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**THE CENTRE OF IMAGE AND MATERIAL ANALYSIS IN CULTURAL
HERITAGE (CIMA) IN VIENNA AND ITS CURRENT ACTIVITIES.
PART III: MATERIAL ANALYSIS***

The third part within the activities of the *Centre of Image and Material Analysis in Cultural Heritage* (CIMA) in Vienna concerns the identification of the materials used for manuscripts and art works. Presently the focus lies on the characterization of the inks and pigments used for the text and the illumination of the manuscripts. Beside this paradigmatic approach of isolating material data the aim of such investigations is to carry out statistical evaluations in order to study the syntagmatic relationship of the single materials, both within the same manuscript and for comparison in specific groups of manuscripts. The results will be stored in a database which can be used for classifying, especially dating and localizing, the objects. Thus, the chemical investigations will increase our knowledge about the materials applied in particular periods and regions. For these tasks various spectroscopic methods are applied which will be described in the following overview.

ANALYTICAL APPROACH

As a result of the growing collaboration between the humanities and the natural sciences during the last decades a fruitful co-operation has been developed between philology, art history and conservation-restoration on the one side and physics, chemistry and biology on the other. This is partly due to the booming development of analytical methods that has recently brought forward a great number of new instrumental micro-analytical techniques with non-sampling (without taking original sample material) and *in-situ* applicability to the object under in-

* The research was funded by the Austrian Science Fund (FWF): P23133 and by the Austrian Federal Ministry of Science, Research and Economy (Structural funds for the Austrian higher education areas, Higher Education Plan 2013).

vestigation, e.g. a manuscript or an artifact. X-ray fluorescence analysis (XRF) (Mantler, Schreiner 2000) plays a unique role in that co-operation: It can be carried out in air, in most cases the analysis is non-destructive or even non-invasive – which means that the objects do not endure any changes or alterations before, during or after the investigation –, and can be carried out at any location. Since the miniaturization in the field of electronics yielded x-ray tubes as well as x-ray detectors of less than one kilogram, the devices can be easily transported to museums, libraries or an archaeological site for analytical investigations (Janssens, Van Grieken 2004).

However, XRF has also a few substantial limitations: In air only the elements with an atomic number higher than 16 (sulfur) can be detected, which gives the possibility to characterize just inorganic components. Furthermore, only the elements present can be determined, while no compound specific information is obtained. Therefore, e.g. in the case of calcium carbonate (CaCO_3) no differentiation between the two modifications calcite and aragonite is possible. Also mixtures of inorganic pigments can hardly be completely characterized; e.g. the detection of lead (Pb) in a red paint layer indicates the presence of red lead (minium – Pb_3O_4), but mixtures of this red pigment with lead white (basic lead carbonate – $2 \text{PbCO}_3 \cdot \text{Pb(OH)}_2$) cannot be clearly identified by using just XRF.

For these reasons, compound-specific methods such as Fourier transform infrared (FTIR) (Griffiths, Haseth 2007) and Raman (Smith, Dent 2005) spectroscopy as well as spectrometry in the UV and visible range (UV-Vis) (Johnston-Feller 2001) seem to be promising complementary techniques, as such measurements also can be carried out in air and in a non-invasive way. FTIR in the transmission mode, where small samples are required, has been applied for decades for the identification of organic as well as inorganic materials in art and archaeology in those cases, where sampling was possible (Derrick et al. 1999). In recent years reflection-FTIR for non-invasive analysis is described in the literature using mirrors (Vetter, Schreiner 2011) or fibers (Miliani et al. 2012) for controlling the optical path from the instrument to the object and vice versa. Raman spectroscopy is complementary to FTIR and has been widely applied for the identification of pigments and inks (Lee et al. 2008; Jean, Brown 2000). It enables us to distinguish not only between pigments of the same color, but also to determine their local and temporal origin due to the way of preparation and/or the raw materials used therefore. Furthermore, this technique has been successfully employed for studying degradation and aging phenomena occurring on parchment stored in libraries or private collections for several hundred years (Garp et al. 2002).

