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Dedicated to Professor Bernhard Wunderlich on the occasion of his 65th birthday

THERMAL ANALYSIS OF CODEX HUAMANTLA AND OTHER MEXICAN PAPERS*

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Abstract

The application of thermal analysis and other techniques to determine the thermal and mechanical history of an object is extended to investigate the method of manufacturing of ancient papers. The Humboldt Fragment number six of the Codex Huamantla and other Mexican papers are analyzed by means of Differential Scanning Calorimetry (DSC) and Thermogravimetry-Mass Spectroscopy (TG-MS). The results reveal mechanical treatment or beating of the raw material and also indicate, that the two cultures exchanged knowledge about the paper making. The simplicity and speed of thermoanalytical methods make them a good choice to screen samples for composition and origin. With the addition of more elaborate techniques, such as X-ray analysis, IR spectroscopy, evolved gas analysis by mass spectrometry and microscopy, a definitive classification can be reached easily.

Keywords: Codex Huamantla, paper making, thermal analysis, thermal and mechanical history, thermogravimetry-mass spectroscopy

Introduction

Paper is a material which played a major role in the development of cultures all over the world. Depending on the vegetation, the discovery of paper is tied to different raw materials. The bark of certain trees has been used as a writing material in various periods and localities. As a result the Latin word for the inner bark, 'Liber' is the basis for our word 'library' [1].

Huun and Amatl were the writing material of the Maya and Aztec people, somewhat related to the papyrus of the Egyptians, Greeks, and Romans. A remnant of this ancient craft as practiced hundreds of years ago in the Western Hemisphere exists to the present day in the work of the Otomi Indians of southern Mexico [2, 3]. Bark-beating among the tribes of Middle America is

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perhaps as ancient as is this aboriginal civilization. Before Christopher Columbus set foot in the Lesser Antilles, a substance resembling paper was in use by the Maya, the foremost tribe of the Yucatan peninsula. The making of this beaten bark material, which was known as *huun* went hand in hand with Mayan intellectual development and finally with the advent of hieroglyphic writing; these ancient peoples actually constructed books.

The amatl paper was made from the inner bark of a noraceous tree; of these trees there are 55 genera and more than 700 species, of wide distribution, nearly 600 being comprised in the single genus *Ficus*. The family also includes the important genera Morus (mulberry), *Cannabis* (hemp, etc.). Several of the species used for making paper were *Ficus padifolia, Ficus involuta,* and *Ficus petiolaris* (fig tree).

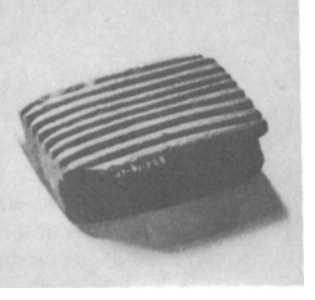


Fig. 1 Stony beater used in the production of ancient Mexican papers

The method of the Otomi paper makers in southern Mexico to make paper is only remotely related to true paper formed from disintegrated fibre upon molds. The bark, an inch or more in width, is taken from the trees in as long strips as possible. The dark outer bark is then removed, leaving the fibrous inner bark as the usable material. The inner bark is boiled over a slow fire in a homemade cauldron containing water and wood ash. If the fibers are old and hard, a liquid residue obtained from cooking corn is used. After boiling the strips of bark fibre, having become disintegrated to some extent, are laid side by side upon a rectangular board that is a little larger in size than the dimensions of the paper being made. The strips of bark, each strip slightly overlapping the next, are then pounded and smoothed with a stone, or in some localities a smoothing tool is made by burning a corncob until it becomes hard. After the strips of bark have been beaten (Fig. 1) and united into a sheet the board with its deposit of crude paper is placed in the sun to dry, when the stratum of fibre can easily be removed. Reports from the days of Columbus indicate that the same method, except for the boiling of the strips, was used 500 years ago.

Papyrus, huun, amatl and tapa can be placed in the same category of paper making. None of these substances is true paper made from disintegrated fibre upon porous molds, the technique conceived and used by the Chinese.

The cultures of Central America invented the making of paper to conserve their knowledge and to communicate it from one location to another as well as others did. The Franciscan Fray Toribio Benavente writes: "Paper is made from 'metl' (agave), and they make much of this today in Tlaxala. There are also trees, whose bark they take to make paper, called 'amatl' (fig tree)" [2–5].

