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Forensic Application of Energy Dispersive X-Ray Fluorescence to Analyse a Vehicle Paint Sample

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Abstract

A paint sample was analyzed by Energy Dispersive X-ray Fluorescence technique by using EDX-720 spectrometer equipped with Si(Li) detector having energy resolution 165eV accessible at Forensic Science laboratory, Madhuban, (Haryana, India). Both sides of the paint flakes were analysed and 8 elements were found common. Ti and Ba are the key element in paint flakes. Various pieces of paint flakes were collected from the scene of crime so that the data can also be supportive in the forensic investigations.

Keywords: Energy dispersive x-ray fluorescence; Paint flakes; Elemental analysis; Forensic science

Abbrevations: XRF: X-ray fluorescence; EDXRF: Energy dispersive X-ray fluorescence; AAS: Absorption Spectroscopy; ICP-AES: Inductively Coupled Plasma Atomic Emission Spectrometry; NAA: Neutron Activation Analysis; FSL: Forensic Science Laboratory

Introduction

Paint is a liquid, liquefiable or mastic composition which after application to a substrate in a thin layer, is converted to a solid film. It is most commonly used to protect colour or provide texture to objects. Pigment and a binder are two basic ingredients of the paint. The application characteristics of the liquid can be changed by adding a solvent (thinner)in paint. In paint, the combination of the binder and solvent is referred to as the paint "vehicle." Pigment and additives are dispersed within the vehicle. Paint evidence can be found in many hit and run cases and other types of crimes where it may prove to have material value. Paint flakes are generally characterized by a number of physical (colour, layer thickness, surface and layer features, and contaminants) and chemical (pigments, polymers, additives) features.

Energy Dispersive X-Ray Fluorescence (EDXRF) is one of the important methods that can be used to analyse different types of forensic samples. Searching for differences between suspected and known samples is the basic principle of forensic paint analysis and comparison. Both suspected and known samples should be properly collected for the forensic paint analysis. The absence of any difference between these samples may leads to the conclusion that the paint samples could have same origin. EDXRF is a non-destructive, qualitative as well as quantitative method for the elemental analysis of solids and liquid samples. When sample is irradiated by an appropriated incident radiations, it emits characteristic X-ray of energies that is of all the elements present in the sample. Compared to some other competitive techniques such as Atomic Absorption Spectroscopy (AAS) [1,2], inductively coupled plasma atomic emission spectrometry (ICP-AES) [3], and Neutron Activation Analysis (NAA)[4], EDXRF has the advantages of being non-destructive in nature, multi elemental, fast and cost effective.

An EDXRF system needs an X-ray source (radioisotope or X-ray tube), an X-ray detection system and a data acquisition system. EDXRF technique can be used for a tremendous variety of elemental analysis applications. This technique is widely used for art conservation and in archaeology [5-6], to analyse modern coloured glasses [7], analysis of Indian nail polish [8], analysis of coins [9-11], analysis of historical painting and paint layers [12-14], house paints study [15], fly ash sample study [16], analysis of under karat jewelry [17], ayurvedic drugs study [18], and in several forensic science investigations [19], it can be carried out on the basis of this technique. Now a days, Portable X-ray fluorescence (XRF) spectrometers are also available which have now wide applications for environmental samples, archaeological objects, and works of art. There are various places where it is not possible for the object to be transferred to a laboratory and destructive sampling is not permitted. In

these conditions, a portable XRF spectrometer is a useful tool for on-site analysis. It is also useful for on-site screening, i.e. distinguishing a sample of specific composition from others.

Present work reports the quantitative determination of different elements of paint flakes collected from the site of a traffic accident by using Energy Dispersive X-ray Fluorescence (EDXRF) technique. The flakes have two opposite sides with dark grey (sample 1) and white colour (sample 2). The small size of collected paint flakes fragments necessitates the use of non destructive and sensitive analytical method like EDXRF which do not require a large sample.

Materials and Methods

The EDXRF analysis of paint flakes has been carried out by EDX-720 spectrometer available at Forensic Science Laboratory (FSL), Madhuban (Haryana, India). X-ray spectrometer is provided with X-ray tube (Rh target) having tube voltage 5-50 KV and tube current lie in range between 1 to 1000 μA. The instrument is equipped with Si(Li) solid state detector having energy resolution of 165 eV at 5.96 KeV Kα Mn line with liquid nitrogen (LN2) cooled. The sample chamber is under observation with CCD camera which gives exact location of sample placement where X-rays are irradiated. The desktop type fluorescence X-ray spectrometer consists of an analyser, workstation and printer. The fundamental parameter with inbuilt program (EDX software version 1.00, release 017) provided by EDX-720 spectrometer was used to determine the relative concentration of all elements present in the sample. The live time for the analysis is 100 sec with off spin and collimator is of size about 3 mm with an air atmosphere.

