XRF and FTIR Analysis of certain African historical documents

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BACKGROUND

Analysis of the history of paper production shows that there was a marked change in the paper making process around 1850 AD. This was mainly due to the shift from using potassium aluminium sulphate (alum) to aluminium sulphate (paper maker's alum) as the sizing agent [1]. It has been observed that such a change in sizing agent was associated with increasing acidity of the paper produced [2]. Transition metals like iron (Fe), copper (Cu) and manganese (Mn) play a significant role in influencing the oxidative degradation of cellulose through their catalytic action. The presence of such transition metal ion species, though in trace quantities, is potentially detrimental to the oxidative stability of paper. It therefore means the detection of these ion species in historical documents is of importance from a document conservation point of view. Knowledge of the compounds used to manufacture the paper and ink, their acidity, and their degradation products allows us to try to describe the degradation mechanisms and consequently to avoid them [3]. Information about compounds found in the composition of degraded inks, as well as the influence of oxidation in cellulose when using different de-acidifying solutions [4] such as calcium hydroxide, calcium bicarbonate, or magnesium bicarbonate—can be very useful when studying the degradation of paper or manuscripts [5].

JUSTIFICATION OF THE STUDY

The material composition of most of African historical documents is not known. It is therefore not possible for curators and conservators to implement a comprehensive conservative action for such documents unless their constituent material composition is determined. This work therefore seeks to determine the material composition of certain historical document obtained from the National Library of South Africa (NLSA) and from Timbuktu. Knowledge of the transition metals ions present in the sampled historical documents is also essential.

Aim and Objectives

The extent to which the composition of the paper itself affects its stability was investigated. In order to achieve this, the following objectives have been identified;

a) Determination of the elemental composition of the documents.

b) Identification of the sizing material, fillers and any other organic inclusions in the paper.

c) Evaluation of the crystallinity and oxidation indices of the fibres of the document samples.

MATERIAL

Table 1: List of historical documents investigated

Sample No.	Title	Classification	Publication date
1	Het Leven en Bedryf	Book	1732
2	South Africa (Barrow)	Book	1803
3	The 19th Century (Vol 33)	Book	1893
4	The Press	Newspaper	1893
5	The 19th Century (Vol 39)	Book	1896
6	The Weekly Press	Newspaper	1897
7	Regulatien:Staatsbiblioteek	Periodical	1897
8	The Weekly Press	Newspaper	1899
9	Timbuktu	Manuscript	Unknown
10	Natal Almanac & Directory	Periodical	1901
11	Die Huisgenoot	Periodical	1918
12	The Standard	Newspaper	1925
13	The Courier	Newspaper	1946
14	Wild Sport of Africa	Book	1844

MATERIAL

TYPICAL SAMPLE IMAGES

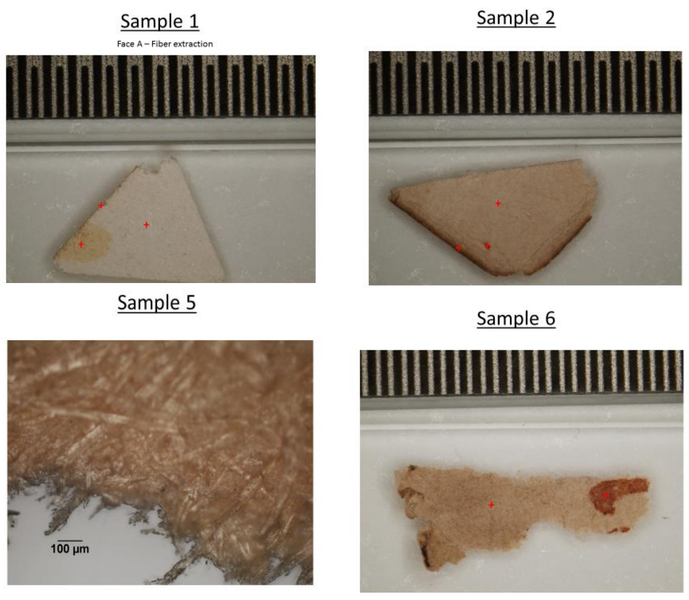

Fig 1. Typical images of some samples listed in table 1.

