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THERMAL ANALYSIS AN IMPORTANT TOOL IN HISTORICAL PAPER INVESTIGATION

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Abstract

Generally, thermal analysis represents a reproductible and practically convenient method to characterize heterogeneous organic material, as paper. In the case of historical paper, the thermal behavior of its main components, as cellulose, hemicelluloses, lignin and fillers can be well investigated with DSC and TGA. Differential scanning calorimetry (DSC) allows a rapid detection and measurement of the physicochemical changes that a polymer undergoes when subjected to heating. Thermo-gravimetric analysis (TGA) provides a method for the determination of mass change in polymer as a function of time and temperature that reflect reactions which occur at the molecular level of the paper. Also the presence of some additives influences the behavior of paper during the thermal degradation. DSC and TGA have been applied to characterize some historical paper, from private collection, from books of the end of the XIX-th century and of the XX-th century. In this way helpful information has been obtained to be used in paper restoration and conservation has been obtained.

Keywords: *historical paper, TGA and DSC analysis*

1. INTRODUCTION

Cellulose is the most extensively used natural polymer and represents a renewable natural source for organic materials. The main reactions acting on the structure of cellulose and causing its alteration are photo-degradation, acid hydrolysis, oxidation, and biodegradation. A complete analysis of them is quite complex, since these phenomena are all related to each other.

Paper stability is a property related to the production processes and to the environmental conditions (temperature, humidity, presence of micro-organisms, etc.) in which the paper is stored. During the time paper undergoes unavoidable ageing processes that cause mainly the degradation of cellulose: these phenomena can involve acid substances and the moisture present in the material (acid hydrolysis), oxidative agents and the atmospheric O_2 (oxidation), micro-organisms (bio-deterioration), or the light (photo-degradation). All these factors act cooperatively and lead to both the progressive shortening of the polymeric chains and the variation of the crystalline content of cellulose [1,2,3,4].

The oxidation reactions of cellulose involve the primary and secondary hydroxyl groups of the pyranose ring and result in carbonyl and carboxyl groups. The reaction can be accompanied by the

opening the pyranose ring. In any cases the glucosidic bond becomes weaker; the formation of carboxyl groups induces a de-polymerization, thus reducing the polymerization degree (DP) and the physical and mechanical strength of the material.

The ageing of paper and cellulose has been studied for about last hundred years. This is not only to understand the mechanism behind the degradation, but also to develop methods for stopping or slowing it down in order to save paper-based cultural heritage word-wide.

2. MATERIALS AND METHODS. EXPERIMENTAL PART

To understand the chemistry of a historical artifact, a restorer must analyze all of its elements, including the substrate, the fillers, the binders and the degradation products. Knowing all the materials in a paper document can also be of great value for determining the most suitable methodology for restoring its' damage or for preserving it against humidity, temperature and light. Chemical analysis must be seen as a complement to the artistic study of a document. Beside the organic components of the paper samples, consist in cellulose, hemicelluloses, lignin and binders, it is important to know the fillers' nature in the paper samples.

Generally, thermal analysis represents a reproducible and practically convenient method to characterize heterogeneous organic material, as paper. Thermo-gravimetric analysis (TGA) provides a method for the determination of mass change in the polymer as a function of time and temperature: thus, this technique reflects reactions which occur at the molecular level of the polymeric material. In the case of paper, the thermal behavior of its main components, as cellulose, hemicelluloses, lignin and additives can be well investigated with TGA and DTG.

Differential scanning calorimetry (DSC) allows a rapid detection and measurement of the physic-chemical changes that a substance undergoes when subjected to heating. Also the presence of some fillers influences the behavior of paper during the thermal degradation.

The present research has been focusing on thermo-analytical methods TGA, DTG, and DSC, that have a valuable place in the identification of raw materials, and then approximate dating and evaluation of manufacturing techniques of the paper. The TGA and DTG analysis have been first tested on eight different types of paper samples from books of the end of the XVIII-th century and of the beginning of the XIX-th century, from private collections. The eight samples were codified as follows:

- M1 the sample from a French book, printed in Paris, in 1871
- M2 the sample from a French book, printed in Paris, in 1894
- M3 the sample from a Romanian book, printed in Bucuresti, in 1783
- M4 the sample from a French book, printed in Paris, in 1899
- M5 the sample from a German book, printed in Berlin, in 1831
- M6 the sample from a French book, printed in Paris, in 1835
- M7 the sample from a Romanian book, printed in Bucuresti, in 1888
- M8 the sample from a Romanian book, printed in Bucuresti, in 1889

Furthermore, for confirmation of the different behavior of the papers depending to the manufacturing process it has been used the DSC analysis for the same samples.

