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Effect of Different Matrices on the Identification of Ignitable Liquid Residue in Post Burn Arson Debris: A Multi-Derivative UV-Visible Spectrophotometric Approach

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Analysis of arson debris is the foremost challenging task to the forensic investigators. Identification of the ignitable liquid residues in the fire debris is one of the prime objectives of forensic quest. This study evaluates the potential of derivative ultraviolet-visible spectrophotometric methods for the analysis and identification of ignitable liquid residues. In this work, arson was simulated using kerosene as an ignitable liquid on various matrices. Derivative UV spectra of kerosene were recorded in their neat state and compared with those obtained from simulated fire debris samples for the identification and detection of ignitable liquid residues. It was observed that different burnt substrates did not cause any interference. The obtained results indicated that the ignitable liquid absorption capacity of the substrate can play an important role in the extraction and identification of ignitable liquid from fire debris. The used technique proved to be rapid, easy, reproducible and efficient.

Keywords: Arson, Forensic, Derivative UV-Vis spectrophotometry, Ignitable liquids, Matrices.

INTRODUCTION

The word 'arson' is routinely employed to describe a crime that involves the intentional burning of any property or person. The term 'arson' typically originates from an Anglo-French word means "the act of burning. 'Arson' can be legally defined as the willful and malevolent burning of a dwelling, vehicles, land, or to one′s property for a wrongful insurance claim. Arson can potentially damage living persons and domestic animals [1]. Arson is mostly committed to taking revenge, to terminate crime traces and evidence or to gain compensation fraudulently. Investigation of fire initiates with the accurate determination of its possible origin and cause. A large variety of ignitable liquids may be used as accelerants to cause arson. Ignitable liquids are typically commercially available fuels or solvents consist of hundreds of components [2]. Most of the frequently used ignitable liquids are petroleum based products such as petrol, diesel, kerosene turpentine oil, *etc.* as they are available and catch fire easily [3]. A fire naturally occurs when fuel comes together with oxygen and a heat source. It is the role of the fire investigator to determine how and why these factors came together and to discover out that the fire was an accident or an intentional act.

The investigation of the scene of arson is one of the most complicated assignments in forensic sciences due to the destructive and spontaneous changing nature of the evidence by the fire. Fire debris commonly consists of fully or partially burnt materials like paper, cloth, carpet, furniture, concrete, wire, *etc.* are transported to forensic laboratories for the identification and characterization of the residues of ignitable liquids. The debris may contain trace amounts of inflammable substances. Detection of an ignitable liquid residue in burnt debris recovered from a fire scene is a critical investigative task for the investigator that may help to establish the cause and origin of fire [4]. Several methods are available for the scientific analysis of extracted ignitable liquid residues (ILRs) from various substrates. Analytical methods can be largely classified into destructive and non-destructive techniques. The fundamental difference between a destructive and nondestructive technique is the consistency of post-analyzed sample quality and repeatability of the analysis by using the same sample. A sample can only be analyzed for a single time by using a destructive technique. While a non-destructive technique can repeat a particular analysis of the same sample for multiple instances. In case of the UV spectrophotometry of an ignitable liquid, sample extraction is necessary but the spectral analysis can be repeated several times on the extracted sample. Gas chromatography [5-8], liquid chromatography [9-11] and thin layer chromatography [12] are most commonly used for the analysis of ignitable liquid residues (ILRs) in fire debris. Although most of the chromatographic techniques (except TLC) are sufficiently sensitive and conclusive, their destructive and interference generating nature is the problematic section during the analysis of ILRs [4].

