# NON-DESTRUCTIVE CHARACTERIZATION OF PAPER AS A SUPPORT OF A GOUACHE COLLECTION

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## ABSTRACT

*Within the framework of the EU INTERREG IIIA project between Slovenia and Austria about the Vine cultural track of the archduke John from Graz to Maribor, which has included also a conservation treatment of the rare collection of 126 illustrations dated 1820 to 1850 representing paintings on paper in a gouache technique of types and sorts of grapevine which were serving as a teaching aid. The 126 originals are the only preserved illustrations of the types of vine that were grown in the area of present-day Slovenia of the Duchy of Styria before the vines were destroyed by phylloxera.*

*The paper presents the results of non-destructive and non invasive analysis of paper as a support to the illustrations. Results were obtained from non-destructive permissible observation and analytical techniques of characterization, such as structural properties, microscopic, optical, and colorimetric and qualitative analysis on selected originals. The results served as a base to determine further conservation and preservation treatments of the exceptional gouache collection.*

## INTRODUCTION

The collection consists of 126 sheets of paper painted using the gouache technique. They feature »portraits« of grapes and vine leaves in vibrant natural colours and in natural sizes. The paintings are outstanding and more credible than any present day colour photograph. They are depicted so that we can imagine without difficulty we are looking at real grapes and vine leaves that seem alive. All sorts of details are painted, including signs of disease on the grapes, stalks and leaves, and therefore they possess extraordinary documentary value. Nowadays the paintings represent the only preserved graphic material on vine sorts that were cultivated in the province of Styria in the Austro-Hungarian monarchy before they were destroyed by wine pests in 1880, and therefore represent a valuable heritage of the history of European ampelography.

*Fig.1: Three typical gouache paintings of vine sorts before the conservation treatment. For a very long period the originals were used as teaching aid, which is reflected also in their material condition. Luckily on the painted parts there is no evident damage.*

The paintings were produced as illustrative material for fruit and wine schools. Due to their extraordinary realism, the originals were used for a very long time as a teaching aid, as reflected also in their material condition or level of damage. Before they were taken to the Conservation Department of the National Archives of Slovenia were kept at the Agricultural Forestry Board (KGZ) Maribor in three already quite damaged cardboard boxes.

The collection comprises 126 works painted in the gouache technique on sheets of paper 430x332 or 476x374 mm in size. The sheets differed among themselves also because several had been trimmed subsequently. On the actual painted parts there is no evident serious damage, which is why there is that much more damage on the paper sheets. This is mainly the result of frequent use, inappropriate storage and the application of unsuitable adhesives. In certain cases the yellowing also reveals the poor maintenance and long-term exposure to light. In order to prevent further wear, most of the pictures were glued onto a fabric approximately 80 years ago (after 1923). The textile support is of good quality and facilitates the preservation of the paintings, but does not solve all the problems of suitable protection of the damaged originals.

In 2001 all of the images have been reproduced in outstanding colour quality in the book A Collection of Ampelographic Images by Vincenzo and Conrad Kreuzer (Zbirka ampelografskih upodobitev Vincenza in Conrada Kreuzerja) edited by Primož Premzel. Besides its intrinsic value, the monograph also has the role of protecting the originals, as the reproductions it contains are of such high quality that they are an aid to top experts. In the reproductions in this book one can see also the extent of the damage on originals. Thanks to this publication the access to the originals is limited only to the most urgent examinations. With the preliminary works having been performed of analyses and characterisation of damage to the paper, guidelines were issued for further conservation and restoration measures. On the basis of the performed examination we determined the extent and range of further conservation action on this outstanding collection.