Thermal analysis have been performed on a Mettler Toledo Thermo-gravimetric Analyzer TGA/ SDTA 823^e, in the range of temperature 25^{0}C to 1000^{0}C, in dynamic air, with 60 ml/min, at a heating rate of 10^{0}C/min, in alumina crucible, for all the paper samples, of 3mg to 5mg .

DSC was performed on a Metter-Toledo Instrument DSC 823^e. Samples (1-2 mg) were loaded into sealed aluminum pans with lids and heated to 600ºC at a heating rate of 10ºC min $^{-1}$ in oxygen flux (100 ml min $^{-1}$). The empty aluminum pan was used as reference and the heat flow between the sample and reference pans was recorded. Measurements were repeated at least three times.

3. RESULTS AND DISCUSSION

This review presents thermal analysis, TGA and DTG, of historical book papers (from a private collection) as a first step in their degradation process. From the literature it is known that the combustion of cellulose comprise two stages – gaseous combustion in which the gaseous degradation products catch fire, and then glowing combustion in which the carbonaceous residue pyrolysis with the evolution of CO, CO_2 and water [5, 6, 7, 8]. Both these processes are exothermic but basically the degradation of the cellulose in the gaseous combustion stage is endothermic. It is only that the exothermic character of the combustion of the gases produced overwhelms the endothermic character of the basic reaction that produces the exothermic observed in DTA plots.

Price and Horrocks examined the gases released from the combustion process of cellulose in an inert atmosphere by mass spectroscopic studies [9, 10]. A significant influence present the organic additives or the cellulose from the paper, because they can increase the carbonaceous residues and alter the combustion-temperature ranges associated with the gaseous and glowing combustion.

The TGA and DTG curves for the each of the eight samples, for the study of thermal stability of the cellulose, are shown in Figure 1 and Figure 2.

In accordance with the literature, it has been established that no degradation takes place until 200ºC. Above this temperature thermal stability gradually decreases and the cellulose decomposition occurs. Generally, at temperatures less than 100ºC the water loss in all the samples takes place. Moreover, TGA analysis gives an insight into the presence of inorganic fillers compounds in the sample by detection, in the derivatives curves, of their decomposition at temperatures usually higher than the decomposition temperature of cellulose. In a first approximation it can be assumed that cellulose does not interact with the fillers. Thus, it can be considered the decomposition of cellulose and the fillers independently.

In the TGA and DTG results discussion, coming from the recorded weight loss curves and their correspondent derivative curves, are reported in terms of:

- Dehydration Temperature of paper- peak 1
- Decomposition Temperature of cellulose (Td $_{cell}$)- peak 2
- Decomposition Temperature of lignin (Td $_{lignin}$)- peak 3
- Decomposition Temperature of fillers (Td $_{fillers}$)
- Residual weight % (RW %) at 1000ºC . This value includes the amount of chairs, unburned components (i.e. inorganic fillers) and final decomposition products produced during the analysis.

All the paper samples show the cellulose decomposition in the range 310-350°C, also when fillers are present in the material. Paper sample M2 shows the highest thermal stability.

Probably due to the high ratio of heating, respectively 10^0C/ min, no peaks related to the inorganic fillers are discovered for all the paper samples.

