



## Assessment of Intergrade Contamination in Refined Petroleum Products Using UV-Vis Spectrophotometry

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### KEYWORDS

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### ABSTRACT

Intergrade contamination, the adulteration of refined petroleum products (PMS, DPK, and AGO) with other petroleum fractions, poses serious risks to safety, public health, and mechanical integrity. This study validates a method for rapid and quantitative measurement of intergrade contamination in binary fuel blends using UV-Vis spectrophotometers. Binary fuel blends of premium motor spirit (PMS), dual-purpose kerosene (DPK), and automotive diesel oil (AGO) were prepared in 20% increments. Spectroscopic analysis revealed characteristic overlapping absorbances in the 220–360 nm range, which are attributed to the aromatic hydrocarbon content of the fuels. Quantitative analysis using the Beer-Lambert law yielded linear calibration curves relating absorbance (a.u.) to contaminant concentration (%). The correlation coefficients ( $R^2$ ) of the linear models were 0.9028 for PMS and AGO, 0.7308 for DPK and PMS, and 0.9155 for AGO and DPK. These high  $R^2$  values demonstrate the accuracy and reliability of the method, establishing UV-Vis spectrophotometers as an accessible and effective analytical tool for fuel quality control and regulatory compliance.

### CITATION

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### INTRODUCTION

Adulteration of refined petroleum products is a significant problem, resulting from the unintentional or intentional mixing of one refined product with another, which can alter the product's fundamental chemical and physical properties (Jenssen, 1996; Wilson and Conrad, 1984). Such adulteration can easily lead to product failure, resulting in loss of life and property due to mechanical impacts and explosions (Egu, 2018). For example, kerosene explosions are often attributed to the adulteration of low-flashpoint fuels such as PMS, while the adulteration of PMS by AGO increases tailpipe emissions (Odebunmi et al., 2002; Jonah and Umar, 2004). This persistent threat underscores the importance of proper and regular quality control testing to verify the composition

of fuels before sale (Ikeora and Nkechi, 2015). While standard analytical methods, such as gas chromatography, fractional distillation (Ikeora and Nkechi, 2015) exists, other such as the neutron reflection techniques to determine (C+O/H) ratio are emerging (Jonah and Umar, 2004). Generally, there is a growing demand for analytical techniques that offer a good balance of accuracy, cost, and speed. The Ultra Violet-Visible (UV-Vis) Spectrophotometry is a photonic technique with these potentials. Like all photonic techniques, UV-Vis Spectrophotometry applies the optical features of light material investigations. It has however been rarely reported for the analysis of hydrocarbon mix, refined petroleum products or intergrade.

Refined petroleum products such as Petroleum Motor Spirit (PMS), Dual Purpose Kerosene (DPK) and Automotive General Gas (AGO) contain a diverse mixture of hydrocarbons, including aromatic compounds that exhibit strong but varying absorption in the Ultraviolet (UV) region of the electromagnetic spectrum. At the molecular level, differences in the energy between two molecular orbitals have been observed to correspond to the energy of visible light. This allows the excitation of electrons from the ground states to higher energy states when light is absorbed. Light wavelengths of unabsorbed light can as such be reflected or transmitted leading to some variation of perception of color observationally. This variation in chromophore concentrations suggests that UV-Vis spectroscopy can be used as a sensitive and simple method to rapidly detect and quantify changes in fuel composition. This study was conducted to interrogate chromophore concentration variation in verifying the effectiveness of UV-Vis spectroscopy for the quantitative analysis of intergrade contamination in binary fuel compositions of PMS, DPK, and AGO.

The sparse report of interrogation of the UV-Vis spectroscopic method is regarded as a strong impetus for this study. David et al. (2014); Echioda et al. (2021); Maci'an et al. (2023); and Dani et al. (2023) all carried out extensive photonics studies targeting different materials with UV-Vis spectrophotometry. While Dani et al. (2023) provided a detailed study of the calculational approach and measurement of solution concentration using UV-Vis spectrum analysis; the report is generally focused and not specific on particular materials, hydrocarbons or intergrades. It however provided details to support measurement in chemical decomposition, photocatalysis, phytoremediation and adsorption process. The idea and application of UV-Vis technique in water quality detection was extensively explored and presented including guidelines for determining the concentration of samples in aqueous solutions. Practical exemplification provided clear details on understanding concentration during the organic decomposition. Meanwhile, Echioda et al. (2021) used UV-Vis Spectrophotometry technique in the determination of heavy metals in environmental, water and biological samples. Synthesized glutaraldehyde phenyl hydrazone was used as the chromogenic reagent in the study. The quantification of these heavy metals, based on the measurement of the increase or decrease of their absorbance reported in Metal Gram Per Hundred Grams

