Scientific investigations on writing materials of Mali (funded by Gerda Henkel Foundation)

Status report by Oliver Hahn, Eva Brozowsky, 31 July 2015

1 Introduction

Archaeological and art historical research is often concerned with the question of origin, dating or attribution of cultural objects. Stylistic and art historical considerations in combination with the investigation of technological treatises and recipes can answer many questions, but in several cases the analysis of the physical properties and the chemical composition of the artefacts is essential. Determination of chemical composition of cultural objects is also crucial for their conservation.

The different collections in Bamako contain a vast number of manuscripts that were written and decorated with different inks on paper. The majority of the manuscripts were produced locally, in *Djenné*, *Timbuktu* or *Kayes*. It is obvious that the manufacture of the writing materials employed local plants, minerals and animals. In addition, a wide range of components and impurities is present in the inks due to a variety of different recipes and the natural origin of raw materials. A better understanding of production processes of manuscripts requires use of analytic techniques for characterisation of writing materials. As an example, determination of the ink type in the codicological description of manuscripts finds ever-growing recognition in manuscript studies.

Fig. 01: Different manuscripts in Bamako with unknown black and coloured inks

A particular requirement for the scientific investigation of the manuscripts in Bamako is the use of techniques that are non-destructive or only need minimal sampling. Furthermore, one has to use mobile equipment. There are several analytical methods which fit to a non-destructive, mobile, "multi-instrumental" approach for manuscript investigation that embraces microscopy, elemental analysis, and chemical characterisation. For the correct interpretation of the data reference materials and appropriate data bases are necessary. Therefore, the main goal of the project is the start of a reference data base construction.

2 Summary

The project aims both at perfecting the analysis techniques used for the identification of parameters that will help to differentiate between various types of inks in the manuscripts from Timbuktu and at observing the changes brought by ageing or decay processes (e.g. ink corrosion). The project comprises several steps:

- Collection and revision of recipes from oral sources in Mali
- Sample preparation
- Scientific analysis: Identification of instrumental parameters to distinguish different types of inks / use of available analytic methods to study the optical, atomic and molecular characteristics of the samples
- Production of a set of databases collecting the data about materials, recipes and scientific results.
- Identification of the peculiar characteristics for each type of ink / degree of deterioration for different types of inks
- Validation of the obtained results applying the analysis to collections from Timbuktu in Bamako

3 Collection and revision of recipes from oral sources

In the first part of the study recipes and plant materials to be used in ink and dye production were collected in Bamako and in Djenné. Up to now no recipes for ink production were available. Thus, ink recipes were collected in interviews with local *Marabouts* and scribes of Djenné. All in all it was possible to summarize 30 basic recipes for colorants and inks. Due to the variety of different recipes and the natural origin of different raw materials, there is a wide range of different components and impurities. The total amount of different samples sums up to about 80 specimens. They were sorted on the basis of the type of inks (soot ink, tannin ink, iron-gall ink, iron-tannin ink, dye ink, pigment ink, mixed ink), of the production method (by sun maceration, by cooking, by squeezing, by pounding), of the side ingredients (binder, colour enhancer) and of quantities.

In the second step different plants, minerals and other ingredients were identified in order to proceed to their acquisition. The set of reference materials includes different leaves (e.g. *Acacia sengalensis*, *Indigiofera tinctoria* / *Indigiofera arrecta*), flowers (e.g. *Hibiscus*), fruits (e.g. *Cola cordifolia* / *Cola nitida*, *Zafrane* (Songai name) and *Acacia senegalensis*), barks (e.g. *Acacia senegalensis*, *Bari* (Songhai name), Vitex Chrysocarpa = *Koronifin* (Songai name), *Pegu* (Bambara name), resins (e.g. Gum Arabic / *Acacia senegalensis*) as well as minerals (e.g. *Laterite*, Gold) (Figs. 02 – 04).[1]

[1] Pères Marcel Forgues et Charles Bailleul: Richesses médicinales du Bénin, Burkina Faso, Mali, Sénégal, Togo. Pays de la zone sahélo-soudano-guinéenne. Éditions Donniya, Bamako 2009.