Paper of the Maya and Aztec Cultures

The investigation of primitive papermaking in American cultures [1] is still inconclusive and the function of paper in Aztec and Mayan civilizations is not fully known. It is known, that the tunics from bark cloth were further developed into sheets to write hieroglyphic symbols. Ever since the bark cloth ceased to be mere body covering but had another use, it was a paper. This paper, called 'huun' by the Mayas, was far superior to the Egyptian papyrus both in texture and durability. The manufacture of these hieroglyphic charts can be followed throughout centuries even through the decline of the Mayas.

The Toltecs assimilated and improved the Mayan techniques of papermaking and writing. In the seventh century they finished the encyclopedic Teoamoxtili, a 'divine book' compiled at Tula in the year 660 by the astrologer, Huematzin. Yet they too, like the Mayas before them, went into eclipse and the Aztec nation appeared between 1100 and 1300 on the cultural horizon. Under their sway, much of Middle America was systemized. Trade and conquest, an inseparable union, expanded together, tribute was levied upon conquered tribes. To keep a record of all this called for precisely written tribute lists. And so there was an insistent demand for paper as in no other primitive American civilization.

The paper of the Aztecs was made from the bast fibers of the amatl-tree; not in a single fragment the paper was made from any other substance than the wild fig free. Neither the Mayas nor Aztecs made paper from the maguey agave [6]. Examination disclosed that the fibers of the Maya codices – which were made from wild fig trees of the tierra caliente – differed in their histology from those taken from the Aztec codices, prepared from the bast fibers of the fig trees and the tierra fria. It is then obvious that the paper of the Mayas came from the species in their own lowland areas, while that of the Aztec fragments was always from those that grew on the plateau and hillsides. Comparative studies of processes and techniques lead to the conclusion that the Mayas preceded the Aztecs. The Aztecs then improved the Maya methods. In order to create a non-blotting surface, they used stone, flat iron-shaped planches which, when heated and pressed upon the paper, closed the pores, and gave it 'surface,' which is more or less the same technique the European paper makers used during the Renaissance in their burnishing, by means of an agate-stone.

Although many rolls and sheets of papers have been discovered, there are only three complete Mayan codices (the Dresdensis, the Peresianus and the Tro-Cortesanius) known and there is scarcely more than a score of Aztec codex

