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STUDY ON THE ROMANIAN HISTORICAL PARCHMENT BY MOLECULAR SPECTROSCOPY TECHNIQUES

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Cunoscând caracteristicile spectrale din domeniile IR si UV-VIS ale unui pergament nou, s-au studiat modificările acestora în pergamente româneşti din secolele XVI – XIX, în scopul identificării mecanismului prin care s-a produs degradarea acestora.

Changes in the IR and UV-VIS spectral characteristics of the Romanian parchments of XVI-XIX centuries were studied based on such characteristics known for a new parchment with the aim of identifying the damage mechanism in the former.

Keywords: spectral techniques, parchment, damage

1. Introduction

In its processing, use and long storage stages, the parchment as any organic structure is subjected to the destructive processes occurring because of some physical (inadequate treatments), physical-chemical (light, humidity, temperature, pollutants etc.) biological and microbiological (bacteria, fungi, micro-organisms) factors that lead to changes in the polypeptide chain structure [1].

Such changes occurring because of the oxidation, hydrolysis and gelatinization processes in collagen can be identified in the IR (middle and NIR) and UV-VIS spectra based on some characteristics bands as compared to those for a new parchment.

The work deals with the main destructive processes that altered the Romanian parchments of XVI-XIX centuries in the CMNM collection of Iassy.

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2. Experimental

Materials

Parchment samples were collected from CMNM-Iassy and ICPI (new kid parchment as control) to perform spectral analysis.

Samples were embedded into spectral KBr (Merck) for the IR analysis and used as such for UV-VIS-NIR analysis with diffuse reflectance accessory ILN-472.

Devices

The spectral analysis was performed by means of the following devices:

- FT-IR 620 Spectrometer, Jasco, Japan;
- UV-VIS-V570 Spectrometer, Jasco, Japan;
- The colour characteristics were measured by CIE-L*a*b* spatial chromatic system [2].

3. Results and discussion

Based on the known spectral characteristics of the parchment in the IR and UV-VIS-NIR [3, 4], some bands specific for the amide structure revealing the structure changes occurring in the damage process in the heritage objects were selected.

Thus, the 3420 cm^{-1} and 1550 cm^{-1} bands assigned to the amide I ($\nu C{=}O$) and amide II (δNH) structures and 3420 cm^{-1} band ($\nu OH + \nu NH$), and the distance between the two amide structures ($\Delta\nu = A_I - A_{II}$) were considered in the IR domain (Fig. 1).

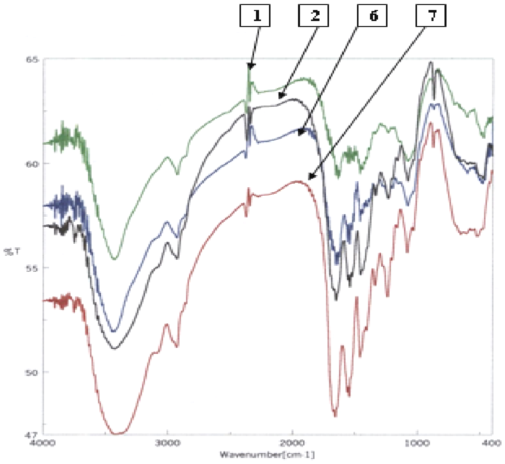

Fig. 1. IR spectra of the samples: 1, 2, 6 and 7

Based on the known absorbance for each absorption band the following parameters were calculated:

- A_I/A_{II} (amide I/amide II) and A_{OH}/A_I ratios providing information on the hydrolysis extent in the peptide chain;
- difference between the wave numbers specific for the amide structures ($\Delta\nu$) providing information on the chain denaturation [5];
- the band at ν = 1710 – 1740 cm^{-1} reveals the carbonyl/carboxyl structures arising in the oxidizing process [6].

In the UV-VIS-NIR domain, the amide structure has been identified by $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ (250-400 nm) transitions, and the hydroxyl structure has been identified by the 1450-1510 band specific for the collagen chain [7-11]. The band shift in the damaged parchment as compared to the initial one has provided information on the hydrogen bond strength in conection with the water content. The original colour changes also occur in the parchment damage. Their assessment by measuring the chromatic characteristics [2] is correlated with the oxidation process extent.

The main spectral characteristics resulting from the IR spectra are shown in Table 1.

Table 1.