Fig. 02: Koronifin (*Vitex Chrysocarpa*)

Fig. 03: Hibiscus (*Hibiscus Sabdariffa*)

Fig. 04: Laterite (Hematite)

4 Sample preparation

Using these recipes and materials different dummy inks were produced and applied to standardized paper (Fig. 5). According to the recipes different plants were extracted with water or potassium carbonate solution. The plants (flowers, fruits, bark, nuts, seeds, and leaves) were ground. The powder was boiled for 30 minutes up to 1 hour at 100 °C in a bath consisting of purified water or potassium carbonate (15 %). The coloured extracts were filtered with Whatman™ filter paper and dried. The plant extracts and/or minerals were mixed with binders (e.g. gum Arabic) that were manufactured specifically.

Fig. 05: Set of reference samples manufactured with artificial inks

5 Scientific investigations

The most important demand for the scientific investigation of manuscripts is the use of techniques that are non-destructive or only need minimal sampling. After analysis, the unchanged sample should preferably be available for further studies. In accordance to Lahanier et al.[2], the ideal procedure for analysing art, historical, or archaeological objects should be non-destructive respecting the physical integrity of the object, but also fast to analyse large numbers of similar objects or to investigate a single object at various locations. In addition, the measurements should be universal to analyse many manuscripts and related objects of various shapes and dimensions, as well as versatile, allowing acquisition of average compositional information but also permitting local analysis of small areas. Final-

[2] Lahanier, Ch., Preusser, F.D., Van Zelst. D.: Study and conservation of museum objects: Use of classical analytical techniques. Nuclear Instrum. Methods Phys. B 14 (1986): 1–9.

ly, the analyses should provide the determination of many elements in a single measurement. The scientific investigations are illustrated by representative examples in the following paragraphs.

The samples were investigated optically (microscopy, Figs. 04 - 06), with ultraviolet (UV) and near infrared (NIR) reflectography (Fig. 07), visible reflectance spectroscopy (VIS, Fig. 08), micro-Raman-spectroscopy (Raman, Fig. 09), Fourier transform infrared spectroscopy (FTIR-ATR Fig. 10), and micro-X-ray fluorescence analysis (XRF, Fig. 11).

5.1 Microscopy

Classification of different ink types is carried out with microscopy (magnification: x 200). In contrast to the pure plant ink and the carbon ink the iron gall ink shows brown haloes around the ink stroke (indicating the presence of tannins). The distinction of different black drawing materials is the starting point for the development of successful restoration or conservation concepts.

Fig. 06: Microscopic image of plant ink (*Koronifin*)

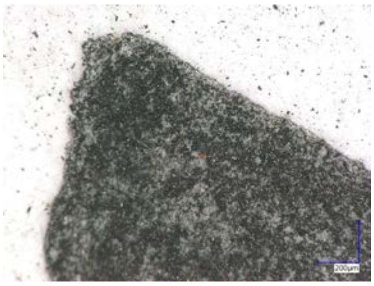

Fig. 07: Microscopic image of carbon ink (lamp black)

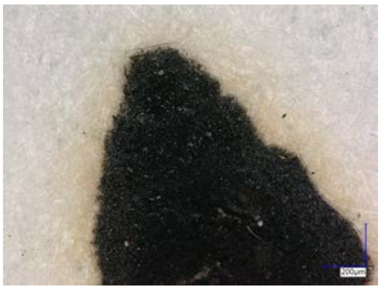

Fig. 08: Microscopic image of iron gall ink (tannin: bark of *Acacia Senegalensis*)

