Article

The Study of Manuscripts: a Natural Scientist's Approach[*]

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Abstract:

The analysis of physical and chemical properties of artefacts provides important data for answering questions that cannot be solved by historical and philological methods alone. In its individual materiality, each manuscript is the result of various influences (e.g. production, storage, restoration, preservation). Given the recent technological developments (e.g. miniaturization of structural units, enlargement of memory capacity), technical diagnostics of art and cultural objects are becoming increasingly sought after in trans-disciplinary research. In this review we present a multi-instrumental approach to the investigation of manuscripts. Several case studies will illuminate our methodology.[*]

1. Introduction

The investigation of manuscripts is often associated with the question of origin, dating, or attribution of these cultural objects. In some cases, the differentiation between different scribes is of special interest. Other questions concern the history of a particular manuscript and examine the relation between the original text and its amendments, corrections, or additions. In this context Mantler and Schreiner indicated that 'styles were sometimes copied at locations and periods completely different from those of their origin', so that physical and chemical investigations 'are helpful and increasingly applied to allocate an object to a particular historic or prehistoric context, to determine the correctness of the claimed provenance or to explore the technology used for manufacturing'.[1] This very general statement also applies to manuscripts. In addition, the development of reversible restoration or conservation concepts requires the knowledge of the material composition and ageing phenomena of the artefacts.

From a scientific point of view, we have to consider a manuscript as a physical object consisting of two types of material. The first one comprises various substrates (e.g. papyrus, paper, parchment, palm leaves), while the second includes writing materials (e.g. carbon ink, iron gall ink, or chalk). In addition, we have to take into account that the examination of writing utensils (e.g. rush, reed, quill, pen, ink wells) may provide useful information about the writing process.

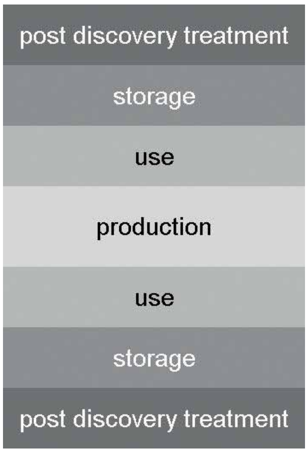

Fig. 1: Cross-sectional scheme of an object with traces from different periods in its history

In general, we may perceive infor-mation acquired during the lifetime of a manuscript as a stack of layers (fig. 1). The first one is the production layer followed by the use, storage, and finally post-discovery treatments. In the ideal case the structure of the layers is preserved; in any real case the phases intermix with one another at the borders, which can even result in the loss of identity of the individual contributions.

2. Analytical techniques

The options of methods and techniques available for the analysis of art objects are diverse. To give an example, the relevance of technical investigations in arts and culture was summarized in the 'European Cooperation in Science and Technology (COST) Action G8 report: Non-destructive testing and analysis of museum objects'[2]. The following compilation contains only a limited choice of investigation techniques that are appropriate for manuscript analyses:

[*] We gratefully acknowledge the support of the German Research Association (DFG) for the sub-project 'Material-Scientific Methods for Reconstructing the History of Manuscripts' of SFB 950 'Manuskriptkulturen in Asien, Afrika und Europa' at the Centre for the Study of Manuscript Cultures
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[1] Mantler, and Schreiner 2000.

[2] Denker et al. 2006

- Image-processing techniques are used to digitalize the objects, map the surfaces, and reveal hidden layers (Multi-Spectral or Hyper-Spectral Imaging, Infrared-Reflectography, various types of radiography), or investigate cross sections (e.g. Scanning Electron Microscopy, SEM).
- X-ray and neutron technologies help to determine elemental compositions (e.g. X-ray Fluorescence (XRF), Particle Induced X-ray Emission (PIXE), Neutron Activation Analysis (NAA), oxidation states of certain elements and their adjacent atoms (X-ray Absorption Near Edge Structure (XANES), Extended X-ray Absorption Fine Structure (EXAFS)), or the crystal phase of pigments (X-Ray Diffraction (XRD)).
- Vibration spectroscopic techniques such as IR and Raman spectroscopy are necessary to determine the chemical composition.

The most important requirement for the investigation of manuscripts is the use of analytical techniques that are non-destructive or require minimal sampling. After the analysis, the unchanged sample should preferably be available for further investigation. According to Lahanier et al.[3], the ideal procedure for analyzing art, historical, or archaeological objects should be 'nondestructive, respecting the physical integrity of valuable and irreplaceable objects; fast, so that large numbers of objects from archaeological excavations and from museum collections, the latter often with little known archaeological context, can be analyzed comparatively; universal, i.e. applicable to many materials and objects of any dimension; versatile i.e. suitable to provide both highly localized analyses of microscopic areas, and average bulk analyses of heterogeneous materials; sensitive and multielemental to furnish a maximum amount of information' However, in some cases sampling may be a basic requirement for a successful analysis. Therefore, the choice of a technique depends strongly on the specific question addressed to the investigator. Ideally, one would apply a number of methods that complement each other to obtain a maximum amount of information belonging to the object.

Band-pass-filter infrared reflectography (IRR) is a useful method for distinguishing between different writing materials. It was invented in the 1960s for investigating paintings. The fact that some pigments and dyes show a low infrared absorption makes it possible to investigate underdrawings.[4] Since infrared light interacts differently with different materials, it is also possible to distinguish between carbon inks and iron gall inks by means of IRR.[5] During analysis the manuscripts are illuminated with infrared light. An infrared-sensitive camera visualizes the radiation, which is invisible to the human eye. Wavelengths ranging from 800 to 1500 nm are most advisable for investigation. Band-pass filters split the whole infrared spectrum into appropriate partitions. Depending on the wavelength, plant inks become transparent at about 800 nm, iron gall inks at between 1000 nm and 1200 nm. Writing materials that contain elemental carbon will absorb the infrared light within the whole mid-infrared range and appear as black lines.