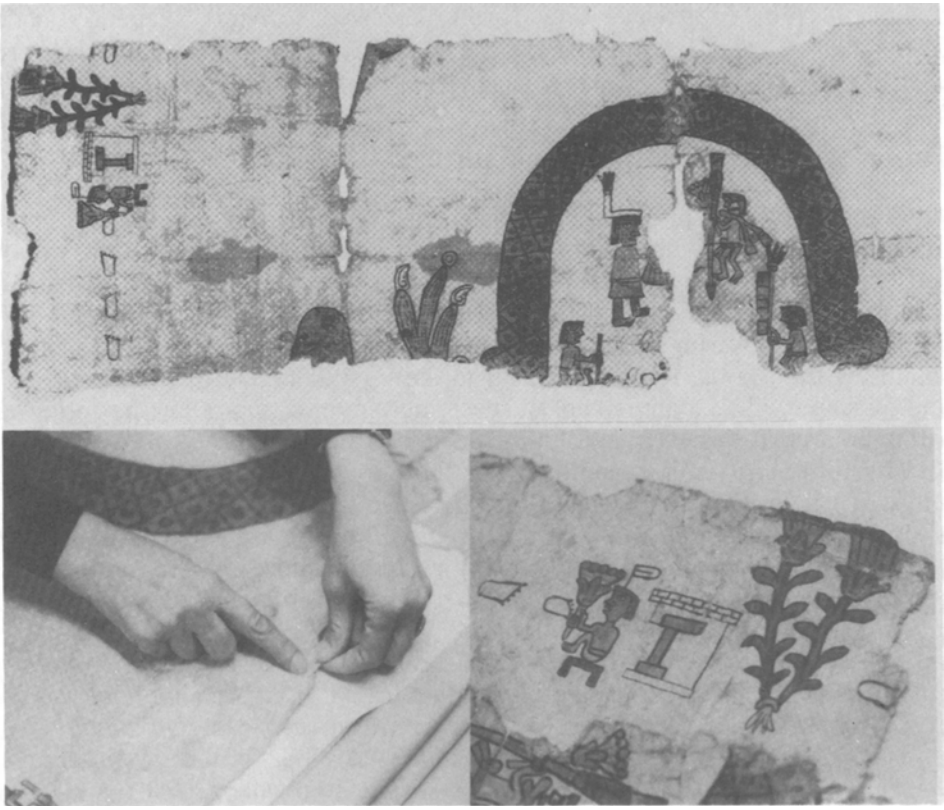


Fig. 2 Top: Codex Huamantla; bottom left: sampling of material for the investigation; bottom right: detail of the Codex Huamantla after removing the sample for investigation

fragments in existence. For the present investigation we had the opportunity to examine original paper material from the fragment number six of the Codex of Huamantla (Fig. 2) which is located in the Anthropological Museum in Mexico-City [7]. The fragments at the Museo Nacional de Antropologia, Mexico and the Humboldt Fragments, located at the Deutsche Staatsbibliothek, Berlin, Germany, are part of a single large painting [3, 4].

Experimental

Instruments

The Mettler Thermosystem TA4000 was used for thermogravimetry (TG) measurements in air. The samples were heated at a rate of 1 K min^{-1} in an alu-

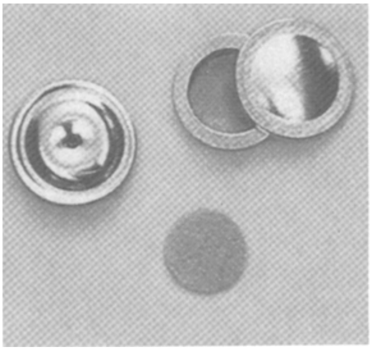


Fig. 3 Sample preparation for the DSC and TG measurements

minum container with a 2 mm diameter hole. The oxidation behavior of the different fibers in air was measured by differential scanning calorimetry (Mettler DSC25) in aluminum pans. The preparation of the circular samples of about 4 mm diameter is shown in Fig. 3. This method was used for both types of experiments.

For the thermogravimetry-mass spectroscopy (TG-MS) combination measurements a Mettler TG50 system was coupled with a Balzers MS-Cube™ (MSC 200). The decomposition products were sampled in close proximity to the crucible in the thermogravimetry oven and transferred to the mass spectrometer in a heated quartz capillary (110°C). The data evaluation was performed with the Quadstar™ 421-Windows™3.1 process control module. The minimum detectable concentrations were 5 ppm/50 ppb with a standard sample pressure of 1000 mbar. The pumping system consisted of a turbomolecular pump and a rotary pump with interstage pumping for gas inlet.

The SEM pictures of a Codex Huamantla fragment as well as a recently produced paper consisting of ficus padafolia were taken in order to determine whether signs of beating of the raw material were visible and to look for fungi mold. The instrumental setup included a SEM 515 Philips, Eindhoven, Netherlands and an EDX TRACORNorthern 5400 and gold sputtered samples.

Materials

The bast fiber samples were taken from the Humboldt Fragment number six of the Codex Huamantla which is kept in the Museo Nacional de Antropologia, Mexico City. Figure 2 shows the fragment and the place where the sample was taken. The reference materials are Mexican papers from recent production. They were manufactured by the Otomi Indians in San Pueblito, Sierra Madre. The agave fibers were taken from fresh plants in 1972 in the vicinity to the Sun and Moon pyramids of Tenochtitlan, Mexico.