## EXPERIMENTAL PART

### Selection of Samples

We performed a comparative analysis of 10 randomly selected originals from the gouache collection of 126 illustrations. On the basis of the visual examination, we selected 5 items (1-5) with a "poorer" appearance and 5 items (6-10) with a "better" appearance, whose identification markings are shown in Table 1.

| Sample | Original classification | Wine sort - German name |
|---|---|---|
| 1 | 234 p. 110 | Weisser Hudler |
| 2 | 75 p. 47 | Blauer Muscateller |
| 3 | 108 p. 74 | Scwarzer Farber |
| 4 | 173 p. 90 | Blauer Ortlieber |
| 5 | 213 p. 106 | Weisser Augster |
| 6 | 54 p. 126 | Slankamenka |
| 7 | 172 p. 89 | Weisser Ortlieber |
| 8 | 212 p. 105 | Blaue Isabella |
| 9 | 96 p. 65 | Rothe Portugieser |
| 10 | 292 p. 123 | Blaue eicheltraube |

*Table 1: Identification markings of the selected originals.*

### Method of Testing

The selected originals (presented in table 1) were acclimatised under standard climatic conditions conforming to SIST ISO 187 at 23°C and 50% relative humidity. We then took measurements of the individual properties to evaluate non-destructive structural, optical and colorimetric properties of the paper as well as microscopy and selected spectroscopy techniques.

On all 10 items we performed standard testing methods of the basic paper properties.

1. Basic structural properties of paper**:** grammage (ISO 536), thickness and specific volume (ISO 534).
2. pH of the paper surface (TAPPI T 529).
3. Optical properties of the paper: ISO brightness (ISO 2470) and yellowness index (DIN 6167).
4. Colorimetric properties of the paper: colour CIE L*a*b* (ISO 5631)

On selected items we performed the following non-destructive and micro-destructive qualitative analyses:

1. FTIR spectroscopy employing the ATR technique (NTF – University of Ljubljana).
2. Presence of lignin in paper (method of identification with fluoroglucinol).
3. Presence of starch in paper (method of identification by colouring with iodine.
4. PIGE and PIXE (Jozef Stefan Institute, Ljubljana) and
5. Microscopical analysis of:
   - paper fibres – measuring at 100x and 200x magnification, optical microscope (ICP method and Research Chem. Laboratory method of the National Archives, Prague).
   - paper surface – measuring light reflection at 60x magnification (ICP - method).
   - protective fabric surface – measuring light reflection at 12x and 60x magnification (ICP - method).
   - painted surface area – measuring light reflection at 60x magnification (ICP- method).

**Analyses on Selected Items**

Basic structural properties of paper: grammage, thickness, specific volume

The structural properties of paper are defined according to ISO 536: grammage, thickness and voluminosity. On the basis of the analyses we can determine that the paper of the originals had a basic grammage of around 150 to 200 g/m$^2$. The values for thickness range from 480μm to 550μm, in which larger differences between the samples are perceptible. The values that are higher by around 50μm were obtained in better preserved items (samples 6-10), which is also confirmed by the values for paper voluminosity. The highest value of specific volume was obtained for samples 6 (54) and 7 (172), which can be placed in the group of better preserved originals.

pH of the paper surface

We took pH measurement readings on the surface of the originals with a special electrode in accordance with TAPPI 529, the results of which are shown in Fig. 3. The results show that the pH values of the surface range from 4.9 to 5.5. The pH values of the paper surface are no lower than pH<4.5, which represents the critical limit where accelerated and more rapid degradation can be expected. Paper sheets that reach a lower value (pH < 5) also have more degraded and shortened fibres. The samples 6 (54) and 10 (292) attain comparatively the best quality in comparison with the other originals.

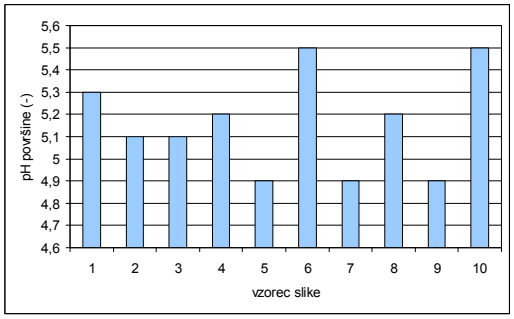
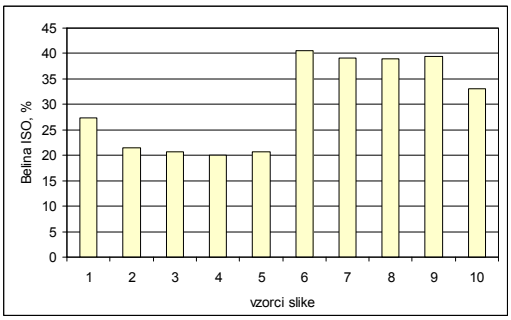



