České vysoké učení technické v Praze, Fakulta jaderná a fyzikálně inženýrská

Czech Technical University in Prague Faculty of Nuclear Sciences and Physical Engineering

Doc. Ing. Tomáš Čechák, CSc.

Použití rentgenfluorescenční analýzy při výzkumu památek

Application of X-ray Fluorescence Analysis in Investigation of Historical Monuments

#### **Summary**

Nuclear techniques and techniques using ionising radiation represent a valuable tool in non-destructive diagnostic applied to archaeological findings and objects of arts, namely for determining the composition of materials used in the production of artefacts. X-ray fluorescence analysis, both in its energy form and in its wave dispersive form, is one of the most widespread methods using ionising radiation to study the elemental composition of materials. It is frequently used for studies of various cultural and historic relicts and objects of art. This work summarizes the author's experience with X-ray fluorescence analysis in investigating historical relicts namely by means of portable spectroscopic devices. Utilization of these methods is demonstrated in the investigation of fresco paintings, metal objects and old manuscripts. The results of these measurements provide the information on the composition of the artefacts, enable the comparison of processes used in the fabrication of fine art pieces by individual artists, and in many cases offer information on how to repair the damaged parts.

#### Souhrn

Jednou z hlavních předností jaderných metod a metod využívajících ionizující záření při analýze archeologických nálezů a uměleckých předmětů, s cílem zjistit jejich chemické složení eventuálně určit dobu vzniku, je skutečnost, že umožňují nedestruktivní analýzu zkoumaných objektů. Rentgenfluorescenční analýza patří mezi metodami využívající ionizující záření k nejrozšířenějším. Tato práce shrnuje autorovy zkušenosti s využitím rentgenfluorescenční analýzy ke studiu památek, především pak s využitím přenosných rentgenfluorescenční analyzátorů pro měření in situ. Použití těchto zařízení je demonstrováno na měření středověkých fresek, historických kovových předmětů a barev a inkoustů ve starých rukopisech. Výsledky analýz umožňují získat informace o složení zkoumaných předmětů, o způsobu výroby, mohou pomoci při určení doby vzniku a v řadě případů určit postup při jejich restaurování.

Klíčová slova: Rentgenfluorescenční analýza, Si(Li) detektory, přenosné analyzátory, energiově disperní analýza, fresky, <sup>55</sup>Fe, <sup>238</sup>Pu

Key works: X-ray Fluorescence Analysis, Si(Li) detectors, portable spectrometers, energy dispersive analysis, fresco paintings,<sup>55</sup>Fe, <sup>238</sup>Pu

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## **1 INTRODUCTION**

The preservation of artefacts, monuments, and archaeological sites frequently requires scientific analysis of cultural materials or testing of specific properties of chemical treatments in order to document their historic evidence, clarify deterioration processes, and specify conservation treatments. Analyses of the variety of materials constituting our cultural heritage require the expertise of many various scientific disciplines. X-ray Fluorescence Analysis is a nondestructive analytical technique used to determine the elemental composition of a sample.

When a primary X-ray excitation beam from a radioactive source or from an X-ray tube strikes a sample, the X-ray photons can either be absorbed by the atom or scattered through the material. The process in which an X-ray source is absorbed by the atom by transferring all of its energy to an innermost electron is called photoeffect. During this process, if the primary X-ray has sufficient energy, electrons are ejected from the inner shells, creating vacancies. These vacancies present an unstable condition for the atom. As the atom returns to its stable condition, an electron from the outer shell are transferred to the inner shell and in the process gives off a characteristic X-rays, whose energy is the difference between the two binding energies of the corresponding shells. Each element has a unique set of energy levels; each element produces X-rays at a unique set of energies allowing one to measure the elemental composition of the sample. Between the proton number Z of the atom emitting characteristic radiation and the energy, or the wavelength of the radiation, the following relationship applies  $E=k(Z-b)^2$ , where E is the energy of the photons corresponding to the transfer between two specific shells, and k and b are constants. The process of emission of the characteristic X-rays is called X-ray Fluorescence (XRF), and the analytical methods using XRF is called X-ray Fluorescence Analysis (XRFA). For the energetic reasons the K and L shells are involved in XRFA. The Fig. 1 gives the schematic of the shells in the atom, indicating the main transfers corresponding to energies (spectral lines), and their notations used for historical reasons. If we are able to measure the energy of spectral lines of the characteristic radiation, we are able to determine the proton number of an element that emits the characteristic radiation. Then, if we know how to measure the number of photons of corresponding energy, we can obtain the information on the concentration of each element in the examined sample.