INSTRUMENTS APPLIED WITHIN CIMA

A transportable x-ray fluorescence (XRF) analyzer was developed and assembled at the Academy of Fine Arts Vienna, in order to permit *in-situ* examinations in museums, libraries and even at archaeological excavation sites (Desnica, Schreiner 2006). The system is based on energy dispersive XRF using an Oxford

XTF5011 50 W-Rhodium x-ray tube, a Röntec XFlash 1000 silicon drift-chamber detector and two lasers for positioning (Figures 1–3). The cross-over of the 2 laser beams (red in Figure 2) coincides with the cross-over of the axes of the primary x-ray beam and the detector (yellow).

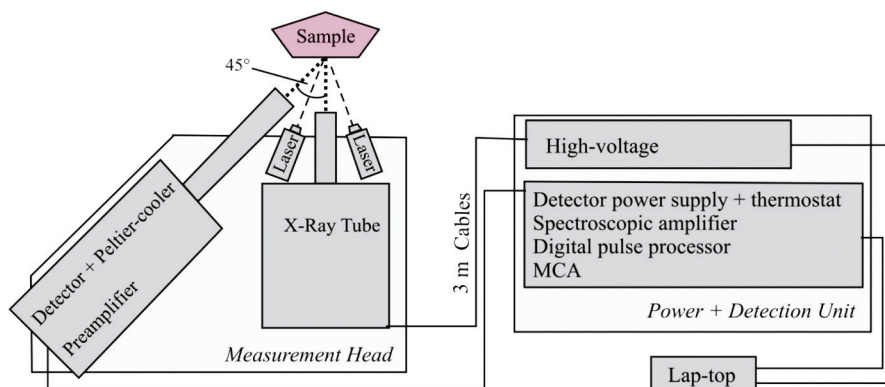


Figure 1. Scheme of the entire self-built XRF system. In reality the plane defined by the two Laser beams is perpendicular to that of the x-ray beam and the detector axis (Desnica, Schreiner 2006)

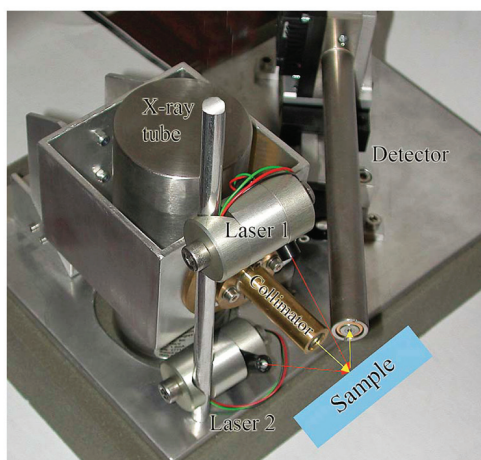


Figure 2. Transportable XRF consisting of an x-ray tube with a collimator and a silicon-drift-chamber detector (weight of the device approximately 4.4 kg)

For non-invasive compound specific analyses we use a novel external reflection-FTIR unit of Bruker Optics, Ettlingen, Germany (Vetter, Schreiner 2011). The reflection module (Figure 4) which can be mounted to the portable Bruker ALPHA FTIR spectrometer (Figure 5) focuses the IR beam to the object via mirrors. The analyzed area is in the range of approximately 4 mm in diameter and the reflected radiation in the region of 2.5–22 μm (4000–450 cm^{-1} wavenumber)

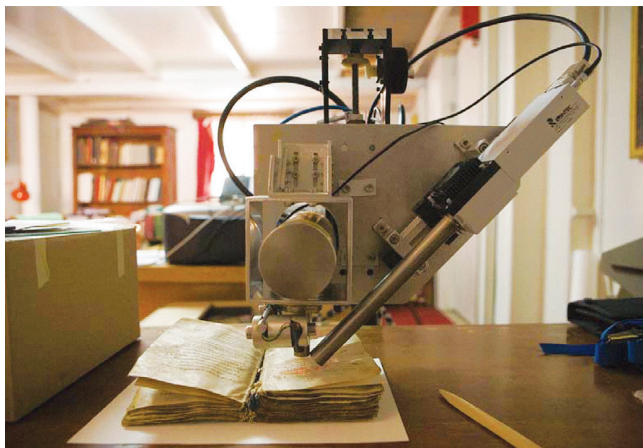


Figure 3. XRF during the measurement of Glagolitic manuscripts in the library of St. Catherine's Monastery in Sinai/Egypt. The red spot on the object is the cross-over of the two lasers and shows the area of analysis (app. 1 mm in diameter)

