IMPLEMENTATION OF METHODS FOR EXAMINATION OF PAPER-BASED LIBRARY MATERIALS

IMPLEMENTACIJA METODA ISPITIVANJA PAPIRNE KNJIŽNIČNE GRAĐE

Maja Kostadinovska
maja.kostadinovska@live.com

Zorica Jakovleska Spirovska
zorica@nubsk.edu.mk
National and University Library "St. Clement of Ohrid"– Skopje

UDK / UDC 025.85
UDK / UDC 027.54(457.7Skopje)
Stručni rad / Professional paper
Primljeno / Received: 5.9.2014.

Sažetak

Članak predstavlja neke konvencionalne i suvremene tehnike koje se koriste u ispitivanju papirne knjižnične građe, a u novije ih vrijeme provodi Laboratorij za konzervaciju i restauraciju Nacionalne i sveučilišne knjižnice "Sv. Kliment Ohridski" - Skopje. Prikazani su najvažniji i najšire primijenjeni pristupi vođenju konzervatorskih istraživanja na raznim oblicima radova na papiru s povijesnom vrijednošću, u smislu njihove primjene i vrste informacija na tvorbenim materijalima papirnih artefakata koji se mogu izdvojiti. U radu su sažeti osjetljivost tehnika, različiti rezultati dobiveni tijekom analize s mogućim interferencijama i najsukladnije suvremene metode. Za prikaz mogućnosti ovih metoda u ispitivanju papira i papirnih aditiva na rukopisima i starim knjigama, od kojih su neke dio pokretne kulturne baštine Republike Makedonije, navodi se niz primjera.

Ključne riječi: metode ispitivanja, papirna knjižnična građa, kulturna baština, Nacionalna i sveučilišna knjižnica "Sv. Kliment Ohridski" – Skopje

---

Vjesnik bibliotekara Hrvatske 58, 3/4(2015), 119-133
ISSN 0507-1925

Summary

This article presents a number of conventional and modern techniques used for the examination of paper-based library materials, which were recently implemented in the Conservation and Restoration Laboratory at the National and University Library "St. Clement of Ohrid" - Skopje. The most important and widely used approaches for conducting the conservation research on many forms of works on paper with a historical value are outlined in terms of their applications and the kind of information on the constituent materials of paper artifacts that can be extracted. Special attention is paid to the conventional methods of micro-chemical analyses of paper artifacts. The sensitivity of the technique, various results obtained during the analysis with possible interferences, and the most compatible modern method are summarised. A set of examples is provided for the demonstration of the capabilities of these methods for examination of paper and paper additives on manuscripts and old print books, some of which are part of the movable cultural heritage of the Republic of Macedonia.

Keywords: examination methods, paper-based library materials, cultural heritage, National and University Library "St. Clement of Ohrid" - Skopje

1. Introduction

In the last several decades, there has been an increased interest in the conservation and restorations of objects of movable cultural heritage in the Republic of Macedonia. The number of publications presented at international conferences and published in journals is steadily on the rise, and the subjects discussed vary from preservation in general to the specifics of the application of particular methods for the extraction of valuable information necessary for authentication and (or) diagnostics[1,2].

The National and University Library "St. Clement of Ohrid" – Skopje has the largest and richest collection of paper-based library materials in the Republic of Macedonia. Paper is found in many forms in historical collections, including books (general), rare books, archive materials, manuscripts, scrap

[1] I. Nastova, O. Grupce, B. Minceva-Sukarova, S. Turan, M. Yaygingol, M. Ozcatal, V. Martinovska and Z. Jakovlevska-Spirovska, Micro-Raman Spectroscopic Analysis of Inks and Pigments in Illuminated Medieval Old-Slavonic Manuscripts, J. Raman Spectrosc. 43(11), 1729-1736, 2012.