METHODOLOGY

XRF MEASUREMENTS

The elemental composition of the samples was determined by energy dispersive X-ray fluorescence (ED-XRF) analysis. This method was chosen for the elemental analysis of the solid paper/document samples because it requires little or no sample treatment or preparation. An energy dispersive X-ray fluorescence spectrometer, Shimadzu EDX-720 was used. The spectra were recorded in air and the instrument energy range was automatically set at 0 to 40 keV.

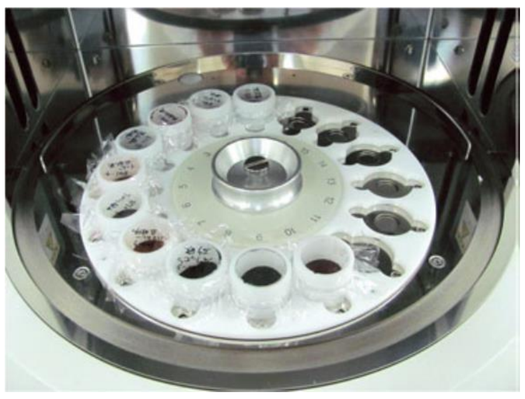

Fig 2. Shimadzu 16-turret solid sample holder used

FTIR MEASUREMENTS

The FTIR measurements were done in reflection mode by use of Attenuated Total Reflection (ATR). A ZnSe ATR crystal was used on a Bruker FTIR machine

Fig 3. Bruker FTIR spectrometer used to determine sizing and crystallinity indices

This crystal has a refractive index of 2.4 at wavenumber of 1000cm^{-1} and a cut-off spectral range of 520cm^{-1}. The penetration depth for this crystal is stated as 2µm meaning that it is a surface analysis instrument. The crystal was pressed against the sample to ensure that there is sufficient contact between the crystal and sample. FTIR spectra were collected for analysis for all samples and the results are presented.

RESULTS

XRF RESULTS

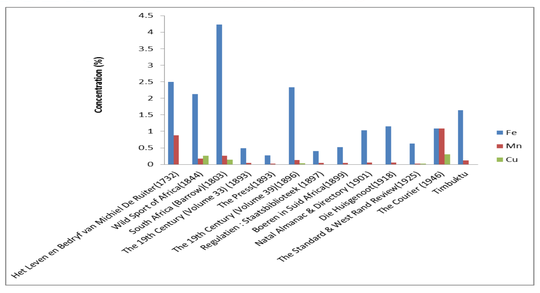

Fig 4 (a). Elemental composition of Fe, Mn and Cu in the samples.

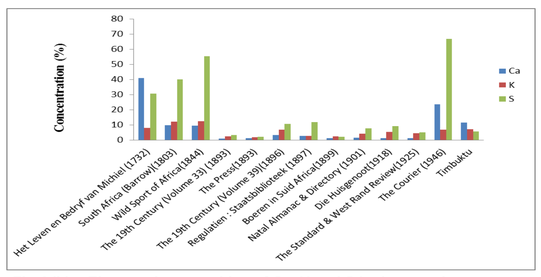

Fig 4 (b). Elemental composition of Ca, K and S in the samples

FTIR RESULTS (selected spectra)

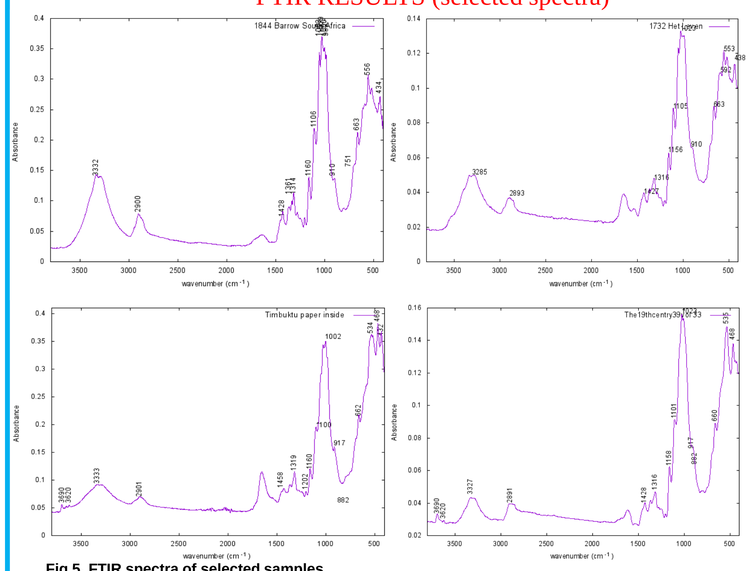

Fig 5. FTIR spectra of selected samples

Table 2: Measurement of Crystallinity Indices: TCI and LOI..

