toward light, weather, heat and chemicals, retention of gloss;
- *Behaviour in binders*: interaction with the binder, dispersibility, compatibility and effect on binder drying.

By their chemical properties inorganic pigments belong mostly to oxides, sulphides, carbonates, chromates, sulphates, phosphates or silicates of metals [2; 7]. There are few pigments that are complex metallo-organic compounds (like Prussian blue ($\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$) or elements in their pure state (such pigments as gold, aluminium and carbon). [2]

Out of the physical properties of pigments the most important is colour. Colour characteristics, the hue, purity and brightness of the light diffused depends upon the colour absorption, size, shape and texture of pigment grains [2].

The important physical-optical properties of pigments are their light-absorption and light-scattering properties. If absorption is very small compared with scattering, then the pigment is a white pigment. If absorption is much higher than scattering over the entire visible region, the pigment is a black pigment. In a coloured pigment, absorption (and usually scattering) is selective (depend on wavelength) [7].

The hiding power is the important property of a pigment, when made into paint, to obscure the surface on which it is applied. The definition of hiding power is based on a black and white contrasting support upon which the film of coating is applied [7]. In the case of white pigments, the ability to reflect light and obscure black is the measure of hiding power; in the case of black pigments the opposite is true. Hiding power of a pigment is proportional to its refractive index, to fineness of particle size and to depth of colour. Usually pigments of compounds of heavy metals have the highest hiding power (except ultramarine and carbon black), alumina based pigments usually have low power (for example lake pigments). [2]

The refractive index is the measure of light-bending power of pigment particles as light passes through them [2]. As light passes from vacuum into a substance, its velocity is reduced and the light is refracted [9]. The refractive index is a ratio obtained by dividing the speed of light in a vacuum by the speed of light as it passes through the substance (material).

² Tinting strength of a coloured pigment is its ability to absorb the incident light and confer colour to the medium in which it is embedded. The tinting strength is an indication of the yield of a colouring material. [8] So, it is the power of a pigment to tint paints as measured by its relative strength in colouring a standard white pigment in oil.

³ Lightening power is the term for ability of a white pigment to raise the lightness of a coloured, grey or black material. Lightening power characterises the yield of a white pigment and corresponds to tinting strength of coloured pigments. [8]

The pigment grains reflect light most strongly, when surrounded with air. The reflection is reduced when the pigment grain is surrounded with binder. Paint reflects light in proportion to the ratio between the refractive indices of pigment and the surrounding binding medium. The higher is the refractive index of the pigment and the lower that on the binding medium, the greater is the light reflection. In the case of e.g white pigments this means greater whiteness and hiding power. [2]

In order to produce paint that can be applied evenly and smoothly on the surface, the pigment grains have to be as fine and uniform as possible. The size and uniformity of the pigment particles influences gloss, hiding power, tinting strength and lightening power [2, 7]. Particle size may be regarded relatively as very fine, fine, medium, large and coarse. The standard unit of measurement is the micrometer. Particle sizes (measured as average particle diameter) of mineral-based pigments vary from approximately 0.3 to greater than 40 μm [9]. The typical particle sizes vary between pigments. For example many earth pigments consist of small, discrete particles which are however very uneven in size and irregular in shape [3].

Individual pigments vary greatly in density or specific gravity and this has to be taken into consideration in the preparation and in the practical use of paints. Pigments with high specific gravity are more prone to settling in liquid paints.

Inorganic pigments are generally chemically stable and are classified as being among the most stable colouring matters (compared to dyes) [7]. In principle a pigment needs only be stable and chemically inert enough to withstand light, air and moisture or environments in which these three are combined. [2; 7] Nevertheless, even paints involving inorganic pigments sometimes show colour or structural changes when are subjected to intense radiation, such as sunlight, or weathering (moisture, air). These changes involve dimming, yellowing (also browning) and darkening, in some cases also chalking and loss of gloss. These processes involve photochemical reactions in which the pigment acts as a catalyst or undergoes chemical changes itself. [2, 6, 7]

Important topic is also pigments behaviour to strong chemical reagents. Carbonates, ultramarine, some oxides and sulphides (for example ZnO , PbO , CdS) are easily decomposed by acids. Prussian blue is sensitive to alkalis. [2] Pigments themselves may have either acidic or alkaline properties. The oxides of heavy metals are basic (alkaline), they can react with free fatty acids of drying oils to form metallic soaps. Zinc oxide and some of the lead pigments have this tendency. For example this is one of the reasons why white lead in oil forms compact, elastic and durable paint film. However titanium oxide is perfectly inert and does not tend to form titanium soap, or react with binders in any way. [2]

2.3. Overview of the most important inorganic pigments

Below overview of the most important inorganic pigments used in paintings is given. Pigments can be classified in different ways. When analytical chemist is dealing with identification of pigments in works of art then the first bit of information that is (usually) effortlessly obtained is the colour of the paint. The colour often forms the starting point for further investigations. Based on this reasoning and underlining the analytical chemical focus of this work the pigments are below classified according to their colour tone.

Table 1 in Appendix 2 summarize the most common traditional inorganic pigments, their chemical compositions, time when the pigments were taken into use, their refractive indices and some general comments.

2.3.1. White pigments

Lead white [$2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$] has been produced artificially (at first made from metallic lead and vinegar) since early historical times and was one of the first artificially prepared pigments [2]. Basic carbonate of lead is chemically equivalent to the naturally occurring hydrocerrusite, however, this mineral has not been used as a pigment source [10, 11]. Lead white was for many centuries by far the most important white pigment and it continues to be the most important of all the lead pigments. It was the only white pigment used in European easel painting until the 19th century when zinc white became a competitor [11]. In the 20th century lead white has been extensively replaced by titanium white (titanium dioxide), which is superior to lead white in several properties [11].

Zinc white (also known as Chinese white) is composed of zinc oxide and is permanent, opaque, non-toxic and has good hiding power. It was first introduced as a watercolour pigment by Winsor & Newton (under the name Chinese white) in 1834 [10, 12]. Zinc white started slowly to be more used after 1850, and it was probably added also to various coloured pigments by manufacturers as a lightening agent [12]. Also zinc white was often mixed with titanium dioxide and lead white paints as a minor component to improve the paint properties [10].

Titanium white has the highest refractive index (2,55) comparing to other white pigments and therefore has the greatest whiteness and hiding power. White lead and zinc white both have refractive index of about 2.0 and have thus lower hiding power than titanium white [2]. Titanium dioxide white pigments were introduced in the first half of the 20th century. Commercial production of these pigments is carried out using several methods [10]. Anatase and rutile are the naturally occurring crystal forms of titanium dioxide (TiO_2) and these forms

both separately also synthesized as pigments [13]. Titanium white is a very stable substance. It is unaffected by heat, by dilute acids and alkalis, and by light and air.

Barium white (barites) is barium sulphate, which may be obtained naturally from the mineral known as barite, barites, or heavy spar, or it can be made artificially (blanc fixe) [2]. Artificial barium sulphate (blanc fixe) has much greater hiding power than the natural material and when co-precipitated with zinc sulphide a pigment called lithopone is formed [2]. Lithopone ($\text{BaSO}_4 + \text{ZnS}$) was first produced about 1874.

Chalk, gypsum, barium white (natural barytes) are more used as fillers (extenders or inertes) in the paint. Chalk and gypsum are also very important primer (ground) components (both have low refractive indices and hence poor hiding powers and so are not in use alone in the oil paints).

2.3.2. Yellow pigments

Orpiment, arsenic trisulphide (As_2S_3), is naturally occurring mineral that was widely used as yellow pigment. Orpiment contains about 60% arsenic [10]. Artificial orpiment is called king's yellow and it has the same composition as the mineral. Natural and artificial orpiment were used until the end of the 19th century. The use of orpiment was discontinued because of its toxicity and its limited supply [2, 13]. The toxicity of orpiment has been known since early times, in spite of that many artists used this anyway [13]. The reasons why it was widely used are its brilliant lemon-yellow tone, very high refractive index (2.40–3.02) and stability to light and air [2, 13]. Natural orpiment is found in historical paintings as yellow pigment and sometimes also mixed with blue (e.g. azurite, indigo) to make green tones [3, 13]. A limitation of orpiment is that can not be mixed with all pigments. For example it reacts with copper- and lead-based pigments [10].

Naples yellow refers primarily to the lead antimony oxide (known also under the name lead antimonate yellow) and it is one of the oldest (like also Egyptian blue) synthetically produced pigments [10, 12]. Pigment's name "Naples yellow" first appears in the end of the 17th century in Rome. Naples yellow is synthesized by roasting (or heating) mixtures of lead and antimony oxides or salts. There are several different recipes of making this pigment [12] that lead to somewhat different chemical composition and different colour tones. In the literature two most frequently cited formulas are $\text{Pb}_3(\text{SbO}_4)_2$ and $\text{Pb}(\text{SbO}_3)_2$ [2, 12, 14]. The pigment is homogeneous, finely divided, has good hiding power and is chemically quite stable [2]. Naples yellow was probably the only yellow pigment during the first seventeen centuries of glass making [12].

Massicot is monoxide of lead and is made by gentle roasting of lead white at the temperature of about 300 °C [2]. At this high temperature, lead white gives off carbon dioxide and water, leaving a soft, yellow powder. Massicot is not

intense yellow but it has good hiding power and is similar to lead white in pigment properties. Massicot name is used also to orthorhombic lead(II)oxide mineral with composition of PbO and that mineral is known since antiquity [10]. It occurs as soft yellow scaly or earthy mass in association with lead ore deposits worldwide. As a colouring pigment artificially made massicot is mostly used.

There are 3 important chromate containing artificial yellow pigments. They all were introduced in the beginning of the 19th century. These are *chrome yellow* (PbCrO₄), *barium yellow* (BaCrO₄), *strontium yellow* (SrCrO₄) [12]. All these pigments were discovered by French chemist Nicolas Louis Vauquelin (he discovered element chromium in 1797 and then the pigments) [2, 3, 12].

Chrome yellow is the most important chromate containing yellow pigment. Chrome yellow (lead chromate) has higher refractive index and also better hiding power than the other two chromate containing yellow pigments. Chrome yellow is made by adding a solution of a soluble lead salt (nitrate or acetate) to a solution of an alkali metal chromate [2]. Lead chromate is a crystalline material. Its colour can vary from lemon yellow to orange, depending upon the particle size (particle size depends upon the condition of precipitation) [2]. Chrome yellow's high tinting strength allows the pure lead chromate to be diluted by extenders such as barium sulphate, calcium sulphate or china clay [12]. Commercial chrome yellow is not chemically pure. It may contain silicates, aluminium phosphate, titanium, aluminium zirconium and other compounds to enhance pigment properties and pigment characteristics such as lightfastness, oil absorption, gloss, etc [12]. Chrome yellow was often mixed with blue pigments to produce a green pigments, traditionally know as chrome green [12]. It was also often added to yellow ochres to brighten the appearance of the ochre colour [3]. The biggest drawback of chrome yellow is it tends to darken with age and become brown. Today that problem is solved and lightfastness of the pigment is achieved by the addition of photochemical stabilizers (for example zinc salts) [12].

Barium yellow is a pale green-yellow pigment made by mixing solutions of neutral potassium chromate or dichromate and barium chloride [2]. Barium yellow is deficient in brightness and hiding power. Barium chromate is said to possess the best long-term stability of the chromate pigments, although like the others, it turns green slowly in light [12]. Barium yellow and strontium yellow are quite similar and are known and sold under the name "lemon yellow". Barium yellow is used in industry as an ingredient of anti-corrosive paint [3].

Strontium yellow is strontium chromate and is prepared like barium yellow except that strontium chloride is used instead of barium chloride. It is a little deeper and brighter in lemon hue and has better hiding power than barium yellow [2]. This pigment tends to be more sensitive to light than barium yellow and gradually develops a green shade [12].

Lead tin yellow. There are two kinds of lead tin yellow: *lead tin yellow type I* and *lead tin yellow type II*. The more frequently used *type I* is lead-tin oxide of

the composition Pb_2SnO_4 [11]. This pigment is prepared from a heated mixture of either lead monoxide (minium) or lead dioxide with tin dioxide [3, 11]. At temperatures around 700–800°C cold lemon yellow colour is obtained. At lower temperatures a slightly warmer shade is obtained [3]. Former times lead tin yellow was a by-product of the glass industry. Earlier this pigment was often incorrectly identified as either Naples yellow or massicot in historical paintings [3]. *Type II* is a second variety of lead-tin oxide that may contain free tin oxide and in addition silicon $[\text{Pb}(\text{Sn},\text{Si})\text{O}_3]$ [10, 11]. It is a yellow lead-glass pigment, a by-product of lead crystal glass manufacturing. The presence of quartz gives a degree of transparency to the pigment.

Nowadays one of the important synthetic yellow pigments is *cadmium yellow* (CdS). It was first recommended as an artists pigment in 1818. Its commercialization began in the mid 1840s. This pigment was initially very expensive and its use by artists remained limited [12]. A cheaper commercial pigment became available in 1920s. It was reproducible, permanent, bright pigment in a wide variety of shades and compatible with most other materials [12]. After that the popularity the pigment increased rapidly. Today different shades of cadmium yellow are available. For example light cadmium yellow contains added zinc sulphide CdS $[(\text{Cd},\text{Zn})\text{S}]$. Cadmium sulphide can be extended with BaSO_4 to give varieties of lithopone: *Cadmium lithopone yellows*. These were developed out of economic necessity because the cost of pure cadmium yellow was very high. Pure cadmium yellow has high refractive index and small particle size, this combination imparts good hiding power and light scattering ability. [2, 12]

Yellow ochres (yellow iron oxide pigments)

Ochres are a subset of the so-called natural earths. Natural earths have been used as artistic pigments since prehistoric times. They can be found in works of art everywhere and in any historic period due to their wide availability, high colouring capacity and stability under a variety of weather conditions [15]. Generally earth pigments (also known iron earth pigments) are derived from minerals, ores and sedimentary deposits of the earth's crust [2]. Earth pigments are distinguished on the basis of colour as ochres (yellow and red ochres), green earths, siennas (it may be darker yellow or brown) and umbers [15, 16]. "Earth" is more general term, since "ochre" refers to a specific type of iron oxide deposit containing clay and silica (quartz). [17]

The colour of an ochre depends on the nature of the iron oxide chromophore – these minerals comprise both oxides and oxide hydroxides of iron [15, 17]. The presence of other minerals, such as clay minerals or other metal oxides can also influence the colours of all the earth pigments. Iron oxides have high pigmenting power and strongly coloured ochres may contain a relatively low concentration of iron minerals compared to the concentration of the other components (additives) [17]. The concentration of iron oxide compared to the accessory minerals depends on the source of the earth and the processing that

the pigment has undergone. All the iron oxide pigments have high refractive indices and thus excellent hiding power [2, 17]. Iron oxide pigments are insoluble in organic solvents and in water and are compatible with most binding media.

In the 19th century synthetic iron oxides, the so-called Mars colours were introduced to painting. Mars colours were produced by dissolving iron salts in water and precipitating the iron oxide with alkali [17]. However natural ochres have never been fully replaced because of their wide availability in nature [16].

Mineral goethite, iron oxide hydroxide (α -FeOOH or $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$), is the most frequently found iron compound among *yellow ochres* [5, 16, 17]. Yellow pigments based on iron oxide hydroxides are referred to by many different names in the literature, including yellow earth, yellow ochre, goethite, etc [17]. Clay minerals, quartz and sometimes calcite are commonly found along with the iron oxide in the yellow ochres. French ochre for example contains kaolinite and quartz mixed with about 20% goethite. Yellow ochre from Georgia in the United States as also from South Africa contains about 50% iron oxide [17]. So that indicates that the weight percentage of iron oxide in the various locations in the world can be different (also mineral accessories can be different).

Raw siennas are goethite containing earths, to which they owe their yellow-brown colour, but are distinct from the yellow ochres in that they contain minor amounts (< 5%) of manganese oxides [10]. Raw sienna pigments, originally found from the quarries near Siena (in Tuscany) but later also from other sources, are generally browner, warmer, more transparent and purer than other yellow earths [10, 17]. Raw sienna contains more iron oxide than yellow ochre [2, 17].

Nowadays different companies sell yellow iron oxide pigments also under other names like *Amberg yellow* (German variety of yellow ochre), *satin ochre* (gold-orange pigment from Tuscany in Italy), *Mars yellow* (synthetic iron oxide pigment) etc.

2.3.3. Red pigments

Cinnabar (vermilion) – a coloured sulphide of mercury (HgS) – is known and used since ancient times [2]. Vermilion is a widely used historic term for the synthetic forms of mineral cinnabar. The earliest reports of making artificial vermilion date from about A.D. 800 and originate from China [11]. Chemically and physically vermilion does not differ from cinnabar. Cinnabar (or vermilion) is an orange-red pigment with excellent hiding power (it has very high refractive index: 3,146–2,819). Although it is toxic pigment [2] it was used extensively until the discovery of cadmium red in the 20th century. Since then its use was dramatically reduced due to its known darkening in the air. [11]

Cadmium red is a deep red pigment composed of cadmium sulphide-selenide ($\text{CdS} + \text{CdSe}$), it has very high refractive index (2,64–2,77) and therefore excellent hiding power. Preparation of cadmium red was patented in 1892 and it was commercialized in 1910. In 1926, co-precipitation method of cadmium red with barium sulphate was developed for production of a less expensive cadmium red lithopone pigment [12].

Realgar, another sulphide-based red pigment is known since antiquity. It is orange-red sulphide of arsenic (As_2S_2) and it is closely related (and chemically associated in nature) with orpiment (these two minerals are often found in the same deposits) [2, 10]. While it is toxic this pigment was used until the 19th century.

Red lead is an important natural red pigment that is used since antiquity. Red lead is chemically Pb_3O_4 or $2\text{PbO} \cdot \text{PbO}_2$ [10]. Although chemically equivalent to the mineral minium, red lead has been synthetically prepared by heating litharge (PbO) or lead white [$2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$] at the temperature of about 480 °C [2]. Red lead is not a very stable pigment. When exposed to strong light the pigment turns chocolate brown. Red lead is no longer used as an artists pigment due its toxicity, poor light stability and colour change upon ageing.

Red ochres (red iron oxide pigments)

Hematite ($\alpha\text{-Fe}_2\text{O}_3$) is the most commonly identified mineral species in red pigments based on iron oxide [17, 18].

Red ochre (or *natural red earth*) contains besides iron oxide (hematite) as mineral additives also clay and (in some regions) also a little quartz and calcite. The weight percentage of iron oxide and clay vary and depend on the locations from where the mineral is mined. For example Spanish red earth, quarried near Málaga, contains 80–85% iron oxide. In very pure hematite ores the concentration of iron oxide may be over 90%. [2, 17] Generally the weight percent of iron oxide in red ochres is higher than that in the yellow ochres.

There are various red iron oxide pigments under different names, some of them differ one another by colour tone (orange to purplish-brown) and also by origin (are mined in different locations and then named after that). Also they may be natural or synthetic red iron oxide pigments. For example *Pompeii red* (also Pompeiian red or Tuscan red) is an orange-red earth pigment which is grained and burnt sienna earth from Toscana and beside iron oxide also contains kaolin [3, 17]. *Venetian red* originally consisted of iron oxide (or red hematite) and had characteristic pinkish shade when admixed with whites. Since the 19th century the term *Venetian red* more often referred to synthetic red iron oxide that is obtained by calcination of ferrous sulphate with chalk (calcium carbonate) [3, 17]. *Caput Mortuum* is reddish-purple or violet pigment which main compound is probably hematite mixed with additives like calcium carbonate, kaolin etc [10]. This pigment is determinable besides its chemical composition also by the particle size and shape in the analyzed sample [19]. *Mars red* is a synthetically prepared red iron oxide pigment. Mars red is one of

the mars pigments developed during the 18th century. Its commercial production began in the middle of the 19th century. It is a permanent pigment with good tinting strength and good oil-drying properties. [17]

2.3.4. Green pigments

There are only two green pigments – green earth and malachite – that are natural mineral pigments, other are synthetically made pigments. Both pigments are known and used since ancient times.

Green earth is prepared principally from two closely related clay minerals celadonite and glauconite, which have layered silicate structures [12, 16]. Glauconite and celadonite do not occur together. Celadonite (has a bluish green tinge) occurs as the alteration product of basaltic igneous rocks (so, is only found in basaltic volcanic areas); the grass green glauconite forms only in marine settings and is well known as a mineral dispersed in sandstones and clay deposits of this origin [10]. Celadonite is traditionally considered a magnesium-rich and glauconite an iron-rich dioctahedral clay compounds [16]. Natural green earth can vary in composition and in shades of colour (it can be yellow-green to pale greenish grey), it is dependent of the locality of the source [2]. With respect to the source locality, other greenish clayey minerals that may be included in green earth pigments are smectites, chlorites, serpentines, kaolinities etc [12, 16, 20]. Admixtures of free ferric oxides such as yellow goethite are also common. Green earth has a low hiding power, especially in oil, but it works well in tempera [2]. The pigment is compatible with all binding media and all other pigments [12].

Malachite is perhaps the oldest known bright green pigment. It is mineral basic copper carbonate with formula $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$ [2]. Malachite forms a secondary mineral in the upper oxidised zones of copper ore deposits. Malachite is commonly found in association with azurite, although malachite is the more abundant copper carbonate [10]. For use as a pigment, malachite was prepared by crushing, grinding, washing [3, 10]. The history of malachite in painting runs closely parallel to that of azurite. Malachite is crystalline, it is unaffected by light and it works, like azurite, better in tempera than in oil [2].

Green pigments include also three chromium containing pigments – chrome green, Chrome oxide green (or chromium oxide), viridian and one cobalt containing pigment – cobalt green.

Chrome green is a complex mixture that is made by mixing chrome yellow (lead chromate) and Prussian blue ($\text{Fe}_4[\text{Fe(CN)}_6]_3$), also some extenders like barites (BaSO_4) and China clay are added [2, 10]. This pigment has excellent hiding power. Its down-side is that it is not light-fast: it has tendency to become blue in strong light because of the darkening of the chrome yellow component [2].

Chromium oxide (or Chrome oxide green) and *viridian* both contain oxide of chromium and they both were introduced during the first half of the 19th century [10, 13]. Chromium oxide is the anhydrous oxide of chromium (Cr_2O_3) and viridian is hydrous oxide of chromium ($\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$) [2]. These pigments are among the most permanent of artists' pigments, although neither has been widely used [13]. Chromium oxide is an opaque dull olive green pigment [10]. Chromium oxide is the most stable of all green pigments, it has good hiding power (refractive index is 2.5) and high tinting strength [2, 13]. Viridian is transparent, bright somewhat bluish green pigment; it has excellent tinting strength and is stable in all mediums, however it has comparatively low refractive index and so the hiding power is only moderately good [2, 13]. Viridian immediately, after the discovery, replaced Schweinfurt green (or Emerald green) for printing and other industrial colouring purposes [2].

Cobalt green ($\text{CoO} \cdot \text{ZnO}$) is similar to cobalt blue except that zinc oxide partially or wholly replaces the aluminium oxide [2, 10]. This pigment was discovered in the end of the 18th century. Cobalt green is semi-transparent and has low hiding power. It is a stable and inert pigment and can be used in mixtures and different techniques.

Green pigments include also some quite complex mixtures like verdigris (basic copper acetate) and emerald green (copper acetoarsenite) which both contain acetate.

Verdigris is artificial pigment that is used since antiquity. It is a transparent bluish-green pigment composed of basic copper acetate [11]. It was prepared in wine-growing areas, by pilling up winemarc and copper plates and subjecting them to a process of fermentation, the resulting formed acetic acid (acetic acid is a by-product of winemaking) reacts with the copper, forming a blue to blue-green crust which is scraped off and ground [11]. Verdigris is the most reactive and unstable of all the copper pigments [2]. Verdigris has always been regarded as a fugitive pigment, darkening dramatically from its original bright green [10]. Because verdigris has poor hiding power in oil-media it often contains high refractive index additives of lead white and/or lead-tin yellow. Lead-tin yellow also changes the bluish green of verdigris to a warmer, more neutral green. [11] Verdigris was often used both in glazes and in opaque paint layers.

Emerald green, composed of copper acetoarsenite, is also known as Paris green or Schweinfurt green [13]. This pigment was introduced in between 1800–1814; however this compound is no longer available as artists' pigment, because of its extreme toxicity. It has unusually brilliant blue-green to green hue and therefore became popular immediately after its discovery. Emerald green has good hiding power due to a combination of a moderately high refractive index and reasonable opacity [13]. It is known that copper arsenic greens will darken in the presence of sulphur containing compounds to form black copper sulphide, so this pigment should not be mixed with such pigment as ultramarine, cadmium yellow, vermilion, lithopone [13]. Emerald green was popular among the French impressionist and post-impressionist artists (like Paul

Gauguin, Paul Cezanne etc) and this pigment has been identified in many of their works [13]. In addition to being sold as an artist pigment, this pigment was used in the decorative art for colouring wallpapers, cloth lampshades, decorating domestic furniture and fabrics, colouring linoleum, a component in paints for toys etc [13].

2.3.5. Blue pigments

The most important and only mineral blue pigments are azurite (the corresponding mineral is also called azurite) and ultramarine blue (mineral is lapis lazuli), other blue pigments are all synthetically made. The most important synthetic blue pigments are Egyptian blue, smalt, Prussian blue, cobalt blue, and cerulean blue.

Egyptian blue ($\text{CaCuSi}_4\text{O}_{10}$) is a copper calcium silicate (other names are blue frit, Pompeian blue, Alexandrian blue etc). It is considered to be the first synthetic pigment and it was prepared and extensively used in Egypt, Mesopotamia and Greece from ca 3100 B.C. until the end of the Roman period in Europe (probably in 395 A.D.). Occasionally it was still used in Italy and central Europe until the Middle Ages [2, 10, 13]. Egyptian blue is generally made by heating together (to temperatures in the region of 850–1000°C) a calcium compound (such as powdered limestone or gypsum or calcium hydroxide), a copper compound (such as copper oxide or a copper salt such as malachite), silica (usually in the form of quartz sand) and may or may not be included a flux such as sodium carbonate, potassium carbonate [10, 13]. Egyptian blue as a pigment was used on such materials as stone, plaster, pottery, wood, papyrus, on canvas and on wall paintings [13]. Egyptian blue which is coarsely crystalline and pure blue in colour is similar in appearance to finely ground azurite. It is completely stable in all media (no change of colour has been observed), is insoluble in acids and is not affected by light or heat [2, 13].

Azurite is bright natural blue pigment composed of basic copper carbonate [$2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$] [2]. The mineral azurite is found in various parts of the world in the upper oxidized portions of copper ore deposits [11]. Azurite mineral is usually associated in nature with malachite. Like preparation of other mineral carefully selected lump of azurite need only to be ground, washed, and sieved to prepare the pigment [2, 11]. Coarsely ground azurite produces dark blue, fine grinding produces a lighter tone. Azurite is stable to light and atmosphere [11]. Although it turns black by heat, by warm alkalis and it is soluble in acids but under ordinary conditions it appears to be a remarkable stable pigment [2]. Traditionally it has been more used in a tempera medium because in oil it would be dark and muddy and would not have the sparkle that it has in tempera. Azurite was the most important blue pigment in European painting from 15th to the middle of the 17th century and in paintings of that

period it is found more frequently than ultramarine [2]. Azurite was largely displaced by Prussian blue when it was discovered at the beginning of 18th century.

Natural ultramarine is a complex sulphur-containing sodium aluminium silicate [11]. Natural ultramarine blue pigment is made from the mineral (semi-precious stone) called lapis lazuli [2]. Lapis lazuli is a complex rock mixture: a mineralized limestone containing grains of blue mineral called lazurite (this is the actual blue component of the mineral lapis lazuli), calcite and pyrites (iron sulphide) with occasional presence of sodium-aluminium-silicate group minerals like haynite and sodalite [2, 11, 21] and some other silicate minerals such as diopside, forsterite, muscovite and wollastonite [11]. In the past, the main source of the mineral was in Asia in the ancient quarries of Badakshan (now in Afganistan) [2, 11]. Lapis lazuli was brought to Europe in mediaeval times [2]. Preparation of the pigment is different from the other minerals (e.g. azurite) – simple grinding and washing produces only a pale greyish blue powder lacking in purity and depth of colour [11]. New improved method of extraction came into use not until 13th century. The principle of the method was that the ground mineral (lapis lazuli) was incorporated into a mixture of melted wax, resins and oils and the molten mass, kneaded under a dilute solution of lye (a solution of potassium carbonate prepared by extracting wood ashes with water). Blue particles of lazurite are washed out by this process and are collected by settling at the bottom of the vessel. The rest of the crystalline material and impurities remain behind in the doughy mass [11]. Chemically ultramarine it is the most complex of all the mineral pigments. The hiding power of ultramarine is higher than would be expected from its low refractive index. It has high stability to light, is unaffected by ammonia or caustic alkalis, but is readily decomposed by acids [11]. Natural ultramarine blue was very expensive, it was more expensive than gold. Because of the high price of the natural ultramarine the scientist looked for the opportunity to make it synthetically. *Synthetic ultramarine* was discovered in 1830s and it quickly gained popularity.

Smalt was the earliest of the cobalt pigments. It is an artificial pigment. Smalt is potash silicate glass strongly coloured with cobalt oxide [2, 3]. Smalt is the only amorphous blue pigment. Smalt was first prepared by roasting native cobalt minerals (e.g. smaltite, cobaltite) to form cobalt oxide (CoO). The obtained cobalt oxide was then added to a mass of molten glass (or it was melted together with quartz and potash) and when thoroughly combined, the molten mass was poured into cold water. The blue melt disintegrated into particles, and these were ground, washed and allowed to settle [2, 11]. Because smalt is a glass, its particles are transparent. It has very low hiding power. For this reason, it must be coarsely ground for use as a pigment [2, 11]. Smalt is quite stable pigment. This pigment is mostly used in aqueous media and in the fresco style. In oil medium smalt is often partially or completely discoloured. One of the reasons for that is the low refractive index (1.46–1.55), which is very

close to that of dried oil [11]. This phenomenon is only observed in dried paint films. When the paint is freshly applied the blue colour remains visible. This problem can be countered by admixing smalt with lead white. [3] Smalt came into use in the 16th century. Its use as an artist's pigment was discontinued around the beginning of the 19th century, when its place was taken by the more satisfactory cobalt blue and by artificial ultramarine [2].

Cobalt blue ($\text{CoO} \cdot \text{Al}_2\text{O}_3$) is nowadays the most important of the cobalt pigments. Its colour varies slightly with different methods of manufacture and with the amount of impurities present [2, 17]. Chemically cobalt blue is very stable: it is insoluble in strong acids and alkalis and is unaffected by sunlight [2, 17]. The pigment is compatible with all the others with which it may be mixed [17]. Cobalt blue may be used reliably in most of the binding media – drying oils, acrylics, alkyds, wax, resin, tempera, watercolour [17]. Cobalt blue strongly promotes curing of drying oils [10].

Prussian blue (other names are for example Berlin blue, Paris blue, Milori blue, Chinese blue) has been called the first of the modern synthetic pigments [13]. Prussian blue is composed of ferric ferrocyanide ($\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$) and has dark blue colour tone [2, 3]. Prussian blue was discovered in 1704 in Berlin by Diesbach [2]. It is the first pigment with well-documented discovery circumstances. Prussian blue is fairly permanent to light and air, it is unaffected by dilute mineral acids, but it is very sensitive to alkalis which cause it to turn brown [2]. Prussian blue can be mixed with all pigments except those that are alkaline [13]. Prussian blue has low refractive index (1.56) but its tinting strength is high [13]. After the discovery the pigment gained very quickly worldwide popularity. Prussian blue has been widely used since the early 1700s and was one of the most commonly used blue pigments until about 1970 when the use started to decrease and now often phthalocyanine blue is used in its place [13].

Cerulean blue is composed of cobalt stannate ($\text{CoO} \cdot n\text{SnO}_2$) and is available since 19th century [2]. It is artificial pigment, which is made by roasting cobalt sulphate, tin salts and silica [3]. It is a stable, inert pigment, it is not affected by light or by strong chemical agents and it has high refractive index [2].

2.3.6. Brown pigments

Umber pigments are earth pigments containing 5–20% MnO_2 and 45–70% Fe_2O_3 and may contain additives such as clay and quartz [10, 17]. Most umbers originally come from Cyprus. The name *umber* did not appear until the 16th century, before that the pigment was known as brown earth. The term *burnt umber* came into use around 17th century and the term *raw umber* before the 19th century. [17] Raw umber is a yellowish-brown earth pigment similar to yellow ochre. It contains goethite and besides that also MnO_2 and may contain additives such as quartz, calcite, dolomite etc [2, 17]. Burnt umber is made by

roasting the raw umber at dull red heat until the desired shade is obtained. Burnt umber is darker reddish-brown calcinated umber. The heating dehydrates the hydrated ferric oxide and the pigment becomes redder and warmer than raw umber. [2, 17]

Burnt sienna is prepared by calcinating raw sienna. During this process the iron hydroxide changes to iron oxide and the colour tone turns to warm reddish brown [2]. Burnt sienna is coloured primarily by hematite (Fe_2O_3) [17]. Burnt sienna differs from the burnt umber by the colour tone (is a little lighter) and by the significantly lower content of MnO_2 .

Brown ochre contains silica, clay, and a mixture of iron oxides along with small amounts of manganese dioxide. Brown ochre is nearly pure limonite [2]. Limonite (most commonly is the mineral species of goethite) is an amorphous light brown to brown colour tone mineral composed of hydrated iron oxide. Limonite is often found mixed with clay and sand in the form of a loose powder. It is often called umber or sienna, depending on its colour.