The XRFA system has two components, i.e., the source and the detector. The source irradiates the sample to produce the characteristic X-rays. The X-ray radioisotope sources will excite characteristic X-rays from an element only if the source energy is greater than the binding energy, or absorption edge energy, of the electrons in a given electron shell. A given source can produce the



Fig. 1 Energy levels and X-ray lines in the atomic shells

characteristic radiation only from certain elements, and for the complex analysis of the sample it is often necessary to use a set of sources with different energies. The analysis is more sensitive for an element with an absorption edge energy similar to, but less than, the excitation energy of the source. Miniature X-ray tube sources are now available. The advantage of the X-ray tubes is that the intensity of the radiation emitted is greater if radionuclide sources are used and the beam enables better focusation. The anode operates at a high enough energy range in order that it can simultaneously excite a range of elements, and a high voltage source (typically 35 - 50 kV) must be used to supply the X-ray tube. But using the high-voltage sources limited the application of equipment with X-ray tube as a portable device a few years ago. A great step forward has been made on the development of small portable X-ray tubes and small portable high-voltage sources recently. Now such devices are fully available. For the possibility to be switched off during transportation, devices based on an X-ray tube can satisfy the radioprotection rules much more easily.

For precise measurements two basic types of detectors are used in XRFA namely. Si(Li) detectors and silicon pin diodes. Si(Li) detectors must be cooled to a temperature of liquid nitrogen but have a greater detection area and higher energy resolution. Silicon pin diode detectors operate near ambient temperatures and can be cooled only by the Peltier effect. These detectors have a smaller detection area as well as and poorer energy resolution till now, but they are used in cosmic research and their quality is being enhanced. Fluorescent and backscattered radiation from the sample is counted by the detector which records the photon and builds a spectrum of pulses whose height depends on the energy of photons absorbed by the detector. The pulses are amplified and analysed by a multichannel analyser. A typical spectrum of pulses from a fresco is seen in Fig. 4. The software integrates the peaks in the spectrum to produce information about elements present in the sample and about their concentrations. There are many factors known as interferences that can affect the detection and quantification of elements in the sample. Some interferences can be inherent in the methods of analysis, while others result from instrumental setup. Other interferences may arise from an outside the source, such as the sample matrix. Some factors can be prevented or minimised by using a special software or special sample preparation. The problem is the detection of low energy X-ray emitted by elements with low Z. Only special XRF devices can be used to measure elements with Z lower than 11. Basic information on the XRFA can be found in [1].

XRFA is widely used for qualitative and quantitative elemental analysis of geological, environmental, industrial and other samples. Compared with other competitive techniques, XRFA has the advantage of being non-destructive, multi-elemental, fast, and cost-effective and it is possible to build and use portable equipment. For these reasons it is very suitable for analyses of cultural heritage [10].

#### **2 EXPERIMENTAL TECHNIQUES**

Two types of X-ray fluorescence equipment were built and are now operated in the Laboratory of Quantitative Methods in the Research of Ancient Monuments at FNSPE. For the in-situ measurements we built an XRF analyser with changeable radionuclide sources in the measurement head and with the Si(Li) detector. See Fig. 2. The radioisotope sources <sup>55</sup>Fe, <sup>238</sup>Pu, and <sup>241</sup>Am, are used. <sup>55</sup>Fe enables the excitation of elements with low Z up to 23, <sup>238</sup>Pu is used for the excitation of elements with Z from 20 up to 39, and <sup>241</sup>Am is used for the excitation of the K shell electrons of elements with higher Z up to 68. The Si(Li) detector is cooled by liquid nitrogen from a 51 Dewar vessel. For special purposes, 2 1 Dewar vessel is available. These small Dewar vessels and the portable multichannel analyser enable in situ measurements. The collimator system of the exited radiation makes it possible to select the irradiated area. Our spectrometr can be used for area mapping or line scan. The detector is equipped with XYZ- stage, which allows maximum movements of up to 250 mm in YZ direction.



Fig. 2 Si(Li) detection equipment during the measurement of the fresco

For higher spatial resolution an energy dispersive analyser with miniaturised X-ray tube, manufactured by Oxford Instruments was built, working with air-cooling. The X-ray tube is suitably shielded. The tube employs the Mo anode and can operate with a maximum current of 0.1 mA and maximum voltage of 30 kV. The detection module consist on Si-PIN, the AMPTECH detector, cooled by a Peltier stage, sealed with a Be window. A laser beam was used for precise location of the X-ray spot on the sample.



