"MATERIALS CHARACTERISTICS OF THE COLLECTION OF ARABIC MANUSCRIPTS OF THE GRANADA PROVINCE ARCHIVE BASED ON THE SCIENTIFIC ANALYSIS OF COMPONENTS"

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INTRODUCTION:

This work includes the results of the research conducted on the material characteristics of the collection of Arabic manuscripts, kept in the Historic Archive of Granada Province **(Figure 1)**. Its importance lies both in its subject matter, of legal character, and by their dating in the years immediately preceding and following the conquer of Granada, and due to the fact that they have all been executed on manufactured paper, although somewhat archaic, following the occidental techniques and processes. This work was supported by the Projects "*Aplicación de tecnologías de análisis específicas para el conocimiento de materiales y la mejora de los procesos de conservación de los manuscritos árabes de la Península Ibérica en los ss. X-XVII"* (MAT2008-02008MAT, granted by the Spanish Ministry of Science and Technology, I+D+I 2008-2011) and "*Caracterización de los materiales de manuscritos árabes de la Península Ibérica para la elaboración de un corpus documental"* (P08-HUM 04188, Excellency Project granted by the Andalusian Government, 2008).

RESEARCH AIMS:

According to the research protocols for the preservation of documentary heritage that our team has developed, the objectives proposed in this work are the following:

- Analyze the material composition of each manuscript.
- Characterize the documents highlighting the aspects related to the paper manufacture **[1]** and the composition of the inks.
- Establish key elements for providing data on the transition period between the Arab paper-making and the adoption of Western techniques and procedures.
- Contribute to a better knowledge of the materials with which to improve the conservation protocols and the specific restoration treatments for this type of document.

Figure 1.- Manuscripts 01, 03, and 07 from the Historic Granada Province Archive

EXPERIMENTAL:

The research was conducted by a multidisciplinary team of professionals from the University of Granada and the Materials Science Institute of Seville, using different techniques for the identification and analysis of materials forming the manuscripts.
Infrared spectroscopy was used. This technique has been scarcely employed on paper samples and on fibres used as binding in manuscripts. FT-IR spectra were recorded using a Nicolet 510 apparatus (source: Globar, detector: DTGS). Fibre samples were ground and prepared into KBr pellets (5 mg of sample in 100 mg of KBr). The spectra were collected in transmission (pellets) mode, in the 4000-400 cm^{-1} range, with a 4 cm^{-1} resolution. Morphological studies of fibres were performed by using an optical (Nikon HOPTIHOT) and scanning electron (HITACHI S-4800) microscopes (SEM). An energy dispersive X-ray analyser (EDX) coupled to SEM, was employed for elemental analysis of inks. The samples were coated with a gold film before the SEM-EDX study.

RESULTS AND DISCUSSION:

OPTICAL AND ELECTRONIC MICROSCOPY: In all the cases, some indications were followed **[2,3]** for the morphological identification of the fibres. Flax was identified in all the fibres analysed **(Figure 2)**. Fibres were damaged and in some cases (fibres 7 and 15), biological activity was observed.

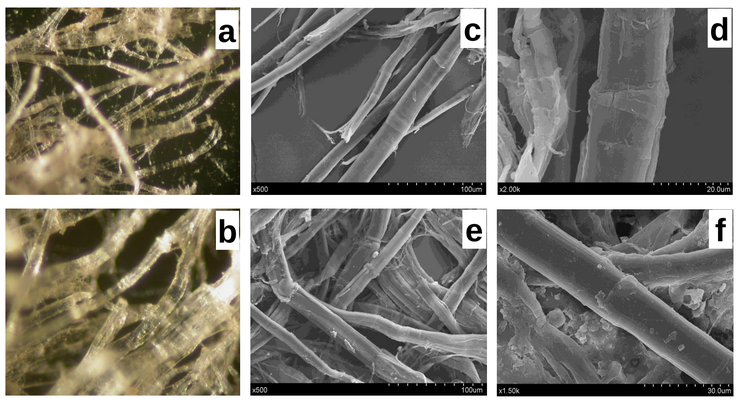

Figure 2.- Microphotographies of: a) fibre 3 (optical microscopy x100); b) fibre 5 (optical microscopy x200), c) fibre 2 (SEM); d) fibre 7 (SEM); e) fibre 9 (SEM); f) fibre 18 (SEM)

