IRON GALL INKS INFLUENCE ON PAPERS' THERMAL DEGRADATION

FTIR SPECTROSCOPY APPLICATIONS[†]

Marta Ursescu[1*], Teodor Măluțan[2] and Sorin Ciovică[2]

[1] *Cultural Heritage Restoration-Conservation Centre, National Complex of Museums 'Moldova', Piata Stefan cel Mare si Sfant, no 1, 700028 Iasi, Romania*
[2] *'Gh. Asachi' Technical University of Iasi, Faculty of Chemical Engineering, P.O. Box 10, Bd. D. Mangeron, no 71, 700050 Iasi, Romania*

Abstract

The paper focuses on investigating the components of some medieval gall inks and the paper – ink assembly, on their behaviour during thermal ageing treatments. The FTIR spectroscopy techniques allow a qualitative interpretation of the main structural changes. The catalytic role of iron and copper ions in the oxidative degradation of cellulose is estimated by means of the absorbance ratio $A_{(1707 \div 1740)\ cm\text{-}1}/A_{1105\ cm\text{-}1}$. The oxidation index for paper thus defined is correlated to the ratio of Fe^{+2} ions and gallic acid (GA) content in the ink solutions -after the tannins hydrolysis processes-.

Keywords: model paper, gall inks, thermal degradation, FTIR spectroscopy

1. Introduction

Works of art on paper are often affected by considerable changes in appearance due to cellulose materials damage, inks and pigments deterioration, as a result of the degrading effect promoted by endogenous and exogenous factors, or by combinations thereof [1, 2].

The internal agents of deterioration include the paper sheet compounds (the type and quality of the fibres, the fillers, coatings and sizing materials, *etc.*) or can be introduced during the pulp and paper manufacturing processes. Different structurally weakened zones in the cellulose lattice (unordered cellulose) may also be mentioned as internal factors, where many chemical changes that occur along the cellulose chains are initiated [2-4].

A decisive element in paper deterioration consists of the fibres' quality in papermaking that reflects the long-term resistance of paper-made objects. Until the first half of the 19th century the raw materials were natural hemp, cotton or linen fibres with a high content of cellulose, the resulting paper having obvious

---

[†] Presented at the Second Symposium on Religious Art Restoration and Conservation, May 8-9, 2008, Iaşi, Romania.
[*] e-mail: marta_ursescu@yahoo.com

considerable durability and longer life span [5, 6]. Developed later, the use of wood fibres, the pulping, bleaching, alum - rosin sizing processes resulted in a poor durability and permanence for papers manufactured after 1850 [2, 5, 6].

The intensity of cellulose natural ageing processes is influenced by the conditions during storage or use; external factors like temperature, relative humidity, light and air pollutants are related to a decreasing chemical stability in any organic material from the cultural heritage. In a suitable environment the rate of degradation reactions like oxidative or hydrolytic decay is very low, while inappropriate storage or handling conditions contributes to pronounced changes in the cellulose materials' performance [3, 7, 8].

Written items like books or documents are subjected not only to the mentioned exogenous damaging factors but also to those related to the printing, writing, decorating, bookbinding conditions and quality, along with bio-deterioration, social factors or natural disasters [5, 8]. A survey of the overall environmental conditions and their parameters' variation is very important when establishing a long term preservation policy for the collections of paper artefacts [8-11].

While taking into account the complexity of the paper degradation mechanisms, along with the atmospheric pollutants one should also consider that the migration of the volatile compounds (VOC) through the stocked sheets affects the chemical stability of the cellulose, their emission during the aging process being substantial [8, 9, 11, 12].

The chemical decomposition of cellulose chains, initiated by radiations emitted either by natural light or by artificial lighting sources can generate cumulative effects on the paper, on writing or drawing materials. Long term exposure to the Vis, IR or UV range wavelengths may produce the brittleness of paper, the fading of dyes and inks, the reduced solubility and flexibility for binders or pigment layers [11, 12].

