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Derivative Ultraviolet Spectrophotometry: A Rapid, Screening Tool for the Detection of Petroleum Products Residues in Fire Debris Samples

Gurvinder Singh Bumbrah[1], Rajinder Kumar Sarin[2], Rakesh Mohan Sharma[1*]

[1]*Department of Forensic Science, Punjabi University, Patiala-147002, India*
[2]*Forensic Science Laboratory, Govt. of NCT of Delhi, Sector-14, Rohini, Delhi-110085, India*

ABSTRACT: The present article describes the potential utility of derivative ultraviolet (UV) spectrophotometric technique to detect petroleum products (gasoline, kerosene and diesel) in fire debris residues. Derivative UV spectra of these petroleum products were recorded in their neat state, and compared with those obtained from fire debris samples in order to distinguish them. Derivative UV spectrophotometry is capable of differentiating between these petroleum products as derivative spectra have more number of points for comparison than their corresponding normal spectrum. Additionally, it was observed that different burnt substrates (water, wire, cloth and foam) did not cause any interference in analysis and interpretation of spectra. Cyclohexane was used to extract traces of petroleum products from fire debris residues. The technique is rapid and could be used for the screening purpose at the initial stage of investigation. Taking into account the results obtained in the present work, it is possible to suggest the use of this technique to distinguish these petroleum products in fire debris samples received in forensic investigations related to arson or the use of improvised incendiary devices.

Keywords: derivative ultraviolet spectrophotometry, fire debris samples, arson, petroleum products, solvent extraction

Introduction

Arson is defined as any wilful and malicious burning of other’s property or burning of one’s own property for some illegal purpose especially with criminal or fraudulent intent. It also involves attempt to burn (with or without intent to defraud) a dwelling house, public building, motor vehicle, personal property of another or one’s own. It is wilful destruction of property by fire. Arson is one of the most difficult crimes to investigate because of its destructive nature. The crime itself destroys the physical evidence at its origin. Most of the evidences are destroy in burning process and rest are destroy during fire extinguish process. Arson is the one crime that destroys, rather than creates evidence as it progresses [1].

Fire debris analysis is an examination of fire debris samples in order to detect and identify ignitable liquid residues. Fire debris samples are most frequently received in cases of suspicious fires such as arson cases, for the detection and characterisation of trace amount of ignitable liquid. Fire debris samples may contain completely or partially burnt clothes, carpet, wood, soil, hairs, paper, concrete, wire and skin, recovered from the body of victim, accused and crime scene and are referred to forensic science laboratories for the detection and characterisation of petroleum residues. These debris may contain trace amounts of inflammable substances [2].

Petroleum products (petrol, kerosene and diesel) are frequently used to initiate the fire due to their easy availability, simple handling, cost effectiveness and storage. These substances are frequently used as a fire accelerant in arson and in bride burning cases [3]. The unexplained presence of these flammable liquids strongly indicates a fire of suspicious origin. Detection and identification of these flammable liquids are therefore helpful in determining origin and cause of fire [4]. Different analytical techniques such as Infra red spectroscopy [5], nuclear magnetic resonance spectroscopy [6], vapour phase ultra-violet spectroscopy [7], thin layer chromatography [8] and gas chromatography [9-11] can be used to analyse fire debris residue samples for the detection and identification of trace amounts of petroleum products. Amongst, gas chromatography is most frequently used for routine analysis of fire debris residue samples due to its high sensitivity, resolution and specificity. Gas chromatography was first applied to fire debris analysis in 1960 [12]. Despite the reasonable success of gas chromatography, it suffers from certain problems. The technique is destructive in nature. Peaks generated from substrate due to burning and pyrolysis products could cause interference in identification. Besides, evaporation of petroleum residues during fire causes loss of its low boiling components which further raises problems in interpretation of chromatograms [13]. Since petroleum products contain large number of components, longer run time is required to resolve these components, and hence the method is time consuming. The complex nature of chromatograms makes the comparison process tedious and raises the question against the reliability of interpretation and identification. Peaks from the background substrates such as cloth, wood *etc.* also enhance the complexity of chromatogram and further complicate the interpretation of chromatogram [14]. Most problems associated with gas chromatography can be minimised or eliminated through the use of UV spectrophotometry in derivative mode.