An interesting task is the 'virtual deletion' of iron gall inks. A variety of fragments of Goethe's Faust II manuscript

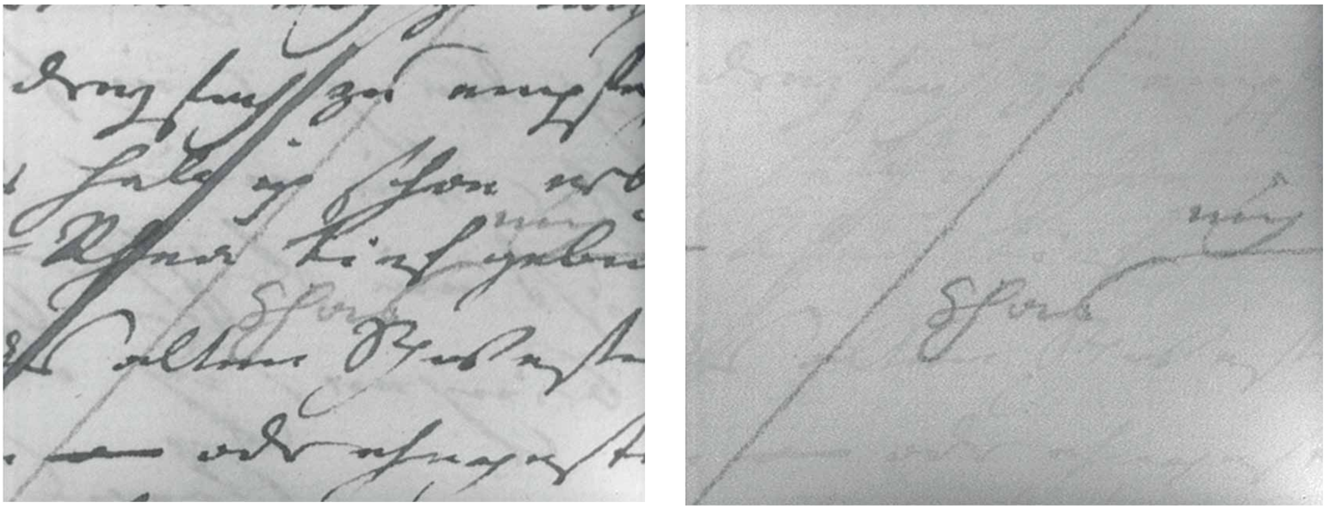

Fig. 2: GSA25/XVII, 8, 12; Johann Wolfgang von Goethe, Faust II, f. 1^{v}; IRR; left: 1000 nm; right: 1300 nm. At 1000 nm the iron gall ink as well as the pencil are visible, whereas at 1300 nm only the pencil is visible.

[3] Lahanier et al. 1986, 1.

[4] Asperen de Boer 1975, 1

[5] Mrusek et al. 1995, 68.

contain conceptual texts written with a pencil. These texts were overwritten with iron gall ink. By means of IRR it was possible to visualize the first conceptual layer in order to compare the concept with the final text (fig. 2). Based on our analysis it was possible to show that most of the initial concept was executed.[6]

Sometimes this method is a useful tool for differentiating iron gall inks. However, different writing materials, restoration treatments, and the variation of ink thickness may influence the result and lead to misinterpretations.[7]

Unlike with IRR, it is possible to determine the elemental composition of writing materials by means of X-ray fluorescence techniques (XRF). XRF is one of the most suitable methods to obtain qualitative and semi-quantitative information on a great diversity of materials. Although XRF is a convenient method for investigatiing inorganic compounds, it is not suited for determining organic materials since their main constituents (carbon, oxygen, nitrogen, and hydrogen) cannot be detected when applying this technique.

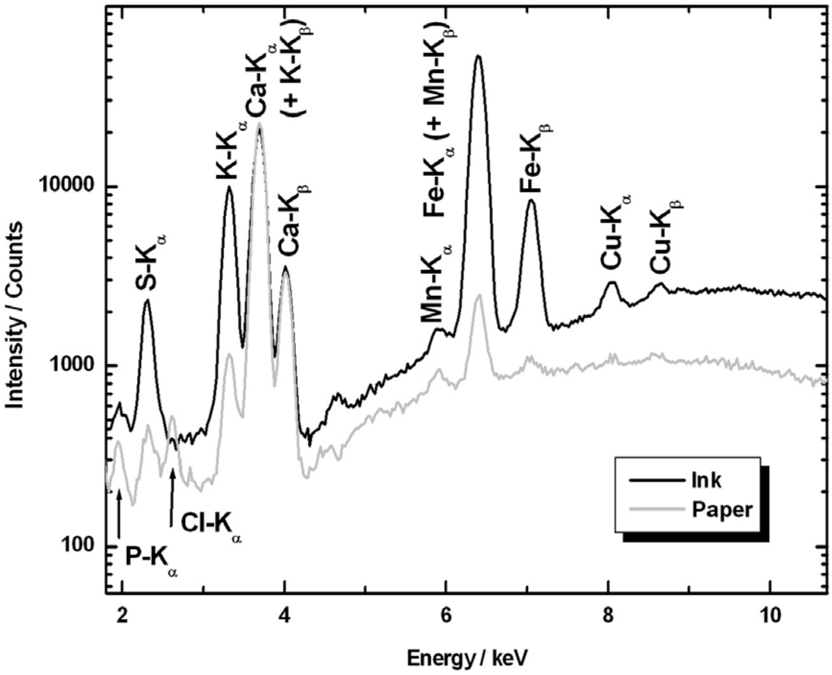

Fig. 3: Representative X-ray spectrum of an iron gall ink and a typical rag paper. The iron gall ink contains iron (Fe), copper (Cu), manganese (Mn), and potassium (K). The diagram shows that the quantitative analysis has to take into account the elements occurred both in the ink and in the paper (e.g. iron, potassium, and calcium).