2.3.7. Black pigments

The most important black pigments that have been used since the earliest times are carbon-based black pigments: lamp black, charcoal or carbon black, graphite, vine black, ivory /bone black. *Carbon black* includes various pigments that are derived from the partial burning or carbonizing of natural gas, oil, wood and other organic materials. Almost none of these products are pure carbon, but all contain mineral impurities and hydrocarbons that are tarry by their nature [2]. For example *lamp black* (slightly bluish in colour) is nearly pure carbon, prepared by collecting carbon from a shooting flame when burning mineral oils, resins, pitch, and tar [2, 10]. *Vine black* (vegetable black), similar to charcoal, is prepared by carbonizing vine twigs or vine wood. *Bone black* (also *ivory black*; animal black) contains besides carbon also calcium phosphate (about 60%) and calcium sulphate (about 20%) [17]. Synthetic black pigment is iron oxide containing *Mars black*. Mars black is one of the mars pigments and its production dates back to the 1920s [3].

2.4. FT-IR spectroscopy

2.4.1. Infrared spectroscopy, general remarks

Infrared (IR) spectral region is in the region of electromagnetic spectrum between the visible and microwave regions. [22]. The infrared region of the electromagnetic spectrum extends from 14000 cm^{-1} to 10 cm^{-1} . The IR region is divided into three regions: the *near-infrared* [$14000\text{--}4000\text{ cm}^{-1}$ ($0.7\text{--}2.5\text{ }\mu\text{m}$)], *mid-infrared* [$4000\text{--}400\text{ cm}^{-1}$ ($2.5\text{--}25\text{ }\mu\text{m}$)] and *far-infrared* [about

400–10 cm^{-1} (25–1000 μm)] [23, 24] The most frequently used region for chemical analysis is the mid-infrared region. The far infrared region is useful for molecules containing heavy atoms such as inorganic and metal-organic compounds. Also the lattice vibrations in crystals are found in the far infrared region [22].

Infrared spectroscopy can also be called vibrational spectroscopy: infrared radiation lies in the same frequency range as the vibrational frequency of molecules. All molecules have specific frequencies at which they rotate or vibrate corresponding to discrete energy levels (vibrational modes). There are three types of vibrational modes in molecules: stretching, bending and torsional modes [22]. In order for a vibrational mode to be active in the infrared region, the vibration must cause a change in the permanent dipole moment of the molecule. The alternating electrical field (oscillating electromagnetic field) of the radiation interacts with fluctuations in the dipole moment of the molecule. If the frequency of the radiation matches the vibrational frequency of the molecule then radiation can be absorbed, causing a change in the amplitude of molecular vibration. [1, 23, 25] The IR spectrum provides energy/frequency information about the IR radiation absorbed or transmitted which can be related to molecular structure [1]. The absorption intensity depends on how effectively the infrared photon energy is transferred to the molecule [24]: the intensity of the absorption band is proportional to the square of the rate of dipole moment change during the vibration [1, 24].

In chemical analysis infrared spectroscopy is almost exclusively used as absorption spectroscopy. When infrared (IR) radiation is passed through a sample, the frequencies corresponding to the active vibrational modes of the molecules of the sample are absorbed, while other frequencies are transmitted through the sample without being absorbed by the sample [22, 25]. Radiation of various wavelengths can be absorbed depending on the chemical composition of the sample. The instrument output is an IR spectrum in which the intensity of IR radiation absorbed or transmitted is plotted on the y-axis against frequency or wavenumber (or wavelength) of the radiation on the x-axis [1]. In infrared spectroscopy, units called wavenumbers are normally used to denote different types of light. The wavenumber (cm^{-1}) is the number of waves in a length of 1 cm and is the reciprocal of wavelength in cm. [1, 23]

Based on its structure, each molecule produces a unique and characteristic IR spectrum. Each peak (or absorption band) in the IR spectrum is associated with a particular vibration mode (or combination of these) [26]. A given structural fragment (functional group) tends to absorb IR radiation at or nearly the same frequency (or wavenumber) in different molecules, regardless of the structure of the rest of the molecules [22, 23]. The position (i.e. frequency or wavenumber) of an absorption band depends on the mass of the atoms in the absorbing group, along with the strengths and angles of the connecting bonds [22]. Functional groups often have chemical properties that are the same (or similar) from molecule to molecule [23]. The vibrational frequencies for any

particular functional group are characteristic of that group. These characteristic vibrations are termed group frequencies and are used for the identification of different materials [22, 23]. The interpretation of infrared spectra involves the correlation of absorption bands in the spectrum of an unknown compound with the known absorption frequencies for types of bonds.

2.4.2. FT-IR spectrometers

Different designs of IR spectrometers exist. The prevalent type is the Fourier Transform Infrared Spectrometer (FTIR) [23]. The heart of an FT-IR instrument is a two-beam Michelson Interferometer controlled by a frequency of a visible light laser. In general terms FT-IR is a method of obtaining infrared spectra by first collecting an interferogram (time-domain spectrum) of the sample signal using Michelson Interferometer. Then a mathematical transformation called a Fourier Transform (FT) is applied on the interferogram to obtain the frequency domain spectrum. This spectrum is then compared to a reference spectrum measured without the sample (called background) to obtain the absorbance or transmittance spectrum. [1, 23, 24]

In the *FT-IR spectrometer*, all frequencies emitted by the IR source (e.g. globar, Nernst glower, heated metal filament) reach the detector (e.g. DTGS, MCT) simultaneously. This results in considerable time saving (the Fellgett advantage) and a high signal-to-noise ratio advantage (Jacquinot' advantage) over dispersive instruments [24]. Additionally, the wavenumber scale of an FT-IR instrument is reliably fixed by the wavelength of the controlling laser (Connes' advantage). This enables performing multiple scans and averaging the spectra to improve the signal-to-noise ratio.

IR spectroscopy has several advantages as a chemical analysis technique [23, 27]:

1. It is a universal technique: solids, liquids, gases, powders, polymers are all routinely analysed (can be analysed organic and also inorganic compounds).
2. IR spectra are information-rich: the peak positions, intensities, widths, shapes in a spectrum all provide useful information.
3. IR spectroscopy is a fast and inexpensive technique.

IR spectroscopy has also some disadvantages:

1. In the IR spectrum of the complex mixtures the absorption bands usually overlap and complex mixtures are generally impossible to analyse without reference IR spectra of pure materials.
2. IR spectroscopy is not a very sensitive technique.

A variety of sampling techniques are available for use with IR spectroscopy. The three most widespread of them are *transmission spectroscopy* (samples is solutions of KBr pellets), *Attenuated Total Reflectance* (ATR, samples without

any treatment can be used) and *diffuse reflectance spectroscopy* (DRIFTS) [1, 22, 24]. In recent years these techniques are increasingly used in the form of FT-IR microspectroscopy, also called FT-IR microscopy [28, 29]. Each of these techniques has its advantages and disadvantages. The technique selected depends on such factors as the information required, the nature of the material being analysed, also the size of the sample. In this dissertation the main sampling technique the attenuated total reflectance (ATR) is described in detail in the following section.

2.4.3. ATR-FT-IR spectroscopy, general aspects

Attenuated total reflectance (ATR) has been developed since 1959 [24] and is now probably the most common sampling technique in FT-IR spectroscopy. ATR generally allows qualitative and quantitative analysis of samples with little or no sample preparation. In principle it is a non-destructive technique. ATR is easily miniaturized so that high-quality spectra can be scanned of samples with a diameter far less than a millimetre.

Generally, in this technique the sample is placed in contact with the internal reflection element (IRE), and IR radiation from the source is directed into IRE at a certain angle (θ) that the light is totally reflected (see Figure 1) [27]. In order to observe total internal reflection the angle of the incident radiation θ must exceed the critical angle θ_c . This angle is a function of the real parts of the refractive indices of both the sample and the ATR crystal. The critical angle is defined as [24]:

$$\sin \theta_c = \frac{n_2}{n_1} \quad (1)$$

where, n_1 is the refractive index of the ATR crystal (or internal reflection element) and n_2 is the refractive index of the sample.

On internal reflection a part of the IR beam (so-called *evanescent wave*) penetrates into the sample to a depth of a few microns (d_p) and is partially (depending on the composition of the sample) absorbed by the sample. The result is a selective attenuation of the radiation at those wavelengths at which the sample absorbs [24, 30, 31]. So generally, due to a sample interaction with the penetrating beam, the beam loses energy at those wavelengths where the sample absorbs and thus an infrared spectrum is obtained.

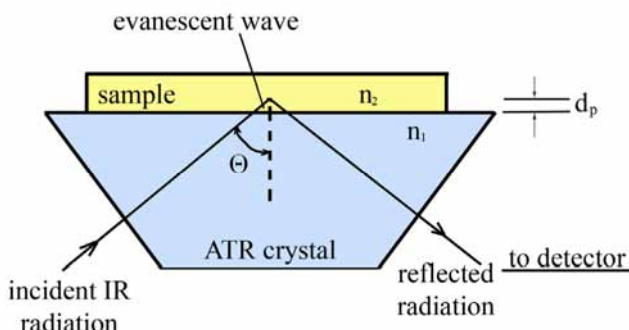


Fig. 1. Schematic representation of total internal reflection

Only the sample surface is analysed since the beam penetrates just a few micrometers into the sample [22]. The intensity of evanescent wave (or the radiation that penetrates into the sample) decays exponentially with distance from the surface of the ATR crystal. As the effective penetration depth is usually a fraction of wavelength, total internal reflectance is generally insensitive to sample thickness and permits thick samples to be analyzed [24]. Due to the low depth of penetration there must be good contact between the sample and the crystal surface. The internal reflection element (IRE) is also called ATR crystal.

High refractive index materials are chosen for the ATR crystal to minimize the critical angle. As the angle of incidence approaches the critical angle, the bands tend to broaden for lower wavenumbers and the minima are displaced to lower wavenumbers. The hardness of the material is also an important characteristic, because in order to obtain good contact with the sample the sample has to be strongly pressed against the crystal.

Table 1. Some ATR crystal materials [22, 27]

Material	Wavenumber range (cm ⁻¹)	Refractive index (n_1)	Comments
ZnSe	10 000–550	2,4	A hard and brittle crystal, water insoluble, resistant to most solvents, slightly soluble in acids
KRS-5	15 000–250	2,37	Soft crystal, water insoluble, soluble in bases, deforms under pressure
AgCl	25 000–400	2,0	very soft crystal that is insoluble in water, sensitive to light
Ge	20 000–600	4,0	A hard and brittle crystal, it is chemically inert
Diamond	40 000–200	2,4	Hard crystal, insoluble, inert, expensive. Very useful for high-pressure or corrosive work.

The ATR accessory consist of a mirror system that sends the source radiation through the attachment and a second mirror system that directs the radiation into the detector [27].

The depth to which the evanescent wave (or IR radiation) extends into the sample is defined as the depth of penetration (d_p). The depth of penetration (of the evanescent wave) is the distance from the crystal-sample interface where the intensity of the evanescent wave decays to 1/e of its original value. It can be estimated by the following eq [32, 33]:

$$d_p = \frac{\lambda}{2\pi n_1 \sqrt{\sin^2 \theta - (n_2 / n_1)^2}} \quad (2)$$

d_p – depth of penetration

n_1 – the refractive index of the ATR crystal,

n_2 – the refractive index of the sample,

λ – the wavelength of the IR radiation

θ – angle of incidence of the IR radiation

Changes in the angle of incidence of the infrared radiation have an effect on the depth of penetration and thus the ATR spectrum of a sample. In most devices it is not possible to vary the angle continuously, usually 30°, 45° and 60° are employed [34]. The angle of incidence must be chosen to exceed the critical angle in order to have internal reflection and produce an ATR spectrum.

ATR-IR spectra are similar, but not identical, to those obtained in the transmission mode [30]. It follows from equation (2) that in order to observe any ATR effect at all the refractive index of the sample (n_2) must be lower than that of the ATR crystal (n_1). If this condition is not fulfilled then internal reflectance will not occur – the light will be transmitted rather than internally

reflected in the ATR crystal. The depth of penetration (and thus the effective path length) is dependent on the wavelength and refractive index of the sample (given that n_1 and θ are constant).

The depth of penetration is proportional to wavelength, and therefore, an increasing depth of penetration is observed at higher wavelengths (lower wavenumbers) [22]. This leads to the increase of the intensity of the bands at low wavenumbers relative to high wavenumbers and is one cause of differences between the ATR-IR spectra and transmission IR spectra.

The refractive index also affects the depth of penetration of the evanescent wave into the sample. By increasing the refractive index of the ATR crystal (or IRE), the depth of penetration will decrease. This will decrease the effective pathlength and therefore decrease the absorbance of the spectrum. [32] Refractive index of a material is also a function of wavelength. In the IR spectral region the change of refractive index with wavelength is not monotonous. At certain wavelengths large nonlinearities are observed [35, 36]. Absorption bands that occur near such nonlinearities can be significantly different from those observed in the transmission mode. This is another cause of differences between IR spectra obtained using transmission and ATR modes.

In order to make the spectra obtained using ATR comparable to the transmission spectra, correction algorithms (so-called ATR correction) have been developed [35].

The ATR technique can be used for solids, liquids, powders, pastes, rubbers, textiles, paper etc. As mentioned above, the efficient depth to which the radiation penetrates into the sample is only few micrometers and is independent of sample thickness. So, ATR spectra can be obtained from many samples that cannot be studied in the transmission mode. These include for example samples that show very strong absorption, resist preparation of thin film, are characteristic only as a thick layers [27].

2.4.4. IR spectroscopy of inorganic pigments, general aspects

Many inorganic compounds – and most inorganic pigments – consist of metal cations combined with anions. With the exception of amorphous silica, the repeating set of molecular units in most inorganic compounds exists as semirigid matrix in a layered, or three-dimensional, crystalline structure (crystal lattice) [22].

The nature of the bonds in such compounds ranges from dominantly covalent (most oxides) to dominantly ionic (most salts). Because of the charges of the ions, the dipole moments of these bonds are high. Thus, the infrared bands of inorganic compounds are typically strong [23]. The atoms involved in the vibrations are usually heavier than in organic compounds, thus in general the absorption bands of inorganic materials occur at lower wavenumbers than the absorption bands of most organic materials [22]. The bands are also generally broader and are fewer in number (because the structures of inorganic

compounds are typically simpler than those of organic compounds) [22]. An inorganic molecule will have useful group vibrations in the mid-infrared region (4000 to 400 cm^{-1}) if it contains a polyatomic ion that contains light elements such as carbon, nitrogen, oxygen, sulphur [23]. Many inorganic pigments (both mineral and synthetic) contain polyatomic ions. The ions most frequently encountered are carbonate, sulphate, chromate and phosphate. In compounds of these types, the binding forces between atoms within the polyatomic ions are appreciably stronger than those between these ions and the metal cations in the crystal lattice [37].

Most inorganic substances (pigments, minerals, clays etc) are crystalline solids. The way in which atoms are arranged in a crystal affects the IR spectrum of a material [23]. This means that IR spectra can be used to distinguish between minerals with the same chemical composition but different structures.

The fundamental vibrations of crystalline compounds containing polyatomic ions may be divided into two classes: 1) internal vibrations of the atoms comprising a single ion; 2) external vibrations (or lattice vibrations), which are either restricted translations of the entire ion or rotations of the ion about a certain axis and do not cause distortions of the equilibrium bond distances and angles within the ion [37]. The lattice structure restricts many molecular motions: translational, rotational and also some vibrational motions. [22]. The external or lattice vibrations usually occur at low wavenumbers (below 300 cm^{-1}) in the far-IR region; the internal vibrations involving the covalently-bonded atoms of the polyatomic ion occur at higher frequencies in the mid-infrared region (but usually below 1500 cm^{-1}) [22, 37].

More complex inorganic compounds (carbonates, sulphates etc) have characteristic bands in the mid-IR region. However, it is usually impossible to tell from mid-infrared spectra of such compounds, which metal ions are present [23]. The cation will have only a slight effect on the position of the absorption bands of the complex anion. In general heavier cations will shift the band to lower frequency [22]. The effect is most prominent in the lower-wavenumber bending vibrations.

Infrared bands due to bonds involving metal atoms, such as metal-oxygen stretching and bending vibrations, appear below 400 cm^{-1} because of the large masses of the metal atoms [23]. Thus simple ionic compounds (for example oxides, sulphides, chlorides etc) will not produce any vibrations in the mid-IR range and their lattice vibrations occur in the far-IR region [22].

In Table 2 in Appendix 3 a general overview is presented of the vibrational frequencies (wavenumbers) for selected complex anionic groups that can be present in the composition of inorganic pigments.

In Appendix 4 some other techniques that are commonly used for analysing inorganic pigments are shortly described. They all have advantages and disadvantages as tools for analysing pigments and in most cases deliver the best results if combined with an independent technique (very often with IR spectroscopy).

3. ATR-FT-IR SPECTROSCOPY IN THE REGION OF 550–230 cm^{-1} FOR IDENTIFICATION OF INORGANIC PIGMENTS [I, II, IV]

3.1. Introduction

IR spectroscopy is one of the well-established methods of analysis in conservation science, because the vast majority of materials (for example: pigments, fillers, oils, waxes, resins and proteins) absorb infrared radiation. The actual interpretation of infrared spectra is conducted by comparing them with reference spectra. IR spectra of complex paint materials are almost impossible to analyse without reference IR spectra of the respective materials [IV].

A number of IR spectral collections of different materials have been published [38–41] and there are also available several IR spectral databases on the World Wide Web [IV]. A number of excellent commercial IR databases available, either on the Internet for example FTIRsearch.com/RAMANsearch.com⁴, Bio-Rad Sadtler's HaveItAll IR⁵, FDM Reference Spectra Databases⁶, S. T. Japan Spectral Library⁷ etc. Most of the databases are, however, quite costly. There are several free IR spectral databases available on the World Wide Web for example IRUG⁸, SDBS⁹, The NIST Webbook¹⁰, IR Spectra at Sigma-Aldrich¹¹ etc, which may contain, some more (for example IRUG) than the others, also conservation and painting related materials. The main limitations that are quite general for the available databases are that the majority of them focus on organic compounds and in most cases the wavenumber range for spectra start from 400 cm^{-1} or even higher. The IRUG database is the largest conservation-relevant database of IR spectra. However the wavenumber range of spectra in IRUG is mostly 4000 to 600 cm^{-1} and in few cases 4000 cm^{-1} to 500 cm^{-1} . [IV] This is a serious limitation because there

⁴ FTIRsearch.com/RAMANsearch.com is available on the Internet at <http://www.ftirsearch.com/>

⁵ Bio-Rad Sadtler's HaveItAll IR is available on the Internet at <http://www.knowitall.com>

⁶ FDM Reference Spectra Databases is available on the Internet at <http://www.fdm spectra.com/>

⁷ S. T. Japan Spectral Library is available on Web Internet <http://www.stjapan.de/>

⁸ IRUG (the Infrared and Raman Users Group) available on the Internet at <http://www.irug.org/>

⁹ SDBS – Integrated Spectral Data Base System for Organic Compounds. Database at http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi?lang=eng

¹⁰ The NIST (The National Institute of Standards and Technology) Webbook available at <http://webbook.nist.gov/>

¹¹ Sigma-Aldrich Catalogue on the Internet available at <http://www.sigmaaldrich.com/>

are many inorganic pigments that have characteristic absorption bands below 500 cm^{-1} .

So, it appears that generally it is difficult to find reference IR spectra of inorganic pigments that have absorption bands in the far-infrared region (below 500 cm^{-1}).

According to the available literature quite some inorganic pigment studies with FT-IR [5, 15, 21, 28, 31, 37, 42–46] have been carried out, usually in the mid-IR region ($4000\text{--}400\text{ cm}^{-1}$). Also ATR-FT-IR spectroscopy has been widely applied to analysis of works of art with the aim of elucidating materials usage [20, 29, 31, 36, 47, 48]. This instrumental technique is very suitable for analysing samples taken from the artefacts because it can be applied as a non-destructive method and micro-ATR accessories make it possible to obtain good spectra from very small samples and samples can be reused many times. Those characteristics are very important because most of the samples that are taken from the artist objects are very small and often very valuable.

The general features of the IR spectra of inorganic pigments, as compared to organic compounds, are: (1) the absorption bands of inorganic pigments are generally broader, (2) are fewer in number and (3) often occur at lower wavenumbers [38]. Although the inorganic pigments (for example ultramarine, lead white, barium white, etc) that contain complex anions (carbonates, sulphates, silicates, etc), have characteristic absorption bands in the mid-IR region ($4000\text{--}400\text{ cm}^{-1}$), there are many pigments that either do not absorb in that region at all (cinnabar, cadmium red, etc) or have absorptions that are at the low wavenumber end of the region and are not characteristic enough for pigment identification (different iron oxide pigments, zinc white, etc.) [22, 38]. Those inorganic pigments that contain simple anions like oxides, sulphides, etc, have often no vibrations in the mid-IR range, and their lattice vibrations are found in the far-IR region [22, 49].

Furthermore, in the IR spectra of paint samples the intense absorptions of other paint components (fillers, organic binder etc) in the mid-IR region complicate identification of pigments. In the mid-IR region, in the complex paint spectrum are very often absorption bands overlapped. Good example is the wavenumber region of $1200\text{--}900\text{ cm}^{-1}$, where silicates, sulphates and phosphates give broad bands, also practically all compounds containing C-O bonds (present in almost all binder materials) absorb in that region. For example, if a sample of light blue paint contains kaolin (or other silicate materials), barium sulphate (to make the colour tone lighter) as a fillers and oil as a binder then this valuable wavenumber region is almost fully blocked by the absorption lines of all the mentioned compounds and identification of the blue (silicate containing) pigment in the mid-IR range is almost impossible.

Due to these reasons, the use of ATR-IR for pigment identification in the mid-IR range has been distinctly more limited than for identification of organic binder materials.

In contrast, in the low wavenumber region (below 500 cm^{-1}) most of the above mentioned materials do not absorb. However, traditionally this low wavenumber range has been inaccessible for routine ATR-FT-IR spectroscopy. This is due to the low intensity of the common IR Sources in this region, the necessity to use more delicate CsI optics in the spectrometer and the opacity of most of the common ATR materials below 500 cm^{-1} . Nevertheless there are currently commercially available ATR accessories, including micro-ATR accessories that, when installed on a spectrometer with CsI optics, permit to access infrared region of 550 to 230 cm^{-1} .

Two main problems emerge when determining pigments with ATR in the low wavenumber region. [I, II]

The first problem is related to the physical basis of the ATR phenomenon that is described above (see chapter 2.4.3). Briefly, in order to observe any ATR effect the refractive index of the sample must be lower than that of the crystal. In addition, the depth of penetration (and thus the effective pathlength) is dependent on the wavelength and refractive index of the sample. Given that many pigments have high refractive indices (to have high hiding power) and the region of 550 to 230 cm^{-1} corresponds to the longest wavelengths in the IR spectrum it is difficult and often impossible to obtain good ATR-FT-IR spectra from pure pigments due to too high absorption of radiation. [I]

In this thesis it is demonstrated that this problem can be overcome by preparing reference samples of the pigments by mixing them with some matrix, e.g. linseed oil. Mixing pigments with a linseed oil allows obtaining spectra of much higher quality in the low wavenumber range. Also, in samples from actual paintings the pigments are always mixed with a binder (very often linseed oil).

The second problem is the overlapping of the absorption bands of the pigments with the absorptions of the very important filler material CaCO_3 (intense absorption band at 300 cm^{-1}) and also with the absorptions of some other pigments (most importantly zinc white). To study calcium carbonate interference in the low wavenumber range some pigments were mixed with linseed oil and chalk (CaCO_3). The interference from chalk when determining some pigments (for example zinc white, lithopone etc) was observed also in the analysis of real samples in the case study section (see chapter 4.3.5).

In this dissertation the historically most widespread inorganic red, white, yellow, blue, green, brown and black pigments are examined and their identification with ATR-FTIR spectroscopy, in particular, using the low wavenumber region, is discussed. This work provides a comprehensive overview of the pigment identification possibilities using ATR-FT-IR as well as a collection of reference spectra in the low wavenumber range (550 – 230 cm^{-1}) and is expected to be a useful reference material for conservation practitioners and material scientists. The usefulness of ATR-FT-IR in the region of 550 – 230 cm^{-1} for identification of pigments is demonstrated by 5 case studies on historic objects.

3.2. Experimental

3.2.1. Equipment

IR spectra were registered on Nicolet 6700 FT-IR spectrometer with the “Smart SplitPea” diamond micro-ATR accessory. The spectrometer has DLaTGS Detector, Vectra Aluminum Interferometer and sealed and desiccated optical bench with CsI optics. Smart SplitPea is a horizontal single-bounce ATR microsampling accessory with angle of incidence of 45° and sampling area diameter of $500\ \mu\text{m}$. It has a diamond ATR crystal (index of refraction 2.418) and calibrated pressure applicator with a 50x viewing microscope. The spectral range available with this equipment is $4000\text{--}225\ \text{cm}^{-1}$. In order to protect the spectrometer from atmospheric moisture it is constantly purged with dry air.

The wavenumber scale of the spectrometer is fixed by the constant wavelength (632.9 nm) of the helium-Neon laser and does not need regular calibration. Check of the wavenumber scale was done occasionally with polystyrene film.

3.2.2. Measurements of ATR-FT-IR Spectra of the reference samples [I, II]

The following spectrometer parameters were used: resolution $4\ \text{cm}^{-1}$, spectral range $225\text{--}4000\ \text{cm}^{-1}$, number of scans: 512, Level of Zero filling: 0, Apodization: Happ-Genzel.

All the self-made reference samples were measured the same way. Small amount (ca $1\ \text{mm}^2$) of reference sample was taken from the glass plate with a scalpel, a sample piece was placed on the ATR crystal and pressure equivalent to 0.5 to 3 kg (i.e. force from 4.9 to 29.4 N; sampling area diameter is $500\ \mu\text{m}$) was applied. The pressure was increased gradually, while monitoring the appearance of the spectrum. When sufficient intensity was reached then the pressure was fixed and spectrum was scanned. The effect of pressure on the spectra is twofold. With too low pressure the contact between the sample (especially if it is a hard material) and the ATR crystal may be insufficient leading to low intensity of the spectrum. On the other hand, in the case of soft samples too high pressure can lead to squeezing the sample into a too thin layer and appearance of the absorption lines of the pressure applicator (sapphire in our case) in the spectrum. In general lower pressures were used for softer paint layers and higher pressures for harder paint layers.

In the ATR spectra the band maxima are slightly shifted from the positions of the same maxima in the transmission spectra. Bands are shifted to lower wavenumber (it is caused by abrupt changes of the sample's refractive index). Most of the reference spectra available in literature have been measured in the

transmission mode [38]. Furthermore, ATR spectra registered using different crystal materials are also different. Therefore ATR-correction was carried out for all the spectra with the aim of obtaining as transmission-like spectra as possible in order to allow better comparison with transmission spectra.

In Fig. 2 is the IR spectrum of chalk is presented with and without ATR correction. In the upper IR spectrum where ATR correction is not carried out is possible to see that CO_3^{2-} anions C-O stretching band is at 1387 cm^{-1} and C-O bending bands at 870 cm^{-1} and 272 cm^{-1} . After the ATR correction was carried out the absorption bands are shifted from the higher wavenumber (see lower IR spectrum): CO_3^{2-} anions C-O stretching band is now at 1425 cm^{-1} and C-O bending bands at 874 cm^{-1} and 299 cm^{-1} .

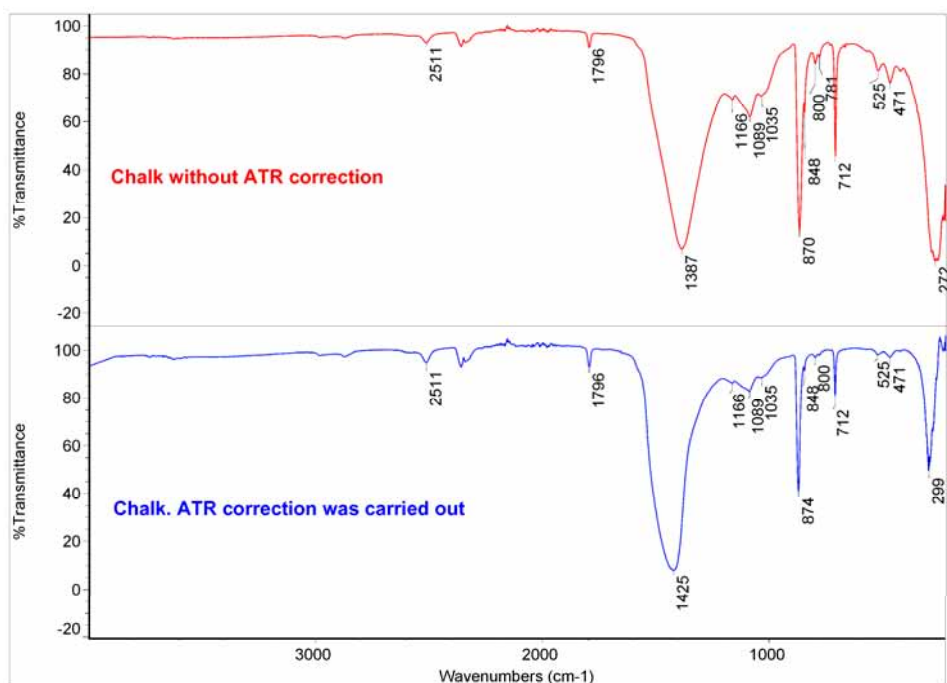


Fig. 2. IR spectra of chalk with and without ATR correction

The ATR correction algorithm [35] recalculates the spectrum into an approximation of the respective transmission spectrum. It uses four parameters: the refractive index of the crystal, the angle of incidence of the radiation, number of bounces and the refractive index of the sample. The sample refractive index is difficult to determine. Samples in cultural heritage research are mostly very small, inhomogeneous and have seldom well-defined composition. In this work the reference samples of the pigments were suspended in the linseed oil matrix and the unknown samples all had oil as one

of the binder materials. Therefore was used the refractive index 1.48 of linseed oil whenever possible. In few cases use of this refractive index led to appearance of “derivative-shaped” min-max peaks in the spectrum. In these cases refractive index in the vicinity of 1.48, such as 1.46, 1.50, etc was used, which did not lead to appearance of these min-max peaks, as suggested by the author of the algorithm [35].

With some complex samples (paint samples) the ATR correction may sometimes give distorted IR spectra. This is because with the complex mixtures it is difficult to specify the parameters that are needed to perform ATR correction.

3.2.3. Measurements of the different paint samples from historic objects

Measurements of ATR-FT-IR Spectra of the paint samples from historic objects (see case studies in the section 4.3)

The reference samples and the paint samples from historic objects were measured the same way and the same spectrometer parameters were used. So, for measuring IR spectra a small sample piece was placed on the ATR crystal and pressure equivalent to 0.5 to 3 kg was applied. Analysed sample pieces were all different in shape and size.

Confirmation of the pigment assignments using SEM-EDS

All pigment assignments made for the historic object samples using the ATR-IR spectra were independently confirmed using the SEM-EDS method.

Paint samples from the tabernacle of the altar of the Church of the Holy Spirit, pink colour sample from the Ludwich von Tolli coat of arms and paint samples from the unknown artist painting were analyzed with a scanning electron microscope -Zeiss DSM940 equipped with an energy dispersive X-Ray detector SAMx 10 mm² SDD (Silicon Drift Detector). The colour sample was fixed on a vacuum-clean double-sticker layer. Magnification was 80–100, the energy of probe electrons was 20 keV. Measurements were done at University of Tartu in Department of Geology.

Red paint samples from the Biestram coat of arms (from the St Mary's Cathedral of Tallinn) was analysed with LEO Supra 35 SEM equipped, with Röntec EDX XFlash 3001 detector. Red paint sample was coated with carbon. Energy of probe electrons was 20 keV. Measurement was done in the Institute of Materials Science of Tallinn University of Technology.

Paint samples from the altar and pulpit of St. Mary church in Vigala were carried out with a scanning electron microscope – micro-analyser JXA-840

(JEOL) equipped with an energy dispersive X-Ray spectrometer (Voyager, Noran), below denoted as SEM-EDS system. Energy of probe electrons was 20 keV.

Before the SEM-EDS analysis cross-sections were prepared from the paint samples. To prepare paint cross-sections the paint sample piece are embedded entirely in a Technovit 2000 LC polymer (single-component mono- and difunctional methacrylate, 2000 LC, Heraeus Kultzer GmbH). Cross-sections of the samples were coated with a thin platinum film using magnetron sputtering, which increased sample surface conductivity and thereby prevented their charging. As a rule different layers of cross-sections were analysed separately. Measurements were done at University of Tartu in Institute of Physics.

3.2.4. Reference samples and their preparation

In this work were used altogether 47 different inorganic red, white, yellow, blue, green, brown and black high quality commercial pigments of 7 different companies products. Table 2 lists common and C.I. generic names¹² of the used pigments, their origin and some of their characteristics.

Many inorganic pigments have quite high refractive indices to have high hiding power. So due to the nature of the ATR phenomenon the high refractive indices of several pigments (for example, cinnabar, chromium green, cadmium red, orpiment, red earths) together with the long wavelengths in the 550–230 cm^{-1} region lead to distorted spectra if scanned from pure pigments. For example cinnabar, chromium green, cadmium red, orpiment and red earths all have higher refractive indices than refractive index of the diamond ATR crystal ($n_D=2.418$), and they all have distorted spectra (see refractive indices of inorganic pigments in Table 1 in Appendix 2). In Fig. 3 is presented example of distorted IR spectrum of pure cinnabar. In the IR spectrum it is possible to see that the baseline is much distorted and also not all the bands appear in the low wavenumber (absorption near 273 cm^{-1}). Also in the low wavenumber region appears intensive negative maximum.

All the iron oxide containing pigments (red and yellow ochres) have relatively high refractive indices (main minerals like goethite $n_D = 2.36$ (average) and hematite $n_D = 2.87$ (average)). In fig. 4 the IR spectrum of Caput Mortuum reddish is presented, this is a hematite-containing red pigment. In the IR spectrum it is possible to see that the baseline is distorted and band in the range of 300–225 cm^{-1} is not well defined.

¹² The C.I. (Colour Index) Name is an internationally recognized name assigned to a particular colorant. The C.I. Name consists of the category (type of dye or pigment), general hue and serial number assigned, based on its chemical constitution. Such information is used by the paint industry to identify ingredients and is also often included on the labelling of artists' colours or associated product information [3].