(GPH), was applied for the determination of Cadmium (Cd), Lead (Pb), Chromium (Cr), and Arsenic (Ar) in environmental, biological, soil, water, and waste samples. The significantly relevant approach of quantification in GPH however was limited to these four heavy metals. Both David et al. (2014) and Maci'an, et al. (2023) attempted to establish a methodological framework for various classes of hydrocarbon-based materials and the associated intergrade problem. While David et al. (2014) studied the detection of biodiesel/diesel blend adulterations with soybean oil using UV-Vis spectrophotometry technique, the study was not extended to refined petroleum products. Multivariate classification techniques were explored in the discrimination of UV-Vis spectra of both the adulterated and non-adulterated combinations and the use of UV-VIS spectrometry was strongly advocated as a simple alternative for detection of vegetable oil adulterations in biodiesel/diesel blends. On the other hand, Maci'an, et al. (2023) attempted an assessment of the application of UV-Vis and Near Infrared (NIR) spectroscopies for the investigation of fuel dilution problems in used engine oils of six different vehicles with various mileages. In its finding, evidence in support of NIR spectroscopy as a preferred method for the quantification of diesel fuel in used engine oils was provided.

Overall, none of these studies addressed fully the need to establish a methodological framework for UV-Vis spectroscopy in petroleum product intergrades despite the multidimensional importance of the subject matter. Ultimately, the need to fully explore chromophore variational optical responses in the characterization of adulterated hydrocarbon as a cheap, fast and accurate technique need to be further explored in detail for various application with economic, fire safety and vehicle performance implications.

## **MATERIALS AND METHODS**

In this study, the Shanghai INESA 723N UV-Vis Spectrophotometer model is used as the principal equipment for the photonic analysis. It is a fixed-slit, single-beam equipment engineered for routine quantitative and qualitative analysis in the ultraviolet and visible spectral regions from 325–1000 nm. It employs a high-stability Tungsten-Halogen lamp for the visible region and a Deuterium lamp for the Ultraviolet region, coupled with a precision Czerny–Turner monochromator and fixed 4 nm spectral bandwidth



Figure 1: Shanghai INESA Model 723N UV-Vis Spectrophotometer with Plastic Stripes Containing Prepared Samples for Analysis

The UV-Vis Spectrophotometry is based on the Beer-Lambert Law which is the combination of Johann Lambert and August Beer. The law states that the amount of light absorbed by a solution under analysis is directly proportional to the concentration of the solute in the solution and the length or thickness of the solution, such that the Beer-Lambert Law is given as Equation (1):

$$A = -\log_{10} \left( \frac{I_T}{I_0} \right) \sim L \text{ or } A = -\log_{10} \left( \frac{I_T}{I_0} \right) \sim C \quad (1)$$

Here; A is the measure of Absorbance, L is the path length, C is the Concentration, while  $I_T$  and  $I_0$  are the Transmitted and the Incident ray of light respectively.

A light sensor, phototransistor transducer is attached to the Spectrophotometer to transmit signal from it to the

Arduino software (Arduino-ide-1.8.13) programmed to receive signal between 400nm to 1000nm operating wavelength. The software processes the received signal using its built-in Analog to Digital Converter (ADC).

Sufficient AGO, DPK, and PMS samples acquired from the same fuel station for consistency and prepared into equivalent portions in plastics cuvettes using graduated measuring cylinder, syringe and plastic stripes as shown in Table 1. This includes the pure 100% samples of AGO, DPK and PMS used as standard for the study; and mixtures of two refined products at 20% concentrations to prepare binary mixtures used to simulate intergrade contamination.

