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ABSTRACT

Ten solvent systems for differentiating the samples of petrol, diesel, and kerosene were studied. The effectiveness of various solvent systems to separate the constituents was examined. Ten solvent systems were inspected from which the solvent system containing xylene: acetone: toluene in the ratio of 20:20:1 (v/v/v) was observed to be best, as the degree of separation is comparatively high. Thin-layer chromatography chromatograms of the petrol, diesel, and kerosene were studied separately under an ultraviolet chamber, and vanillin with concentrated sulfuric acid was used as a spraying agent. This study can help to determine the adulteration in petrol and diesel and kerosene and also for analysis of residues generally encountered as accelerants in fire and arson cases.

Key words: Diesel, Petrol, Kerosene, Thin-layer chromatography, Solvent system, Separation.

1. INTRODUCTION

Petroleum is a liquid mixture of hydrocarbons that exists as a liquid in subsurface reservoirs in nature and remains liquid at ambient temperature. It is created at a natural gas processing facility from the processing of liquid hydrocarbons, and it includes both crude oil and petroleum products when delivered to the surface. Due to the rising population, urbanization, development activities, and lifestyle changes, India's use of petroleum products is expanding, resulting in widespread degradation of the environment [1-3]. Petrol is a light crude oil product with a hydrocarbon distribution ranging from C4 to C12. Kerosene (K) is made up of hydrocarbons with carbon atoms ranging from C8 to C18, but diesel (D) is substantially heavier and made up of hydrocarbons with carbon atoms ranging from C8 to C40 [4]. Kerosene shortages have been a primary cause of kerosene adulteration, forcing customers to use other alternative hydrocarbon substances, which have resulted in deforestation, large-scale carbon monoxide production, and other depleting substances. It has also pushed up the price of cooking gas by putting pressure on household gas demand [5]. The most common accelerant, petrol (P), is composed of parts containing hydrocarbon that is substantially lighter than kerosene or diesel. It has far higher volatility, and when ignited, it can rapidly generate an explosive air-vapor mixture that will do extensive damage [6]. After petrol, kerosene is the most widely used accelerant. Although it is more challenging to ignite because of its lower volatility, if properly ventilated, it will burn longer and hotter. Kerosene is the most prevalent incidental accelerant because, unlike petrol, which is primarily used as a motor fuel, it may be found in a range of ordinary household products, such as paint thinner and charcoal lighters [7]. Similar to diesel, kerosene contains a greater percentage of lighter hydrocarbon components, increasing its volatility, and a wider boiling range [8].

Various hyphenated and sophisticated instrumental techniques are existing for the analysis of petroleum products, such as thin-layer chromatography (TLC) [9], gas chromatography (GC), high-performance thin-layer chromatography, GC/mass spectrometry (GC-MS), and direct analysis in real time-MS (DART-MS) were reported to identify various flammable compounds [10-12], but these methods should be adapted when the sample size is small and there is a necessity to cause minimal damage to the sample while performing analysis.

The instruments such as GC, GC-MS, and DART-MS were destructive techniques, and they are very expensive also [11,13,14], whereas TLC is inexpensive, easy to carry, and rapid development technique. The hyphenated techniques generally require sample preparation or pre-treatment before analysis, whereas TLC does not require any specific sample preparation. The spectroscopic techniques such as Fourier-transform infrared spectroscopy, near IR, and fluorescence spectroscopy were coupled with chemometrics [15,16] to classify and differentiate kerosene, gasoline, and diesel. Even, quantification of the adulterants can also be estimated. The disadvantages of these techniques over TLC are costly and, un-portable heavy instruments, and interpretation of the data obtained needs sound knowledge of the instrument along with a good understanding of statistical analysis.

TLC is a flexible chromatographic analytical method that can be used in forensic investigations to analyze arson cases and find adulteration in samples of gasoline, fuel, and kerosene [17]. Therefore, if the investigator is looking for flammable and volatile petroleum compounds, this study can aid in the preliminary evaluation of arson evidence. Thus, an attempt was undertaken to test petroleum products (P, D, and K) using TLC and to evaluate the efficacy of various solvent systems for their separation.