Table 2. White, yellow, red, green, blue, brown, black pigments that are used in the investigation.

Pigment name	C.I. Name	Source of the pigments
WHITE PIGMENTS		
Lithopone	Pigment White 5	Kremer 46100
Lead white (Flake white)	Pigment White 1	Maimeri ¹³ 012
Zinc white (lead free)	Pigment White 4	Kremer 46300
Titanium white (mineral: rutile)	Pigment White 6	Kreidezeit ¹⁴
Chalk	Pigment White 18	Tempera Oy ¹⁵
Gypsum	Pigment White 25	Tempera Oy
YELLOW PIGMENTS		
Massicot (contains besides Massicot also Litharge ¹⁶)	Pigment Yellow 46	Kremer 43010
Cadmium yellow medium	Pigment Yellow 35/37	Kremer 21040; Maimeri
Naples yellow, light	Pigment Yellow 41	Kremer 4310
Yellow Ochre	Pigment Yellow 43	Kreidezeit
Italian Gold ochre, light (contains iron oxide and minerals)	Pigment Yellow 43	Kremer 40220
Amberg yellow (contains iron oxide and minerals)	Pigment Yellow 43	Kremer 40280
Satin Ochre (contains iron oxide and minerals)	Pigment Yellow 43	Kremer 40260
Orpiment, genuine	Pigment Yellow 39	Kremer 10700
Barium yellow	Pigment Yellow 31	Kremer 43940
Strontium yellow	Pigment Yellow 32	Kremer 4392
RED PIGMENTS		
Cinnabar (or Vermilion)	Pigment Red 106	Kremer ¹⁶ 10625
Red lead	Pigment Red 105	Kremer 42500
Cadmium red no.1 light	Pigment Red 108	Kremer 21120
Natural red earth (or red ochre)	Pigment Red 102	Kremer 40500
Caput Mortuum reddish	Pigment Red 102	Kremer 48700
Venetian Red	Pigment Red 102	Kremer 40510
Pompeii red	Pigment Red 102	Kremer 40440

¹³ Detailed information about used pigments of Maimeri company is available at <http://www.maimeri.it/index.asp>

¹⁴ In the table is Kreidezeit Naturfarben GmbH name shortened in Kreidezeit. Detailed information about used pigments is available at <http://www.kreidezeit.de/>

¹⁵ Detailed information about used pigments of Tempera Oy is available at <http://www.tempera.com/>

¹⁶ In the table is Kremer Pigmente GmbH & Co name shortened in Kremer. Detailed information about used pigments is available at <http://www.kremer-pigmente.de>

Table 2. Continue

Pigment name	C.I. Name	Source of the pigments
GREEN PIGMENTS		
Cobalt green	Pigment Green 19	Kremer 4410
Malachite natural standard	Pigment Green 39	Kremer 10300
Chromium oxide (chrome oxide green)	Pigment Green 17	Maimeri 336; Kreidezeit
Viridian green	Pigment Green 18	Kremer 44250
Verdigris	Pigment Green 20	Kremer 44450
Bohemian green earth (<i>Iron-rich clay*</i>)	Pigment Green 23	Kremer 40810
Vagone green earth (<i>green earth with additives*</i>)	Pigment Green 23	Kremer 41750
Raw umber greenish dark	Pigment Brown 8	Kremer 40630
BLUE PIGMENTS		
Egyptian blue	Pigment Blue 31	Kremer 10060
Ultramarine blue, deep	Pigment Blue 29	Schmincke ¹⁷
Lapis lazuli		Kremer 10520
Smalt	Pigment Blue 32	Kremer 10000
Prussian blue	Pigment Blue 27	Maimeri 402
Azurite (natural)	Pigment Blue 30	Kremer 10200
Cobalt blue	Pigment Blue 28	Kremer 4514
Cobalt blue dark	Pigment Blue 74	Kremer 45700
BROWN PIGMENTS		
Burnt umber (calcined natural iron oxide)	Pigment Brown 7	Winsor & Newton ¹⁸
Burnt umber	Pigment Brown 7	Sennelier ¹⁹ 202
Brown ochre	Pigment Brown 6	Kremer 11650
Fawn Ochre (light greenish brown)	Pigment Yellow 43	Kremer 40241
BLACK PIGMENTS		
Charcoal	Pigment Black 10	Kremer 47800
Bone black	Pigment Black 9	Kremer 47100
Ivory black (<i>calcined animal bones</i>)	Pigment Black 9	Winsor & Newton
Vine Black (<i>pure plant black</i>)	Pigment Black 8	Kremer 47000
Mars black	Pigment Black 11	Maimeri 777

* The exact composition of these pigments depends on the origin and the producer of the pigment. Further composition information is available from the producer.

¹⁷ Detailed information about used pigment of Schmincke company is available at <http://www.schmincke.de>

¹⁸ Detailed information about used pigments of Winsor & Newton is available at <http://www.winsornewton.com/>

¹⁹ Detailed information about used pigment of Sennelier company is available at <http://www.sennelier.fr/>

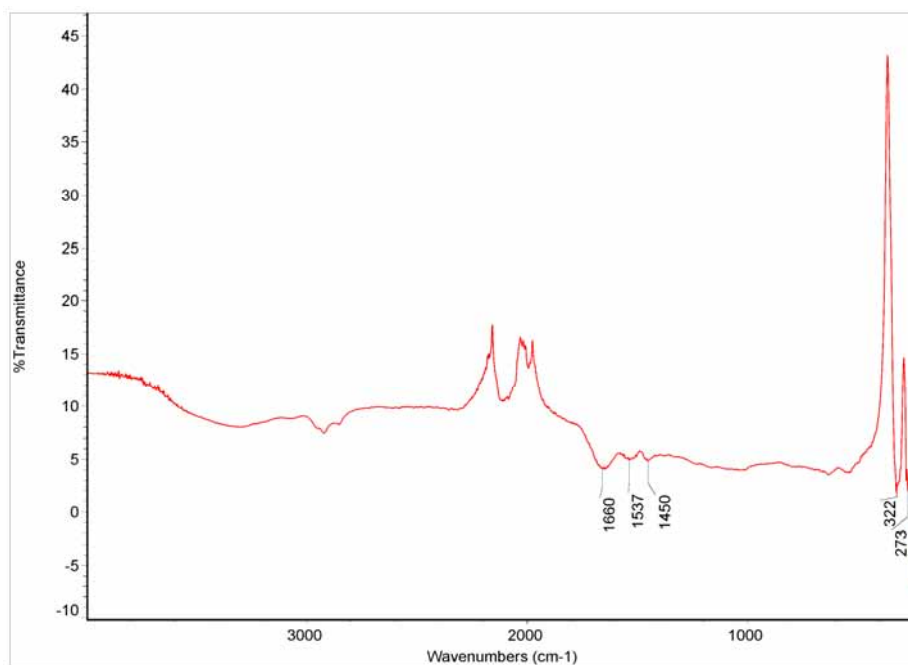


Fig. 3. ATR-IR spectrum of pure cinnabar (ATR-correction was not carried out)

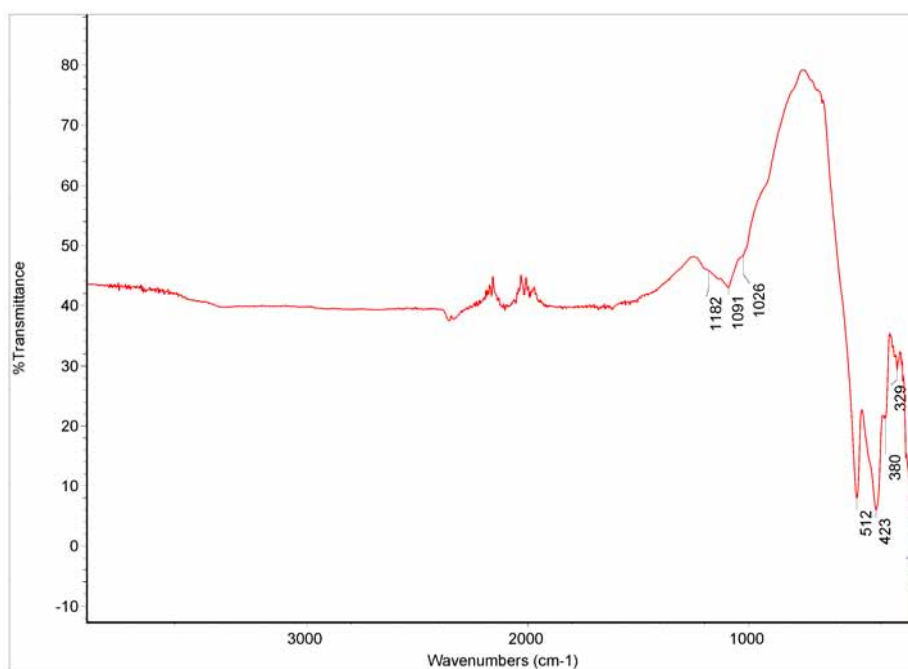


Fig. 4. ATR-IR spectrum of pure Caput Mortuum reddish (ATR-correction was not carried out)

Also there are some pigments (for example, gypsum, chalk, verdigris, smalt) that have quite low refractive indices (1.46–1.66). Due that gypsum and chalk are usually used as primers and fillers. These pigments of low refractive indices have normal ATR spectra (see fig. 2) without distortion in the spectrum.

Solution for the distorted spectra and IR spectra quality improvement in the low wavenumber range is to mix the pure pigment powder with some matrix. Mixing matrix material with the powdered pigment decreases the refractive index of the mixture and makes it possible to get better quality IR spectra whereby also the absorption bands in the low wavenumber range ($550\text{--}230\text{ cm}^{-1}$) are well visible.

In real paint samples the pigments are never pure, but also mixed with some binder material, very often linseed oil (the most common binder material in historic paintings). Therefore linseed oil (refractive index is $n_D^{20} = 1.480$) is a good choice to use it as matrix material for preparation of reference samples of pigments for identification.

Linseed oil is one of the drying oils and most widely used as a binder in paintings. IR spectrum of the used linseed oil is presented in Fig. 5 (interpretation of the IR spectrum of the linseed oil is given in Table 3 in Appendix 5).

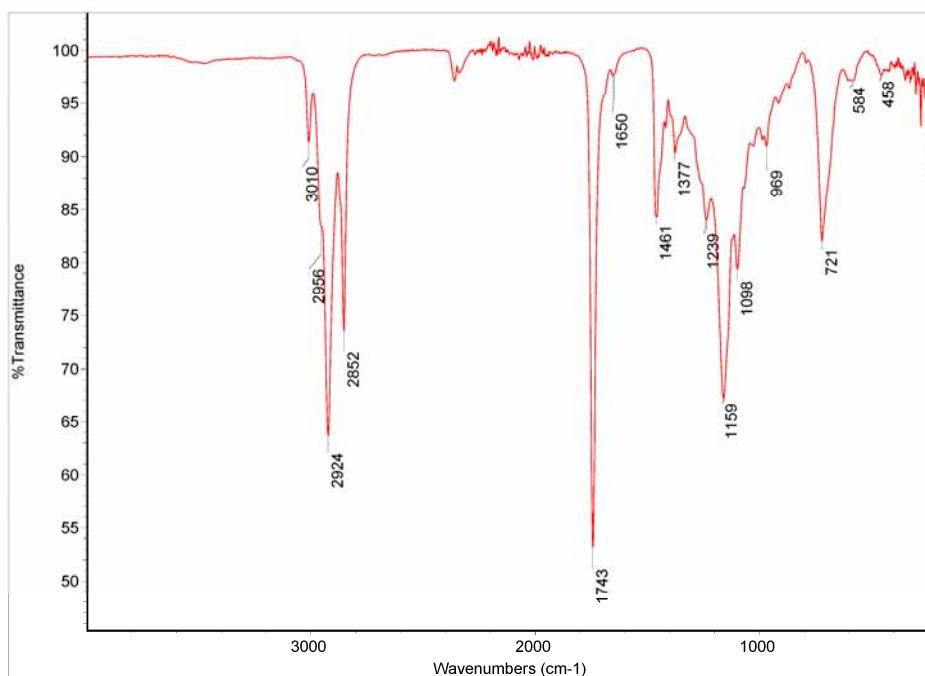


Fig. 5. IR spectrum of linseed oil (product of Distrei Group OÜ)

Linseed oil has one very weak absorption line in the range of $550\text{--}230\text{ cm}^{-1}$ (band at 458 cm^{-1}), its intensity is very low and it does not interfere because in the mixtures it is covered by more intensive absorption bands of the pigments. So it may be said that linseed oil does not have any characteristic intensive absorption bands in the range of $550\text{--}230\text{ cm}^{-1}$ and is suitable matrix material. Preparation of the reference paint layers (mixtures) was done as follows:

Pigment + linseed oil

A small weighed amount of the powdered pigment was placed on a glass plate, linseed oil was added with a pipette and then the components were thoroughly mixed on the glass plate with the small palette-knife. The mass ratio of the pigment and linseed oil ranged from 3:1 to 1:3 and was in most cases near 1:1 (the mass ratio is not critical for the quality of spectra). Each pigment absorbs linseed oil differently: some pigments need more binder than others. Eventually drying linseed oil with pigment forms a cohesive paint paste. The paint paste was then spread with the small palette-knife on the glass plate and was left for drying on the glass plate at room temperature ($20\text{--}23^\circ\text{C}$). Drying time of the paint layer depends on the pigment, thickness of the paint layer also on temperature, humidity, illumination conditions, etc. The paint layers were dried until they were dry to the touch, which took 3–6 days. After that IR spectrum of the paint layer was recorded. Some measurements were also done few weeks to couple of months after preparing the paint layer. No noticeable changes in the pigment absorptions were observed. The thickness of the layers varied from approximately $20\text{ }\mu\text{m}$ to $100\text{ }\mu\text{m}$.

Pigment + chalk (CaCO_3) + linseed oil.

Identification of pigments (oxides, sulphides) in paint samples taken from artefacts in the low wavenumber region is often complicated by the presence of chalk (CaCO_3 gives intense absorption band at 300 cm^{-1}). To study this interference some red pigments was mixed with linseed oil and chalk.

Small weighed amounts of the red pigment and chalk were placed in the ball mill and were thoroughly mixed for about 2 minutes. Then a small weighed amount of that mixture was placed on a glass plate and approximately equal weighed amount of linseed oil was added with the pipette and then the components was thoroughly mixed on the glass plate with the small palette-knife. The paint paste (mixture of pigment, chalk and linseed oil) was then spread with the small palette-knife on the glass plate and was left for drying on the glass plate at room temperature ($20\text{--}23^\circ\text{C}$). After few days the IR spectrum of the paint layer was measured.

Mass percentages of the pigments mixed with linseed oil and pigments mixed with linseed oil and CaCO_3 are given in Tables 4 and 5 in the Appendix 6.

In Figs. 6 and 7 the IR spectra of pure cinnabar and Caput Mortuum reddish with the IR spectra of same pigments mixed with linseed oil are compared. With these IR spectra baseline and ATR-correction was not carried out.

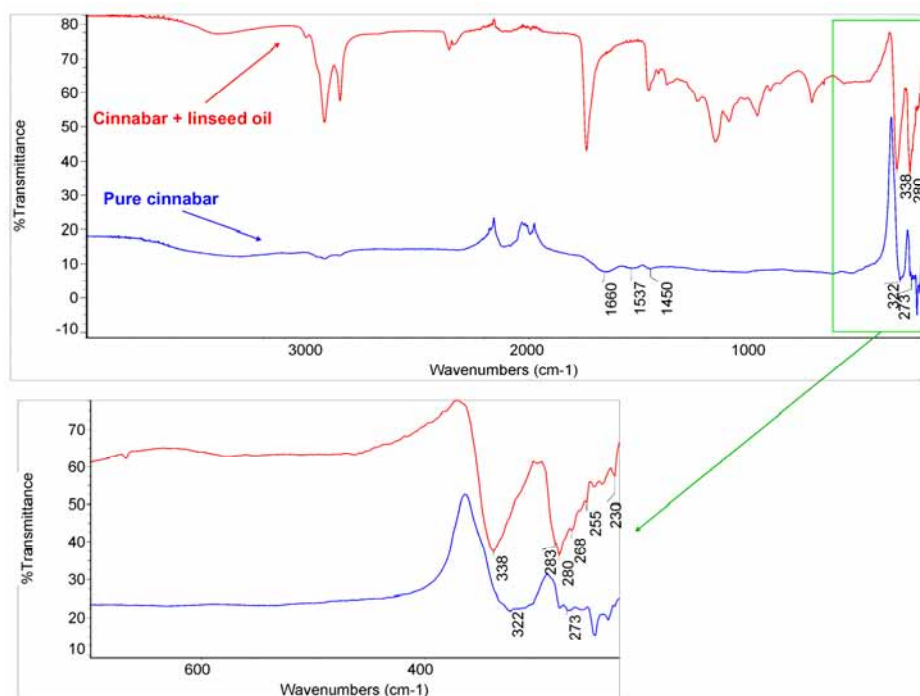


Fig. 6. IR spectra of pure cinnabar and cinnabar mixed with linseed oil

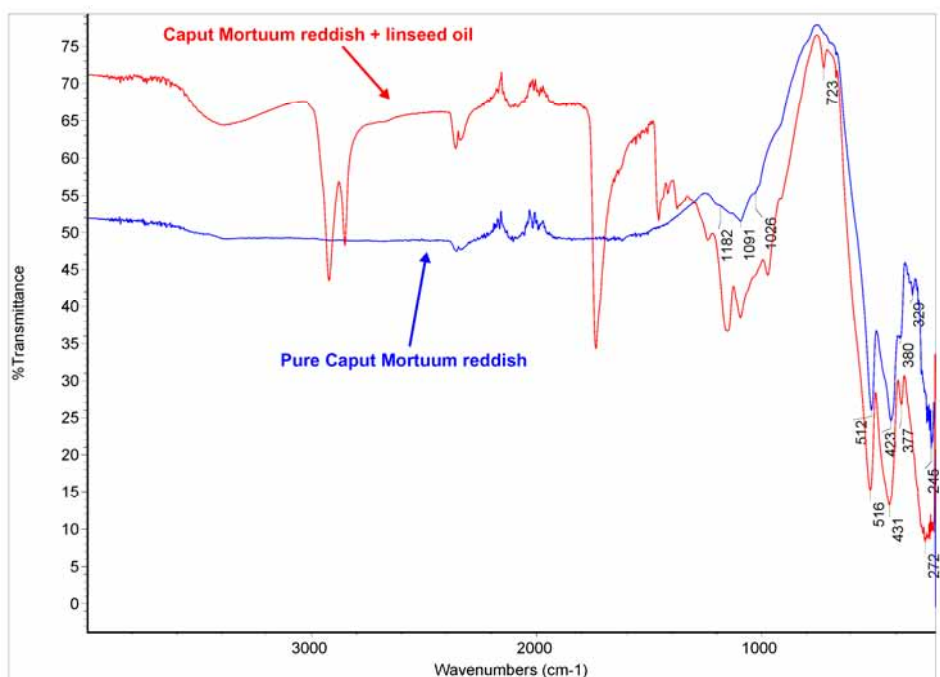


Fig. 7. IR spectra of pure Caput Mortuum reddish and Caput Mortuum reddish mixed with linseed oil

In Figs. 6 and 7 it is possible to see that IR spectra of pigments mixed with linseed oil have much better quality than IR spectra of pure pigments. In these IR spectra bands in the far-IR region are slightly shifted to the higher wavenumber.

4. RESULTS AND DISCUSSION

4.1. IR spectra of pigments in the region of 550–230 cm⁻¹

All the recorded IR spectra of the inorganic pigments are classified by the colour tone and are observed and analysed together. IR spectra of the same colour tone are presented in the same figure. Only the low wavenumber region of the spectra is presented.²⁰

The IR spectra of 47 red, white, yellow, green, blue, brown, black pigments in the linseed oil matrix in the low wavenumber range are presented in Figs. 8–12, 14, 15, 17 and 18. The characteristic bands of all the analysed pigments in the region of 550–230 cm⁻¹ are listed in Table 3.

Table 3. Characteristic bands wavenumbers of all the analysed pigments in the region of 550–230 cm⁻¹.

Pigment name	Characteristic bands wavenumbers (cm ⁻¹) in IR spectra ^a
WHITE PIGMENTS	
Lithopone	311, 300, 284
Lead white	414, 393 , 363
Zinc white	472, 431
Titanium white (rutile)	506, 392 , 348, 308 , 272 , 240
Chalk	305, 231
Gypsum	457, 420, 278, 248
YELLOW PIGMENTS	
Yellow Ochre	536, 504, 466, 430, 397, 368, 342, 275
Amberg yellow	524, 465, 423, 397, 372, 280 , 268, 237
Satin Ochre	461, 409, 288, 271, 266, 243
Italian Gold ochre, light	463, 407 , 379, 300 , 284, 275 , 251, 239, 233
Cadmium yellow medium	<i>Maimeri</i> (Cadmium yellow medium): 274, 262, 249 ; <i>Kremer Pigmente</i> (Cadmium yellow No.6 medium): 261, 247
Naples yellow, light	462, 397, 340 , 229
Massicot, Litharge	503, 495 , 484, 468, 375, 353, 289, 279 , 268, 255, 243, 230
Orpiment, genuine	541, 526, 492, 480, 459, 392, 380, 363 , 353, 346 , 312, 295, 282 , 266, 256, 245, 239 , 228
Barium yellow	418, 391, 374, 336
Strontium yellow	445, 428, 407, 392, 378, 345, 337

²⁰ Detailed discussion of the vibrational modes of the compounds is outside of the scope of this thesis and therefore they are discussed only briefly, in cases where data are available.

Table 3. Continue

Pigment name	Characteristic bands wavenumbers (cm⁻¹) in IR spectra^a
RED PIGMENTS	
Cinnabar (or Vermilion)	342, 284 (shoulder at 280)
Red lead	528, 454, 381, 326 (shoulder at 318), 280
Cadmium red	300–230 (broad band in that region)
Natural red earth (or red ochre)	537, 467, 431, 396, 366, 344, 276
Caput Mortuum, reddish	528, 458, 379, 294
Venetian Red	460, 422, 377, 354, 301, 237
Pompeii red	534, 466, 428, 318, 272
GREEN PIGMENTS	
Cobalt green	409, 327
Malachite	523, 501, 464, 427, 355, 322, 295, 283, 264, 251
Chrome oxide green	<i>Maimeri and Kreidezeit have similar bands: 571</i> (broad band in that area), 445, 416, 307
Viridian green	559, 496, 422
Verdigris	521, 460, 374, 327, 288, 271, 253, 239, 229
Bohemian Green earth	497, 462, 437, 397
Vagone Green Earth	519, 498, 465, 415, 315, 278, 246
Raw umber greenish dark	463, 404, 310, 303, 274, 258, 234
BLUE PIGMENTS	
Egyptian blue	521, 483, 424, 343, 281, 237
Ultramarine blue, deep	445
Lapis lazuli	507, 446, 410, 391, 332, 309, 295, 251, 241
Smalt	456, 395, 365, 293, 280, 263
Prussian blue	497, 455, 385, 259, 245
Azurite	532, 492, 457, 450, 403, 343, 308, 303, 252, 238
Cobalt blue	564 (broad band in that area), 480, 431, 383
Cobalt blue dark	549, 495, 235
BROWN PIGMENTS	
Burnt umber (<i>Winsor & Newton</i>)	528, 454, 396, 320
Burnt umber (<i>Sennelier</i>)	527, 464, 426, 340, 307, 290, 265, 246
Brown ochre	492, 432, 420, 396, 378, 332, 289, 276, 263, 244
Fawn Ochre	516, 462, 422, 395, 370, 287, 276, 261, 243
BLACK PIGMENTS	
Charcoal	In that region is no absorption bands
Bone Black	469, 348, 289, 273, 253, 239
Ivory Black	468, 344, 289, 274, 243
Vine Black	537, 470 (these bands may belong to this pigment)
Mars black	556 (broad band in that area), 370, 343, 330, 307, 288, 263, 241

^a The most characteristic bands for identification of pigments in the IR spectra of real-life paint sample layers are given in bold.

4.1.1. IR spectra of white pigments

Altogether 6 white pigments were analyzed. The IR spectra of chalk, zinc white, gypsum, lead white, titanium white (rutile) and lithopone in the linseed oil matrix are presented in Fig. 8. These pigments are the most important white pigments (some of them are also important fillers).

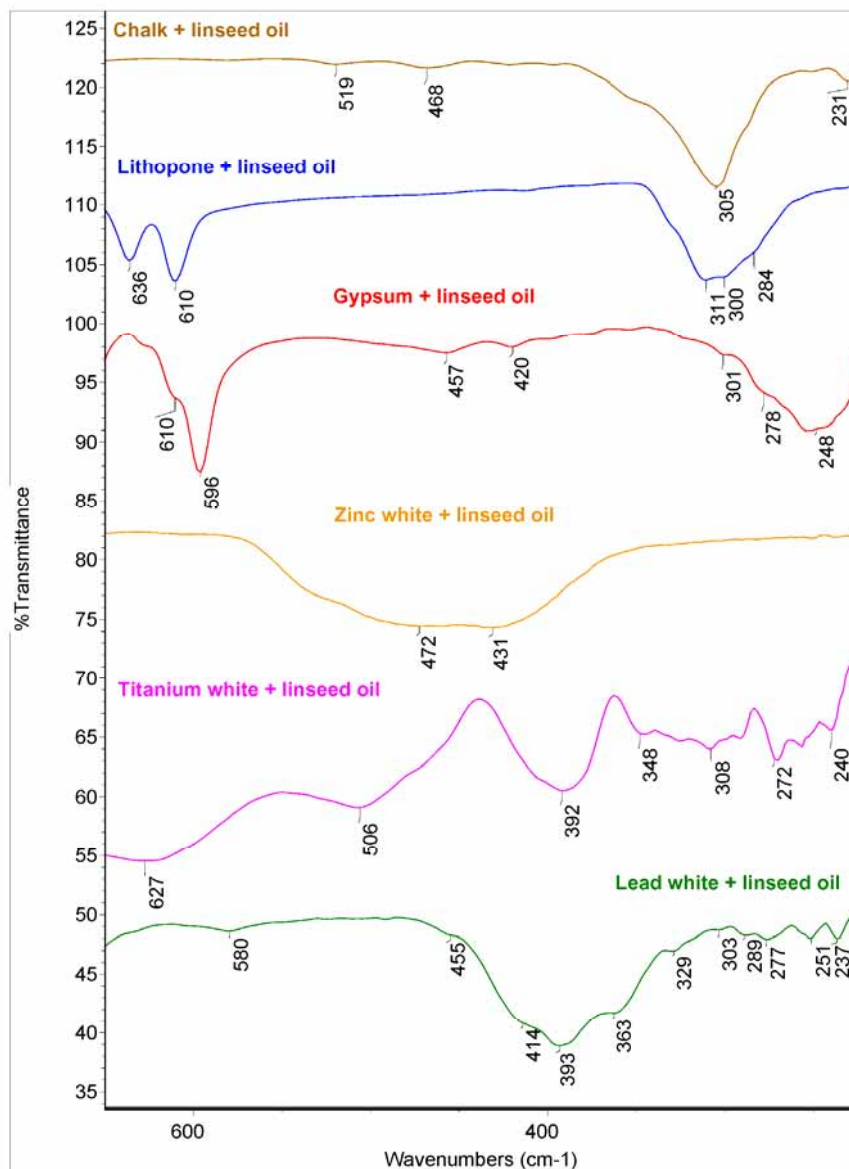


Fig. 8. IR spectra of white pigments mixed with linseed oil

All these pigments have characteristic absorptions in the region of 550 to 230 cm^{-1} .

The absorption bands of these pigments are quite broad, especially for titanium white and zinc white. Zinc white (ZnO) has only one broad band while titanium white has one broad intensive band and about 4 smaller bands.

Zinc white has the very broad and very characteristic Zn-O stretch band in the wavenumber range of 550–350 cm^{-1} .

Titanium white (TiO_2) is mainly produced by synthesizing such minerals like anatase and rutile. These minerals can be differentiated from each other and from other white pigments on the basis of their IR spectra. In this investigation rutile-based titanium white is used. The analysed titanium white has broad absorption bands in the end of mid-IR region, but besides that there are several characteristic bands in the far-IR region at 392 cm^{-1} , 348 cm^{-1} , 308 cm^{-1} , 272 cm^{-1} , 240 cm^{-1} .

Chalk and lithopone both have absorption bands in the region of 350–250 cm^{-1} , but in lithopone the band is much broader. That is because lithopone consists of two compounds – BaSO_4 and ZnS and they both have absorptions below 300 cm^{-1} (BaSO_4 lower than ZnS) [38, 50].

Also gypsum has one characteristic broad band (at $\sim 248 \text{ cm}^{-1}$) in the far IR region at a lower wavenumber than chalk's (occur at $\sim 305 \text{ cm}^{-1}$) and lithopone's bands (at $\sim 311 \text{ cm}^{-1}$).

Lead white has a characteristic broad absorption band at 393 cm^{-1} (with two shoulders at 414 cm^{-1} and 363 cm^{-1}) and this belongs to PbO modes [11]. Besides that there are some smaller bands at the lower wavenumbers that are not very characteristic.

The spectra of the white pigments are sufficiently different from each other to allow differentiation between the pigments.

4.1.2. IR spectra of yellow pigments

Altogether 10 yellow pigments were analyzed. The IR spectra of cadmium yellow, massicot, yellow ochre, satin ochre, Amberg yellow, Italian gold ochre light, Naples yellow light, orpiment, barium yellow and strontium yellow in the linseed oil matrix in the low wavenumber region are presented in Fig. 9 – Fig. 11.

Four yellow iron oxide hydroxide ($\alpha\text{-FeOOH}$, mineral goethite) containing pigments (yellow ochre, satin ochre, Amberg yellow, Italian gold ochre light) were selected to compare them with each other (see Fig. 9). It is evident that the IR spectra of these pigments differ.

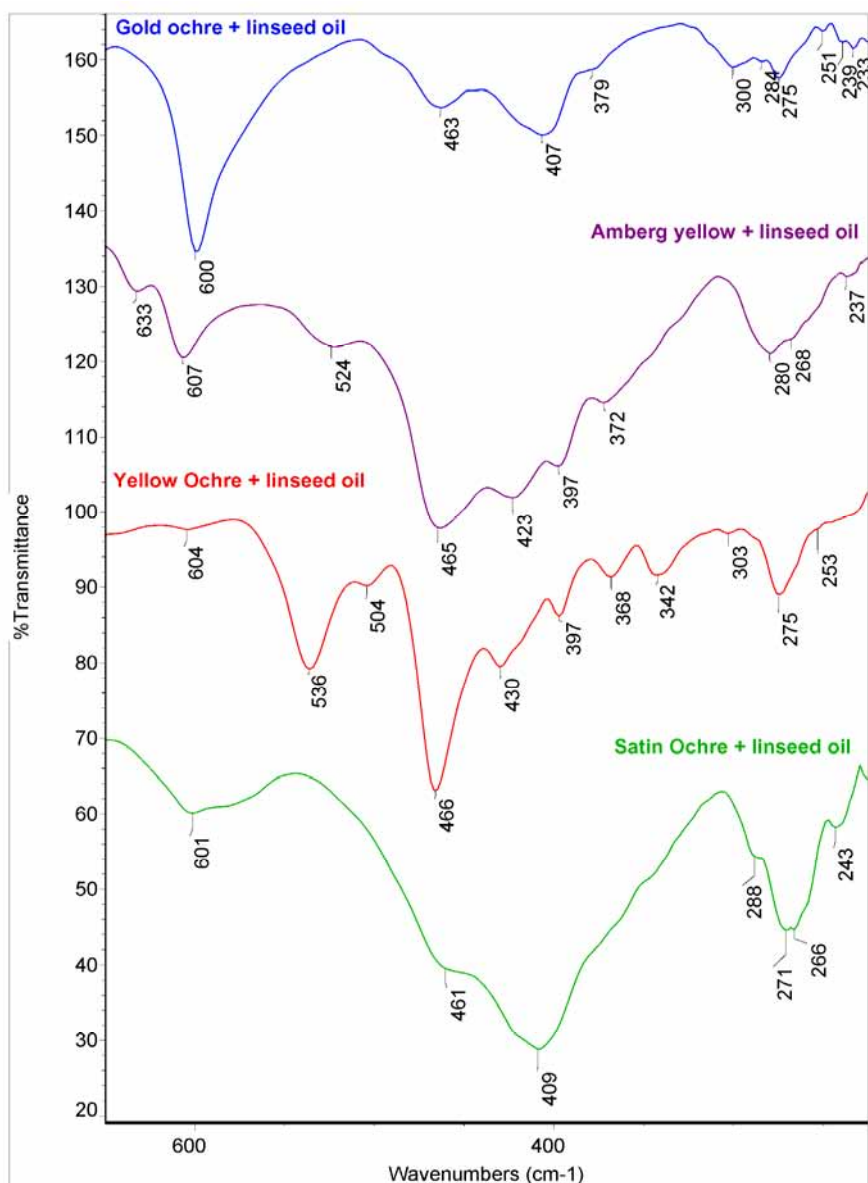


Fig. 9. IR spectra of 4 yellow iron oxide pigments mixed with linseed oil

The positions and intensities of the infrared bands of the iron oxides vary with crystallinity, particle size and shape, and the partial substitution of iron by other cations [17]. The position of the infrared absorptions of goethite (natural or synthetic goethite) is variable. According to literature in the low wavenumber (below 700 cm^{-1}) region goethite (natural and synthetic goethite) has the

following IR absorptions: Fe-O stretches (lattice modes of FeO_6) in the region of $615\text{--}640\text{ cm}^{-1}$, $449\text{--}465\text{ cm}^{-1}$ and $397\text{--}409\text{ cm}^{-1}$; sharp Fe-O maximum in the region of $263\text{--}270\text{ cm}^{-1}$ [17, 18, 51–53]. Yellow iron oxide pigments contain different additives (gypsum, minerals like kaolin, quartz and other silicate minerals) and if the additive content is high then the bands of the additives can mask the characteristic goethite bands. In some cases the IR spectra are dominated by the absorptions of the additives rather than iron oxide hydroxide bands.