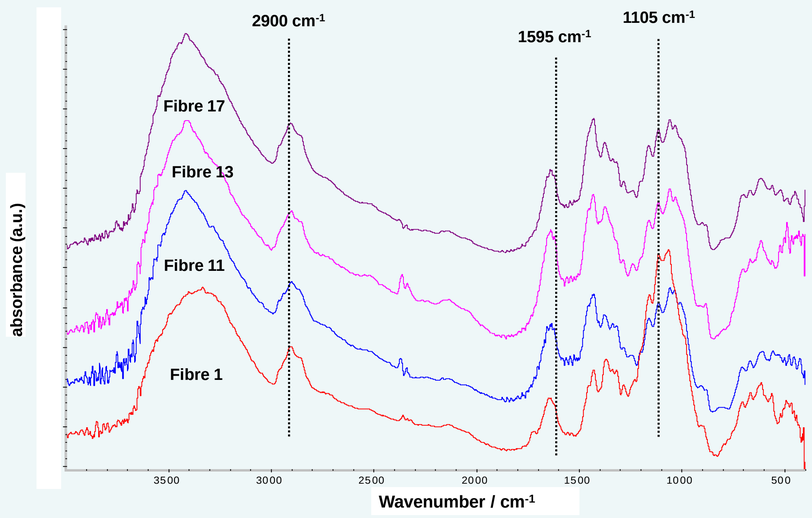

Figure 3.- Infrared spectra from fibres 1, 11, 13 and 17

INFRARED SPECTROSCOPY: Two ratios were calculated to distinguish between fibres: $R1=I_{1595}/I_{1105}$ and $R2=I_{1595}/I_{2900}$ (**Figure 3** and **Table 1**). Bands in spectra situated at 1595 cm^{-1} were referred to groups C=C and assigned to lignin; bands at 1105 cm^{-1} to glycosidic band C-C in polysaccharides (cellulose compounds); and bands at 2900 cm^{-1} were associated to general organic material (groups $-CH_2$, $-CH_3$, methyl and ethyl) **[4,5]**. Depending on the theoric cellulose, hemicellulose, pectin and lignin percentages, and on the ratios R1 and R2, four different theoretical regions were defined, corresponding to flax, jute, hemp and cotton (**Figure 4**). Infrared spectra corresponding to twelve of the samples were collected and the ratio values calculated. The results indicate that all the samples correspond to flax fibres (**Figures 3** and **4**, and **Table 1**).

Fibre Sample	I_{1105}	I_{1595}	I_{2900}	R_1	R_2	Identification
1	0.125	0.039	0.078	**0.31**	**0.50**	Flax
2	0.024	0.012	0.027	**0.50**	**0.44**	Flax
4	0.028	0.020	0.024	**0.71**	**0.83**	Flax
5	0.058	0.023	0.027	**0.40**	**0.85**	Flax
9	0.048	0.019	0.023	**0.40**	**0.83**	Flax
10	0.048	0.032	0.039	**0.67**	**0.82**	Flax
11	0.094	0.060	0.108	**0.64**	**0.55**	Flax
13	0.057	0.030	0.052	**0.53**	**0.58**	Flax
15	0.037	0.033	0.015	**0.89**	**2.20**	-
17	0.092	0.048	0.100	**0.52**	**0.48**	Flax
19	0.048	0.042	0.058	**0.87**	**0.72**	Flax
20	0.149	0.108	0.124	**0.72**	**0.87**	Flax

