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Trace Evidence Analysis of Paint in a Serious Accident Case by Simultaneous Thermal Analysis and Energy Dispersive X-Ray Microanalysis Techniques

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Abstract

Physical evidence plays an important role in forensic investigation of any crime. In accidents or hit and run cases, comparison on paint of vehicles at collision site are examined using elemental analysis and microchemical tests. Sometimes microscopic examination of paint layers is also studied. In the present paper, a very small piece of paint scrapping was found inside the back side of tipper vehicle. The sample size was too small to determine the microchemical test. So, in addition to elemental analysis, Simultaneous Thermal Analysis (STA) technique was applied to examine the thermal behavior pattern of paint scrapping. Thermal analysis of paint scrapings found on suspected vehicle tallied with the control paint sample of the damaged vehicle and helped in solving the case successfully despite very small sample size.

Keywords: Paint; Micro XRF; Differential Scanning calorimetry; Thermogravimetric analysis; Elemental analysis; Comparison; Forensic

Abbreviations: XRF: X-ray Fluorescence; STA: Simultaneous Thermal Analysis

Introduction

Paint is important physical evidence in forensic analysis [1]. Generally, queries regarding the paint comparison are asked by investigating officers in different cases such as hit and run cases and accident cases. Different types of paints have different properties. Paint consists of multiple components such as pigment binder, solvent, additives along with organic and inorganic constituents [2,3]. Based on the properties of constituents in paints, chemical and physical examination are carried out in forensic examinations [4]. The use of scientific instruments is found to be very helpful in confirmation of paint. Different types of chemical and instrumental techniques for paint comparison have been reported in literature [5]. During analysis, the sample collected from the crime scene plays an important role. Sample size collected from the scene decides the nature of analysis to be opted for comparison. If the sample size is satisfactory, each parameter can be examined successfully. Sometimes very few scrapings are sent by investigating officers that is insufficient for all examination. In such cases microscopic examination along with instrumental methods are opted for comparison. In many cases of paint comparison, non-destructive techniques such as microscopic analysis- such as fluorescence spectroscopy, stereomicroscopy, scanning electron microscopy are used [6-10]. Similarly instrumental techniques like, Fourier transform infrared spectroscopy, Pyrolysis Gas chromatography- mass spectroscopy infrared spectroscopy Raman spectroscopy techniques are also reported for paint comparison [6-12].

X-ray fluorescence (XRF) is an efficient technology for spot analysis of metal coating on vehicles. It is a nondestructive technique and capable of analyzing small paint samples. Hence the paints were compared using Micro XRF technique as major

physio-chemical evidence. Thermal method of analysis is also a very important technique in forensic examination and has been rarely applied for paint comparison. This method has been used in solving many forensic cases such as fiber, rubber, and cardboard comparison [13-15]. In the present paper along with stereo microscopic analysis and micro XRF technique, use of simultaneous thermal analysis (STA-Thermogravimetry and differential scanning calorimetry) has been successfully applied in solving an important accident case.

Case History

Tavera vehicles carrying people returning from the family function dashed to the tipper from the back side. In this accident the front part of white colored Tavera was badly deformed and flattened. This serious accident was so severe that seven people in Tavera died on the spot. The incident happened at night due to the negligence of the tipper driver. The driver in the tipper ran away from the spot with his tipper. The incident was registered under IPC section 279 (about road accident) 304 (A) (causing death by negligence) and IPC 338 (grievous hurt) along with motor vehicle Act. Police caught the driver and seized his tipper. The suspected tipper involved in the collision was observed carefully. Some white colored paint sample was found on the back side of tipper. The following samples were collected and sent to the Forensic science laboratory for comparative analysis.

i. Exhibit 1- Paint from the Tavera from collision site.

ii. Exhibit 2- Control white paint sample of Tavera.

iii. Exhibit 3- Control (Bluish- Grey colored) paint sample from Tipper.

iv. Exhibit 4- White colored paint sample collected from back side of (collision site) of tipper.

Experimental

Preliminary examination

Surface of the exhibits were observed under Motic stereo microscope.

Elemental Composition

The elemental composition of the sample was analyzed on Horiba Micro XRF XGT 7200. A piece of paint scraping collected from both vehicles was directly mounted on stage. The analysis was performed under a partial vacuum for 100 seconds with XGT Dia. 1.2 mm, X-ray tube vol. 50 kV & current 1.000 mA.

Simultaneous thermal analysis

The STA measurements were performed using NETZCSH STA 449 F3 (Jupiter) instrument using aluminum crucible with pierced lid and nitrogen as purge gas at a flow rate of 40ml /min. About 4-5 mg samples were used in this study. During study, samples of paint were trimmed into fine particles and placed in the center of the aluminum crucible with tweezers and each specimen was encapsulated. The analysis was performed in the range of 50 ^{0}C to 600 ^{0}C at the rate of 20K/min. Data was analyzed using NETZCSH protease software.