Derivative ultraviolet spectrophotometry is an analytical technique in which normal zero order spectrum of sample is mathematically differentiated into a derivative (first- or higher derivatives), and thereby enhances the “fingerprint” of a sample and provides cleaner spectrum. It isolates qualitative and quantitative information from overlapping bands of the analytes and interferences and useful for analysis of mixture of multi-components. This technique improves resolution bands, eliminates the influence of background or matrix and provides more defined fingerprints than traditional ordinary or direct absorbance spectra. It can separate superimposed curves for quantitative measurements and is able to suppress matrix effects [1,15,16].

Verweji and Bonte [17] detected the carboxyhaemoglobin in blood samples by using second derivative ultraviolet spectrophotometry. Cruz *et al.* [18] also determined carboxyhaemoglobin and total haemoglobin in carbon monoxide intoxicated patients using third derivative ultraviolet spectrophotometry. Randez-Gil *et al.* [19,20] simultaneously determined nitrazepam and clonazepam in urine and blood plasma samples by high order (fourth and fifth) derivative ultraviolet spectrophotometry. Sharma *et al.* [21] analysed some commonly abused over the counter drugs by derivative ultraviolet spectrophotometric method. Kaur *et al.* [22] analyzed some undetonated explosives by derivative ultraviolet spectrophotometry.

Saini *et al.* [23] compared some lipstick smears by ultraviolet-visible spectrophotometry operated in derivative mode and pointed out that derivative spectrophotometry provides more points for comparison than conventional ultraviolet spectrophotometry. Meal [24] analysed the fire debris samples using second derivative ultraviolet spectroscopy and observed a unique and easily recognisable second derivative UV spectrum of petrol, kerosene and diesel. Absence of minima at 251 nm and maxima at 261 nm in second derivative spectrum of kerosene differentiate it from diesel. Zerlia *et al.* [25] analysed different petroleum products using ultraviolet spectrometry and suggested that present method could be used as a tool for rapid screening of petroleum products in petroleum field without performing chromatographic separation prior to analysis by ultraviolet spectrometry.

It is observed that very little work had been done on the detection of petroleum products in fire debris samples using derivative ultraviolet spectrophotometry. Therefore, in the present study, UV spectrophotometry in normal and derivative mode is used to analyse fire debris samples. In this paper, we describe the potential utility of normal and derivative UV spectrophotometry in the analysis of fire debris residues.

Materials and Method

Reagents and Samples

Anhydrous sodium sulfate, Whatman filter paper no. 1 and cyclohexane of analytical grade were purchased from Loba Chemie, Ambala. The petroleum products (petrol, kerosene and diesel) analysed in the present study were purchased from petrol stations and oil depot of Patiala city, Punjab. These samples were of Hindustan Petroleum (HP) brand. Insulated wire, cloth piece and foam were purchased from local market of Patiala.

Instrument and Operating Conditions

Double beam UV-VIS spectrophotometer with model 1700 PharmaSpec (Shimadzu Corporation, Kyoto, Japan) was used to record the absorbance of samples in normal and derivative mode. Quartz cells of 1 cm path length were used. Instrument was operated in spectrum mode to record the zero, first and second order derivative spectra of samples. All samples were scanned from 320 to 245 nm region of ultraviolet band. Sample concentrations were adjusted to provide a sample absorption maximum of within unity. Cyclohexane was used as extracting solvent as well as reference. The following instrumental parameters were kept constant throughout the present study:

- Measurement mode – ABS
- Scanning range – 320-245 nm
- Absorbance recording range – 0.00 A ~ 1.00 A
- Scan speed – Fast
- Number of scans – 1
- Display mode – Overlay

Sample preparation

Neat samples

Neat samples of petroleum products (petrol, kerosene and diesel) were prepared by dissolving 20 µl petroleum product in 10ml of cyclohexane. Three different samples of each petroleum product in their neat state was analysed three times, making up to a total of 27 spectra.

Tap water samples

Tap water samples were prepared by dissolving 1 ml of petroleum product in 10 ml of tap water. 5 ml of it was then extracted trice with 10 ml of cyclohexane. Cyclohexane extracts the high boiling components of petroleum products [24]. The organic layers were collected, combined and filtered through Whatman filter paper containing anhydrous sodium sulfate to remove traces of water from it. Three different samples of each petroleum product in tap water was analysed three times and total of 27 spectra were recorded.

Other samples

Different matrices (insulated wire, cloth and foam) were moistened with petroleum products, ignited and extinguished with water. Each matrix was ignited and extinguished (with water) three times and three replicates of each sample was analysed. In this way, a total of 72 spectra (27 for burnt insulated wire, 27 for burnt cloth and 18 for burnt foam) were recorded. Burnt matrices were collected and subjected to solvent extraction procedure described in previous section. The filtered extracts were subjected to UV spectrophotometry and spectrum was recorded in the range of 320 to 245 nm.