By lowering the relative humidity to the critical level of chemically bounded water the cellulose destruction will occur, while a relative humidity level above limits can stimulate hydrolysis or bio-deteriorating mechanisms affecting the papers' structure strength. An enhanced acid-catalysed hydrolysis will result in the case of acidic papers [6, 13, 14].

For written or illuminated manuscripts, during relative humidity variations accompanied by temperature extremes the mechanical stresses induced by dimensional fluctuations may arise and affect the pigments' or inks' cohesion to the cellulose substrate [2, 7, 14].

In recent years, damage survey of collections consisting of historical documents or artistic drawings on paper concluded that iron gall inks, widely used until the 20th century poses a threat to many of these objects [15].

Iron gall inks contain a mixture of a soluble iron ($FeSO_4 \cdot 7H_2O$) and/or a copper soluble salt ($CuSO_4 \cdot 5H_2O$) and gallic acid (resulted upon some tannins hydrolysis), the two main components in the black iron (III) - gallic acid complex formation, along with gum Arabic as a binder or other components included in different historical recipes [15-17].

The various proportions of inks components, strongly depending on provenance and production methods but also on the preparation manner of the ink, results in degradation mechanisms like acid hydrolysis of the cellulose and oxidation reactions catalysed by an excess of metal ions (Fe^{2+}, Cu^{2+}) in paper. [15, 18-21].

The IR spectroscopy techniques are widely used for characterisation of cellulose and paper [22], providing valuable information focused on degradation studies at molecular levels [18, 23-27]. A considerable number of applications of FTIR for identification of gall ink components on historical papers or for the characterisation of gall inks' influence on the cellulose degradation mechanisms during natural or accelerated aging of cellulose [28-31] is highlighting the possibilities and limitations of using the FTIR methods for the analysis of manuscripts on paper.

2. Experimental

2.1. Materials

The model paper M is made from cotton linters submitted to an alkaline delignification, un-sized and containing no fillers, with a grammage of 25 g/m^2. The six different ink solutions that were manually applied had preparation methods according to Romanian Middle Age historically representative recipes [32-35] and the composition given in Table 1.

Table 1. Inks composition.

Ink	FeSO$_4$·7H$_2$O	Fe^{2+}/GA *	CuSO$_4$·5H$_2$O	Cu^{2+}/GA	GA	Arabic Gum	pH
	mol/l	mol/mol	mol/l	mol/mol	mol/l	g/l	
1	0.507	2.164	-	-	0.251	98.2	2.45
2	0.057	0.357	0.048	0.302	0.159	55.9	2.11
3	0.190	0.965	-	-	0.197	18.0	2.51
4	-	-	0.086	0.402	0.215	52.9	2.81
5	-	-	-	-	0.231	26.1	4.26
6	0.086	0.09	-	-	0.950	-	1.98

* The amount of gallic acid (GA) content, after the tannins hydrolysis processes.

Ink 5 formula consists of eliminating the soluble metal salt, basic compound in ink colour formation, while in ink 6 the binder (gum Arabic) is omitted as it only contains FeSO4·7H$_2$O and gallic acid.

2.2. Methods

The model paper (M), the papers containing gall ink solutions (abbreviations C1, C2, C3, C4, C5 and C6), along with the ingredients used in the experiments (FeSO$_4$·7H$_2$O, CuSO$_4$·5H$_2$O, gallic acid, gum Arabic and

quebracho tannins) were submitted to thermal ageing conditions performed at 105°C according to ISO 5630 1991/ASTM-D776-87 standards.

All FTIR spectra were recorded using a DIGILAB FTS 2000 spectrometer, in KBr pellets, averaged over 24 scans for the region 4000-400 cm^{-1}, with a resolution of 4 cm^{-1}.

3. Results and discussion

3.1. Gall ink components characterisation

3.1.1. Arabic gum

The FTIR spectra recorded for Arabic gum (Table 2) exhibits a broad band at ~3422 cm^{-1} assigned to the OH functional groups from the alcohols in polysaccharides and to the N-H vibration in the amines, while the peak in the range 2928-2930 cm^{-1} reflects the C-H absorption [36].