Results

The damaged Tavera vehicle is presented in Image (1) while suspected vehicle Tipper is shown in image (2). Preliminary examination of exhibits was done using stereomicroscope with following observations Image 1 & 2:

i. **Paint of Tavera from collision site**: White colored paint with blackish-brownish stains were seen under microscope and presented in Figure 1. The stains, when observed carefully revealed slight rust like portion. The rust like portion found on the collision site on Tavera paint may be due to rusted portion of tipper.

ii. **Control white paint sample of Tavera**: White colored paint seen under microscope is presented in Figure 1.

iii. **Control (Grey colored) paint sample from Tipper**: Bluish-Grey colored paint scrapping was found under microscope as shown in Figure 1.

iv. **White colored paint sample collected from back side of (collision site) of tipper**: White colour paint with blackish stain found clinging on collision site of tipper is shown in Figure 1. Microscopic observations of above exhibits revealed that white paint piece clinging on tipper from back side tallies with control paint of Tavera. Similarly rust like portion observed on exhibit 1 is due to the rusting portion of tipper.

Elemental composition of Paint by Micro XRF

After preliminary observation under microscope, elemental composition of exhibits was determined using micro Xrf. The spectrochemical composition of white paint in Ex no. 1, Ex no. 2 and 4 were found to be matching as shown in Table 1 and Figure 2. Similarly blackish brownish stains in exhibits 1 and 4 show similar spectrochemical composition as shown in Table 2 and Figure 3 and Figure 4. Hence, it was the paint that acted as physical evidence that linking the collision between accused vehicle and victim vehicle.

Simultaneous thermal analysis

Thermogravimetric measurements of paint degradation study mainly provide information on the thermal stability, composition, thermal decomposition process and its products. Thermal analysis of Ex no. 1, 2 and 4 shown in Figure 5 indicates decomposition temperature 300-500 °C with mass change of 48%. The Figure 6 shows two DSC curves at temperature of 211 °C and 414-425°C. The results of differential scanning calorimetric depicted in Figure 6 clearly show the perfect matching temperatures of Ex no. 1, 2 and 4. The results of STA depicted in Table 3 clearly show the perfect matching of TG and DSC curves of Ex 1, 2 and 4.

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Table 1: Elemental composition of white paint in exhibits 1, 2 and 4 by Micro Xrf.

Elements	% Mass			Atomic %		
	Ex 1	Ex 2	Ex 4	Ex 1	Ex 2	Ex 4
Si	3.49	3.46	5.08	5.85	5.86	8.43
S	0.28	0.14	0.09	0.41	0.21	0.13
Ca	0.99	0.42	0.07	1.17	0.49	0.08
Ti	91.29	92.91	91.44	89.88	91.13	89.07
Fe	2.1	1.74	2.03	1.77	1.47	1.69
Zn	0.11	0.11	0	0.08	0.08	0
Br	0.02	0	0.01	0.01	0	0
Sr	0.41	0.37	0.13	0.22	0.2	0.07

Table 2: Elemental composition of black stain in exhibit 1 and 4 by Micro Xrf.

Elements	% Mass		Atomic %	
	Ex 1	Ex 4	Ex 1	Ex 4
Si	22.92	10.04	33.7	16.72
S	2.85	1.15	3.68	1.68
K	0.37	0.18	0.39	0.22
Ca	3.27	0.61	3.37	0.72
Ti	58.38	53.43	50.35	52.14
Cr	0.98	0	0.78	0
Mn	0.13	0.36	0.1	0.31
Fe	8.94	33.06	6.61	27.67
Zn	0.54	0.03	0.34	0.02
Sr	0.51	0.11	0.24	0.06

Table 3: STA of Exhibits 1, 2 and 4.

Ex	Weight	Exothermic peak Temp peak Temp (℃)	Degradation peak Temp (℃)	Mass Change (%)
1	5.3	211.8	419.5	-48.95
2	5.6	211.4	425.3	-48.3
4	5.2	211.9	414	-48.27

Image 1 & 2: Damaged Tavera vehicle is presented in Image (1) while suspected vehicle Tipper is shown in Image (2).