Spectrophotometry is the most frequently applied technique in forensic evidence analysis due to its simplicity, rapidity, sensitivity, accuracy, precision, conclusiveness, robustness and cost-effective nature [13,14]. Except for atomic absorption spectroscopy (AAS), atomic emission spectroscopy (AES) and mass spectroscopy (MS), all the spectroscopic methods are relatively non-destructive [15,16]. Derivative ultraviolet-visible (UV-Vis) spectrophotometry is one of the non-destructive spectroscopic techniques used for the qualitative and quantitative analysis of numerous functional groups based on their specific absorption on different wavelengths [13]. In this spectrophotometric method, the obtained raw spectra are further differentiated into its higher derivatives (first-order derivative to higher ones) by mathematical algorithms to reduce the background noise and positively enhance the resolution. By properly obtaining the higher derivatives, the minute spectral features of the original absorption spectra become more defined [13]. Derivative UV-visible spectrophotometry is frequently used in different industries for analytical purposes as well as in forensic science for the analysis of ink [17,18], drugs [19,20] and petroleum products [4]. This specific technique is effectively established for the analysis of remaining volatile components in arson scenes such as ILRs in the unburnt absorbed liquid state and vapour state by solvent extraction and activated charcoal strip (ACS) extraction methods, respectively [21]. In the present study, the effect of commonly encountered matrices *i.e.* wood, tile and polyvinyl chloride (PVC) on the identification of ILRs *i.e.* kerosene is analyzed by derivative UV spectrophotometry.

EXPERIMENTAL

Kerosene, purchased from the Government authorized public distribution system (PDS) in Jhansi, India, was selected as an ignitable liquid. Common households like wood, tile and PVC floorings were selected as the matrices. Hexane of analytical grade was used as the extraction solvent. The collection of kerosene residue from burnt matrices was done by the preparation of simulated miniature arson scenes in the laboratory.

Sample preparation: Tile and wood pieces of 12 cm × 12 cm × 0.8 cm dimension, PVC sheet pieces of 12 cm × 12 cm × 0.3 cm dimension and cotton cloth pieces of 12 cm × 12 cm × 0.1 cm dimension were prepared as matrices. Each piece of the matrix was moistened with 5 mL kerosene measured in a measuring cylinder and left for 4 min. The matrices were ignited in a fume hood and extinguished after 60 s by placing a beaker inverted over the burning sample to forcefully stop the oxygen supply. From all the burnt matrices, tile and wood pieces of 4 cm × 4 cm × 0.8 cm dimension, PVC sheet pieces of 4 cm × 4 cm × 0.3 cm dimension and cotton cloth pieces of 4 cm × 4 cm × 0.1 cm dimension were separated and placed in a 500 mL glass beaker filled with 15 mL of hexane and closed with a lid. Aluminium foil was tightly wrapped around the lid to minimize sample evaporation or external interferences. The sealed containers were further placed on an ultrasonicator for 10 min for the fine extraction of residual kerosene. Additionally, negative samples were also prepared. Burnt and unburnt matrices of the same dimensions as mentioned above were placed in hexane and ultrasonicated.

Operational conditions: A double beam UV-visible spectrophotometer (model: 1700 Pharm-Spec, Shimadzu Corporation, Kyoto, Japan) was used to obtain the spectral data from the burnt samples in zero and higher derivative modes. A 1 cm path length of quartz cell was used. Zero and higher-order derivative spectra of the samples were collected by placing the instrument in spectrum mode. The spectral data of all the samples were collected between 320 to 245 nm of the ultraviolet region. Before spectral data collection, each extracted sample was filtered by using a 0.2 µm syringe filter. Firing and extinguishing were performed three times for each sample as well each sample was analyzed thrice so a total of 45 spectra (15 for each matrix) were recorded by UV-Vis spectrophotometer. A sample absorption maximum was provided by adjusting the concentration of the sample. Some instrumental modes were kept consistent throughout the data collection procedure (Table-1).

TABLE-1
LIST OF DIFFERENT PARAMETERS AND THEIR CONDITIONS KEPT FOR THE MEASUREMENTS IN THE PRESENT EXPERIMENT

Parameters	Condition
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

RESULTS AND DISCUSSION

In present work, the derivative UV-visible spectrophotometry was used to assess the effect of different matrices on the identification of burnt kerosene samples in simulated arson scenes. Table-2 consists of all the absorption maxima and minima of the zeroth to fourth-order spectra of standard and extracts from three matrices burnt with kerosene.