The paint flake that has been taken having two layers with different colours. One side is with dark grey colour and opposite side with white colour named as sample 1 and sample 2 respectively. No further preparation is required for the sample analysis.

Result and Discussion

The results of XRF analysis with comparative percentage composition of paint sample 1 and sample 2 are depicted in Table 1. Major elements Ti and Ba were found in paint sample 1 with elemental concentration observed to be 52.12% and 33.75% respectively.

Table 1: Comparative Quantitative Result of sample 1 and sample 2.

Sr. No.	Analyte	Elemental Concentration (%) of Paint Sample 1	Elemental Concentration (%) of Paint Sample 2
1	Ti	52.217	93.087
2	Si	1.724	2.334
3	Fe	3.327	1.856
4	Zn	2.259	0.841
5	S	–	0.834
6	Bi	0.566	0.406
7	Ca	0.367	0.175
8	Cr	–	0.135
9	Mn	–	0.116
10	Sn	0.068	0.092
11	Co	–	0.052
12	Zr	–	0.043
13	Sr	0.026	0.027
14	Ba	33.757	–
15	P	5.689	–

Some minor elements namely P, Fe, Zn and Si were also observed with concentration in the range 1.72-5.69%. Traces of Bi, Ca, Sn and Sr were observed with concentration in the range 0.026-0.566%. But paint sample 2 have major concentration of only Ti that is about 90.087%. Two elements Si and Fe were found with elemental concentration of 2.334% and 1.856% respectively. Other elements like Zn, S, Bi, Ca, Cr, Mn, Sn, Co, Zr and Sr were found as traces whose concentration was below 1%. Surprisingly Ba was found absent here. The enormous contents of Ti pigments in the paint sample gave special properties to the paints that allow the paint to be more durable. For these purpose, manufacture also add Zn and Pb in the paint. But in the present case it is interesting to see that both are in a very inconsequential quantity. If we study paint guideline [20], and data we observe that Pb, Ti and Zn are the main elements of different paints. But in our case we observe the presence of Ti and Ba as major constituent.

All data available here can be used for the forensic purpose where sample has to be compared with the standard data or sample in different types of investigations of crime cases. Forensic science investigators mostly use this technique for elemental analysis of paint sample for measuring elemental compositions. In particular, the information of elemental analysis provides important evidence in a criminal investigation. XRF spectra of paints samples are shown in Figure 1 and 2. A commonly encountered overlap is observed of Ba L lines with the Ti K lines in case of sample 1. Here in sample 1, Ba is present in sufficient quantities; hence Ba K lines were also detected. With the available software PCEDX, the concentrations were obtained for various elements.

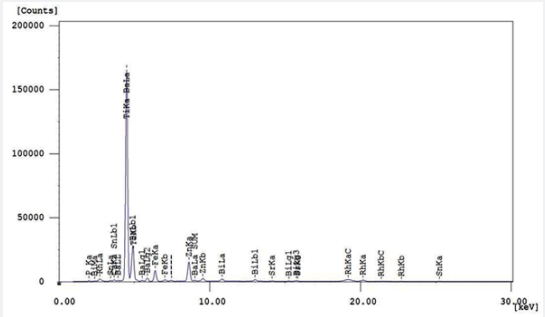

Figure 1: EDXRF Spectra of Sample 1.

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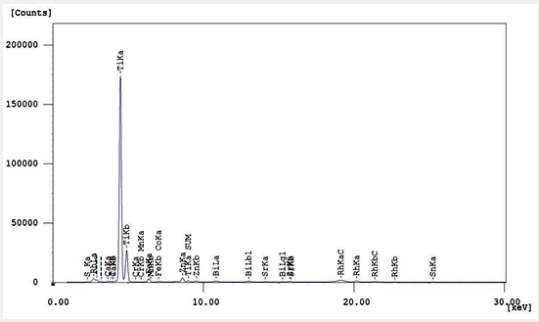

Figure 2: EDXRF Spectra of Sample 2.

Conclusion

XRF analysis is a powerful and widely used tool, which can be successfully applied to analyse the paint samples. It is non-destructive in the sense that a prepared specimen is usually not altered by the analytical procedure and with special instruments it is possible to analyze objects without taking samples and without physical contact. XRF method also facilitates the process of identification of unknown forensic sample. Physical and chemical properties of a coat of paint often allow us to determine the particular type of paint it is made up of, and to establish the degree of similarity between the evidence and the comparative materials. The present work was performed in order to judge the usefulness of results obtained by these methods for forensic purposes. In a hit and run case when there is no known suspected evidence, paint analysis with Paint Database can still be a very useful tool. Known standards from any painted or plastic objects involved should be collected for such type of analysis. With the help of country specific Paint Database and any automotive parts left at the scene of crime, may be useful to identify the make and model of an unknown vehicle.

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