The object under analysis is irradiated with X-rays. As a result, the external primary excitation beam interacts with the atoms within the sample. An electron of the inner shell is ejected, creating a vacancy. In the next step another electron from an outer shell fills the vacancy. The energy of the emitted X-ray fluorescence is characteristic for a certain element, whereas the signal intensity allows the quantification of the element.[8]

As mentioned above, one has to consider that the character of artefacts entails several problems that may affect the interpretation of the results. ‘Even plane objects such as manuscripts are usually not ideal but of complex shape, heterogeneous composition; they consist of several layers (support and colouring agent) and may show surface alteration’.[9]

This requires the development of specific procedures to quantify the composition of the inks and the supporting materials in an appropriate way. In case of iron gall inks, a fingerprint model was conceived based on inorganic compounds such as iron, manganese, zinc, and copper.[10] The well-known fingerprint method relies on the determinationof characteristic elemental compositions in samples.[11] The micro-XRF measurements of the iron gall inks were quantified using the composition fingerprint model, which is based on fundamental parameter procedures leading to the value W_i (weight concentration of the element i relative to Fe).[12] The respective calculations are based on a model ink containing a certain amount of iron sulphate as a constant parameter.[13]

Similarities of, and differences between, the IRR and XRF techniques have been illustrated using two pages from Wolfgang Amadeus Mozart’s *Magic Flute* (f.34^{r} und f.38^{r}, State Library Berlin) as an example.[14] The visual characterization of f.34^{r} indicates two different types of ink: light brown ink and dark brown ink (fig. 4a). Regarding f.38^{r}, it is possible to distinguish three different inks with the naked

[6] Henke 2000, 387.

[7] Hahn, and Maurer-Zenck 2003, 2.

[8] Hahn et al. 2004, 234.

[9] Hahn 2010, 43.

[10] Malzer et al. 2004, 229.

[11] Hoffmann et al. 2000, 92; Werner et al. 1975, 158; Rye 1993, 39.

[12] The composition fingerprint value Wi mainly involves three different parameters: the experimentally determined transmittance of the entire layered system, the penetration depth of the writing material into the paper, and a normalized absorption coefficient that takes into account the matrix composition.

[13] Malzer et al. 2004, 231.

[14] Hahn 2006, 148.

eye (fig. 4c). This differentiation is confirmed by means of IRR (tab. 1). The dark brown ink from f. 34^{r} is visible up to 1100 nm, whereas the light brown one is only visible up to 1000 nm (fig. 4b). The three ink types from f. 38^{r} may be classified into two groups: the light brown and the brown ink disappear at about 1100 nm, whereas the dark brown ink is still visible (fig. 4d).

After carrying out the XRF analysis, we obtained a different result. Figure 5 shows the composition fingerprint of zinc as a function of the fingerprint of copper. All things considered, it is possible to distinguish two different types of ink: type I and type II.