[2] Kostadinovska, M., Jakovleska-Spirovska, Z. and Minčeva-Šukarova, B. A spectroscopic study of inks from a rare Old Slavic manuscript : Liturgical Collection of chronicles, scriptures, etc., 2nd Virtual International Conference on Advanced Research in Scientific Areas (ARSA-2013), Slovakia, 2-6 December 2013, p. 311-316. Available at: http://www.arsa-conf.com/archive/?vid=1&aid=2&kid=60201-95

books, serials, newspapers, maps, posters and works of art. Many historical collections possessed by our library also may contain parchment and vellum that are not paper-based, but these will not be in the focus of this article.

Recently our cultural institution has re-evaluated preservation responsibilities required by a comprehensive programme to preserve historical collections according to the Law on Protection of Cultural Heritage (Official Gazette of the Republic of Macedonia No.20/04). One core responsibility is *Conservation Research* which utilises material science to characterise the nature, technology, and deterioration of collections, but also helps to test and evaluate preventive and interventive care protocols for collections and to develop and modify treatment practices in order to improve preservation policies.

Paper-based materials, especially objects referred to as movable cultural heritage which arrive in the Conservation and Restoration Laboratory in Skopje for conducting of any kind of preservation programme, need to be subject to conservation research.

There are several problems addressed by art owners, museums, and dealers we often face with as conservators. Among them is determining the origin and age of artwork (i.e. authentication and discovery of forgery) and pre-conservation diagnostics (i.e. material characterisation). Traditionally the approach to these problems was based on the personal expertise of an expert or the conservator themselves; with time it has become apparent that this alone may not be enough. Today these problems are evaluated through the application of scientific studies based on conventional methods of analysis and modern "high-tech" instruments.[3]

The work presented here discusses a number of examination techniques – both conventional and modern – which were recently implemented at our laboratory in Skopje in order to conduct a comprehensive preservation programme based on a scientific examination of paper artifacts. The information that may be extracted by each technique will be summarised, along with an indication of the strengths and weaknesses of the methods. Special attention will be paid to the methods of micro-chemical analysis, most of which are based on optical microscopy for fiber and binder/filler of paper substrate identification.

[3] Whitmore, P. M. The Scientific Examination of Works of Art on Paper. *In:* Scientific Examination of Art : Modern Techniques in Conservation and Analysis. The National Academies Press. 2005. pp. 40–57. [Online]. Available from http://www.nap.edu/openbook.php?record id=11413.

2. Brief history on examination methods

The history of systematic scientific analysis of paper artifacts dates back to the first half of the 20th century. At that time different libraries and museums began using more thorough examination methods, such as optical microscopy of paper fibers and chemical analysis of extracted pigment samples, either in collaboration with research institutions or by making use of their own scientific laboratories.

Today the arsenal of techniques available to the conservator and art scientist is large, but still limited. Majority of the existing methods for the inspection of the chemical structure and physical properties of paper originate from the paper industry where they are used for quality control, research for new products and improvement of quality, yield and performance. With very few exceptions, no methods have been developed specifically for the evaluation of the suitability of paper conservation treatments. This happens for a number of reasons:

- Paper conservation is a relatively new scientific field involving a limited number of scientists. On the contrary, paper industry has a long history and the industrial associations have standardised the quality control processes. Scientific journals date from the beginning of the 20th century;
- Until recently, paper conservation was a craft based on secret recipes practiced by highly skilled but empirically educated individuals. Dedicated scientific journals appeared in the early seventies.

3. Spot tests

Spot tests refer to two types of testing performed during the examination of paper artifacts. The first (termed "micro-chemical testing") consists of testing a small sample, removed from either the artifact (e.g. a single paper fiber or a fraction of the cellulosic medium) or extraneous materials (e.g. adhesives, binders, fillers), with very small amounts of chemical reagents. Characteristic reactions of these reagents aid in identifying the materials present. The second type of testing (termed "pretreatment testing") is performed directly on small areas of the artifact and tests possible treatment methods and reagents in order to predict the reactivity, sensitivity, or vulnerability of the paper support or media. The latter are not in the focus of this article and therefore they will not be additionally explained.