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2. EXPERIMENTAL

2.1. Chemicals and Materials

All the chemicals were reagent grade and used exactly as received. These include highly pure petroleum products (petrol [P], diesel [D], and kerosene [K]): toluene, hexane, xylene (procured from Central Drug House Pvt. Ltd., Mumbai, India), diethyl amine, ethyl acetate, chloroform, methanol, and acetone (Sisco Research Laboratories Pvt. Ltd., Mumbai, India). The experimental work was carried out using TLC Silica gel 60 F254 (20 cm \times 20 cm) plates.

Highly pure standards of petrol, diesel, and kerosene were procured from the oil company with properties as mentioned in Table 1 and were used to load in the TLC plate. Ten different solvent systems were prepared for purpose of separation of the mentioned petroleum products toluene: hexane (60:40) (S1), toluene: diethyl amine (80:20) (S2), xylene: hexane:diethyl amine (30:10:1) (S3), toluene (50 mL) (S4), toluene: ethyl acetate (80:20) (S5), hexane: ethyl acetate (80:20) (S6), chloroform: methanol (70:30) (S7), xylene: acetone:toluene (20:20:1) (S8), hexane: acetone:toluene (8:1:1) (S9), and acetone: toluene (40:1) (S10), respectively.

2.2. Procedure for TLC analysis

The aluminum-backed TLC Silica gel 60 F254 (20 cm \times 20 cm) was procured from Merck. The plates were activated by keeping them in the

oven at 110°C. Afterward, using a syringe (5 μ L), aliquots of standard petrol, diesel, and kerosene were placed over the activated plates. The solvent solutions were used to completely saturate the solvent chamber first. In this saturated solvent chamber, the spotted TLC plates were positioned at a 45° angle, and the chamber was properly closed with a lid. The solvent front was permitted to move to a level of 10 cm above the origin. The developed plates were removed from the process once it was completed and left to air dry at room temperature. The separated color spots of the samples were visualized using a reagent (vanillin + H₂SO₄) [18] and ultraviolet (UV) light of 100–290 nm and 320–400 nm wavelengths [19], as shown in Figure 1, and their respective Rf values were obtained using the equation:

 $R = \frac{\text{Distance covered by spot(solute) from origin}}{\text{Distance covered by spot(solute) from origin}}$

Distance covered by solvent from origin

4. RESULTS AND DISCUSSION

A comparative study of the effectiveness of ten different solvent systems for the separation of petrol, diesel, and kerosene through the TLC technique was carried out. Toluene, hexane, xylene, diethyl amine, ethyl acetate, chloroform, methanol, and acetone were utilized to prepare the solvent systems used in this study. The TLC plates were examined in strong daylight using a reagent (vanillin + H_2SO_4). The result obtained in terms of Rf, and the relative difference of the obtained

Table 1: Physical and chemical properties of Petrol, Diesel, and Kerosene.

Property	Gasoline	Diesel	Kerosene 170	
Molar mass	108	198		
Boiling point	64–65°C at 1.013 hPa	338–617°F at 760 mmHg	149–304°C	
Density	$0.7-0.8 \text{ g/cm}^3$	0.82–0.86 kg/L	0.8 g/cm^3	
Composition of hydrocarbon	C ₄ -C ₁₂	$C_{10}H_{20}$ - $C_{15}H_{28}$	$C_{12}H_{26}\!\!-\!\!C_{15}H_{32}$	
Flash point	11°C closed cap	>55°C	38–52°C c.c.	
Specific gravity	0.8 at 59°F	0.88 at 60° F	0.8 to <1.0	
Water solubility	Insoluble	Insoluble	Insoluble	
Color	Clear, white, or slightly amber	Clear or slightly green	Pale yellow or colorless	

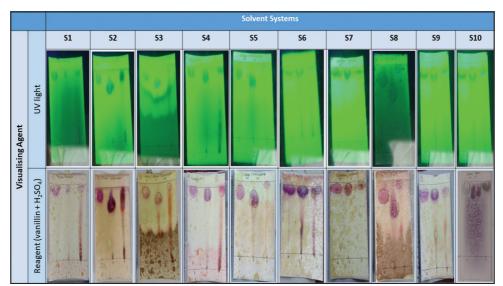


Figure 1: Thin-layer chromatography plates used in solvent system S1–S10 were visualized using ultraviolet light and reagent (vanillin + H_2SO_4).

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Rf values of each sample of petrol (P), diesel (D), and kerosene (K) with the respective solvent systems in terms of δ (P-D), δ (K-P), and δ (K-D) are shown in Table 2.

