Comparation of Cardboard Pieces as Physical Evidence in Murder Case Using Simultaneous Thermal Analysis

Keshav S. Kapgate*
Regional Forensic Science Laboratory, Nagpur, Maharashtra, India.
*Corresponding Author

Renuka V. Phadke
Regional Forensic Science Laboratory, Nagpur, Maharashtra, India.

Charansing B. Ghoti
Regional Forensic Science Laboratory, Nagpur, Maharashtra, India.

Shivangi S. Apte
Regional Forensic Science Laboratory, Nagpur, Maharashtra, India.

Vijay J. Thakre
Regional Forensic Science Laboratory, Nagpur, Maharashtra, India.

Abstract
Physical evidence obtained at crime scene is important basic evidence in forensic science. In such examination along with classical methods, instrumental analysis plays a major role. Very few studies have been performed for cardboard comparison as physical evidence with reference to forensic examination. Examination and comparison of cardboard found in murder case was successfully performed using thermal methods of analysis. The results were also matched with control samples. The analysis is found to be helpful in identification and linking of physical evidences at crime scene. The results obtained from the simultaneous thermal analysis of cardboard seized at crime scene and company office showed that all the three layers in cardboard show similar thermal properties and differences found in the thermal properties were due to their treatment in making originating from binder in cardboard making. The adhesive material used in preparation of corrugated cardboard box results in exothermic degradation peak while endothermic peak was observed for corrugated cardboard box without adhesive material. The differences in results are found out with help of control sample as well as simulated study.

Introduction
Forensic science is an integrated part of judiciary system. The collection, sampling, preservation and analysis of evidences are important aspects of forensic investigations. Forensic evidences may be biological, physical or audio-visual and generally involve detection or comparison method. Most of the cases submitted in forensic science laboratories (FSL’s) need comparison between articles collected from crime scene and from accuse or victim. Analysis of those evidences requires specific method and technique to reach final conclusion. Analytical instrumental techniques are valuable and integrated part in forensic investigations. The physical evidences that are commonly submitted to FSL are earth, metals, glass, fibre and polymer etc. In a rare case cardboard has become an important linking evidence in murder case. Thermal analysis of cardboard box has become imperative and is been done using simultaneous thermal analysis. Corrugated cardboard is stiff, strong and lightweight and hence mainly due to its strength, cardboard boxes are generally used for packaging and transportation. Cardboard boxes are generally made from pine tree’s bark. The bark mainly composed of cellulose, hemicelluloses and lignin. The pine bark chips are treated in a pressurised tank containing sodium hydroxide to remove its glue like material called lignin which holds wood fibres together. The process is called Kraft Process. In this process wood chips breaks down in to fibrous pulp and used for making cardboard. The cardboard has two flat liner sheets on either side of the corrugated sheet (medium) on the middle, bound together with corn starch glue.

Thermal properties of cardboard have been extensively studied with relevance to its recycle, reuse, safety purposes in storehouses and environmental impact28,29. The present case gives emphasis on comparison of two cardboard boxes found at crime scene and from accuse, using simultaneous thermal analysis.

In present case accused used a cardboard box to dispose off a body in murder case. A cardboard piece along with label stucked to it was seized from riverside. The cardboard piece thrown in river to dispose the body has company label stucked on it. The same label was observed on the cardboard boxes seized from the export company office. Thermal properties of cardboard boxes at crime scene and from suspected site were found to be different. The peak observed at about 357°C was of opposite nature. A study for this difference was performed using different conditions and using different cellulose based materials. The results of analysis revealed that the cardboard used to dispose the body was obtained from the same office.

2.0 Experimental
2.1 Preliminary analysis:
Label examination- Details of printed words such as hue, font size, background colour and words printed on labels were compared on intact cardboard box in exhibit no. 1 and piece of cardboard in exhibit no. 2. Similarly colours of words were also observed under UV cabinet. Thermal properties of label were studied using STA.