All four analysed yellow earth pigments have different additives: yellow ochre contains kaolin (bands at 536 cm^{-1} , 466 cm^{-1} , 430 cm^{-1}), satin ochre contains some silicate (very broad absorption in the region of $500\text{--}300\text{ cm}^{-1}$), Amberg yellow contains probably kaolin ($\sim 524\text{ cm}^{-1}$, $\sim 465\text{ cm}^{-1}$, $\sim 423\text{ cm}^{-1}$) and Italian gold ochre light contains gypsum (600 cm^{-1} , $\sim 463\text{ cm}^{-1}$).

These additives do not interfere much with identification of some goethite Fe-O vibrations below 500 cm^{-1} . In Fig. 9 it is possible to see that yellow ochre has Fe-O bands at 397 cm^{-1} and 275 cm^{-1} ; satin ochre at $\sim 461\text{ cm}^{-1}$, 409 cm^{-1} and $\sim 271\text{ cm}^{-1}$; Amberg yellow at 397 cm^{-1} and band in the region of $280\text{--}268\text{ cm}^{-1}$ (maybe also band at 465 cm^{-1} but it is mostly masked by kaolin bands); Italian gold ochre light has Fe-O vibrations at $\sim 463\text{ cm}^{-1}$, 407 cm^{-1} , 275 cm^{-1} .

In some cases also pigments from different companies were compared. In Fig. 10 are presented the IR spectra of cadmium yellow medium from two different companies (Kremer Pigmente and Maimeri) and the spectra are similar, differing slightly by the shape of the characteristic broad CdS lattice vibration in the region of $300\text{--}230\text{ cm}^{-1}$. The lines at 609 and 633 cm^{-1} in the spectrum of cadmium yellow medium (Kremer Pigmente) are most probably due to BaSO_4 additive.

It is evident from Fig. 10 that orpiment and massicot (PbO , contains also a small amount of litharge) have numerous bands in the region of $550\text{--}230\text{ cm}^{-1}$ while Naples yellow light has three quite broad and characteristic bands and one low-intensity band (229 cm^{-1}).

Orpiment (As_2S_3) has complex molecular structure and because of that also very complex IR spectrum. In the IR spectrum of orpiment bands at 459 cm^{-1} , 392 cm^{-1} , 380 cm^{-1} , 363 cm^{-1} , 346 cm^{-1} , 312 cm^{-1} are found and belong to the As-S stretching modes [54, 55].

It is of interest to compare the spectra of the two chromate pigments (barium yellow and strontium yellow). Their IR spectra are presented in Fig. 11. The spectra differ from one another. Both barium yellow (BaCrO_4) and strontium yellow (SrCrO_4) have intense sharp bands. Barium yellow has four characteristic Cr-O bending vibrations in the CrO_4^{4-} anion at 418 cm^{-1} , 391 cm^{-1} , 374 cm^{-1} and 336 cm^{-1} [36, 37, 49]. Strontium yellow has the same bands (although slightly shifted) and in addition several bands of lower intensity. In spite of the same anion (CrO_4^{4-}) these two pigments can be easily distinguish from one another, also in the real paint samples.

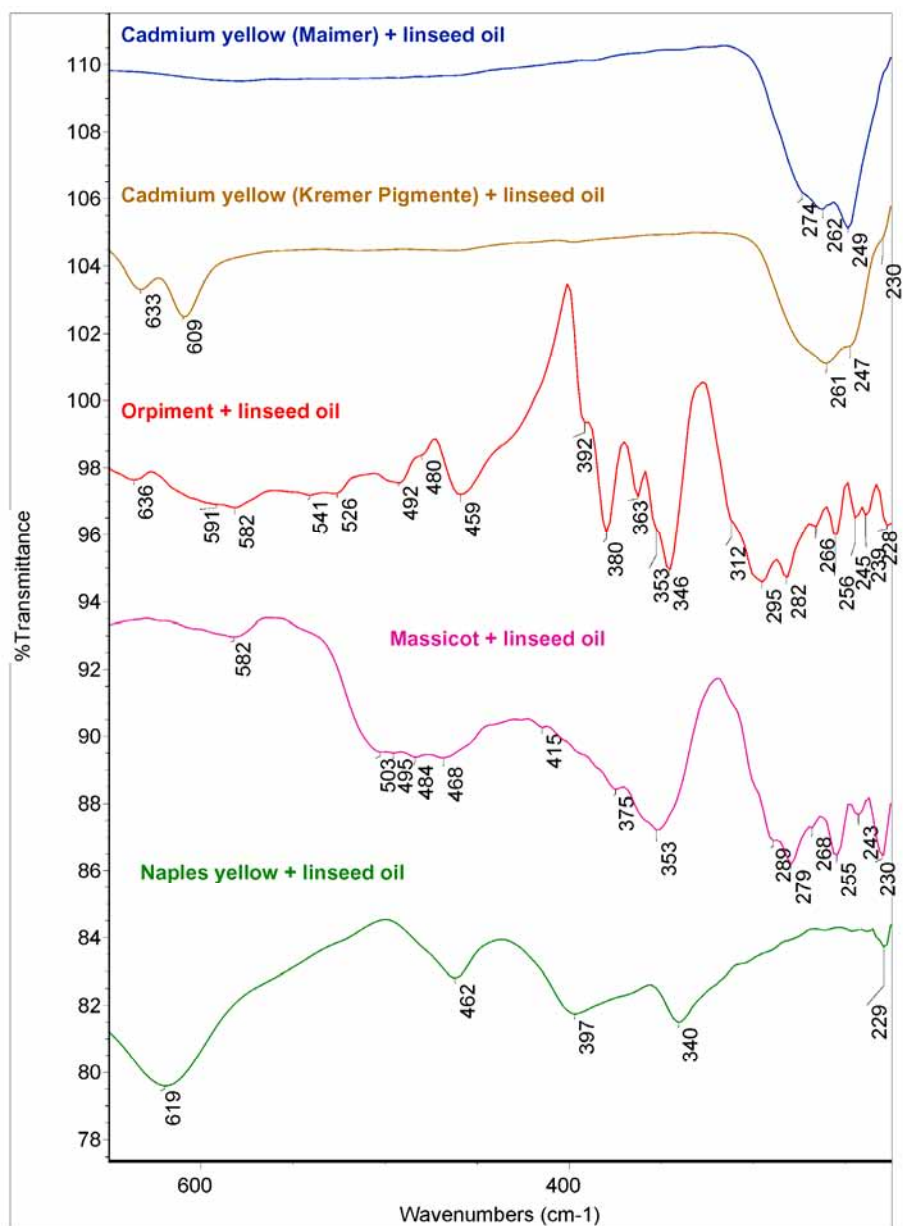


Fig. 10. IR spectra of cadmium yellow, orpiment, massicot, Naples yellow mixed with linseed oil

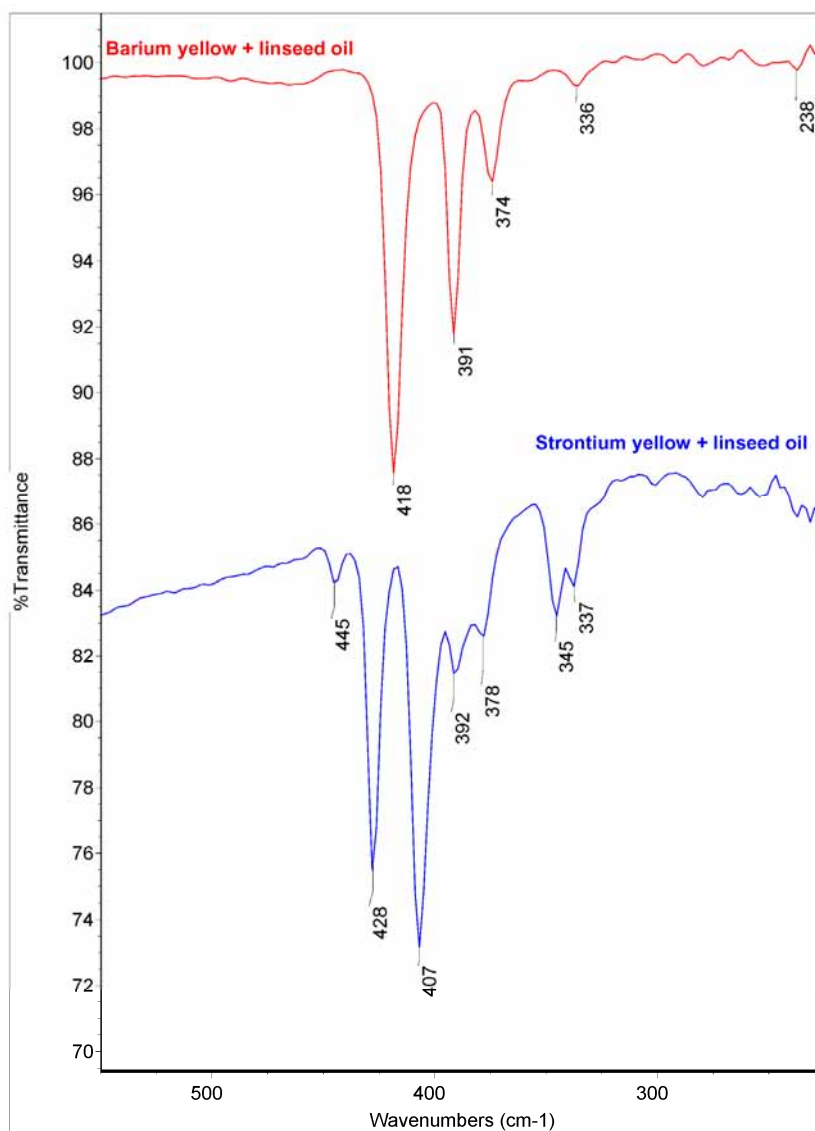


Fig. 11. IR spectra of barium yellow and strontium yellow mixed with linseed oil.

All the yellow pigments have absorption bands in the investigated spectral range and the spectra are sufficiently different to permit differentiation between the pigments. Nevertheless complications may arise with identification of cadmium yellow when a large amount of chalk is present in the sample and also the spectra of the yellow iron oxide pigments can be different depending on the origin of the pigment, thereby complicating the identification.

4.1.3. IR spectra of red pigments

Altogether 7 historically important red pigments were analyzed. The IR spectra of red lead, cinnabar, cadmium red, natural red earth, Pompeian red, Venetian red and Caput Mortuum reddish in the linseed oil matrix are presented in Fig. 12.

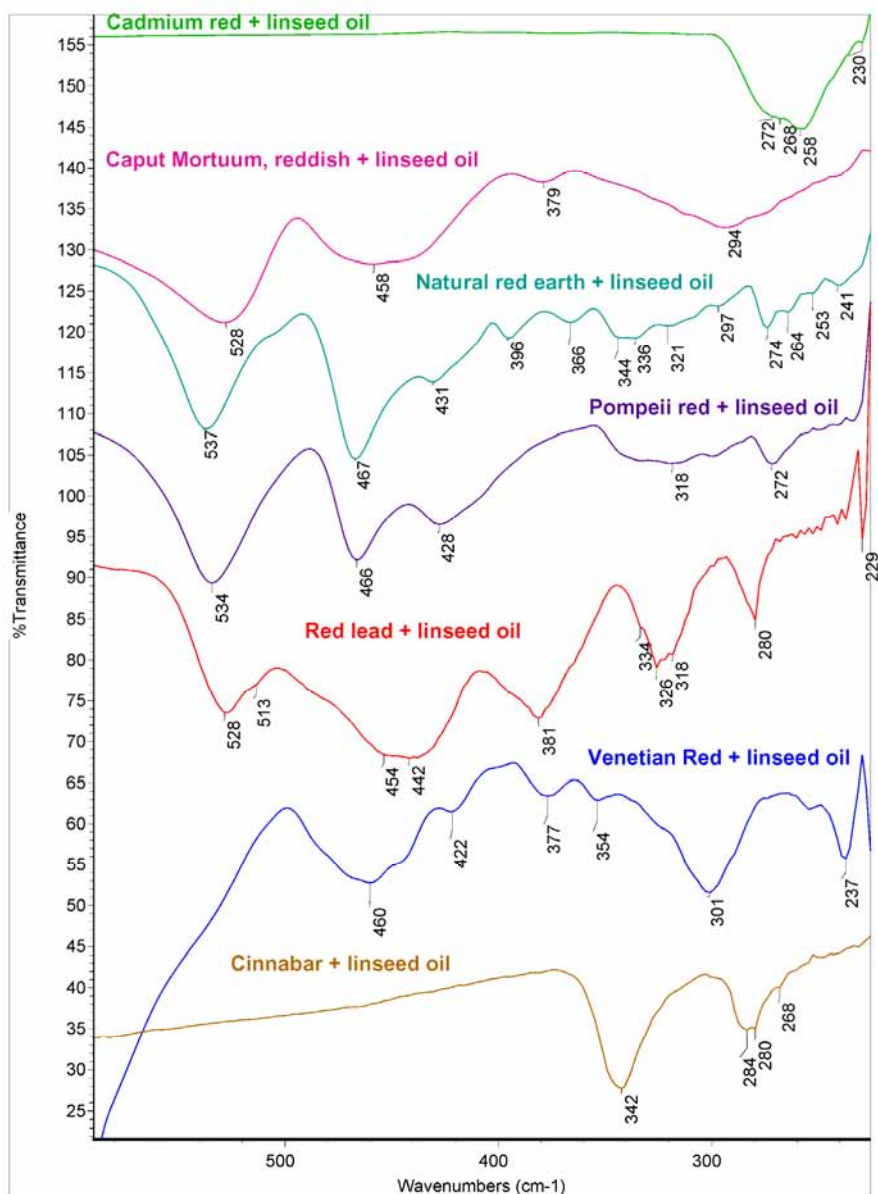


Fig. 12. IR spectra of red pigments mixed with linseed oil

Cinnabar and cadmium red have fewer absorption bands in the region of 550–230 cm^{-1} than the other red pigments.

Cinnabar (or vermilion) has in the IR spectrum three characteristic vibration bands, one is at about 341 cm^{-1} and other two bands in the region of 284–280 cm^{-1} (actually one band is split in two). In the IR spectrum of cadmium red there is one broad and intense band in the region of 300–230 cm^{-1} . Cadmium red is composed of cadmium sulphide-selenide ($\text{CdS} + \text{CdSe}$). Probably cadmium sulphide and cadmium selenide have characteristic absorption band in the same area and that explains broad band in the spectrum.

Red lead (Pb_3O_4) has 5 clearly distinguishable absorptions. Pb-O vibration bands are at about 528 cm^{-1} , 454 cm^{-1} (quite broad absorption), 381 cm^{-1} , 326 cm^{-1} (has a shoulder at 318 cm^{-1}), 280 cm^{-1} .

Altogether 4 different red iron oxide pigments – natural red earth, Pompeian red, Venetian red and Caput Mortuum reddish – were measured with the main goal to compare them to each other. All these pigments have iron oxide ($\alpha\text{-Fe}_2\text{O}_3$, mineral is hematite) as their main component but the additives are different. In the spectra of these pigments wavenumbers of bands may shift somewhat depending on the pigment origin. Also hematite-based pigments can show variations in the position of the hematite bands in IR spectra due to differences in particle shape and size [43].

According to literature in the low wavenumber (below 600 cm^{-1}) region hematite has the following IR absorptions (probably Fe-O stretches): in the region of 525–560 cm^{-1} , 436–480 cm^{-1} , 378–397 cm^{-1} , 325–349 cm^{-1} , 297–312 cm^{-1} , 220–233 cm^{-1} [17; 51, 52, 56–58].

In the IR spectrum of natural red earth kaolin's bands dominate and these mask almost all the iron oxide bands (see Fig. 13).

In the IR spectrum of kaolin there are strong absorption bands at 527 cm^{-1} , ~455 cm^{-1} and a series of weak bands in the region of 450–240 cm^{-1} . In the natural red earth IR spectrum the characteristic bands are at 431 cm^{-1} (Pompeii red has the same band at 428 cm^{-1}), also at 396 cm^{-1} and 276 cm^{-1} .

Pompeii red contains beside iron oxide also kaolin. In the IR spectrum of Pompeii red vibration bands occur at 534 cm^{-1} , 466 cm^{-1} , 428 cm^{-1} , 318 cm^{-1} , 272 cm^{-1} (last two bands may belong to hematite). IR spectrum of natural red earth and IR spectrum of Pompeii red are more similar compared to IR spectra of Caput Mortuum reddish and Venetian red.

Venetian red contains beside iron oxide gypsum (or calcium sulphate) as additive (has a low-intensity band at 457 cm^{-1}). Gypsum masks (or interferes with) hematite absorptions at 525–560 cm^{-1} and 436–480 cm^{-1} . Maxima at 422 cm^{-1} , 377 cm^{-1} , 354 cm^{-1} , 301 cm^{-1} and 237 cm^{-1} may belong to hematite (Fe-O) absorptions.

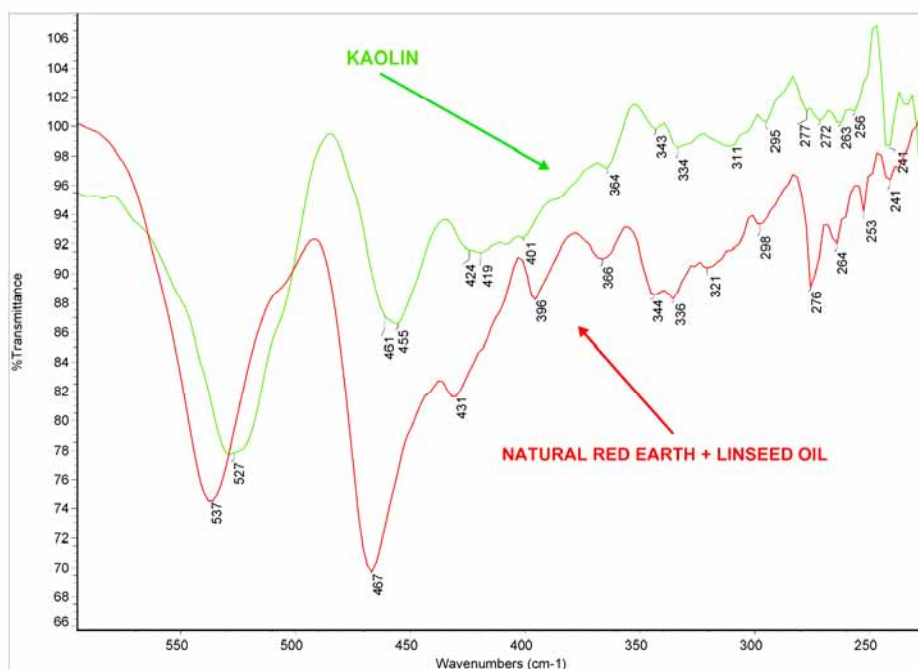


Fig. 13. Comparison of IR spectrum of natural red earth mixed with linseed oil and IR spectrum of pure kaolin

The IR spectrum of Caput Mortuum reddish displays absorption bands at 528 cm⁻¹, 458 cm⁻¹, 379 cm⁻¹ and 294 cm⁻¹, characteristic to hematite. In Fig. 4 the IR spectrum of pure Caput Mortuum reddish is presented. It is possible to see that this red pigment does not have many additives, only in small amount, probably some silicates.

All these 7 red pigments have characteristic absorptions in the region of 550 to 230 cm⁻¹ and can be distinguished from each other.

4.1.4. IR spectra of green pigments

Altogether 8 green pigments were analyzed. The IR spectra of verdigris, malachite, chrome oxide green, raw umber greenish dark, Vagone green earth, Bohemian green earth, viridian green and cobalt green, in the linseed oil matrix in the low wavenumber region are presented in Fig. 14.

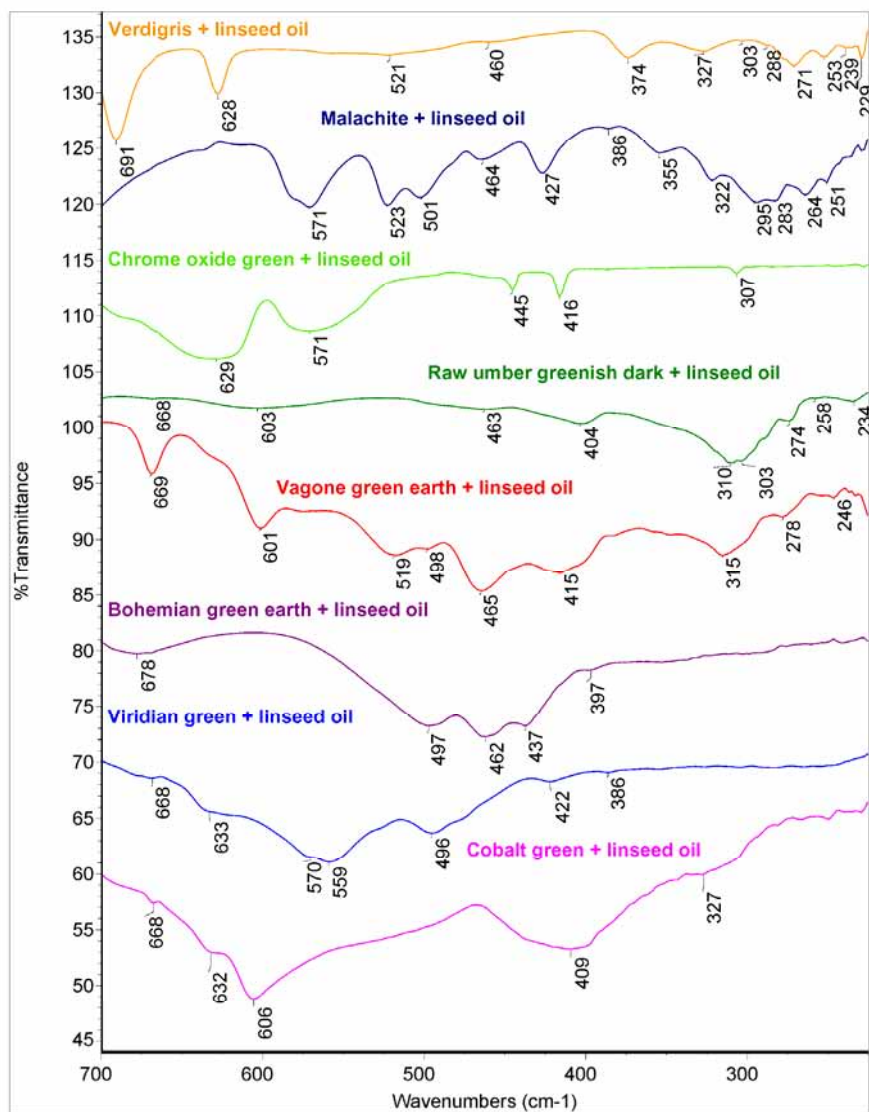


Fig. 14. IR spectra of green pigments mixed with linseed oil

Among the analysed green pigments there are two copper (malachite, verdigris) and two chromium (chromium oxide, viridian) containing pigments.

Malachite $[\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2]$ and verdigris $[\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 2\text{Cu}(\text{OH})_2]$ are widely used since antiquity. Although both contain copper, in their composition they are different and so the IR spectra of those two pigments are quite different. Both of them have a number of characteristic absorption bands in the region of $550\text{--}230\text{ cm}^{-1}$.

In the IR spectrum of malachite below 550 cm^{-1} the stretching vibrations of the Cu-O skeleton appear at 523 , 501 , 427 cm^{-1} (also band at 571 cm^{-1}) and the bending vibrations of the Cu-O skeleton appear at 322 , 295 , $\sim 283\text{ cm}^{-1}$ and 264 cm^{-1} [11, 49]. Verdigris has numerous characteristic vibration bands in the range of 521 (possibly Cu-O stretch) – 229 cm^{-1} .

Chromium oxide green is the anhydrous oxide of chromium (Cr_2O_3) and viridian green is the hydrous oxide of chromium ($\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$). Although these pigments both contain oxide of chromium their IR spectra are quite different. In both IR spectra there are bands of quite low intensity in the region of 550 – 230 cm^{-1} . Chromium oxide green and viridian green both have in the region of 550 – 230 cm^{-1} three characteristic absorption bands. Chromium oxide absorbs IR radiation only at the long wavelength end of the mid-IR region. In Cr_2O_3 the strongest band at $\sim 571\text{ cm}^{-1}$ is probably due to various combinations of O^{2-} and Cr^{3+} displacements in the lattice. The sharp bands at 445 and 416 cm^{-1} correspond to two specific O^{2-} displacement vibrations in the lattice. In viridian green the absorptions (at 559 cm^{-1} , 496 cm^{-1} , 422 cm^{-1}) are probably due to similar types of displacements (as chromium oxide), whose frequencies have been shifted due to the presence of water in the structure. [13, 37]

IR spectra of the three green earth pigments (raw umber greenish dark, Vagone green earth, Bohemian green earth) differ from each other. However there are similarities between the IR spectra of raw umber greenish and Vagone green earth. Both contain the chalk's (CaCO_3) band at $\sim 310\text{ cm}^{-1}$. Vagone green earth (product of Kremer Pigmente) is the most complex of commercial green pigments. This pigment contains different additives and its exact composition depends on the origin and the producer of the pigment. In the IR spectrum of Vagone green earth there are numerous characteristic absorption bands in the range of 519 cm^{-1} – 246 cm^{-1} . Bohemian green earth has in the spectrum quite characteristic absorption band group, where three bands at 497 cm^{-1} , 462 cm^{-1} and 437 cm^{-1} are together. In the IR spectrum of raw umber greenish the only intensive band in the region of 550 – 230 cm^{-1} is at 310 cm^{-1} and it belongs mostly to calcium carbonate with some contribution probably from Fe_2O_3 . The rest of the bands at 463 cm^{-1} , 404 cm^{-1} and 274 cm^{-1} have lower intensity. Due to the low intensity of the bands determination of this pigment in paint samples may be complicated. These green earth pigments are complex mixtures, containing different additives.

Cobalt green has quite interesting IR spectrum. In the region of 550 – 230 cm^{-1} there are only two broad bands at 409 cm^{-1} and 327 cm^{-1} .

All the analysed green pigments have characteristic absorption bands in the region of 550 to 230 cm^{-1} and can be distinguished from each other.

4.1.5. IR spectra of blue pigments

The IR spectra of Prussian blue, smalt, ultramarine blue (natural) deep, azurite, lapis lazuli, Egyptian blue, cobalt blue and dark cobalt blue in the linseed oil are presented in Fig. 15. Altogether 8 blue pigments were analyzed.

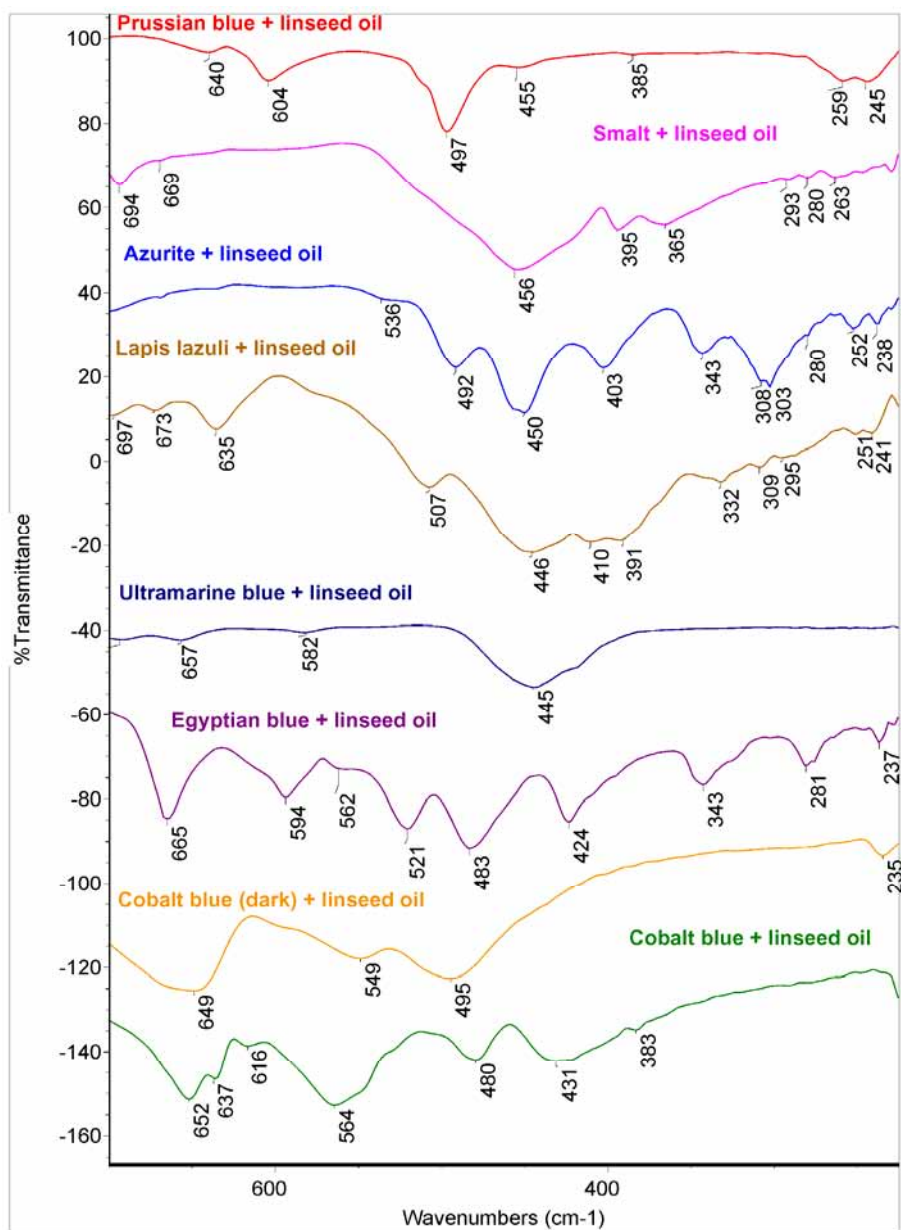


Fig. 15. IR spectra of blue pigments mixed with linseed oil

Four of the investigated pigments are silicate-containing pigments: smalt, ultramarine blue (natural) deep, lapis lazuli, Egyptian blue. In the mid-IR region all these pigments have absorption bands in the range of 900–1100 cm^{-1} . However, these bands in this region are very common in paint samples and are therefore of low diagnostic value. At the same time in the region of 550–230 cm^{-1} it is much easier to distinguish between these pigments. Egyptian blue ($\text{CaCuSi}_4\text{O}_{10}$) has especially characteristic IR spectrum and differs considerably from the other silicate-containing pigments. Numerous absorption bands in the Egyptian blue spectrum are almost evenly spread across the 550–230 cm^{-1} range. Also the IR spectrum of lapis lazuli, which is the mineral of ultramarine blue, is different from the IR spectrum of ultramarine blue itself: natural ultramarine is purified from ground lapis lazuli which contains several additives [2, 3]. Lapis lazuli has many absorption bands in the low wavenumber region compared to ultramarine, which has only one absorption band. In lapis lazuli the blue coloration is caused by the presence of sulphur radical anions S_3^- and S_2^- in the aluminosilicate structure [11, 59]. In the fig. 15 it is possible to see that ultramarine blue (natural) deep and smalt have both similar broad absorption bands in the range of 500–400 cm^{-1} . Smalt has besides the broad band also two smaller absorption bands at 395 cm^{-1} and 364 cm^{-1} . However, complications can arise when distinguishing smalt from ultramarine in complex mixtures with low pigment content, because the main absorption bands are similar and at low pigment contents the additional bands of smalt may not be reliably detectable.

In fig. 15 spectra of two cobalt pigments are presented: cobalt blue and cobalt blue dark (both are products of Kremer Pigmente). Their IR spectra differ. The colour of cobalt blue can vary, depending on how it was produced. Also there can be different amounts of additives and impurities present. Both cobalt blue pigments have characteristic oxide bands in the IR spectra, with peaks between ~564 and 235 cm^{-1} . In that range the cobalt–oxygen stretching frequencies appear, associated with the vibrations of Co–O, Al–O, and Co–O–Al bonds. [60, 61]

Usually Prussian blue ($\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$) is identified in the mid-IR region using the characteristic $\text{C}\equiv\text{N}$ stretching band at ~2083 cm^{-1} [13, 22] and use of the low wavenumber region is unnecessary. Nevertheless, according to fig. 15 Prussian blue has 3 distinguishable absorption bands in the low wavenumber range. The most intense band at 497 cm^{-1} is assigned to Fe–C and C–Fe–C *in-plane* bending or Fe–C \equiv N bending mode, while the less intensive bands at 259 cm^{-1} and 245 cm^{-1} are associated with similar stretching vibrations [13, 36, 62].

Azurite [$2\text{CuCO}_3\cdot\text{Cu}(\text{OH})_2$] has below 550 cm^{-1} Cu–O skeleton stretching vibrations at 492 cm^{-1} , 450 cm^{-1} , 403 cm^{-1} , 343 cm^{-1} and 305 cm^{-1} and Cu–O skeleton bending band at 238 cm^{-1} [11]. While azurite mineral is usually associated in nature with malachite [$\text{CuCO}_3\cdot\text{Cu}(\text{OH})_2$], then in fig.16 the IR spectra of these pigments are compared in the region of 550–230 cm^{-1} .