Table 1.- I_{1105}, I_{1595} and I_{2900} cm^{-1}, and R1 and R2 values, corresponding to the 12 samples studied by spectroscopic methods

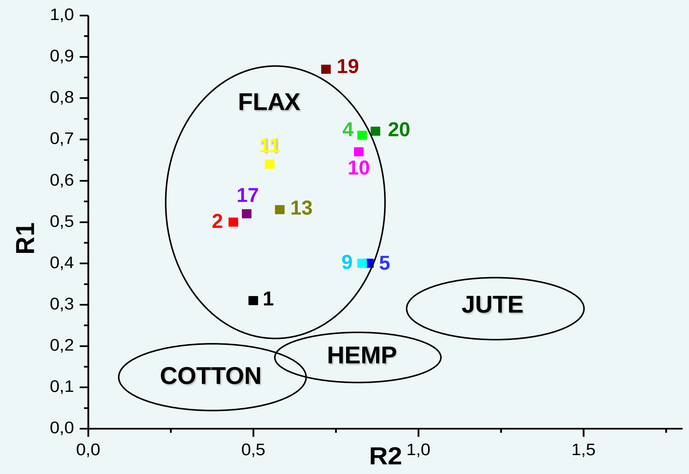

Figure 4.- Representation R1⊥ R2 of the 12 samples studied by infrared spectroscopy, defining the different types of cellulose fibres