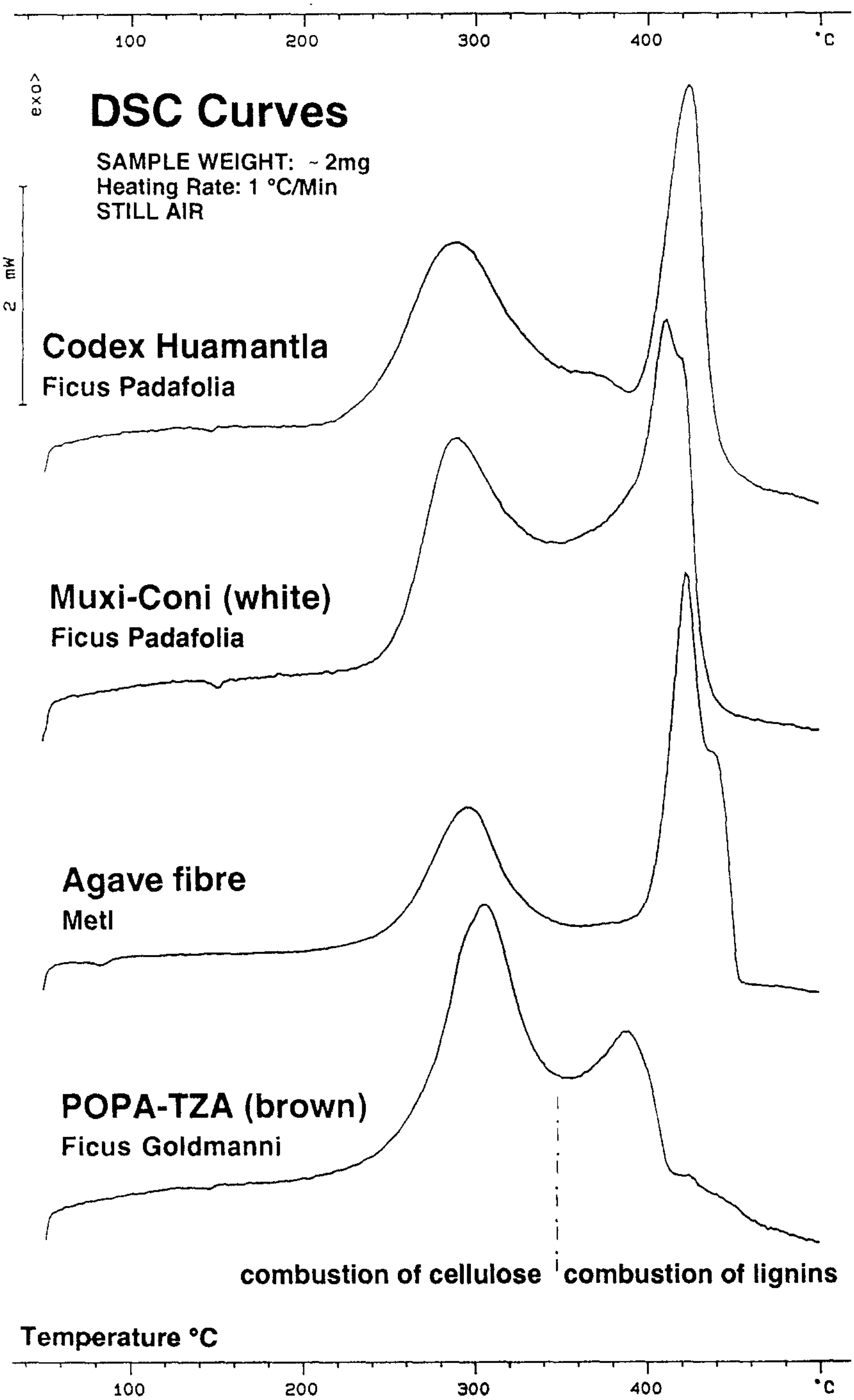


Fig. 4 DSC curves of the Codex Huamantla and other recently produced Mexican bast papers

Table 1 Heats of combustion of cellulose and lignin

Origin	$\Delta H_{dehydr.}$/ J g^{-1}	T_{peak}/ °C	$\Delta H_{cellulose}$/ J g^{-1}	T_{peak}/ °C	ΔH_{lignin}/ J g^{-1}	T_{peak}/ °C
Ficus Padafolia* Codex Huamantla	5.9	147.2	4985.8	290.3	4427.2	367.2/424.2
Ficus Padafolia* White Amatl	12.0	150.8	4148.6	290.3	5012.7	411.4
Agave fiber Metl			4850.1	297.0	6411.3	422.6
Ficus Goldmannii* Brown Amatl	2.9	147.2	6031.8	306.8	2988.1	389.3/424.0

Test conditions: 2 mg sample weight, heating rate 1°C min^{-1}, Al crucible, air
* mechanically treated during processing