Results and Discussion

In the present study, ultraviolet spectrophotometry in normal and derivative mode is used to analyse fire debris samples. The potential utility of this technique in screening of different petroleum products is observed. Tables 1-3 reflect the characteristic peak wavelengths of petrol, kerosene and diesel in neat and in different burnt matrices along with type of spectrum recorded.

Neat Samples

The zero order spectrum of petrol shows a broad absorption region at 255.5 nm (Fig. 1). However, in case of its first and second order derivative, the spectra are bipolar with more points for comparison. In its first order spectrum, maximum absorbance occurs at 251.9 nm while in second order spectrum of petrol, this characteristic peak shifts to 267.0 nm (Fig. 2).

Table 1: Characteristic peaks of petrol in their normal and higher order derivative spectra (1st and 2nd) in different matrices

Spectrum Order	Matrices									
	Neat		Water		Wire		Cloth		Foam	
	Max (nm)	Min (nm)	Max (nm)	Min (nm)	Max (nm)	Min (nm)	Max (nm)	Min (nm)	Max (nm)	Min (nm)
Zero	268.2, 264.7, 261.5, 259.7, 255.5[a]	267.1, 263.9, 260.8, 257.2	272.4, 264.9, 259.7[a], 255.5	271.3, 263.9, 256.2	254.9[a]	-	253.5[a]	-	NR	NR
First	272.1, 267.6, 264.7, 261.3, 257.9, 251.9[a], 247.4	275.5, 269.5, 266.0, 262.6, 260.2, 256.1, 249.7	286.0, 271.8, 267.5, 264.4, 261.1, 257.6, 251.9[a], 247.1	288.6, 275.6, 269.3, 266.1, 262.7, 260.3, 256.5, 249.6	296.0, 271.9, 264.2, 251.6[a]	306.9, 280.0, 264.9, 261.0	312.8, 306.1, 291.1, 285.8, 272.6, 267.1, 264.4, 258.1, 251.6, 246.5[a]	314.1, 307.4, 294.9, 289.7, 276.2, 269.3, 266.3, 262.6, 257.5, 247.8	NR	NR
Second	279.7, 276.5, 273.0, 270.6, 267.0[a], 263.6, 260.7, 257.3, 251.3	277.5, 274.1, 273.3, 268.4, 265.1, 261.7, 259.8, 255.4, 248.0	279.7, 273.0, 270.7[a], 267.0, 263.7, 260.7, 256.5, 251.2	274.2, 272.4, 268.4, 265.2, 261.7, 259.8, 255.4, 247.7	254.9[a]	255.6	280.4, 270.8[a], 266.4, 264.1, 254.3, 251.2	273.9, 268.8, 264.9, 255.5, 253.5, 247.4	NR	NR

"a" – Indicates wavelength of maximum absorbance
NR – Not recorded

Table 2: Characteristic peaks of kerosene in their normal and higher order derivative spectra (1st and 2nd) in different matrices