*Fig. 2: pH values of the paper surface*

Optical properties of the paper

We measured the brightness (ISO 2470) and yellowness index (DIN 6167) of the paper on all selected samples using a DataColor spectrophotomer. Whiteness is a measurement for the reflectance of blue light at 457nm and is used to determine paper whiteness.



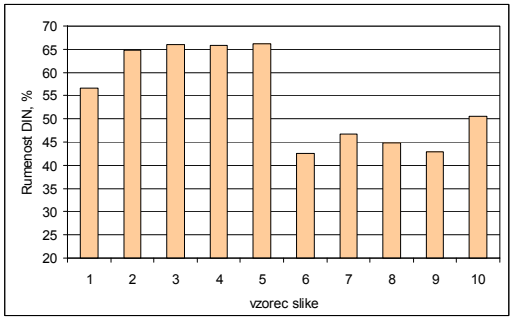




*Fig. 3: Values obtained for paper brightness. Fig. 4: Values obtained for paper yellowing.*

The results are confirmed by the better and worse visual appearance of the originals, on the basis of which the conservator may estimate the visual quality of the examined object.

Colorimetric properties of paper

We also decided to define the colorimetric properties, which nowadays are more often used to characterize articles on paper.

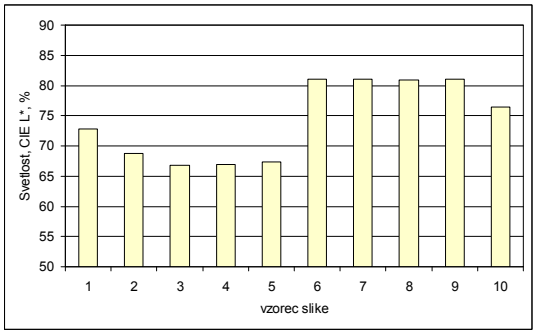
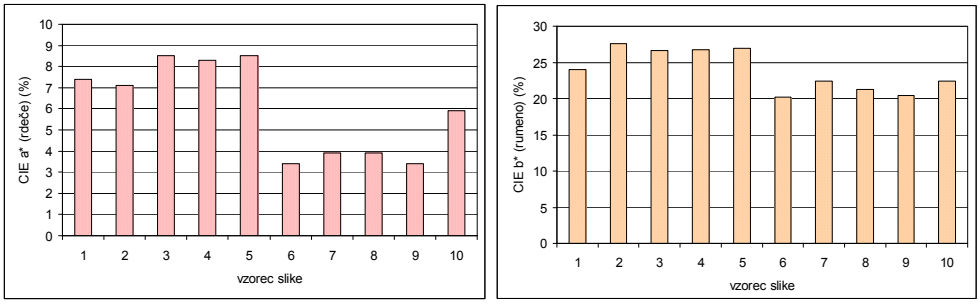



*Fig. 5: Values obtained for paper lightness CIE L*.*

The values obtained for lightness CIE L* confirm the figures obtained for brightness and yellowing. The highest values ranging from 75% to 80% were obtained in the best preserved originals, i.e. 6 to 10. On the samples of poorer quality (samples 1 to 5) the values obtained range from 66% to 73%.




*Figs. 6 and 7: Colorimetric properties of paper, CIE a*b* (6 –red, 7-yellow)*

Positive values at axis +a/-a are showing the red colouring of the paper surface. On better preserved originals the values are lower, ranging from 3 to 5, and in worse preserved originals from 7 to 9. The values obtained for colours at axis +b/-b reveal that the samples had a strong yellow coloration. Better preserved originals had a value of up to 20, while worse preserved originals had a value of around 25.