Results and discussion

As can be seen in the DSC curves in Fig. 4, there is a small endothermic peak at approximately 150°C preceding the combustion of both cellulose and lignin. The authors speculated that this peak, which is observed in three out of four samples, indicates mechanical treatment of the raw material since the X-ray analysis of the papers with this peak indicates the presence of calcium oxalate. The beating of the raw material causes the break down of the cell walls which contain oxalic acid. The release of oxalic acid and the presence of calcium ions in the water then leads to the formation of measurable quantities of calcium oxalate. Therefore, the peak at 150°C can be attributed to the dehydration of calcium oxalate monohydrate. The Agave fibre paper does not show any peak around 150°C and is assumed to have a different mechanical history. The analysis of the heats of combustion as well as the heat of dehydration of the calcium oxalate monohydrate is summarized in Table 1.

The oxidative decomposition of cellulose occurs between 140 and 350°C while the lignin of the fig tree and the mulberry tree decomposes in the range between 350 and 500°C (Figs 4, 5). The step analysis by thermogravimetry is summarized in Table 2.

Table 2 Step Analysis of brown amatl (Ficus Padafolia)

	Steps	Weight loss/ mg	Weight loss/ %
A)	water	–0.25	–6.57
B)	cellulose	–2.53	–67.30
C)	lignin, cross-linked	–0.97	25.97
D)	ash	0.01	0.06
	total	3.760	100.00

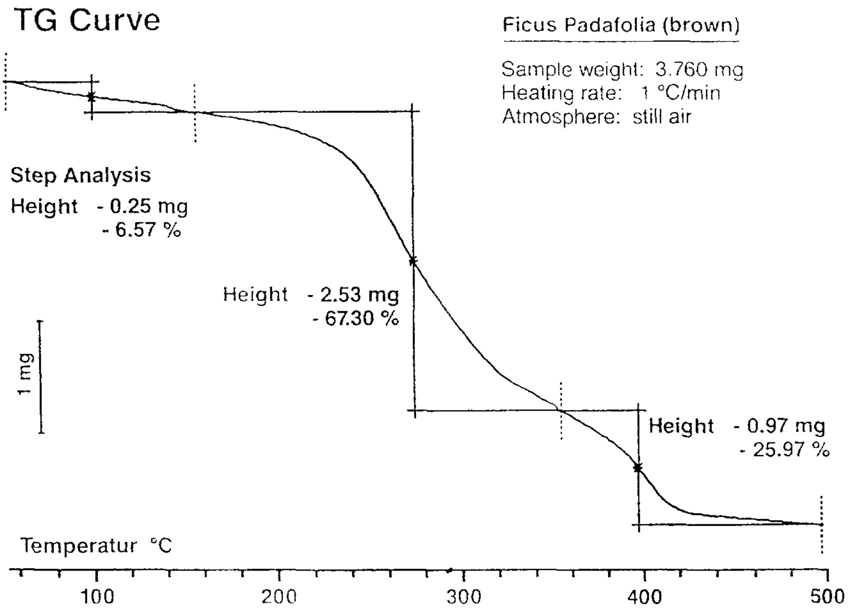


Fig. 5 Step analysis of a TG curve of a ficus goldmanii bast paper, recently produced

The analysis of the Codex Huamantla by scanning electron microscopy (SEM) was performed to check for visible effects of the beating to the material and signs of fungi attack. While the difference between beaten and unbeaten material is not visible, both the traces of fungi attack and some fungi were found (Fig. 6a). Due to the scarcity of the fungi the more representative pictures, only shown the scars of the fungi attack, are shown in Fig. 6b. Thermal analysis alone gave no indication of the fungi growth.