Spectrum Order	Matrices									
	Neat		Water		Wire		Cloth		Foam	
	Max (nm)	Min (nm)	Max (nm)	Min (nm)	Max (nm)	Min (nm)	Max (nm)	Min (nm)	Max (nm)	Min (nm)
Zero	272.7[a], 268.1	317.5, 270.3	272.6[a], 268.1	317.8, 270.2	272.3, 268.2[a]	270.7, 249.0	314.9, 273.0[a], 268.8	317.2, 313.7, 270.1	319.0, 272.6[a], 268.3	317.8, 269.9
First	291.1, 286.1, 282.4, 276.9, 271.5, 264.0[a], 260.8, 257.8, 252.0	294.9, 289.1, 283.9, 279.7, 274.4, 269.4, 262.4, 259.8, 253.4	310.9, 291.1, 286.0, 282.3, 276.9, 271.5, 263.9[a], 261.0, 258.0, 252.0	312.2, 294.9, 282.2, 283.6, 279.7, 274.5, 269.1, 262.3, 260.3, 253.4	314.5, 291.1, 286.0, 282.4, 277.0, 271.5, 263.9[a], 258.6	315.5, 295.2, 289.3, 283.6, 279.7, 274.5, 269.2, 262.4, 245.8	291.3, 286.1, 282.4, 276.2, 271.5, 264.1[a], 260.7, 257.9, 251.2, 248.6	295.2, 289.2, 283.9, 279.7, 274.5, 270.0, 262.2, 259.4, 254.2, 249.9	291.0, 286.1, 282.4, 276.9, 271.4, 263.9[a], 258.3, 251.9	295.1, 289.3, 283.8, 279.7, 274.4, 269.3, 262.3, 253.3
Second	308.3, 289.5, 284.2, 279.5, 273.9, 269.2[a], 265.4, 262.7	291.0, 285.6, 281.7, 277.3, 271.6, 267.0, 264.1, 246.0	290.2, 285.0, 280.6, 275.1, 270.7[a], 266.3, 263.5	294.0, 287.4, 282.9, 278.5, 272.8, 268.3, 264.6, 261.6	280.5, 275.3, 270.4[a], 267.5, 246.0	294.5, 278.9, 272.8, 268.4, 264.7	306.2, 298.7, 296.0, 293.2, 290.2, 284.5, 281.0, 275.3, 270.6[a], 265.8, 263.9	305.6, 298.1, 293.9, 291.8, 287.5, 283.1, 278.3, 273.4, 268.4, 264.8, 252.3	290.2, 280.5, 275.6, 270.3[a], 266.7	286.9, 278.6, 273.0, 268.3, 264.7

"a" – Indicates wavelength of maximum absorbance

Table 3: Characteristic peaks of diesel in their normal and higher order derivative spectra (1st and 2nd) in different matrices

Spectrum Order	Matrices									
	Neat		Water		Wire		Cloth		Foam	
	Max (nm)	Min (nm)	Max (nm)	Min (nm)	Max (nm)	Min (nm)	Max (nm)	Min (nm)	Max (nm)	Min (nm)
Zero	255.2^a	317.1	255.2^a	-	254.9^a	-	272.4, 255.3^a	315.7, 271.1	254.6^a	247.9
First	303.6, 296.6, 292.2, 286.4, 271.8, 264.2, 251.8^a	305.6, 299.2, 295.0, 288.6, 279.7, 262.1	298.0, 291.8, 286.1, 271.7, 268.3, 264.3, 251.9^a	299.0, 294.6, 287.8, 280.0, 269.3, 265.3, 260.6	304.3, 292.2, 286.3, 275.4, 271.8, 268.2, 264.3, 251.8^a	305.5, 295.0, 287.7, 280.0, 274.2, 269.2, 265.0, 260.5	318.8, 291.8, 286.3, 275.0, 273.0, 264.2, 250.8^a, 245.9	300.9, 288.5, 280.0, 274.1, 265.0, 260.0, 247.2	300.0, 296.0, 292.0, 271.7, 251.7^a	307.2, 298.7, 294.8, 279.9, 260.7, 245.8
Second (D_2N_3)	309.6, 290.6, 284.5, 275.7, 270.2, 266.6, 262.6, 248.9^a	293.5, 287.5, 278.3, 273.2, 268.2, 265.1, 255.3, 247.2	284.3, 276.0, 270.6, 266.7, 262.6, 249.4^a	293.4, 278.7, 273.0, 268.5, 265.4, 255.3	290.8, 284.7, 275.9, 270.2, 266.7, 262.4, 249.0^a	293.5, 288.7, 278.6, 273.2, 268.3, 265.1, 255.3	309.1, 302.6, 296.7, 290.3, 284.5, 275.5, 270.3, 266.7, 262.6, 248.8^a	306.1, 298.7, 294.0, 287.6, 278.5, 273.3, 268.0, 265.3, 254.8, 247.6	284.4, 276.3, 266.7, 248.4^a	293.3, 278.6, 273.2, 255.2

"a" – Indicates wavelength of maximum absorbance

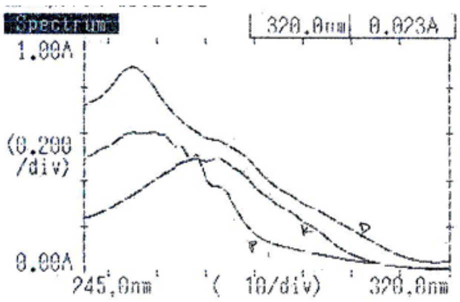

Fig. 1: Normal UV spectra of neat petrol (P), kerosene (K) and diesel (D) samples.