INK SAMPLES	DESCRIPTION	ELEMENTAL COMPOSITION
t2-1 (42/115)	Main ink	**C**, **O**, Na, Mg, Al, Si, Cl, K, **Ca**, Fe
		C, **O**, Na, Mg, **Al**, **Si**, S, Cl, **K**, **Ca**, **Fe**
		C, **O**, Na, **Mg**, **Al**, **Si**, K, Ca, Ti, Fe
		C, O, Al, Si, **S**, **Cl**, K, **Ca**
		C, **O**, **Si**
		C, **O**, Na, Mg, **Al**, Si, S, Cl, K, **Ca**, Fe
t2-2 (60/147)	Margin ink	C, **O**, Na, **Al**, **Si**, S, K, Ca, Fe
		C, **O**, Mg, **Al**, **Si**, S, K, **Ca**, Fe
		C, O, Na, Mg, **Al**, **Si**, K, Ca, Fe
		C, **O**, Na, Mg, Al, Si, **S**, K, **Ca**, **Fe**
		C, O, Na, Mg, Al, Si, **S**, K, **Ca**, Fe
		C, **O**, Na, Mg, Al, Si, S, K, **Ca**, **Fe**
t2-3 (103/60)	Signature	C, O, **Al**
		C, O, Al, S, Ca
t3-1 (150/95)	Main ink	C, **O**, **Mg**, **Al**, **Si**, P, K, **Ca**, Fe
		C, O, **Mg**, **Al**, **Si**, P, K, **Ca**, Fe
		C, O, Mg, Al, **Si**, K, **Ca**, Fe
t3-2 (195/130)	Margin ink	C, O, Al, Si, **P**, S, Cl, K, **Ca**, Fe
		C, **O**, Mg, **Al**, Si, **S**, K, **Ca**, **Fe**
		C, O, Mg, Al, Si, S, K, **Ca**, Fe
t4-1 (90/60)	Main ink	**C**, O, **S**, Cl, **Ca**
		C, **O**, Na, **Al**, **Si**, **S**, Cl, **Ca**
		C, O, Mg, Al, Si, S, Cl, **Ca**, Fe
		C, O, S, Cl, **Ca**
		C, O, Na, Mg, **P**, **S**, Cl, K, **Ca**
t4-2 (140/170)	Margin ink	C, **O**, **Si**, Ca
		C, **O**, Mg, Al, Si, S, Cl, K, **Ca**, Fe
t5 (160/245)	Main black ink	**C**, **O**, Na, Mg, Al, Si, S, K, Ca, **Fe**
		C, **O**, Na, Mg, Al, Si, **P**, **Pb**, K, **Ca**, Fe
t8 (15/50)	Main black ink	**C**, O, Na, S, Cl, K, Ca
		C, **O**, Mg, **Al**, **Si**, Ca, **Fe**
		C, **O**, Mg, Al, Si, S, K, **Ca**, **Fe**
		C, **O**, Na, Mg, Al, Si, S, Cl, K, **Ca**, **Fe**
		C, **O**, Na, Mg, Al, Si, **S**, K, **Ca**, Fe
t10 (200/230)	Main black ink	C, **O**, Na, Mg, **Al**, **Si**, S, K, Ca, Fe
		C, O, Mg, Al, Si, **P**, **Ca**
		C, O, Mg, **Al**, **Si**, K, Ca, Fe
		C, O, Al, Si, Ca
t12-1 (22/60)	Black ink (reverse)	**C**, **O**, Na, Mg, **Al**, Si, P, S, K, **Ca**, **Fe**
		C, **O**, Na, Mg, **Al**, Si, P, S, K, Ca, **Fe**
		C, **O**, Na, Mg, **Al**, Si, P, S, K, **Ca**, **Fe**
t12-2 (58/60)	Black ink (anverse)	**C**, **O**, Na, Mg, **Al**, Si, S, K, Ca, Fe
		C, **O**, Na, Mg, **Al**, **Si**, **K**, Fe
		C, **O**, Na, Mg, **Al**, Si, S, Cl, K, Ca, **Fe**
t13 (40/18)	Black ink	**C**, O, S, Cl, K, Ca
		C, **O**, Na, Mg, Al, Si, S, K, **Ca**, Fe
		C, O, **Al**, **Si**, S, K, **Ca**, Fe
		C, O, **Al**, **Si**, **S**, **K**, **Ca**, **Fe**
		C, **O**, Na, Al, Si, **S**, K, Ca, **Fe**
t15 (15/13)	Black ink	**C**, **O**, Na, Mg, Al, Si, P, S, K, **Ca**, Fe
		C, **O**, Na, **Al**, **Si**, S, K, Ca, Fe
		C, **O**, Al, Si, **S**, **Ca**, K, Fe
		C, **O**, Al, Si, S, K, Ca, **Fe**
		C, **O**, **Al**, **Si**, S, K, Ca, Fe
		C, **O**, **Mg**, **Al**, **Si**, K, Ca, Fe
t17 (110/15)	Black ink	**C**, **O**, Na, Mg, **Al**, Si, S, K, **Ca**, **Fe**
		C, **O**, Na, Mg, Al, Si, S, K, **Ca**, Fe
t18-1 (86/86)	Black ink 1 (reverse)	**C**, **O**, Na, Mg, Al, Si, S, Cl, K, Ca, Fe
		C, **O**, Mg, Al, Si, S, Cl, K, **Ca**, Fe
		C, **O**, Mg, Al, Si, S, Cl, K, Ca, Fe
		C, O, Na, Mg, Al, Si, P, S, Cl, K, Ca, Fe
t18-2 (23/125)	Black ink 2 (anverse)	**C**, O, Na, Mg, Al, Si, S, K, Ca, Fe
		C, O, **Al**, **Si**, **K**, Fe
t20-1 (19/62)	Black ink	C, **O**, Na, Mg, **Al**, **Si**, **S**, K, **Ca**, **Fe**
		C, **O**, **Al**, Sr, **P**, S, Ca, Fe
		C, O, Na, Mg, Al, Si, S, K, **Ca**, Fe
		C, **O**, Mg, **Al**, **Si**, S, Cl, K, Ca, Fe
		C, **O**, Na, Mg, Al, Si, **S**, K, Ca, **Fe**
t20-2 (135/75)	Signature and corrections	C, O, Mg, **Al**, **Si**, **K**, Ca, Ti, Fe
		C, O, Al, Si, K, Ca, **Fe**
		C, **O**, **Si**
t21 (65/160)	Black ink	C, O, **S**, **K**, **Ca**, Fe
		C, **O**, Mg, **S**, K, Ca, Fe
		C, **O**, **Mg**, **Ca**
		C, **O**, Na, Mg, Al, Si, **S**, K, Ca, Fe
		C, O, S, **K**, **Fe**

Table 2.- Results obtained from elemental analyses performed on inks by SEM-EDX (some analyses were performed on each ink sample). Boldface letters indicate those elements whose intensity is higher than the others.