Qualitative analysis of the presence of lignin in paper

The results of the qualitative method of characterising the presence of lignin in paper revealed that none of the examined samples contained lignin in the paper. On this basis we can ascertain that all of the paper was made from cellulose fibre that originated from annual plants (flax, hemp, cotton).

Qualitative analysis of the presence of starch on the paper surface

The results of the qualitative method of characterising the presence of starch in paper has revealed that all the examined samples of paper have a high starch content in the structure and on the paper surface. The results confirm the preliminary finding that the paper was hand made and probably then partly dried and finished with a starch solution on the surface.

PIGE and PIXE qualitative analysis on selected originals

Paper samples were taken from the left margin of the samples 5 (213) and 9 (96) for the PIGE and PIXE analyse. The analyses were performed at the Josef Stefan Institute in Ljubljana. The results are presented in table 2. and table 3.

| Sample | Na | Mg | Al |
|---|---|---|---|
| 9 (96) margin | 1100 | 1300 | **3400** |
| 5 (213) margin | 500 | 400 | 1400 |

*Table 2: Concentrations of elements (in ppm), results obtained by PIGE.*

| Sample | S | Cl | K | Ca | Ti | Cr | Mn | Fe | Ni | Cu | Zn | Pb |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 9 (96) margin | 2920 | 1180 | 3270 | 1410 | 41 | 9 | 47 | 663 | 77 | **3300** | 61 | 191 |
| 5 (213) margin | 1690 | 540 | 880 | 350 | 137 | 3 | 3 | 326 | 85 | **2470** | 46 | 68 |
| Scotch tape | 2010 | 510 | 340 | 140 | 211 | | | 259 | 85 | 1480 | 3 | 28 |

*Table 3: Concentrations of elements (in ppm), results obtained by PIXE.*

From the obtained data we notice, that the measurements on the fragment taken from the margin of sample 9 (96) and 5 (213) are shoving some higher concentration of aluminium, and copper. All the other detected elements are in range of normal concentrations for rag paper. The presented data are informative. For more precise results deeper investigation should be performed.

Qualitative analysis of raw materials (fibre, filling and additives) in the paper samples employing FTIR-ATR spectroscopy

On the upper and back sides surface of three examined samples; 1 (234), 9 (96) and 5 (213), we took spectral shots employing FTIR-ART spectroscopy, comparative shots on the reference samples of filler (calcium carbonate, kaolin) and additives (starch, gelatine). The results are shown in Figs. 8.

The spectral shots of the paper surface confirm the presence of starch and gelatine. We found no traces of kaolin in the paper, and to a lesser extent in some samples 1 (234) and 5 (213) we traced the presence of calcium carbonate on the paper surface – probably it was added to the agent to give the surface finish. The results of the spectral shots for the selected items confirm the preliminary findings of fibre microscopy analysis.