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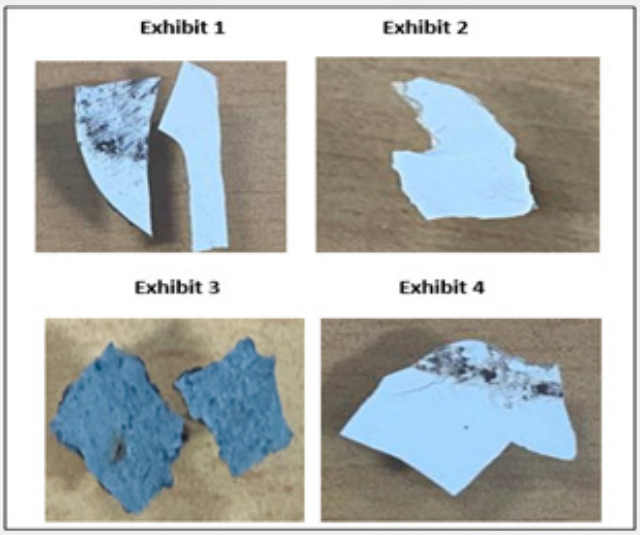

Figure 1: Microscopic examination of paint scrapings.

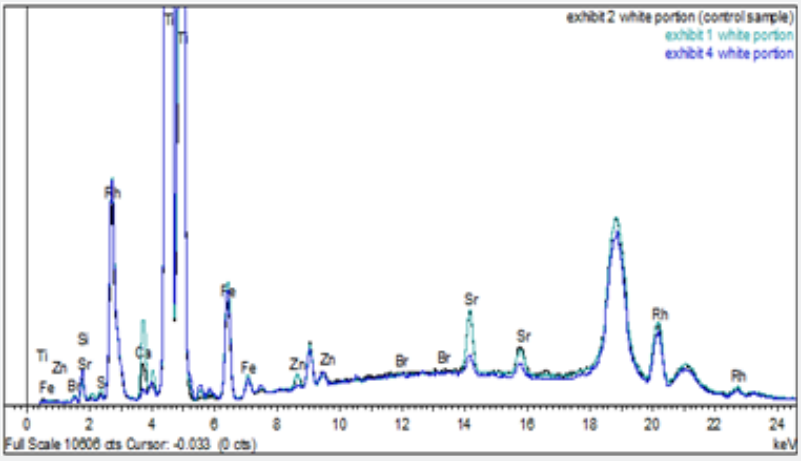

Figure 2: graph of Elemental composition of white paint in exhibits 1, 2 and 4 by microXrf.

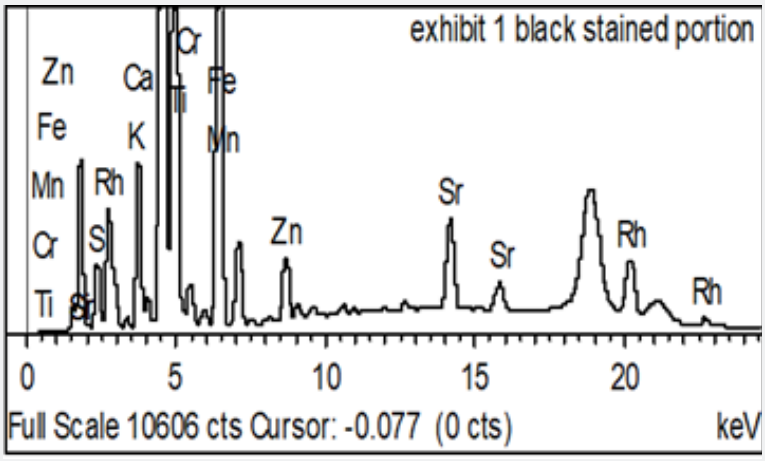

Figure 3: Elemental composition of black stain in exhibit 1 by Micro Xrf.

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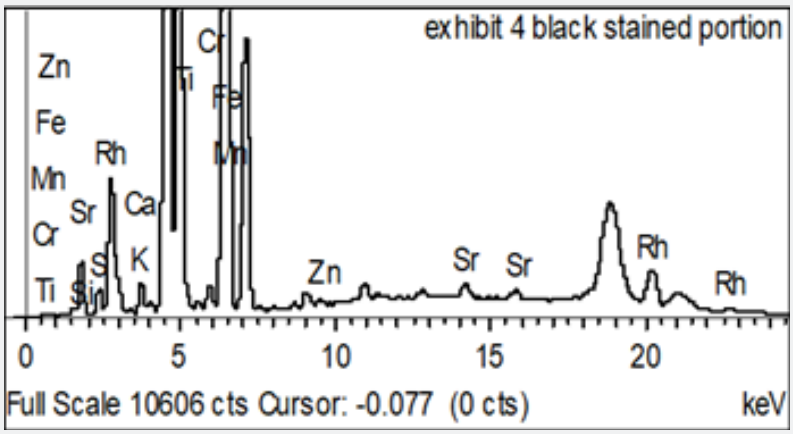

Figure 4: Elemental composition of black stain in exhibit 4by Micro Xrf.