3.1. Micro-chemical testing

Micro-chemical spot tests assist in the technical examination of the artifact by identifying or suggesting the materials used, including those contributing to the current condition of the artifact. Spot tests included herein are conventional chemical methods, most of which are destructive to the sample and they do not allow us to perform them directly on the object. Therefore, tests are performed on a microscopic sample removed from the object. In our laboratory, trained and highly skilled personnel with background on chemical and biological sciences trigger the chemical reactions and interpret the obtained results. Most chemical reactions induce a visible colour, precipitate or generate gas evolution, which can be detected by the analyst or by the use of more sophisticated equipment such as compound light microscope (NIKON YS100).

The micro-chemical tests implemented for the examination of paper and paperboard (see Table 1) and paper sizings (see Table 2) are outlined in terms of sensitivity of the technique, the results obtained during the analyses with the possible interferences, and most compatible modern method which we conduct in order to confirm the authentication of the artifact based on the results. These tests have been performed on real authentic micro-samples taken from manuscripts and old print books in last several months. Images of some of the tests are shown below to demonstrate the capabilities of these techniques (see Figure 1, 2 and 3).

Although an array of tests is listed, it is likely that only a few are appropriate for a given artifact. A specific test should be selected wisely since micro-chemical testing generally consumes the entire sample. Sampling sites should be chosen to represent the component being analysed. It may be necessary or advantageous to take samples from different locations in order to achieve appropriate results that represent the object overall. Particular care must be taken to distinguish areas of previous restoration. The sample selected should be as free as possible from extraneous material. Since micro-chemical spot tests are designed to test for specific substances, results can be confusing or complicated when samples contain mixtures. More sophisticated analytical instrumentation may be advantageous in this instance, where a small sample can simultaneously be evaluated for a broad range of components.

TABLE 1. Micro-chemical testing (spot tests) Used in Conservation Research Referred to as Conventional Examination Methods for Paper and Paperboard.

Paper and paperboard					
Method/Technique	**Sensitivity**	**Results**	**Caution/Interference**	**Confirmation method**	**Authentication**
Acidity (pH) – SkincheckÔ					/
Lignin ***(Phloroglucinol Test) – Light microscopy***	Very sensitive. Trace amount (less that 5%) of ligneous fibers can be detected. Individual fibers can be seen with a hand lens or the naked eye. (Grant 1961, 377)	A bright- or deep-red or magenta colour indicates mechanical or semi-mechanical wood pulp, unbleached chemical pulp, or other lignified fibers such as jute.	Some dyestuffs also give a red color with hydrochloric acid (Grant 1961, 377). The dye metanil yellow can turn red with phloroglucinol (TAPPI T401). A purple color reaction indicates the presence of iron (Browning 1977, 318).	*FTIR (peak at 1505 cm^{-1})*	*Dating of artifact: mechanical or semi-mechanical wood pulp (19th century – 1949)*
General Fiber Content ***(TAPPI T 401) – Light microscopy*** 1. ***Graff "C" Stain Test***	Very good for separating pulp types	Yellow indicates high lignin content, which could be mechanical or semi-mechanical pulp. Blue indicates well-purified pulp. Red indicates absence of lignin.	Some old rag fibers may not stain intensely red and instead appear yellow, possibly influenced by acidity or degradation products. The stain oxidizes readily and is not permanent. Slide should be read within 10-15 minutes.	*FTIR (different peaks depending on the type of the fiber)*	*Discovery of the fiber type can be used for dating the artifact and for determining the place of creation*
2. ***Herzberg Stain Test***	Much sharper distinction is made between rag, mechanical pulps, and chemical pulps. Not useful for separating chemical pulp types.	Generally, chemical pulps from wood and most grasses stain blue; rag and bleached abaca (manilla hemp) stain pink-purple; alpha-cellulose pulp stains a reddish color; mechanical pulp (ground wood), and unbleached jute and raw cooks of abaca and grasses stain yellow. Bleached jute stains yellow-green.	/		

Figure 1. Microscopic view (x200) of Cotton fibers stained with Graff "C" stain.