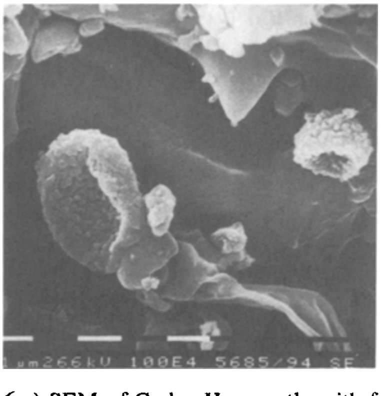


Fig. 6 a) SEM of Codex Huamantla with fungi

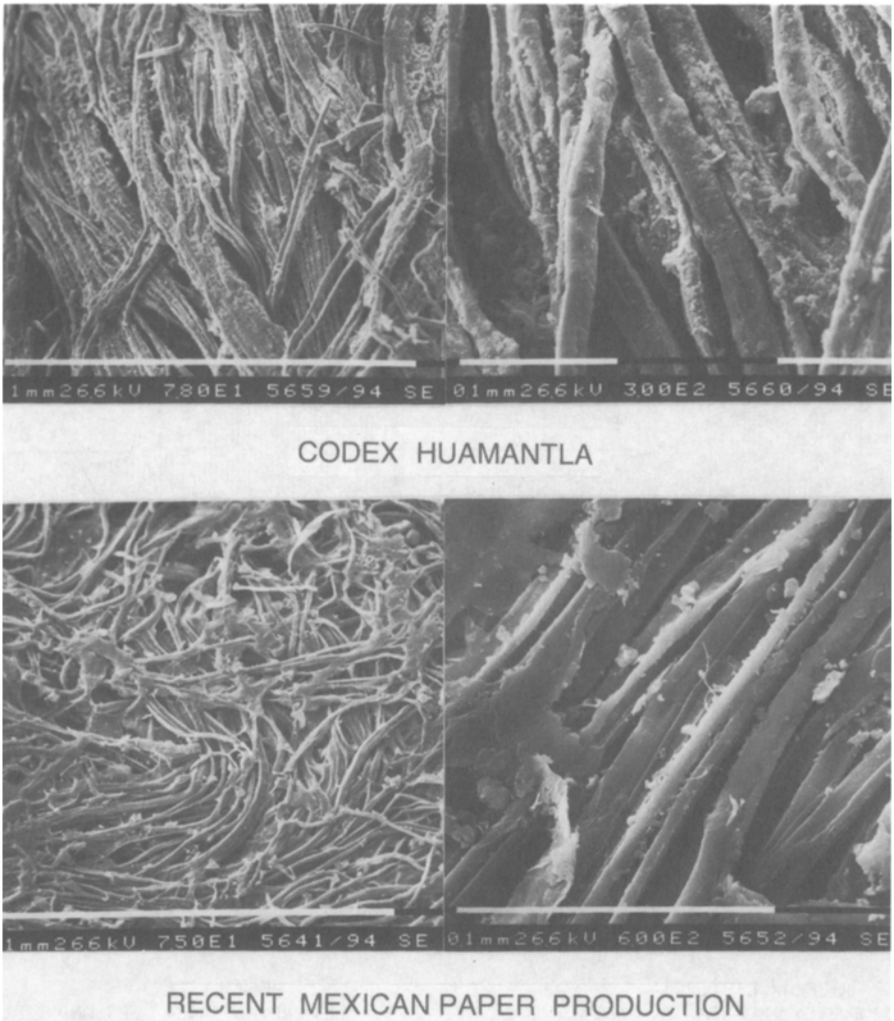
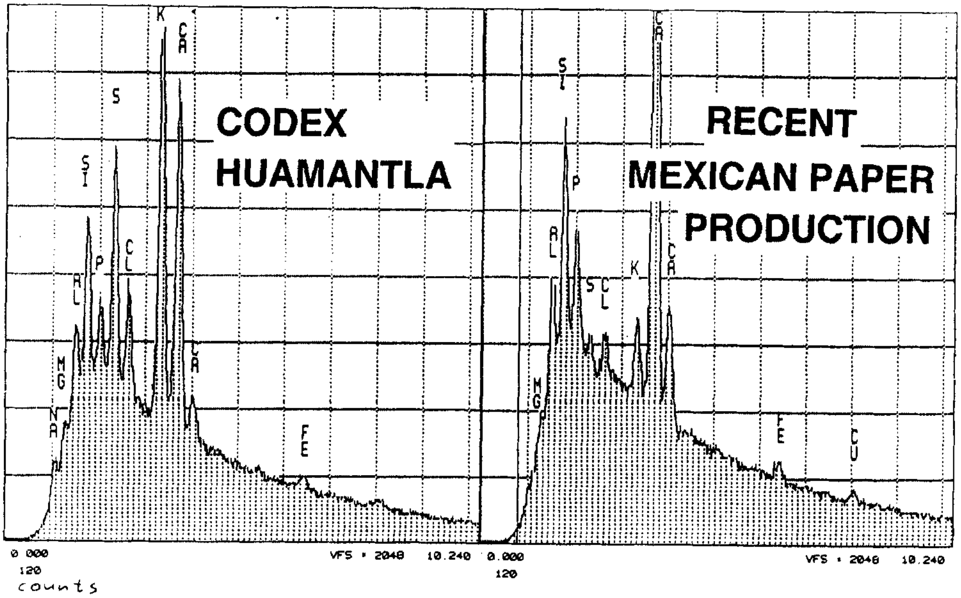