Sample Name	Publication date	I_{1372} (1339 -1390) cm^{-1}	I_{2900} (2830 -2959) cm^{-1}	Total Crystal.Index	I_{1420} (1458 -1407) cm^{-1}	I_{1372} (917 -882) cm^{-1}	LOI
Het Leven en Bedryf	1732	0.432	0.054	0.125	0.121	0.04	3.03
South Africa (Barrow)	1803	0.814	0.134	0.165	0.206	0.087	2.37
Wild sport of Africa	1844	0.531	0.077	0.145	0.143	0.050	2.86
The 19th Century (Vol 33)	1893	0.712	0.083	0.117	0.179	0.144	1.24
The Press	1893	0.325	0.033	0.101	0.067	0.228	0.29
The 19th Century (Vol 39)	1896	0.164	0.012	0.073	0.030	0.031	0.97
Regulatien:Staatsbiblioteek	1897	0.512	0.056	0.109	0.128	0.097	1.32
Timbuktu	Unknown	0.528	0.106	0.200	0.103	0.295	0.35
Natal Almanac & Directory	1901	0.034	0.394	0.086	0.103	0.163	0.63
Die Huisgenoot	1918	0.716	0.094	0.132	0.145	0.296	0.49
The Standard	1925	0.291	0.051	0.175	0.074	0.164	0.45
The Courier	1946	0.265	0.073	0.275	0.053	0.025	2.12

Table 3: A summary of filler material detected in the samples under investigation. The detected fillers are shown with a tick (√) together with the observed absorption bands in cm^{-1}.

Sample	Filler												
	Kaolin				Calcium Carbonate			Gelatine		Clay			
	1032	1004	524	470	1415	874	710	1650	1550	3690	3620	1000	910
The Courier	√		√	√		√	√						
Timbuktu	√	√	√	√			√	√	√	√	√	√	√
The Standard			√	√						√	√	√	√
Die Huisegnoot	√	√	√	√						√	√	√	√
Natal Almanac										√	√	√	√
Regulatien	√	√	√	√						√	√	√	√
The Press	√	√	√	√						√	√	√	√
The19th Cent. V33										√	√	√	√
Het Leven en	√		√	√	√		√			√	√	√	√
Wild Sport Africa	√	√	√	√						√	√	√	√
Barrow South Africa	√	√	√	√	√	√	√			√	√	√	√

CONCLUSION

The concentration of Fe remained considerably high for all the samples studied. These results emphasize the importance of Fe in paper degradation and that conservation efforts should aim to slow down/arrest the adverse effects of Fe. The catalytic effect of Fe can be inhibited in an alkaline environment. This means that mass de-acidification undertaken by some libraries and archives can effectively extend the shelf lives of their collections. The presence of Ca also ensured that there is a sufficient alkaline buffer so that the paper remains of archival quality. The samples are made up mainly of cellulose with the exception of *The Courier*. This sample also showed absorption peaks of hemicellulose and lignin. The samples studied had Total Crystallinity Index (TCI) values that ranged from 0.073 (19th Century Vol. 39) to 0.275 (The Courier). The *Het Leven* sample had the Lateral Order Index (LOI) of 3.03 while the *Timbuktu* and *The Press* samples had the lowest LOI values of 0.35 and 0.29 respectively. All samples except *The Courier* had clay as the filler material. Traces of $CaCO_3$ were found only in *The Courier, Timbuktu, Het Leven* and *South Africa (Barrow)*. *Het Leven and South Africa (Barrow)* also had high levels of Ca and these two samples are also in good physical condition. The Timbuktu sample had only a weak shoulder band at 710 cm-1. This may mean that the detected $CaCO_3$ was in small concentrations.

ACKNOWLEDGEMENTS

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