Studies in Manuscript Cultures (SMC)

Ed. by Michael Friedrich, Harunaga Isaacson, and Jörg B. Quenzer

Writing is one of the most important cultural techniques, and writing has been handwriting throughout the greater part of human history, in some places even until very recently. Manuscripts are usually studied primarily for their contents, that is, for the texts, images and notation they carry, but they are also unique artefacts, the study of which can reveal how they were produced and used. The social and cultural history of manuscripts allows for ‘grounding’ the history of human knowledge and knowledge practices in material evidence in ways largely unexplored by traditional scholarship. With very few exceptions, the history of the handwritten book is usually taken to be the prehistory of the (printed Western) book, thus not only denying manuscripts their distinct status as carrier medium, but also neglecting the rich heritage of Asian and African manuscript cultures from which, according to conservative estimates, more than ten million specimens survive until today.

The series Studies in Manuscript Cultures (SMC) is designed to publish monographs and collective volumes contributing to the emerging field of manuscript studies (or manuscriptology) including disciplines such as philology, palaeography, codicology, art history, and material analysis. SMC encourages comparative study and contributes to a historical and systematic survey of manuscript cultures.

Publisher: de Gruyter, Berlin

From volume 4 onwards all volumes are available as open access books on the De Gruyter website:
https://www.degruyter.com/view/j/45146
http://www.manuscript-cultures.uni-hamburg.de/Studies_e.html

Just published

Archives are considered to be collections of administrative, legal, commercial and other records or the actual place where they are located. They have become ubiquitous in the modern world, but emerged not much later than the invention of writing. Following Foucault, who first used the word archive in a metaphorical sense as ‘the general system of the formation and transformation of statements’ in his ‘Archaeology of Knowledge’ (1969), postmodern theorists have tried to exploit the potential of this concept and initiated the ‘archival turn’. In recent years, however, archives have attracted the attention of anthropologists and historians of different denominations regarding them as historical objects and ‘grounding’ them again in real institutions. The papers in this volume explore the complex topic of the archive in a historical, systematic and comparative context and view it in the broader context of manuscript cultures by addressing questions like how, by whom and for which purpose were archival records produced, and if they differ from literary manuscripts regarding materials, formats, and producers (scribes).
CONTENTS

2    Editorial
    by Christian Brockmann, Oliver Hahn, Volker Märgner, Ira Rabin, and H. Siegfried Stiehl

ARTICLES

3    Hard Science and History
    by Marina Bicchieri

17   Ink Study of Herculaneum Papyri
    by Ana S. Leal, Silvia Romano, and Vito Mocella

21   The ‘Decorative Style’ Group of Byzantine Manuscripts Seen with Different Eyes: Initial Explorations, Further Thoughts, Implications and New Avenues for Research
    by Marina Toumpouri

41   The Quest for the Mixed Inks
    by Claudia Colini, Oliver Hahn, Olivier Bonnerot, Simon Steger, Zina Cohen, Tea Ghigo, Thomas Christiansen, Marina Bicchieri, Paola Biocca, Myriam Krutzsch, and Ira Rabin

49   Ignatius of Loyola’s Exercitia Spiritualia: Spectroscopic Monitoring and Nanomaterials for an Integrated Conservation Methodology on Ink-degraded Manuscripts
    by Melania Zanetti, Alfonso Zoleo, Luca Nodari, and Maddalena Bronzato

63   Image Processing Software for the Recovery of Erased or Damaged Text
    by Keith T. Knox

73   High Performance Software in Multidimensional Reduction Methods for Image Processing with Application to Ancient Manuscripts
    by Corneliu T. C. Arsene, Stephen Church, and Mark Dickinson

97   Three Complementary Non-invasive Methods Applied to Historical Manuscripts
    by Bernadette Frühmann, Federica Cappa, Wilfried Vetter, and Manfred Schreiner

109  Palaeography and X-Ray Fluorescence Spectroscopy: Manuscript Production and Censorship of the Fifteenth Century German Manuscript, State and University Library Hamburg, Cod. germ. 1
    by Marco Heiles, Ira Rabin, and Oliver Hahn

133  Advanced Codicological Studies of Cod. germ. 6: Part 2 (Hamburg, Staats- und Universitätsbibliothek)
    by Mirjam Geissbühler, Georg Dietz, Oliver Hahn, and Ira Rabin

