Non-destructive analysis of black inks in medieval monastery manuscripts of Moldavia (Romania)

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Abstract:
In Moldova (Romania), many monastic collections of valuable medieval manuscripts are being preserved, as a result of the long term efforts of the local monks. Today, monasteries such as Sucevita, Dragomirna, Putna, Neamt, Secu and others have medieval manuscripts of inestimable value. The article entitled „Non-destructive analysis of black inks in medieval monastery manuscripts of Moldova (Romania)" aims to identify the black inks of some medieval manuscripts of Moldavian region, in order to initiate a database of inks used in this area. The scientific analysis of manuscripts, using non-destructive methods, is a constant concern of the cultural heritage conservators and restorers, offering information about constitutive materials of manuscripts and their preservation state.

Keywords*: non-destructive analysis, manuscript, black ink, carbon ink, metal gall ink*

1. Introduction

Slavic-Romanian and Romanian-Cyrillic writings and manuscripts most often used black ink. In some manuscripts from the 18th-19th centuries are mentioned several recipes for inks preparation. Ink could be of plant origin, prepared from different plants, from soot, by combining with other substances or from different ferrous substances, obtaining iron gall ink. In this context, it should be noted that the inks in Valahia and Moldova were of superior quality to those in Transylvania (Dragnev 2003: 76).

Through ages the monasteries were truly cultural centers where thousands of documents and books were copied, hand-written or typed.

The Scriptoriums in Moldavian monasteries were the main centers for copying religious manuscripts. In Moldova, many monastic collections of valuable medieval manuscripts are being preserved, as a result of the long term efforts of the local monks. Today, monasteries such as Sucevita, Dragomirna, Putna, Neamt, Secu and others have medieval manuscripts of inestimable value.

At this moment, the information referring to the paper support document research aren't limited only to a historical analysis, but is essential needed a deeper knowledge about the material components, theirs' properties and alterations through time, in order to set a correct diagnosis and use the efficient conservation and restauration treatments.

The scientific analysis of manuscripts, using non-destructive methods, is a constant concern of the cultural heritage conservators and restorers, offering information about constitutive materials of manuscripts, their preservation state and efficiency of conservation treatments.

X-Ray Diffraction (XRD) technique and Fourier Transform Infrared (FTIR) spectroscopy, along with IBA techniques, can be considered complementary: some of them give information at an elemental level (PIXE and RBS), while others detect the presence of compounds or molecular structure (XRD and FTIR respectively) (Figueiredo Vigas 2014: 10).

The non-destructive analysis respect the physical integrity of the art object; usually this eliminate completely sampling or limits it to very small amounts of material. It is considered that among the truly non-destructive methods are the spectroscopies based on UV, Vis and IR radiations and the X-ray based methods (Janssens, Van Grieken 2004: 2).

The identification of the metal gall ink or the organic ink through FTIR spectroscopy one appears to be very difficult due the fact that the cellulose absorption bands covers the other ink components absorption bands (Neevel 2000: 125-134).

New approaches (Ursescu, Mureșan, Ciovică 2012: 3-14) affirm that using color measurements referenced according to the CIE system, allowed a fast, non-destructive and quite accurate identification of the main gall ink classes iron gall inks, copper gall inks, incomplete inks, and also for the estimation of the degradation processes in historical papers.

Scientific investigations of medieval ink include the following non-destructive analytical methods: Particle Induced X-ray Emission (PIXE) and X-ray Fluorescence (XRF).

PIXE is an Ion Beam Analysis (IBA) technique that allows the precisely identification of the inks on paper and the study of the interaction between inks and papers. Previous researches (Remazeilles and all, 2001: 681-687; Viegas and all 2013: 593-602) on iron gall inks showed that PIXE technique permits to evaluate the migration of some elements, such as sulphur, iron and calcium around inscriptions, to identify different inks in the same document or different paper manufacture techniques.

On the other hand, X-ray Fluorescence is a non-destructive analysis technique that provides data on the elementary chemical composition of the materials. XRF allows ink characterization, setting up technical aspects and chronological classification of different inks used.

Previous our researches (N. Melniciuc Puică, E. Ardelean, N. Vornicu 2013: 75-87) are focused on composition of red inks in some illuminated manuscripts of Moldavia book deposits, from 16 and 19 century. It was made qualitative and quantitative investigations, using micro-X-ray fluorescence analysis, and the presence of cinnabar red in studied samples was demonstrated.