Fig. 3 Si-PIN detector and X-ray tube during the measurement

#### **3 RESULTS AND DISCUSSION**

#### **3.1 Fresco paintings**

Pigment compositions on the fresco paintings vary with the locale and date. White, for example, may be produced with Pb, Zn and Ti oxides, but ZnO was not produced before 1870, and Titanium White was not used before 1920 [2]. Therefore, if neither Zn nor Ti is found in the white areas of supposed fresco paintings from the Renaissance period, those paintings were restored or they are a forgery. A more subtle study of the fresco paintings of several works of a particular artist to determine the pigments characteristically used by him or his disciples would reveal frescos that were particularly typical of the artist and possibly, the times. Differences between countries or areas and time periods would most certainly be revealed, and differences between works of fresco artists in the same place at the same time period might show up, too.

The overall results of XRFA on frescos are multielement spectra indicating the main elements of pigments present. Usually, this step makes it possible to identify inorganic pigments under consideration. In many cases useful details about the minor and trace elements can be obtained [18].

Several measurements have been carried out directly in the field in order to verify the method and receive information about Gothic fresco paintings. The valuable fresco paintings from the Žirovnice Castle were investigated in this way. Surprisingly many pigments were used on these frescos, which was not typical of the Bohemia region at the end of 15<sup>th</sup> century. For all basic paints, a few pigments and their combinations was used. Local common pigments e.g., Green Earth and Yellow Ochres were used together with expensive imported pigments such as Vermilion, Saturn Red and Azurite and with pigments which were used very seldom on the fresco paintings, e.g., Antimonate Yellow, and Manganese Brown. Artists took into account not only the colour and shade of the pigments but also the significance of the imaginary persons and their position in the church hierarchy. Most expensive pigments and gilding were used on the vesture of most important persons. Other less important persons and architecture are painted only by ochres. Fresco paintings of the Žirovnice Castle have never been repainted and the first restoration dates to 1997 - 2000. During the restoration investigation of the frescos by XRFA was performed. Comparison of X-ray spectra from fresco paintings of the Žirovnice Castle is shown in Fig. 4 [3].



Fig. 4 Fresco of the Virgin Mary with Child of the Žirovnice Castle. Spectrum Sp1-small angel, green pigment, Spectrum Sp18-mantle of kneeling figure, red pigment.

Cu, Cl, Fe and Pb peaks can be seen in spectrum Sp1.

 $Cu - Malachite (CuCO_3.Cu(OH)_2 appeared mostly on wall paintings from the 7<sup>th</sup> through 18<sup>th</sup> century; other copper-based pigments, for example Mountain–Green or Sheeel's Green were not considered applicable because in the years when the paintings had been finished, Copper-Green (Cu(CH_3COO)_2. Cu(OH)_2.nH_2O had not been used for the wall paintings$ 

Cl - additive of Malachite made in Czech Lands from the mineral chlorite

Fe – additive Earth-Green (mixture of indefinite composition of hydro-silicates, containing glauconite or seladonite, the colouring element was  $Fe^{2+}$ ). Use of Earth–Green was not time restricted.

Pb - possible composition included additive lead-tin yellow (Pb<sub>2</sub>SnO<sub>2</sub> or Pb<sub>2</sub>Sn<sub>2</sub>SiO<sub>7</sub>) - used from the 13<sup>th</sup> through 17<sup>th</sup> century, or lead white (2PbCO<sub>3</sub>.Pb(OH)<sub>2</sub>) used with no time restriction. However, the set-up of the measuring equipment did not make possible to estimate additives S or As, which were normally accompanying elements in a natural source of Lead White. The other possible source of lead is massikote, known as Lead-Yellow (PbO) that has been used in Europe since the 15<sup>th</sup> century.

The red pigment on the Sp18 is cinnabar (HgS); its use is not time-restricted. In this case it is natural mind cinnabar that may contain other mineral additives [4, 11, 12].

The mediaeval fresco of St. Hyeronymus was discovered in the Church of Our Lady before Týn behind a side Baroque altar. This fresco was unique not only for its preserved state, but also the techniques, used: It was a classical fresco painted without organic materials. This type of the fresco is very valuable in the Bohemia region. The investigation has confirmed pigments commonly used in this period. It was Iron Oxide Reds and Red Ochres, Azurite, Malachite and Lead White. See Fig. 5 [6, 13].



Fig. 5 XRF spectrum of the blue pigment. Mixture of Ochres, Azurite and Lead White on fresco of St. Hyeronymus

Investigation of the fresco paintings at the Karlštejn Castle aims to date the particular parts of the frescos restored in the 19<sup>th</sup> century, during the reconstruction of the castle. Analysis of XRF spectra of the pigments can give information about the type of the pigments. The 14<sup>th</sup> century painters used other types of pigments than in the 19<sup>th</sup> century, and application of XRFA enables to differentiate mediaeval and new parts of the fresco.