**Table 1: Binary Mixture of Refined Petroleum Products AGO, DPK and PMS**

PMS/AGO MIX		PMS/DPK MIX		AGO/DPK MIX	
PMS (%)	AGO (%)	PMS (%)	DPK (%)	AGO (%)	DPK (%)
100	0	100	0	100	0
80	20	80	20	80	20
60	40	60	40	60	40
40	60	40	60	40	60
20	80	20	80	20	80
0	100	0	100	0	100

The acquired spectra for the standards and the intergrades were acquired following the process below:

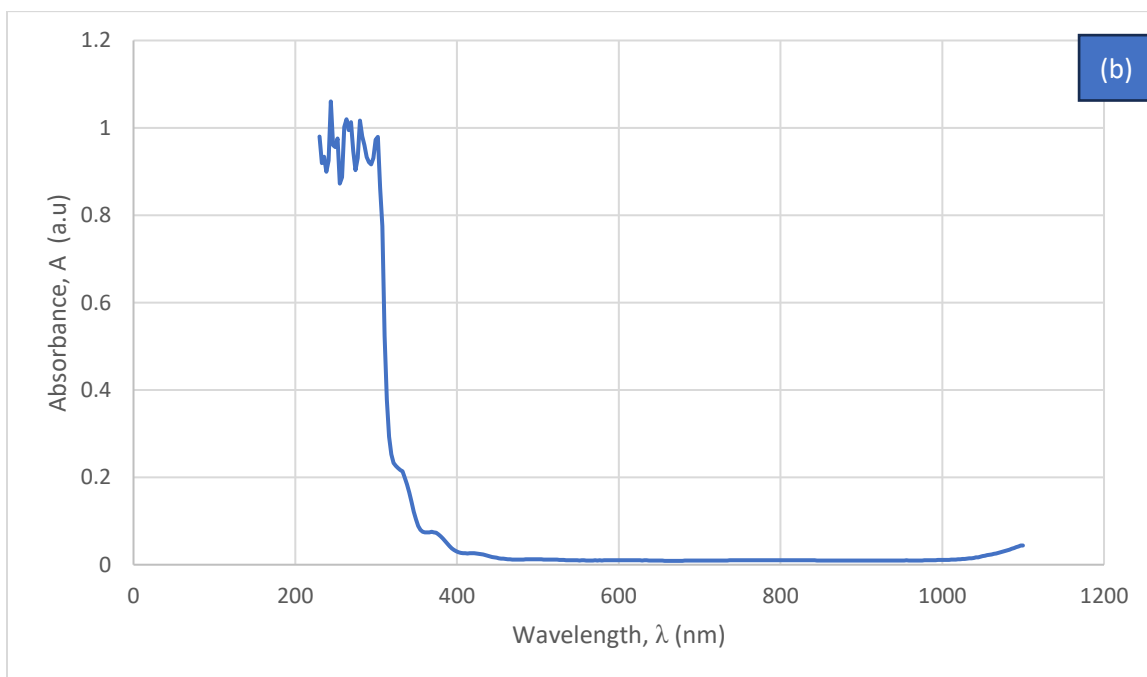
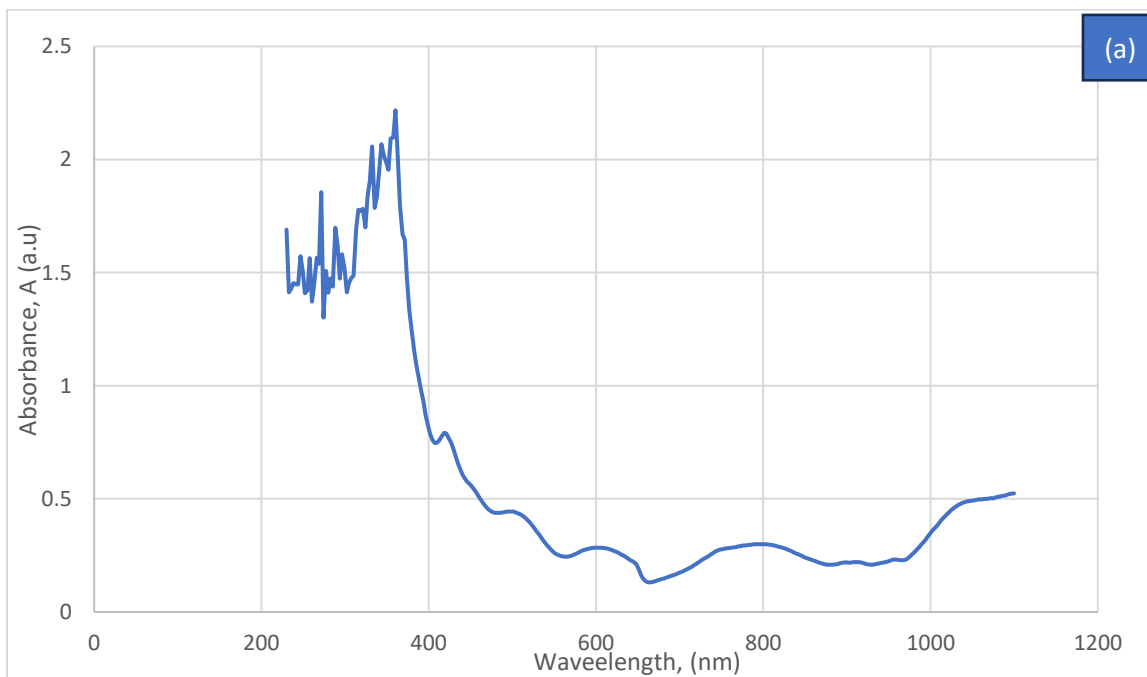
1. The UV-VIS Spectrophotometer is put on and allow to stay for about 20 minutes to to ensure voltage stability.
2. For calibration, the wavelength range was set between 400nm to 1000nm which is the instruments scanning range.
3. The black standard reference is measured by blocking the light source on an empty cuvette, pressing the start button and allowing scanning between 400nm to 1000nm.
4. The Result is read and recorded as displayed by the Arduino software installed and launched on a PC.
5. This procedure was repeated for an empty cuvette by not blocking the light source. The result for the empty cuvette was read and recorded.
6. Using 2 mL aliquots of each standard sample of 100% AGO, 100% DPK, and 100% PMS, the Spectrophotometer was allowed to scan within the reference wavelength.
7. Results were read and recorded from the Arduino software to obtain the full spectra showing the function of absorbance (a.u.) vs. wavelength ( $\lambda$ ) in nm