5.2 Reflectography

In general, IR reflectography is used to reveal underdrawings in paintings. The method is based on the fact that certain materials (e.g. pigments) absorb very little infrared radiation in the spectral range between 0.8 and 2 µm (near infrared). Radiation incident on carbon-based underdrawings is strongly absorbed and becomes "visible" by means of appropriate cameras. In addition, the method provides an appropriate technique to distinguish between carbon-based (carbon ink, bistre) and non-carbon-based (iron gall ink, plant ink) drawing and writing materials.[3]

Ultraviolet (UV) photography is a convenient tool to visualize older compositions, hidden signatures, and retouched areas of works of art.[4] UV fluorescence is a kind of luminescence. A substance (e.g. binding material) irradiated by UV light emits light in the visible range of color. Under UV light, old paint or varnish layers emit more fluorescent light than "modern" materials do. Retouched or restored areas appear darker under investigation. UV reflectography is a convenient tool to visualize text fragments that became discolored over time. Furthermore, it can be used to analyze the binding media used for paper preparation.

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[3] Ralf Mrusek, Robert Fuchs, and Doris Oltrogge, „Spektrale Fenster zur Vergangenheit - Ein neues Reflektographieverfahren zur Untersuchung von Buchmalerei und historischem Schriftgut", *Naturwissenschaften* 82, Heidelberg (1995), p. 68-79.

[4] Miroslav Hain, Ján Bartl, and Vlado Jacko, "Multispectral analysis of cultural heritage artifacts", *Measurement Science Review* **3** (2003), p. 9-12.

The measurements were carried out with a three-color USB microscope (Dino-lite AD413T-I2V), which was extremely useful in determining the ink typology and surface morphology. The microscope possesses in-built LED illumination at 395 and 930 nm and an external white light source (Fig. 07).

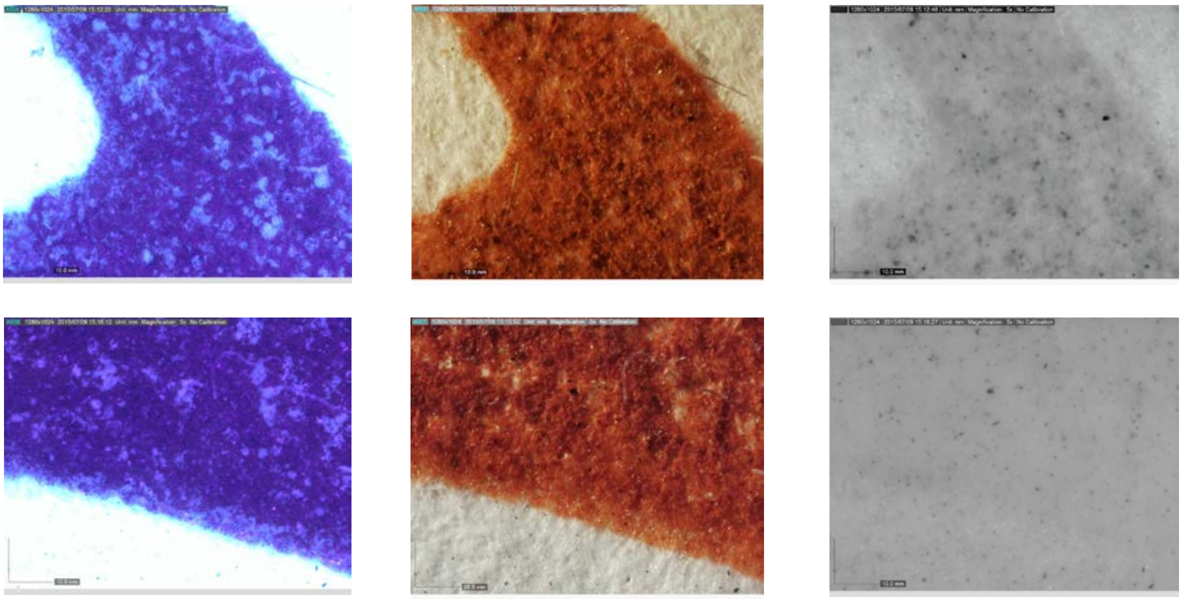

Fig. 09: From left to right UV/VIS/NIR-micrographs of Laterite (upper row) and Zafrane (bottom row). The NIR-reflectography (right column) shows the difference between both red colorants: the dye Zafrane completely disappears at 930 nm whereas the pigment Laterite is still visible.