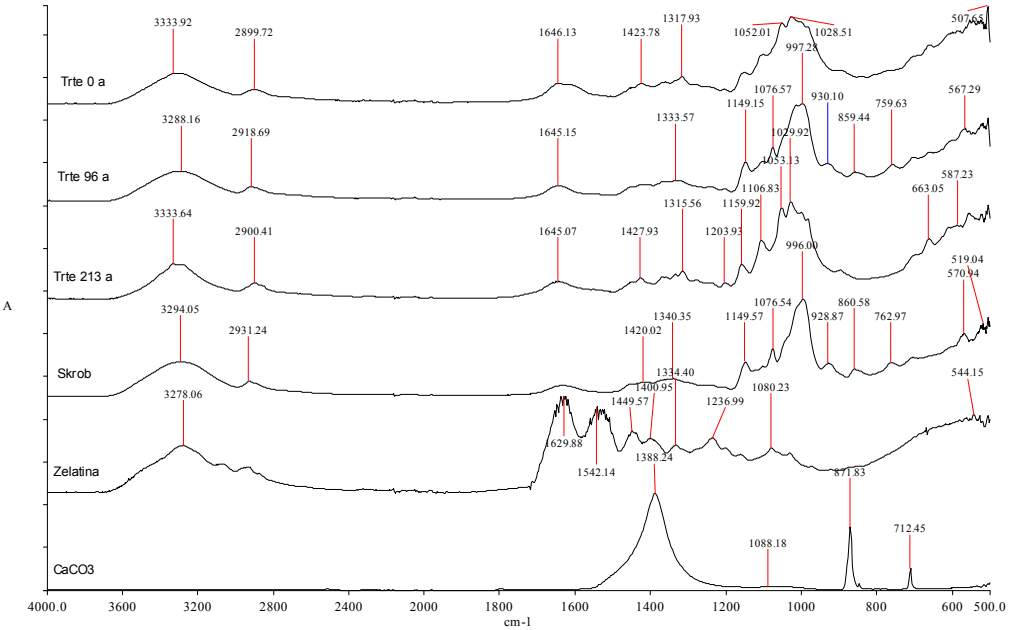


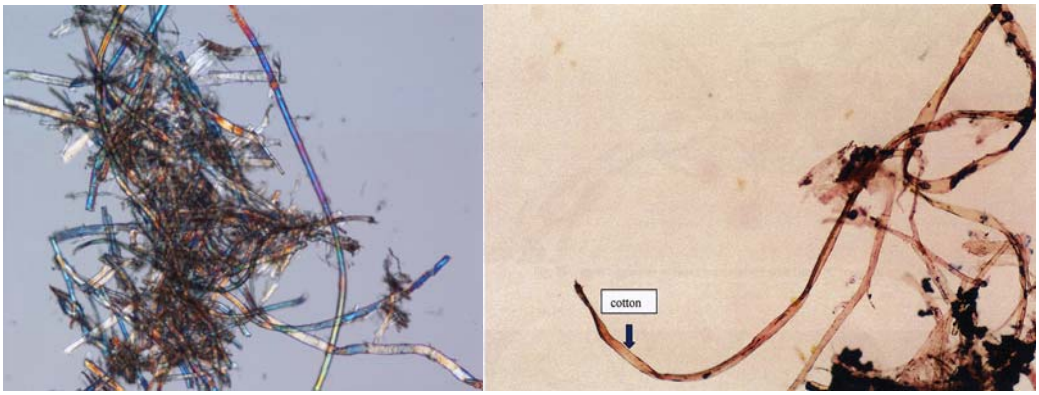

*Fig. 8: FTIR-ATR spectrum of three items:1 (0), 9 (96) and 5(213) on the upper surface and comparison with spectrum of calcium starch (skrob), gelatine (zelatina) and carbonate (CaCO3).*

Qualitative microscopy fibre analysis of paper

Microscopic photos of the paper surface were taken at 60x and 12 x magnification with ICP method on stereo microscope Wild 352873.

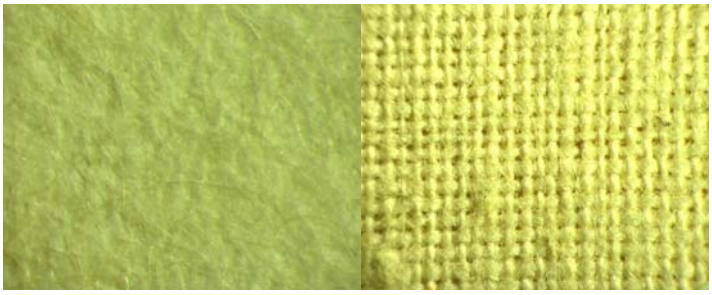
The fibre composition was specified in greater detail using staining solutions according to ISO 9184, Herzberg and Graff"C" staining test, examined under Nicon Eclipse E 400 microscope and ICP method under Nicon Eclipse 80i both at 100 x and 200x magnification.