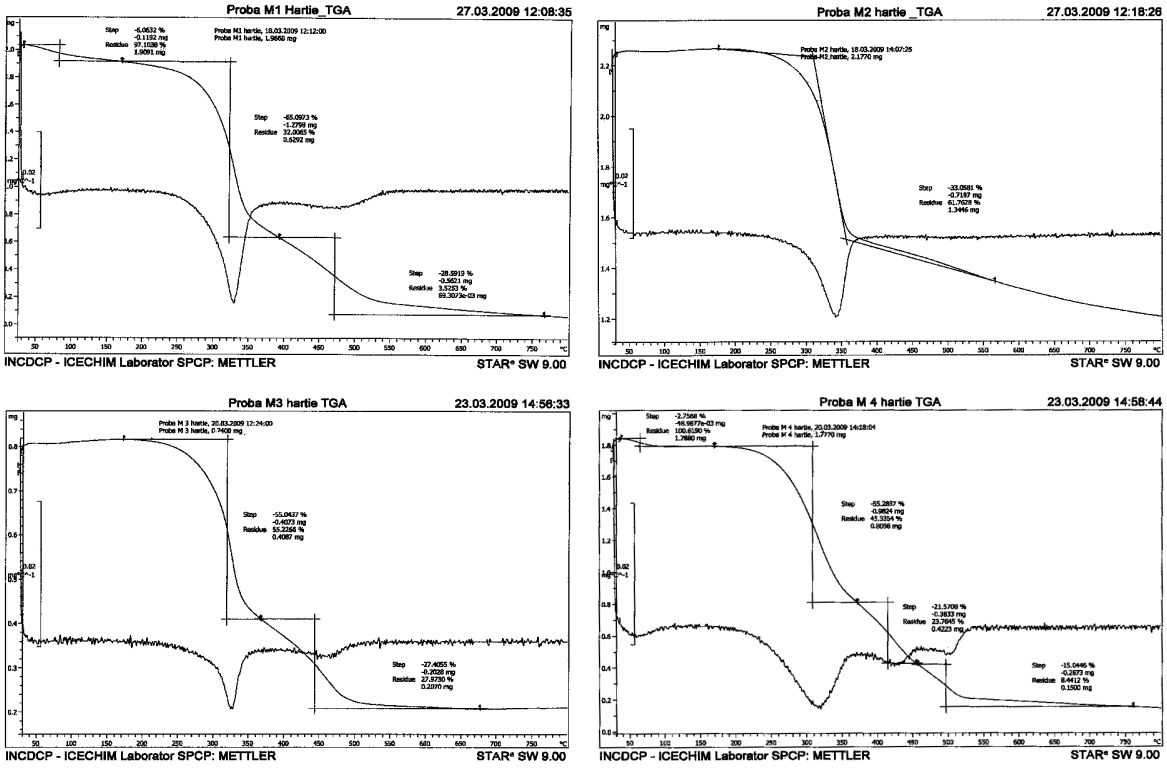


Figure 1. TGA and DTG curves for paper samples M1, M2, M3 and M4

The data are tabulated for all paper samples investigations in Table 1: sample type, initial temperature T_i [^{0}C], peak temperature T_p [^{0}C], final temperature T_f [^{0}C] of the DTG plot and the mass % of residue of inorganic salts and oxides, at 1000°C.

First peak of the DTG curves represents the dehydration process, the second one represents the oxidative combustion of cellulose, each type of paper being characterized by different degradation velocity, at different temperatures. All kind of samples have the third peak of combustion that represents the oxidative degradation of lignin. In the case of the paper M4 and M8, there is one more peak of oxidative degradation. This peak could not be assigned to the fillers because in the literature reports the oxidative degradation of the inorganic fillers occurs above 700-750^{0}C. The fourth peak appears at 490-505^{0}C.