5.3 Visible spectroscopy

By means of a spectral photometer, the color value of a colorant can be quantitatively determined on the basis of its reflective spectrum in the range of visible light (380 nm to 730 nm). This is an optical method of analyzing the surface. The sample to be examined is illuminated with visible light. The sample material interacts with the visible light by absorbing or reflecting it in a specific way, thereby appearing colored. The reflected light characteristic of a specific pigment is measured with a photometer and recorded in the form of a characteristic reflection curve. This curve represents the correlation between the intensity of the reflected light and its wavelength. Comparison with a databank makes it possible to ascribe the pattern to a particular pigment or dye.[5] The examinations were carried out with the aid of the spectral photometer SPM 100 made by the Gretag Imaging AG company (Regensdorf, Switzerland).

[5] Robert Fuchs and Doris Oltrogge, "Painting materials and painting technique in the Book of Kells", *The book of Kells, Proceedings of a Conference at Trinity College Dublin (09/1992)*, Dublin (1994), p. 133-171, p. 147-191, p. 603.

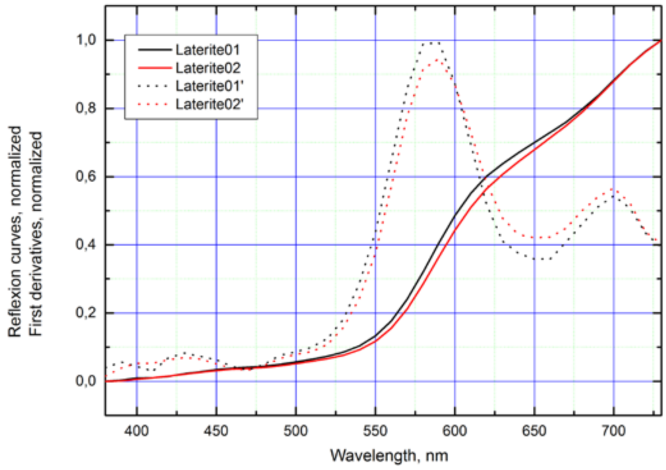

Fig. 10: Visible spectroscopy of Laterite (Hematite), characteristic bands indicate the red colorant

5.4 Raman spectroscopy

Raman spectroscopy is a technique that relies on the scattering of monochromatic light in the visible, near-infrared, and near-ultraviolet range, used in particular to provide vibrational information specific to different chemical bonds and molecules. It has proved to be a specifically powerful tool for identifying inorganic as well as organic materials. In the field of scientific manuscript analysis, it is now routinely used to identify pigments, binders and tannins, whose spectra are tabulated.

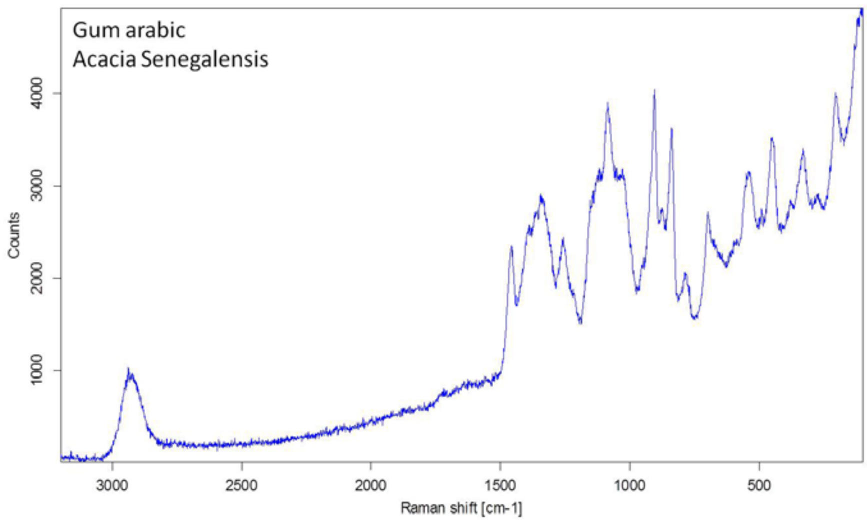

Fig. 11: Raman spectrum of gum Arabic (resin of Acacia Senegalensis); characteristic bands of carbohydrates lead to unequivocal identification of this binder.