Cardboard examination-
Three layers of each corrugated cardboard (outer layer -liner, middle layer -medium /flute, and inner layer –liner) in Exhibit no. 1 and Exhibit no.2 were separated and assigned as (a) (b) and (c) respectively. Each layer was observed under Motic SMZ-168 series stereomicroscope. Physical parameters such as thickness and weight of known dimensions were studied using Digimatic Vernier caliper and digital balance (Metter Toledo) respectively for comparison. The thermal properties of each layer was studied using STA.

2.2 Simultaneous thermal analysis:
The STA measurements were performed using NETZSCH STA 449, aluminium crucible with pierced lid and nitrogen as purge gas at a flow rate of 40 ml/min About 4-5 mg samples used in this study were heated in the range of 50 °C to 600°C at the rate of 20K/min. Data was analyzed using NETZSCH STA 449.
3.0 RESULTS AND DISCUSSIONS

Label stuck on both cardboard in exhibit no 1 and 2 have same hue, wordings and physical appearances as shown in fig 1, similarly STA analysis of label found on ex 1 and 2 also show similar TG as well as DSC curves as shown in fig.2. Thus labels on cardboard box from company office in ex 1 and cardboard piece seized from riverside tally with each other in morphological and thermal characteristics.

Each layer of cardboard as described in section 2.1 was studied for hue and microscopic appearance. All layers of cardboard in exhibit no. 1 and 2 resembles with each other on the basis of hue. The images under stereomicroscope of each layer are shown in fig.3. The results of physical parameters indicate that the width and Weight of known dimensions of cardboard piece are same. Thus on the basis of preliminary examinations the pieces of cardboard on ex 1 and 2 appears to be same.

Thermogravimetric analysis- The thermal stability of cardboard is determined by testing the onset of degradation temperatures. TG curve for all the layers for ex no. 1 and 2 (fig 4 to Fig 6) show decrease in the curve at about 300°C. Cellulose absorbs moisture and this moisture loss generally found in the range 75°C-127°C. Cardboard generally consist of cellulose fibres. The decrease in weight of the cellulosic fibres was observed at 206-400°C with the maximum decrease in weight loss about 80-85% in these temperatures. Literature on thermal degradation study of cellulose fibre reveals that decomposition of major components of the cellulose fibres and the depolymerization of hemicellulose occurs between 180 and 350°C [5] and the random cleavage of the glycosidic linkage of cellulose between 275 and 350°C [6]. The cellulose molecule is a very long polymer of glucose units, and its crystalline regions improve the thermal stability of fibres [7]. Higher thermal stability of Celluloses is attributed to the hydrogen bonds between cellulose chains that can lead to more ordered and packed cellulose regions, and hence increasing the thermal decomposition temperature of cellulose [8].

The cardboard piece obtained from river side was wet and STA was performed on drying the exhibit. The DSC analysis of each layer of cardboard box namely a, b and c obtained from river side show endothermic peak at 354-357°C, however the exothermic peak was observed at same temperature from cardboard box seized from office. The discrepancy in the DSC results was found for both exhibits. Hence similar control samples were used from fresh cardboard box. The piece of cardboard was kept in water for 24 hours and then dried. The results are presented in Fig 7 to fig 9. The DSC of the control sample was performed and it was found that the nature of peak at 357°C was endothermic. Thus it was found that cardboard box show exothermic peak at 357°C while after getting moistened followed by drying, it shows endothermic peak. The water extract of the residue of cardboard box was tested. water extract was alkaline (pH 9) along with sulphate and traces chloride.

The probable reason for the phenomenon is hidden in formation of cardboard box. When cardboard piece get moistened with water, the glue used to stick the medium or corrugated sheet get dissolved in water and only cellulose left behind show endothermic peak instead of exothermic peak for the same cellulose without glue. The phenomenon was again confirmed using cotton and filter paper as control sample. Whatman filter paper is made up of high quality cotton linters which have been treated to achieve a minimum alpha cellulose content of about 98%. The DSC of pure whatman paper show endothermic peak at 358°C in absence of glue and when the glue is sticked to it an exothermic peak is observed at 388°C. The same experiment was performed using cotton and the similar results obtained are shown in table 1.