Observing the performance of X-ray Fluorescence analysis, the ability of scanning large areas and the absence of collection of samples, this study aims to identify the black inks of some medieval manuscripts of Moldavian region, in order to initiate a database of inks used in this area.

2. Theoretical Part

The most important writing materials of the ancient manuscripts were carbon inks and metal gall inks. Along time, choosing a carbon or metal gall ink is related to the choice of the support (papyrus, parchment or paper), the properties of the surface support, and its ability to form the ink suspension. Although the term iron gall is the most commonly used term, the correct term is metal gall because the active principle of this type of inks is either copper gallotannate or iron gallotannate.

First known varieties of ink include Egyptian ink, long time considered made by burnt wood and oil mixed with a binder in aqueous media. Acacia tree provided an important ingredient as binder for ink (Arabic gum).

Recent researches (Christiansen and all 2017: 15346), using synchrotron-based micro X-ray fluorescence (XRF) and micro X-ray absorption near-edge structure spectroscopy (XANES) prove that black inks on old Egyptian papyri contains copper (from different mineral: azurite, cuprite and malachite).

Although most of the Dead Sea scrolls were written with carbon ink (powdered charcoal), other Hebrew manuscripts show some metallic content (Avrin 2001: 115).

Carbon inks

Carbon inks were known in the Roman world as "Antramentum scriptorum" or "Antramentum". Roman naturalist Pliny the Elder describes the carbon-based ink (without metal in composition) used at that time (Eichholz 2016: 3751-3754).

The Greek Philon from Byzantium (ca. 250-200 BC) describes the process of obtaining a „sympathetic ink": the invisible text with ink made from dried tree galls, would be discovered by passing a sponge dipped in a solution of copper sulphate above written papyrus. The remarkable fact is that he anticipated the ink that had been used by scribes into Middle Ages (Houston 2016).

Sometimes, modern research has found traces of different metals as component of antique inks. So, lead was found recently as constituent in the writing in carbonized Herculaneum scrolls (79 AD), by Multi-scale X-ray fluorescence micro-imaging, Monte Carlo quantification and X-ray absorption microspectroscopy experiments(Tack and all 2016: 20763).

In 5th century, with the more intense use of parchment as a writing aid, metallic blends have been used to improve ink adhesion to the new support. In the first half of Middle Ages carbon inks and metal gall inks coexists, but in the last half, iron gal inks are preferred.

Generally, carbon inks were made up of a black pigment (derived from calcined products, soot or carbon black) held in suspension in a binder. The binder could be sugar (Arabic gum, honey), protein (gelatine, egg white, skin or fish glue) or lipid (sizable oils like nut oil, olives oil). Sometimes perfume is added. The inks were kept in powder form, which at the time of use is dissolved in solvent - usually rain water.

Degradation of carbon inks is observed under exposure to oxidizing agents, and especially when different impurities are present.

Metal gall ink

The first recipe of metal gall ink appears only in the 11th century in the Arab world, but the oldest recipe in Europe dates back only from the 13th century. Metal gall inks were used endlessly until the second half of the nineteenth century, their place being taken by the synthetic inks developed since the discovery of the aniline by William Henry Perkin in 1856.

The hard removal of ink from old documents surface and the color strength are the main advantages of metal gall inks.

The main ingredients of medieval gall inks are: tannin acid (product from hydrolysis of gall nuts or other plant tannins), metal salt, a binder and water.

Tannins used in the production of medieval iron gall inks were hydrolysable tannins. In most ink recipes, tannins came from gall walnuts. Gall walnuts are formed by some insects who sting and lay eggs on the oaks trees leafs. Typically, the metal salt was iron sulphate or copper sulphate. In old recipes, metal salts are called copper-vitriol and salmartes. In ink gall composition were used the same types of binders as in carbon inks, but especially Arabic gum.

The colored complex is obtain by combining ferrous sulphate ($FeSO_4$) with gall acid ($C_6H_2(OH)_3COOH$). Due to the pale color when applied to the substrate, the color intensification was supplemented with various additives: Indigofera Tinctoria extract (for indigo color), Brazil wood (for red color), black carbon ink, etc. Other additives was ethylic alcohol, acetic acid or ground glass. (N. Melniciuc Puică, E. Ardelean 2010: 163-164).