A comparative analysis of fibre types has revealed that the paper sheets contain cellulose that originates from rag fibres, as cotton and flax fibre is present in examined samples of paper. Analyses of degraded areas taken form the margins of paper sheets are showing shortened and very brittle fibres. They break further on handling. The morphological characteristics are suppressed by the degree of working. (Figs. 9 and 10)




*Figs.9 and 10: Microscopic photos of a degraded paper fibres taken from the margins of sample 9 (96/65 red portugal), magnification fig. 9:100x (ICP) and fig. 10: 200x (National Archives in Prague).*

*Microscopic photos of the paper surface at* 60x magnification for all the samples reveal that the paper surface in the samples 6 (54), 8 (212), 9 (96) and 10 (292) are considerably less damaged in comparison with the other samples of worse quality in which product decomposition and impurities can be locally perceived.



*Figs. 11, 12 and 13: Microscopic photos of the sample 9 (96): paper surface at 60x magnification ( fig. 11); paper surface (fig. 12) and the protective fabric (fig. 13) under 12x magnification..*

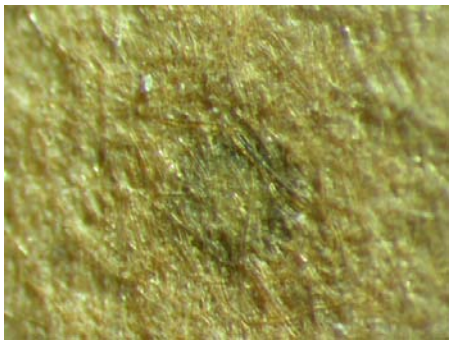


*Fig. 14: Microscopic photos (60x) of local impurities on the surface sample 3 (108).*

*Microscopic photos of the protective fabric surface (on the back)* at 12x and 60x magnification for all the analysed samples reveal only slight differences between individual samples.

*Microscopic photos of the picture surface* at 60x magnification for all the picture originals reveal that the colour conceals the paper surface very well; only in sample 6 (54) can one perceive fibre beneath the applied paint surface. The quality of the painted areas demonstrates good properties.

## CONCLUSION

On the basis of the historic data together with the results obtained from the visual examination and the results of the analysis of the structural properties, surface pH, optical and colorimetric properties and microscopy shots of the selected samples of paper from the original gouache collection we my conclude that the comparative analysis has shown that the analysed samples of paper were damaged in different ways. The general finding is that the quality of the examined samples of paper within the group has similar properties. There are considerable differences, however, in the level of degradation between individual samples, mainly in the most decomposed locations. Protective fabric prevented even greater mechanical damage occurring to the originals. Due to its protective role it made no sense to remove it. We did not remove or unpeel it also because that would have required a wet process – something that is almost impossible to perform on the objects painted using the gouache technique. In this case the process was also entirely unnecessary because the paper is in good condition except for the most damaged places that are, fortunately, only along the edges.

The fact that the paper has still preserved its required physical and chemical properties is confirmed by all the analyses performed on randomly selected samples. Although the paper is well aged in appearance and also in fact quite decomposed in places along the edges, the colour images are still remarkably vibrant and almost undamaged as testified by the exceptional choice of pigments, superb painting technology and paper quality. Today all of these extraordinary and precious Kreuzer depictions of vine sorts are conserved, safeguarded with suitable paspartu in protective boxes, and stored under suitably climatic conditions in Maribor Provincial Museum.