The bending modes of water molecules adsorbed in the sample are evidenced by the specific band at 1640 cm^{-1}.

Table 2. Absorption bands (expressed in cm^{-1}) in the FTIR spectra of un-aged and thermally degraded Arabic gum.

Un-aged	After 72 hours
3422	3424
2923	2928
	1645
1622	1616
1427	1429
1381	1381
1314	1312
1260	1260
1146	1144
1072	1072
910	
839	839
773	773
709	710
615	613
549	569
	457
434	439

The region 1200-1500 cm^{-1} - where some bands partially overlaps - covers distinct absorptions, due to the alcoholic OH functional group, to C-O and C-H vibrations. The peak at 1381 cm^{-1} is indicating the presence of the -CH_3 functional group, specific to some monosaccharide like rhamnose in the gum Arabic structure [36].

The intense peak at 1072 cm^{-1} may be assigned to the pyranose ring structure (C-O and C-C deformation vibrations) and C-O vibrations in alcoholic groups. The peaks at 910, 839 and 773 cm^{-1} reflects the 5- and 6- member rings in monosaccharide but also the -OH deformation vibrations in alcohols and carboxyls.

The FTIR spectrum recorded for the 72 hours thermally aged gum Arabic does not show essential changes in the absorption levels.

3.1.2. Gallic acid

Table 3. Peak table variations in the FTIR spectrum of gallic acid due to thermal ageing treatment (given in cm^{-1}).

Un-aged	After 72 hours
3489	3495
3366, 3287	3283
3065	3061
3010	2992
	2891, 2841
	2746
2656	2671, 2631
	2573
	2511
	1832
1707	
	1667
1620	1611
1541	1539
1468, 1447	1481, 1425
1373	1387
1339	
1310	1319
1246, 1204	1267, 1217
1101	1098
1026	1026
964	959
	903
868	864
789, 764, 730, 702	797, 768, 732
658	635
573	557, 530
436	471

The bands in the 3400-3500 cm^{-1} region are assigned to different OH functional groups (from carboxyl or phenols) and those between 2800 and 2980 cm^{-1} belong to stretching vibrations of the aliphatic and aromatic –CH (Table 3).

The peaks at 1707 cm^{-1} and 1246 cm^{-1} indicate the presence of carboxylic groups. The aromatic character of the compound is confirmed by the absorption bands at 1600-1620 cm^{-1}, along with the intense absorption at 864–868 cm^{-1}. The bands between 1200 and 1270 cm^{-1} represent the C-O deformation vibrations of phenols and carboxyl [37].

After 72 hours of accelerated ageing treatment, most of the bands in the FTIR spectrum of the gallic acid are broadened and shifted, thus reflecting the oxidative structural changes induced by the prolonged thermally ageing treatment.

Absorption in the range 3400-3200 cm^{-1} is increased, with peaks merged under the distinct bands at 3496 and 3283 cm^{-1}. The peak at 1707 cm^{-1}, attributed to C=O vibrations is shifted to 1667 cm^{-1}. The thermal treatment of gallic acid results in an increased absorption, with bands formation at 1425, 1320 and 905 cm^{-1} and broadening peaks at ~1380, 1267 and ~730 cm^{-1}, an indication on possible interactions between the functional groups of the acid.

3.1.3. FeSO4·7H2O

The OH group presence in the sulphate is marked as a broad absorption band between 3200 and 3500 cm^{-1}, with an increased intensity leading to a visible peak at ~3450 cm^{-1} after 72 hours of thermal ageing (Table 4). The bending vibrations of the adsorbed water molecules correspond to the characteristic band at ~1640 cm^{-1} [38].

Table 4. The peak positions (in cm^{-1}) from the iron sulphate ($FeSO_4 \cdot 7H_2O$) FTIR spectrum, before and after 72 hours of thermal ageing.