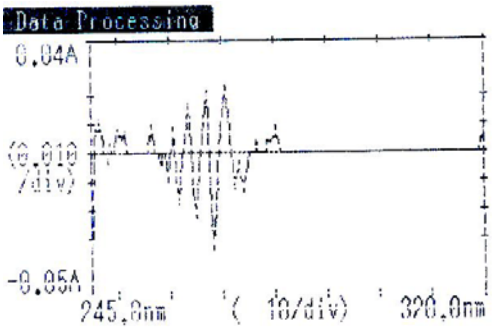

Fig. 2: Second order derivative UV spectrum of neat petrol sample.

In case of petrol, as we increase the derivative order, no specific pattern is observed in characteristic peak shift. In case of petrol, number of maxima and minima points increases with derivative order (*i.e.*, from zero to second order derivative). The second order derivative spectrum has more number of maxima and minima points than their corresponding first order derivative spectrum (Table 1). Meal [24] observed characteristic minima at 274 nm in second order derivative spectrum of gasoline.

The zero order spectrum of kerosene shows a broad absorption region at 272.7 nm (Fig. 1). In its first order spectrum, maximum absorbance occurs at 264.0 nm while in second order spectrum of kerosene, this characteristic peak shifts to 269.2 nm. In this case, second order derivative spectrum has one less maxima and minima point than their corresponding first order derivative spectrum (Table 2). The zero order spectrum of diesel shows a broad absorption region at 255.2nm (Fig. 1). In its first order spectrum, maximum absorbance occurs at 251.8 nm. In second order derivative spectrum of diesel, characteristic absorption peak is observed at 248.9 nm (Figure 3). In case of diesel, with increase in the derivative order, characteristic absorption peak shifts to shorter wavelength (Table 3). Meal [24] observed characteristic strong minima at 276 nm in second order derivative spectrum of kerosene.

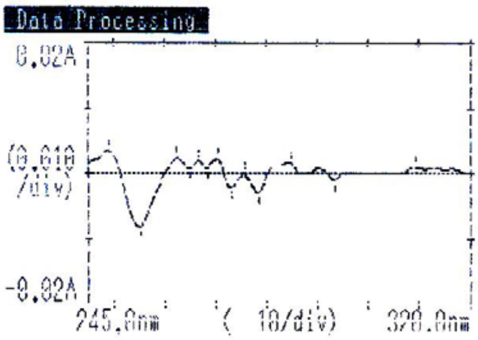

Fig. 3: Second order derivative UV spectrum of neat diesel sample.

Kerosene can be easily distinguished from petrol and diesel by observing the strong maxima at 272.7 nm in their zero order spectrum while it is difficult to distinguish between petrol and diesel by comparing their zero order spectra since both have characteristic absorption peak at 255.5 nm and 255.2 nm respectively. Therefore, higher order derivative spectra are recorded to distinguish petrol from diesel. In first order derivative spectra of petrol and diesel, characteristic absorption peak is observed at 251.9 nm and 251.8 nm respectively. However, in the second order derivative spectra of petrol and diesel, characteristic absorption peak is observed at 267.0 nm and 248.9 nm respectively and both spectra have different number of maxima and minima points and can be easily distinguished by visual comparison of their second order derivative spectra. Higher order derivative spectra (*i.e.*, second order derivative) have potential to distinguish these petroleum products (petrol, kerosene, and diesel) with certainty. However, Meal [24] reported that absence of strong minima at 251 nm and strong maxima at 261 nm in second order derivative spectrum of kerosene to be differentiated from diesel.

Comparison of Spectra of Petroleum Products Residues in Water

The zero order spectrum of petrol shows a broad absorption region at 259.7 nm. In case of its first and second order derivative, spectra show points of minima's along with maxima points. In its first order spectrum, maximum absorbance occurs at 251.9 nm while in second order derivative spectrum of petrol, this characteristic peak shifts to 270.7 nm (Fig. 4). In first and second derivative spectra of petrol, numbers of maxima and minima points are the same and more than their corresponding zero order spectrum (Table 1).

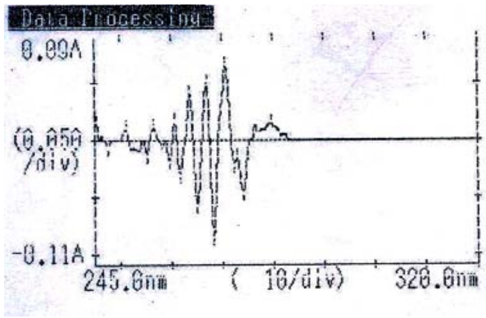

Fig. 4: Second order derivative UV spectrum of petrol extracted from water.