## ACKNOWLEDGEMENTS

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## BIBLIOGRAPHY

1. Baker M., van den Reyden D., Ravenel N., FTIR Analysis of Coated Papers, The Book and Paper Group Annual 8 (1989) http://aic.stanford.edu/sg/bpg/annual/v08/bp08-01.html, 22. 2. 2007.
2. Barrett T.D.: Early European papers/contemporary conservation papers. A report on research undertaken from fall 1984 through fall 1987. The paper conservator. Volume 13, 1989. Institute of Paper Conservation 1989. ISSN 0309-4227.
3. Barrett T.D. & Mosier C.: The role of gelatin in paper permanence. JAIC 1995, Volume 34, Number 3, Article 2 (pp. 173 to 186)
4. Browning B.L., Analysis of Paper, Marcel Dekker, Inc., New York and Basel, 1977.
5. Burgess H.D. &. Binnie N.E.: The development of a research approach to the scientific study of cellulosic and ligneous materials. JAIC 1990, Volume 29, Number 2, Article 3 (pp. 133 to 152).
6. Černič-Letnar M., Vodopivec J.: Influence of Paper Raw Materials and Technological Conditions of Paper Manufacture on Paper Ageing, Restaurator 18 (1997) 73–91.
7. Degrigny, C., Vodopivec, J.: Degradation processes, corrosion and weathering of museum artefacts: an interdisciplinary field greatly supported by COST G8. V: *Non-destructive analysis and testing of museum objects: COST Action G8, final workshop, Intercollege,*

*Nicosia, Cyprus, 18-20 May 2006: programme and abstract book*. [Brussels: COST], 2006, str. 13-14.
8. Engeldrum P.G.: A Theory of Image Quality: The Image Quality Circle, The Journal of Imaging Science and Technology, 5 (2004) 447–457.
9. Feller R.L.: Aspects of chemical research in conservation: the deterioration process. JAIC 1994, Volume 33, Number 2, Article 2, pp. 91 to 99.
10. ISO 536: Paper and board – Determination of grammage, 1995.
11. ISO 534: Paper and board – Determination of thickness and apparent bulk density or apparent sheet density, 1997.
12. ISO 2470: *Paper, board and pulps — Measurement of diffuse blue reflectance factor (ISO brightness).* 1999.
13. ISO 5631: *Paper and board — Determination of colour (L*a*b*), C/2° — Diffuse reflectance method.* 2000.
14. DIN 6167: Yellowness index. Description of yellowness of near-white or near-colourless materials. 1980.
15. ISO 9706: Informacija in dokumentacija – Papir za dokumente – Zahteve za trajnost (∞) (Information and Documentation - Paper for Documents - Requirements for Permanence (∞).
16. ISO 11108: Informacija in dokumentacija – Arhivski papir za dokumente – Zahteve za trajnost (∞) (Information and Documentation - Archive Paper for Documents - Requirements for Permanence (∞)).
17. Kentta E., Determination of SB-latex distribution on paper coating surface with ATR-FTIR spectroscopy, in: COST action E32 Research Conference, 30 September, Helsinki, 2004, http://www.pfi.no/gary/Presentations.htm.
18. Marcus R.T.: The Measurement of Color, K. Nassau (Ed.), Color for Science, Art and Technology, Elsevier, Amsterdam, 1998, pp. 31–96.
19. McCrone W.C.: Polarized light microscopy in conservation: A personal perspective. JAIC 1994, Volume 33, Number 2, Article 3, pp. 101 to 114.
20. TAPPI T529 om-04: Surface pH measurement of paper, 2004.
21. Paulus. H.: Determination of fibre Composition of Samples, Research Chem. Lab. of the Preservation Department National Archives, Prague, 2007.(internal document)
22. Smith B.C.: Fundamentals of Fourier Transform Infrared Spectroscopy, CRC Press, Boca Raton, 1996.
23. Stanley T.: Digital video microscopy: A practical visual analysis technique for the conservator. JAIC, Volume 39, Number 2, article 2.
24. Stuart B., Infrared Spectroscopy: Fundamentals and Applications, John Wiley & Sons, Chichester, 2005.
25. Vodipovec, J., Budnar, M., Pelicon, P.: Application of the PIXE method to organic objects. *Nucl. instrum. methods phys. res., B Beam interact. mater. atoms*. [Print ed.], 2005, vol. 239, str. 85-93.
26. Zbirka ampelografskih upodobitev Vincenza in Conrada Kreuzerja (*A Collection of Ampelographic Images by Vincenzo and Conrad Kreuzer)*, Umetniški kabinet Primoz Premzel, Maribor, 2001.

Back to Top