Un-aged	After 72 hours
3462, 3381, 3252	3458
1655, 1624	1638
1101	1125, 1015
989	
	827
	640
610	
	588
	536
	469
432	

The peaks in the FTIR spectrum sharply defined at ~1100 and 610 cm^{-1} are indicative for the SO_4^{2-} ions presence, along with bands visible at 989 cm^{-1} and 432 cm^{-1} [39, 40]. After accelerated ageing, the 1101 cm^{-1} band splits into two distinctive peaks at 1015 and 1125 cm^{-1}. The peaks occurring at 989 cm^{-1} and 610 cm^{-1} shift toward lower wave-numbers (827 cm^{-1} and 536 cm^{-1}), while new peaks appear in the spectra at 588 and 640 cm^{-1}.

3.1.4. $CuSO_4 \cdot 5H_2O$

The cooper sulphate contains adsorbed water molecules showing a large O-H stretching between 3200 cm^{-1} and 3500 cm^{-1} and a strong O-H bending at 1630 cm^{-1} [40].

Fundamental vibration bands of the SO_4^{2-} ions occurs in the 1100–1200 cm^{-1} domain (split into two components) and at 580-660 cm^{-1} [39, 40]. Intense vibrations are shown at 995 and 961 cm^{-1}.

Among peaks of lesser intensity at 1101, ~870, ~793, ~520 and 451 cm^{-1} in the IR spectra, the one at 1101 cm^{-1} disappears after the 72 hours duration of thermal treatment.

Table 5. The main absorption bands in the FTIR spectrum of $CuSO_4 \cdot 5H_2O$, un-aged and after being submitted to thermal accelerated ageing.

Un-aged	After 72 hours
3431	3426
1630	1632
1200	1202
1159	1153
1101	
995	995
961	961
864	870
795	793
660	660
604, 588	604, 588
521	519
451	451

3.1.5. The model paper

The IR crystallinity index for the cellulose in the model paper was evaluated as the intensity ratio between absorptions at 1427 cm^{-1} and 893 cm^{-1}

[41-43]. Figure 1 show how the IR crystallinity index changes during the thermal degradation, in agreement to the corresponding X-ray crystallinity index.
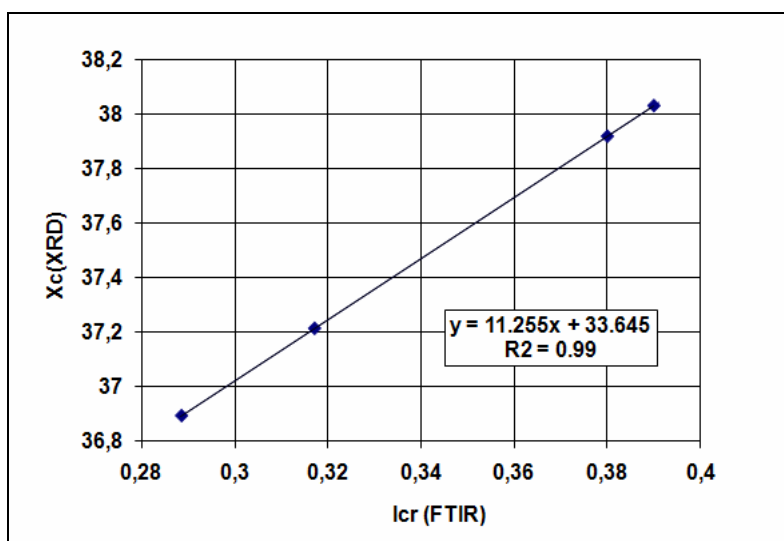

Figure 1. Correlation between IR crystallinity ($I_{Cr} = A_{1429}/A_{893}$) and X-ray ($X_C$, %) indices of cellulose, during the thermal degradation.

It appears that the slight advance in cellulose crystallinity during the thermal ageing is strongly related to the treatment time and implying only the amorphous fraction of cellulose. Along the thermal ageing processes, a certain amount of the bound water is eliminated through dehydration, leading to an increased density of hydrogen bonds between OH functional groups in cellulose without the involvement of water molecules. Under those circumstances, the oxidative decay of cellulose could not be accurately evaluated by means of FTIR techniques.

