

Importance of Polycyclic Aromatic Hydrocarbons and Application of Spectrofluorimetry in Petro-forensic Investigation

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ABSTRACT

Polycyclic aromatic hydrocarbons are ubiquitous in nature present in petroleum products in varying concentrations. They are used as a marker for chemical fingerprinting of crude oil, adulteration detection of kerosene in petrol and diesel, source liability determination in environmental contamination, and oil spill cases. In forensic investigation chromatographic methods used are expensive and increases cost of analysis per sample. Hence, replacement of chromatographic technique with low cost, simple, and sensitive method of analysis is required. Conventional fluorescence spectroscopy and synchronous fluorescence spectroscopy (SFS) method was compared for their application in forensic study. Pure kerosene, diesel and petrol samples, and six different brands of diesel samples were analyzed with conventional method. Six diesel samples were analyzed with developed SFS method. For adulteration detection, diesel sample was simulated with kerosene sample 0.1 to 50% concentration and then analyzed with SFS. Conventional fluorescence spectroscopy does not show sharpness in fluorescence intensity, whereas SFS shows well separated sharp fluorescence intensity peaks. As the concentration of kerosene increases in the diesel, it causes self-quenching of diesel fluorescence, subsequently decreasing the intensity of fluorescence spectra. From present study, it is concluded that synchronous spectrofluorimetry needs to be developed and included in forensic laboratories for routine petroleum product analysis that can replace traditional method of analysis.

Key words: Adulteration, Oil spill, Petroleum product, Polycyclic aromatic hydrocarbons, Synchronous fluorescence spectroscopy.

1. INTRODUCTION

Petro-forensic is an emerging specialized field of forensic investigation related to the petroleum products which includes source identification, adulteration determination, detection of environment contaminant, and liability allocation. Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in environment, consist of two or more fused benzene ring aromatic compounds with various structural configurations. It is an organic contaminant, mutagenic, and carcinogenic in nature. It consists of simple to complex ring structures based on benzene ring formed due to different combination of carbon and hydrogen atoms that give it different physical, chemical, and toxicological properties. These are formed due to incomplete combustion and thermal decomposition of and subsequent recombination of organic molecules. Four ring PAHs are considered as light PAHs whereas more than four rings are considered as heavy PAHs [1-3].

Petroleum products are distillation fraction of crude oil, and crude oil is a mixture of more than 1700 aromatic hydrocarbons. Out of these major group consists of PAHs. Crude oil samples obtained from different location consists of varying type and concentrations of PAHs; hence, distillation fractions obtained from different crude oil consist of different varieties and concentrations of PAHs which help in forensic chemical fingerprinting [4]. PAHs profile varies with boiling point of the petroleum compound, low boiling point compounds consist of two or less than two benzene fused rings of PAHs compound, whereas higher boiling compounds consist of three or more than three number of PAHs fused ring compounds. Diesel, lubricant oils, and crude oil consist of high number of PAHs fused rings [5].

PAHs helps forensic investigator in oil spill cases to determine the source identification of petroleum spill oil such as crude oil, lubricating oil, petrol, and diesel and adulteration detection in petrol and diesel. In environmental forensic investigation, it helps in liability determination for waste material produced due to industry. Liquid-liquid extraction, Soxhlet extraction, sonication, supercritical fluid extraction, solid phase extraction, and column chromatography are few methods used for the extraction of PAHs [6-9]. Instrumental techniques such as Gas Chromatography-mass spectrometry (GC-MS), high-performance liquid chromatography, Ultraviolet (UV)-visible spectrometry, Fourier transform infrared spectrometry, Graphene nanosensors, and fluorescence spectroscopy are used for analysis [1,9-15].

Chromatography techniques are expensive to use for routine analysis whereas UV-Visible spectroscopy techniques have limitations because various PAHs have similar chemical properties; hence, spectroscopy analysis shows limitation in characterization of different PAHs compounds. Fluorescence spectroscopy or spectrofluorimetry is used for the identification of compounds based on their fluorescence properties. When compound is excited at specific wavelength, it

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emits visible radiation of specific wavelength, hence it is found to be sensitive technique. However, conventional spectrofluorimetry is a simple, rapid, and sensitive analytical method [16] but does not provide spectral resolution in multi component analysis and does provide overlapping spectra for multi components. Conventional spectrofluorimetry technique is based on single emission or excitation and thus provides insufficient information about the spectra. However, synchronous spectrofluorimetric overcome the disadvantage of conventional spectrofluorimetric and provides narrow resolved bands for different PAHs components characterization [3,17-19].