Intra-comparison

Standard spectra: A total number of 4, 11, 14, 16 and 18 absorption maxima were observed from zero to fourth-order derivative spectrum (Fig. 1a-e) of standard kerosene, respectively. Among all the absorption maxima 267.6 nm in the zeroth order (Fig. 1a), 264.2 nm in the first order (Fig. 1b), 269.1 nm in the second order (Fig. 1c) and 270.3 nm in the third and fourth order derivative (Fig. 1d and e) spectrum has the highest absorbance. In the standard spectra of kerosene 3, 11, 15, 14

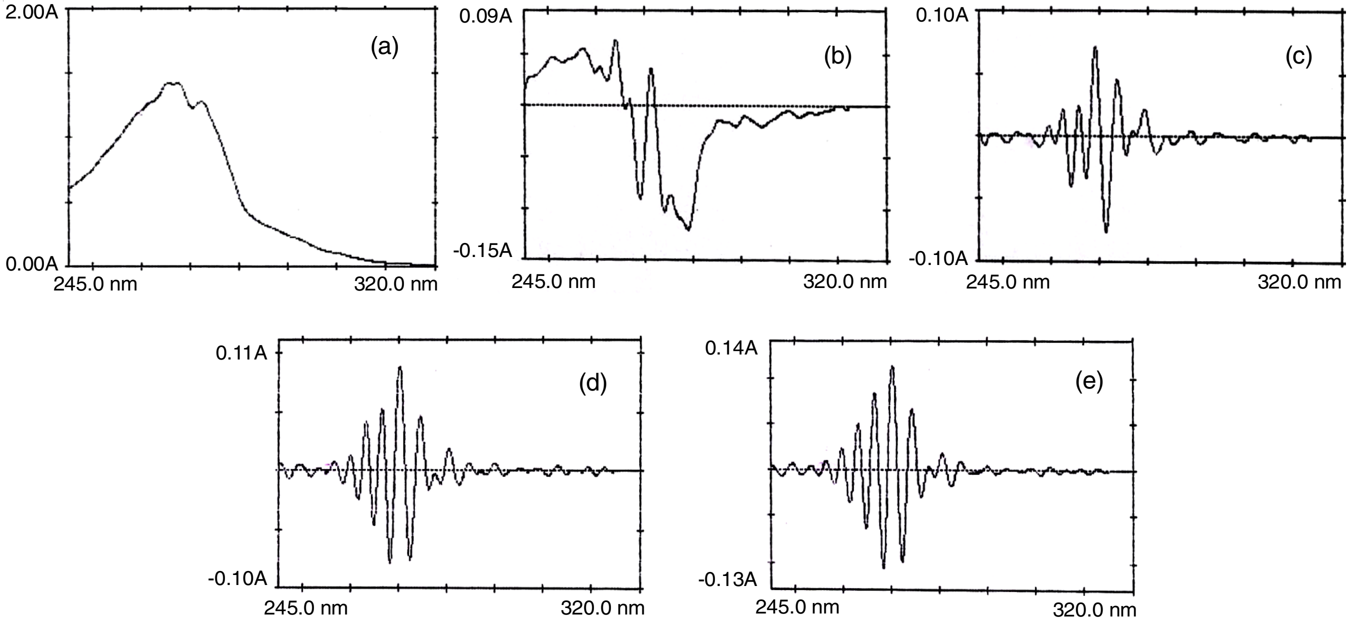

Fig. 1. UV absorption spectra of standard kerosene (a) zeroth order, (b) first order, (c) second order, (d) third order, (e) fourth order

TABLE-2
COMPLETE ABSORPTION PEAKS FROM ZERO ORDER TO FOURTH ORDER ABSORPTION SPECTRUM OF STANDARD AND EXTRACTED KEROSENE BURNT WITH WOOD, TILE AND PVC MATRICES