The zero order spectrum of kerosene shows a broad absorption region at 272.6 nm. In its first order spectrum, this characteristic absorption peak shifts from 272.6 nm to 263.9 nm while in second order derivative spectrum of kerosene, this characteristic peak further shifts to 270.7 nm (Fig. 5). The number of maxima and minima points is more in first order spectrum than their corresponding zero and second order derivative spectra (Table 2). The zero order spectrum of diesel shows a characteristic absorption peak at 255.2 nm. In its first order spectrum, the maximum absorbance occurs at 251.9 nm. In second order derivative spectrum of diesel, characteristic absorption peak shifts to 249.4 nm (Fig. 6). The peak of maximum absorbance shifts to shorter wavelength as we proceed from zero to second order derivative spectra of diesel (Table 3).

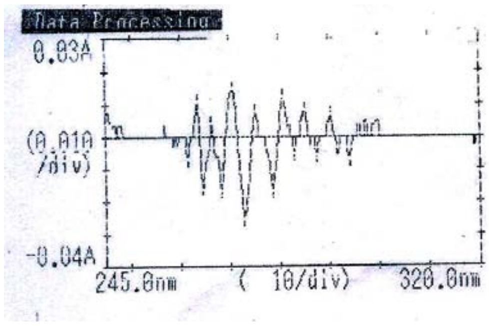

Fig. 5: Second order derivative UV spectrum of kerosene extracted from water.

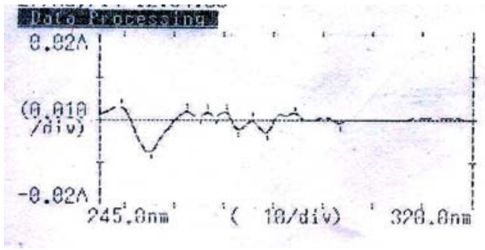

Fig. 6: Second order derivative UV spectrum of diesel extracted from water.

Comparison of Spectra of Petroleum Products Residues on Wire

The zero order spectrum of petrol shows a characteristic absorption peak at 254.9 nm. In its first order spectrum, this characteristic absorption peak shifts to 251.6 nm which further shifts to 254.9 nm in its second order derivative spectrum. The number of minima points are lesser in its second order derivative spectrum than their corresponding first order derivative spectrum, in contrast to case of its neat samples. It could be due to the excessive evaporation of petrol during the burning of wire (Table 1). The zero order spectrum of kerosene shows a broad absorption region at 268.2 nm (Fig. 7). In its first order spectrum, the characteristic absorption peak shifts from 268.2 nm to 263.9 nm. In its second order derivative spectrum, this peak further shifts to 270.4 nm. The number of maxima and minima points are higher in first order derivative spectrum than their corresponding zero and second order derivative spectra. No characteristic pattern is observed in peak shift with change in derivative order of spectrum (Table 2).

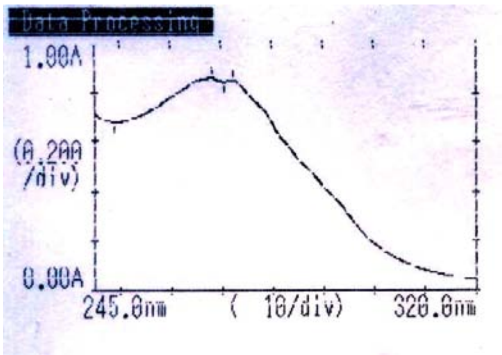

Fig. 7: Normal UV spectrum of kerosene extracted from wire.

The zero order spectrum of diesel shows a characteristic absorption peak at 254.9 nm. In its first order spectrum, this characteristic absorption peak shifts from 254.9 nm to 251.8 nm which further shifts to 249.0 nm in its second order derivative spectrum (Fig. 8). The numbers of maxima and minima points are higher in first order derivative spectrum than their corresponding zero and second order derivative spectra which is in agreement as in case of spectra of water as matrix. The characteristic absorption peak shifts towards lower wavelength with increase in derivative order of spectrum (Table 3).