In 1980s, Synchronous fluorescence was introduced and this technique, initially developed by Lloyd for qualitative and quantitative analysis of machine oil. In forensic application Lloyd first compared conventional and synchronous fluorescence spectra of anthracene, benzo(a)pyrene, perylene, and benzo(k)fluoranthene mixtures in different engine oil, also studied crime scene samples quantitatively with synchronous spectrofluorimetry, also characterized PAHs forensic interest in rubber, tar, soot, petroleum residue, and oil spots [3,20]. It is a convenient method used for the simultaneous determination of multifluorophoric compounds such as PAHs. In general, synchronous spectra are obtained by scanning both excitation and emission wavelength by keeping fixed wavelength interval between them. Lloyd characterized petroleum products according to their high relative molecular weights and successfully used synchronous spectrofluorimetry for forensic purpose [21-23].

It is available in three modes, that is, constant wavelength synchronous, constant energy synchronous, and variable angle SF spectrometry. Constant wavelength synchronous includes the measurement of simultaneous fluorescence of excitation and emission wavelength at same velocity by keeping constant or variable wavelength difference between excitation and emission wavelength. Constant energy synchronous includes the measurement of fluorescence while keeping constant energy difference between excitation and the emission monochromators at variable angles. SF spectrometry involves the measurement by keeping different scan speeds for the excitation and emission monochromators [24].

1.1. Adulteration Detection

In developing country like India, petrol and diesel are adulterated with kerosene. Kerosene is highly subsidized in local market and cheaply available to everyone and it is of low cost; hence, it is commonly used for adulteration purpose. This type of adulteration affects efficiency of petrol and diesel utility engine, engine start up control, engine heating, causing faster wear and tear of piston of engine, and also leading formation of suits due to incomplete burning of kerosene, diesel, and petrol together which affects the environment [25]. The presence of PAHs in petroleum product makes spectrofluorometric technique more useful for the characterization and identification of possible adulterants in petroleum products [18,25,26]. When this technique combines with chemometrics, is also used to measure cetane number, biodiesel percentage, heat of combustion gross and color in biodiesel and diesel blends [17].

1.2. Fuel Quality

Due to increasing demand of hydrocarbon fuel, ethanol and biodiesel blends in petrol and diesel, respectively, at certain ratio. Current marketed vehicles do not support with these blended mixtures; hence, ethanol and biodiesel need to be blended with certain ratio. However, this blending affect efficiency of engine, causes blockage of fuel pipes, valves and filters, causes corrosion of metallic parts of the engine, high concentration of ethanol, and biodiesel leads to increase in high consumption rate of fuel. Hence, monitoring of percentage of ethanol

in petrol and biodiesel in diesel is important in quality determination of fuel. GC-MS method used for qualitative and quantitative identification of ethanol and biodiesel in petrol and diesel, respectively. However, this technique is expensive and requires lot of sample preparation steps; hence, it is time consuming technique. Synchronous fluorimetry technique is new emerging technique used for the qualitative and quantitative identification of ethanol and diesel because of presence of PAHs in petrol and diesel, whereas biodiesel is made up of animal fat and vegetable oil that contains fluorescent pigment which act as a marker for the identification [27]. synchronous spectrofluorimetry characteristics such as emission, excitation, and wavelength relate with physical and chemical characteristic of crude oil such as density; hence, it aids in quality assessment of petroleum product. They also studied density parameter of Brazilian crude oil with synchronous spectrofluorimetry. Heavier petroleum product exhibits shorter fluorescence lifetime than lighter petroleum product [28,29].