IR characteristics of the samples

No.	Sample name	A_I/A_{II}	$\Delta\nu$	A_{OH}/A_I	$\nu_c = 0$
1	Incunabulum, sec. XV	1.04	96	1.128	-
2	Incunabulum back, sec. XV	1.03	111	1.100	-
3	Sewing Ligament, sec. XV	1.03	112	1.059	+
4	Anastasie Crimca, sec. XVII	1.02	111	0.976	+
5	G.D.Bibescu (1844)	1.02	112	1.140	-
6	V.Lupu (1635)	1.02	98	1.025	+
7	M.Basarab’s signet (1639)	1.02	110	1.074	-
8	Legislative Divan (1820)	1.06	90	0.983	+
9	Signet (Ghica Voda) (1855)	1.04	101	1.010	+
10	Ghica Voda (1856)	1.04	97	0.988	+
11	M.G.Sturza (1845)	1.06	99	1.129	-
12	Kaimacanul Domniei (1857)	1.05	114	1.243	-
13	Matei Basarab (1639)	1.03	110	1.059	-
14	Control (kid parchment- ICPI)	1.02	108	1.063	-

Allthough the samples were collected from parchments of different ages (XVI, XVII and XIX centuries), they have shown comparable hydrolysis levels (A_I/A_{II}) and only 4 % higher than in the control. The samples exceeding 110 cm^{-1} have shown more advanced denaturation assessed by means of $\Delta\nu$ value.

Hydrolysis level assessed from the A_{OH}/A_I ratio has shown generally values above 1.10 and a larger spreading because of the complex structures of both bands considered (3420 cm^{-1} and 1650 cm^{-1}). The samples ‘A. Crispea’ and

‘Divan legislativ’ have shown ν_{OH} bands below 3400 cm^{-1} (at 3337 cm^{-1} and 3365 cm^{-1}, respectively), revealing some associations made by inter-/intramolecular hydrogen bonds. Band shifts to values of 3420 cm^{-1}- 3440 cm^{-1} in the other samples suggested a molecular disturbance. Bands of very low intensities such as 1710 cm^{-1} – 1725 cm^{-1} for some samples have only shown some carbonyl/carboxyl structures resulting from the oxidation of lipids associated with collagen.

In the UV-VIS domain (Table 2), the bands assigned to –CONH- groups have shown bathochrome shifts by 10 nm up to 128 nm as compared to the control, thus revealing some structures with extended conjugation resulting most likely by oxidation of organic acids existent in the system.

Table 2

UV-VIS-NIR characteristics of the samples

No.	**Sample name**	**Λ_{CONH}**	**λ; nm**	**$\Delta\lambda_{OH}$**
		250-400	**NIR**	**NIR**
1	Incunabulum, sec. XV	284	1484	+23
2	Incunabulum back, sec. XV	306; 364	1476	+15
3	Sewing ligament, sec. XV	312; 398	1494	+33
4	Anastasie Crimca, sec. XVII	304; 348	1490	+29
5	G.D.Bibescu (1844)	306; 354	1484	+23
6	V.Lupu (1635)	298; 326	1500	+39
7	M.Basarab’s signet (1639)	302; 356	1484	+23
8	Legislative Divan (1820)	296	1492	+31
9	Signet (Ghica Voda) (1855)	308; 400	1482	+21
10	Ghica Voda (1856)	308; 358	1490	+29
11	M.G.Sturza (1845)	304; 348	1468	+7
12	Kaimacanul Domniei (1857)	304; 360	1490	+29
13	Matei Basarab (1639)	310; 402	1474	+13
14	Control (kid parchment- ICPI)	274	1461	=

The λ_{OH} bands in the heritage parchments have shown bathochrome shifts of 7 nm up to 39 nm as compared to those in the new parchments (λ = 1461 nm) in the NIR domain. Such shifts to higher wave lengths (lower wave numbers) revealed molecular associations by means of hydrogen bonds of inter-/intramolecular type [11].