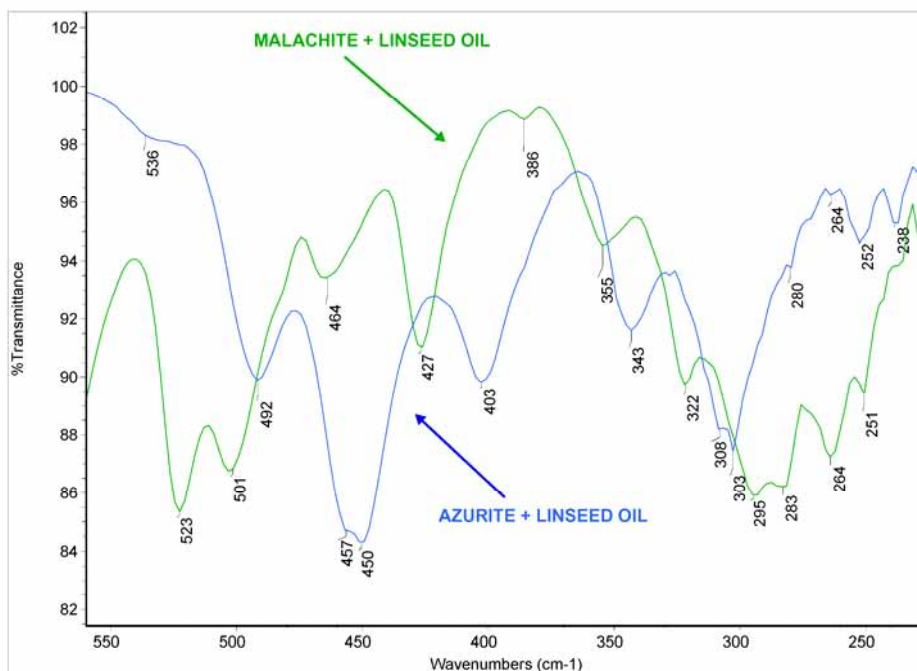


Fig.16. IR spectra of azurite and malachite both mixed with linseed oil

Fig. 16 reveals that the spectra differ markedly and the structural differences between azurite and malachite are clearly revealed.

All the investigated blue pigments have characteristic absorptions in the studied spectral region and can be distinguished from each other.

4.1.6. IR spectra of the brown pigments

The IR spectra of brown ochre, fawn ochre and two varieties of burnt umber in the linseed oil matrix are presented in Fig. 17. All of them are iron oxide containing pigments and depending on their source they also may contain different amounts silica, kaolin and may contain other minerals. Burnt umber contains higher amount of manganese oxide (MnO₂).

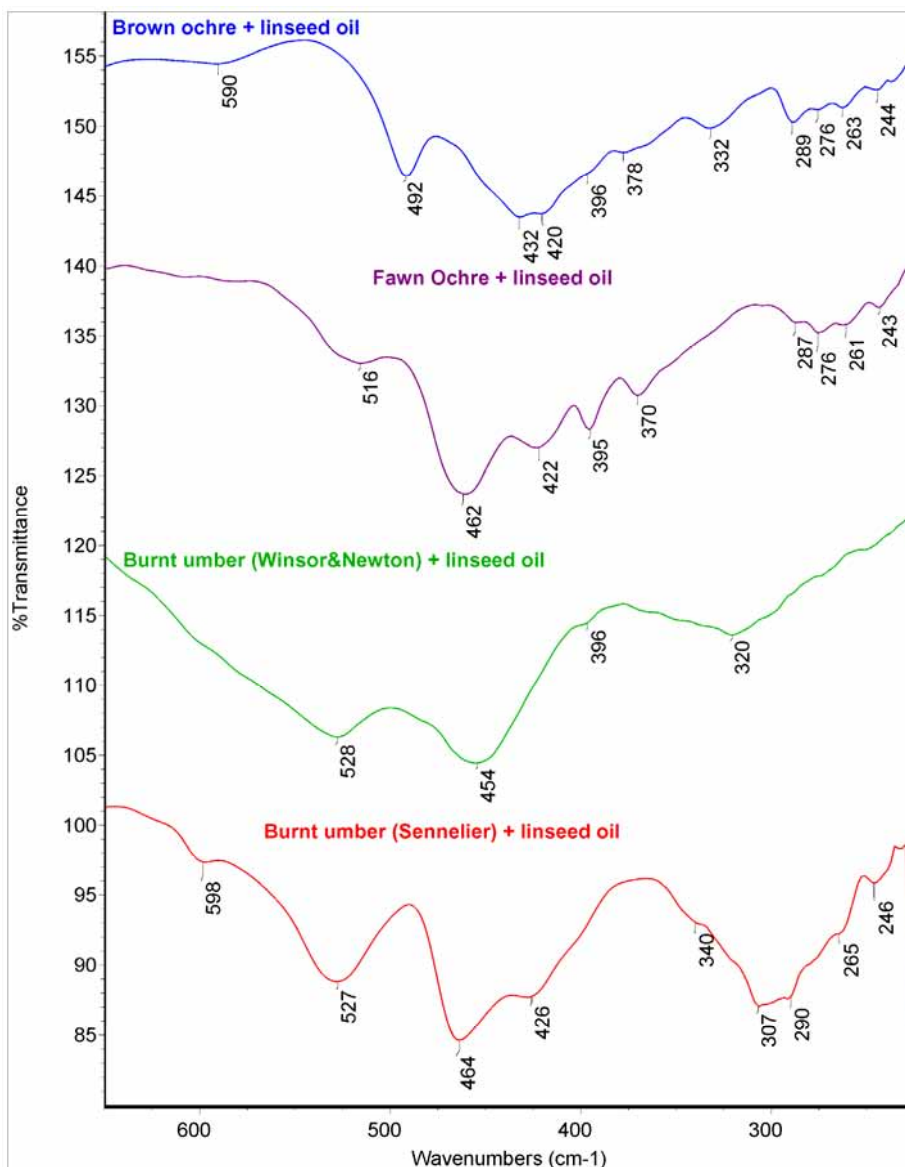


Fig. 17. IR spectra of brown pigments mixed with linseed oil

Brown pigments are complex mixtures and in the IR spectra in the region of 550–230 cm^{-1} they contain series of broad and partially overlapping absorption bands. The bands at 430–470 cm^{-1} and the group in the range of 525 to 560 cm^{-1} are related to iron oxide, although as mentioned above also kaolin gives bands in the same area. According to literature also the manganese oxides give bands at around $\sim 465 \text{ cm}^{-1}$, $\sim 525 \text{ cm}^{-1}$ and also $\sim 315 \text{ cm}^{-1}$. These bands are the

stretching modes of the MnO_6 (Mn-O stretching mode) octahedra that are the fundamental building blocks of the manganese oxide mineral structures. In most cases Mn-rich deposits contain at least some iron (in the form of iron oxide). [63]

The IR spectra of the two burnt umber samples from different companies (Winsor & Newton and Sennelier) display in broad terms similar spectra but the exact positions, shapes and relative intensities of the bands differ. The differences come from different additives (fillers). Burnt umber that is produced by Sennelier contains kaolin and the product of Winsor & Newton may contain some silicate compound (or compounds) other than kaolin. In the appendix 7 in Fig. 2 the full-size IR spectra of the two burnt umber samples are presented.

Also complex mixtures like brown ochre and fawn ochre have several characteristic absorptions in the region of 550 to 230 cm^{-1} .

All analysed brown pigments are natural earths (iron oxide containing pigments) and their IR spectra differ somewhat from each other. All analysed brown pigments have recognizable absorption bands in the IR spectra and these can be used for identification of brown pigment in the paint sample.

4.1.7. IR spectra of black pigments

The IR spectra of ivory black, bone black, mars black, vine black and charcoal, in the linseed oil matrix are presented in Fig. 18. All these black pigments contain carbon (C) except Mars black.

Charcoal has no bands in the IR spectrum, because it contains only carbon. The very high absorption coefficients on carbons across almost the entire infrared-visible-ultraviolet spectrum make absorption spectroscopy difficult and IR spectroscopy is not a practical method for identification of charcoal [17]. Also vine black contains mainly carbon and so the low intensity bands in the IR spectrum belong to additives (or impurities). The absorption bands of ivory black and bone black belong to calcium phosphate $[\text{Ca}_3(\text{PO}_4)_2]$ (probably P-O vibrations in the PO_4^{3-} anion), which is typically present in these pigments. Mars black is a synthetic black pigment and is based on iron oxide mineral magnetite. This is the reason why the IR spectrum of Mars black is distinctly different from other black pigments and also from the other iron oxide pigments (based on hematite and goethite).

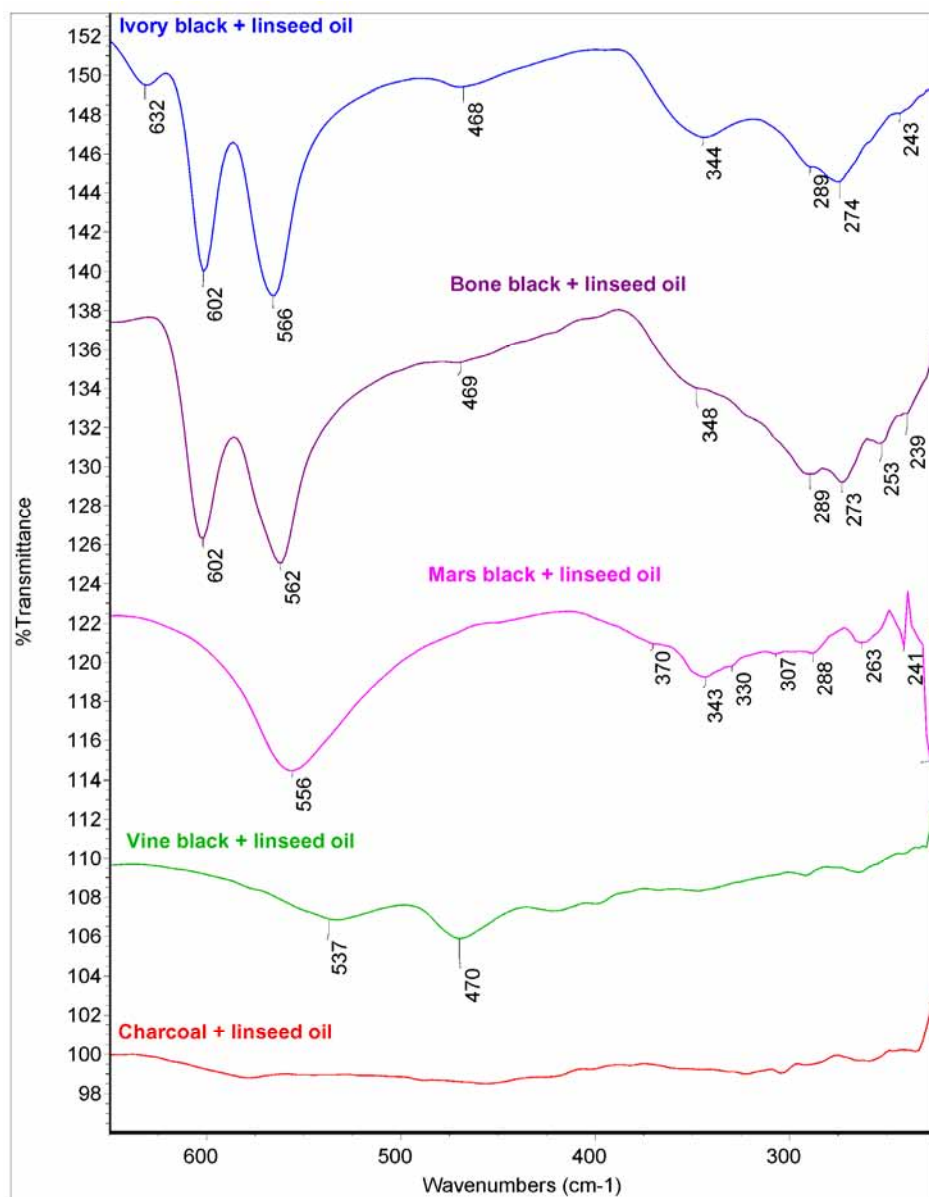


Fig. 18. IR spectra of black pigments mixed with linseed oil

4.2. Interference of chalk in the low wavenumber region

There is a strong absorption band in the spectrum of chalk (mostly CaCO_3) with maximum in the range of 305 cm^{-1} (see figs 2 and 8) that overlaps with the characteristic absorptions of several pigments. This is of high importance, because chalk (CaCO_3) is the most common filler in paints.

To study this interference two red pigments (red lead and cinnabar) were mixed with linseed oil and chalk (see figs. 19 and 20). Equal amounts of pigment and chalk were taken (see Table 5 in the Appendix 6).

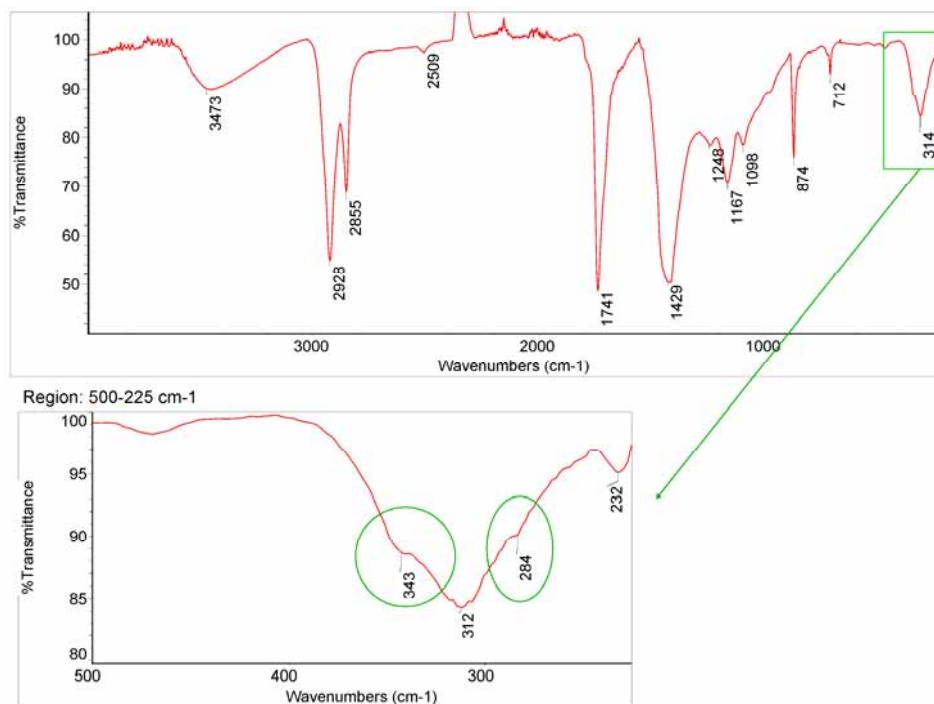


Fig.19. IR spectrum of the cinnabar (HgS) mixed with chalk and linseed oil

From the IR spectrum of Fig.19 it is possible to see that the CaCO_3 absorption band has two shoulders at 343 cm^{-1} and 284 cm^{-1} caused by cinnabar. These bands are of low intensity and in the unknown paint samples only by these maxima cinnabar cannot be identified. So cinnabar is difficult to identify if an equal amount of CaCO_3 are present.

Also in the IR spectrum of red lead the CaCO_3 maximum at 305 cm^{-1} interferes with identification of red lead (see Fig. 20). However, because red lead has

more absorption bands in the region of 550–230 cm^{-1} red lead is still identifiable by the absorption maxima at 527 cm^{-1} and 459 cm^{-1} .

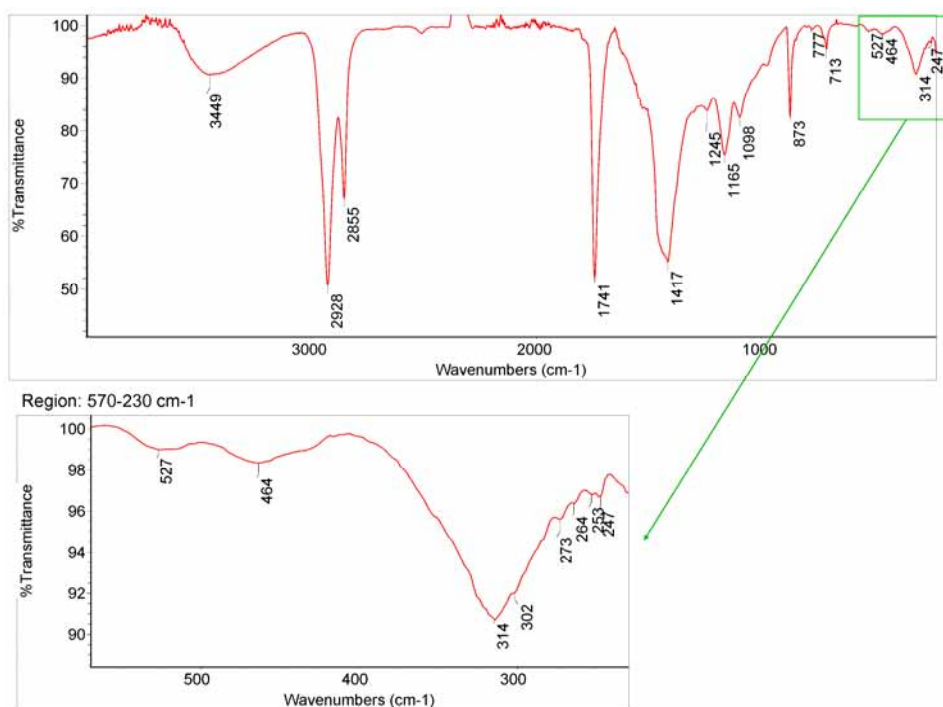


Fig. 20. IR spectrum of the red lead (Pb_3O_4) mixed with chalk and linseed oil

At the same time, for example the red iron oxide pigments (Fig. 12) can in some cases be identified by their absorptions between 400 and 600 cm^{-1} where the CaCO_3 band at 305 cm^{-1} does not interfere. So, when some inorganic pigment has absorption band (or bands) exactly in the same range as calcium carbonate, then in the IR spectrum the maximum gets broader and it is difficult or impossible to identify the pigment. In these cases it is more reasonable to use other absorption bands in the low wavenumber range if available.

If a large amount of CaCO_3 is present then this complicates identification of many of the pigments investigated and use of complementary techniques (SEM-EDS, XRF, etc) is highly beneficial as well as treatment with dilute HCl or HF to remove CaCO_3 [64, 65].

Further discussion about the possible interference of chalk is presented in the case studies section.

4.3. Case studies

The following case studies demonstrate the usefulness of ATR-FT-IR in the region of 550–230 cm⁻¹ for identification of inorganic pigments and allow assessing the capabilities and limitations of ATR-FT-IR spectroscopy for identification of pigments in the low wavenumber range.

For the case studies art objects have been selected, some of them important in Estonian art history. The paint samples have been taken from the different objects and the analysis has been carried out in the frameworks of different projects that involved comprehensive material and pigment studies.

4.3.1. Paint samples from the tabernacle of the altar of the Church of the Holy Spirit in Tallinn

INTRODUCTION

The Church of the Holy Spirit, built in the 13th century, is one of the oldest churches in Tallinn. Different construction works continued until the 14th century and since then the architecture and interior of the church has been preserved mostly in the same form until nowadays. [66]

The most remarkable feature of the church interior is the altar – an excellent masterpiece made by Bernt Notke in 1483 (see Photo 1).²¹

The upper part of the altar is octagonal tabernacle, which was designed as a chapel with lacy ribbed top. Inside of the tabernacle the scene of the Coronation of Mary is presented (see Photos 1 and 2).

In 2009 the tabernacle was conserved in the Conservation Centre Kanut and during these conservation works paint samples from the tabernacle were taken. The aim of the investigation was to elucidate the materials usage of the tabernacle. An important part of the investigation was identification of the used original inorganic pigments.

²¹ Bernt Notke was a very important painter and sculptor (wood-carver) in Germany and in Northern Europe in 15th century. He was born probably between 1430–1440 in Lassan in Pomerania and died in Lübeck in 1509 [67]. There are only 3 works still existing for which his authorship can be proved by historical records (all others have been assigned to him based on dating and style). One of these is the altar in the Church of the Holy Spirit. It is noteworthy that out of his most important (for the whole Europe) works two are exhibited in Estonian churches (the other is the “Death dance” in the St. Nicholas’ church).

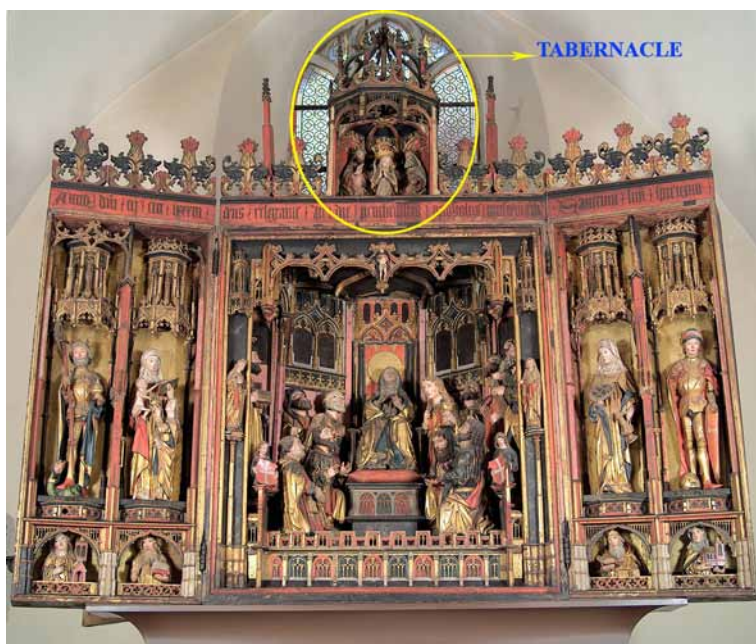


Photo 1. The altar of the Church of the Holy Spirit in Tallinn (photo by Jaanus Heinla, Conservation Centre Kanut, Tallinn, Estonia)


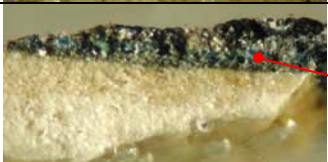
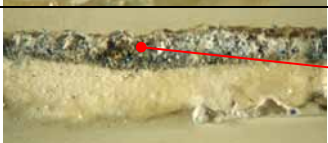






Photo 2. Tabernacle after conservation (photo by Jaanus Heinla, Conservation Centre Kanut, Tallinn, Estonia)

SAMPLES

Seven out of ca 40 paint samples were selected into this dissertation. Samples were taken from different places of the tabernacle with a sharp scalpel and tweezers. The sizes of the analysed sample pieces were in the range of 2 to 4 mm². In the appendix 8 are presented figures where the locations of the samples are marked on the tabernacle. Table 4 shows cross-sections of the samples and with the arrow are indicated analysed paint layers.

Table 4. Analysed paint layers.

Sample No	Locations of the samples	Picture of cross-section	Analysed paint layers
1.	On the rib of the roof of the tabernacle		Dark blue layer
2.	On the concave black surface		Dark blue layer
3.	Inside of the corpus, in the middle of baldachin		Dark blue layer
4.	From the upper part of the roof fleche		Red layer
5.	On the thin slat		Red layer
6.	Inside of the corpus on the background		Red layer
7.	On the corner of the pillar		Yellow layer

RESULTS

Dark blue layers (samples no 1–3)

All three IR spectra of blue layers that were taken different places of the tabernacle were analyzed together (see Fig. 21). It is evident that all three IR spectra in the region of 550–230 cm^{-1} are very similar and thus the same blue pigment was used on the different areas of the tabernacle.

The spectra agree very well with that of Azurite, see Fig. 21.

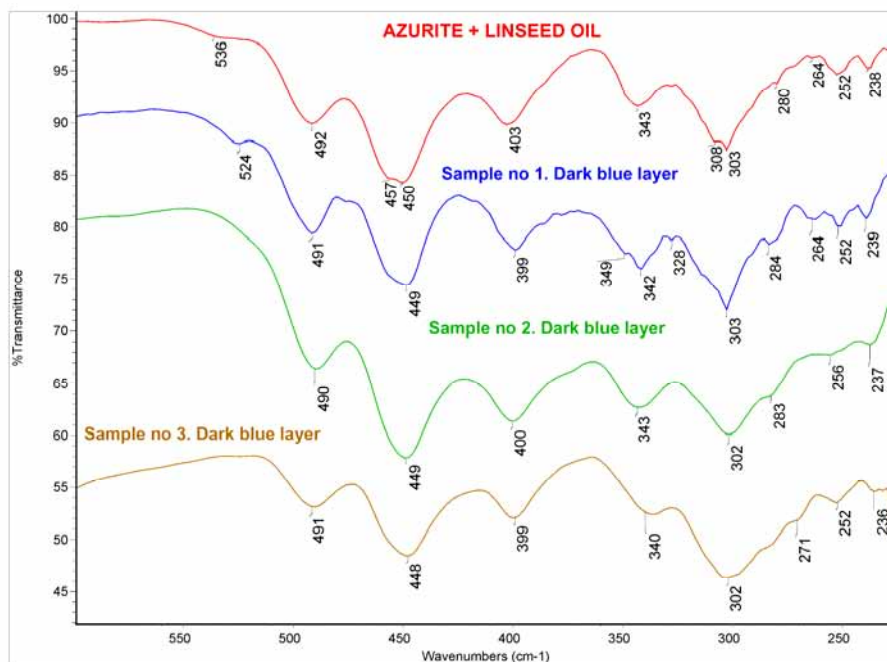


Fig. 21. IR spectra of dark blue layers and azurite + linseed oil.

Azurite has the absorption bands at 492 cm^{-1} , 450 cm^{-1} , 403 cm^{-1} , 343 cm^{-1} , 308 cm^{-1} , 303 cm^{-1} , 280 cm^{-1} , 252 cm^{-1} , and 238 cm^{-1} and all these bands match very well the absorption bands of the blue pigments. The blue sample layers contain also a small amount chalk (CaCO_3) and some silicates as fillers. In the IR spectra of samples no 2 and no 3 the bands at $\sim 302 \text{ cm}^{-1}$ are broader than the band in the IR spectrum of azurite mixed with linseed oil. This is due to an overlap with the chalk absorption band at 305 cm^{-1} (see Fig. 8). However, this overlap does not hinder the identification of azurite, which is also fully supported by the SEM-EDS results (see Fig. 4 in appendix 9).

In appendix 9 in figure 3 the full size IR spectrum of the sample no 3 of blue layer is presented and in Table 6 the results of the ATR-FTIR analysis are

summarized. Since all the IR spectra of blue layers are similar, then only one IR spectrum was selected.

Thus the results indicate that the original blue layers contain azurite, some fillers (chalk, silicates) and protein binder. According to the cross-sections, under the blue layer is a dark grey layer, most probably a preparative layer for the blue layer (this was probably made to increase the intensity and brightness of the azurite containing blue colour tone).

Red layers (samples no 4–6)

Fig. 22 presents the IR spectra of the 3 red layers together, for comparison are in the figure added reference IR spectra of cinnabar and chalk (both mixed with linseed oil).

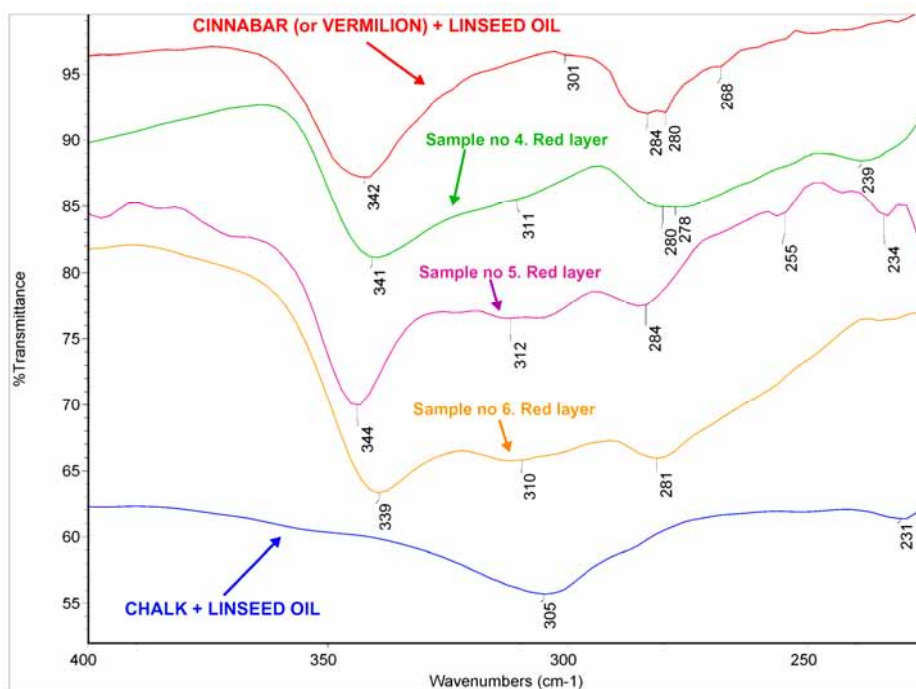


Fig. 22. IR spectra of red layers and reference IR spectra of cinnabar and chalk both mixed with linseed oil

In the IR spectra of red layers the cinnabar's characteristic bands at 342 and 284 cm^{-1} are well identifiable although the wavenumbers are slightly shifted and the bands are broader. As demonstrated by Fig. 22 the additive is chalk, contributing the broad band around 300 cm^{-1} . The amount of chalk in the

samples is small and chalk's band presence does not hinder the identification of cinnabar. The conclusion is that the main red pigment in all samples is cinnabar and one of the fillers is chalk. This is fully supported by the SEM-EDS results. In appendix 10 in figure 5 the full-size IR spectrum of the sample no 6 of red layer is presented and in Table 7 the results of the ATR-FTIR analysis are summarized. Since the IR spectra of red layers are quite similar, then only one IR spectrum was selected. In appendix 10 in Fig. 6 also the SEM/EDS spectrum of red layer is presented.

Yellow layer (sample no 7)

The ATR-IR spectrum of the yellow layer is presented in Fig. 23 together with a reference spectrum of yellow ochre mixed with linseed oil.

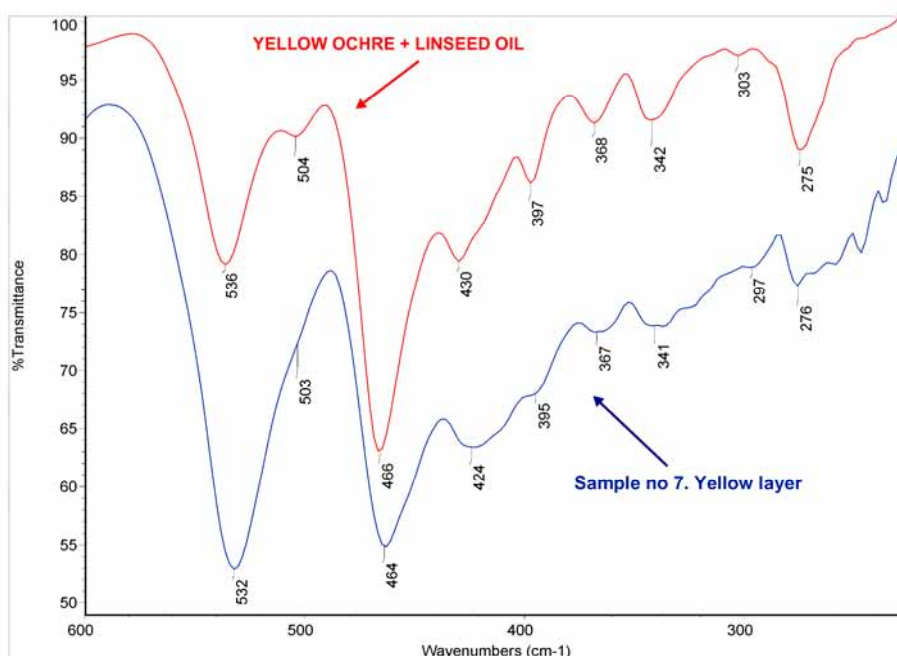


Fig. 23. IR spectrum of yellow layer and reference IR spectrum of yellow ochre mixed with linseed oil.

The absorption bands of yellow layer match well with the yellow ochre absorption bands. The pigment yellow ochre contains kaolin and in the IR spectrum displays probably kaolin's ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) and iron oxide's (Fe-O) bands overlapping. This is the reason why the bands at 532 cm^{-1} , 464 cm^{-1} and 424 cm^{-1} are broader (also Fe-O gives band that area).

The conclusion is that the pigment is yellow ochre. This is fully supported by the SEM-EDS results (see Fig. 8 in the appendix 11). In appendix 11 in figure 7 the full size IR spectrum of the yellow layer is presented and in Table 8 the results of the ATR-FTIR analysis are summarized.

The investigations of the cross-sections indicated that all over the corpus of the tabernacle below yellow layer is a gold layer and below that a dark red bole layer (preparative layer of the gold). According to the historical notes the yellow layer on the gold layer was probably made in the 19th century, i.e. was not made originally by Notke.

As a result of this study there is now systematic information available on the materials usage of this tabernacle.

4.3.2. Pink paint sample from the Ludwich von Tolli coat of arms from the Kaarma Church of Saints Peter and Paul in Saaremaa

The church of Kaarma parish on the island of Saaremaa, dedicated to St. Peter and St. Paul, was constructed across from Kaarma stronghold. It was built possibly in the middle of 1270–1280 [68]. In the church of Kaarma there are many historical art objects, including the coat of arms of Ludwich von Tolli²². The coat of arms was prepared in the polychrome technique and dating back to the 17th century (see photo 3).²³ This coat of arms has not been overpainted and all the paint layers are original and date back to the 17th century. For the most part the paint is destroyed, only some of the paint layers are still there.

²² This coat of arms belongs to Ludwich von Tolli (1646 – 1693), an important figure in Estonian history, the owner of the Meedla manor and a Chief Lieutenant of the Swedish Royal Army.

²³ The work comes from the workshop of Christian Ackermann, the most distinguished of Estonian Baroque wood carvers and an innovator of the local tradition of coat of arms [69].



Photo 3. Coat of arms of Ludwich von Tolli (photo by Jaanus Heinla, Conservation Centre Kanut, Tallinn, Estonia)

In 2007 the coat of arms was submitted for conservation in the Conservation Centre Kanut in very bad condition. During that time also the paint samples for the analysis were taken. The purpose of the analysis was to determine the chemical composition of the original paint layers and elucidate the materials usage of the coat of arms.

For this dissertation one paint sample is selected as an example and only the results that were obtained by analysing ATR-FTIR spectra of the pink paint layer are discussed here. The size of the analysed sample piece with the pink upper layer was very small, having area in the range of few mm².