1.3. Source Identification in Pollution Cases

Crude oil is an important element of economy. Most of the industries work on crude oil. Petroleum products are distillate fractions of crude oil and this fraction is used in economy in different forms. Like petrol and diesel are used in vehicles, lubricating oil and heavy fractions used in industries in functioning of machinery. Crude oils are exported or imported based on the economy and availability of these natural resources in the country and it is quite expensive to export from other countries; hence, spectrofluorimetry helps in source identification of crude oil. PAHs are important content of crude oil they are present in every crude oil sample but with different concentration. This feature helps in source identification. Light petroleum product such as petrol and kerosene gives fluorescence emission spectra between 310 and 400 nm whereas heavy petroleum product such as diesel and lubricating oil gives fluorescence emission spectra between 420 and 500 nm [21]. Pollution due to crude oil consumption in industry is emerging pollution problem and it is important in environmental forensic to identify unknown contaminants and their sources to settle down the liabilities; hence, synchronous spectrofluorimetry plays key role in main pollutant identification and source determination [30].

1.4. Oil Spill Cases

Oil spill in water ecosystem is of great concern because it is hazardous to the marine life and environment. Hence, it is important to identify the spilled oil and to determine their source using accurate qualitative and quantitative analysis method to determine the liability of contamination. Traditional GC-MS method was used, however, recently synchronous spectrofluorimetry used in contaminant determination in oil spill cases because of its sensitivity and selectivity toward PAHs compounds present in spilled oil [29].

Cristescu *et al.* (2009) successfully used synchronous fluorimetry in soil contaminant identification in Romanian crude oil. PAHs are carcinogenic in nature and they enter in the environment through the industrial waste and through accidental or intentional oil spill, etc., in such cases contaminated, soil, water, and sewage sludge were collected analyzed for the presence of PAHs with spectrofluorimetry [31,32]. Crude oil characterization by synchronous spectrofluorimetry was first evaluated by John and Soutart, they studied effect of solvent, wavelength increment on different crude oil samples collected from different locations. Synchronous spectrofluorimetry was successfully used in cresol and phenol content determination in coal gasifier waste water and discriminate between the three isomers of cresol. When oil concentration is high, it produces fluorescence spectra due to higher ring PAHs and quenching fluorescence of lower ring PAHs [20]. In deep water marine spill oil case, crude oil spilled in Gulf of Mexico for 87

days in 2010. Synchronous spectrofluorimetry was successfully used in characterization of petroleum compound for source identification. Fluorescence in petroleum product appears due to the presence of carbon-carbon bond within aromatic compound, starts from benzene to PAHs compounds, heavy ring compounds emit low-intensity fluorescence with shorter intensity life-span [33].

In the present study, author is explaining how synchronous spectrofluorimeter can be used for the adulteration detection in diesel sample by kerosene, how to differentiate between diesel sample of three different origin and comparison between conventional and synchronous spectrofluorimetry in adulteration detection. In spectrofluorimetry, parameter $\Delta\lambda$ needed to be optimized in synchronous fluorescence spectroscopy (SFS) and this optimization can be carried out by measuring the SFS spectra at various [21].

2. MATERIALS AND METHODS

Diesel, petrol, and kerosene samples obtained from local distribution center at Gandhinagar, Gujarat, India, were used as reference. Similarly, six diesel samples of different brand were collected from the petrol pump of Gandhinagar Gujarat. For extraction cyclohexane, hexane, dichloromethane, and methanol of analytical grade solvents were used. Both conventional and synchronous spectra were compared for better resolution. JASCO FP 6500 spectrofluorometer was used for the analysis. Initially petrol, diesel, and kerosene and all six different diesel samples of each 1 mL were diluted with 9 mL cyclohexane and were analyzed with spectrofluorometer with emission spectra measurement mode, excitation band width, and emission band width is 3 nm, respectively, response – 1 s, sensitivity – high, measurement range – 230 nm–750 nm, data pitch – 0.5 nm, excitation wavelength – 220 nm, and Scanning speed – 500 nm/min. In second part diesel, samples were analyzed by synchronous spectrofluorometer, each diesel sample of 1mL was diluted with 9 mL cyclohexane solvent. For adulteration study, out of three diesel samples, one diesel sample was mixed with kerosene sample in the concentration of 5%, 10%, 25%, and 50% on large scale analysis. For small scale analysis diesel sample mixed with kerosene sample 0.1%, 0.2%, 0.3%, 0.4%, 0.5%, 0.6%, 0.7%, 0.8%, 0.9%, 1%, 1.1%, and 1.2%. Pure diesel samples and simulated fractions were analyzed with spectrofluorometer with synchronous spectra measurement mode, excitation, and emission band width set at 3 nm, response – 0.5 s, sensitivity – medium, measurement range – 400 - 700 nm, data pitch – 1nm, delta wavelength – 30.0 nm, and scanning speed – 500 nm/min.