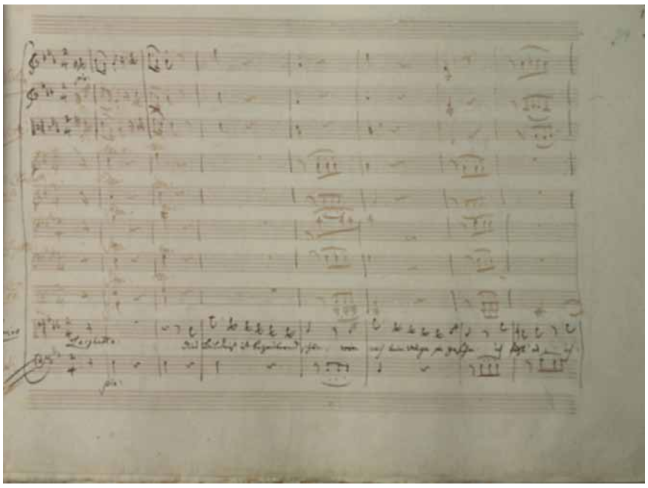

Fig. 4a: f.34^{r}, VIS

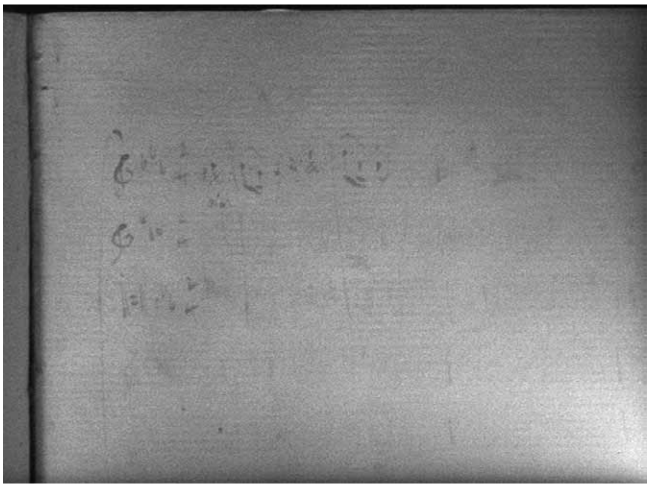

Fig. 4b: f.34^{r}, IRR, 1100 nm

Fig. 4c: f.38^{r}, VIS

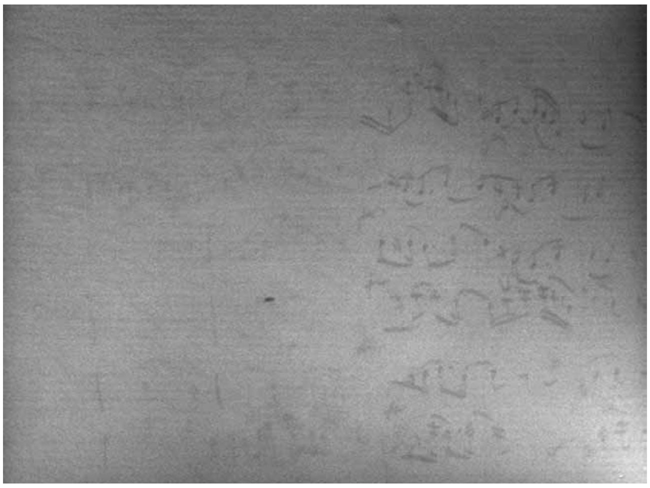

Fig. 4d: f.34^{r}, IRR, 1100 nm

Table 1: IRR, f.34^{r} f.38^{r}

Folio	Visual Characterization	Visible up to a wavelength of ... nm					
		900	950	1000	1100	1200	1300
34r	dark brown	x	x	x	x		
	light brown	x	x	x			
38r	dark brown	x	x	x	x		
	brown	x	x	x	((x))		
	light brown	x	x	x	((x))		

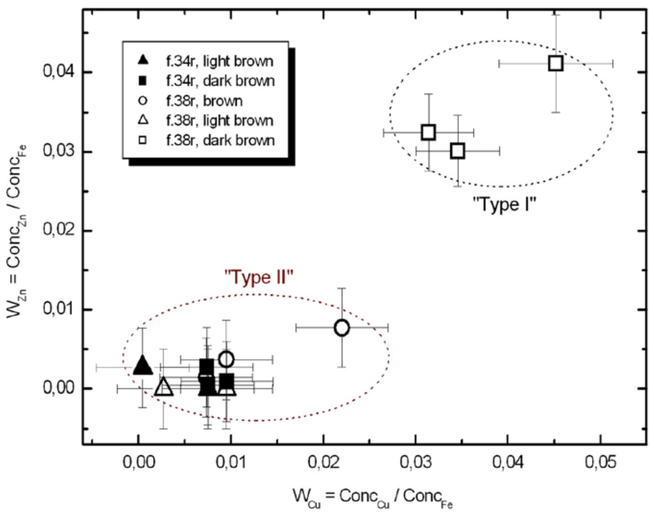

Fig 5: Composition fingerprint of zinc [Zn]/[Fe] as a function of the fingerprint of copper [Cu]/[Fe]; results of the XRF analysis, f.34r, f.38r.

On the basis of the inks on f. 38r, the IRR results were confirmed by XRF. The dark brown ink is an independent ink type (type I), whereas the two brown inks belong to another ink type (type II). The different colours of the inks presumably result from different layer thicknesses. The two inks on f. 34r certainly belong to one ink type (type II). The difference in the visual appearance as well as the different result of the IRR can be explained by different layer thicknesses or by a dilution of the ink with water during the writing process.

Unlike XRF, vibration (i.e. Infrared and Raman) spectroscopy techniques provide information on chemical composition and are thereforeapplied routinely to screen unknown assays. Both techniques take advantage of the fact that the bonds of atoms in a molecule interact with light at characteristic frequencies in the infrared region of the light spectrum. Therefore, their detection in an IR or Raman spectrum reveals the chemical identity of the materials under investigation. The type of interaction measured by infrared spectroscopy differs from that detected by Raman in such a way that they complement each other. Historically, IR spectroscopy has been commonly used for investigatiing organic materials. It is therefore a well-established method for classifying binding media. To perform a conventional measurement (so-called transmission mode), a thin or powdered sample is placed in the beam pass and the amount of transmitted light detected as a function of wavelength or frequency, producing an infrared spectrum. Hence, this method required samples to be extracted from an object. To reduce the sample size, special diamond cells were developed. Rapid technological progress in this field led to the appearance of non-destructive methods such as Attenuated Total Reflection Fourier Transform Infra-Red (ATR-FTIR) spectroscopy[15] to study surfaces, fibre-optic FTIR spectroscopy in reflection,[16] and synchrotron-based FTIR spectroscopy.[17] The miniaturization of infrared sources and detectors led to a new generation of portable FTIR spectrometers, for example a hand-held Exoscan.[18]

It is noteworthy, however, that none of these analytical techniques can be used for the direct dating of an art object. Only special techniques such as radiocarbon dating of organic materials (C14-method),[19] dendrochronology for wooden artefacts,[20] and the analysis of thermoluminescence for ceramics[21] permit age determination.

2. Writing support

Leather and parchment

Leather and parchment are skin-based writing materials known in the Mediterranean since Antiquity. Leather rolls were in use in Ancient Egypt at least since the seventeenth century BCE; the spread of the Aramaic language in Mesopotamia was accompanied by writing on leather; Herodotus reports that in Antiquity Ionian Greeks used leather as a writing material.[22] In contrast to leather, the oldest known parchment documents, the Dead Sea Scrolls, are dated to the third century BCE. Unlike leather, parchment is prepared by drying an un-haired skin under tension and is usually not tanned.

In the Roman Empire, the replacement of papyrus with parchment coincides with the change from 'scroll' to 'codex' in the third and fourth centuries. However, the main cause for these changes is unclear. For a millennium, parchment becomes the main writing material in Europe.