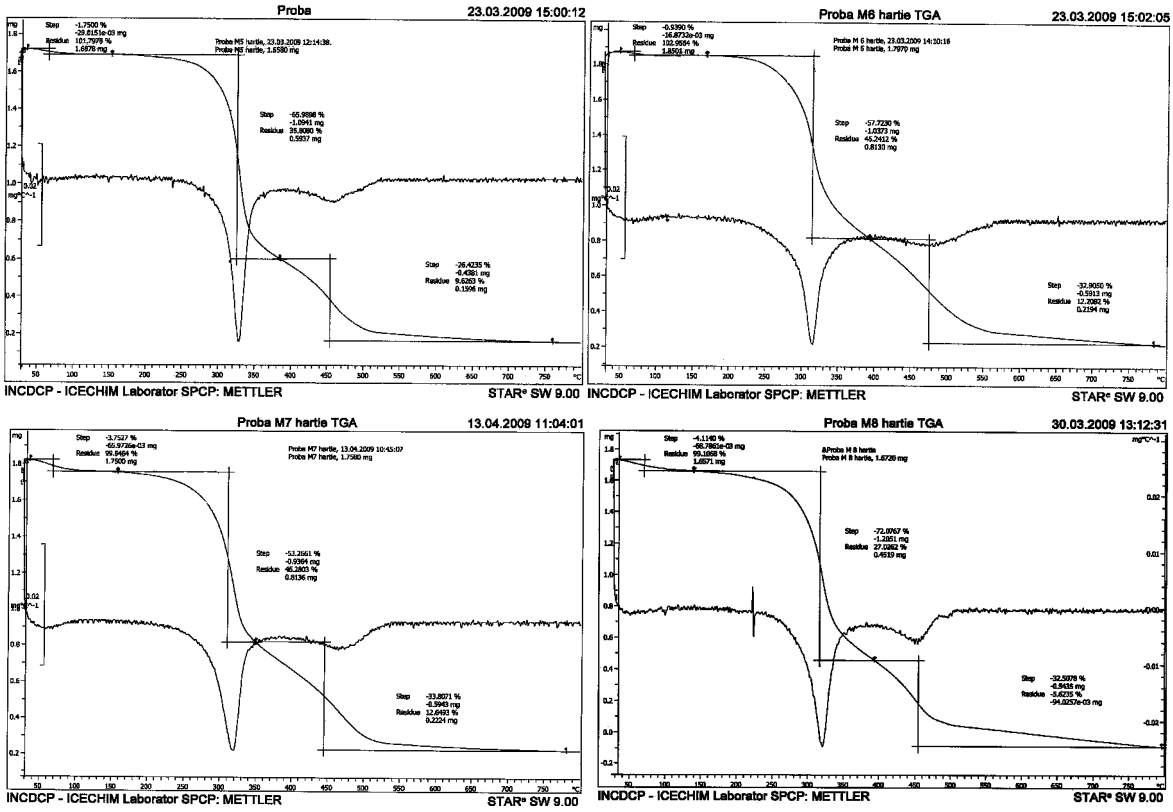


Figure 2. TGA and DTG curves for paper samples M5, M6, M7 and M8

Comparable results for the value of the residue of inorganic salts and oxides at 1000^0C are obtained for the M4, M5, M6 and M7 book paper samples, that means they have approximately the same amount of filler agents in their composition.

There are the M1 and M8 paper samples that have the smallest mass % of residue of inorganic salts and oxides, at 1000°C, 3,52% respectively 0,16%. At the opposite side, M2 paper sample, has the biggest mass % of residue at 1000°C, namely 55,91%, and M3 sample has also a very high mass % of residue at 1000°C, respectively 27,97%, that means the amount of fillers is very high.

A great importance has the second oxidative degradation step from the TGA curve that represents the oxidative combustion of cellulose, for all samples.

As the peak temperature corresponding to the second peak of the DTG curve is higher, the thermo destructive resistance of the paper is higher, and in this case is M2. That means that the paper resists better to thermal variations of the environment, so it presents the advantage of a better conservation. Very close values of the maximum temperatures of the second peak means that the cellulose from the studied papers is of the same type.

Samples	peak	T_i [^{o} C]	T_p [^{o} C]	T_f [^{o} C]	mass % of residue of inorganic salts and oxides at 1000 ^{o}C.
M1 French book, Paris, 1871	1	30	80	115	-
	2	172	328	396	-
	3	402	421	549	-
					3.52%
M2 French book, Paris, 1894	1	30	68	110	-
	2	180	345	413	-
	3	413	560	770	-
					55.91 %
M3 Romanian book, Bucuresti, 1783	1	30	64	130	-
	2	182	327	368	-
	3	368	470	510	-
					27.97 %
M4 French book, Paris, 1899	1	30	64	120	-
	2	185	320	370	-
	3	370	426	465	-
	4	465	503	545	
					8.44 %
M5 German book, Berlin, 1831	1	30	58	120	-
	2	160	328	387	-
	3	387	459	529	-
					9.63 %
M6 French book, Paris, 1835	1	30	69	120	-
	2	171	315	394	-
	3	394	477	574	-
					12.21 %
M7 Romanian book, Bucuresti 1888	1	30	63	108	
	2	160	318	350	
	3	350	467	542	
					12.65 %
M8 Romanian book, Bucuresti, 1889	1	30	67	120	
	2	140	316	387	
	3	387	448	477	
	4	477	491	510	
					0.16 %