3.2. The characterisation of papers containing gall ink solutions

The changes detected after 24 hours and 72 hours in the absorbance levels of the FTIR spectrum, for the thermally degraded papers that were treated with gall ink solutions are presented in Table 6 and Table 7.

The complexity of a system consisting of ink and paper allows only for qualitative interpretation of the papers´ behaviour during thermal ageing treatments. The changes due to modifications of the papers´ structure or of the gall inks´ components are reflected in the shape, the intensity but also in the position of some peaks from the cellulose FTIR spectrum.

Table 6. The main absorption bands in the FTIR spectrum for the thermally degraded papers that were treated with gall ink solutions (C1, C3 and C6).

C1			C3			C6		
Un-aged	After 24 hours	After 72 hours	Un-aged	After 24 hours	After 72 hours	Un-aged	After 24 hours	After 72 hours
3449	3451				3451		3516	
3397				3397				
3335	3333		3327	3321	3300	3329	3319	3319
3298	3292			3267		3281	3296	
		3279	3275		3260		3269	3265
				3007	3080			2988
		3084			3005			
2914	2914	2914	2930	2913	2914	2926	2913	2943
2891	2889		2899	2872		2899	2882	2901
2859	2853	2853	2855		2855	2859	2859	
		2785		2779				
1738								
1722			1701				1726	
		1707	1684		1695	1701		1707
		1645	1645		1647	1638		
1599	1599			1595			1597	1612
			1558			1558	1547	
	1541	1537		1533		1543	1531	1530
1508	1530		1524		1518			
			1456		1462			
1423	1423	1423	1423	1423	1425	1425	1423	1425
1362	1356	1368			1368			1323
1321	1319	1319	1315	1315	1317	1315	1314	
1246	1236	1244		1236	1238		1233	1256
			1200			1207		
1153	1155	1153	1155	1155	1155	1153	1158	1153
1103	1109	1103	1103	1107	1107	1103	1111	1101
1016			1020			1020		
986	982	988	989	989	988	991	983	991
		903	901					899
818			791	835				
779	762			762		764	752	

Table 7. The main absorption bands in the FTIR spectrum for the thermally degraded papers that were treated with gall ink solutions (C2, C4 and C5).

C2			C4			C5		
Un-aged	After 24 hours	After 72 hours	Un-aged	After 24 hours	After 72 hours	Un-aged	After 24 hours	After 72 hours
	3397	3443	3528	3397			3447	3514
3325	3325	3319	3323	3327	3316	3329	3329	3319
	3294		3281	3296	3273		3304	
3271		3262			3227	3279	3272	3269
				3196	3146			3144
				3003	2953		3011	2986
2901	2911	2913	2924	2918	2901	2903		2899
	2882		2891	2872		2857	2914	
		2859		2859			2886	
	2777			2783			2777	
				2741				
			1788		1773			1771
1726			1734			1728		1732
			1715					
		1692	1686	1701				
	1628	1647	1643			1634		
1595	1597			1595	1601	1591	1595	1603
1531	1535	1545	1539	1535	1522		1537	1514
1425	1422	1423	1427	1420	1422	1423	1422	1423
		1366						
1315	1314	1317	1315	1315	1319	1315	1315	1319
1271								
	1240	1242	1244	1234	1248		1236	1254
1204	1200					1207	1202	
1155	1155	1153	1155	1155	1150	1155	1157	1152
1101	1103	1101	1103	1109	1097	1103	1107	1099
1020			1015	1045		1020		
993	993	988	989	984	988	997	988	989
901					899	905		903
		835		762	853		760	
816				712		800		
785	756							

Although hydrolytic pathway is prevalent in the paper degradation processes induced by gall inks [13, 44, 45], the catalytic role of transition metals (Fe, Cu) in the cellulose oxidative mechanism was recently pointed out using different analytical methods [46], including FTIR spectroscopy [47-49]. Therefore, an oxidation index for paper has been proposed as a ratio of integrals of bands at 1730 cm^{-1} to that at 1620 cm^{-1}, for the purpose of following the degradation of aged cellulose [49].