5.5 FTIR spectroscopy

Similar to Raman spectroscopy IR spectroscopy has been commonly used for the investigation of organic materials. It is therefore a well-established method for classifying binding media. We used attenuated total reflection Fourier transform infra-red (ATR-FTIR) spectroscopy to study plant extracts, and FTIR in reflection, for the analyses of different inks.

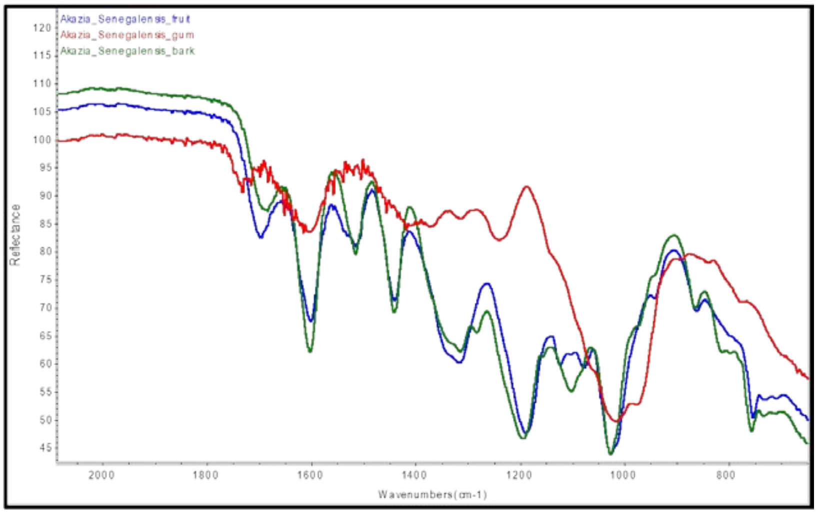

Fig. 12: Comparison of FTIR-ATR spectra of gum, fruit, bark from *Acacia Senegalensis*; the differentiation of raw materials by means of FTIR spectroscopy is obvious.

5.6 XRF spectroscopy

After classification of the writing materials with microscopy, reflectography or chemical analysis, we have to ask whether the script was executed with one or more than one carbon ink. Thus, the next step is the analysis of possible trace elements in the writing inks. In addition to colorants and binders, writing inks contain secondary components, such as salts of the elements potassium, calcium, copper, iron, manganese, or aluminum, among others. The varying composition of these different components is a characteristic property of writing inks and makes possible their exact determination.

Ageing phenomena have no influence on the applied XRF, because even if the chemical composition of the binder and the colorants may change due to chemical corrosion processes that alter the organic material, the proportion of metal components, i.e., the elemental composition, remains the same. To estimate the presence and the real amount of trace elements, we performed line scans with XRF. A line scan consists of a number of single measurements along a chosen line. As an example, Figure 11 (bottom) displays the net peak intensities as a function of distance extracted from the single measurements; (top) displays the image corresponding to the line scan.