The decrease in temperature at endothermic peak with respect to exothermic peak is due to loosening cellulose carbon hydrogen bond and less energy is absorbed to break the bond. The present study successfully interprets the cause of differences in thermal properties during analysis and thus helpful in forensic investigations of comparison of exhibits to come to the final conclusion. TG results-Generally decomposition temperature of any material is found to be low due to less moisture content in dry condition and it shifts to higher value.

CONCLUSION:

In a murder case cardboard box was used to dispose the body. The results of comparison of cardboard box obtained in the present study show similar STA results for label. In exhibit but show discrepancy in cardboard box results. DSC results show first endothermic peak for moisture loss and second degradation peak show opposite nature. The adhesive material used in preparation of corrugated cardboard box results in exothermic peak while endothermic peak was observed for the corrugated cardboard box without adhesive material. The differences in results were found out with the help of control samples as well as simulated study. Hence the observations are further useful in solving and establishing evidence of cardboard box in similar type of medicolegal case.

Figure no. 1: Images of label on cardboard paper in Exhibit no. 1 and 2

Lable in Exhibit no. 1

Lable in Exhibit no. 2

Figure no. 2: STA analysis of label in Exhibit no. 1 and 2 of cardboard box

Figure no.3: Images of three layers of cardboard paper in Exhibit no. 1 and 2 in Stereo Microscope

Exhibit no. 1a

Exhibit no. 2a
Table 1: Summery of STA results

<table>
<thead>
<tr>
<th>Exhibit</th>
<th>Weight taken for analysis (mg)</th>
<th>DSC</th>
<th>Mass change (TG %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Label in Ex. No. 1</td>
<td>2.7</td>
<td>162.1</td>
<td>469.2</td>
</tr>
<tr>
<td>Label in ex. No. 2</td>
<td>2.7</td>
<td>162.3</td>
<td>461.7</td>
</tr>
<tr>
<td>Exhibit no. 1a</td>
<td>5</td>
<td>116.6</td>
<td>362.4</td>
</tr>
<tr>
<td>Exhibit no. 1b</td>
<td>5</td>
<td>133.7</td>
<td>364.3</td>
</tr>
<tr>
<td>Exhibit no. 1c</td>
<td>5.2</td>
<td>117.7</td>
<td>365.0</td>
</tr>
<tr>
<td>Exhibit no. 2a</td>
<td>4.3</td>
<td>117.2</td>
<td>359.7</td>
</tr>
<tr>
<td>Exhibit no. 2b</td>
<td>5.0</td>
<td>118.9</td>
<td>354.4</td>
</tr>
<tr>
<td>Exhibit no. 2c</td>
<td>5.4</td>
<td>119.7</td>
<td>359.7</td>
</tr>
<tr>
<td>Ex. 1a (after treatment)</td>
<td>4.3</td>
<td>115.2</td>
<td>357.7</td>
</tr>
<tr>
<td>Ex. 1b (after treatment)</td>
<td>5.0</td>
<td>122.0</td>
<td>353.6</td>
</tr>
<tr>
<td>Ex. 1c (after treatment)</td>
<td>5.3</td>
<td>114.3</td>
<td>355.0</td>
</tr>
<tr>
<td>Whatman filter paper</td>
<td>3.9</td>
<td>110.6</td>
<td>358.9</td>
</tr>
<tr>
<td>Whatman filter paper with gum</td>
<td>4.6</td>
<td>130.0</td>
<td>388.0</td>
</tr>
<tr>
<td>Cotton</td>
<td>5.0</td>
<td>104.5</td>
<td>357.0</td>
</tr>
<tr>
<td>Cotton with gum</td>
<td>4.3</td>
<td>107.6</td>
<td>358.0</td>
</tr>
</tbody>
</table>

Acknowledgement

The authors are thankful to Director, Directorate of Forensic Science Laboratories and Director General (legal and technical) Mumbai, Government of Maharashtra, for their valuable guidelines and encouragement for the preparation of this paper.

REFERENCES

3. Pyrolysis and oxidation of cardboard Gaurav Agraval, Ganu liu and Brian Lattimer124-4e safty science and proceeding of the eleventh international symposium pp 124-137.

Exhibit Weight taken for analysis (mg) DSC Mass change (TG %)
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