We have considered that an useful index could be defined as a ratio of peaks indicative for the global state of oxidation in cellulose (arising from groups like –CHO, -C=O, etc.) namely A(1707 ÷1740) cm^{-1} and the absorption at 1105 cm^{-1} (assigned to –C-O-C- vibrations in the pyranose ring). Table 8 is containing values that resulted on this basis for the papers treated with gall ink solutions.

Table 8. Values of the ratio of peaks indicative for the global state of oxidation in cellulose for the papers treated with gall ink solutions.

Sample	Ageing time, hours	$A_{1707, 1720, 1740}$ / A_{1105} ratio	Oxidation index (72h)/(0h)
C1	0	0.06	4.35
	72	0.261	
C2	0	0.04	7.15
	72	0.286	
C3	0	0.222	2.26
	72	0.503	
C4	0	0.062	1.28
	72	0.08	
C5	0	0.063	0.71
	72	0.045	
C6	0	0.182	0.93
	72	0.175	

In case of iron gall inks (samples C1, C3 and C6), the oxidation index displays a linear correlation to the Fe^{+2}/GA ratio (Figure 2), justifying the use of terms like 'balanced ink' or 'worst-case ink' in the paper conservation field [46, 50].

The results in Table 8 are supportive of the Cu^{2+} high catalytic potential and are suggesting that gum Arabic has a contibution in slowing down the deterioration process, although the hypothesis needs further investigations.
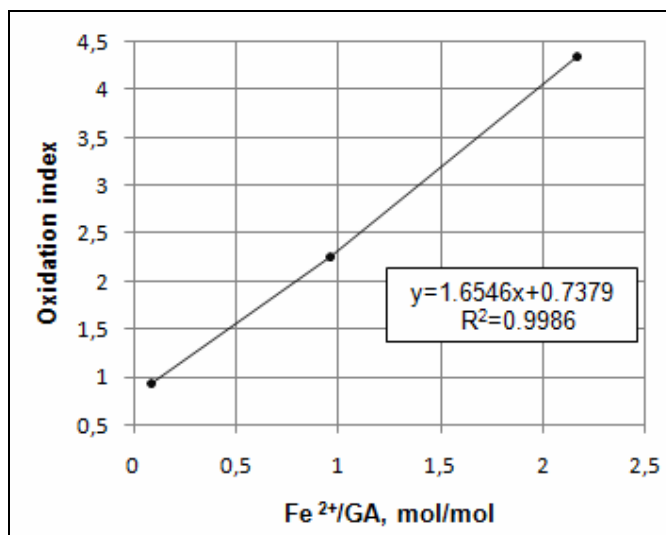
Figure 2. Correlation between the composition and the oxidising potential of iron gall inks.

5. Conclusions

- The FTIR spectroscopy techniques serve as effective tools for the global survey on changes promoted during accelerated ageing, not only in the iron gal ink components but also in the paper – ink assembly.
- For the studied model paper, the thermal ageing process is implying only the amorphous fraction of the cellulose.
- The catalytic role of iron and copper ions in the oxidative degradation of cellulose has been confirmed, in accordance to the literature, by means of the absorbance ratio $A_{(1707 \div 1740)\ cm^{-1}}/A_{1105\ cm^{-1}}$. The oxidation index for paper thus defined displays a linear correlation to the ratio of the main components in the gall inks, while gum Arabic exhibits a protective feature.