The red and black pigment was used as a marker of the mediaeval part of the fresco. See Figs. 6 and 7. The red pigment used in the  $14^{th}$  century was a mixture of Vermilion, Saturn Red, and Red Ochres. Red Ochres with Chinese White were used as a red pigment in the  $19^{th}$  century. Admixture of the Mars Black with Saturn Red and Verdigris was used for tinting the black pigment in the  $14^{th}$  century. This pigment differs from the black pigment used in the  $19^{th}$  century (Mars Black with traces of Zn ) [14, 15, 16].

XRF facilities can measure the thickness and perform composition analysis of coating layers; This equipment is used industrially [8, 9]. For the oil paintings where the oil pigments were used, the situation is much more complicated because the thicknesses of separate layers are not constant. For the fresco paintings the situation is simpler. The covering layer on definite areas can have a more or less constant thickness in many cases. The aim of this type of layer analysis is to separate qualitatively the presence of pigments from the covering layer and to identify the pigments and their position in the substrate layer by means of a non-destructive technique [9].



Fig. 6 XRF spectrum of the red pigments on the fresco on the Karlstejn castle Red pigment used in the 14<sup>th</sup> century was the mixture of Vermilion, Saturn Red and Red Ochres. Red Ochres with Chinese White was used as a red pigment in the 19<sup>th</sup> century.



Fig. 7 XRF spectrum of the black pigments on the fresco on the Karlstejn castle

The basic principle of the measurements of thickness h of a coating deposited on a substrate material is given in the following equation. For a given

excitation spectrum, the intensity of the fluorescence radiation emitted from the substrate layer and measured by a detector depends on the angle of excitation  $\psi_i$  and the angle of detection  $\psi_f$ , with h as a parameter. In fact, the total fluorescence emitted by the substrate depends on the thickness of the substrate layer; it is supposed now that the thickness is so big that the signal does not depend on it. The intensity of the measured fluorescence emitted from the substrate can easily be calculated for a simple model defined by the following condition: single-element coating deposit and single element substrate, monochromatic excitation at energy  $E_0$ , flat and smooth surface area, substrate of infinite thickness and only primary fluorescence are considered.

Under this assumption, the fluorescence intensity  $I_{\text{SF}}$  measured by the detector is given by

$$I_{SF} = I_0 \varepsilon \tau \left( E_0 \right) \frac{\Delta \Omega}{4 \pi} \eta \left( E_s \right) \exp \left\{ - \left[ \frac{\mu_c \left( E_0 \right)}{\sin \psi_i} + \frac{\mu_c \left( E_s \right)}{\sin \psi_f} \right] p_c h \right\} \times \frac{1}{p_s \sin \psi_i} \frac{1}{\frac{\mu_s \left( E_0 \right)}{\sin \psi_i} + \frac{\mu_s \left( E_s \right)}{\sin \psi_f}} \right]$$

where  $I_0$  is the intensity of the incident radiation,  $\varepsilon$  is the excitation factor for the respective X-ray line of the substrate. When considering a K line,  $\varepsilon$  is the product of the absorption jump factor for the creation of K vacancy, fluorescence yield for the decay of the K vacancy, and relative emission rate for the specific K line with respect to other K lines.  $\tau(E_0)$  is the photoelectric absorption coefficient of the substrate at the energy  $E_0$ ;  $\Delta\Omega/4\pi$  is the fraction of the emitted photons collected within the detector solid angle,  $\eta(E_S)$  is the detection efficiency at the fluorescence energy of the substrate  $E_S$ ;  $\rho_S$  is the density of the substrate;  $\rho_C$  is the density of the coating; and  $\mu_S(E_0)$  and  $\mu_S(E_S)$  are mass absorption coefficients of the substrate at energies  $E_0$  and  $E_S$ , respectively; and  $\mu_C(E_0)$  and  $\mu_C(E_S)$  are the mass absorption coefficients of the coating at energies  $E_0$  and  $E_S$  respectively [9].

In principle, knowing the coating density, for this very simple model it is possible to determine also analytically the coating thickness h, by using the measured intensities. From the model, it is possible to define the energy of primary radiation which is necessary for irradiation of the atoms in the substrate layer and Z of atoms whose characteristic radiation can be detected.