Nowadays researches highlights the presence of many impurities in the gall ink composition, depending on different formulations.

In the Middle Ages, the iron gall ink was known as the "encaustum" ("burn in the interior" of Latin), a property characteristic of this type of ink. The corrosiveness of iron gall inks causes serious conservation documents problems.

By means of PIXE analysis previous researches were identified sulphur, calcium, iron etc. By XRD, gallic acid and glucose were identified in the tannin sources and different iron sulphate hydrate compounds in the vitriol. PIXE revealed traces of zinc in the inks, also identified in the Arabic gum (Figueiredo Vigas 2014: 60).

XRF offers new approaches for novel application and prospective for new research in art and archaeology; a recent study (Kumar 2017: 1-11) shows its importance for color, manuscripts, miniature, textiles and photographic materials.

Recent studies (Targowski and all 2015: S167-S177) demonstrated that of the two non-invasive techniques – macro-XRF and OCT – applied to the iron–gall ink lettering of a sixteenth-century manuscript on parchment for the first time, the macro-XRF technique seems to be much the more useful.

3. Experimental part

In order to establish the chemical composition of inks the investigation was performed on some documents with a portable spectrometer XRF type Innov-X Systems Alpha 4000 with iPAQ Pocket PC technology.

The excitation source is an X-ray tube, with W anode, maxim parameters being 35–40 μA. The fluorescence radiation was detected and analysed with Si PiN diode detector, with thermoelectric cooler.

The XRF analysis were carried out at the "Tabor" Research Center of the Moldavia and Bucovina Metropolitanate.

4. Results and discussions

We performed composition analysis of text portions from many manuscripts inscribed with black ink.

This paper presents the analysis of five manuscript (called diptych or pomelnic) dated to about 17^{th} century, belonging to Dragomirna Monastery from Suceava County (Moldavian region of Romania).

Other two studied manuscripts are dated to about 19^{th} century, belonging to Secu monastery, from Neamt County (Moldavia region of Romania). Because this manuscript is made of bundles of paper from different workshops, multiple pages analysis was performed.

The notation of the samples are presented in Table 1.

Sample notation	Sample description
1	Manuscript, 17th century, black pigment
2	Manuscript, 17th century, black pigment
3	Manuscript, 17th century, black pigment
4	Manuscript, 17th century, black pigment
5	Manuscript, 17th century, black pigment
6	Manuscript, 19th century, black pigment
7	Manuscript, 19th century, black pigment
8	Manuscript, 19th century, red pigment

Table 1. The notation of the analysed samples

The results were presented in Figures 1-7.

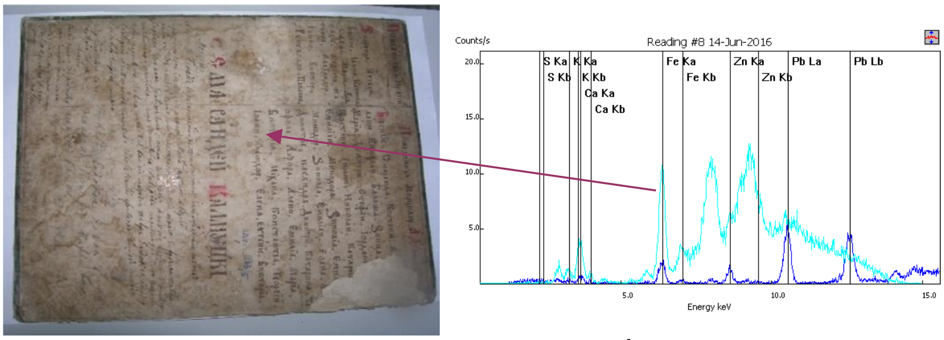

Figure 1. XRF spectrum of sample 1 (Manuscript, 17th century, black pigment)