is focused again by mirrors to the DTGS-detector (Deuterated Triglycine Sulfate – IR detector material). In a reflection-FTIR spectrum, the intensity of the reflected radiation is plotted against the wavenumber. The reflection-spectra obtained have to be mathematically treated by the Kramers-Kronig-Transformation (KKT) in order to achieve so-called absorption index-spectra, which can be evaluated by comparison with database absorption-spectra measured in the transmission mode (IRUG database 2007).

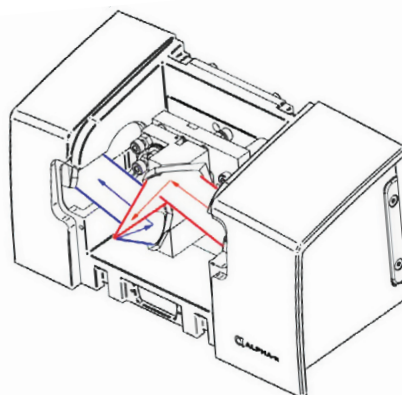


Figure 4. Optical path of the external reflection module for the FTIR instrument ALPHA of Bruker. Angle of incidence = angle of reflection = ca. 20°. © Bruker Optics, Ettlingen/ Germany

In special cases, a MSP400 spectrometer (J&M Analytik AG, Aalen, Germany) can be employed for fiber optic reflection-UV-Vis analyses. Quartz fiber optic cables are used to control the beam from the 75 W xenon light source to the object and from the object to the spectrometer. The application of a collimator yields a beam of 1.5 mm in diameter on the object. The measuring geometry is 0°/45° and reflection spectra are collected in the region of 350–1000 nm with a 1024 linear diode array detector. The obtained spectra are evaluated by



Figure 5. The FTIR instrument ALPHA of Bruker, Germany during the measurement in the Austrian National Library in Vienna

comparison with database spectra of materials from the pigment collection of our institute.

Finally, for the Raman measurements an instrument of Enwave Optonics, USA, type ProRaman-L-Dual-G analyzer, could be purchased for CIMA, which will enlarge our possibilities for compound specific characterization of the materials (pigments, inks and parchment degradation). The instrument represents a fully integrated and portable Raman spectrometer (Figure 6), equipped with a Diode Laser of 785 nm and an energy of approximately 350 mW for the excitation. The detector is a two dimensional temperature regulated CCD (Charged-coupled Device) array, the integrated microscope equipped with a 1.3 Mpixel CMOS (Complementary Metal-oxide-semiconductor) camera with In-Line LED (Light-emitting Diode) illumination.

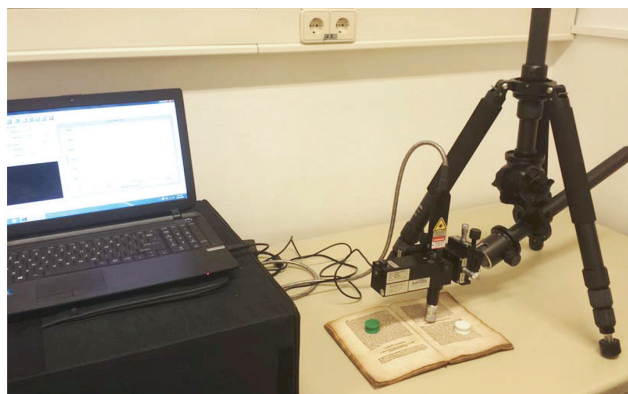


Figure 6. The ProRaman-L-Dual-G analyzer from Enwave Optonics recently purchased for CIMA

SOME RESULTS

In forerunner research projects dealing with Old Church Slavonic-Glagolitic manuscripts of the 11th century material analyses by using mainly XRF and FTIR were carried out in order to determine the inks and pigments used for writing and decoration (Miklas et al. 2008). In the case of the Sinaitic Euchology (Figure 7) the XRF results revealed that in the blue areas the elements silicon (Si), sulfur (S), potassium (K), calcium (Ca) and iron (Fe) are the main constituents, indicating the application of the blue mineral lapis lazuli. In the red parts of the