The Rf values of P, D, and K, and their relative differences were plotted using a bar chart separately, as shown in Figures 2 and 3. In the solvent system S1, the relative differences of Rf values δ (P-D) and δ (K-P) for

Solvent system (ratio [v/v])		Calculated <i>Rf</i> values			Relative differences in Rf values		
		Petrol (P)	Diesel (D)	Kerosene (K)	δ(P-D)	δ(K-P)	δ(K-D)
S1	Toluene:Hexane (60:40)	0.875	0.812	0.937	0.063	0.062	0.125
S2	Toluene:Diethyl amine (80:20)	0.95	0.866	0.95	0.084	0	0.084
S3	Xylene:Hexane:Diethyl amine (30:10:1)	0.75	0.68	0.732	0.07	0.018	0.052
S4	Toluene (50 mL)	0.937	0.678	0.975	0.259	0.038	0.297
S5	Toluene:Ethyl acetate (80:20)	0.857	0.785	0.971	0.072	0.114	0.186
S6	Hexane:Ethyl acetate (80:20)	0.916	0.933	0.966	0.017	0.05	0.033
S7	Chloroform:Methanol (70:30)	0.942	0.928	0.971	0.014	0.029	0.043
S8	Xylene:Acetone:Toluene (20:20:1)	0.825	0.662	0.962	0.163	0.137	0.3
S9	Hexane:Acetone:Toluene (8:1:1)	0.912	0.875	0.95	0.037	0.038	0.075
S10	Acetone:Toluene (40:1)	0.885	0.828	0.971	0.057	0.086	0.143

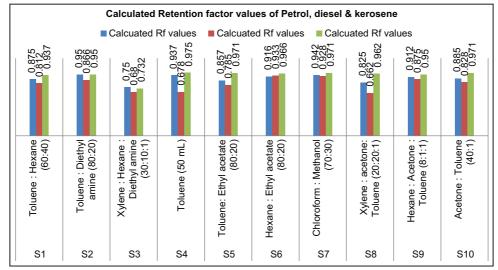


Figure 2: The calculated values of *Rf* for the ten solvent systems S1–S10.

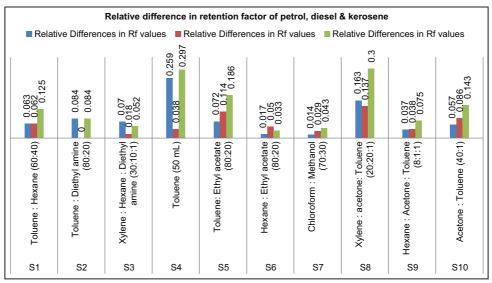


Figure 3: The relative differences in the *Rf* values of δ (P-D), δ (K-P), and δ (K-D).

solvent system S1 were nearly the same but the differences in Rf values show that it can separate the mixture of P, D, and K. The solvent system S2 was not effective for the separation of the mixture of K and P, as their Rf value was the same, and the relative difference of Rf is also found to be 0. The δ (P-D), δ (K-P), and δ (K-D) values in the S3 solvent system were less and could not be effective. Similarly, solvent systems S6, S7, S9, and S10 showed less value in relative differences in Rf values of P, D, and K. The relative difference in Rf values of the S4 and S8 solvent systems was high as compared to the rest of the solvent systems. Both solvent systems (S4 and S8) were capable to separate the mixture of P with D and K with D, but δ (K-P) value in the S4 system was less (0.038) which infer its inefficiency in differentiating the mixture of P and K whereas δ (K-P) value is S8 is high as compare to S4. Hence, the solvent system S8 seems to be more effective for the present study.

5. CONCLUSION

The trial made for the identification of spots of kerosene, petrol, and diesel using TLC with ten different solvent systems was performed. The reliability and effectiveness of TLC were proven to be appropriate for the preliminary examination of these petroleum products. After the comparative examination of the chromatograms of each solvent system, it is well established that the spot of petrol, diesel, and kerosene can be distinguished easily using solvent system S8 (xylene: acetone:toluene) in the ratio of 20:20:1 (v/v/v). Under the same experimental conditions, the TLC plates provide excellent visualization of the spots in all solvent systems when seen under UV light and also with the reagent (vanillin + H₂SO₄), and each solvent system displayed a different pattern of spots with varied Rf values.

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*Bibliographical Sketch



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