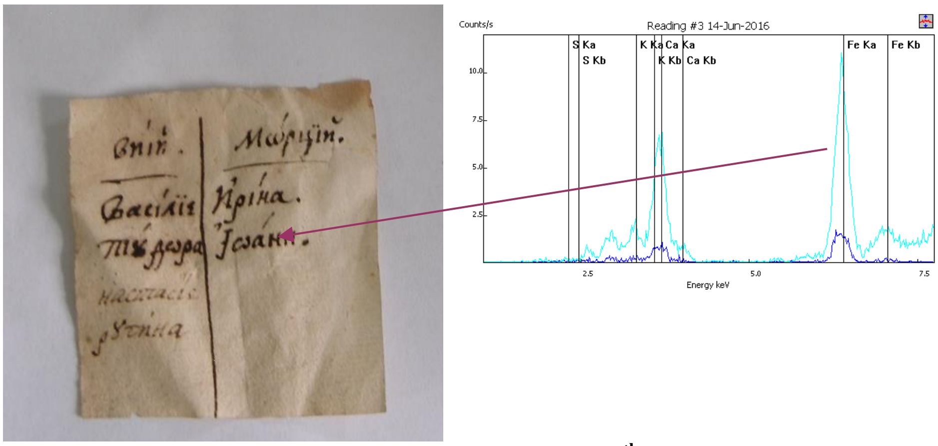

Figure 2. XRF spectrum of sample 2 (Manuscript, 17th century, black pigment)

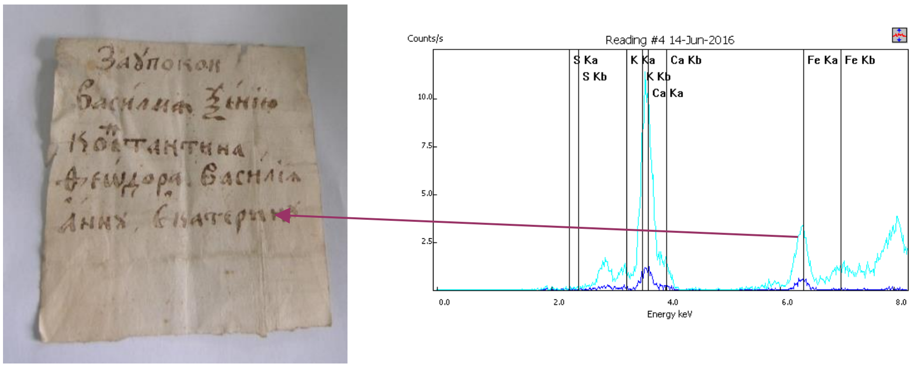

Figure 3. XRF spectrum of sample 3 (Manuscript, 17th century, black pigment)

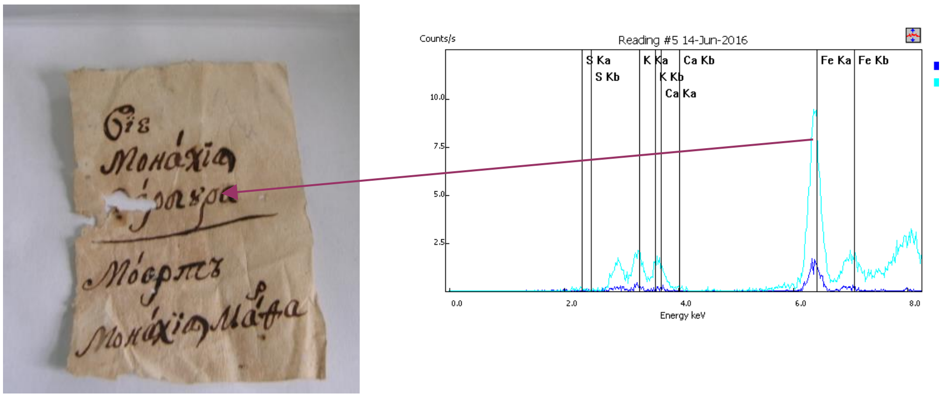

Figure 4. XRF spectrum of sample 4 (Manuscript, 17th century, black pigment)

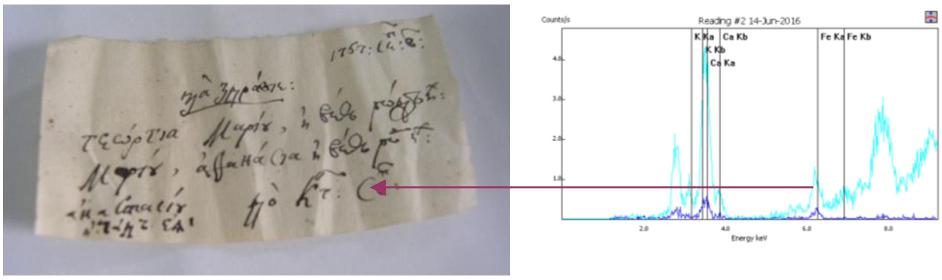

Figure 5. XRF spectrum of sample 5 (Manuscript, 17th century, black pigment)