3. RESULTS AND DISCUSSION

Forensic investigation of adulteration of diesel was studied by comparing two modes of spectrofluorometer. In part one diesel samples along with petrol and kerosene was analyzed with emission measurement mode to see how these three samples differ from each other. However, different diesel samples were also analyzed in emission measurement mode to see how different brands of diesel differ from each other. In second part, synchronous mode was studied to check how different brands of diesel differ from other brands of diesel, second, kerosene sample was simulated with diesel sample with high concentration fractions, that is, 5%, 10%, 25%, and 50%. Kerosene sample was also simulated with diesel sample at low concentration fraction range, that is, 0.1%, 0.2%, 0.3%, 0.4%, 0.5%, 0.6%, 0.7%, 0.8%, 0.9%, 1%, 1.1%, and 1.2% to obtain the minimum level at which forensic expert can detect adulteration.

3.1. Emission Measurement Mode

Figure 1 showed emission spectra of kerosene, petrol, and diesel sample, in which kerosene, petrol, and diesel excited with 220 nm and emission spectra for kerosene obtained at 338.5 and 660.5 nm,

petrol emission spectra obtained at 327 nm, and diesel emission spectra obtained at 328 nm and 650 nm. Emission spectra intensity was found to be high for all three samples that showed the presence of PAHs in high concentration in pure diesel, petrol, and kerosene samples. Figure 2 showed emission spectra of six different brands of diesel samples, D-1 showed emission spectra at 327 nm and 625.5 nm, D-2 showed emission spectra at 328 nm and 650 nm, D-3 showed emission spectra at 327.5, 579, and 613.5 nm, D-4 showed emission spectra at 327, 576, and 652 nm, D-5 showed emission spectra at 327 and 653 nm, and D-6 showed emission spectra at 328 nm and 653.5 nm. All samples showed emission spectra near to each other; however, emission spectra obtained were non-linear when concentration kept constant. A. Taksande and C. Hariharan (2007) conducted similar study on absorption and emission criteria, they found that changes seen in absorption and emission spectra are non-linear, hence conventional emission mode fluorimetry fails in adulteration quantitation [25].

3.2. Synchronous Spectra Mode

With change in delta wavelength ($\Delta\lambda$), change in spectral bandwidth and intensities reported in the previous literature. When $\Delta\lambda$ set at lower value produces high-intensity synchronous features, lower intensity synchronous spectra obtained with higher value of $\Delta\lambda$ nm SFS taken with varying $\Delta\lambda$ at 10, 20, 30, 40, 50, and 60 nm and based on the peak intensity and sharpness of spectra, the synchronous spectra optimize at 30 nm $\Delta\lambda$ and excitation and emission slit width at 3 nm. Intensity sharpness and emission signal were used as an optimal criterion for $\Delta\lambda$ evaluation [5]. (Kulathunga and Mahanama, 2013) Figure 3 showed synchronous spectra for D-1 at 414, 450, 474, 662, and 669 nm, D-2 at 414, 436, 445, 464, 472, 543, 660, and 673 nm, and D-3 at 414, 476, 550, 669, and 675 nm. SFS has three maxima toward shorter wavelength for pure diesel sample; however, SFS shows three intense maxima with additional fluorescence wavelength for diesel and kerosene mixture when excitation and emission slit width kept constant at 3 nm. Kulathunga and Mahanama (2013) studied mixture of diesel and kerosene at $\Delta\lambda$ 30 nm and excitation and emission slit width at 1.5 and 3 nm, respectively, author found two maxima toward shorter wavelength for mixture of diesel and kerosene. As compared to emission spectra, synchronous spectra give more informative and well separated peak; synchronous spectra also showed difference in different brand of diesel sample based on concentration of fluorescent substances present in diesel samples. Pure diesel sample simulated with kerosene sample at 5%, 10%, 25%, and 50% concentration and analyzed by synchronous measurement mode. Diesel, petrol, and kerosene are distillate fraction of crude oil, each contain PAHs such as fluorescent compounds of different molecular weight, these fluorescent compounds help in identification of adulteration in petroleum products. As the molecular weight of the fluorescent compound increases, it emits high-intensity of fluorescence. However, kerosene contains low molecular weight fluorescent compounds, as the concentration of kerosene increased in diesel sample, it quenches the fluorescence of diesel sample, which is found in Figure 4, in which pure diesel samples gives high intensity of fluorescence whereas as the concentration of kerosene increases by 5%, 10%, 25%, and 50%, it quenches the fluorescence. In addition to, prominent fluorescence maxima at 441, 436, and 450 nm additional wavelengths observed at 526, 529, 540, 661, and 663 nm. Maximum decrease in fluorescence observed in 50% of sample. Figure 5 synchronous spectra of simulated diesel samples at 0.1%, 0.2%, 0.3%, 0.4% 0.5%, 0.6%, 0.7%, 0.8%, 0.9%, 1%, 1.1%, and 1.2%. It is found that even at minimum level if concentration of kerosene increases, it decreases the fluorescence of diesel sample. Similar study conducted by Corgozinho *et al.* (2008) [26] wherein diesel sample simulated with B2 oil and residual oil, and it was found that as concentration B2 oil and residual oil increases in diesel it causes