141  The Atri Fragment Revisited I: Multispectral Imaging and Ink Identification
    by Sebastian Bosch, Claudia Colini, Oliver Hahn, Andreas Janke, and Ivan Shevchuk

157  An Attempt at a Systematic Study of Inks from Coptic Manuscripts
    by Tea Ghigo, Olivier Bonnerot, Paola Buzi, Myriam Krutzsch, Oliver Hahn, and Ira Rabin

165  Contributors
In this article, we would like to share our observations concerning the inks produced by intentionally mixing soot or charcoal with tannin extracts or iron-gall ink. Aside from Zerdoun’s mention in her outstanding review of written sources, *Les encre noir au Moyen-Âge*¹, this ink category has received little if any attention from scholars and scientists. And yet, if analytically attested, the use of such inks could serve as an additional category to classify and distinguish the writing inks on the historical socio-geographic map of the writing inks we are trying to build.

In the collection of recipes from Arabic sources that one of us investigated, we found that explicit recipes for mixed inks constitute some 20% of the collection². It would be extremely interesting and important for our enterprise to obtain a chronological and geographic attribution of the recipes from the Orient, beyond those of Dioscorides³ and Philo of Byzantium⁴. However, the overall scarcity of copies per treatise and the young age of the manuscripts make it difficult for the current state of the art to understand when and where a certain formula was introduced and changes were made. In addition, we observed that the transmission of recipes from one treatise to another is massive, but at the same time extremely fluid, since small but mostly reasonable changes are introduced every time, often resulting in modifications to the formulas (concerning the quantities, ingredients, or technique employed). Although great respect was accorded to the authors, especially if they were eminent figures, their texts and words were not untouchable and unchangeable. This ‘active’ transmission⁵ suggests at the same time a living tradition with practical applications, as otherwise there wouldn’t be the need to change the content and the formulas, but only the form. For this reason, a more detailed study not only of the origin, but also of the transmission of these texts⁶ will contribute to establishing a chronology of the modifications of the single recipes, which will be useful when comparing with specific manuscripts.

Mixed inks appear also in the Jewish sources associated with the Jewish Diaspora in the Orient. The best-known among these recipes was suggested in the twelfth century by Maimonides, a Jewish philosopher from Spain and Egypt, for inscribing phylacteries.⁷ It is very similar to the one attributed to Ibn Muqla, a famous calligrapher from the Abbasid period.⁸ However, Maimonides argued against the practice of adding iron-gall ink to carbon, another popular mixed ink. It is also interesting to notice that none of the five Maimonides autographs we analyzed contained inks that followed his recipe. Analysis of the codices in the Jewish National Library in Jerusalem (Heb. 5703_2) and the Bodleian Library in Oxford (Huntington 80, fol. 165r, signature) revealed that these manuscripts were written using pure iron-gall inks. But the letter preserved in Cambridge University Library (T-S 12.192) was penned in carbon ink. Most interestingly, the manuscript containing ‘The guide for the perplexed’ (T-S 10 Ka 4.1) displayed both carbon and iron-gall ink on different pages and corrections both written by Maimonides himself.

These results correlate well with the study of the inks used in the legal documents found in the Cairo Genizah, which stated that both ink types were employed in mediaeval Fustat.⁹ In our study of the inks of the manuscripts produced in the Diaspora, we have found indication that Jews used the same

---

¹ Zerdoun 1983.
² Colini to be published in the PhD thesis 2018.
³ *Materia Medica* V.181; Zerdoun 1983, 80.
⁴ Zerdoun 1983, 92.
⁵ Meaning the copyist’s deliberate intervention in the text; Varvaro 1970, 87.
⁶ Few contributions started a research in this sense: Zakt 2011, Fani 2013, Raggetti 2016.
⁷ Zerdoun 1983, 111.
⁹ Cohen, PhD thesis to be published in 2019.
writing materials as their non-Jewish neighbors. Therefore, the Jewish records might be an excellent source for studies of the technology that corresponds to the place and time of the source. In this respect, it is interesting to compare the ink of Rashi (Rabbi Salomon ben Isaac), a Jewish author who lived in Northern France in the eleventh century, with the commentaries of Maimonides. In the Orient, Maimonides was familiar with the palette of all possible inks: carbon, plant, iron-gall, and mixtures of carbon inks with plant or iron-gall inks. In contrast, the arguments of Rashi allow us to conclude that mostly plant and maybe iron-gall ink were in use in northern Europe during the eleventh century. It is noteworthy that mixtures of carbon and iron-gall ink were found in some drawings of German artists in the fifteenth and sixteenth centuries.