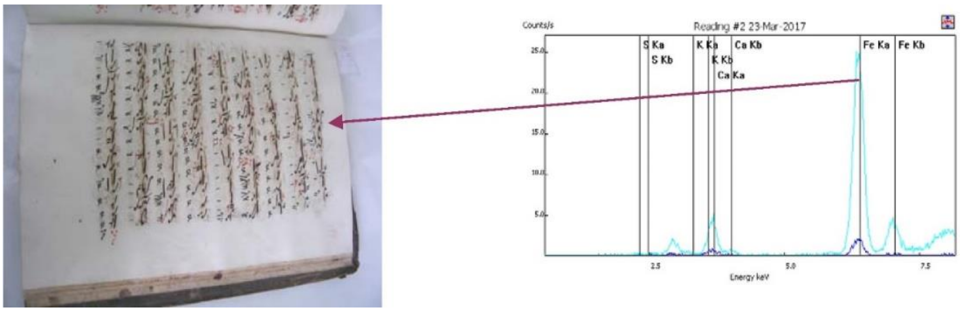

Figure 6. XRF spectrum of sample 6 (Manuscript, 19th century, p. 21, **black pigment)**

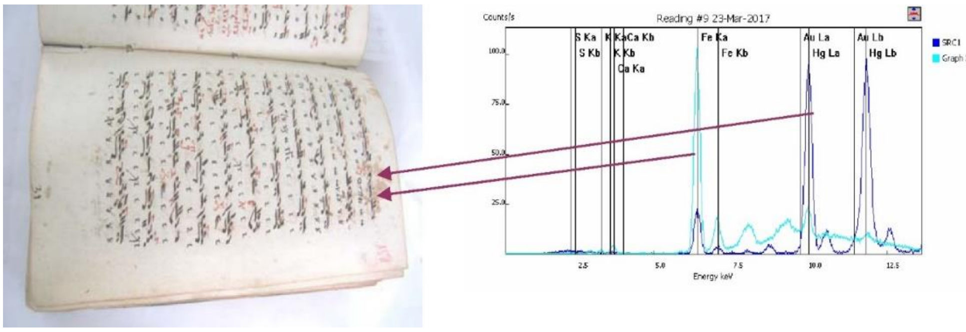

Figure 7. XRF spectrum of samples 7 and 8 (Manuscript, 19th century, p. 30, black and red pigment)

XRF spectrum (Figures 1-7) indicate the existence of Fe element in all black pigments used in writing of studied manuscripts. It was observed also high concentration on Fe element especially in black pigments sample 1, 2, 4, 6 and 7. It has been concluded that the documents in Moldova dated in Late Middle Ages may have been written with black iron gall ink.

In addition, XRF performed in the writing text from sample 8, at red decoration, shows the presence of Hg element as red cinnabar. As we have described in previous research, red cinnabar is present in many medieval decorated manuscripts in Moldova.

Present research brings novelty by the fact that at the level of the red decoration it was identified the gold element. That means the use of a red ink from 19th century manuscript made by a mixture of red cinnabar with gold, as a consequence of the importance that the writer gave to his work.

Conclusions

Today, monasteries such as Sucevita, Dragomirna, Putna, Neamt, Secu and others have medieval manuscripts of inestimable value.

Making a database of the type of ink used in Moldova (Romania) is an ambitious approach, quite difficult, but particularly useful for conservators and restorers.

For this purpose, the X-ray fluorescence analysis (XRF) is a very useful instrument. Information about chemical composition of inks, provenance of raw constituents, preservation state of old documents and efficiency of its conservation treatments can be obtained by XRF.

In this study, few medieval documents are analysed by XRF. It has been concluded that the documents in Moldova dated in Late Middle Ages may have been written with black iron gall ink. The use of a red ink from 19th century manuscript made by a mixture of red cinnabar with gold, is a consequence of the importance that the writer gave to his work.

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