Transmission of characteristic ( $K_{\alpha}$  and  $K_{\beta}$ ,  $L_{\alpha}$  and  $L_{\beta}$ ) radiation through a layer of painting material will result in modification of the intensity ratio  $I_{\alpha}/I_{\beta}$ . This effect becomes obvious, if attenuation is sufficiently different for the  $\alpha$  and  $\beta$  radiation components. Maximum  $I_{\alpha}/I_{\beta}$ . modification is expected for selective absorption, i.e., if the element of strongest absorption in the pigment (Hg in Cinnabar and Pb in Lead White) has an absorption edge just between the  $K_{\alpha}$  and  $K_{\beta}$  or  $L_{\alpha}$  and  $L_{\beta}$  energy of the penetration radiation [17]. In order to search for pigment combinations, i.e. top layer - subjacent layer, where layer position studies via the  $K_{\alpha}/K_{\beta}$  or  $L_{\alpha}/L_{\beta}$  intensity ratios are practicable, estimations are very useful on the basis of single elements. For this, modification of the intensity ratio  $I_{\alpha}/I_{\beta}$  is expressed by a gain factor for the characteristic element of the pigment:

$$g = \frac{I_{\alpha}(e,a) / I_{\beta}(e,a)}{I_{\alpha}(e) / I_{\beta}e}$$

where (e,a) represents the emitter – absorber layer system and (e) denotes only the emitter without attenuating top layer. It is well known that this gain factor g(S) = exp(Sd) is a function of the absorption selectivity:

$$S = [(\mu/\rho)_{\alpha} - (\mu/\rho)_{\beta}]\rho$$

where  $(\mu/\rho)_{\alpha}$  and  $(\mu/\rho)_{\beta}$  denote the mass attenuation coefficients for the considered system and  $\rho$  and d represent the top material density and thickness respectively [25].

For a realistic situation, both models mentioned above are too simple. The Monte Carlo method must be use to calculate of intensities of K and L lines of characteristic radiation from the subjacent layer. MCNP-IVC code is very useful for this calculation [26] and this code is available in our laboratory.

In Franciscan Monastery in Kadaň, an extremely precious Gothic fresco was found. Unfortunately, this fresco was superimposed by a new layer of fresco in the Renaissance period. The Renaissance fresco is also valuable and taking down of this fresco will be very hazardous and expensive. XRFA can help here to investigate the subjacent layer of the Gothic fresco.

For the non-destructive elemental analysis of the pigments used in the frescopaintings, XRFA is the preferred technique for routine work. This is because of the mobility of equipments which ensure that the object is kept as its stationary position during the measurement.

#### 3.2 Metal objects

The Reliquary of St. Maurus was restored in the last decade by A. Šumbera and his co-workers. The difficulty of the restoration work necessitated the

application of modern research and analytical methods. XRFA was used to analyse of the metal parts of the Reliquary.

The Reliquary of St. Maurus is one of the most valuable mediaeval works of art in the Czech Lands. It is an outstanding example of Romanesque goldsmith work from the first quarter of the 13<sup>th</sup> century, originating from the Abbey at Florennes, Belgium. Onto a basic core of oak-wood, rich ornamentation of gilded silver and gilded copper was applied, using the techniques of embossing, filigree, and enamelling. The filigree plaques are adorned with precious stones and antique gems. The Reliquary was considerably damaged after the World War II, when was hidden in the floor ballast in the chapel of the Castle Bečov in West Bohemia.



Fig. 8 Spectrum of characteristic radiation obtained from one component of the Reliquary. Higher content of Hg in the gold plating -Annealing at lower temperature.

Various parts of relief decoration were analysed by XRFA from both the outer and the inner side, and the measurements from the inner side were carried out also in the joints. The composition of the silver alloy, especially the ratio of copper to silver, was the main subject of interest. The type of the gilding was also a subject of interest. The ratio of Hg and Au peaks in X-ray spectra depends on the temperature which was used during the gilding by the amalgam technique. It was discovered that various pieces had been annealed by different methods. Spectra of characteristic radiation obtained from various components of the Reliquary decoration are shown in Fig. 8 and 9. It can be seen that sample A (Fig. 8) contains a relatively high amount of Hg in the surface layer in the comparison with sample B (Fig. 9), while most of the Hg has been removed from sample B (annealing at higher temperature).



Fig. 9 Spectrum of characteristic radiation obtained from one component of the Reliquary. Lower content of Hg in the gold plating -Annealing at higher temperature.

Analyses carried out from the inner side enabled the decorations to be divided provisionally into five groups:

- 1. The bas-reliefs contain between 30 and 33.3 mass percent of copper
- 2. Most of the sculptures of apostles, including the larger statues of Christ and St. Maurus from the front side of the Reliquary, are purer then the first group and contain between 18.7 and 23 % of cooper. The two larger statues differ from the others by the greater thickness of the sheet, probably for mechanical reasons, so that no diffusion of gold and mercury up to the inner surface was detected.
- 3. The third group consists of the statues of St. Peter and St. Paul with 14.2% of copper, the relief of Salome is also close to them, having 11.1% of copper.
- 4. The ornament and pinnacle on the ridge of the Reliquary are made of gold plated copper. They are also thicker, and no diffusion of gold and mercury to the inner surface was detected.
- 5. Some later repairs and additions have a different composition, e.g., the hand of St. Matthew contains more copper than silver (61%), the cross is made of brass, and the verification plate of the relics is made of lead.