Table 1. TGA results for the paper samples: M1, M2, M3, M4, M5, M6, M7, M8

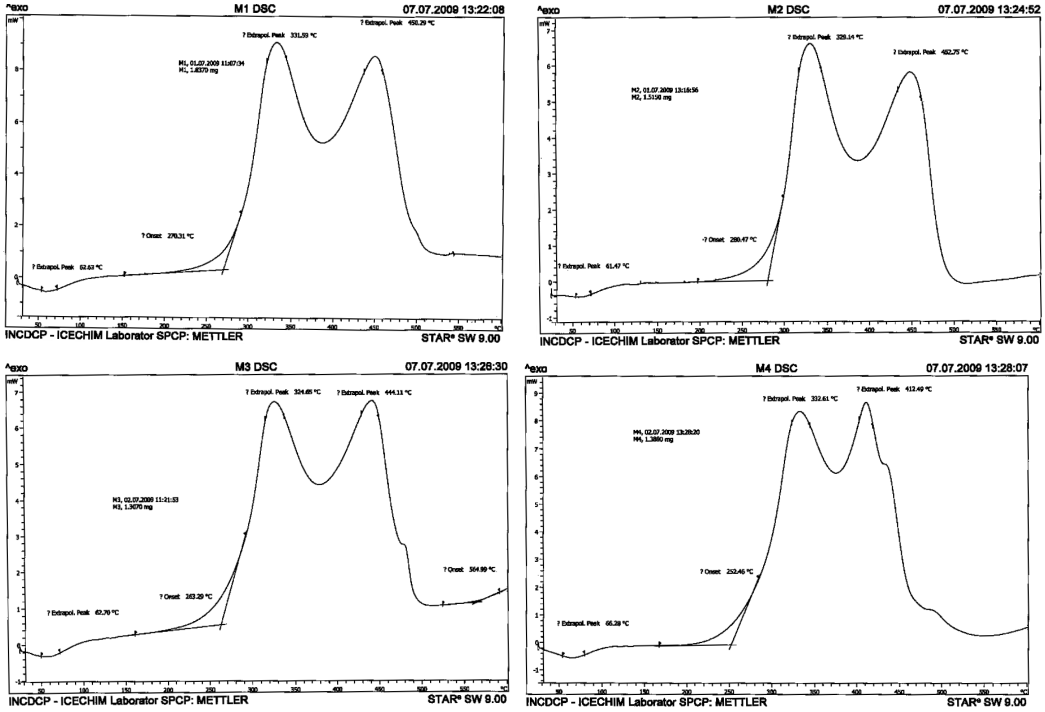
Although no peaks related to the inorganic fillers are revealed for the paper samples, it is important to note that EDXRF analysis detected the presence of the inorganic fillers in all the paper samples.

DSC curves showed a different behavior depending on the parts of the plant used and of the way of manufacturing of the paper sheets.

The difference in the shape of the curves can probably be explained by the different amount of cellulose and lignin present in the different portions of the plant.

As can be seen in the DSC curves in Figure 3 and Figure 4, there is a small endothermic peak at approximately 150^0C, preceding the combustion of both cellulose and lignin. The literature mentioned that this peak, which is observed six out of eight samples, respectively at M1, M3, M4, M6, M7 and M8 samples, indicates mechanical treatment of the raw material. The beating of the raw material causes the breakdown of the cell walls of the plant, which contain oxalic acid[11]. Therefore, the peak at 150^0C can be attributed to the dehydration of calcium oxalate monohydrate. The M2 and M5 fiber papers do not show any peak around 150^0C, and that is assumed that they have a different mechanical history.