Fibers were extracted from paper pulp of an illuminated Old-Slavonic manuscript, "The Octoechos of Kruševo" (IMK Ms.1), 3rd quarter of 15th century, belonging to the Historical Museum of Kruševo

(Picture in Press for the 4th Balkan Symposium on Archaeometry, 27th – 30th September 2014, Nessebar, Bulgaria)

TABLE 2. Micro-chemical testing (spot tests) Used in Conservation Research Referred to as Conventional Examination Methods for Paper Sizings and Additives.

Sizing (adhesives, binders)					
Method/Technique	**Sensitivity**	**Results**	**Caution/Interference**	**Confirmation method**	**Authentication**
Gums (sugar)	No straightforward micro-chemical tests are found to confirm the presence of a sugar gum (arcacia, tragacanth, etc.) that are practical to perform on a very small sample (often composed of low concentrations and/or containing complex mixtures or impurities). The Iodine Potassium Iodide Test for starch is used by some reporting a yellow-brown color reaction. However, this is a negative reaction showing only the absence of starch and dextrin.			*FTIR*	/
Starch *(Iodine Potassium Iodide Test, TAPPI T 419)*	Extremely sensitive to small concentrations of starch.	Formation of deep blue to black color indicates starch. Dextrins prepared from starch yield red-violet to red colors. A faint blue or violet coloration should be disregarded. A yellow-brown color is a negative response.	Starch derivatives may also exhibit blue color formation. Modified starches react somewhat differently from unmodified: generally, modified starches are more evenly dispersed and give a more uniform stain.	*FTIR (peak at 999 cm^{-1})*	*Dating of artifact: starch (11^{th}–13^{th} century) & modified starch (1949 – onward)*
Proteins 1. *Non-specific proteins* *(Buiret Test)*	Not sensitive to small concentrations of protein.	Purple color indicates presence of protein.	Disregard a blue reaction.	*FTIR (Amide I, I and III bands)*	/
2. *Gelatine* *(Ehrlich's Reagent) (TAPPI T 504)*	The test is applicable to glue hardened with formaldehyde, alum, or amonioformaldehyde resins.	Development of a rose-red or pink color within ten minutes indicates the presence of animal glue or gelatin.	Specific test for gelatin or animal glue, other nitrogenous materials do not interfere.	*FTIR (Amide I and amide II bands)*	*Dating of artifact: mid-13^{th}–16^{th} century*
Alum *(Aluminon Test)*	/	Formation of bright or deep pink indicates alum. Deep purple formation indicates the presence of iron. Pinkish-purple probably indicates presence of both iron and alum (Barrow 1969, 13).	The reagent can also turn pink-red in the air after approximately two hours. Possible positive reaction with some dyes used to color paper.	*FTIR (peak at 1100 cm^{-1})*	*Dating of artifact: 16^{th}–18^{th} century*
Rosin *(Raspail Test)*	/	A pink to raspberry color indicates rosin is present. No color or brown indicates the absence of rosin. A positive test can indicate either gelatin/rosin or alum/rosin and may obscure the red color reaction. Charring of the fibers indicates presence of ground wood (mechanical wood).	Positive color is often faint pink and difficult to see on badly yellowed papers. Color is fleeting and will disappear in a few minutes. Casein may also give a similar red reaction (Lee 1935, 10).	*FTIR (peak at 1694 cm^{-1})*	*Dating of artifact: 19^{th} century – 1949*
Resins and Fats *(Sudan IV Test)*	/	Resins and fats are stained red, while the fibers remain colorless.	/	/	/
Synthetic polymers (Cellulose derivates) *(General Test with Benzene)*	/	All cellulosics show a blue or green ring between the two liquid phases except for ethylcellulose, which shows a violet ring (Browning 1977, 242).	This test works for water-soluble ethers.	/	*Dating of artifact: 1949 – onward*