The alloy for making the Reliquary was probably obtained by melting down various gifts, jewels, coins, etc. It seems that several different meltings were used in the same period in order to produce it. Additional measurements referred to the composition of the solders, which can in some cases provide information about the approximate date of the repairs to the Reliquary:

1. The analysed joints of the statue of St. James the Minor revealed pure silver solder. They are probably original.

- 2. The joints of St. Matthew's fingers confirmed the finding that the fingers were later repairs. The solder contains zinc, which was recognised and started to be used only in the 19<sup>th</sup> century. The same conclusion can be drawn about the joint between the head and the body of St. James the Major.
- 3. Some joints were made with solders containing lead (between the head and the body of St. Maurus, the chest of St. Maurus, and relief of St. Apolinar blessing St. Maurus). These joints correspond with high probability to historic repairs using a Pb/Ag soft solders.

The results obtained by XRFA together with the results of other investigations carried out by other laboratories have served as the basis for restoration works, returning the Reliquary to its original form [7].

The Holy Trinity Column in Olomouc was restored between 1999 - 2002. During the recent restoration, various parts of the Holy Trinity were investigated by XRFA. The composition of solders based on copper and lead used in historical repairs was a major subject of interest of both historians and restorers, mainly with the aim to use materials of similar composition for the restoration.



Fig. 10 XRF spectrum from the head of Christ from the Holy Trinity Column in Olomouc, measured with a <sup>238</sup>Pu radiation source. The grey line corresponds to the background [5].

Other recent major restoration works were carried out on the so-called "Golden Gate" of St. Vitus' Cathedral. The XRFA measurements attempted to find some remains of the original polychromy of the grating. However the

results were negative confirming the hypothesis that during the restoration at the turn of  $20^{\text{th}}$  century the grating was carefully sand blasted and then gilded.

The Prague Jewish museum owns a large collection of Jewish silver prayer objects from the whole of Bohemia. Most of them are from the period after the Napoleon wars. The XRFA investigation attempted to find the composition of the objects and help the historians to determine the producers.



Fig. 11 XRF spectra of characteristic radiation obtained from the Jewish silver prayer objects. Ratio of peaks of Ag, Cu and Pb characterises the individual performers.

#### 3.3 Manuscripts

Analytical identification of pigments and also of inks used in the paintings and manuscripts can provide insights into pieces of art of historical relevance. Pigments were used for all colours of the pallet because of their high colouring power and stability against changes of temperature and light. Some natural mineral or organic pigments have been known since antiquity, whereas others are more recent discoveries. Several inorganic pigments were discovered during the past 500 years, and most of the organic pigments were first synthesized no more than 100 years ago [2].

The pallet of pigments used in historical manuscripts includes more than one hundred types. Each of these is characterised by its colour and by several different elements, which allow the pigment to be identified. Nevertheless, their identification is not always easy. Occasionally, compounds which differ in only a mass fraction of some constituent elements can produce the same pigment. Others, e.g. Ultramarine, are found as either natural or artificial pigments which can be distinguished by their impurities only. Pigments may also have different crystallographic modifications, e.g. Titanium Oxide, which can appear as either Rutile or Anatase. Obviously, if pigments are mixed to obtain a particular colour, identification of the individual components may be hampered, but in many cases identification remains unproblematic and the XRFA can allow the mixing ratios to be determined [19].

To test the applicability of XRFA in the investigation of the pigments used in historical manuscripts, a set of standard samples of typical pigments was prepared by the chemical laboratory of the National Library. This set includes about 30 typical pigments. All samples were measured by XRFA method and the library of spectra is used to determine the unknown samples.



Fig. 12 XRF spectrum of the cobalt blue measured with an X-ray tube

The investigation of old manuscripts was made in the collaboration with the National Library of the Czech Republic. The pigments and inks from various manuscripts were analysed from the collection of this Library. Fragments of parchments, even from around the 8<sup>th</sup> century, the manuscript of the Homiliary of the Opatovice Monastery from the 12<sup>th</sup> century, Gradual of České Budějovice and some other precious folios have been measured in an attempt to identify the composition of pigments, inks, bindings materials, papers etc.

Recently ink analysis was used to study a series of 15<sup>th</sup> and 16<sup>th</sup> century manuscripts from the collection of the National Library. The problem was to determine of inorganic compounds in iron gall inks. From the 15<sup>th</sup> to 18<sup>th</sup> centuries manuscripts were written in iron gall ink. This ink was made by mixing iron vitriol with gallnut extract. The black indelible iron galet complex

was created following oxidation on exposure to air [21]. Because of the use of naturally occurring raw materials, the composition of the ink has variable amounts of main and side components and contamination. Consequently due to the analysis of the components a definite characterization of the inks could be made.