References

[1]   R.I. Capotă, *Abordarea strategică a conservării preventive a patrimoniului cultural mobil muzeal în România*, in *Restaurare. Ştiinţă şi artă*, C2 Design, Braşov, 2006, 7.
[2]   A. Moldoveanu, *Conservarea preventivă a bunurilor culturale*, 2nd edn., Centrul pentru Formare, Educaţie Permanentă şi Management în Domeniul Culturii, Bucureşti, 2003, 8.
[3]   M. Strlic, J. Kolar and S. Scholten, *Paper and Durability*, in *Ageing and Stabilisation of Paper*, M. Strlic & J. Kolar (eds.), National and University Library, Ljubljana, 2006, 3.
[4]   E. McCrady, Abbey Newsletter, **23** (1999) 4.
[5]   M. Cedzova and I. Gallova, Restaurator, **27** (2006) 35.

[6]   A. Baransky, A. Koniecna-Molenda, J.M. Lagan and L.M. Proniewicz, Restaurator, **24** (2003) 36.

[7]   J.M., Cardamone, K.M. Keister and A.H. Osareh, *Degradation and conservation of celluloses and their esters,* in *Polymers in Conservation,* N.S. Allen et al. (eds.), Cambridge Royal Society of Chemistry, London, 1992, 108.

[8]   J. Havermans and T. Steemers, *Air pollution and its prevention*, in *Ageing and Stabilisation of Paper,* M. Strlic & J. Kolar, (eds.), National and University Library, Ljubljana, 2006, 165.

[9]   M. Strlic, J. Kolar and D. Kocar, *Thermo-oxidative degradation*, in *Ageing and Stabilisation of Paper*, M. Strlic & J. Kolar, (eds.), National and University Library Ljubljana, 2006, 111.

[10] P. Bégin, Restaurator*,* **20** (1999) 1.

[11] G.R. Cass, J.R. Druzik, D. Grosjean, W.W. Nazaroff, P.M. Whitmore and G.L. Wittman, Research in Conservation*,* **5** (1989) 43.

[12] J. Kolar, M. Strlic, J. Malesic, J. Lemaire and D. Fromageot, *Photooxidative degradation,* in *Ageing and Stabilisation of Paper,* M. Strlic and J. Kolar, (eds.), National and University Library, Ljubljana, 2006, 149.

[13] A. Baranski, J.M. Lagan and T. Lojewski, *Acid-catalysed degradation*, in *Ageing and Stabilisation of Paper*, M. Strlic and J. Kolar, (eds.), National and University Library, Ljubljana, 2006, 93.

[14] R. Teygeler, Preserving paper: recent advances, in Managing preservation for libraries and archives. Current Practice and Future Developments, J. Feather (ed.), Loughborough University, Ashgate, 2004, 83.

[15] T. Steemers, *Damage survey of archives containing iron gall inks*, in *Iron gall inks: on manufacture, characterisation, degradation and stabilization*, J. Kolar and M. Strlič (eds.), National and University Library, Ljubljana, 2006, 20.

[16] A. Stijman, *Iron Gall Inks in History: Ingredients and Production*, in *Iron gall inks: on manufacture, characterisation, degradation and stabilization*, J. Kolar and M. Strlič (eds.), National and University Library, Ljubljana, 2006, 25.

[17] H. Neevel, *The development of in-situ methods for identification of iron gall inks*, in *Iron Gall Inks: on Manufacture, Characterisation, Degradation and Stabilisation*, J. Kolar and M. Strlič (eds.), National and University Library, Ljubljana, 2006, 147.

[18] P. Calvini and A. Gorassini, Restaurator, **23** (2002) 48.

[19] C. Remazeilles, E. Rouchon-Quillet and J. Bernard, Restaurator, **25** (2004) 220.

[20] P. Calvini, M. Silveira, E-Preservation Science, **5** (2008) 1.

[21] B. Sivakova, J. Senvaitiene and A. Kareiva, Mater. Sci., **14** (2008) 1.

[22] J. J. Jr. Workman, Appl. Spectrosc., **36** (2001) 139.

[23] V. Mosini, P. Calvini, G. Mattogno and G. Righini, Cell. Chem. Technol., **24** (1990) 263.

[24] K. Pandey, J. Appl. Polym. Sci., **71** (1999) 1969.

[25] K.L. Kato and R.E. Cameron, J. Appl. Polym. Sci., **74** (1999) 1465.