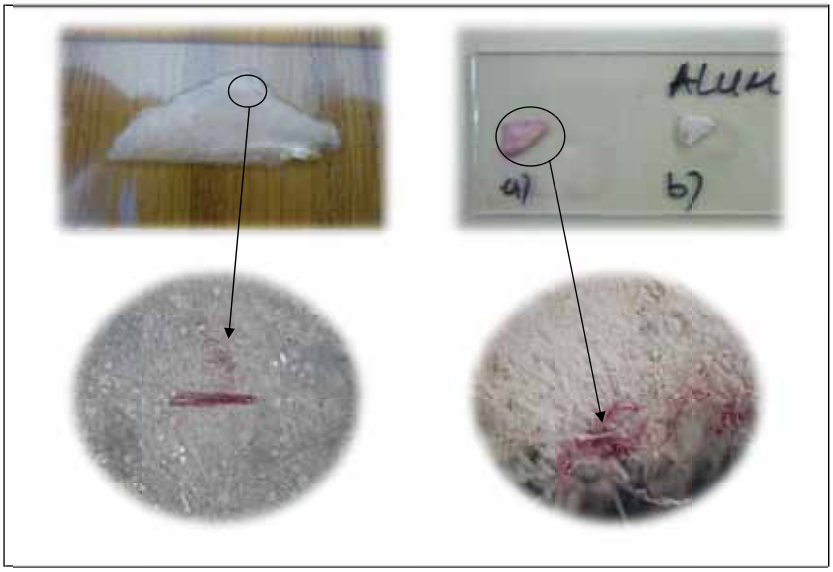


Figure 2. Micro-chemical (spot) tests for detection of lignin and alum (above – macroscopic view and below – microscopic view at 100X).

Left: Phloroglucinol Test on a sample of paper removed from the Old-Slavonic Manuscript "Liturgical Collection of chronicles, scriptures, etc." (IMK Ms. 2), 16th century, belonging to the Historical Museum of Kruševo).

Right: Aluminon Test on paper samples from the Bible, old print book, 19th century, belonging to the "St. John the Baptist - Bigorski" Monastery (a) Original paper (most pages of the book) – positive for alum and (b) Original paper (paper on book cover) – negative (Pictures are in Press for the 4th Balkan Symposium on Archaeometry, 27th – 30th September 2014, Nessebar, Bulgaria)

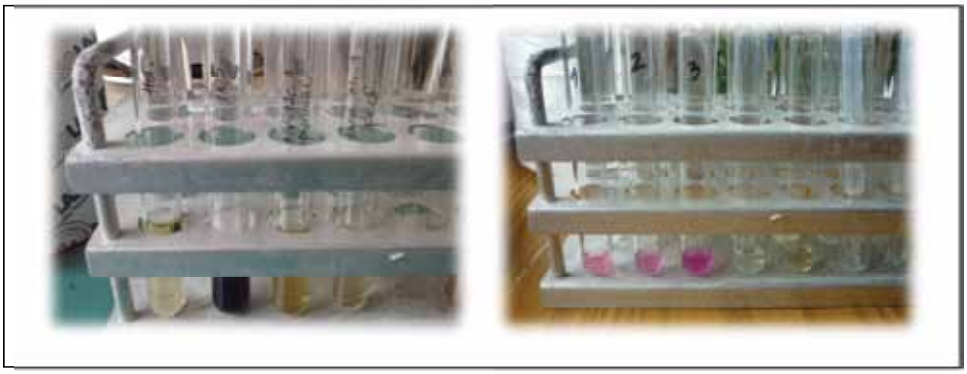


Figure 3. Micro-chemical tests for detection of starch and gelatin performed on samples from IMK Ms.1.

Left: Iodine Potassium Iodide Test according to TAPPI T 418.

Right: Ehrlich's Reagent according to TAPPI T 504

4. Modern examination methods

Micro-chemical testing is considered by more authors as a confirmation of results obtained using other modern and more sophisticated examination analytical techniques, such as infrared spectroscopy, micro-Raman spectroscopy, x-ray diffraction, or x-ray fluorescence, even though such examination may be more appropriate in terms of providing further information and more detailed data on the materials after their detection with the micro-chemical tests.