The problem of the manuscripts written by the iron gall ink is ink corrosion. The reasons of this destruction are not fully understood yet. The origin for the destructive mechanism of inks is a result of complex overlapping of various processes. Of importance in this context are the natural ageing of paper, the composition of the inks, and their ability to enter chemical reactions with the carrier or the medium [22].

The applicability of XRFA to old ink investigation was demonstrated by an analysis of a 12<sup>th</sup> century book of homilies. The measurements provide information on chemical elements present in the ink as well as in the parchment. Several different types of inks were identified. Fig. 13 shows the spectrum of characteristic radiation obtained from the ink with high iron content. Fig. 14 represents a spectrum of ink containing iron, copper, mercury and lead. The beam of X-ray tube has been used for this measurement. The beam of X-ray tube can be focused on an area less than 1 mm<sup>2</sup> [24]. The use of special collimator is planned, to reduce this value.



Fig. 13 XRF spectrum of characteristic radiation obtained from the ink sample, the Manuscript of the Homiliary of the Opatovice Monastery. Ink with high iron content.



Fig. 14 XRF spectrum of characteristic radiation obtained from an ink sample, the Manuscript of the Homiliary of the Opatovice Monastery. The ink contains iron, copper, mercury, and lead.

The scribes used metal points for annotations and for drawing and ruling. which had left a trace element on the writing surface. These marks vary in appearance according to the metal used, a ferrous point leaving a brown mark, silver and lead leaving a silver-gray trace, and copper alloys sometimes a greygreen marks. The marks produced are more discreet than those made with the ink but more visible than those made with a hard point. Metal points increased in use from the 11<sup>th</sup> century on. Graphite, derived from carbon, was not generally used before the 17<sup>th</sup> century. Lead in Fig. 13 and partly in Fig. 14 was contained in the ruling. The type of these metal points can give information about the scribe's workshop. These metal points can be found not only in the scripts, but can also be superimposed by the pigment layers in the initials or miniatures. XRFA is able to identify the metal points under the pigment layer, which are not visible. In this case, the technique using the intensity ratios of  $K_{\alpha}/K_{\beta}$  or  $L_{\alpha}/L_{\beta}$  lines is very useful. Experiments with complex layout and ruling patterns to accommodate glosses, commentaries, and other parallel texts took place during the Carolingian period and, notably, also in university book production from the 13<sup>th</sup> and 14<sup>th</sup> century. The information about the ink composition can help to date of these glosses and commentaries [20].

## **4 CONCLUSIONS AND THE OUTLOOK**

XRFA is a method that can be successfully used to investigate old monuments. Compared to other competitive techniques, XRFA has an advantage of being non-destructive, multi-elemental, fast, and cost-effective. Thanks to advances in miniaturization of electronics, detectors, cooling equipment and X-ray tubes, it is possible to build and use portable equipment for the XRFA. XRFA is preferred technique for the routine work.

The lecture has presented a review of utilising XRFA in the investigation of fresco paintings, metal objects and old manuscripts.

The investigation of fresco paintings and metal object was carried out in the collaboration with the National Institute of Care of Monuments. The National Institute of Care of Monuments has the chemical laboratory and used many analytical methods, e.g. electron microprobe analysis, in the collaboration with other institutions. But the application of portable XRF analyzer extends the possibilities of the field measurement mainly. The investigation of pigments and inks on the old manuscripts was made in the collaboration with the National Library of the Czech Republic.

The XRFA along with thermoluminiscence dating will remain an important technique used in the Laboratory of Quantitative Methods in the Research of Ancient Monuments at FNSPE. In the future research work, using also the small X-ray tubes is planned for the research of fresco paintings. The use of X-ray tube beams can increase the area resolution of the method. Better collimation of the beam renders possible the application of more precise software for quantitative analysis. Thanks to fruitful collaboration with the National Institute of Care of Monuments it is possible to compare the XRFA results with the results obtained by other methods, e.g. electron microscopy and last but not least, collaboration with the PIXE laboratory of FNSPE also gives some interesting results.

In the near future, measurements of the fresco paintings in the right chapels of St. Vitus Cathedral and in the Franciscan Monastery in Kadaň are planned. In Franciscan Monastery in Kadaň, two superimposed fresco paintings were found, one Gothic and one from the Renaissance period. The results of the investigation of the subjacent Gothic fresco are anxiously awaited. Continued collaboration with the Náprstek Museum and the Jewish museum is also expected.