after which the relevant UV absorption region were analyzed.

8. For the various prepared intergrade contaminant mixtures, the experimental procedures were repeated and the result read and recorded.

**RESULTS AND DISCUSSION**

Figure 1 (a) – (c) presents the full spectra from the UV Vis Spectrophotometer for the pure uncontaminated AGO, DPK and PMS respectively with the assumption of no prior binary mixing. They were acquired in each cycle of the UV Vis spectrophotometer. The results present the Absorbance, A, in Absorbance Unit, (a.u) as a function of the Wavelength,  $\lambda$  in Nanometer (nm).



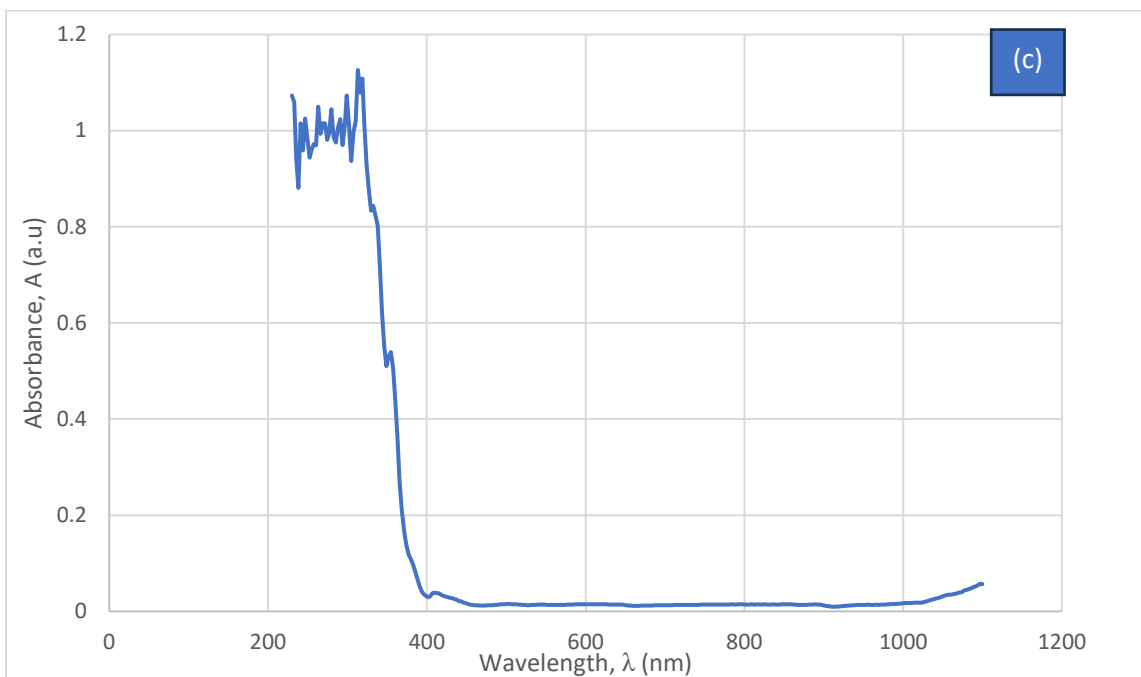


Figure 2: UV-Visible Spectra for 100% Pure (a) AGO (b) DPK and (c) PMS

In Figure 2 (a), the spectra for 100% pure AGO covered wavelength of 229.99 to 360.19nm. Within this wavelength the absorbance values ranged from 1.6896 to 2.2176 a.u. The spectrum peak features are given as 2.2176 a.u at 360.19 nm. Similarly, in Figure 2 (b) the spectra covered wavelength of 229.99 to 243.84nm with the absorbance values ranging from 0.9803 to 1.0605 a.u. The peak features in this case can be observed as 1.0605 a.u at 1.0605 nm. Also, in Figure 2 (c), the spectra covered wavelength of 232.77 to 318.63nm with absorbance values ranging from 1.059 to 1.1087au and peak features as 1.1262 a.u at 313.10 nm wavelength. Comparatively, Figure 2(a) - (c) shows important characteristics of overlapped wavelength of absorption. This overlap ranged from 232.77 to 360.19nm within which the

uncontaminated samples of AGO, DPK, and PMS absorb. The absorbance values in this case are between 0.9803 to 2.2176 a.u. However, unlike DPK and PMS, which show no absorption as the wavelength increases from 360nm upwards, AGO absorption spectrum depicts slight absorbance in this range.

**UV-Vis Spectrum Analyses of Binary Intergrade Contamination of Petroleum Products**

Similar spectra were obtained for the binary intergrades of the petroleum products. Table 2 gives the Wavelength, λ (nm) and Absorbance, A (a.u) characteristics of the spectra obtained for different of PMS/DPK, PMS/AGO and AGO/DPK in 80/20%, 60/40%, 40/60% and 20/80% which implies 20% variation for each binary mix.

**Table 2: Wavelength, λ (nm) and Absorbance, A (a.u) Features of Binary Intergrade Contaminated Petroleum Products**

Conc. (%)	Features	PMS/DPK MIX	PMS/AGO MIX	AGO/DPK MIX
80/20	λ <sub>R</sub> (nm)	230.00-313.10	232.77-326.94	257.69-354.65
	A <sub>R</sub> (a.u)	1.0194-1.0846	1.1368-1.4779	1.1370-1.9025
	λ <sub>p</sub> (nm)	313.10	326.94	354.65
	A <sub>p</sub> (a.u)	1.0846	1.4779	1.9025
60/40	λ <sub>R</sub> (nm)	235.53-321.40	318.63-338.03	246.61-271.54
	A <sub>R</sub> (a.u)	1.1193-1.3078	1.2212-1.3951	1.0714-1-1.1084
	λ <sub>p</sub> (nm)	321.40	338.03	271.54
	A <sub>p</sub> (a.u)	1.3078	1.3951	1.1084
40/60	λ <sub>R</sub> (nm)	229.99-315.86	229.99-351.88	238.31-340.80
	A <sub>R</sub> (a.u)	1.0146-1.3315	1.6825-1.2487	0.8611-1.2534
	λ <sub>p</sub> (nm)	315.86	351.88	340.80
	A <sub>p</sub> (a.u)	1.3315	1.2487	1.2534