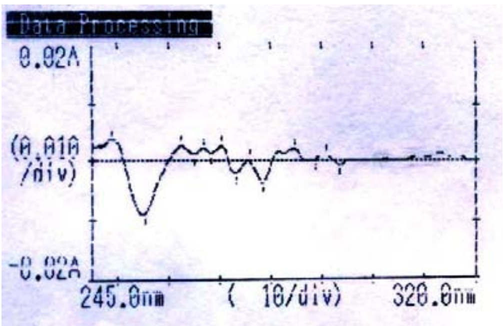

Fig. 8: Second order derivative UV spectrum of diesel extracted from wire.

Comparison of Spectra of Petroleum Products Residues on Cloth

A characteristic absorption peak at 253.5 nm is observed in zero order spectrum of petrol. In its first order spectrum, maximum absorbance occurs at 246.5 nm which shifts to 270.8 nm in its second order derivative spectrum (Fig. 9). The number of maxima and minima points is higher in first order derivative spectrum than their corresponding zero and second order derivative spectra, in contrast to spectra (zero, first and second order derivative) of neat petrol sample (Table 1).

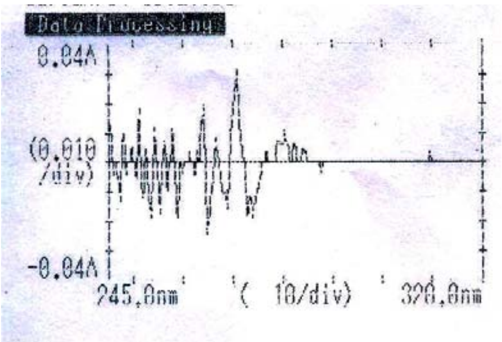

Fig. 9: Second order derivative UV spectrum of petrol extracted from cloth.

The zero order spectrum of kerosene shows a characteristic absorption peak at 273.0 nm. In its first order spectrum, this characteristic absorption peak shifts to 264.1 nm which further shifts to 270.6 nm in its second order derivative spectrum (Fig. 10). The numbers of maxima and minima points are higher in second order derivative spectrum than their corresponding zero and first order derivative spectra (Table 2). The zero order spectrum of diesel shows a broad absorption region at 255.3 nm. In its first order spectrum, the maximum absorbance occurs at 250.8 nm. In second order spectrum of diesel, characteristic absorption peak shifts to 248.8 nm. The number of maxima and minima points is higher in second order derivative spectrum than their corresponding zero and first order derivative spectra which are in agreement as in case of spectra of neat diesel sample but in contrast to spectra of diesel sample extracted from burnt wire and water matrices. Again in this case, increase in derivative order of spectrum shifts the characteristic absorption peak towards lower wavelength region (Table 3).

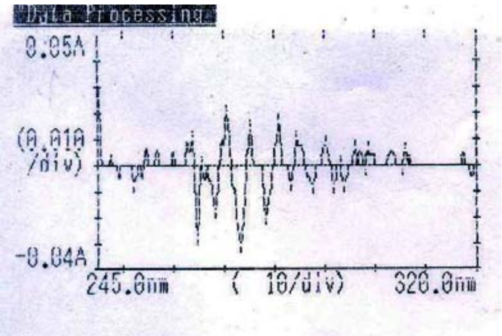

Fig. 10: Second order derivative UV spectrum of kerosene extracted from cloth

Comparison of Spectra of Petroleum Products Residues on Foam

Spectra (zero, first and second order derivative) are not recorded in case of petrol. It may be due to complete evaporation of petrol during burning process. The porous nature of foam may absorb petrol in trace quantities. But since foam is a synthetic material and it completely burns in fire and forms combustion or pyrolysis products during burning so it may be possible that such conversion at high temperature of fire also evaporates or burns that trace amount of petrol present in foam. The zero order spectrum of kerosene shows a characteristic absorption peak at 272.6 nm (Fig. 11) which shifts to 263.9 nm in its first order derivative spectrum. This characteristic absorption peak further shifts from 263.9 nm to 270.3 nm in case of its second order derivative spectrum. The numbers of maxima and minima points are higher in first order derivative spectrum than their corresponding zero and second order derivative spectra which are in agreement as in case of spectra of neat diesel sample and diesel sample extracted from burnt wire and water matrices but in contrast to spectra of diesel sample extracted from burnt cloth. As such no specific pattern is observed in shifting of wavelength region of characteristic absorption peak with change in derivative order (Table 2).