There are no written sources on the preparation of ancient leather and parchment as writing materials. It is believed that animal skins were de-haired enzymatically (e.g. with urine or flour paste) prior to drying under tension. Chemical investigation of the Dead Sea Scrolls suggested that the parchments were superficially tanned at the finishing stage.[23]

15 Marengo et al. 2005, 225.

16 Miliani et al. 2007, 3293.

17 Salvado et al. 2005, 3444 and Bartoll, et al. 2008, 1.

18 A2 Technologies, 2011, accessed 15 September 2011.

19 Jull et al. 1995, 11.

20 Schweingruber 1988.

21 Goedicke 2007, 31.

22 Diringer 1982, 189.

23 Poole, and Reed, 1962.

The modern definition of parchment includes the depilation of a precursor animal skin using lime in addition to the aforementioned drying under tension. However, this preparation technique is mentioned for the first time in the eighth century CE in the Lucca manuscript.[24] Theophilus Presbyter describes the use of lime for the preparation of leather and parchment in his *Schedula diversarium artium* in the early twelfth century. It is unclear when and where the use of lime was introduced.

Palm leaves and tree bark

Before paper was introduced, palm leaves of *Talipot* or *Talipat* (*Corypha umbraculifera*, C. taliera) and *Palmyra* (*Borassus flabellifer*) were a common writing material in South Asia. According to Diringer, however, it is only leaves of the *Talipot* palm that were used throughout India in the early times, whereas *Palmyra* palm was introduced much later and was mostly in use in South and East India.[25] The precursor palm for a manuscript can be easily determined by visual inspection. *Talipot* leaves are thinner and possess marked rills, whereas *Palmyra* leaves appear pitted.

Agraval reports that techniques for preparing palm leaves for writing varied from place to place. However, practically all techniques involved drying the leaves, boiling them in water (alternatively, in lime water or milk), and polishing using turmeric paste or sesame oil.[26] No advanced studies of the composition of the palm leaf manuscripts have been reported. However, the use of local materials during their processing raises hopes that palm leaf manuscripts could be sorted according to their origin.

The bark of birch trees was another writing material commonly used besides palm leaves in India. It is a naturally layered material held together by tree gum and bark knots. Usually, one peeled off the bark from the tree, dried it, smoothed it with oil, and polished it. Then the sheets were cut to the desired size. Diringer remarks that in ancient times a full length of peeled-off bark may have been used similarly to the papyrus rolls. In the Assam region, one used rather the bark of the agar wood tree (*Aquilaria malaccensis lamk*).[27] Traditional processing of bark consists of several steps described in great detail by Goswamee.[28] It is noteworthy that preparation involves dyeing with arsenic sulphide and/or mercury sulphide, which are easily determined by X-ray fluorescence.

Paper

Paper is best defined as a thin, matted sheet of intertwined fibres formed from a aqueous pulp suspension by means of a sieve-like screen. The invention of paper is traditionally attributed to Cai Lun in the early second century CE. After having been in use for at least several centuries, Cai Lun probably standardized and possibly also improved already-known processes: breaking textile fibres down into a pulp and draining the water through a sieved mould producing a matted layer of fibres.[29] Although technological progress considerably affected each step of the manufacture, the essence of the invention remains unchanged until today.

Papermaking reached Europe in the eleventh century through the Arab world, where it was known from the eighth century CE. However, it became popular and largely replaced parchment only after the invention of the printing press in the fifteenth century. By that time, water-powered paper mills considerably improved the process of breaking the fibres down into a pulp. In the nineteenth century, another revolutionary invention introduced wood pulp instead of textile fibres and led to the mass production of paper.

Archaeometric studies of the paper concentrate on precursor fibres that can be determined by means of microscopy,[30] mould imprints, and watermarks.[31]

3. Writing materials

Carbon or soot ink

According to its generic recipe, one of the oldest writing and drawing pigments are produced by mixing soot with a binder dissolved in a small amount of water. Thus, along with soot, binders such as gum Arabic (ancient Egypt) or animal glue (ancient China) belong to the main components of soot inks. From Pliny's detailed account on the manufacture of various soot-based inks[32] we learn that, despite its seeming simplicity, the recipe for the production of pure soot of high quality was no easy task in Antiquity. Therefore, we expect to discover various detectable additives that may be indicative of the time and place of the production.

Among the first raw materials employed in the Arabian sphere to produce inks were soot from stone pine resin, fish

[24] Reed 1975.

[25] Diringer 1982, 358.

[26] Agraval 1984, 24.

[27] Diringer 1982, 361.

[28] Goswamee 2006, 73.

[29] Needham 1985,1–3. – In recent decades, archaeological finds have prompted scholars to antedate the beginning of the use of paper by at least two hundred years: in Xuanquan, Gansu, a piece of paper with written characters dated 140–7 BCE was excavated in 1990. Already four years earlier, a map drawn on a fragment of paper dated 176–141 BCE had been unearthed in Fangmatan, also in the Gansu province; see Pan 2011.

[30] Helman-Ważny, and Van Schaik 2012.

[31] Dietz et al. 2012, 1505.

[32] Pliny, *Naturalis Historia*, Book XXXV, 25

glue, and gums. Later, more expensive raw materials were used, like sandarac resin from the *Sandarac Tree*, styrax resin from the bark of the *Oriental Sweet Gum*, and ladanum resin from various species of rock roses.[33]

In Europe, the smooth carbon material came from burnt oil. Due to its quality, sesame oil was preferred for the preparation in China. Baldinucci mentioned in 1681 the preparation of 'inchiostro della China'. Many recipes were known for the preparation of carbon inks at that time.[34] One differentiated between one's own European products and materials produced in the Far East.[35] In general, carbon inks were used as printing inks, but also for drawing, especially washes.

Plant ink

The brown ink – best-known as blackthorn or Theophilus' ink – is usually produced from the blackthorn bark and wine. In the early European Middle Ages, inks of this kind were widely used in the production of manuscripts in monasteries.[36]

Usually, they are light brown,[37] so sometimes small amounts of iron sulphate were added, which led to what was called an 'imperfect' iron gall ink. The difference between 'classic' iron gall ink and such imperfect ink is therefore unclear, and the distinction – especially with the naked eye – is impossible.