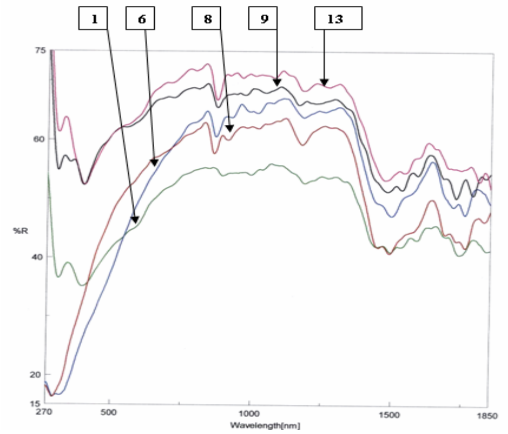

Fig. 2. UV-VIS spectra of the samples: 1, 6, 8, 9, 10

The data resulting from the spectral investigations on the heritage parchments of XVI-XIX centuries have revealed an ageing process occurring predominantly by denaturation in a relatively long period of time and leading to:

- irregular structures as a proof of the spread values for the A_{OH}/A_I ratio;
- oxidized structures in some parchments ($\nu = 1710\ cm^{-1}$ -$1740\ cm^{-1}$);
- structures showing extended conjugation, revealed in the 310 nm- 400 nm region;
- inter-/intramolecular crosslinked structures by removing water from the peptide chains with the involvement of OH groups in making inter-/intramolecular hydrogen bonds as a proof of the changes occurring in the 1450 nm-1510 nm region [12].

The whole ageing process has been developing by changes within the molecular geometry by the rearrangement of the inter-/intramolecular hydrogen bonds that was also revealed by the correlation of data on the OH group progress monitored by middle-IR and NIR spectra (Figure 3).

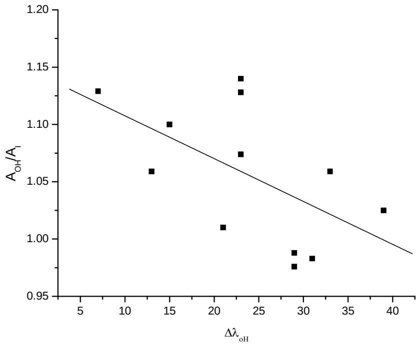

Fig.3. Change of A_{OH}/A_I ratio (IR mid) with $\Delta\lambda_{OH}$ (NIR)

The denaturation process has resulted to be predominant, mainly due to the changes in the levels of free water and water associated by hydrogen bonds in different ways.

4. Conclusions

Parchment samples collected from heritage objects of XVI-XIX centuries were investigated by IR (mid and NIR) and UV-VIS spectra to establish the mechanism they have been damaged. Based on the resulting data, the collagen denaturation with changes in the level of free water and water associated by inter-/intramolecular hydrogen bonds and formation of irregular and oxidized structures has been revealed to be predominant.

REFERENCES

[1] *Chiriță G., Chiriță M.* – „Chimia pielii”, the II-ed., Polytechnical Institute-Iassy, 1987.

[2] *** DIN 174, CIE-Lab, 1976 (Germania).

[3] *L. Miu, M. Giurginca* – Rev. Chimie, **57**, 1 (2006), p. 42 – 44.

[4] *T. Tite, L. Miu, M. Giurginca, A. Meghea* - Rev. Chimie, **57**, 5 (2006), p. 466.

[5] *M. Derrick* – „Evaluation of the State of Degradation of Dead Sea Scroll Samples Using FT-IR Spectroscopy”; Annual of the Book and Paper Group, the American Institute for Conservation, **10**, 1991.

[6] *A.T. Balaban., M. Banciu, I. Pogany* – „Aplicații ale metodelor fizice în chimia organică”, Ed. Ştiinţifică şi Enciclopedică, Bucureşti, 1983.

[7] *M. Egawa, T. Furuhara, M. Takahashi, Y. Ozaki* – Applied Spectroscopy, **57**, 4 (2003), p.473.

[8] *V.H. Segtman, S. Šašić, T. Issakssou, Y. Ozaki* – Anal. Chem **73** (2001), p. 3153.

[9] *S. Šašić, V.H. Segtman, Y. Ozaki*– J. Phys. Chem. **A106** (2002), p.760.

[10] *Y. Wang, K. Murayama., K. Myojo, R.. Tsenkova, H. Hayash., Y. Ozaki,* – J. Phys. Chem. **B102,** (1998), p. 6655.

[11] *Y. Wu, B. Czarnik-Matsusewicz, K. Murayama, Y. Ozaki,* – J. Phys. Chem., **B104** (2000), p. 5840.

[12] *I. Bădilescu, S. Bădilescu* – „Legătura de hidrogen”, Ed. Ştiinţifică şi Enciclopedică, Bucureşti, 1981.

[13] *E. Badea, L. Miu, P. Budrugeac, M. Giurginca, A. Masic., N. Badea, Della Gatta G.* – J. Thermal Analysis Calorimetry **91**, (2008), p.17-27.