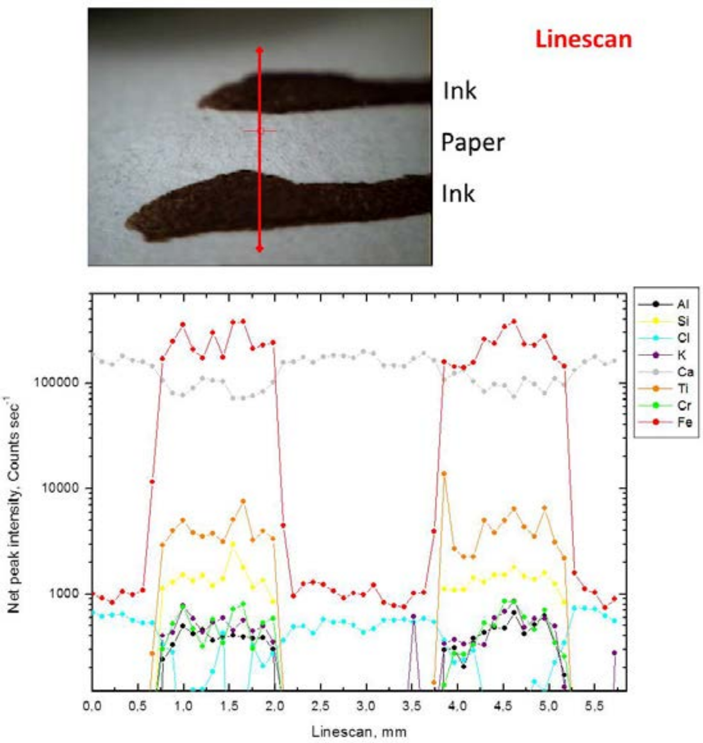

Fig. 13: XRF – Linescan of two red *Laterite* ink strokes. The main colorant is iron oxide (e.g. hematite; Fe_2O_3). The presence of characteristic traces of aluminium (Al), silicone (Si), titanium (Ti), chrome (Cr) and potassium (K) reveals the mineral nature of the raw material.

6 Ink Corrosion

As mentioned before different decomposition reactions can take place, leading to changes in the ink colour, and occasionally, to iron gall ink corrosion. There are two main reasons for the ink corrosion, first of all the acid components in the inks (e.g. tannins) which lead to hydrolytic splitting of the cellulose, and second, the capacity of soluble metal ions that act as catalyst for the oxidative decomposition of the cellulose. The reconstructed samples in this study reveal that the beginning of the corrosion may take place at an early date (Fig. 8) and strongly depends on the ink composition. These findings are very important for the development of appropriate conservation concepts.

7 Conclusions

The first results of the scientific analyses indicate that it is possible not only to classify writing inks (typology) but also to differentiate between the different inks of the same type (fingerprinting). After the end of the first step (07/2015) of this research project it is possible to create a first structured collection of traditional recipes for producing black and coloured inks. We intend to publish these results in the *Journal of Cultural Heritage* within the end of 2015.

The reference database has to be completed adding more materials and analyses (see time schedule) and will be validated by comparison with original samples. However, even at this stage it is absolutely clear that the analytic work on the original manuscripts in Bamako can be started. The manuscripts to be analysed will be selected after classification on the basis of the type of inks (pigment inks, dye inks, etc.) on the type of applicable analyses and on the kind of sampling allowed by the libraries they belong to. A codicological record will be produced for each manuscript, with particular regard to inks. Analyses were carried out in close cooperation with Dr. Bondarev.

In general, material analysis of the manuscripts can assist scholars in their work on codicology, paleography, textual criticism and text editing, cataloguing, and in addition, in the conservation and preservation of manuscripts. The development of reversible conservation treatments or restoration concepts requires the detailed knowledge of material compositions and ageing phenomena of the manuscripts. Our scientific investigations will provide essential information for the preservation of the manuscripts.

Time schedule (until October 2015)

Task	02/2014	04/2014	06/2014	08-11/2014	11/2014	12/2014 - 01/2015	02-03/2015	04-05/2015	06/2015	07/2015	08-09/2015	10/2015
Conference about "inks and writing materials"												
Interviews												
Collection of first raw materials												
Reconstruction / preparation of the writing inks												
Preparation of the samples												
Documentation												
Microscopy												
Elemental analysis												
Vibrational analysis												
Data Evaluation												
Compilation data base												
Investigation of original samples												