Fig. 6 b) SEM of Codex Huamantla and a recently produced Mexican paper from ficus padafolia without fungi

The SEM was also used to compare the physical appearance of the fibers of ficus padafolia in a recently produced paper and the Codex Huamantla, which shows good agreement (Fig. 6b).

In order to obtain knowledge of the presence of metal atoms the energy dispersive X-ray analysis (EDX) of the samples used for the electron microscopy was performed (Fig. 7). The differences in metal contents may in the future lead to more knowledge about the manufacturing techniques. A significant difference in the two samples was only seen in the content of sulfur and potassium.



QUALITATIVE ELEMENT IDENTIFICATION

SIBLE IDENTIFICATION
K KA OR IN LA?
CA KA KB
S KA
SI KA
CL KA
AL KA
P KA
NA KA
FE KA
MG KA

PEAK LISTING

	ENERGY	AREA	EL. AND LINE
1	1.034	1141	NA KA
2	1.250	511	MG KA
3	1.483	3328	AL KA
4	1.744	8537	SI KA
5	2.021	3086	P KA
6	2.312	13132	S KA
7	2.633	5664	CL KA
8	3.324	24239	K KA OR IN LA?
9	3.695	19486	CA KA
10	4.037	2136	CA KB
11	6.418	827	FE KA

POSSIBLE IDENTIFICATION
CA KA KB
SI KA
P KA
AL KA
K KA OR IN LA?
CL KA
S KA
FE KA
CU KA
MG KA

PEAK LISTING

	ENERGY	AREA	EL. AND LINE
1	1.233	498	MG KA
2	1.482	4687	AL KA
3	1.745	10965	SI KA
4	2.025	5845	P KA
5	2.324	1186	S KA
6	2.633	2589	CL KA
7	3.324	4043	K KA OR IN LA?
8	3.700	53600	CA KA
9	4.037	5854	CA KB
10	6.412	1175	FE KA
11	8.046	759	CU KA

Fig. 7 EDX analysis indicates the presence of various elements on the surface of the samples

