IRA RABIN AND **MARCELLO BINETTI**

NIR REFLECTOGRAPHY REVEALS INK TYPE: PILOT STUDY OF 12 ARMENIAN MSS OF THE STAATSBIBLIOTHEK ZU BERLIN.

Introduction

For some time now, our group has been focusing on the history of the writing inks in Europe and Middle East. This work is partly inspired by my participation in the COMSt and the reviews dedicated to medieval inks in different scribal practices. (Bausi et al. 2014, Zerdoun 1983, Schopen 2004, Schreiner & Oltrogge 2011). In particular, the exhaustive research on the early written sources that Zerdoun presented allowed her to conclude that only experimental studies could produce a record of the inexorable expansion of iron-gall-ink. Our study of the corrosive ink in the Genesis Apocryphon scroll, which turned out to be carbon ink with a substantial amount of copper in accordance with Dioscurides recipe from the Antiquity, served as a second strong motivation to build a bridge from the carbon inks of Antiquity to the iron-gall-inks that became the most popular writing media far beyond Europe from 12th century AD. At the same time, carbon ink preserved its importance at least in the Middle East.

Unfortunately, a search through the literature shows that manuscript studies do not include determination of the ink type. Admittedly, the spread of the non-destructive techniques among the conservation labs throughout the world resulted in exhaustive studies of some illuminated or otherwise singularly important manuscripts. We anticipate, however that standard determination of the inks type will expand codicology and lead to much better understanding of the development of the practices of the individual cultures and trans-cultural relationships.

Let us turn now to the different type of inks that we encounter in the Middle Ages and to their properties that will allow us to differentiate between them. Unfortunately, their “color” (black, gray or brown) results from the combination of such factors as manufacture receipt, corrosion and aging and cannot be used as a criterion for distinction.

Soot, plant, and iron-gall inks form different typological classes of historical black writing materials used in manuscript production. Soot ink is a fine dispersion of carbon pigments in a water-soluble binding agent;

plant-based ink is a solution of the tannins extracted from tree barks; iron-gall ink, produced by mixing iron (II) sulphate with a tannin extract from gall nuts, presents a boundary case between soot and plant ink – a water soluble preliminary stage (similar to inks from the second group) oxidizes and evolves into a black, insoluble material (similar to the carbon pigments of the first group) when the writing is exposed to air. Each ink class has distinct properties that would readily permit their easy differentiation, if only the inks used throughout history always belonged to just one of these classes. Carbon inks do not penetrate the substrate (whether papyrus, parchment or paper) and stay well localized on the surface. In contrast, plant inks and iron-gall inks are absorbed by the substrate, and the degree of their absorption depends to a great extent on the nature of the substrate.

Iron-gall inks are best studied by means of the X-ray fluorescence (XRF) technique. Natural vitriol, the main component of the historical iron-gall inks, consists of a mixture of metal sulfates (iron sulfate, copper sulfate, manganese sulfate, and zinc sulfate) with relative weight contributions characteristic of the vitriol source or purification procedure (Krekel 1999). This very property of the iron-gall inks can be used to compare them and to distinguish among them. Specifically, the development of the fingerprint model based on the qualitative and quantitative detection of inorganic components of iron-gall inks allows their reliable classification (Hahn et al. 2004). Furthermore, physico-chemical studies of the inks could lead to establishing of the production sites of non-provenanced manuscripts. (Khajakyan 1984).

In addition to inks of pure classes, mixed inks containing components of different classes are well known. In such cases, the ink usually has a type-defining component and "picture smearing" additives. In this respect, a recipe from Dioscurides is remarkable among ancient Roman recipes for the production of soot inks. Along with soot ("condensed smoke") and gum, the recipe mentions chalcanthon, a copper compound. Mediaeval sources in Arabic report frequent use of inks containing soot and iron-gall ink. Transition from the purely plant (that is, tannin) inks to the iron-gall type presents an especially difficult case since a small addition of vitriol to a tannin ink would produce a preliminary stage of an iron-gall ink. Moreover, metals like iron and copper can occasionally be present in the tannin inks due to the water or tools used in the production process. Though a full elucidation of the composition of such inks requires the combination of XRF, Raman and IR reflectography (IRR) (Rabin et al. 2012), the determination of the main components can be accomplished using their optical properties alone, that is, their opacity in the spectral range 700-1200 nm.

The Jewish Diaspora in Europe and Middle East led to the production of distinct geo-cultural traditions that could be roughly classified as Ashkenazi, Sephardic, Italian, Byzantine, Oriental and Yemeni according to the areas of residence. Our recent works on Hebrew manuscripts indicate that the Jewish scribes were using local writing materials to produce their manuscripts. Though no systematic study of inks in the medieval Hebrew manuscripts has been yet conducted our results show that iron-gall inks were found indiscriminately in European and extra-European manuscripts. (Rabin 2014)

Recently, we started testing inks of Armenian medieval manuscripts to assess the types of inks used at different production sites. Most of the codices under investigation showed the characteristic deep black colour commonly associated with carbon inks, seemingly in contrast with the wealth of Armenian recipes for iron-gall inks (Galfayan 1975). Indeed we will show below that conclusions based on the colour might be erroneous. In this contribution we present results obtained by NIR reflectography alone. We plan to add XRF studies in the very near future. We also hope that based on our work, the classification of the ink types followed by the determination of their composition will become standard in the codicological description of manuscripts.