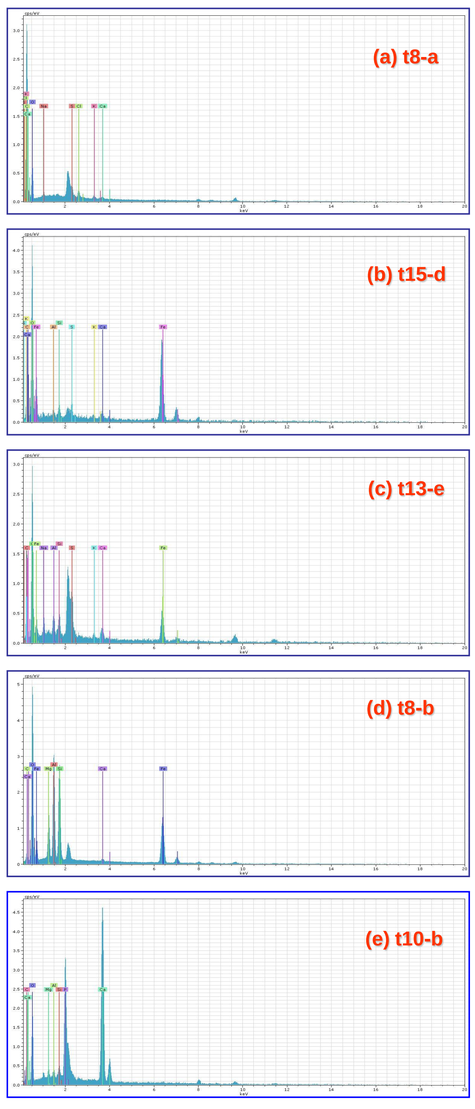

Figure 5.- EDX spectra corresponding to some of the analyses performed on the following black inks: (a) t8-a; (b) t15-d;(c) t13-e; (d) t8-b; (e) t10-b

SCANNING ELECTRON MICROSCOPY-ENERGY DISPERSIVE OF X-RAYS (SEM-EDX): Among the black ink components, carbon has been detected in high amounts in some of the EDX analyses (**Table 2** and **Figure 5a**). The identification of carbon in this type of samples is difficult due to the fibres composition itself. Iron was also detected, only (**Table 2** and **Figure 5b**) together with sulphur in some ocassions (**Table 2** and **Figure 5c**), and silicon and aluminum in others (**Table 2** and **Figure 5d**), which we respectively attribute to the presence of iron oxide, iron gall ink and possibly of some type of alumino-silicate compounds contaning iron. In addition, the presence of phosphorus has been observed (**Table 2** and **Figure 5e**), which can be attributed to the addition of ivory black that had been added to give the ink a deeper black hue. Calcite, dolomite, quartz and gypsum particles were also detected. In some analyses, aluminium in high amount appears, which together to the presence of silicon show that some type of iron-based earth compound was employed in the fabrication of the iron gall ink.

CONCLUSIONS:

This study includes the most outstanding characteristics related to the elaboration of this type of documents, their physical examination and chemical analysis of both paper and inks during this period. Physical examination shows that the manufacture of paper continued the Italian papermaking protocols, though in a somewhat archaic way. Chemical analysis indicate that the materials and procedures used by the Arab tradition continued. Our aim is to contribute to the reconstruction of the history of paper in Spain, providing new data about the transition from Arab to Western paper in this period of the Iberian Peninsula history.

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