Iron gall ink

Iron gall ink is the most widely used drawing and writing material in Western history.[38] In general, it is produced from four basic ingredients: galls, vitriol, gum Arabic as a binding media, and an aqueous medium such as wine, beer, or vinegar. By mixing gallic acid with iron sulphate, a water-soluble ferrous gallate complex is formed. Due to its solubility, the ink penetrates the parchment surface, making it difficult to erase. When exposed to oxygen, a ferric gallate pigment is formed. This complex is not water-soluble, which contributes to its indelibility as writing ink. Normally, when mixing gallic acid and iron sulphate, the presence of oxygen leads directly to the formation of the ferric gallate pigment. Gum Arabic acts like a suspension agent for the insoluble pigment particles. It also modifies the viscosity of the ink. Due to the variety of recipes and the natural origin of raw materials, there is a wide range of different components and impurities in historical iron gall inks.

Vitriol, the main source of iron in the iron gall inks, was obtained from different mines by means of various techniques.[39] Therefore, inks contain many other metals, like copper, aluminium, zinc, and manganese, in addition to the iron sulphate. These metals do not contribute to colour formation in the ink solution, but possibly change the chemical properties of the inks. In Goslar, Germany, for instance, a large concentration of natural vitriol served as a major supply in the Middle European market.[40] The determination of different inorganic components in iron gall inks provides the basis for differentiating these writing materials.

Colour inks

Colour inks based on pigments such as cinnabar or azurite were used since Antiquity.[41] The minerals were finely ground and then dispersed in a binding media.[42] In general, water-soluble binders such as gum Arabic or egg white were used. As an example we cite the medieval prescription for preparing red inks:

> When you paint cinnabar or red lead on a parchment to form capital letters, take a well-slit quill, but not solely for this colour, but also for blue. For green colour, it should be less slit, because one applies it more thinly.[43]

4. Case studies

The first two examples deal with the investigation of iron gall inks. As mentioned above, the distinction between these writing materials based on the amount of manganese, iron, copper, zinc, and lead is a suitable way to answer many cultural-historical questions. The analyses were carried out by means of a mobile X-ray fluorescence technique with helium purging. Details concerning the method are described elsewhere.[44] The third example shows the investigation of different parchments in order to distinguish between different preparation techniques. The last example focuses on the investigation of pigments in illuminated manuscripts by means of X-ray diffraction.

33 Schopen 2004, 10.

34 Krekel 2005, 631.

35 Koschatzky 1996, 135.

36 Trost 2011, 89.

37 Hahn, 2011, 116.

38 Krekel 1998, 25.

39 Hickel 1963, Lucarelli, and Mando 1996, 644.

40 Kraschewski 2001, 344

41 Oltrogge, and Hahn 1999, 383.

42 Oltrogge 2005, 535.

43 'Cum membrana vermiculum vel minium inposueris ad formandum capitalis litteras, habeto pennam bene fixam; non solum autem ad istum colorem, verum etiam at ad azorium; ad viridem vero colorem minus sit fissa, eo quod tenuiter inponitur' Straub 1965, 98 und Trost 2011, 89.

44 Bronk et al. 2001, Hahn et al. 2004, Wolff 2009.

Fig. 6: The Erfurt Hebrew Giant Bible (State Library Berlin, Ms. or. fol. 1210/1211) under investigation.[45]

Mass in B Minor

The *Mass in B Minor* (BWV 232) is now kept in the State Library in Berlin. It is a musical setting (or more formally a *missa tota*) of the *Latin Mass* by Johann Sebastian Bach. Although parts of the *Mass in B Minor* date to 1724 (and the model for one parody even to 1714), the whole was assembled in its present form in 1749, just before the composer's death in 1750.[45]

After the death of Johann Sebastian Bach, the composition was passed on to his son, Carl Phillip Emanuel Bach. He studied the composition of his father intensely. Looking at the manuscript, it is obvious that the composition contains various amendments and corrections. It is possible to ascribe most of them to Johann Sebastian Bach or to Carl Philipp Emanuel Bach. However, the manuscript shows a certain amount of remnants and slurs whose correct attribution was previously impossible. By means of the XRF method it became possible to distinguish Johann Sebastian's from Carl Phillip Emanuel's ink.[46]

Although the manuscript was subject to a conservation treatment, the splitting of the paper, the characteristic distinctive features were conserved. The inks used by Johann Sebastian Bach contain lead sulphate, which probably originated from the transportation of tap water in lead pipes. The inks used by Carl Phillip Emanuel show no lead content.

The Erfurt Hebrew Giant Bible

Another valuable manuscript kept in the State Library in Berlin is the *Erfurt Bible* (fig. 6). The two-volume giant codex is a unique Jewish cultural artefact and extraordinary textual, material, and artistic product of the medieval German Ashkenazi heritage. Many pages are decorated with the arrangements of the text of the *Masora*, notably the beginning of the book of *Genesis*. It contains the whole Hebrew Bible, written on totally equalized parchment. In addition it includes the Aramaic translations, also written in Hebrew characters, which follow the Hebrew version verse by verse. The text is accompanied by the grammatical and lexical notes known as the *Masora Magna*, written on the upper and lower margins, and the *Masora Parva*, written between and beside the three columns of the biblical text, in a minute script.

The investigation of the inks in the second volume shows a wider ink variation than in the first volume. These findings reflect the chequered history of this part of the book. Fire, the presence of water, and restoration interventions may have considerably influenced the ink composition. However, it was possible to analyze a variety of different inks, which allows us to reconstruct the complex history of the production of the *Erfurt Bible*. As an example, on the opening page of the duplicate quire, which was left unused, primary text, vocalization, both *Masoras*, and micrography were carried out with a single ink. This fact can be considered as a confirmation of the palaeographic hypothesis that the abandoned quire served as a sample before the Bible was commissioned. Moreover, the result that the same ink was used for the primary text in the second quire renders further support for the palaeographic reconstruction of events: after the Bible hade been commissioned, the scribe went on copying from the second quire.