Experimental

Optical properties reflect the interaction of a material with light from ultraviolet (UV), visible (VIS), and infrared (IR) regions of the electromagnetic spectrum. IR reflectography has been traditionally used to study soot-based pigments or carbon inks: the colour of soot inks is independent of the illumination wavelength in the range 300–1,700 nm; plant inks lose opacity between 750 and 1,000 nm, whereas iron-gall inks become transparent only at a wavelength > 1,000 nm. Similarly, multispectral imaging for the visualization of palimpsests can allow one to differentiate between soot-based and tannin-based inks, since only the latter become transparent in the infrared region of the spectrum. A conventional multispectral imaging set-up employs LED illumination with up to thirteen different wavelengths ranging from UV to near IR region (Christens-Barry et al. 2011). But to identify the ink types a simplified, 2-wavelength reflectography is sufficient since our main goal is to investigate the opacity in the spectral range 700–1000 nm. Our hand-held USB microscope (Dino-Lite AD413T-I2V) is equipped with a visible and a 940 nm light source.

Results and discussion

For our analysis in the Staatsbibliothek zu Berlin we have chosen a set of 12 manuscripts from 14th and 15th centuries.

List of the manuscripts investigated in this study.

Call number	Date	Place of origin
Phillipps 1398	1317	Ancona
Hs. or. 10910	1336	Vansee
Ms. or. oct. 279	1337	Syownik
Minutoli 287	1358	Krim
Ms. or. quart. 304	ca. 1353	
Petermann I 35	1361	Berg Sinea
Ms. or. quart. 381	1364	
Ms. or. oct. 1924	1451	Syounik
Minutoli 291	1450	Vansee
Ms. or. oct. 167	1447	Ayrivank'
Minutoli 285	1432	Karaman?
Petermann I 138	15th century	

We will start with a very simple case: the identification of the ink found in Phillipps 1398, a manuscript produced in Italy. The inks are of a characteristic dark brown colour that immediately allows us to exclude the carbon ink type. Fig 1a. presents a micrograph with 50 times magnification of a portion of the text written on the hair side of the parchment. Already the heterogeneous texture of the ink strongly suggests that we deal here with iron-gall-ink. The final proof is delivered by the micrograph in Fig. 1b: under illumination at 940nm the inks loses its intensity. Note that the central letter becomes almost transparent. The heterogeneous texture of the ink, its present colour and its response to the near infrared light indicate iron-gall-ink in an advanced stage of degradation.

Iron-gall-inks commonly have different appearance on the hair and flesh side of the parchment. The characteristic flaking off often observed on the flesh side can also help in determination of the ink type. Let us have a look at the flesh side of the same folio (Fig.2). Similarly to the previous figure, the micrograph on the left is taken in visible light, whereas the right image was shot at 940 nm.

First of all, the colour of the inks seems to be of a considerably lighter shade of brown (Fig. 2a). Some of the ink disappeared leaving blank parchment behind. In the corresponding NIR-micrograph, we see now only a shadow of the ink that turned almost transparent. However, the fact that the ink is still discernible proves beyond doubt the ink type, i.e. iron gall.

Let us turn now to a more complicated case: the inks of a deep black colour we found on the majority of the manuscripts tested in this work.

Here, a cursory glance might suggest that the inks are of a carbon type (Fig. 3a). However, a close inspection under microscope reveals ink browning, especially on the borders of the letters. The brown spots show the onset of the ink deterioration and serve as an indication of the ink type. Investigation of the same text portion under NIR (Fig. 3b) displays a variable transparency that cannot be detected in the visible light. Here, the ink almost disappears also at the locations where no apparent ink deterioration is observed under illumination with white light. As mentioned before, carbon ink would stay equally opaque throughout the range probed here.

In general it is advisable to check different letters under magnifycation since iron-gall-inks are prone to deterioration that does not occur homogeneously.

Conclusions

With this study we illustrate the possibility to classify the ink types present in ancient manuscripts using portable USB-microscope. Such investigations conducted at the manuscript storage site could be entered in the catalogues. In unclear cases other mobile non-destructive techniques (e.g. XRF) could be also employed onsite. The material information gathered with such studies is an important complement to the standard codicological analysis of the manuscripts.

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Իռա Ռաբին, Մարչելլո Բինետտի

Թանաքի տիպի բացահայտումը NIR ռեֆլեկտոգրաֆիայի օգնությամբ. Բեռլինի Պետական գրադարանի 12 հայերեն ձեռագրի փորձնական ուսումնասիրություն

Ներկայացնում ենք 12 հայերեն ձեռագրի թանաքների փորձնական ուսումնասիրությունը։ Ցույց ենք տալիս հին ձեռագրերում առկա թանաքի տիպերի դասակարգման հնարավորությունը շարժական եռագույն USB-*մանրադիտակի օգնությամբ։ Ձեռագրապահոցներում անցկացրած հետազոտության արդյունքում բացահայտված թանաքի տիպերի մասին տեղեկությունները կարելի է ներմուծել ձեռագրացուցակներ։ Բարդ դեպքերում տեղում կիրառելի են նաև այլ շարժական և ձեռագրերը չվնասող տեխնոլոգիաներ (օրինակ,* XRF)։ *Նման ուսումնասիրությամբ ստացված նյութական ինֆորմացիան սովորական ձեռագրագիտական վերլուծության կարևոր լրացում է։*