Spectrum order	Matrices							
	Neat		PVC		Wood		Tile	
	Peak	Valley	Peak	Valley	Peak	Valley	Peak	Valley
Zero	318.8	317.0	274.7	262.1	318.4	317.0	274.3	262.6
	272.4	270.5	–	–	272.2	270.6	–	–
	267.6	266.5	–	–	265.3	–	–	–
	265.6	–	–	–	–	–	–	–
First	304.6	305.9	281.3	285.1	310.5	305.7	299.4	302.5
	300.0	302.3	271.4	277.1	304.7	302.2	291.4	293.7
	290.9	294.4	267.3	268.7	299.9	294.5	286.3	288.4
	285.7	289.0	–	245.8	290.9	289.0	277.6	279.2
	275.4	278.9	–	–	285.7	279.1	275.6	276.7
	271.4	274.1	–	–	275.5	274.1	271.7	274.0
	267.0	269.1	–	–	271.4	269.1	267.2	268.9
	264.2	266.1	–	–	264.1	262.4	261.9	263.4
	261.0	262.3	–	–	260.9	260.0	250.2	256.4
	257.5	259.8	–	–	257.7	253.4	–	–
	251.0	253.3	–	–	250.9	–	–	–
Second	308.1	310.3	287.0	283.1	316.8	318.0	298.0	300.3
	302.2	304.1	279.8	275.3	308.9	312.2	290.1	292.3
	294.6	300.0	270.5	267.7	303.3	306.0	284.8	287.0
	289.0	290.9	263.4	258.2	297.8	301.1	280.5	283.2
	283.9	285.4	256.4	252.0	290.0	292.3	274.7	278.2
	279.3	281.8	248.6	247.1	284.4	288.0	270.4	272.0
	277.0	277.7	246.8	–	280.7	283.2	260.6	267.6
	273.7	275.5	–	–	277.2	278.1	257.3	259.2
	269.1	271.4	–	–	274.9	276.4	248.2	251.5
	265.7	267.3	–	–	270.3	271.8	–	–
	262.5	264.2	–	–	266.4	267.8	–	–
	259.6	261.0	–	–	263.2	265.1	–	–
	253.1	257.8	–	–	260.5	261.3	–	–
	248.3	251.0	–	–	256.7	258.8	–	–
	–	246.4	–	–	249.3	252.2	–	–
	–	–	–	–	–	246.9	–	–

Third	312.8	311.0	284.5	291.6	302.8	299.7	288.1	285.9
	309.3	304.8	276.9	281.8	294.4	291.0	273.7	271.9
	303.2	301.1	269.2	271.8	289.0	285.7	269.3	261.7
	295.4	291.9	252.9	264.7	284.6	281.9	253.4	250.9
	290.0	288.1	246.1	250.3	279.8	275.8	246.6	–
	284.6	282.5	–	–	273.8	271.9	–	–
	280.1	278.7	–	–	269.2	267.2	–	–
	277.1	276.3	–	–	265.8	264.6	–	–
	274.5	272.4	–	–	262.8	261.4	–	–
	270.3	268.3	–	–	259.5	257.8	–	–
	266.5	264.9	–	–	253.0	250.7	–	–
	263.1	261.7	–	–	–	–	–	–
	260.1	258.5	–	–	–	–	–	–
	256.8	254.9	–	–	–	–	–	–
	253.2	252.0	–	–	–	–	–	–
	249.7	247.4	–	–	–	–	–	–
Fourth	312.7	311.1	292.0	289.9	305.3	316.8	292.2	297.8
	309.3	307.7	288.7	286.2	301.0	303.1	287.2	289.5
	306.4	304.8	283.1	280.4	292.2	297.7	282.7	284.7
	302.7	301.1	275.6	272.7	287.2	289.9	278.6	280.5
	298.9	297.3	272.9	270.4	283.0	284.8	272.5	274.5
	294.0	291.8	268.2	264.5	277.6	280.7	268.2	270.3
	290.0	286.6	259.1	253.6	272.7	274.8	259.0	261.0
	284.5	282.5	251.7	249.3	268.2	270.3	252.0	254.9
	280.7	279.1	248.4	247.2	265.0	266.4	–	249.5
	277.9	276.3	–	–	261.5	263.1	–	–
	274.4	272.3	–	–	258.4	260.1	–	–
	270.3	268.4	–	–	251.9	256.9	–	–
	266.6	264.9	–	–	247.2	249.4	–	–
	263.2	261.5	–	–	–	–	–	–
	259.9	258.3	–	–	–	–	–	–
	256.7	255.2	–	–	–	–	–	–
	253.6	251.6	–	–	–	–	–	–
	249.6	247.5	–	–	–	–	–	–

and 18 absorption minima (Fig. 1a-e) were observed from zeroth to fourth-order, respectively. A 317.0 nm in the zeroth-order (Fig. 1a), 278.9 nm in the first order (Fig. 1b), 271.4 nm in the second order (Fig. 1c), 268.3 nm in the third-order (Fig. 1d) and 268.4 nm in the fourth-order (Fig. 1e) were the absorption minima with maximum intensity. Bumbrah *et al*. [4] reported similar results in their study on petroleum product residues from fire debris samples. In this study, the highest absorption maxima and minima in second order derivative spectra of standard kerosene sample were observed at 269.1 and 272.6 nm, respectively.