Other results suggest that a change of the scribes may have taken place during the production of the manuscript.

[45] Hahn, 2011, 206.

[46] Wolf et al. 2010, 117.

The successive similarity of the inks used for the primary text, vocalization with *Masora Parva* and *Masora Magna*, beginning exactly where the ink of the primary text changed, may indicate that the masorete alone completed the commission. At the end of the manuscript the masorete uses the ink of the *Masora Magna* for the corresponding colophon, which proves that he signed the manuscript immediately after completing the last step of work.[47]

The Temple Scroll (11QTa)

The Dead Sea Scrolls (DSS) were discovered between 1947 and 1956 in eleven caves in and around the Wadi Qumran on the western shore of the Dead Sea. The collection consists of approximately 900 highly fragmented manuscripts produced between the end of the second century BCE and 68 CE. The aforementioned material study conducted in the 1950's suggested that the production process of the Jewish ancient parchment involved vegetable surface tanning at the finishing state.[48] This treatment is consistent with the brown colour of the majority of the fragments in the collection as well as the practices prescribed in the *Talmud*. In contrast, the *Temple Scroll* (11QT^a) was written on a particularly light-coloured parchment uncommon for tanned parchment. Text must have been written onto an easily detachable layer rather than directly on the parchment surface, since part of the text was found as a mirror image imprint on the back of the columns in contact leaving blank surface behind. Furthermore, on the basis of the palaeographic examination it was concluded that the scroll consisted of two parts considerably separated in time: the main scroll (columns VI-LXVII) and the 'repair' part (columns I-V)[49].

Systematic visual examination of the parchment surface of the scroll shows two obvious differences: the first columns have a greyish tint, whereas the rest of the scroll varies in colour from pale ivory to lemon yellow and brown; the surface of the first sheet is of uniform roughness while the powdery texture of the surface throughout the rest of the scroll displays multiple cracks and grooves (fig 7: columns V and LII). These differences are especially evident near the ruling lines, which are much more pronounced in the main part of the scroll. The examination of the surface of the selected fragments with stereomicroscopy at a higher magnification confirms these observations. Despite the advanced degradation and rather aggressive attempts to preserve the first columns, one can still deduce that the differences in the texture result from the original treatment in Antiquity rather than post-discovery intervention.

To understand the origin of these differences, we have investigated a number of fragments from the first and the second part of the scroll by means of scanning μ-XRF, SEM, ATR-FTIR, and Raman techniques.[50] Scanning electron microscopy and XRF analysis revealed that the parchment of both parts had a layered structure with an inorganic top layer that contained the elements sulphur, calcium, aluminium,

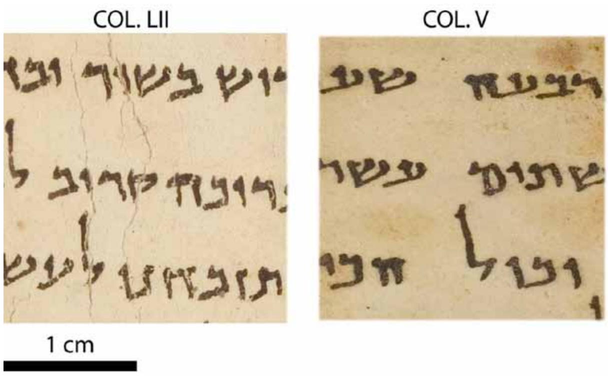

Fig. 7: The *Temple Scroll* (11QT^a), details from col. LII and col. V.

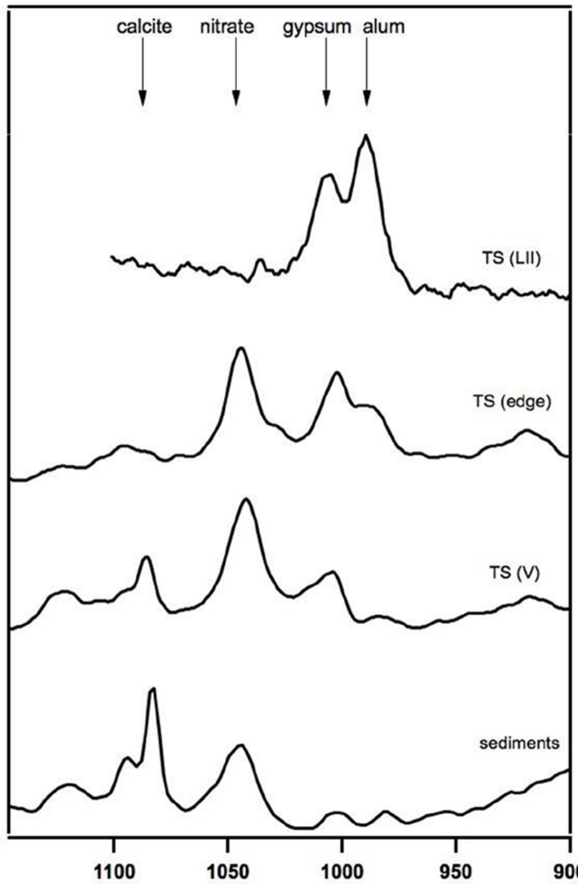

Fig. 8: Raman spectra of the *Temple Scroll* fragments and of the sediments from the Cave 11 in Qumran.

[47] Hahn et al. 2008, 16.

[48] Poole, and Reed, 1962.

[49] Yadin, 1983.

[50] Rabin et al. 2010.

Fig. 9: *Tucherbuch* (Nuremberg), detail. Posnjakite was used for the coloration of the bluish-green pleats; the green areas were colorized with malachite.