Figure 7. Glagolitic-OCS Cod. Sin. Slav. 1/N, 11th c.; red circles and numbers mark the areas of analysis

same manuscript only lead (Pb) could be determined; here the conclusion can be drawn that red lead (minium – Pb_3O_4) was applied. In the green paint only copper (Cu) was detected. As several green pigments containing copper, mainly malachite and verdigris, were known and used for manuscripts at this time, further investigations by Raman or UV-Vis spectroscopy will be necessary for a clear identification.

Contrary to these results in the red ink of the Western Rusian codex Hankensteinianus (Vind. Slav. 37) of the Austrian National Library from the 12th/13th c. (Figure 8) the elements mercury (Hg) and sulfur (S) have been detected by XRF, which indicates the application of cinnabar (HgS). This well-known red pigment could also be identified, e.g., in the well-known Greek Dioscurides-manuscript of the Austrian National Library (Vind. Med. Gr. 1) ca. a. 512, as well as in the famous medieval miniature paintings for Emperor Maximilian I. preserved in the Vienna Albertina, which were executed on parchment by A. Altdorfer in Regensburg/Germany around 1513.

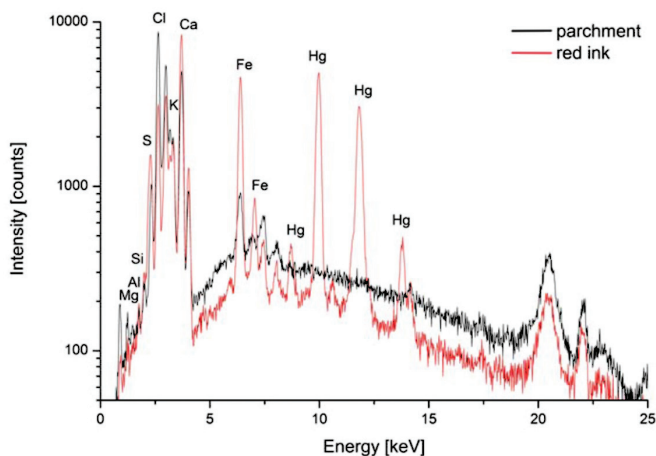
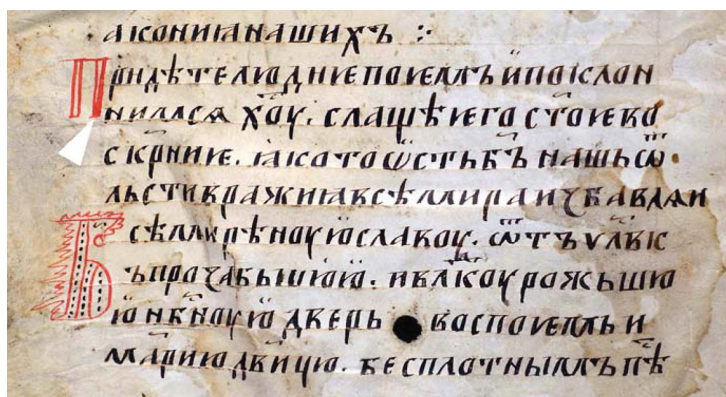


Figure 8. Western Rusian Cyrillic Cod. Vind. Slav. 37, folio 1v, 13th c. (above); XRF spectra of the parchment and the red ink: main elements mercury (Hg) and sulfur (S) indicating cinnabar (HgS) (below)



Figure 9. FTIR analysis of ink on parchment (left) and area of analysis (red), seen by the CCD camera of the instrument (right)

Similar to the XRF investigations, FTIR is carried out by acquiring spectra in the area of interest and by comparing them with results obtained at the pure support (papyrus, parchment, paper etc.). Figure 9 depicts the ALPHA instrument during the analysis of a Glagolitic fragment and the area of analysis, documented by the CCD camera of the instrument. As the diameter of the IR beam is in the range of 5 mm (for XRF it is just 1 mm), the identification of ink materials can be quite difficult or is even limited in many cases.