[26] M. Ali, A.M. Emsley, H. Herman and R.J. Heywood, Polymer, **42** (2001) 2893.

[27] L.M. Proniewicz, C. Paluskiewich, A. Weselucha-Birczynska, A. Baranski, D. Dutka, J. Molec. Struct., **614** (2002) 345.

[28] J. Senvaitiene, A. Beganskiene and A. Kareiva, Vib. Spectrosc., **37(1)** (2005) 61.

[29] J. Burandt, The Book and Paper Group, **13** (1994) 9.

[30] J. Senvaitiene, S. Beganskiene, L. Salickaite-Bunikiene and A. Kareiva, Lithuanian Journal of Physics, **46(1)** (2006) 109.

[31] P. Calvini, S. Vassallo, E-Preservation Science, **4** (2007) 13.

[32] Dionisie din Furna, *Erminia picturii bizantine,* Sophia, Bucureşti, 2000, 46.

[33] T. Pamfilie and M. Lupescu, *Cromatica poporului român*, Bucureşti, Academia Română, 1914, 211.

[34] M. Zerdoun Bat-Yehouda, *Les encres noires au Moyen Age (jusqu'à 1600)*, Editions du C.N.R.S., Paris, 1983, 306.

[35] I. Constantinescu, *O lume într-o carte de bucate. Manuscris din epoca brâncovenească,* Fundaţia Culturala Româna, Bucureşti, 1997, 169.

[36] S. Caruso, *Caratterizzatione ed invecchiamento di leganti pittorici a base di gomme vegetali*, Tesi di Laurea, Universita' degli Studi di Torino, Torino, 2006, p. 40, online http://aperto.unito.it/bitstream/2318/100/1/tesi_laurea_fulltext.pdf.

[37] D. Slawiñska, K. Polewski, P. Rolewski, J. Slawiñski, Int. Agrophysics, **21** (2007) 199.

[38] A. Pui and D.G. Cozma, *Bazele chimiei compuşilor coordinativi*, 2nd edn., Matrix Rom, Bucureşti, 2006, 162.

[39] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Theory and Applications in Inorganic Chemistry,* Wiley-Interscience, 2009, 392.

[40] N. Durães, I. Bobos and E. Ferreira da Silva, Revista de la sociedad española de mineralogía, **10** (2008) 126.

[41] H. Kasprzyk and K. Wichlach, Acta Sci. Pol., Silv. Colendar. Rat. Ind. Lignar., **3(1)** (2004) 73.

[42] Y. Kataoka and T. Kondo, Macromolecules, **31** (1998) 760.

[43] T. Röder, J. Moosbauer, M. Fasching, A. Bohn, H.P. Fink, T. Baldinger and H. Sixta, Lenzinger Berichte, **86** (2006) 34.

[44] X. Zou, T. Uesaga and N. Gurnagul, Cellulose, **3** (1996) 243.

[45] J. Kolar, and M. Strlič, *Ageing and stabilisation of paper containing iron gall ink,* in *Iron gall inks: on Manufacture, Characterisation, Degradation and Stabilisation,* J. Kolar & M Strlič (eds), National and University Library, Ljublijana, 2006, 181.

[46] A. Potthast, U. Henniges and G. Banik, Cellulose, **15** (2008) 849.

[47] L. Csefalvayova, B. Havlinova, H. Paulusova, A. Makova, M. Petrovicova, Chem. Listy, **99** (2005) 555.

[48] J. Kolar, M. Strlič and B. Pihlar: *Methodology and analytical techniques in studies of iron gall ink and its corrosion*, in *Iron gall inks: on manufacture characterization, degradation and stabilization,* J. Kolar & M. Strlič (eds.), National and University Library, Ljublijana, 2006, 95.

[49] J. Lojewska, P. Miskowiec, T. Lojewski and L.M. Proniewicza, Polym. Degrad. Stabil., **88** (2005) 512

[50] M. De Feber, J. Havermans and P. Defize, Restaurator, **21** (2000) 204.