Visual and microscopic examinations indicate that there are two layers – pink paint layer and the primer layer. Following is presented results of pink paint layer. The ATR-IR spectrum of the pink paint layer is presented in Fig. 25.

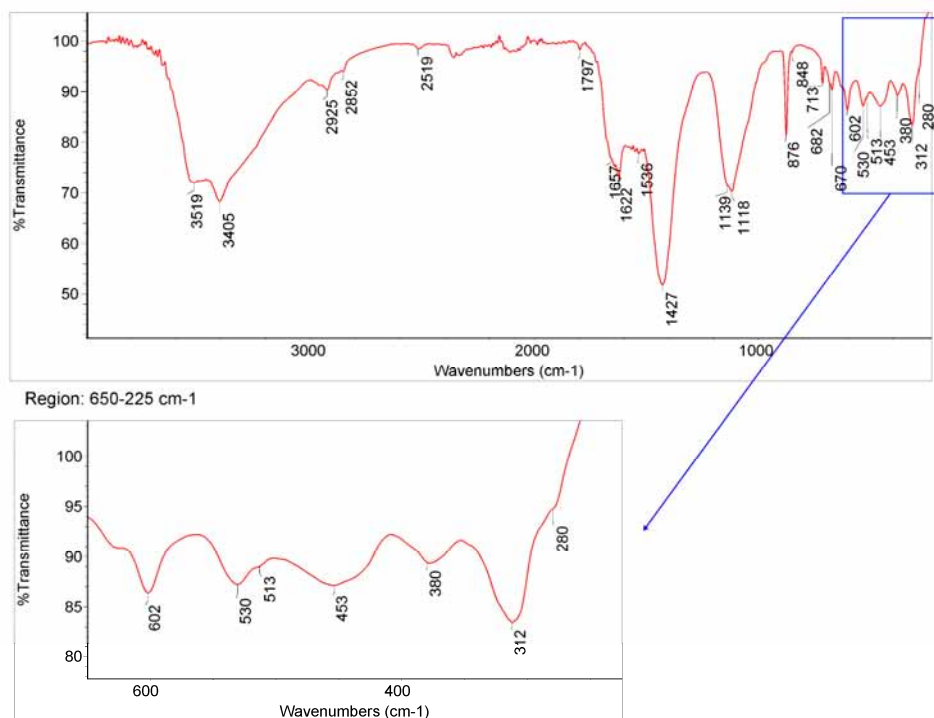


Fig. 25. The ATR-IR spectrum of the pink paint layer

Comparing the ATR-IR spectrum of the pink paint layer with the IR spectrum of red lead (Pb_3O_4) mixed with linseed oil in the low wavenumber range, it is possible to see those IR spectra match quite well (see Fig. 26).

Fig. 26 reveals that the absorption bands of the pink layer at 530 cm^{-1} , 453 cm^{-1} , 380 cm^{-1} and $\sim 312\text{ cm}^{-1}$ agree very well with Pb-O absorptions of Pb_3O_4 (as mentioned above linseed oil does not give any characteristic absorptions below 550 cm^{-1}). As an additional confirmatory feature, the shoulder of the 530 cm^{-1} peak at 513 cm^{-1} is present, exactly as in the case of Pb_3O_4 . The bands of Pb_3O_4 at 326 cm^{-1} and 280 cm^{-1} are masked in the sample spectrum by the large peak of CaCO_3 (has band at $\sim 305\text{ cm}^{-1}$). Nevertheless the 280 cm^{-1} peak is visible as a shoulder on the CaCO_3 peak.

Thus, the red component of pink colour of this sample is red lead (Pb_3O_4). Pink tone was presumably made by mixing red lead pigment with fillers such as chalk, gypsum and silicates. This conclusion is fully supported by the SEM-EDS results (see Fig. 9 in the appendix 12). Table 9 in appendix 12 summarizes the results of the ATR-FTIR analysis of analyzed pink paint layer.

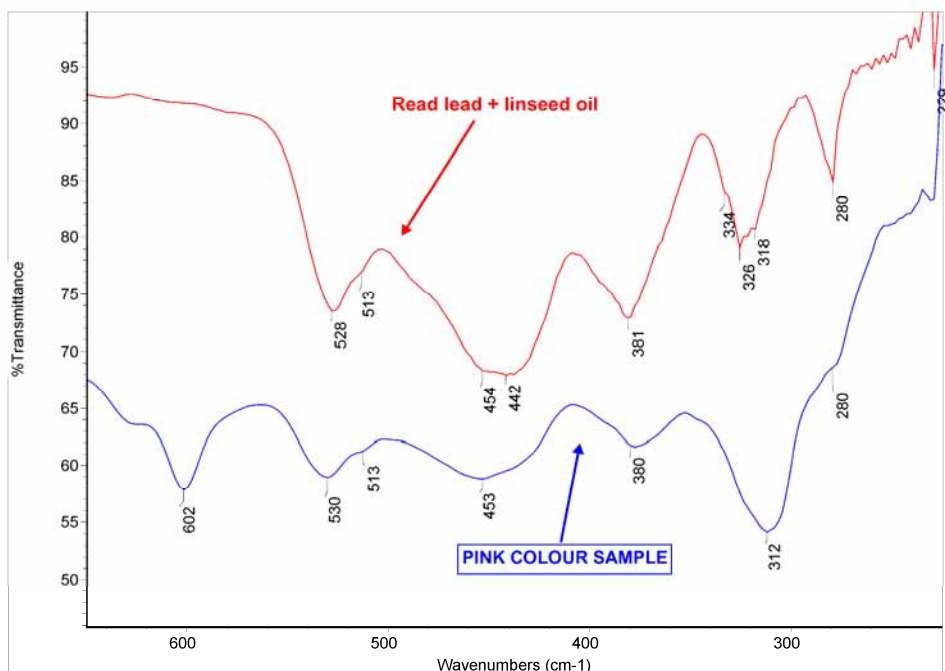


Fig. 26. The ATR-IR spectrum of the pink colour sample and reference spectrum of read lead mixed with linseed oil

4.3.5. Red paint sample from the Bengt Hinrich von Biestram coat of arms of the St Mary's Cathedral in Tallinn

The Cathedral of Saint Mary the Virgin (known in everyday usage as the Dome Church) is one of the oldest churches in Tallinn and is located on Toompea Hill.²⁴

In the Dome church there are numerous historical objects and artefacts including numerous coats-of arms from the 17th–20th centuries. [70]. The coats-of arms collection is the biggest in Europe with the total number of 109 (see photo 4) [71].

²⁴ The first wooden predecessor of the present church was built in 1219 probably by the Danes. Construction of the stone church (which replaced the existing wooden one) was initiated by Dominican monks, who lived in Toompea during 1229–1233 [66]. First time the church in Toompea was mentioned in 1233 when the monks left and bishop continued building the church. The construction works were completed in 1240 and it was also named cathedral and consecrated in honour of Virgin Mary. [70].



Photo 4. The wall full of coat of arms in Dome church (photo by Jaanus Heinla, Conservation Centre Kanut, Tallinn, Estonia)

On the one coat of arms, which belongs to the Bengt Hinrich von Biestram²⁵, there was a paint investigation carried out (see photo 5). The coat of arms was made probably in the 18th century.



Photo 5. Coat of arms of Bengt Hinrich von Biestram (photo by Jaanus Heinla, Conservation Centre Kanut, Tallinn, Estonia)

²⁵ Bengt Hinrich von Biestram was land advisor and head of the Estonian knighthood.

During the restoration work, red paint sample was taken from the coat of arms and the main goal was to determine its composition (especially the pigment) of original upper red paint layer. The area of the red sample pieces was in the range of 2 to 4 mm². The IR spectrum of the upper red paint layer is presented in Fig. 27.

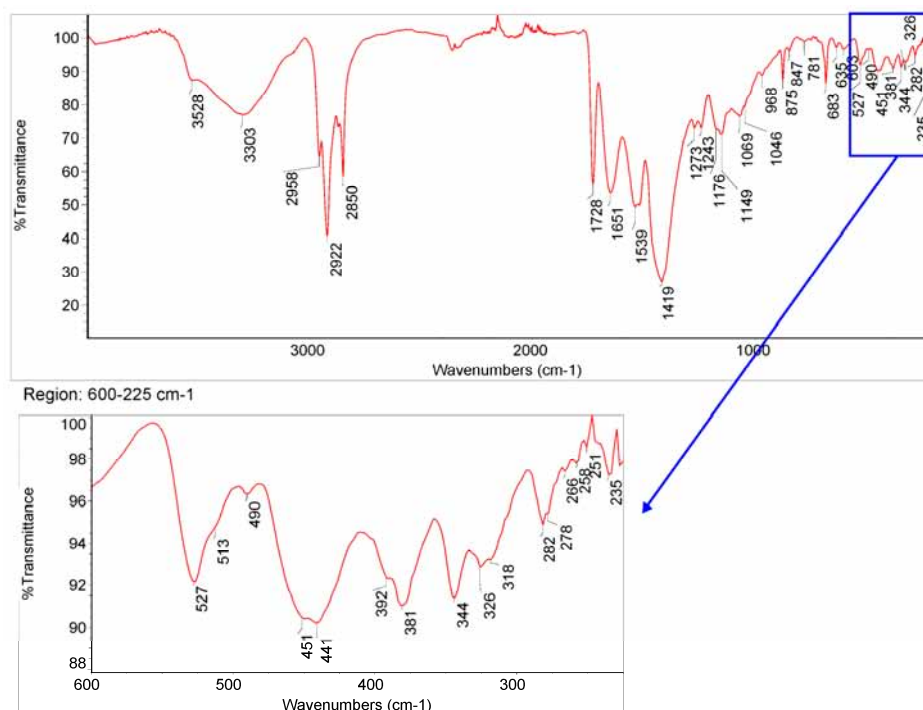


Fig. 27. The ATR-IR spectrum of the red colour sample

Interpretation of the IR spectrum showed that the red paint layer contains two red pigments (see Fig. 28). The absorption bands at 344 cm⁻¹, ~282 cm⁻¹ and 266 cm⁻¹ agree well with those of cinnabar (HgS). The bands at 527 cm⁻¹, 451 cm⁻¹, 441 cm⁻¹, 381 cm⁻¹, 326 cm⁻¹, 318 cm⁻¹ and ~278 cm⁻¹ agree well with the bands of red lead (Pb₃O₄).

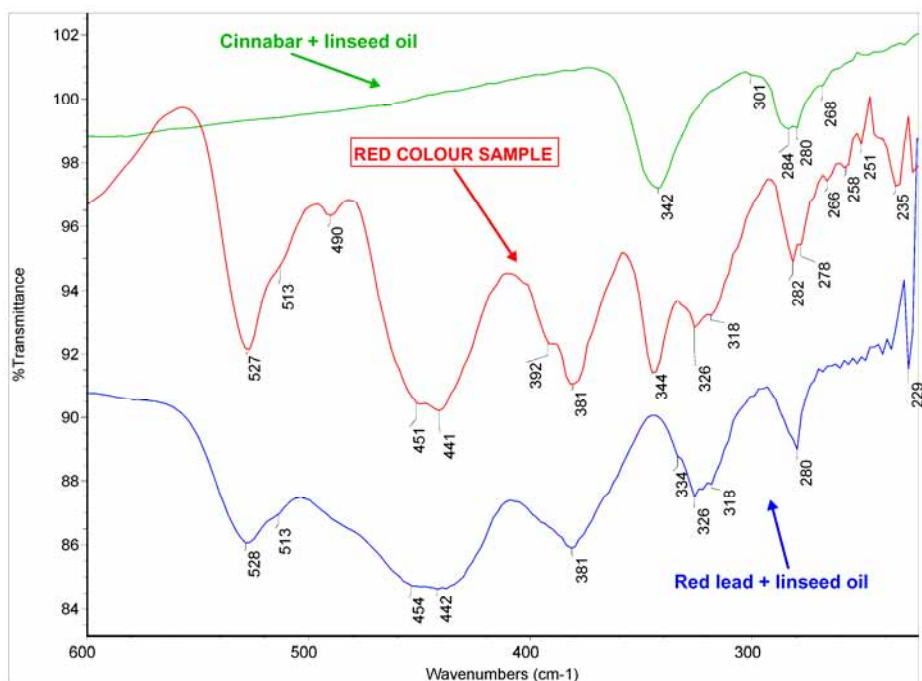


Fig. 28. The ATR-IR spectrum of the red colour sample from Bengt Hinrich von Biestram coat of arms and reference spectra of red lead and cinnabar mixed with linseed oil

Thus the red colour was made by mixing red lead (Pb_3O_4), cinnabar (HgS) pigments and some fillers. This conclusion is fully supported by the SEM-EDS results (see Fig. 10 in the appendix 13). Table 10 in appendix 13 summarizes the results of the ATR-FTIR analysis of analyzed red paint layer.

This is a good example of analysing pigments in the region of $550\text{--}230\text{ cm}^{-1}$ because all the bands are clearly identifiable. This example also demonstrates that in favourable cases pigments can be easily determined even in mixtures.

4.3.4. Paint samples from the unknown artist painting

Paint samples were taken from the unknown artist's painting (see photo 6). This painting belongs in the private collection and there is not much information about this painting. The pigment analysis helped in dating this work of art.

Yellow and brown paint samples were analysed. The sizes of the analysed sample pieces were very small, having area in the range of 0.5 to 1 mm^2 .



Photo 6. The unknown artist's painting (photo by Anu Teearu)

Yellow paint sample

The ATR-IR spectrum of the yellow paint sample is presented in Fig. 29. There are characteristic bands at 444, 428, 406, 390, 379, 346, 338 cm^{-1} , which exactly match those of strontium yellow (SrCrO_4) (Fig. 30). The presence of strontium yellow in the sample is confirmed by the SEM-EDS analysis (see Fig. 11 in the appendix 14). Table 11 in appendix 14 summarizes the results of the ATR-FTIR analysis of yellow paint layer.

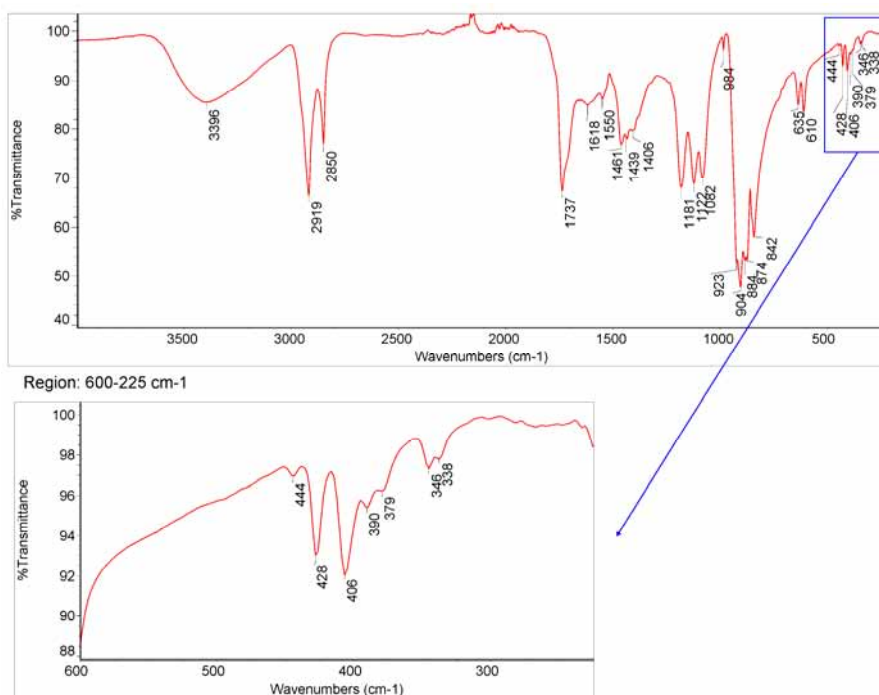


Fig. 29. The ATR-IR spectrum of the yellow paint sample.

This paint sample has a high content of strontium yellow. Strontium yellow was discovered in the beginning of 19th century and so the painting can not be made earlier than that time.

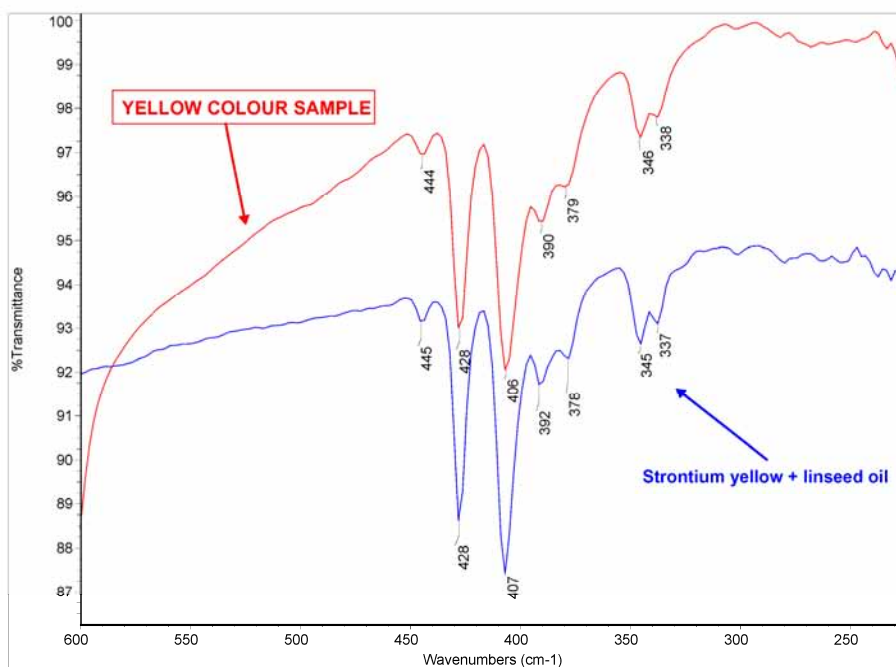


Fig. 30. The ATR-IR spectrum of the yellow paint sample and reference spectrum of strontium yellow mixed with linseed oil.

Brown paint sample

The IR spectrum of the brown paint sample is presented in Fig. 31.

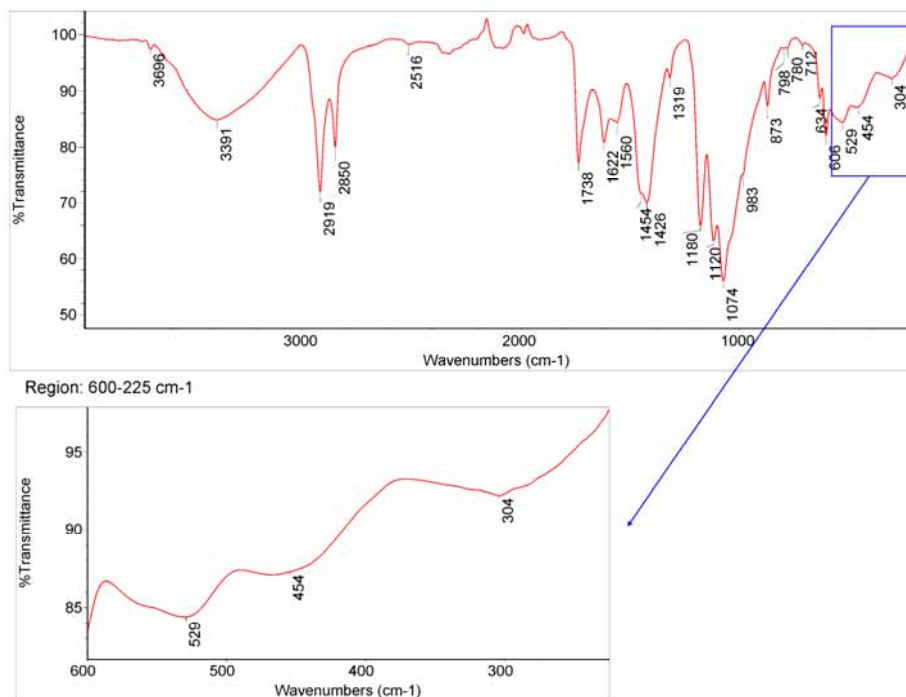


Fig. 31. The ATR-IR spectrum of the brown colour sample

The group of three broad partially overlapping bands at 529, 454 and ~ 304 cm⁻¹ matches very well with that of burnt umber (Fig. 32) from Winsor & Newton.

The sample contains also fillers such as chalk, barium sulphate and some silicates. In the IR spectrum the band at 304 cm⁻¹ is slightly shifted to lower wavenumbers compared to the same band in the IR spectrum of burnt umber mixed with linseed oil. In the spectra of iron oxide (Fe₂O₃) containing pigments the wavenumbers of bands may shift somewhat depending on the pigment particle shape and size, origin and pigment additives [17]. The conclusion that the pigment is burnt umber is fully supported by the SEM-EDS results (see Fig. 12 in the appendix 15). Table 12 in appendix 15 summarizes the results of the ATR-FTIR analysis of brown paint layer.

Usually in the IR spectra of complex paint samples it is difficult to distinguish between different iron oxide-containing pigments, such as burnt umber and brown ochre. In this case distinguishing was successful and this case study shows how useful can the reference IR spectra of pigments be, in particular in the low wavenumber region.

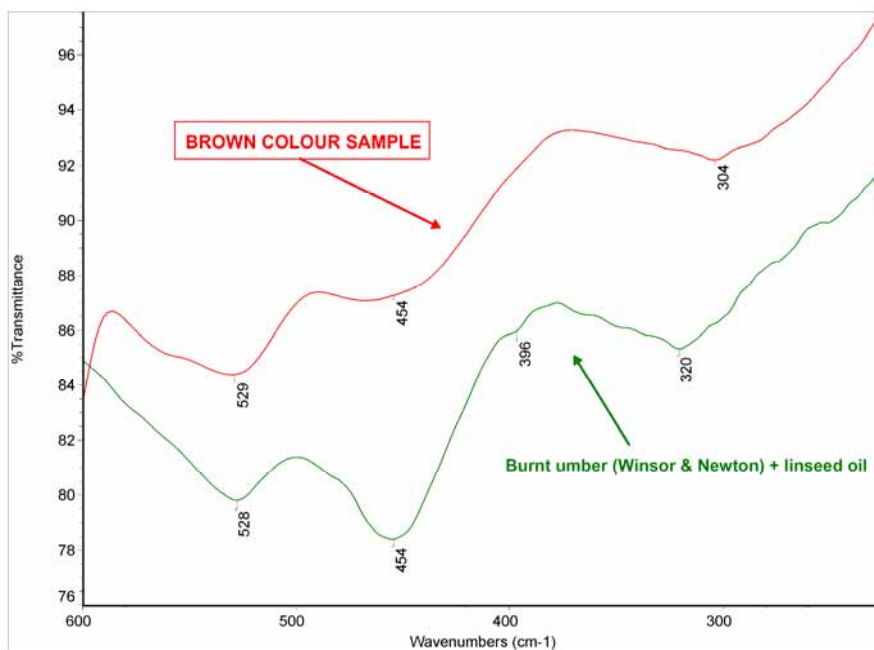


Fig. 32. The ATR-IR spectrum of the brown colour sample and reference spectrum of burnt umber (Winsor & Newton) mixed with linseed oil

4.3.5. Paint sample from the altar and pulpit of St. Mary church in Vigala, Estonia [III]

The altar and the pulpit of the Vigala²⁶ church are among the most beautiful and original woodcarving works preserved in rural churches in Estonia, and are two of the most important interior elements of the Vigala church [72, 73]. See appendix 16, Figs. 13 and 14 where altar and pulpit are displayed before overpainting. Both, the altar and pulpit, were made by Christian Ackermann, a leading woodcarver in Estonia in the second half of the seventeenth century.

In autumn 2005, upon the initiative of the priest of the Vigala St. Mary's church and without permission from the National Heritage Board of Estonia, the altar and pulpit were overpainted with exterior and artists paints (alkyd resin and oil paints) leading to the loss of their historical value (see figs. 15–17 in appendix 16, where are altar and pulpit after the overpainting).

Initiated by this unfortunate overpainting, a comprehensive historical and material study of the overpainted altar and pulpit was carried out with the aim to elucidate the colour schemes and paint materials used during different time

²⁶ St. Mary's church in Vigala was probably built at the end of the thirteenth century [72].

periods and to decide whether to attempt removing the overpainting or not. The altar's and pulpit's colour scheme was investigated using different analyse methods. This was the first study of this kind in Estonia and it is expected to provide reference material for similar investigations in the Baltic and Northern-European region.[III]

This study demonstrates some of the limitations of ATR-FT-IR identification of pigments in the low wavenumber range. Analysis of one paint layer – the red paint layer from the altar – is included in this dissertation. The IR spectrum of the red layer demonstrates very well the problems that occur when there are broad additive bands that overlap with pigment bands in the IR spectrum. Similar problems occurred also with some other paint layers that were taken from the altar and pulpit.

Red paint layer

The sample piece was taken from the lower part of the robe of the round plastic sculpture „Love“ from the altar and the red middle layer was analyzed (see in appendix 16 in figure 15 is marked the location of the sample). In figure 33 the cross-section of the analysed paint sample is presented and the analysed red middle layer is indicated. In figure 34 the IR spectrum of the red middle layer is presented.

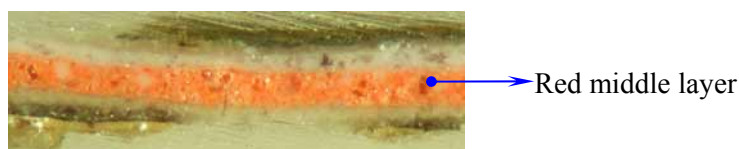


Figure 33. Cross-section of the paint sample where analysed red middle layer is indicated

On the basis of the IR spectrum (fig. 34) in the region of $550\text{--}230\text{ cm}^{-1}$ it is possible to see one very broad band and the some smaller bands. These bands cover almost the entire wavenumber region of $550\text{--}230\text{ cm}^{-1}$. The broad band in the range of $550\text{--}350\text{ cm}^{-1}$ matches well with the absorption band of zinc white (ZnO). The other band, in the range of $320\text{--}250\text{ cm}^{-1}$, matches well with the absorption bands of calcium carbonate (CaCO_3) and lithopone ($\text{ZnS} + \text{BaSO}_4$). On the basis of that IR spectrum, it is very difficult to say whether in the red layer is chalk or lithopone or both. The comparison of the red layer and reference IR spectra is presented in fig. 35.

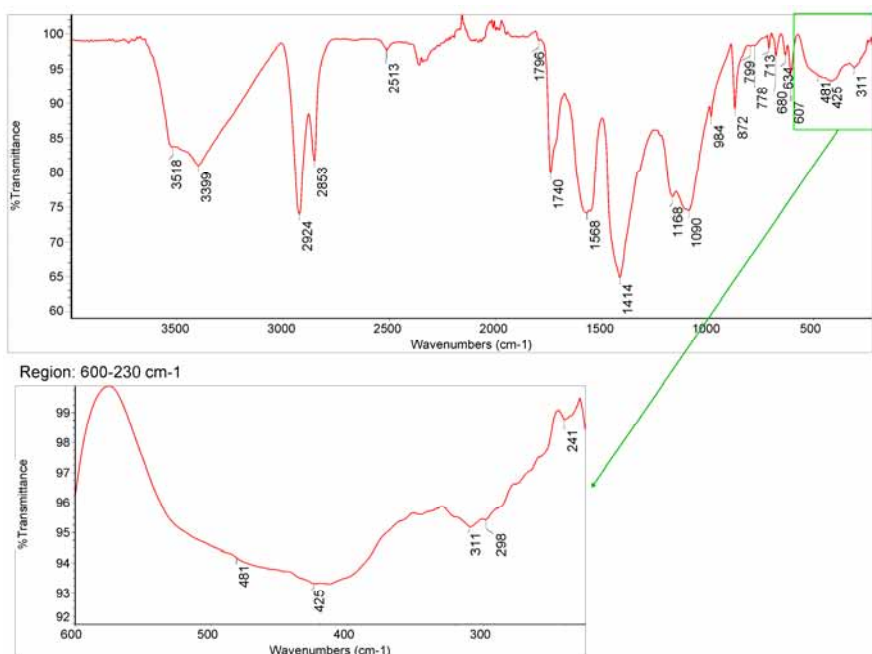


Fig. 34. IR spectrum of red middle layer

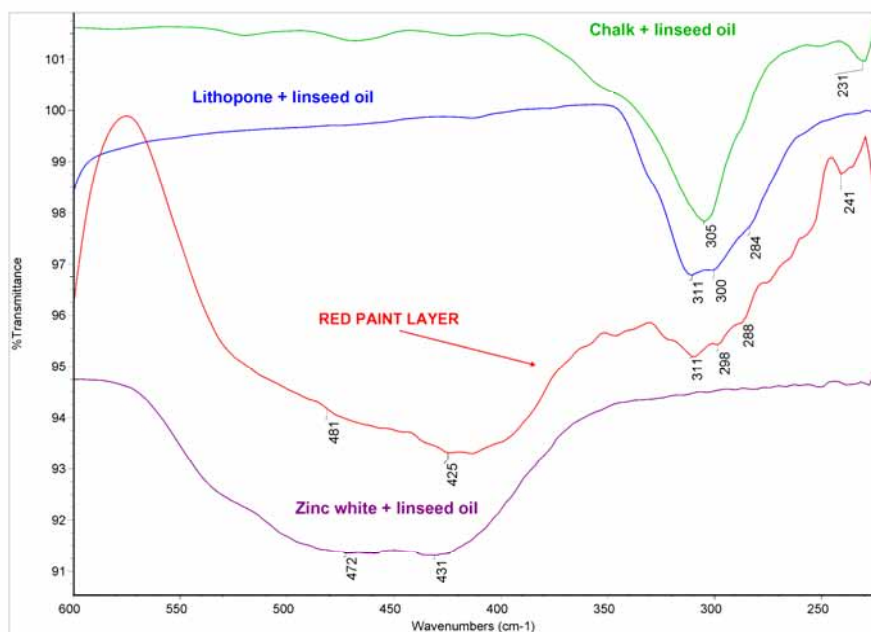


Fig. 35. The ATR-IR spectrum of the red layer and reference spectra of zinc white and chalk mixed with linseed oil

On the basis of these IR spectra (figs. 34 and 35) it is impossible to determine red pigment in the region of $550\text{--}230\text{ cm}^{-1}$, because its content is low and the two broad bands in the spectra overlap or interfere red pigments appearance.

In this case to get information about red pigment, other analyse method (SEM/EDS) was used (see SEM/EDS spectrum of red pigment in appendix 17) and the result is that cinnabar (HgS) is the red colour tone giving pigment.

So, the red middle layer according to the different analysis (ATR-FTIR and SEM/EDS) is composed of cinnabar, zinc white and some additives like chalk or lithopone or both and maybe also barium carbonate. It is important to mention that the amount of the red pigment in paint samples is often lower than the amount of fillers or other additives.

This IR spectrum of red layer is a good example showing the limitations of ATR-FT-IR analysis of pigments in the region of $550\text{--}230\text{ cm}^{-1}$. Nevertheless, there are very few pigments that have as broad bands as zinc white. When zinc white is in the spectrum it gives a band in the range of $550\text{--}350\text{ cm}^{-1}$, so in the further analysis the lower part of the IR spectrum can be used (around $350\text{--}230\text{ cm}^{-1}$). However, when in the region of $550\text{--}230\text{ cm}^{-1}$ there are two broad bands (one belongs to zinc white and the other to some other pigment or filler that absorbs at lower wavenumber) then it can be very difficult to analyse other compounds (pigments) using the low wavenumber range.

5. CONCLUSIONS

The results of this work significantly expand the applicability of ATR-FT-IR spectroscopy in the analysis and identification of inorganic pigments by using the low wavenumber region $550\text{--}230\text{ cm}^{-1}$. The advantages (and possibilities) of ATR-FT-IR for identification of inorganic pigments in the low wavenumber region $550\text{--}230\text{ cm}^{-1}$ are the following:

- The absorption bands of many inorganic pigments are very characteristic. Actually most inorganic pigments can be determined using that wavenumber region.
- It is possible to determine oxide- and sulphide-based pigments such as cinnabar, orpiment, cadmium red, cadmium yellow, massicot that are undetectable in the mid-IR region because they lack characteristic absorption bands in the mid-IR region.
- There are many pigments that have absorption bands in the mid-IR region but are still problematic to determine in real-life samples because of limited characteristicity of the bands (e.g. blue silicate-containing pigments) or overlapping of the bands by those of other paint components (binder, additives). Many of these problems are absent in the far-IR region.
- Most of the characteristic bands of the binders (linseed oil, tempera, etc) and fillers (chalk, gypsum etc) that are likely to interfere with pigment determination occur in mid-IR region and many of those materials lack bands in the far-IR region.

The limitations of ATR-FT-IR for identification of inorganic pigments in the low wavenumber region $550\text{--}230\text{ cm}^{-1}$ are the following:

- The bands of some fillers (most importantly chalk) and also pigments (zinc white, lithopone) can overlap with the pigment bands.
- In the ATR spectra the band maxima are slightly shifted compared to transmission spectra and ATR correction algorithm is necessary to carry out. With the complex mixtures (paint samples) it is difficult to know the parameters that are required for the correction because these have seldom well-defined composition and therefore the result after ATR correction is some times distorted bands in the IR spectra.

6. SUMMARY

The present work focused on expanding the possibilities and usefulness of micro-ATR-FT-IR spectroscopy in identification of different inorganic pigments in historic artefacts.

The main goals of this dissertation were successfully fulfilled:

1. An analytical method for determination and identification of inorganic pigments in paint layers by micro-ATR-FT-IR using the wavenumber region of $550\text{--}230\text{ cm}^{-1}$ was developed.

Due to the nature of the ATR phenomenon, the high refractive indices of many pigments and the long wavelength in the $550\text{--}230\text{ cm}^{-1}$ spectral region low quality spectra are obtained if recorded directly from pure pigments. Mixing the powdered pigment with linseed oil decreases the refractive index of the mixture and makes it possible to obtain high-quality IR spectra. These reference IR spectra can be used for analysis of paint layers. Since in the samples the pigment is inevitably mixed with a binder, this above described problem does not appear when recording spectra of samples.