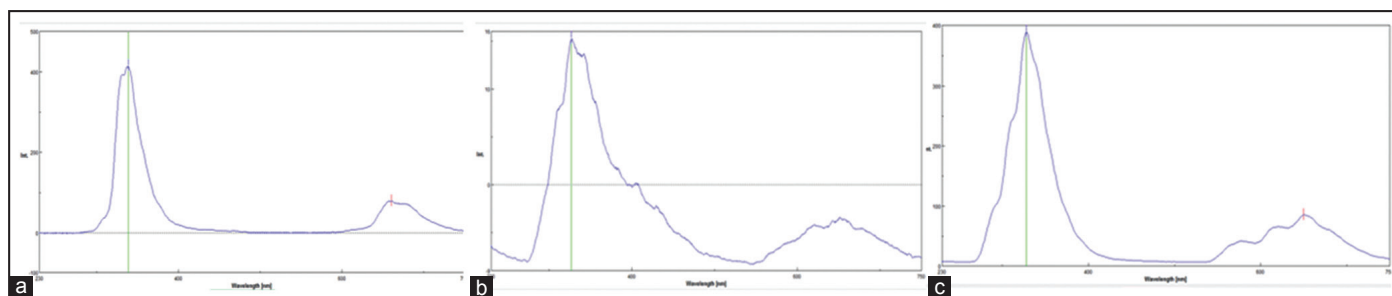


Figure 1: Emission spectra of pure (a) Kerosene, (b) petrol, and (c) diesel sample in cyclohexane.