Spectra of extracted residue from PVC: A significant drop in the number of absorption maxima was observed in the extracted residue of kerosene from burnt PVC samples. A total number of 1, 3, 7, 5 and 9 absorption maxima (Fig. 2a-e) were observed from zero to fourth-order derivative spectrum of kerosene extracted from burnt PVC, respectively. Among all the maxima, 274.7 nm in the zero-order (Fig. 2a), 271.4 nm in the first order (Fig. 2b), 287 nm in the second-order (Fig. 2c), 279.8 nm in the third-order (Fig. 2d) and 246.8 nm in the fourth order (Fig. 2e) derivative spectrum has the highest absorbance. 1, 4, 6, 5 and 9 absorption minima (Fig. 2a-e) were observed from zero to the fourth-order of burnt kerosene samples with PVC matrices, respectively. The absorption minima with maximum intensity at 262.1 nm in the zeroth-order (Fig. 2a), 285.1 nm in the first order (Fig. 2b), 283.1 nm in the second-order (Fig. 2c), 281.8 nm in the third-order (Fig. 2d) and 247.2 nm in the fourth-order (Fig. 2e) were observed.

Spectra of extracted residue from wood: The number of absorption peaks remained relatively constant in the sample extracted from burnt wood. A total number of 3, 11, 15, 11 and 13 absorption maxima (Fig. 3a-e) were observed from zero to fourth-order derivative spectrum of kerosene extracted from burnt wood respectively. Among all the maxima, 265.3 nm in the zero-order (Fig. 3a), 264.1 nm in the first order (Fig. 3b), 270.3 nm in the second-order (Fig. 3c), 269.2 nm in the third-order (Fig. 3d) and 272.7 nm in the fourth-order (Fig. 3e) derivative spectrum has the highest absorbance. Similarly, 2, 10, 16, 11 and 13 absorption minima (Fig. 3a-e) were observed from zeroth to the fourth-order of burnt kerosene samples with wood matrices, respectively. The absorption minima with maximum intensity at 317.0 nm in the zeroth-order (Fig. 3a), 279.1 nm in the first order (Fig. 3b), 272.8 nm in the second-order (Fig. 3c), 271.6 nm in the third-order (Fig. 3d) and 270.3 nm in the fourth-order (Fig. 3e) were also observed.

Spectra of extracted residue from tile: The number of absorption peaks observed in the samples extracted from burnt tiles was comparatively less than wood but more than PVC. A total number of 1, 9, 9, 5 and 8 absorption maxima (Fig. 4a-e) were observed from zero to fourth-order derivative spectrum of kerosene extracted from burnt tile, respectively. Among all the maxima, 252 nm in the zero-order (Fig. 4a), 250.2 nm in