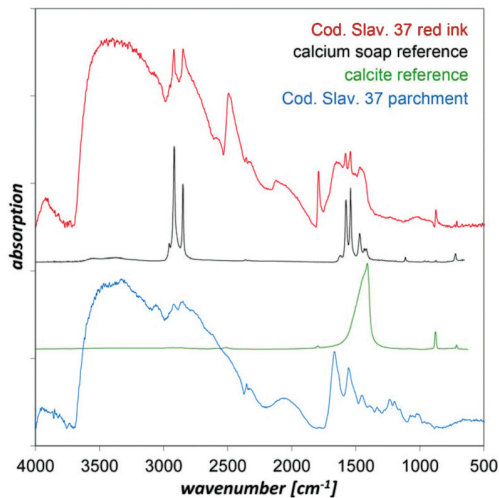


Figure 10. FTIR-spectrum of one red ink (red) on folio 1v of the Cod. Vind. Slav. 37 with spectra of the parchment (blue) as well as reference spectra of calcium soap (black) and calcite (green)

Even so, reflection-FTIR has enabled the identification of several organic materials on the hitherto investigated objects, such as calcium soaps, calcium oxalates, waxes or indigo, revealing information about the production and even the use of the manuscripts. Furthermore, in many cases it allows an unambiguous interpretation of the XRF-results. For example, when calcium was detected by XRF, a clear identification of the various calcium compounds became possible. Figure 10 shows that two calcium components, in particular calcium soaps and calcite (CaCO_3), were contained in one red ink instance of the above mentioned Codex Hankensteinianus. In contrast, cinnabar from the red ink (Hg and S detected by XRF) does not absorb mid infrared and can therefore not be identified by FTIR. This example clearly shows the benefits of the application of complementary methods. Furthermore, it also was possible to clarify the use of the lead components red lead and lead white by reflection-FTIR.

CONCLUSION

CIMA's activities aim at improving our knowledge about historical written documents (manuscripts) in an interdisciplinary cooperation between philology, computer science and material analysis. For the non-invasive chemical analysis of the inks, pigments and dyes in manuscripts the analytical techniques of x-ray fluorescence analysis (XRF) and Fourier transform infrared (FTIR) spectroscopy have already proven their applicability. However, limitations of these techniques have also been observed, especially concerning the area of analysis due to the diameter of the primary beams used for the excitation of the various materials. Since in most cases handwritten texts have a fine structure, the instrumentation has to be adjusted to these proportions. Moreover, it has become clear that complementary investigations by methods such as Raman spectroscopy have to be employed, too.

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ВИЕНСКИЯТ ЦЕНТЪР ЗА АНАЛИЗ НА ИЗОБРАЖЕНИЯТА И МАТЕРИАЛИТЕ
 ОТ КУЛТУРНОТО НАСЛЕДСТВО И НЕГОВИТЕ ТЕКУЩИ ДЕЙНОСТИ.
 ЧАСТ III: АНАЛИЗ НА МАТЕРИАЛА

(Резюме)

Екипът на СИМА използва разнообразни аналитични техники за анализ на състава на боите и мастилата, както и за характеризиране на пергаментата: рентгенов флуоресцентен анализ (XRF) за идентифициране на наличните елементи и инфрачервена трансформация на Фурие (FTIR), както и Раман-спектроскопия, като допълнителни методи за определянето на различните съставки. Голямото предимство на тези методи за анализ е тяхното прилагане във въздушна среда. В повечето случаи анализът е неструктивен (без да се взема проба от оригиналния материал) или дори неинвазивен, което означава, че преди, по време или след изследването не се появяват никакви изменения в ръкописа. Освен това миниатюризацията в сферата на електрониката доведе до произвеждането на инструменти, които могат лесно да бъдат транспортирани в музеи, библиотеки или галерии. В публикацията е направен кратък преглед на техниките и са представени някои от постигнатите досега резултати от работата с глаголически, гръцки и латински ръкописи, в които се идентифицираха както различни пигменти, така и мастила в зависимост от произхода и времето на тяхното написване.

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