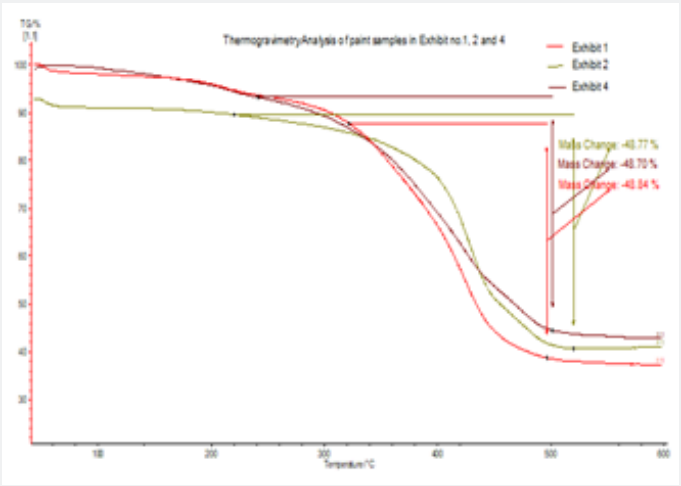

Figure 5: Graph of Thermogravimetric Analysis of Exhibits 1, 2 and 4.

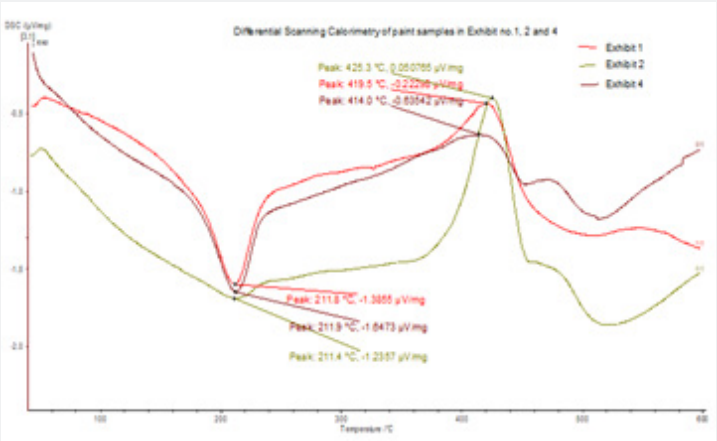

Figure 6: Graph of Differential Scanning Calorimetry of Exhibits 1, 2 and 4.

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Discussion

During the accident/ collision front side of Tavera badly intruded inside the back side of tipper. The back side of the tipper was so heighted that the paint colour of the tipper could not be transfer on front side of Tavera. The lower side of tipper had some rusted portion near middle of the rear wheels where the collision took place. The rust got transferred on the front side of Tavera and paint piece of the Tavera was found clinging to the back side of tipper near the collision position. Thus, in the present case, transfer of rusted part of the tipper on Tavera successfully link the incident. XRF is an efficient technology for spot analysis of metal coating on vehicles. Sometimes analysis of the evidence is challenging because of trace quantity. It is a nondestructive technique and capable of analyzing small paint samples. In the present study a small white paint scraping was found on back side of suspected tipper at collision site. Chemical tests such as the effect of various solvents on the scrapping was not possible to determine for such a small quantity. Hence the paints scrapings were compared using Micro XRF technique as major physio-chemical evidence. Elemental analysis of very few white colored paint particles adhered to suspected tipper in Ex no. 4 and white paint scrapping of Ex no. 1 and 2 were found to be matching. Hence it was the paint that acted as physical evidence that proves the collision of accused vehicle with victim vehicle. Thermal properties of paint were further studied using simultaneous thermal analysis. The advantage of STA is that both Thermogravimetry analysis and differential Scanning calorimetry are performed at same conditions. The results of paint comparison using thermal analysis and differential scanning calorimetric of the paint at the crime scene tallied with paint collected from accused tipper. Thus, physical evidence left at the crime scene when properly collected and examined form important evidence to link the accused with the crime.

Conclusion

Modern instrumental methods can now be used as successful tools to establish the similarity or dissimilarity of the physical evidence in hit and run cases in absence of eyewitness in such crime. The physical evidence left at the crime scene and on the suspected vehicle when properly collected and examined from important evidence to link the accused with the crime. The present study focused on comparison of paint samples using STA that incorporate both TG and DSC. Similarly, despite too small quantity of paint at site of collision of suspected vehicles, analysis was successfully carried out using Micro XRF. Thus, a case of road accident which took precious life of seven people was solved through comparative analysis of paint samples.

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