4.1. Infrared Spectroscopy

Infrared spectroscopy is one of the most important analytical techniques available for confirmation of results obtained by micro-chemical tests. One of the greatest advantages of the infrared spectroscopy is that virtually any sample in any state may be analysed. For example, liquids and solutions (like pulp), dry fibers, powders (adhesives, binders) can all be examined with a judicious choice of sampling technique. Infrared spectroscopy has

been successfully applied to the analysis of papers and inks.[4,5] The analysis of papers and inks using a microscope with a diamond cell or ATR objective is useful in identifying compounds such as lignin, gelatin, and starch in papers (see Figure 4). The ATR technique as a universal sampling accessory to FTIR provides reproducible qualitative and quantitative analysis of samples and is a non-destructive method for detection of the molecular composition of a sample. Therefore, a paper sample can be analysed several times.

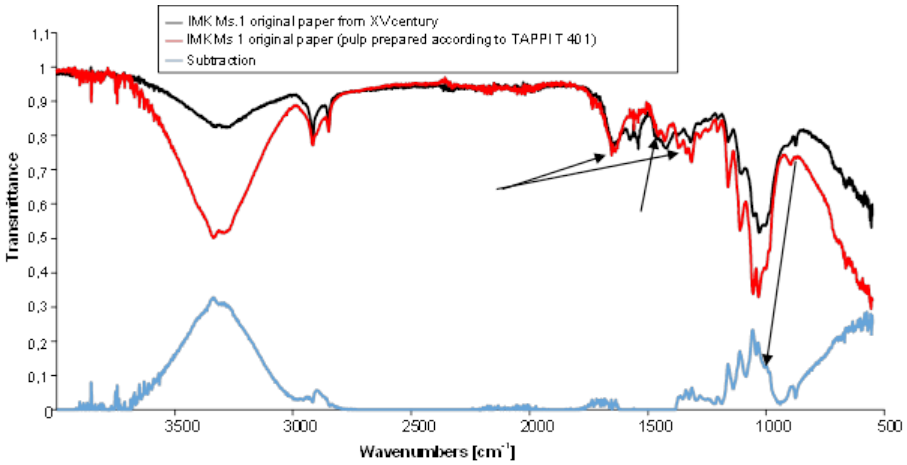


Figure 4. Identification of gelatin, lignin and starch in paper and pulp samples from manuscript IMK Ms.1 by FTIR spectroscopy in the ATR mode.

[4] Kostadinovska, M., Jakovleska-Spirovska, Z. and Minčeva-Šukarova, B. A spectroscopic study of inks from a rare Old Slavic manuscript : Liturgical Collection of chronicles, scriptures, etc., 2nd Virtual International Conference on Advanced Research in Scientific Areas (ARSA-2013), Slovakia, 2-6 December 2013, p. 311-316. Available at: http://www.arsa-conf.com/archive/?vid=1&aid=2&kid=60201-95

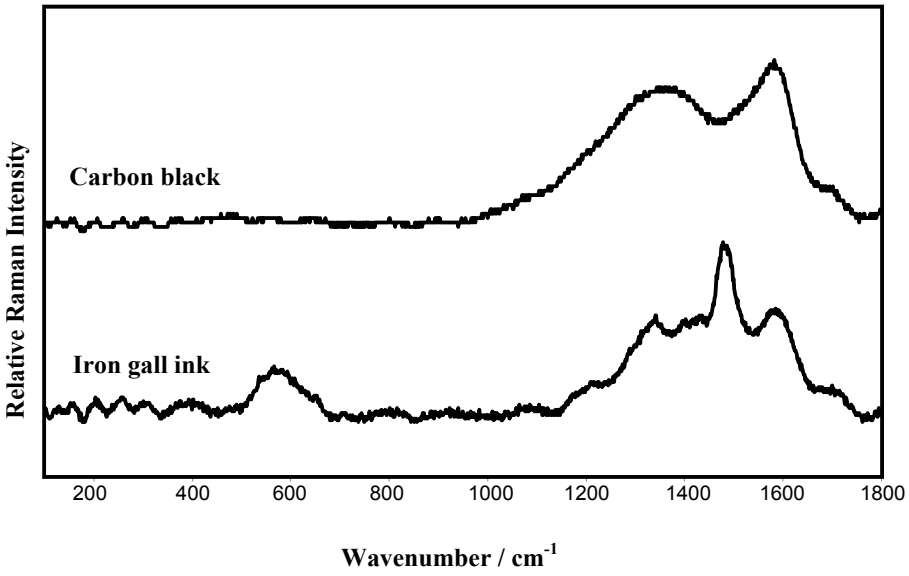
[5] Kostadinovska, M., Minčeva-Šukarova, B., Z. Jakovleska-Spirovska, O. Grupče. Spectroscopic and Microscopic Techniques for the Characterization of a 15th Century Old-Slavonic Illuminated Manuscript: A Case Study, Fourth Balkan Symposium on Archaeometry, 27th – 30th September 2014, Nessebar, Bulgaria. Available at: http://bsa4.issp.bas.bg/wp-content/uploads/P8-4_M_Kostadinovska.pdf