It was demonstrated that with few exceptions the analyzed inorganic pigments have characteristic absorption bands in the low wavenumber region ($550\text{--}230\text{ cm}^{-1}$) and can be determined and identified using ATR-FT-IR in this spectral region.

2. Using the developed method, reference samples of the 47 white, yellow, red, green, blue, brown, black inorganic pigments were prepared by mixing them with linseed oil and their IR spectra were measured and analysed. These spectra form a useful collection of reference spectra for identification of pigments in the low wavenumber range.
3. Via five case studies it was demonstrated that ATR-FT-IR in the low wavenumber range ($550\text{--}230\text{ cm}^{-1}$) can be well used for identification of inorganic pigments in paint samples from historic objects and the spectra of the self-made samples of inorganic pigments can be successfully used as reference spectra. The main limitation of the approach – interference from chalk, if present in large quantity – was also demonstrated. Art objects, several of them important in Estonian history, were selected for the case studies.

As a result of this work the application area of ATR-FT-IR spectroscopy for determination of inorganic pigments was significantly expanded. In fact, it is now possible to determine and identify all paint components – pigment, binder and additives – by ATR-FT-IR spectroscopy.

7. SUMMARY IN ESTONIAN

ATR-FT-IR spektroskoopia võimaluste laiendamine anorgaaniliste pigmentide analüüsimisel

Käesolevas doktoritöös keskenduti mikro-ATR-FT-IR spektroskoopia võimaluste hindamisele ja rakendusala laiendamisele erinevate anorgaaniliste pigmentide uurimisel.

Püstitatud eesmärgid saavutati:

1. Töötati välja meetodika värvikihtides anorgaaniliste pigmentide analüüsimiseks mikro-ATR-FTIR meetodil kasutades lainearvude vahemikku 550–230 cm^{-1} .

Tulenevalt ATR meetodi iseärasustest, pigmentide kõrgetest murdumisnäitajatest ja kasutatavast madalate lainearvude piirkonnast (550–230 cm^{-1}), saadakse puhastest pigmentidest enamasti halva kvaliteediga ATR-IR spektrid. Segades pigmenti linaseemneõliga, pigment lahjeneb ja segu murdumisnäitaja alaneb, võimaldades saada märksa parema kvaliteediga IR spektreid, kus ka madalatel lainearvudel on kõik neeldumismaksimumid eristatavad. Saadud võrdlusspektreid saab kasutada pigmentide tuvastamisel värvikihtides. Uuritavate proovide korral eelpool mainitud probleemi ei esine, sest pigment esineb proovides alati segatuna kilemoodustajaga.

Demonstreeriti, et väheste eranditega omavad analüüsitud anorgaanilised pigmendid karakteristlikke neeldumisjooni madalatel lainearvudel (550–230 cm^{-1}) ja välja töötatud ATR-FT-IR-põhise meetodika abil on võimalik analüüsida värviproovides pigmente kasutades kaug-IR piirkonda.

2. Rakendades välja töötatud meetodikat, valmistati võrdlusproovid 47 valgest, kollasest, punasest, sinisest, rohelisest, pruunist ja mustast pigmendist. Registreeritud spektritest koostati võrdlusspektrite kogumik pigmentidest, mis neelavad madalatel lainearvudel (550–230 cm^{-1}).
3. Viie rakendusnäite põhjal demonstreeriti, et ATR-FTIR meetodil on võimalik madalatel lainearvudel edukalt identifitseerida värviproovides pigmente, kasutades selleks välja töötatud meetodika abil valmistatud võrdlusproovide spektreid. Toodi välja ka meetodi puudused, millest olulisimaks on kriidi (sageli esinev täiteaine) segav mõju. Rakendusnäidete värviproovid võeti kunstiobjektidelt, millest mitmed on Eesti kunstiajaloo olulisel kohal.

Töö tulemusena laiendati oluliselt ATR-FT-IR meetodi kasutusvaldkonda anorgaaniliste pigmentide identifitseerimisel. Nüüd on võimalik ATR-FTIR spektroskoopia abil põhimõtteliselt analüüsida ja identifitseerida kõiki värvi komponente: pigmente, täiteaineid ja sideaineid.

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APPENDIX I

Short description of two most common binders

Here only two most common binder material types – oils and proteins – are discussed, because these are in the composition of the paint samples that were taken from art objects (look case studies in section 3.4).

Oils

Oils can be divided into drying, semidrying and non-drying oils.

Drying vegetable oils are suitable binders in paints, because they form a dry film upon exposure to air (drying time can be about 2–4 days) [14, 74]. The solid film can be very different: matt or shiny, porous or glazed, depending on the quantity and the nature of the pigments or of the coating technique [75]. The most important drying oils are linseed oil, poppy-seed oil and walnut oil [74]. Linseed oil is the most widely used drying oil in paints. Linseed oil dries faster than poppy seed and walnut oils. Semi-drying oils are for example sunflower oil, soybean oil etc. Semi-drying oils dry much longer than drying oils and are therefore rarely used in paints [14]. Non-drying vegetable oils are for example rice oil, olive oil, castor oil etc [2] and these are not suitable for painting.

Drying oils are natural triglycerides containing high percentage of polyunsaturated fatty acids (linolenic, linoleic, oleic acid) and also minor amounts of saturated fatty acids (palmitic, stearic acids and also lauric, myristic acids) [75–77]. The drying power is related to the concentration of polyunsaturated fatty acids in the oil, because their C=C double bonds enable polymerization and oxidation reactions which promote the formation of the film (for rapid drying the presence of linolenic acid is essential) [75].

Drying oils have replaced step by step the egg tempera medium since 15th century, although they may have been used already in 12th century [74, 75]. Drying oils have been the most popular binder for many centuries and are often used also nowadays.

Proteins

Proteins are polymeric substances composed of chains of amino acids [22, 75]. The proteins present in living organisms consist of various combinations and proportions of twenty naturally occurring amino acids [22]. Proteins are amongst the most important components of living cells. Such diverse materials as bone and ivory; silk, wool and hair; skin products such as leather and parchment are made of, or contain, protein [78].

Proteins from eggs (egg white, egg-yolk) also milk have been long used as binding media; animal and fish glue, casein as adhesives [78].

Tempera is a painting medium in which pigments are mixed with a water-soluble binding agent (such as egg, glue, honey, milk (in the form of casein) and a variety of plant gums). After drying, this binding agent becomes insoluble and permanent. Egg is oldest binding agents and term “Egg tempera” is used [3]. Other forms of tempera are for example gum tempera, glue tempera, casein tempera [2, 3].

Traditional (used for centuries) pure egg tempera was made by the simple process of mixing finely powdered inorganic pigments, water and dilute egg yolk (vinegar was sometimes added as preservative and to make the medium less greasy) [2, 3].

APPENDIX 2

Table 1. General common traditional inorganic pigments [2, 3, 9–13, 17]

Pigment name	Chemical composition	Time when the pigment was in common use	Refractive index (n_D)	Comments
WHITE PIGMENTS				
Lead white	$2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$	Antiquity –20 th century	1.94–2.09	One of the first artificial pigments. Was later replaced by titanium white
Barium white (Barytes or barite)	BaSO_4	Natural: since antiquity; Artificial: since 1830	Barite (nat): 1.636–1.648; Blanc fixe (art.): 1.62–1.64	Natural from the mineral barite. Artificial called blanc fixe.
Lithopone	$\text{BaSO}_4 + \text{ZnS}$	Since 1874	2.3 (ZnS); 1.64 (BaSO_4)	Synthetically made pigment, has greater hiding power than zinc white
Zinc white	ZnO	Since 1834	2.00–2.02	Was used as a lightening agent in various coloured pigments.
Titanium white	TiO_2	Since 1920s	2.6–2.9	The highest whiteness and hiding power of the white pigments.
Chalk	CaCO_3	Since antiquity	1.49–1.66	Mineral form of calcium carbonate is calcite. In painting important filler and primer (ground) component
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Since antiquity	1.52–1.53	In painting important filler and primer (ground) component

Table 1. Continue

Pigment name	Chemical composition	Time when the pigment was in common use	Refractive index (n_D)	Comments
YELLOW PIGMENTS				
Yellow Ochre	α -FeOOH + clay, quartz	Since antiquity	2.36 (average) (goethite)	Mineral is goethite
Massicot	PbO	Since antiquity	2.51–2.71	Synthetically made pigment
Cadmium yellow	CdS	Discovered in 1817; widespread use since early 20 th century	2.35–2.48	Synthetically made pigment
Naples yellow	$Pb_3(SbO_4)_2$ or $Pb(SbO_3)_2$	16 th century B.C.	2.01–2.28	One of the oldest synthetically produced pigments. Also known under the name lead antimonate yellow.
Orpiment, genuine	As_2S_3	B.C. until the end of the 19 th century	2.40–3.02	Mineral is orpiment. Toxic pigment.
Chrome yellow	$PbCrO_4$	First recognised as a pigment in 1804	2.3–2.7	Synthetically made pigment. Most important chromate-containing yellow pigment
Barium yellow	$BaCrO_4$	Since 1809	1.94–1.98	synthetically made pigment
Strontium yellow	$SrCrO_4$	Since 1800s	1.92–2.01	synthetically made pigment
Lead-Tin-Yellow, type I	Pb_2SnO_4	13 th century–1750; rediscovered in 1941	2.29–2.31	synthetically made pigment
Lead-Tin-Yellow, type II	$Pb(Sn,Si)O_3$	Probably 13 th century-1750; rediscovered in 1941	2.29–2.31	synthetically made pigment

Table 1. Continue

Pigment name	Chemical composition	Time when the pigment was in common use	Refractive index (n_D)	Comments
RED PIGMENTS				
Cinnabar (or Vermilion)	HgS	Since antiquity	3,146–2,819	Mineral is cinnabar
Red lead	Pb ₃ O ₄	Since antiquity	2.42	Artificially made
Cadmium red	CdS+CdSe [or CdS(Se)]	first commercialized in about 1910	2.64–2.77	synthetically made pigment
Natural red earth (or red ochre)	Fe ₂ O ₃ + clay	Since antiquity	2.87 (average) (hematite)	Mineral is hematite
Realgar	As ₂ S ₂	B.C.–19 th cent.	2.46–2.61	Mineral is realgar
Mars red	Synthetic red iron oxide pigment	Commercially produced since middle of the 19 th century	2.78–3.01 (probably)	Mars red is one of the mars pigments
GREEN PIGMENTS				
Malachite	CuCO ₃ ·Cu(OH) ₂	Since antiquity	1.655–1.909	Mineral is malachite
Green earth	The general formula: K[(Al, Fe ^{III}), (Fe ^{II} , Mg)] (AlSi ₃ Si ₄)O ₁₀ (OH) ₂	Since antiquity	1.62	Primary source minerals are glauconite and/or celadonite
Chromium oxide	Cr ₂ O ₃	Known since 1809; available as an artist's pigments since 1862	2.5	Synthetic pigment. Most stable of green pigments.
Verdigris	Cu(CH ₃ COO) ₂ ·2Cu(OH) ₂	Since antiquity	1.53–1.56	Synthetic pigment. The most reactive and unstable of all the copper pigments.
Cobalt green	CoO·ZnO	Since 1780	1.94–2.0	Synthetic pigment.
Viridian green	Cr ₂ O ₃ ·2H ₂ O	Discovered 1838	1.62–2.12	Synthetic pigment. After the discovery, replaced Emerald green.

Table 1. Continue

Pigment name	Chemical composition	Time when the pigment was in common use	Refractive index (n_D)	Comments
Emerald green (or Schwein-furt green)	$3\text{Cu}(\text{AsO}_2)_2 \cdot \text{Cu}(\text{CH}_3\text{COO})_2$	Discovered in between 1800–1814	1.71–1.78	Synthetic pigment. Its extremely toxic pigment.
Chrome green	$\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 + \text{PbCrO}_4$	Since in the first quarter of the 19 th century	2.4	Synthetic pigment.
BLUE PIGMENTS				
Egyptian blue	$\text{CaCuSi}_4\text{O}_{10}$	ca 3100 B.C.	1.59–1.63	One of the oldest synthetically produced pigments. Mostly used in ancient time.
Ultra-marine blue	the approximate compositional formula $3\text{Na}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{Na}_2\text{S}$	natural: 13 th –19 th , artificial: since 1828	1.5	Mineral is lapis lazuli. Chemically it is the most complex of all the mineral pigments.
Smalt	potash silicate glass with cobalt oxide	16 th –19 th century	1.46–1.55	The earliest of the cobalt pigments. It is synthetic pigment. The only amorphous blue pigment.
Prussian blue	$\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$	Since 1704	1.56	Well-documented synthetic pigment.
Azurite	$2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$	Since antiquity until at the beginning of 18 th century	1.730–1.838	Mineral is azurite. Largely was replaced by Prussian blue.
Cobalt blue	$\text{CoO} \cdot \text{Al}_2\text{O}_3$	Discovered by L.J. Thénard in 1802	1.74	Synthetic pigment.

Table 1. Continue

Pigment name	Chemical composition	Time when the pigment was in common use	Refractive index (n_D)	Comments
Cerulean blue	$\text{CoO} \cdot n\text{SnO}_2$	First introduced in 1821; widely available and into use since 1860	1.84	Synthetic pigment.
BROWN PIGMENTS				
Raw umber	$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O} + \text{MnO}_2 + \text{clay}$	Since antiquity	1.87–2.17	Natural pigment
Burnt umber	$\text{Fe}_2\text{O}_3 + \text{MnO}_2 + \text{clay}$	Since antiquity	2.2–2.3	Natural pigment
Brown ochre	$\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$, silica, clay	Since antiquity	1.8–2.2	Natural pigment
BLACK PIGMENTS				
Charcoal	C	Since antiquity	Opaque	Natural pigment
Bone black	$\text{C} + \text{Ca}_3(\text{PO}_4)_2$	Since antiquity	1.65–1.70	Natural pigment
Ivory black	$\text{C} + \text{Ca}_3(\text{PO}_4)_2$	Since antiquity	1.65–1.70	Natural pigment
Vine black (pure plant black)	C	Since antiquity	Opaque	Natural pigment
Mars black	$\text{FeO} \cdot \text{Fe}_2\text{O}_3$ (Synthetic black iron oxide)	Since 1920s		Synthetic pigment

APPENDIX 3

Table 2. The group wavenumbers of inorganic anions [22, 23, 37, 79]

Vibrations	Wavenumbers (cm ⁻¹)	Comments
CARBONATES (CO₃²⁻)		
C-O stretch (strong)	1550–1350	Inorganic carbonates have three equivalent C-O bonds arranged in a trigonal planar pattern around the carbon atom, with a bond angle of 120°. The following pigments and fillers are carbonate-based: calcite (CaCO ₃), lead carbonate (or cerussite; PbCO ₃), azurite (2CuCO ₃ ·Cu(OH) ₂) and malachite (CuCO ₃ ·Cu(OH) ₂). In anhydrous compounds (for example calcite) the stretching band is smooth, symmetrical and broad. In hydrated carbonates (for example malachite) the stretching absorption band is split. The carbonate bending bands show measurable frequency differences corresponding to the attached cation. For example the out-of-plane bending vibration for calcium carbonate (calcite) occurs at 872 cm ⁻¹ , for lead carbonate the same vibration occurs at 841 cm ⁻¹ . Calcium carbonate has absorption band also around ~300 cm ⁻¹ . Hydrated carbonates (azurite, lead white, malachite etc) have stretching O-H bands due to hydration in the region of 3535–3320 cm ⁻¹ and sharp O-H bending vibrations at 1100–1000 cm ⁻¹ .
C-O out-of-plane bend (sharp)	880–820	
C-O In-plane bend (sharp)	~740–650	
SULPHATES (SO₄²⁻)		
S-O Stretch (strong and broad)	1200–1050	Sulphates contain four equivalent S-O bonds with formal bond order of ca 1.5 and thus nine fundamental vibration modes, several of which are degenerate. Gypsum (CaSO ₄ ·2H ₂ O), anhydrite (CaSO ₄) and barite (BaSO ₄) are sulphate-based. Gypsum contains besides S-O bands also O-H stretching bands from 3550 to 3400 cm ⁻¹ and the bending bands at 1684 and 1621 cm ⁻¹ . Gypsum has broad absorption band at around ~250 cm ⁻¹ .
S-O Bends (sharp)	680–600	

Table 2. Continue

Vibrations	Wavenumbers (cm ⁻¹)	Comments
SILICA AND SILICATES		
SiO-H stretch	3700–3200	Nearly all types of glass (amorphous silica) produce an absorption band that is similar in appearance, even though glass is composed of a wide range of mixture of materials. The similar IR spectra occur because the basic glass structure contains a Si-O backbone. So, glass type can not differentiate with IRS. Silicates have a fully ordered crystalline lattice structure. This produces a well-defined Si-O absorption band at 1200–800 cm ⁻¹ . The hydration absorption bands for silicates (kaolin, talc) occur as sharp, well defined bands in the region of 3700–3600 cm ⁻¹ .
Si-O (or Si-O-Si) asymmetric stretch	1200–800	
Si-O bending bands	800–400	
CHROMATES (CrO₄²⁻)		
Cr-O stretching bands	950–800	Similarly to sulphate the tetrahedral chromate anion possesses nine fundamental vibrations, several of which are degenerate in the free ion. The respective chromate absorptions occur at lower wavenumber values than the corresponding sulphate ones. Such pigments like chrome yellow (PbCrO ₄), barium yellow (BaCrO ₄) and strontium yellow (SrCrO ₄) belong to chromates.
Cr-O bending bands	450–300	
PHOSPHATES (PO₄³⁻)		
P-O stretch (broad and strong)	1100–1000	P-O stretching appears between 1100 and 1000 cm ⁻¹ . Also sulphates and silicates have strong, broad bands in this region and thus this band is of low diagnostic value for phosphate determination. So in order to identify phosphates the secondary bands, such as bending vibrations and bands in the far-IR region are very important. Bone (or ivory) black [C+Ca ₃ (PO ₄) ₂] is a pigment that contains phosphate.
P-O bends	600–500	
WATER BANDS		
O-H stretching band (broad)	3800–3200	Inorganic compounds generally contain polar bonds and charged fragments. Therefore the polar ends of the O-H bond in a water molecule can easily form hydrogen bonds to inorganic molecules.

APPENDIX 4

Other commonly used methods for analysing inorganic pigments

Optical microscopy methods

Light microscopy (LM)

Light or optical microscopy involves passing visible light transmitted through or reflected from the sample through a single or multiple lenses to allow a magnified view of the sample and determining the colour of the pigment. Light microscopy (optical microscopy) has been used to characterize particles down to the micrometer size scale. It is also used in the investigation of paint cross-sections. Cross-sections are prepared from multi-layered samples taken from an art objects. Paint cross-sections are normally embedded entirely in a polyester or poly-acrylate resin. It is used to investigate the colour, thickness, and particle size distribution of the different layers. The colour and form of pigment particles can in many cases be used for their identification. [31] Most cases, using light microscopy alone is not enough, it may be difficult to distinguish one pigment (or particles) from another pigment, for example hematite (Fe_2O_3) from vermilion (HgS). These two pigments can be distinguished then by instrumental methods. [17]

Polarized light microscopy (PLM)

Polarized light microscope utilizes polarized light (light is polarized by the polarizing filters) to form a highly magnified image of a sample [22]. The simplest polarized light microscope is essentially a brightfield microscope with a rotating stage and plane-polarizing filters placed below (the polarizer) and above (the analyzer) the specimen. Polarized light microscopes have a high degree of sensitivity and can be utilized for both quantitative and qualitative studies targeted at a wide range of anisotropic specimens. The polarized light microscope allows to observe (and also photograph) samples that are visible primarily due to their optically anisotropic character.

For pigment analysis PLM provides refractive index, particle size, size distribution, color, shape, pleochroism, optical properties, and morphology data which are useful for the identification of the type of pigment and its source. PLM cannot directly determine a material's crystal structure or chemical composition. [80]

Raman Spectroscopy

Raman spectroscopy (also Raman microscopy) is widely used in the pigment identification due to its high reproducibility, high sensitivity and non-destructiveness. [29]

Raman spectroscopy (as also infrared spectroscopy) is classified as vibrational spectroscopy. [31] Raman spectroscopy is based on Raman scattering (or Raman effect). The electromagnetic radiation, colliding with a molecule, can be transmitted, absorbed, or scattered [50]. When monochromatic radiation is scattered by molecules, a small fraction of the scattered radiation is observed to have a different frequency from that of the incident radiation, this is known as the Raman effect [27]. So the Raman effect arises when a beam of intense monochromatic radiation passes through a sample that contains molecules that undergo a change in molecular polarizability as they vibrate.

For a vibration to be active in the Raman effect, the polarizability of the molecule must change during the vibration. [27] In Raman spectroscopy, as it is scattering technique, samples are simply placed in the laser beam and the backscattered radiation is analysed [24].

Although vibrational Raman spectra are related to infrared absorption spectra, a Raman spectrum arises in a different manner and thus often provides complementary information to IR spectrum. Vibrations that are active in Raman scattering are often inactive in the infrared, and vice versa. [27]

Frequent problems when collecting Raman spectra of paint samples are (1) fluorescence [50] and (2) heating and possible degradation of the sample under the intense laser radiation. The primary disadvantage of Raman spectroscopy is the fluorescent background that accompanies intense laser irradiation of many materials. Relative to the Raman signal, the fluorescent background can be enormous and interfere with the spectrum. Although the problem can be partially resolved by careful sample preparation, time resolved spectroscopy or coherent anti-Stokes Raman spectroscopy (CARS), there will always be experiments that remain difficult to perform. [27]

X-ray Diffraction (XRD)

With XRD is possible to analyze only crystalline substances. XRD provides information on structures, phases, preferred crystal orientations (texture), and other structural parameters.

Generally, X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. Each crystalline substance has a unique repeating three-dimensional array of atoms and produces a unique X-ray diffraction pattern [81]. Diffraction patterns can be used as “fingerprints” for identification of crystalline phases.

X-ray diffraction experiments are performed by irradiating a crystalline sample with a beam of X-rays, X-rays interact with the sample in such a way that the x rays are emitted in all directions. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy the Bragg's Law ($n\lambda = 2d \sin \theta$). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. A diffractometer can be used to obtain the diffraction pattern of any crystalline solid. So, both the diffraction angle and the intensity of each of the diffracted beams (diffraction peaks) are then measured, processed and counted. The intensity of diffracted X-rays is plotted as a function of diffraction angle 2θ [81]. When a crystal is mounted and exposed to an intense beam of monochromatic X-rays, it scatters the X-rays into a pattern of spots or reflections that can be observed on a screen behind the crystal. The intensities of these reflections may be recorded with a photographic film, an area detector or with a charge-coupled device (CCD) image sensor. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. [27, 81, 82]

XRD has been used to analyze inorganic pigments, because most of them have crystal structure. XRD has also some disadvantages. Different substances may have similar diffraction patterns (at least in part). Misidentification can occur when the sample contains several crystalline phases producing a complex diffraction pattern [81]. With XRD is impossible to analyze amorphous materials (this of course can also be an advantage – amorphous constituents of the samples do not interfere). The sample size required for the analysis is usually larger than what is needed for most other techniques

(ATR-FTIR, XRF, SEM-EDS etc). This often complicates the analysis of paint samples that are taken on the art objects, which are mostly very small and containing many paint layers.

Elemental analysis techniques

Scanning electron microscopy –energy dispersive X-ray spectrometry (SEM-EDS)

SEM-EDS is useful for the spatially resolved analysis of pigments, which have a characteristic elemental composition. [31] Scanning electron microscope (usually abbreviated SEM) is a technique that is routinely used in the investigation of paint surfaces and also cross-sections. Due to its excellent spatial resolution it allows detailed surface analysis at high imaging magnifications and is thus a very suitable method for cross-section analysis. Energy dispersive X-ray spectrometer (EDS) allows carrying out elemental analysis of different materials (including pigments). SEM, in addition to providing image of the surface also serves as excitation source for EDS. The interaction of the SEM beam with the sample creates X-rays that are detected and identified by EDS. [1]

Scanning electron microscope (SEM) operates by generating a beam of electrons in a vacuum. The beam is focused by electromagnetic lenses within a column, and directed downwards toward the sample. The interaction of the electron beam with the sample causes electrons to be dislodged from the atoms within the sample. The electrons generated by this sample-beam interaction are detected, amplified and displayed on a screen. High magnifications are made possible by scanning smaller areas of the sample and displaying that smaller area on the display screen. [1] Image formation in the SEM is achieved by the detection of the backscattered and secondary electrons that arise from the sample.

Energy dispersive X-ray spectrometer (EDS) detects and identifies emitted X-rays. X-rays are produced when the incident electron beam interacts with the inner shell electrons of the atom. The ejected produces a hole that is filled by an electron of the outer shells. The transitions result in the emission of X-rays. The emitted X-rays have an energy characteristic for each element. [50] Energy dispersive X-ray analysis uses this characteristic X-ray emission to identify the elemental content of the sample.

When performing interpretation of the EDS spectra, many elements have lines that overlap with one another. Sometimes the peak from one element will obscure the peak from another. Some of the notorious overlaps encountered in paint analysis are titanium/barium (Ti/Ba), sulphur/lead/mercury (S/Pb/Hg), chromium/manganese (Cr/Mn), iron/manganese (Fe/Mn) and nickel/zinc (Ni/Zn) [1].

Particle (or Proton) Induced X-ray Emission (PIXE)

Pigments on the surface of a painting can be analyzed also by PIXE. This method is non-destructive, no sample preparation is needed and with this method small samples can be analyzed [83]. PIXE provides multi-elemental analysis based on the energies of X-rays emitted upon irradiation with high-energy protons [31]. More exactly, the PIXE technique relies on the emission of X-rays induced by the interaction of energetic light ions (most frequently protons of a few mega-electronvolts) with constituent atoms of materials [50]. In PIXE measurements the proton-induced X-rays are detected with an energy dispersive semiconductor detector [83]. Almost all elements of the periodic table can be analyzed simultaneously with the exception of the lightest ones (H to Ne) [50]. Also previous investigations indicate that inorganic pigments containing light elements

(such as ultramarine) can not be detected by PIXE due their low X-ray energies [29]. Due to the limited range of proton energy the method is only well suited for the analysis of thin paint layers but does not allow looking deeply into the painting. However, PIXE is frequently combined with another ion beam analytical technique, called PIGE (particle-induced gamma ray emission) for the measurement of some light elements (F, Na, Al, Si) [50].

X-ray fluorescence spectroscopy (XRF)

XRF and also EDXRF are among the most important techniques for qualitative and semi-quantitative analysis of elements in paint samples, since they allow identification of chemical components through the entire thickness of the painting. There are also portable XRF systems and these have been widely used for in-situ non-destructive analysis. [29]

All X-ray fluorescence spectrometers share the common principle that X-rays are directed onto the sample to excite secondary emission of X-rays i.e., X-ray fluorescence, which consists of wavelengths characteristic of the element or elements that are present in the sample [81]. It is important is that every element emits X-rays at characteristic wavelengths. Most XRF spectrometers are capable of detecting the elements of the periodic table from sodium to uranium. However, the limit of detection increases rapidly as the atomic number decreases below that of sodium [81].

X-ray fluorescence spectrometers of two design principles are available: wavelength dispersive X-ray fluorescence spectrometers (WD-XRF) and energy dispersive X-ray fluorescence spectrometers (ED-XRF). WD-XRF produces a spectrum by using a crystal monochromator to diffract the fluorescent X-rays, a single wavelength at a time, onto a detector that measures their intensity. ED XRF permits the fluorescence radiation emitted at all wavelengths to reach the detector simultaneously and use a pulse-height discriminator to electronically classify the energy of the X-ray photons that strike the detector. [81]

SEM-EDS, XRF, PIXE are elemental analysis techniques and can provide information on the elemental composition only, without revealing information about the chemical surroundings of the atoms (chemical bonds, molecular structure). These methods do not distinguish in the paint sample one pigment from another if the heavy elements that the pigments contain are the same, for example they do not distinguish red lead (Pb_3O_4) from lead white ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$). Also paint samples contain besides pigments also fillers and other additives and they all give peaks in the spectra and sometimes it is difficult to distinguish, what elements belong to pigments and what elements belong to fillers.

Chemical spot tests

Chemical spot tests can also be used to identify certain pigments. Chemical spot tests are based on chemical reaction whereby the use of a drop of a test solution or a reagent will provide some identification for the presence of a particular elements (or cations or anions). This kind of analysis is complicated and often unreliable in the case multi-component mixtures; also this method requires larger sample size than is usually available.

APPENDIX 5

IR spectrum of linseed oil and its interpretation

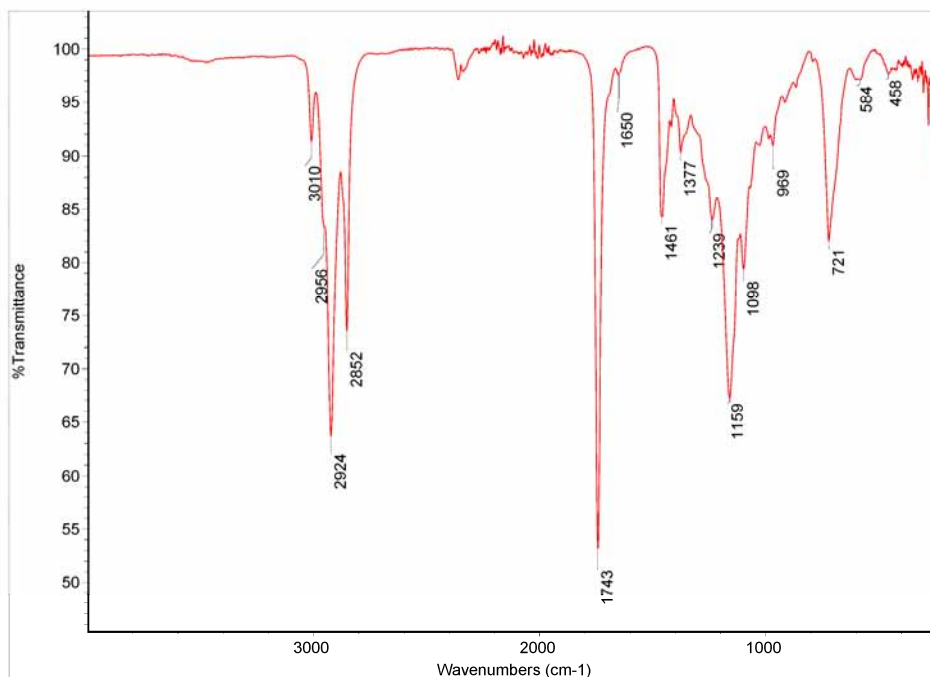


Fig. 1. IR spectrum of fresh linseed oil

Table 3. Assignment of the absorption bands in the IR spectrum of fresh linseed oil [31, 74 77, 84]

Wavenumber (cm ⁻¹)	Assignment
3010	<i>cis</i> C-H stretching in -CH=CH-
2956	C-H asymmetric stretching of CH ₃
2924	C-H asymmetric stretching of CH ₂
2852	C-H symmetric stretching of CH ₂
1743	C=O stretching in the ester groups
1650	C=C stretching of <i>cis</i> -CH=CH-
1461	C-H bending of CH ₂ , CH ₃
1377	C-H symmetric bending of -C-CH ₃
1239	C-O stretching in ester
1159	C-O-C asymmetric stretching in ester
1098	C-O-C symmetric stretching
722	C-H <i>rocking</i> bending in -C-CH ₂ - (+ C-H <i>wagging</i> bending in -CH=CH-)

APPENDIX 6

Table 4. Compositions of inorganic pigment mixtures with linseed oil

Paint mixture	Mass percent of the pigment	Mass percent of linseed oil
White pigments + linseed oil		
Lithopone + linseed oil	46	54
Lead white + linseed oil	64	36
Zinc white + linseed oil	45	55
Titanium white + linseed oil	53	47
Chalk + linseed oil	59	41
Gypsum + linseed oil	49	51
Yellow pigments + linseed oil		
Yellow ochre + linseed oil	53	47
Amberg yellow + linseed oil	59	41
Satin ochre + linseed oil	48	52
Gold ochre + linseed oil	53	47
Cadmium yellow (Maimeri) + linseed oil	54	46
Cadmium yellow (Kremer Pigmente) + linseed oil	41	59
Naples yellow + linseed oil	76	24
Massicot + linseed oil	61	39
Orpiment + linseed oil	46	54
Barium yellow + linseed oil	45	55
Strontium yellow + linseed oil	45	55
Red pigments + linseed oil		
Red lead + linseed oil	66	34
Cinnabar + linseed oil	59	41
Cadmium red no.1 light + linseed oil	51	49
Natural red earth + linseed oil	63	37
Caput Mortuum, reddish + linseed oil	51	49
Venetian red + linseed oil	59	41
Pompeii red + linseed oil	61	39
Green pigments + linseed oil		
Cobalt green + linseed oil	59	41
Malachite + linseed oil	57	43
Chromium oxide green + linseed oil	42	58
Viridian + linseed oil	46	54
Verdigris + linseed oil	54	46
Bohemian green earth + linseed oil	49	51
Vagone green earth + linseed oil	48	52
Umber greenish + linseed oil	55	45

Table 4. Continue

Paint mixture	Mass percent of the pigment	Mass percent of linseed oil
Blue pigments + linseed oil		
Egyptian blue + linseed oil	52	48
Ultramarine blue + linseed oil	25	75
Lapis lazuli + linseed oil	55	45
Smalt + linseed oil	52	48
Prussian blue+ linseed oil	32	68
Azurite + linseed oil	52	48
Cobalt blue + linseed oil	55	45
Cobalt blue dark + linseed oil	46	54
Brown pigments + linseed oil		
Burnt umber (Winsor&Newton) + linseed oil	36	64
Burnt umber (Sennelier) + linseed oil	53	47
Brown ochre + linseed oil	47	53
Fawn ochre + linseed oil	53	47
Black pigments + linseed oil		
Charcoal + linseed oil	14	86
Bone black	46	54
Ivory black + linseed oil	51	49
Vine black + linseed oil	36	64
Mars black + linseed oil	60	40