Figure 3. DSC curves for paper samples M1, M2, M3 and M4



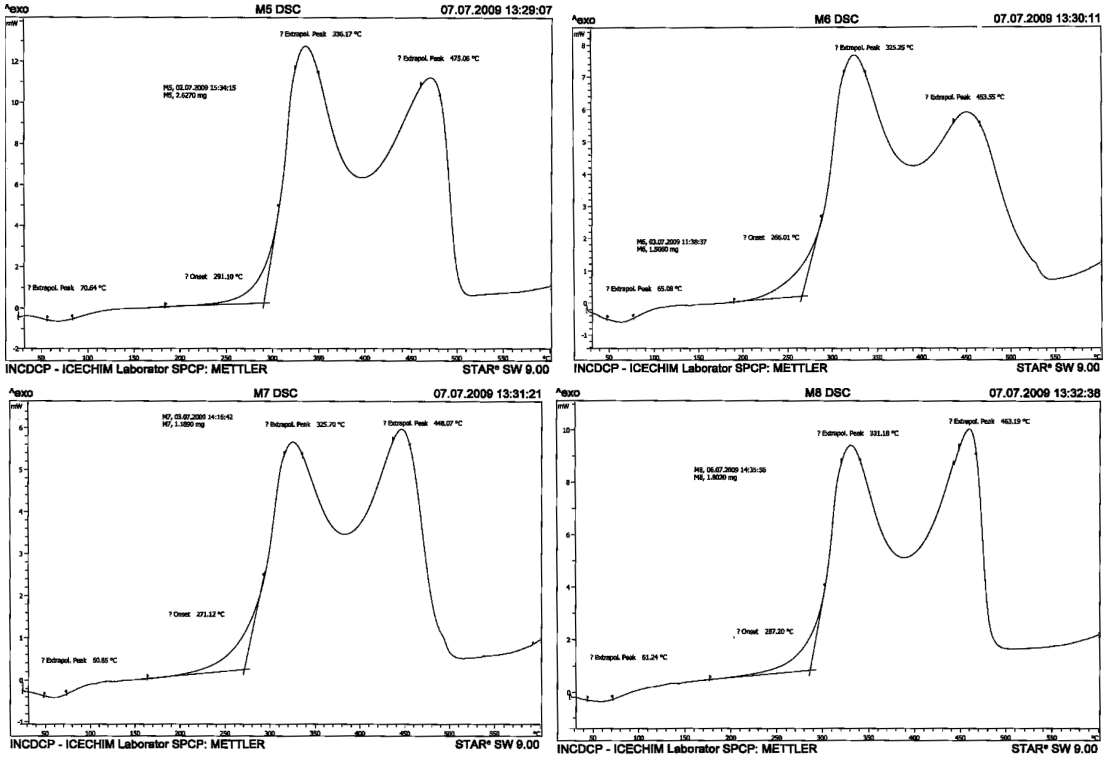


Figure 4. DSC curves for paper samples M5, M6, M7 and M8

The oxidative decomposition of cellulose occurs between 150^0C and 350^0C, while the lignin decomposes in the range between 350^0C and 500^0C. For the M1, M3, M4, M6, and M7 samples there is a shoulder at approximately 500^0C, which was also attributed to the lignin, Table 2.

Samples	T peak 1 °C	T peak 2 °C	T peak 3 °C	T peak 4 °C	T peak 5 °C	T peak 6 °C
M1 French book, Paris, 1871	62.63	150	331.59	450.29	-	500
M2 French book, Paris, 1913	61.47	-	329.14	425.75	-	-
M3 Romanian book, Bucuresti, 1914	62.70	150	324.65	441.11	-	500
M4 French book, Paris, 1929	66.28	150	332.61	412.49	450	500

M5 German book, Berlin, 1931	70.64	-	336.17	475.06	-	-
M6 French book, Paris, 1935	65.08	150	325.25	453.55	-	525
M7 Romanian book, Bucuresti, 1888	60.85	150	325.70	448.07	-	500
M8 Romanian book, Bucuresti, 1889	61.24	150	331.18	463.19	-	-

Table 2. DSC results for the paper samples M1, M2, M3, M4, M5, M6, M7 and M8

4. CONCLUSIONS

The analyzed naturally aged paper samples, M1 to M8, have different provenience, age and composition: therefore these samples give the possibility to investigate the effect of the natural weathering at various level of degradation.

This paper established a relationship between TGA, DTG and DSC techniques for evaluation of thermal stability of the paper samples.

Also, these techniques help to determine the history of the paper samples, the method of manufacturing of the historical papers.

All these results highlighting how some characteristics are in function of their composition and provenance, and allowed a first assessment of age determination and technological manufacturing classification of the paper samples.

Moreover, TGA, DTG and DSC analysis of the paper samples showed that the different manufacturing methods cause the different behave of the thermal curves.

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