4.2. Raman spectroscopy

Raman spectroscopy has been shown to be important in the forensic analysis of trace evidence and documents. Document analysis can be broken down into a few categories of investigation, including authentication of documents of value, determination of document alteration, and evidences for a suspected origin or place of origin. For example, the proper dating of a paper artifact or artwork often requires information on the pigments that were available to the artist. This data becomes useful when spectroscopic analysis of materials is conducted. It can easily be compared to some documented information (e.g., spectra database).[6]

Raman spectroscopy, like infrared spectroscopy, is highly specific method for chemical identification, because it accesses fundamental modes of vibration of the molecules which are observed as unique fingerprints in spectra (see Figure 5a and 5b).

a)



[6] Robin J. H. Clark. Raman Microscopy in the Identification of Pigments on Manuscripts and Other Artwork. *In:* Scientific Examination of Art : Modern Techniques in Conservation and Analysis. The National Academies Press. 2005. pp. 40-57. [Online]. Available from http://www.nap.edu/openbook.php?record id=11413.

b)

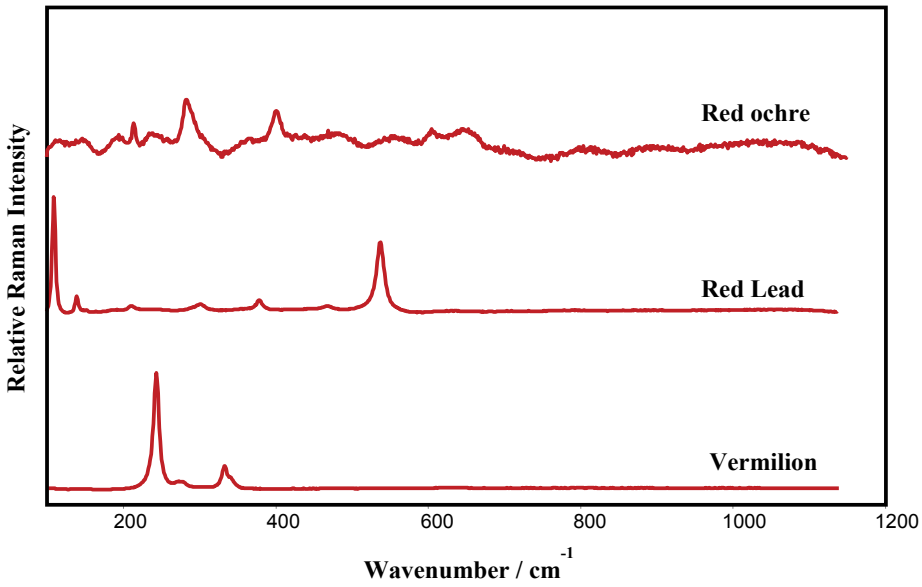


Figure 5. Chemical identification of black (above) and red (below) ink/pigments examined in handwritings of IMK Ms. 1 and IMK Ms. 2 by micro-Raman spectroscopy. Pigments have unique fingerprints in spectra at different wavelength regions.

Modern Raman microscopes routinely allow the detection and identification of inorganic pigments that frequently have spectral signatures down to ~100 cm^{-1} (see Figure 6). Unfortunately, there are a few obstacles to the successful Raman analysis of documents. First, paper frequently exhibits fluorescence upon visible excitation, where the fluorescence signal dwarfs the Raman signal. Secondly, many synthetic dyes found in textiles, inks, and paints also exhibit fluorescence. Third, paper sizings and other additives may be difficult to be detected as most of them are of organic nature.