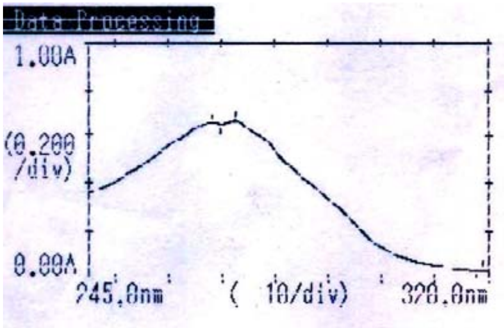

Fig. 11: Normal UV spectrum of kerosene extracted from foam.

The zero order spectrum of diesel shows a characteristic absorption peak at 254.6 nm. The maximum absorbance occurs at 251.7 nm in its first order derivative spectrum. This characteristic absorbance peak further shift to 248.4 nm in its second order derivative spectrum (Fig. 12). The number of maxima and minima points is higher in first order derivative spectrum than their corresponding zero and second order derivative spectra. The point of maximum absorbance shifts to lower wavelength with successive increase in derivative order of spectra (Table 3).

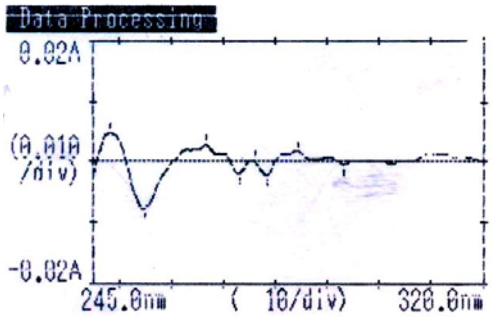

Fig. 12: Second order derivative UV spectrum of diesel extracted from foam

No significant change is observed in the position of characteristic peak with change in matrices. Rojas and Ojeda [16] and Meal [24] also suggested that peaks from background matrices did not interfere in interpretation and identification process and it also did not lead to false positive results. Peak shifts from zero to first order spectrum are very close in case of petrol and diesel and it is in contrast to case of kerosene with higher peak shift. However, a significant change is observed in peak shifts from first to second order spectrum of petrol and diesel. Thus peak shifting is a useful parameter to distinguish petrol from diesel on the basis of their second order derivative spectra. Therefore, peak shifting along with the visual inspection of normal and higher order derivative spectra are useful to discriminate petroleum products in neat as well as in fire debris samples. The presence or absence of maxima or minima point in derivative spectra (first and second) can be used to establish the differentiation between samples and could be helpful in exclusion of suspected petroleum product in fire debris residues. Although the technique is incapable of identifying the petroleum product in debris residues yet it is very useful and effective in screening. Derivative spectra not only provide more points for comparison than their corresponding normal zero order spectrum but it also enhances the certainty in exclusion of samples. Transformation of normal UV spectrum into derivative (first and second) spectra also enhances the discriminating potential of this technique.

Derivative UV spectrophotometric technique can be very useful and helpful for the screening of petroleum products in fire debris residues in cases where gas chromatograph is not available in laboratories. In addition to this, the technique can be used for initial screening purpose and final identity can be established by analysing the same sample with more sophisticated instrumental techniques such as gas chromatography-mass spectrometry.

Conclusion and Future Work

Derivate Ultraviolet spectrophotometry is an effective, non-destructive, well established analytical technique for the analysis of petroleum products as it provides much better fingerprints of petroleum products than the conventional UV spectrophotometry by resolving the overlapped and hidden peaks in spectra of petroleum products. It is observed that it is a reliable screening technique for the analysis of fire debris samples and elimination of sample can be rapidly done by visual comparison of derivative spectra of sample with their corresponding standard at the initial stage of analysis process. The technique is free from substrate interference and enhances the resolution of spectra of complex matrices.

Advent of gas chromatographic technique has simplified the issue of fire debris analysis due to its high sensitivity and resolution. However, gas chromatography has its limitations with regards to skilled manpower, analysis time and financial issues involved. In cases where gas chromatograph is not available in laboratories, UV spectrophotometric technique in their derivative mode can be very useful and helpful for the screening of petroleum products in fire debris residues. The present technique can be useful for screening of petroleum products in neat state and in case where it is extracted from fire debris samples; in examination of small quantity of samples recovered from crime scene.

Further studies including effect of different levels of evaporation of petroleum products on UV spectra is in progress. More kinds of substrates including plastics, rubber, wood, soil will be analysed under similar conditions using derivative UV spectrophotometry.

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Conflict of Interest

The authors declare that they have no conflict of interest.

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Additional information and reprint request:
Gurvinder Singh Bumbrah
Department of Forensic Science
Punjabi University
Patiala-147002, India
Email: bumbrah85@gmail.com