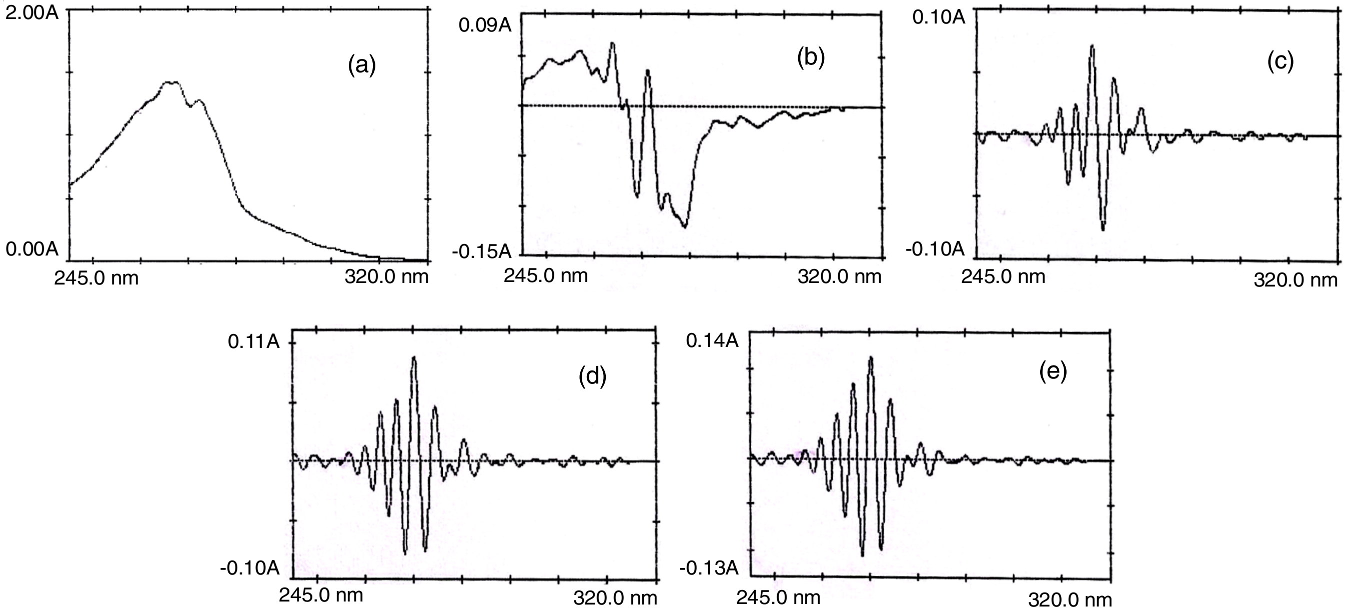

Fig. 2. UV absorption spectra of kerosene burnt with PVC (a) zeroth order, (b) first order, (c) second order, (d) third order, (e) fourth order

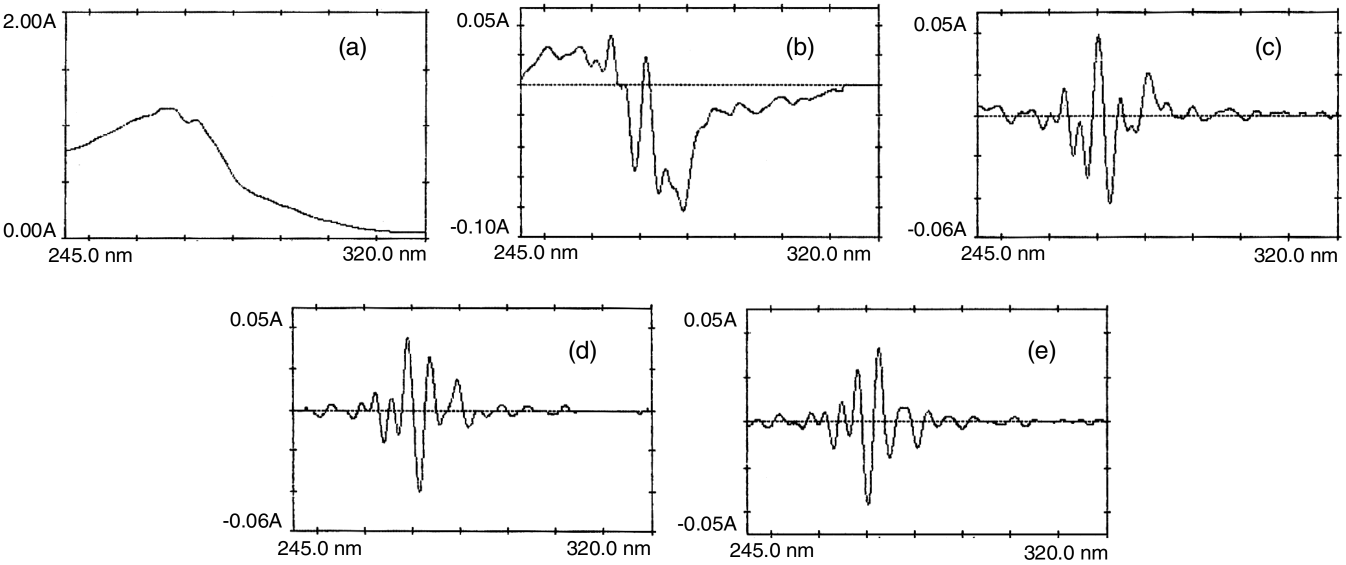

Fig. 3. UV absorption spectra of kerosene burnt with wood (a) zeroth order, (b) first order, (c) second order, (d) third order, (e) fourth order