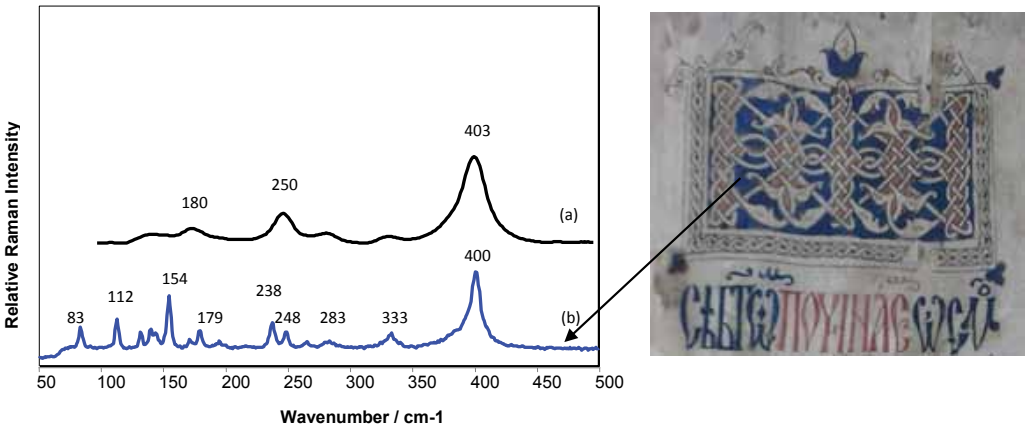


Figure 6. Micro-Raman analysis of blue pigment/ink in the arabesque of the illumination of IMK Ms.1: (a) reference spectra for azurite* and (b) azurite from examined sample

*retrieved from Clark R.J.H., Bell I. M., Gibbs P.J. (1998) - Raman Spectroscopic Library http://www.chem.ucl.ac.uk/resources/raman/index.html

5. Conclusion

This article was intended to give a description of some chemical tests that work reasonably well when scaled down to a size appropriate for testing tiny samples. Scientists have directed a lot of effort toward developing ways to make chemical tests on tiny samples using a microscope to interpret the results. Most of these tests have become obsolete in recent years, but they still offer useful and fairly low cost methods that paper conservators can use for testing paper-based materials.

The need for implementing these methods in examination of paper artifacts at our Conservation Laboratory was seen for several reasons:

First, for the purpose of carrying out preservation of paper-based materials which are part of the movable cultural heritage according to the local regulations of the country.

Secondly, conservators have to carefully study the objects and the materials used for their preparation in order to understand and determine the potential threats to the physical integrity of the objects and to plan an appropriate conservation treatment.

Third, the last but not the least one, was the need to raise the solving preservation issues to a scientific level based on concrete results rather than on observable data of subjective examination such as the personal experience of the conservator.

REFERENCES

Association of Official Analytical Chemists (AOAC), Official Methods of Analysis. Washington, DC: AOAC, 1990.

Claire McBride. A Pigment Particle & Fiber Atlas for Paper Conservators. Graphics Conservation Laboratory, Cornell University, Ithaca, 2002.

Henry, Walter, et al. Spot tests. Chap. 10 in Paper Conservation Catalog. Washington D.C.: American Institute for Conservation Book and Paper Group, 1990.

Isenberg, I.H. Pulp and Paper Microscopy. Appleton, Wisconsin: Institute of Paper Chemistry, 1967.

Radosavljević B., Petrović R. Konzervacija i restauracija arhivske i bibliotečke građe i muzejskih predmeta od tekstila i kože. Beograd, 2000.

TAPPI Publications (Technical Association of the Pulp and Paper Industry):

T 401 om-08 Fiber Analysis of Paper and Paperboard

T 419 om-11 Starch in Paper

T 504 cm-97 Glue in Paper (Qualitative and Quantitative Determination)