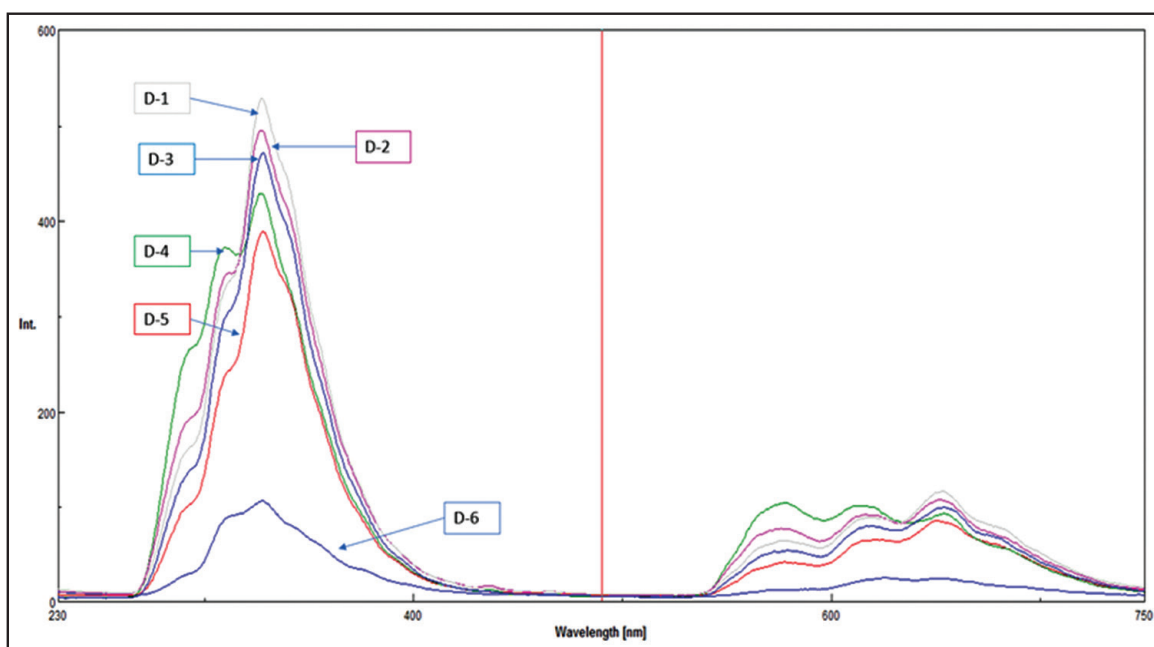


Figure 2: Emission spectra of all six pure diesel samples in cyclohexane.

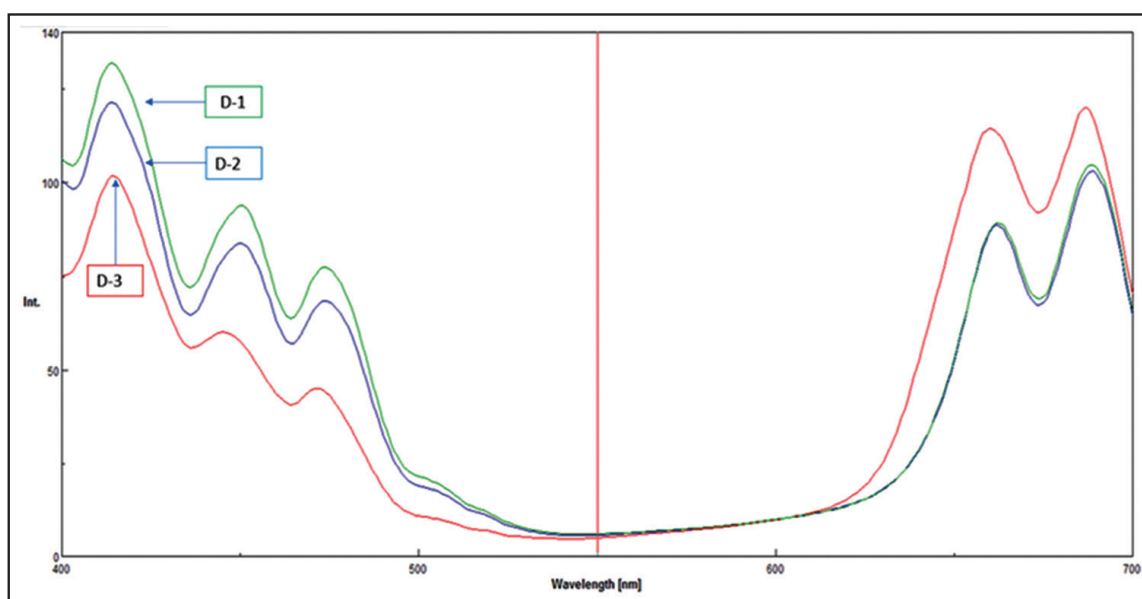


Figure 3: Synchronous spectra of pure diesel D-1, D-2, and D-3 samples diluted in (1:1) ratio with cyclohexane.

self-quenching of fluorescence PAHs present in diesel sample. Routine conventional adulteration techniques such as viscosity, flash point, and boiling point can detect adulteration up to 30%; however, synchronous spectrofluorometer can detect adulteration <30% and up to 0.1%

concentration. This is because of characteristic polycyclic aromatic compound present in petroleum product at varying concentration and varying molecular weight.