the first order (Fig. 4b), 248.2 nm in the second-order (Fig. 4c), 253.4 nm in the third-order (Fig. 4d) and 252 nm in the fourth-order (Fig. 4e) derivative spectrum has the highest absorbance. In the same way, 1, 9, 9, 4 and 9 absorption minima (Fig. 4a-e) were observed from zeroth to the fourth-order of burnt kerosene samples with tile matrices, respectively. 247.4 nm in the zeroth-order (Fig. 4a), 256.4 nm in the first order (Fig. 4b), 252.1 nm in the second-order (Fig. 4c), 250.9 nm in the third-order (Fig. 4d) and 270.3 nm in the fourth-order (Fig. 4e) were the absorption minima with maximum intensity.

Inter-comparison

Previous researchers explored derivative UV spectra of different ignitable liquids up to the second order as McCurdy *et al.* [22] used vapour phase ultraviolet spectroscopy to analyze accelerants from fire debris. This study concluded that except alkenes and polycyclic hydrocarbons ultraviolet spectroscopy is a very good screening technique for the identification of petroleum products and can be useful to distinguish individual accelerants in a mixture. In the present study, matrix interference has been added as an additional factor to check their effect on the identification of residual kerosene from burnt debris. The derivative UV spectra of all the extracted samples from different burnt matrices were obtained up to the fourth order to investigate whether the higher derivative spectra contribute to the identification of the residual kerosene. Table-3 summarizes the similar absorption maxima and minima of the extracted samples from burnt wood, PVC and tile pieces up to fourth order with the standard kerosene. From Table-3, it is clearly visible that the number of similar absorption maxima for samples obtained from burnt wood is relatively greater than PVC and tile up to third order derivative spectra. But very few similar

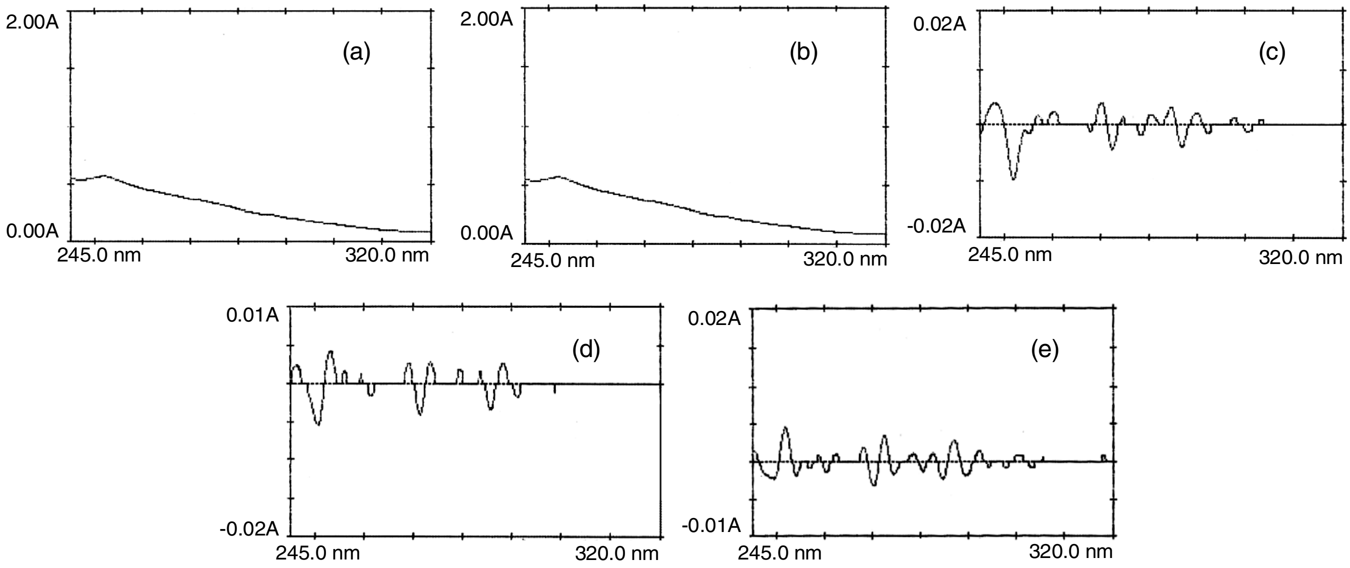

Fig. 4. UV absorption spectra of kerosene burnt with tile (a) zero order, (b) first order, (c) second order, (d) third order, (e) fourth order