Table 5. Compositions of red pigment mixtures with CaCO_3 and linseed oil

Number of paint mixture	Paint mixture	Mass percent of the pigment	Mass percent of CaCO_3	Mass percent of linseed oil
1.	Cinnabar + CaCO_3 + linseed oil	20	20	60
2.	Red lead + CaCO_3 + linseed oil	27	27	46

APPENDIX 7

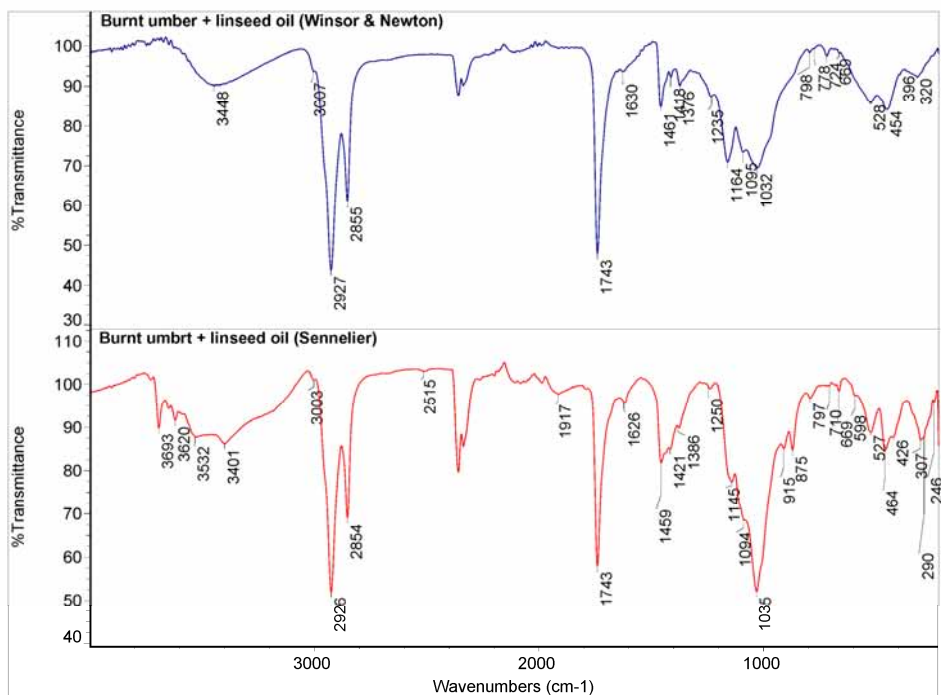
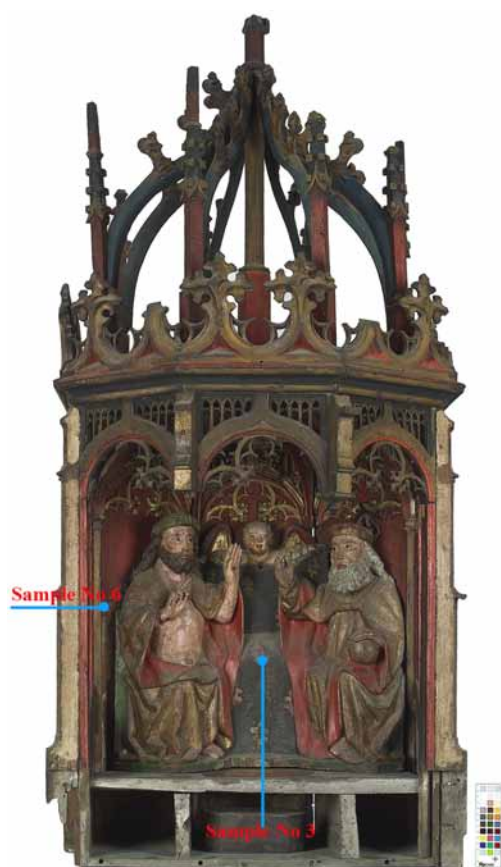


Fig. 2. Burnt umber (from the two different companies) mixed with linseed oil

APPENDIX 8

Locations of samples on the tabernacle of the altar from
the Holy Spirit Church in Tallinn



APPENDIX 9

Sample from the tabernacle of the altar from the Holy Spirit Church in Tallinn

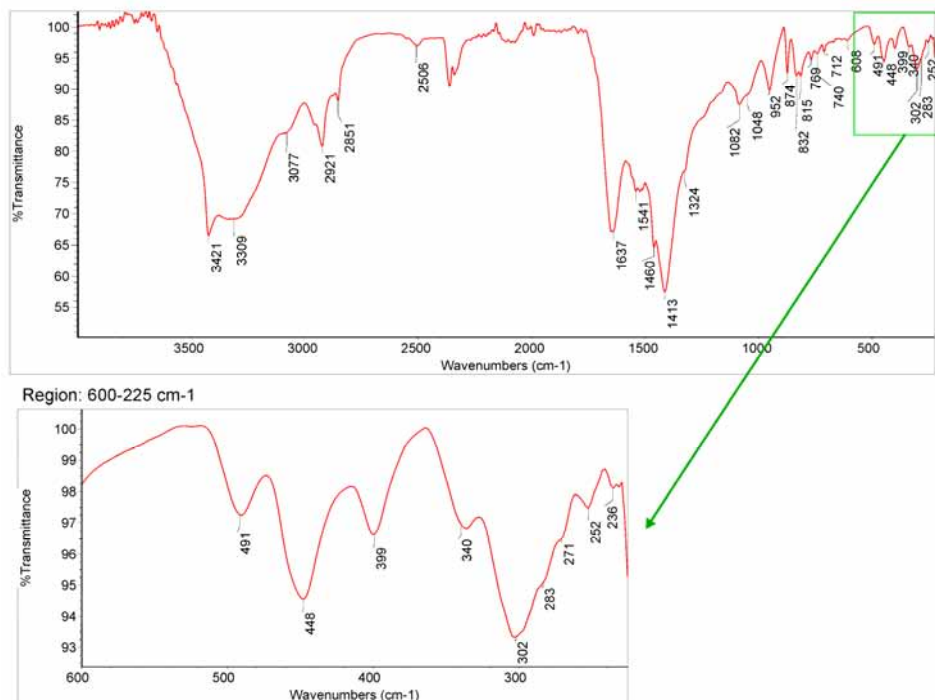


Fig. 3. Sample no 3. IR spectrum of the dark blue layer

Table 6. Interpretation of the ATR-IR spectrum of the dark blue layer (sample no 3)

	Materials	Band wavenumbers (cm ⁻¹)
Pigment	Azurite [2CuCO ₃ ·Cu(OH) ₂]	<i>bands in the region of 550–230 cm⁻¹: 491, 448, 399, 340, ~302, 283, 252, 236</i>
Fillers (additives)	Chalk (CaCO ₃)	~2506, band in the region of 1450–1400, 874, 712, ~302
	Silicates	1100–1000, 769, 740
Binder	Protein	3309, 3077, 2921, 2851, ~1637 (amide I), 1541 (amide II), 1460

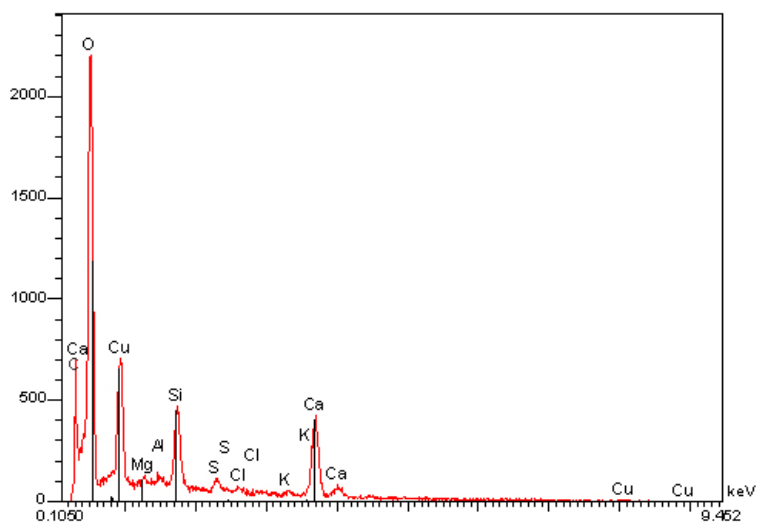


Fig. 4. SEM-EDS spectrum of the dark blue layer (sample no 3)

APPENDIX 10

Sample from the tabernacle of the altar from the Holy Spirit Church in Tallinn

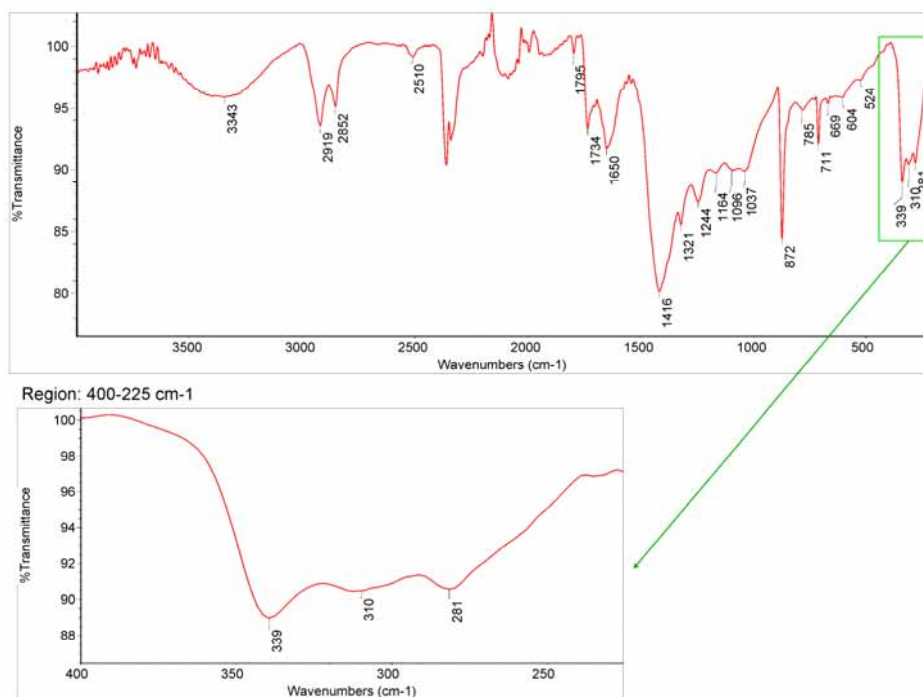


Fig. 5. Sample no 6. Red layer

Table 7. Interpretation of the ATR-IR spectrum of the red layer (sample no 6)

Materials		Band wavenumbers (cm ⁻¹)
Pigment	Cinnabar (HgS)	339, 281
Fillers (additives)	Chalk (CaCO ₃)	2510, 1795, ~1416, 872, 711, 310
	Silicates	1100–1000, 785
Binder	Oil	Broad band in the region of 4000–3000, 2919, 2852, 1734, 1244 (probably also 1164, 1096)

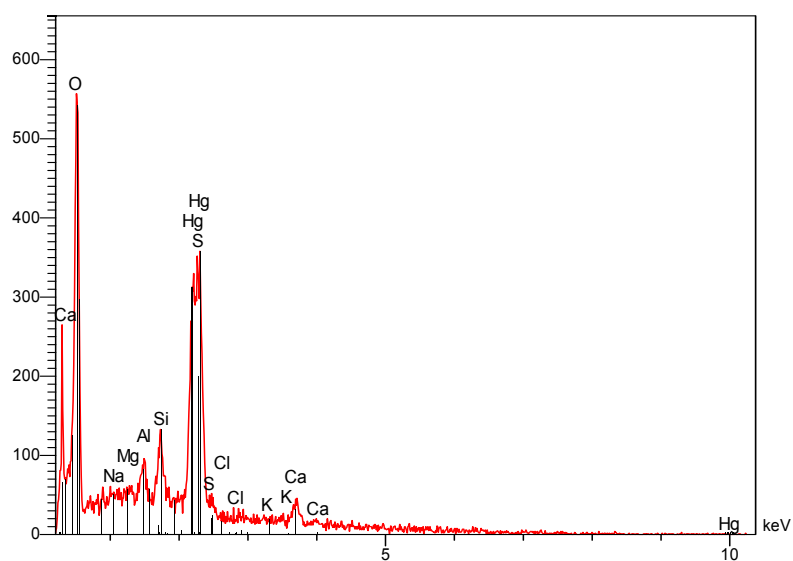


Fig. 6. SEM-EDS spectrum of the red layer

APPENDIX II

Sample from the tabernacle of the altar from the Holy Spirit Church in Tallinn

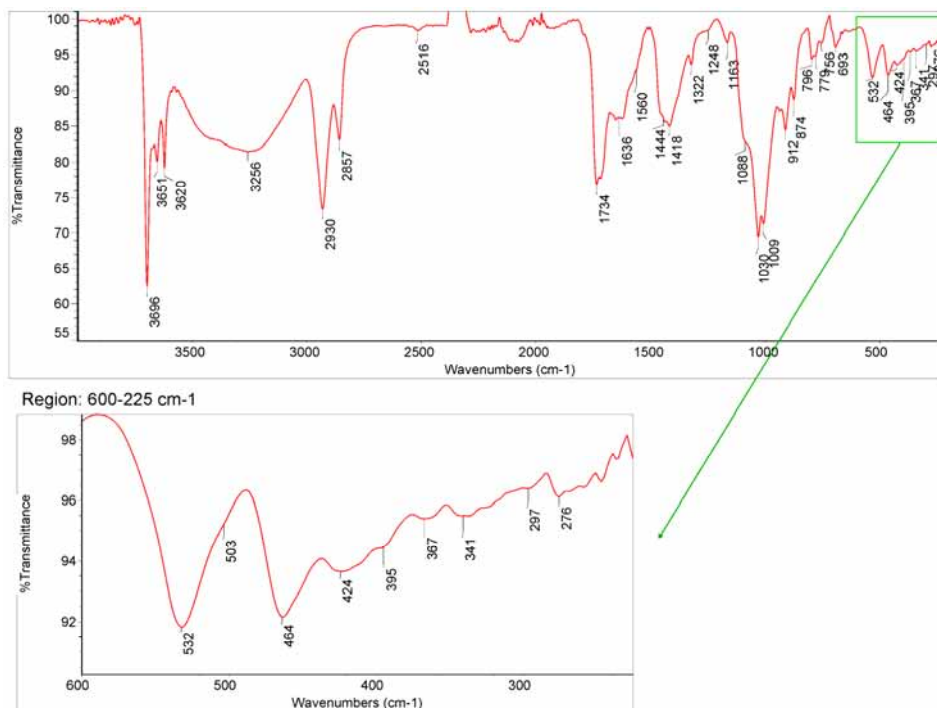


Fig. 7. Sample no 7. Yellow layer

Table 8. Interpretation of the ATR-IR spectrum of the yellow layer (sample no 7)

Materials		Band wavenumbers (cm ⁻¹)
Pigment	Yellow ochre (α -FeOOH + kaolin)	<i>bands in the region of 550–230 cm⁻¹: 532, 464, 424, 395 (probably Fe-O band), 367, 341, 297, 276 (probably Fe-O band)</i>
Fillers (additives)	Chalk (CaCO ₃)	2516, ~1418, 874
Binder	Oil	Broad band in the region of 4000–3000, 2930, 2857, 1734, 1444, 1248 (probably also 1163)

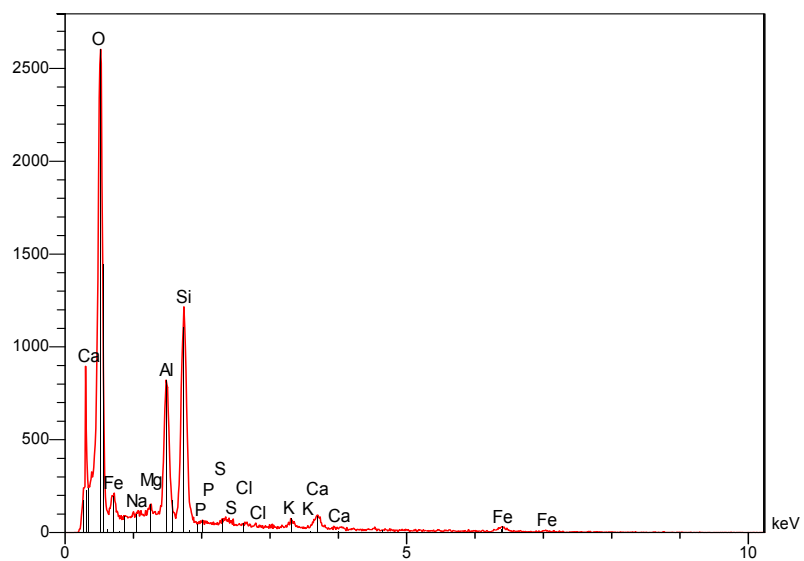


Fig 8. SEM-EDS spectrum of the yellow layer

APPENDIX 12

Pink paint sample from the Ludwich von Tolli coat of arms from the Kaarma Church of Saints Peter and Paul in Saaremaa

Table 9. Interpretation of the ATR-IR spectrum of the pink paint layer (see IR spectrum in Fig. 25)

Materials		Band wavenumbers (cm ⁻¹)
Pigment	Red lead (Pb ₃ O ₄)	530, 513, 453, 380, 312, 280
Fillers (additives)	Chalk (CaCO ₃)	2519, 1797, 1427, 876, 713
	Gypsum (CaSO ₄ ·2H ₂ O)	3519, 3405, 1622, 1139, 1118, 670, 602
	Silicates	1100–1000
Binder	Protein	2925, 2852, ~1657 (amide I), 1536 (amide II)

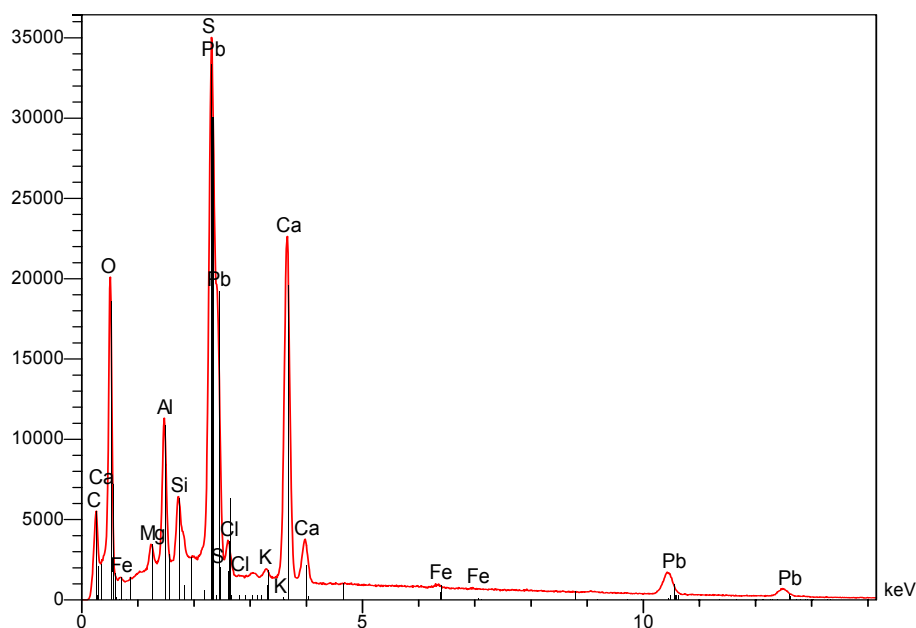


Fig. 9. SEM-EDS spectrum of the pink paint layer

APPENDIX 13

Red paint sample from the Bengt Hinrich von Biestram coat of arms of the St Mary's Cathedral (Dome Church) in Tallinn

Table 10. Interpretation of the ATR-IR spectrum of the red paint layer (see IR spectrum in Fig. 27)

Materials		Band wavenumbers (cm ⁻¹)
Pigment	Read lead (Pb ₃ O ₄)	527, 513, 451, 441, 381, 326, 318, ~278
	Vermilion (HgS)	344, ~282, 266
Fillers (additives)	Lead white (2PbCO ₃ ·Pb(OH) ₂)	3528, band in the region of 1450–1400, 1046, 683
	Silicates	1100–1000, 781, 751
	Possibly also chalk (CaCO ₃)	band in the region of 1450–1400, 875
Binder	Protein	Broad band in the region of 4000–3000, 1651 (amide I), 1539 (amide II)
	Oil or possibly acrylic resin	Broad band in the region of 4000–3000, 2958, 2922, 2850, 1728, 1243 (maybe also 1176 and 1149)

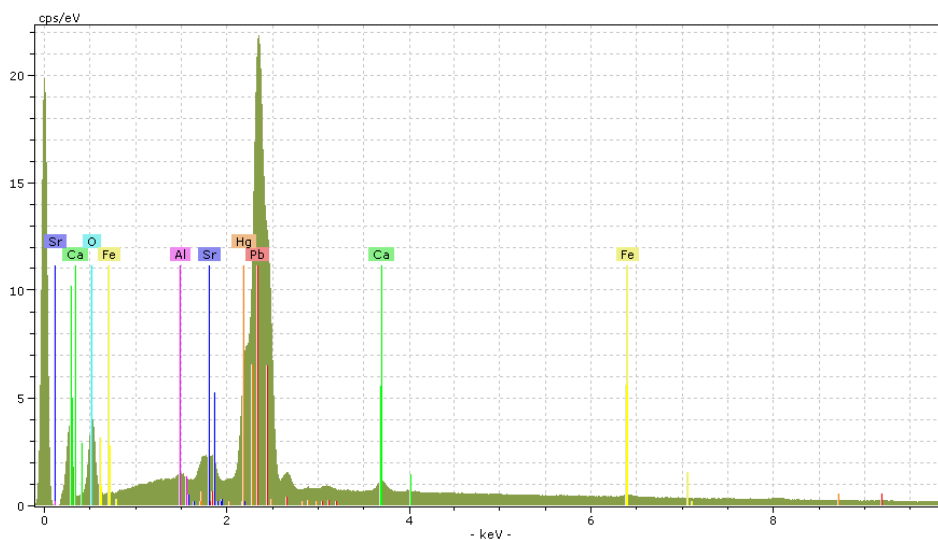


Fig 10. SEM-EDS spectrum of the red paint layer

APPENDIX 14

Paint samples from the unknown artist painting

Table 11. Interpretation of the ATR-IR spectrum of the yellow paint layer (see IR spectrum in Fig. 29)

Materials		Band wavenumbers (cm^{-1})
Pigment	Strontium yellow (SrCrO_4)	<i>bands in the region of 550–230 cm^{-1}: 444, 428, 406, 390, 379, 346, 338 (probably Cr-O bendings in the CrO_4^{4-} ion)</i>
Fillers (additives)	Barium sulphate (BaSO_4)	1181, 1122, 1082, 984, 635, 610
Binder	Oil	3396, 2919, 2850, 1737, 1461

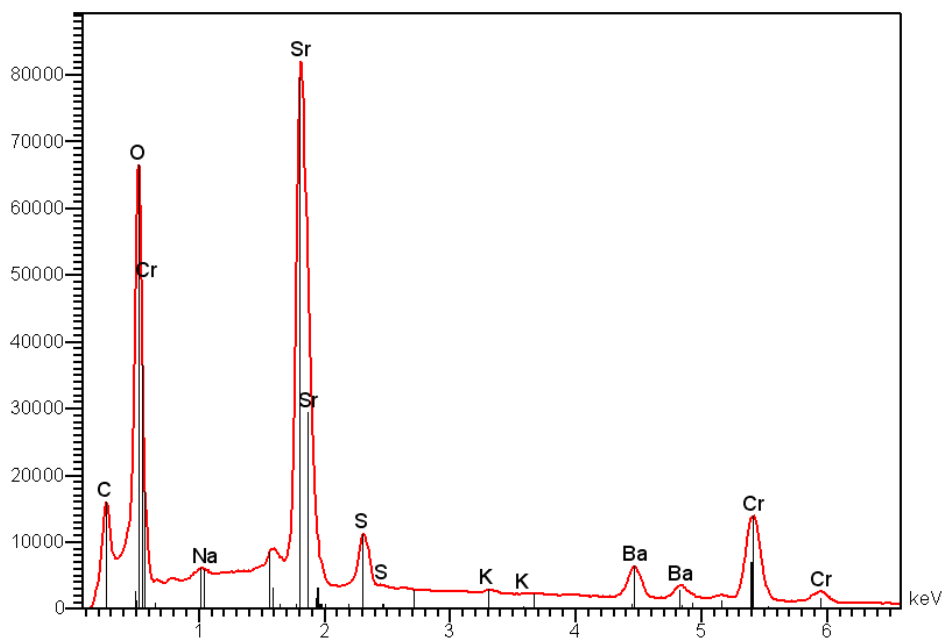


Fig 11. SEM-EDS spectrum of the yellow paint layer

APPENDIX 15

Paint samples from the unknown artist painting

Table 12. Interpretation of the ATR-IR spectrum of the brown paint layer (see IR spectrum in Fig. 31)

Materials		Band wavenumbers (cm^{-1})
Pigment	Burnt umber ($\text{Fe}_2\text{O}_3 + \text{MnO}_2 + \text{clay}$)	<i>bands in the region of 550–230 cm^{-1}: 529, 454, 304</i>
Fillers (additives)	Barium sulphate (BaSO_4)	1180, 1120, 1074, 983, 634, 606
	Chalk (CaCO_3)	2516, band in the region of 1450–1400, 873, 712, 304
	Silicates	1622 (maybe), 1100–1000, 798, 780
Binder	Oil	3391, 2919, 2850, 1738, ~1454, 1319

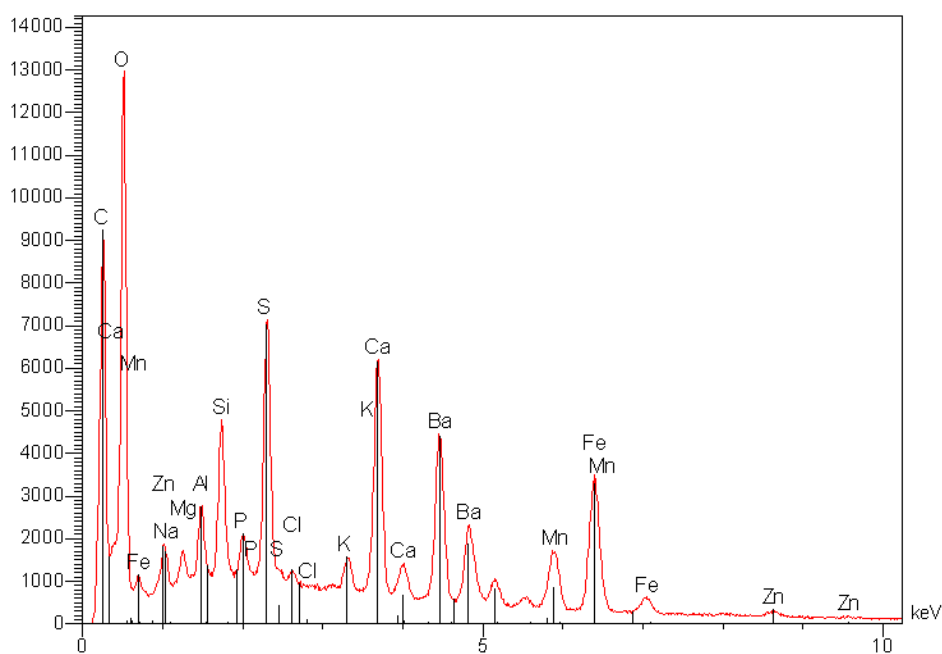


Fig 12. SEM-EDS spectrum of the brown paint layer

APPENDIX 16



Fig. 13. The altar before the overpainting in 2005 (photo by Peeter Säre)



Fig. 14. The pulpit before the overpaintings in 2005 (photo by Peeter Säre).



Fig. 15. The altar after the overpainting in 2005 (photo by Jaanus Heinla, Conservation Centre Kanut)



Figs. 16 and 17. The sounding-board and the pulpit after the overpaintings in 2005
(Photo by Jaanus Heinla, Conservation Centre Kanut)

APPENDIX 17

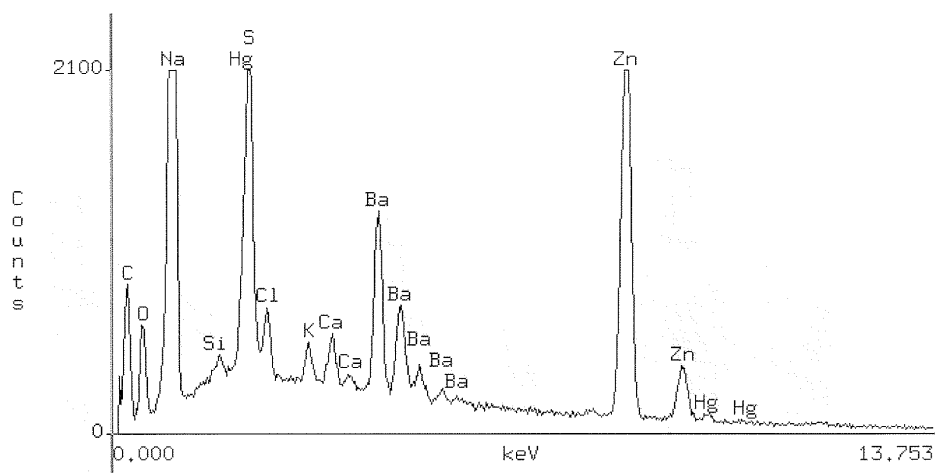


Fig 18. SEM-EDS spectrum of the red paint layer (sample from the altar of St. Mary church in Vigala, Estonia)

PUBLICATIONS

CURRICULUM VITAE

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Main scientific publications

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2. **Vahur, S.**; Knuutinen, U.; Leito, I. ATR-FT-IR spectroscopy in the region of 500–230 cm^{-1} for identification of inorganic red pigments. *Spectrochimica Acta Part A*, **2009**, 73, 764 – 771.
3. **Vahur, S.**; Sibul, K.; Ehasalu, P.; Sammelselg, V.; Leito, I. Paint investigations of altar and pulpit in the church of St Mary, Vigala, Estonia. *e-Preservation Science*, **2009**, 6, 43–52.

4. Nummert, V.; Piirsalu, M.; Mäemets, V.; **Vahur, S.**; Koppel, I. Effect of ortho substituents on carbonyl carbon C-13 NMR chemical shifts in substituted phenyl benzoates. *Journal of Physical Organic Chemistry*, **2009**, 22, 12, 1155–1165.
5. Nummert, V.; Piirsalu, M.; **Vahur, S.**; Travnikova, O.; Koppel, I. A. Kinetic study of hydrolysis of benzoates. part xxvii. ortho substituent effect in alkaline hydrolysis of phenyl esters of substituted benzoic acids in aqueous Bu₄NBr. *Coll. Czech. Chem. Comm.*, **2009**, 74, 1, 29–42.
6. Nummert, V.; Travnikova, O.; **Vahur, S.**; Leito, I.; Piirsalu, M.; Mäemets, V.; Koppel, I.; Koppel, I., A. Influence of substituents on the infrared stretching frequencies of carbonyl group in esters of benzoic acid. *Journal of Physical Organic Chemistry*, **2006**, 19, 10, 654–663.
7. **Vahur, S.**; Virro, K.; Leito, I. Web-based Infrared Spectral Databases Relevant to Conservation, *J. CAC*, **2005**, 30, 10–17.

Attended conferences

1. “Non-destructive and Microanalytical Techniques in Art and Cultural Heritage Research” (TECHNART 2007). April 25–28, 2007, Lissabon, Portugal.
2. “International Workshop Characterisation of organic materials (binding media, varnishes, pigments) in paint cross-sections”, 20–21 september, 2007, Bologna, Italy.
3. “Third International Architectural Paint Research Conference”, January 17–19, 2008, New York, USA.
4. “The Object in Transition: A Cross Disciplinary Conference on the Preservation and Study of Modern and Contemporary Art”, January 25–26, 2008, Los Angeles, USA.
5. “8th international conference of the Infrared and Raman Users’ Group” (IRUG 8), March 26–29, 2008, Vienna, Austria.

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Ülikooli Keemia Instituut; keemik (0,4 k)
2003– ... Ennistuskoda Kanut, Polükroomia restauraator (0,6 k)

Tähtsamad teaduspublikatsioonid

1. **Vahur, S.**; Teearu, A.; Leito, I. ATR-FT-IR spectroscopy in the region of 550–230 cm^{-1} for identification of inorganic pigments. *Spectrochimica Acta Part A*, **2010**, 75, 1061 – 1072.
2. **Vahur, S.**; Knuutinen, U.; Leito, I. ATR-FT-IR spectroscopy in the region of 500–230 cm^{-1} for identification of inorganic red pigments. *Spectrochimica Acta Part A*, **2009**, 73, 764 – 771.
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5. Nummert, V.; Piirsalu, M.; **Vahur, S.**; Travnikova, O.; Koppel, I. A. Kinetic study of hydrolysis of benzoates. part xxvii. ortho substituent effect in alkaline hydrolysis of phenyl esters of substituted benzoic acids in aqueous Bu₄NBr. *Coll. Czech. Chem. Comm.*, **2009**, *74*, 1, 29–42.
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Osalemine konverentsidel

1. “Non-destructive and Microanalytical Techniques in Art and Cultural Heritage Research” (TECHNART 2007). 25–28. aprill 2007, Lissabon, Portugal.
2. “International Workshop Characterisation of organic materials (binding media, varnishes, pigments) in paint cross-sections”, 20–21. september, 2007, Bologna, Itaalia.
3. “Third International Architectural Paint Research Conference”, 17–19. jaanuar, 2008, New York, USA.
4. “The Object in Transition: A Cross Disciplinary Conference on the Preservation and Study of Modern and Contemporary Art”, 25–26. jaanuar, 2008, Los Angeles, USA
5. “8th international conference of the Infrared and Raman Users’ Group” (IRUG 8), 26–29. märts, 2008, Viin, Austria.

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