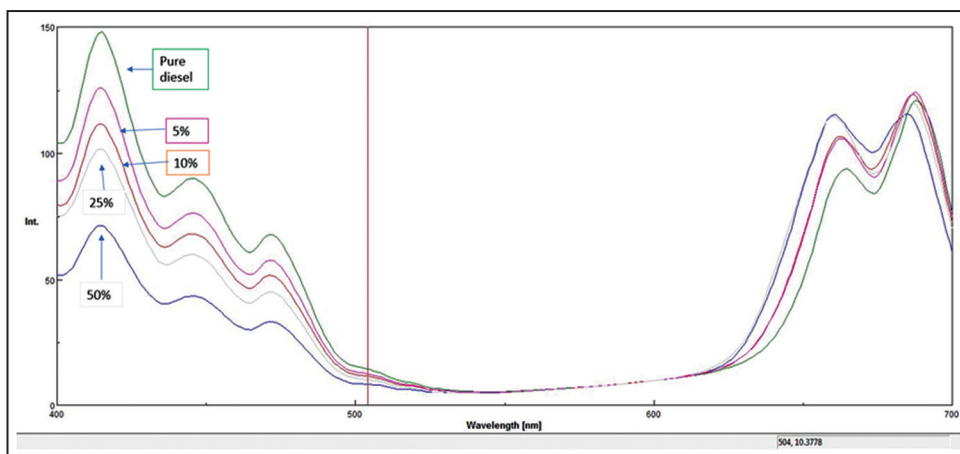


Figure 4: Synchronous spectra of pure diesel and 5%, 10%, 25%, and 50% simulated diesel samples.

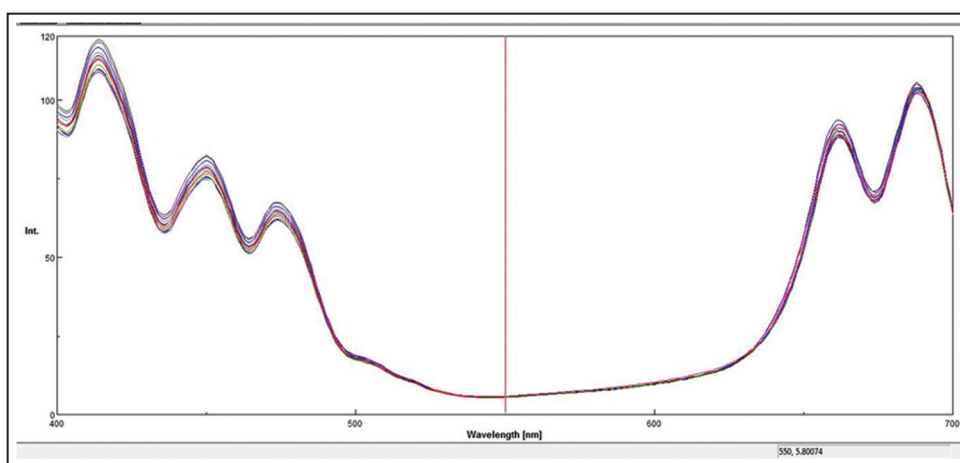


Figure 5: Synchronous spectra of 0.1%, 0.2%, 0.3%, 0.4%, 0.5%, 0.6%, 0.7%, 0.8%, 0.9%, 1%, 1.1%, and 1.2% simulated diesel samples.

4. CONCLUSION

Forensic investigation involves use of highly sophisticated instruments such as GC-flame ionization detection, GC-MS, and Headspace-GC these instrumental techniques are highly expensive, time consuming, and required proper maintenance for working. Due to increase in cases of adulteration, quality assessment, oil spill cases, and forensic laboratories receiving maximum number of cases every day and that has to be reported in stipulated time. Because of increase in cases, it is always not possible to used highly sophisticated instrument. In forensic laboratories, petroleum investigation requires minimum 1 litre of sample to check parameters such as density, American Petroleum Institute gravity, specific gravity, flash point, aniline point, and distillation points this increases the sample size collection; hence, all identification cannot be possible on small amount of sample. Synchronous spectrofluorimetry is simple, selective, cheap, technique, requires small amount of sample that helps in forensic investigation in adulteration detection, origin identification, and quality assessment. From present study, it is concluded that synchronous spectrofluorimetry need to be developed and included in forensic laboratories for routine petroleum product analysis that can replace traditional method of analysis.

5. DECLARATIONS

5.1. Ethics Approval and Consent to Participate

Not Applicable.

5.2. Consent for Publication

Not applicable.

5.3. Availability of Data and Material

Data generated or analyzed during this study are included in this published article.

5.4. Competing Interest

The authors declare that they have no competing interests.

5.5. Funding

Not Applicable.

5.6. Author's Contribution

AP, AS, and IP equally contributed in sample collection, extraction, analysis, and interpretation. All authors read and approved the final manuscript.

5.7. Acknowledgement

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***Bibliographical Sketch**

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