The wealth of recipes for the black mixed inks in the Orient, on the one hand, and the absence of analytical evidence of their existence, on the other, raises two questions:

1. Is there a simple method for recognizing these inks?
2. Why would one use a mixture of two black inks?

Let us start by looking at the methods employed in the ink studies. Raman spectroscopy has been extensively used to identify materials such as pigments in paintings and archeological artefacts. Generally, Raman spectroscopy probes the change in the wavelength of light that occurs when a light beam interacts with molecular vibrations (Raman scattering). Reliable Raman identification of mediaeval black inks started to emerge during the past decade and shows that soot, logwood, and iron-gall inks have characteristic Raman spectra that provide a recognition pattern. Therefore, Raman spectroscopy presents the cleanest and the most straightforward method to identify carbon and iron-gall inks and is therefore well suited to document a mixture of both. In the example below, mixed carbon and iron-gall inks were found in addition to the pure iron-gall inks of the main text of a Syriac manuscript (a sacred text, fourteenth century). The amount of added carbon was variable: ink A in Fig.1 contains less carbon than ink B, so that the features related to iron-gall (blue curve) are more evident in spectrum A, whereas spectrum B look similar to the carbon ink (black). The Raman peak at about 577 cm\(^{-1}\) and the XRF control test on both inks confirmed the presence of iron in the ink.

Unfortunately, despite the recent development of portable Raman spectrometers, black ink analysis using Raman technique still often requires a bench instrument or the extraction of samples in addition to trained personnel. Furthermore, Raman measurements on plant inks, i.e., inks based on tannin but not containing metals, yield no conclusive spectra with lasers in the VIS wavelength range whereas better results can be obtained by exciting the sample with a laser in the near-infrared. In many cases strong fluorescence (= emission of light after excitation) of organic molecules considerably disturbs the spectrum. To overcome this difficulty, it has become customary to use Surface-Enhanced-Raman-Spectroscopy (SERS) in studies of modern paints and dyes. SERS is a powerful technique in which the Raman scattering of molecules is enhanced by several orders of magnitude (up to a factor of \(10^{11}\)) due to their adsorption by plasmonic metal surfaces (e.g. gold or silver nanoparticles) or nanostructures. The simultaneous quenching of fluorescence allows measurements of strongly

---

10 Rabin et al. 2014
12 Lee et al. 2008.
15 Pozzi and Leona 2015.
16 Schlücker 2014; Pozzi and Leona 2015; Lee and Meisel 1982.
fluorescent materials as well. Many different procedures for synthesizing and modifying SERS substrates have been described to optimize SERS for different kinds of materials.\textsuperscript{17} SERS is a micro-invasive technique that, depending on the selected substrate, requires a certain amount of sample. Attempts have been made, for cultural heritage purposes, to reduce the sample amount to a minimum and to optimize it.\textsuperscript{18} In the case of tannin and iron gall ink, our first SERS tryouts yielded positive results. However, an optimized substrate and procedure for SERS on tannins and mixed inks need still to be defined. This means that, for the time being, we cannot use Raman technique to detect mixed inks on a large scale in situ and have to find a simpler way to conduct a primary classification similar to the one adopted in our ink test protocol.\textsuperscript{19}

In short, we use the comparison of the images recorded under white and near-infrared light to quickly classify the inks by type (carbon, plant, or iron-gall). The simplicity of the test encouraged many codicologists and paleographers to adopt our methodology and share with us the results of their own field studies. As a result, a considerable number of papyri from the turn of the era started undergoing routine reflectographic checks in various collections. The knowledge of the ink type helps select which inks to study more closely. In such cases, following the reflectographic screening, we perform X-ray fluorescence analysis (XRF) on selected inks to determine their elemental composition and, in the case of the iron-gall inks, their fingerprint.\textsuperscript{20} For the carbon inks, 

\textsuperscript{17} Pozzi and Leona 2015; Fan et al. 2011; Le Ru and Etchegoin 2009.

\textsuperscript{18} e.g. Pozzi and Leona 2015; Lofrumento et al. 2012; Gomez and Lazzari 2014.

\textsuperscript{19} e.g. Ghigo et al., present volume.