As mentioned in Chapter 1, XRFA has to deal with the problem detecting elements with low Z. A local helium gas atmosphere around the measuring head can enable measurements of elements with Z lower than 11 and can increase the sensitivity measurements of elements with Z within the interval of 11 - 22. The detector window is another limitation for the measurement of light elements.

Making use of a multitarget X-ray tube, where the anticatodes are exchangeable without breaking the vacuum, or use of a set of X-ray tubes with different anticatodes, can excite most of the elements from the Mendeleev's Table and make the application of XRFA more flexible.

The chapters about the XRFA are parts of the following courses; namely Introduction in the Application of the Ionising Radiation and Application of Ionising Radiation in Science and Technology, and of Practical Exercises run by the Department of Dosimetry and Application of Ionizing Radiation. Application of XRFA in Investigation of Historical Monuments is the subject of the Degree project and Doctoral dissertations.

Pigment analysis or analysis of metals is also an extremely important aid in restoration, since it can help to distinguish the original sections of painting from the restored or later added ones. Thus the pigment or metal characterisation may be very important in making a decision whether to remove spurious layers or choose of the most closely matching process of the restoration. The important purpose for analysing pigments in frescos or in manuscripts is in conservation. Depending on their nature, pigments may be sensitive to light, humidity gaseous atmospheric pollutants, or heat, which requires specific storage or display conditions. Additionally, one may want to identify the pigments before applying any chemical or other treatment aiming at reversing or at least stopping the deterioration process. And the characterisation of the pigments may help in assigning a probable date to the painting, in reconstructing its restoration and conservation history, and in detecting forgeries.

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# Doc. Ing. Tomáš Čechák, CSc.

# **CURRICULUM VITAE**

## **Education:**

MSc.(Ing.) 1971, Czech Technical University in Prague, Faculty of Nuclear Sciences and Physical Engineering (FNSPE)
Ph.D.(CSc.) 1981 Czech Technical University in Prague, FNSPE
Assoc. Prof. (Doc.) 1994 Czech Technical University in Prague, FNSPE

## **Professional Positions:**

1971-1972 Research Fellow FNSPE, CTU
1972-1975 Ph.D. Student FNSPE, CTU
1975-1992 Research Assistant, Department of Dosimetry and Application of Ionizing Radiation, FNSPE, CTU
1992 -present Head of Department of Dosimetry and Application of Ionizing Radiation, FNSPE, CTU
1994 Associate Professor

## **Educational activities:**

Lecturer at the Faculty of Nuclear Science and Physical Engineering, CTU in Prague Courses on: "Mathematical Methods in Dosimetry" (1980 -89) Courses on: "Dosimetry of Ionizing Radiation" (1991- 92) Courses on: "Mathematical Methods and Computer Technique in Dosimetry" (1993 - 97) Courses on: "Application of Ionizing radiation in Science and Technique" (1993 - 2004) Lecturer at the Faculty of Mechanical Engineering, CTU in Prague Courses on: "Radiation protection" (1993 - 2004) Supervisor of Ph. D. students and M. S. diploma theses Head of Council for Ph.D. Studies. Specialization: Experimental nuclear physics.

## **Publications:**

Author or co-author of 49 scientific papers in scientific journals and 55 papers in conference proceedings. Co-author of 6 patents

## **Recent Grants Awarded:**

Investigator or co-investigator of 14 grants (Grant BARANDE, EURECA, GA CR, IGA, CTU Development found ect.)

#### **Other activities:**

Member of Scientific Board of Institute of Dosimetry AS CR (1993 – 95) Member of Scientific Board of FNSPE, CTU in Prague (1993 – ) Member of Scientific Board of State Institute of Nuclear Safety (2003 – ) Member of Scientific Board of Institute of Biomedical Engineering, CTU in Prague (2003 – )

Member of International Radiation Physical Society

Member of Executive Committee of Czech Society for Radiation Protection Member of EURADOS (European Radiation Dosimetric Group) (2003 - ) Member of NATO/CCMS Committee: Cross-Border Environmental Problems Emanating from Defence –Related Installations and Activities, (1995-98)

Member of Organising/Programme Committee of four international conferences: European Conference on Protection against Radon at Home and at Work, 1997 Prague, 8th International Symposium on Radiation Physics, 2000 Prague, LUMDETR, 2003, 5th European Conference on Luminescent Detectors and Transformers of Ionizing radiation, 2003 Prague, European Conference on Protection against Radon at Home and at Work, 2004 Prague Reviewer for project proposals for GA CR

## **Research profile:**

Research into application of ionizing radiation in geology and industry, X-ray fluorescent analysis, dosimetry

Technology innovation in co-operation with various institutions in application of ionizing radiation in coal industry and geology