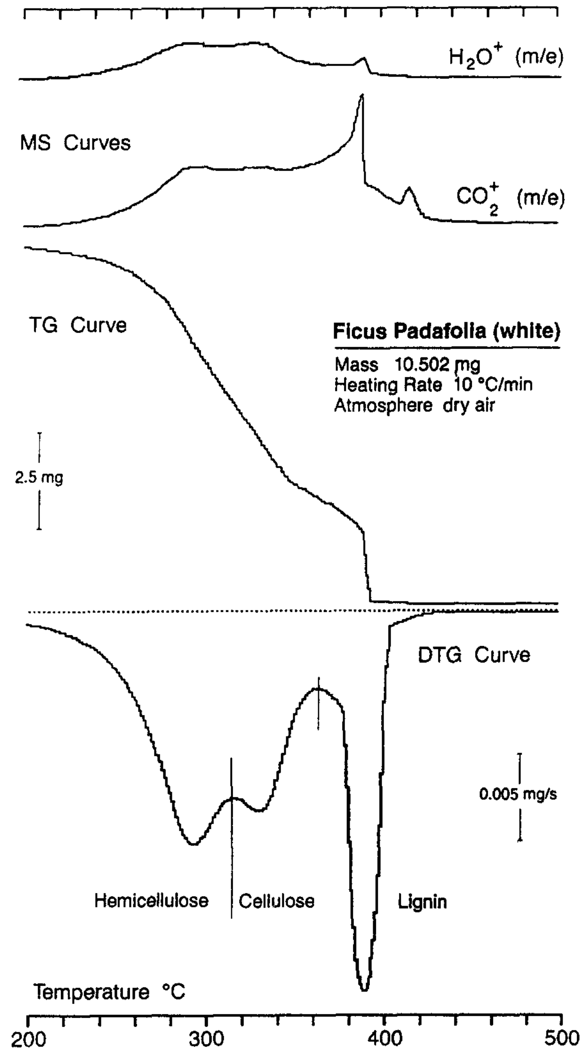


Fig. 8 Overlay of simultaneously recorded Thermogravimetry – mass spectroscopy curves. The top curves show the total ion current of H_2O^+ and CO_2^+ (i.e. *m/z* 18 and 44)

Recent Mexican paper contains a twelve-fold amount of sulfur in contrast to a six times lower amount of potassium compared to the Codex Huamantla. As of now no theory on how this may originate from different manufacturing procedures has been established.

The simultaneous measurement of thermogravimetry and evolved gas mass-spectroscopy (TG-MS) is shown in Fig. 8. With increasing temperature the decomposition of hemicellulose, cellulose and lignin can be seen. It is interesting to observe that the first derivative of the TG curve (DTG) and the ion current

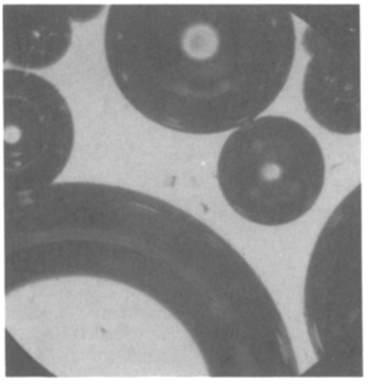


Fig. 9 Picture of the evolution of hydrogen during the heating of coniferyl alcohol at 100°C (heating rate 10 K min^{-1})

curves of the MS exhibit the same features but with different intensities. The individual ion current curves allow for the distinction of different decomposition reactions, while the total ion current mirrors the first derivative of the thermogravimetry curve almost perfectly. The differences in thermogravimetry and mass spectroscopy, i.e., mass loss and counting of ions of different masses accounts for only small differences in the two curves. For this reason the total ion current is omitted in Fig. 8. The ratios of evolved water to carbon dioxide mirrors the differences in decomposition between carbohydrates and the polycondensate which contains unsaturated hydrocarbons. After the steep decomposition step at 390°C the remains consist mainly of polycondensate with a very limited amount of hydrogen atoms. In the subsequent decomposition around 420°C only the carbon dioxide peak can be observed in the mass spectroscopy curve (Fig. 8) since there is not enough hydrogen left for the formation of a significant amount of water vapor. The polycondensation of coniferyl alcohol to lignin was observed in a separate experiment on a hot-stage under a microscope [8]. The bubbles in Fig. 9 are attributed to the hydrogen formation during the polycondensation of coniferyl alcohol.

Conclusion

The experimental evidence in the present paper shows that the thermoanalytical methods have a valuable place in the identification of raw materials, approximate dating and the evaluation of manufacturing techniques of ancient paper materials.

* * *

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References

1 D. Hunter, Papermaking, The History and Technology of an Ancient Craft, Dover Publications New York 1978.
2 B. Rudin, Making Paper, A look into the History of an Ancient Craft, Rudins, Vällingby, Sweden 1990.
3 R. Schwede, Ueber das Papier der Maya Codices, Dresden, Verlag von Richard Bertling 1912.
4 J. B. Glass, Catalogo de la Coleccion de Codices, Museo Nacional de Antropologia, Mexico (1964).
5 M. F. Cline, Guide to Ethnohistorical Sources, Handbook of Middle American Indians, Vol. 14, University of Texas Press, Austin, USA, 1973, pp. 133, 140.
6 W. Sandermann, Papiergeschichte, 20, 11 (1970) , p. 61.
7 W. von Hagen, The Aztec and Maya paper makers, New York, Hacker Art Books 1977.
8 H. G. Wiedemann, R. Riesen, A. Boller and G. Bayer, From Wood to Coal: A Compositional Thermogravimetric Analysis, Compositional Analysis by Thermogravimetry, ASTM STP 997, C. M. Earnest, ED., American Society for Testing and Materials, Philadelphia, 1988, pp. 227–244.