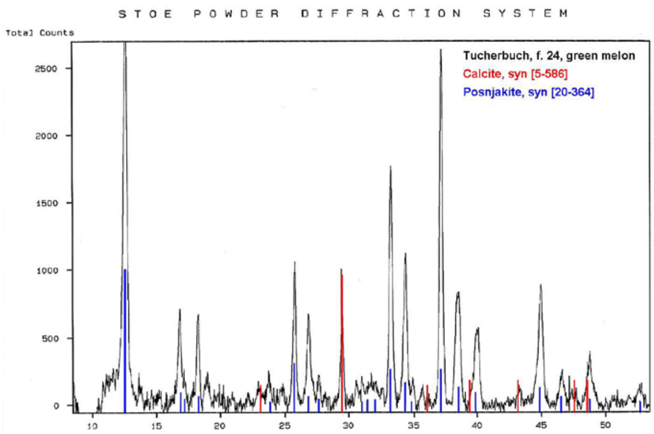

Fig. 10: X-ray diffractogram of a green area: posnjakite is mixed with calcite.

and potassium, suggesting that the surface layer at least partly consisted of alum $KAl(SO_4)_2$ x 12 H_2O and a calcium-containing substance. The spectrum of the collagenous layer contained very little inorganic substance, suggesting that the finishing process of the parchment preparation included treatment with a dressing in the form of a paste rather than a powder. Parchments processed with dry chalk finishing would have displayed much deeper penetration of calcite particles into the fibre structure. Quantitative analysis indicated that potassium, sulphur, and aluminium were by far more abundant on the parchment of the main part of the scroll. ATR-FTIR and Raman spectroscopy helped us identify the inorganic compounds in the top layer of the main part as alum and gypsum ($CaSO_4$ x 2 H_20). Thus we may conclude that the skin was first tawed with alum and then dressed with gypsum to prepare the surface for writing, which was a common practice in Antiquity. The results of the top layer of col. V did not provide conclusive evidence a alum and gypsum presence. Instead, vibration spectra displayed a calcite ($CaCO_3$) peak. In this case we cannot exclude skin tawing in Antiquity, since water-soluble alum could have been easily removed during a rather aggressive conservational treatment of the fragments studied. The presence of calcite, however, proves unequivocally that the skins of the main scroll and the repair sheet were dressed differently. In the latter case, a chalk-containing paste was used. The use of paste dressing in either case explains why a transfer of writing text occurred indiscriminately in both parts of the scroll.

In addition, we found an interesting fingerprint on the first sheet and outer parts of the *Temple Scroll*: bat guano abundant in Cave 11 left a considerable trace on all the objects discovered in this cave. Figure 8 shows Raman spectra recorded on the main scroll column LII, on the edge part of the main scroll, on column V, and sediments from Cave 11 in Qumran (from top to bottom). The main scroll was treated with alum and gypsum in Antiquity, whereas the first columns bear calcite instead. The nitrate peak appears only on column V and the edges of the main scroll. We believe that ammonia, whose stinging odour was noticed in the cave, could not penetrate the inner parts of the tightly rolled scroll. Hence only the outer parts of the scroll and textiles carry nitrate traces, which are also found in the sediments (bottom curve). One should note that the doublet at the position of the carbonate does not correspond to calcite but to aragonite and dolomite, which are characteristic of the natural caves.

A rare copper green pigment in an illuminated manuscript

The *Tucherbuch* (Nuremberg) is characterized by elaborate and grand book illuminations containing a variety of different dyes and pigments. The genealogy of the Tucher family was commissioned in 1590 and completed in 1596. The manuscript contains a personal register of all family members up to 1618 and detailed prefaces concerning each family member, followed by a short biography including birth, profession, wedding, and death. Each biography is combined with a precious miniature. Overall, the manuscript contains 95 miniatures and overshadows all other genealogies originated in Nuremberg. The miniatures were designed and partly executed by Jost Amman. After Amman's death, the illuminations were finished by Georg Hertz.

XRD in transmission mode is a convenient method for investigating colour inks used in book illumination. The whole sample, which means parchment or paper as well as painting layers, is virtually transparent for the X-ray beam. Furthermore, the organic matrix has no disturbing effect on the XRD results.[51]

In the *Tucherbuch*, the rare pigment posnjakite was used for the coloration of the bluish-green areas. Figure 9 provides an example of the appearance. When posnjakite was used, it was not mixed with other colouring pigments such as malachite, but with lead white or calcite (fig. 10). Furthermore, figure 9 makes it clear that this pigment was used in a very distinct way. It was identified in seven of 33 investigated miniatures, whereas malachite was identified in only two miniatures. Some single proofs of wroewolfeite or chalcocyanite combined with posnjakite allow the assumption that the mineral was produced artificially for use as a pigment.

[51] The experiments were carried out with a STOE STADIP diffractometer (STOE & Cie GmbH, Darmstadt, Germany). The modular system offered the possibility of transmission measurements by use of a special stage. With a combination of a focused Kα1 incident beam (copper target) from a Germanium monochromator with a transmission goniometer and a linear position-sensitive detector (PSD), the equipment provides data of sufficient angular resolution and reliable intensities within reasonable acquisition times.

5. Conclusion

This paper presents a short overview of the use of different methods for the analyses of manuscripts written or drawn with different inks. The determination of inorganic components by means of XRF provides elemental composition fingerprints that allow a differentiation between materials that do not differ on visual examination.

Additionally, vibration spectroscopy allows the identification of the different materials by determining their chemical composition.

The resulting classification of different writing supports and materials allows us to address questions concerning the origin and genesis of manuscripts or the ascription of later amendments or corrections.

Further developments such as combining micro-spectroscopy with fast imaging at a high resolution would provide information on all the materials simultaneously, including degradation patterns of each individual material. Rapid technologic progress raises hope that new instruments will combine high functionality, transportability, and ease of operation.

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