\textsuperscript{20} Hahn et al. 2004; Rabin 2014.
we have used XRF to identify trace elements that could indicate characteristic contaminations. It was XRF analysis of the carbon inks that led to a successful identification of metals whose amounts hinted at intentional admixture rather than unintentional contamination.\textsuperscript{21} In general, NIR reflectography is a quick and perfect method when dealing with an ink of a pure class, since carbon, plant, and iron-gall inks have very distinct optical properties. However, no unequivocal identification of mixed inks seems possible, since a considerable amount of carbon ink should mask the presence of any other component when illuminated with NIR light. On the other hand, tannin’s property of quenching fluorescence and enhancing the contrast between a fluorescing background and the text makes UV illumination highly effective in recovering lost writing done in iron-gall ink. Since tannin ink contains tannins, it stays in it even if the text is removed from the surface. Therefore, the contrast enhancement achieved by UV light illumination has been widely used to recover lost writing done in iron-gall ink.\textsuperscript{22}

In the example below, we analyzed the ink in the Sahidic papyrus fragment from Cambridge University Library (Ms. Thompson HT 110.1). In the top part of Fig. 2, we present the individual intensities of the elemental components resulting from a line scan across a heterogeneously degraded letter shown in the three bottom images. Note that the curve form of each element in the graphics follows that of iron, the main component of iron-gall ink, revealing the composition of the ink. Iron, copper, and zinc represent the vitriol used in the recipe, sulfur indicates that the ink indeed contained vitriol, i.e., a mixture of metallic sulfates, and potassium is strongly associated with the tannins and gum arabic that was traditionally used as a binder. The varying thickness and degradation of the ink are reflected by the variability of the signal for iron and its satellites within the inked area. The changes in the opacity of the iron-gall inks can be seen in the bottom part of the same picture. Here the left, middle, and right images present micrographs taken under white, near-infrared (NIR), and ultraviolet (UV) light, respectively. The text penned in iron-gall ink that is perfectly visible under normal illumination becomes almost transparent when illuminated with NIR light, but regains its opacity under UV light. The latter picture shows the presence of tannin in the iron-gall ink.

We hope that tannins or the carbon/plant or carbon/iron-gall inks would be also detectable if they suffered damage and have been partially removed from the surface. Meanwhile, we started employing XRF for a routine screening of carbon inks to identify metals in metal-containing carbon inks. The fragment below is part of a demotic text concerning dream divination. It comes from Tebtynis and dates to c. 100–200 CE. It derives from clandestine excavations and was acquired by the Carlsberg Foundation on the antiquities markets of Cairo sometime between 1931 and 1938.\textsuperscript{23}

The images in the top row of Fig. 3 show that there is no change in the opacity and intensity of the black color when the illumination is switched to NIR, proving the carboniferous nature of the ink. At the same time, the images in the bottom row show that the distributions of Ca and Fe correlate with the text, suggesting their presence in the ink. Strictly speaking, the presence of iron can’t be considered unequivocal proof of iron-gall ink, since iron could have wandered into the ink as unintentional contamination. Here, however, ink contains also the element Ca, which has been detected many times in iron-gall inks. Therefore, we can assume here that we are dealing here with a mixed carbon and iron-gall ink, even though no Raman test for an unequivocal identification of iron-gall ink has been conducted.

The very early date of this ink correlates well with the detection of iron-gall ink coeval with the Coptic codex.\textsuperscript{24} Therefore, we can assume that iron-gall ink was indeed in use in Egypt as early as the third century CE. However, it is not clear whether the production technology was always based on vitriol. In our example above, no copper, zinc, or other common iron satellites from vitriol could be detected. It is possible that metallic iron from nails was used: when soaked for a prolonged time in vinegar, the oxidation will result in the production of iron ions ready to react with tannins. We find that some of the oldest recipes in the Arabic collection prescribe using iron filings with or without acid.\textsuperscript{25}

After establishing that the scarcity of analytical evidence results from the difficulties of unequivocal identification, we are left with a historical question of the emergence of the

\textsuperscript{21} Nir-El and Broshi 1996; Brun et al., 2016; Christiansen et al., 2017; Rabin 2017.

\textsuperscript{22} Rabin et al. 2015.

\textsuperscript{23} Christiansen et al. 2017.