TABLE-3
SUMMARIZED TABLE OF MULTIPLE DERIVATIVE SIMILAR ABSORPTION MAXIMA AND MINIMA OF STANDARD AND BURNT KEROSENE WITH VARIOUS SUBSTRATES

Derivative orders	Standard	Matrices		
		Wood	Tile	PVC
		Maxima		
Zero	318.8, 272.4, 265.6	318.4, 272.2, 265.3	No similar peaks	No similar peaks
First	300.0, 290.9, 285.7, 275.4, 271.4, 267.0, 264.2, 261.0, 257.5, 251.0	299.9, 290.9, 285.7, 275.5, 271.4, 264.1, 260.9, 257.7, 250.9	291.4, 275.6, 271.7, 267.2	271.4, 267.3
Second	308.1, 302.2, 294.6, 289.0, 283.9, 279.3, 277.0, 273.7, 269.1, 265.7, 262.5, 259.6, 253.1, 248.3	308.9, 277.2, 266.4, 260.5	290.1, 284.8, 248.2	279.8,248.6
Third	303.2, 295.4, 290.0, 284.6, 280.1, 277.1, 274.5, 270.3, 266.5, 263.1, 260.1, 256.8, 253.2, 249.7	302.8, 284.6, 279.8, 262.8, 259.5, 253.0	273.7, 253.4	284.5, 276.9, 252.9
Fourth	306.4, 302.7, 298.9, 290.0, 284.5, 277.9, 274.4, 270.3, 266.6, 263.2, 259.9, 256.7, 253.6, 249.6	277.6	278.6, 259.0	259.1
		Minima		
Zero	317.0, 270.5	317.0, 270.6	Not found	Not found
First	302.3, 294.4, 289.0, 278.9, 274.1, 269.1, 266.1, 262.3, 259.8, 253.3	302.2, 294.5, 289.0, 279.1, 274.1, 269.1, 262.4, 260.0, 253.4	302.5, 293.7, 279.2, 274.0, 268.9	268.7
Second	300.0, 277.7, 275.5, 271.4, 267.3, 261.0, 257.8, 251.0, 246.4	278.1, 271.8, 267.8, 261.3, 246.9	300.3, 278.2, 272.0, 267.6, 251.5	275.3, 267.7, 258.2, 247.1
Third	291.9, 282.5, 276.3, 272.4, 268.3, 264.9, 261.7, 258.5	281.9, 275.8, 271.9, 264.6, 261.4, 257.8	271.9, 261.7	291.6, 281.8, 271.8, 264.7
Fourth	297.3, 286.6, 272.3, 264.9, 261.5, 255.2, 247.5	297.7	261.0, 254.9	286.2, 272.7, 264.5, 247.2

absorption maxima are obtained in the fourth order for all the three matrices, while in absorption minima, a similar trend is also visible. In contrast to the absorption maxima, a relatively greater number of minima are observed in the fourth order spectra for PVC than wood and tile. This result summarizes that the similar absorption minima found in the higher derivative spectra than the second order can contribute to the identification of residual kerosene.

Conclusion

In the present study, derivative UV-visible spectrophotometry was used to investigate the effect of different matrices on the identification of burnt kerosene residue. Results showed that kerosene can be identified from all three matrices. But the efficiency of the identification in better for the extracted samples from burnt wood than tile and PVC as it is a porous matrix. Wood potentially absorbed the kerosene more than PVC and tile and left with more kerosene residue after the burning. Moreover, in this study, the spectral collection extended to fourth order to investigate its effect on positive identification. Results showed that residual unburnt and semi-burnt kerosene from wood can be successfully identified within the first and second order derivative spectra due to the porous nature of the matrix. While the maximum amount of kerosene was destroyed during the burning process on PVC and tile. Hence, the third and fourth order derivative spectra of kerosene extracted from these two matrices significantly contributed to the identification as a considerable number of similar absorption minima with the standard kerosene were found. The instrumentation technique used in this study proved to be very useful for the identification of kerosene residue and it will also be explored in other petroleum products to check the effect of matrices on them after burning in simulated arson scenes.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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