\textsuperscript{24} Ghigo et al., present volume.

mixed inks. The very early appearance of iron-gall inks and a high number of papyri inscribed with this ink overturn the generally accepted opinion that iron-gall ink accompanied the change of the substrate from papyrus to skin-based writing surfaces. Moreover, thousands of the Dead Sea Scroll fragments inscribed with carbon inks speak strongly against this theory.

We believe that the explanation can be found in the entry 'Atramentum' of the very first encyclopedia preserved in the Western world: *Natural History* of Pliny (35.25). He recounts a number of ways to obtain black writing inks, where salts or dried leaves could be used in addition to soot. In other words, in the late Roman period, inks produced according to different recipes were in use. Given that Pliny mentions blue vitriol (copper sulfate) as ‘shoemaker black’ (34.123), it is rather obvious that the Romans had not yet arrived

---

26 Diringer 1982, 551.
at the understanding that only green vitriol (iron sulfate) reacts with tannins to produce black substance. It is highly probable that early iron-gall ink was brown like tannin inks, so that carbon was added to obtain black ink. Alternatively, expensive carbon ink could have been adulterated by adding various dark liquids.

In any case, once we are aware of the existence of the mixed inks, we will be able to develop a suitable method for detecting them.

ACKNOWLEDGEMENT

A considerable part of the research presented in this article was carried out in the context of the SFB 950 ‘Manuskriptkulturen in Asien, Afrika und Europa’ funded by the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG) and within the scope of the Centre for the Study of Manuscript Cultures (CSMC).

We would like to acknowledge the help of the personnel of the museums, archives and libraries who permitted us access and supported our work. Our special thanks go to the Cambridge University Library: to the scholars, Ben Outhwaite and Yasmin Faghihi, the staff of the conservation department, especially Anna Johnson and Jim Bloxam for preparing the documents and the literature, and every member of the digital contents unit, especially to Blazej Mikula and Maciej Pawlikowski for hosting us and taking care of the equipment transport.
REFERENCES


Colini C., *From Recipes to Material Analysis: the Arabic Tradition of Black Inks and Paper Coatings (9th to 20th century)* (PhD thesis)

Cohen Z., *Composition Analysis of Writing Materials in Geniza Fragments* (PhD thesis)


**Sources**


Studies in Manuscript Cultures (SMC)

Ed. by Michael Friedrich, Harunaga Isaacson, and Jörg B. Quenzer

Writing is one of the most important cultural techniques, and writing has been handwriting throughout the greater part of human history, in some places even until very recently. Manuscripts are usually studied primarily for their contents, that is, for the texts, images and notation they carry, but they are also unique artefacts, the study of which can reveal how they were produced and used. The social and cultural history of manuscripts allows for ‘grounding’ the history of human knowledge and knowledge practices in material evidence in ways largely unexplored by traditional scholarship.

With very few exceptions, the history of the handwritten book is usually taken to be the prehistory of the (printed Western) book, thus not only denying manuscripts their distinct status as carrier medium, but also neglecting the rich heritage of Asian and African manuscript cultures from which, according to conservative estimates, more than ten million specimens survive until today.

The series Studies in Manuscript Cultures (SMC) is designed to publish monographs and collective volumes contributing to the emerging field of manuscript studies (or manuscriptology) including disciplines such as philology, palaeography, codicology, art history, and material analysis. SMC encourages comparative study and contributes to a historical and systematic survey of manuscript cultures.

Publisher: de Gruyter, Berlin

From volume 4 onwards all volumes are available as open access books on the De Gruyter website:
https://www.degruyter.com/view/journals/43546
http://www.manuscript-cultures.uni-hamburg.de/Studies_e.html

Archives are considered to be collections of administrative, legal, commercial and other records or the actual place where they are located. They have become ubiquitous in the modern world, but emerged not much later than the invention of writing. Following Foucault, who first used the word archive in a metaphorical sense as ‘the general system of the formation and transformation of statements’ in his ‘Archaeology of Knowledge’ (1969), postmodern theorists have tried to exploit the potential of this concept and initiated the ‘archival turn’. In recent years, however, archives have attracted the attention of anthropologists and historians of different denominations regarding them as historical objects and ‘grounding’ them again in real institutions. The papers in this volume explore the complex topic of the archive in a historical, systematic and comparative context and view it in the broader context of manuscript cultures by addressing questions like how, by whom and for which purpose were archival records produced, and if they differ from literary manuscripts regarding materials, formats, and producers (scribes).