20/80	$\lambda_R$ (nm)	230.00-351.87	252.15-351.87	238.31-332.49
	$A_R$ (a.u)	1.2453-1.3506	1.0133-1.6833	0.9179-1.4442
	$\lambda_p$ (nm)	351.87	351.87	332.49
	$A_p$ (a.u)	1.3506	1.6833	1.4442

For the 80/20 % PMS/DPK, data shows just a little shift from the wavelength and absorbance range of the 100% pure PMS. As the wavelength increase from about 320nm, there is no recorded absorbance. This is also similar to that of 100% pure PMS UV-Vis spectra shown in Figure 1(c) above. Thus, it is noted that the 20% contamination of PMS by DPK shows apparently little shift in the wavelength and absorbance range by UV-Vis spectrometry analysis.

For all the other mixes, similar observations of the spectra show that as the percentage concentration of the contaminant intergrade increases from 20% to 80%, the shift in wavelength and abundance increases away from that of the 100% pure product while the shift towards the 100% pure contaminant decrease in significance. such that the

#### Determination of Peak Characteristics ( $A_p$ , $\lambda_p$ ) of the Intergrade Mixes From the UV-Vis Spectra of the Pure and Intergrade Mixed Samples of Refined Petroleum Products

The Peak Absorbance ( $A_p$ ) and corresponding Peak Wavelength ( $\lambda_p$ ) of all the pure and different intergrade

mixes were deduced from the UV-Vis Spectra and presented in table 3. In a UV-Vis spectrophotometric analysis, the peak absorbance value and its corresponding wavelength are two of the most important parameters used to characterize a substance. They provide information about the concentration of the analyte and the nature of its electronic transitions. The peak absorbance is the highest absorbance recorded in the UV-Vis spectrum. It indicates the wavelength at which the sample absorbs light most strongly. Within the linear range of a UV-Vis Spectrophotometric machine, a higher absorbance generally indicates a higher concentration of the absorbing species, provided the measurement remains within the instrument's linear range. The absorbance also depends on the compound's molar absorptivity which represents its ability to absorb light. For purposes of quantitative analysis, absorbance values between 0.2 to 1.7 are generally preferred because they provide the best accuracy in analysis. 77.78% of the Peak Absorbance values in this study falls within this range.

**Table 3: Deduced Wavelength and Absorbance for the Pure and Intergrade Contamination of PMS/AGO, PMS/DPK and DPK/AGO**

Conc (%)	PMS/AGO		PMS/DPK		DPK/AGO	
	$\lambda_p$ (nm)	$A_p$ (a.u)	$\lambda_p$ (nm)	$A_p$ (a.u)	$\lambda_p$ (nm)	$A_p$ (a.u)
100/0%	318.63	1.1087	318.63	1.1087	360.19	1.0605
80/20%	326.94	1.2779	313.10	1.1046	357.42	1.4442
60/40%	338.03	1.3951	321.40	1.1028	268.78	1.3842
40/60%	349.10	1.7057	315.86	1.1015	343.57	1.5867
20/80%	357.42	1.6566	318.64	1.0901	332.49	1.8232
0/100%	360.19	2.2176	243.84	1.0605	243.84	2.2176
$\lambda_R$ (nm)	319.00-361.00		243.00-319.00		244.00-361.00	
$A_R$ (a.u)	1.1087-2.2176		1.1087-1.0605		1.0605-2.2176	

The Peak Absorption Wavelength ( $\lambda_p$ ) corresponding to the Peak Absorbance ( $A_p$ ) is characteristic of the molecular structure of the material because it corresponds to a specific electronic transition. Its value also depends the the degree of conjugation, the presence of functional groups or chromophores, Solvent polarity, pH of the solution and the temperature which usually has a smaller effect.

For this study, an increasing trend in wavelength and Absorbance is observed for the PMS/AGO intergrade mix with increasing impurity. For both the PMS/DPK and DPK/AGO mixes, the trend is less clear with increasing Impurity concentration. DPK's transparent colouration in these two set of intergrade mixes might be accountable for

this unclarity in trend. While little change in the wavelength and absorbance value when PMS is contaminated with AGO is noted, this becomes more significant when the contaminant increase by 60% and a little decrease in absorbance was observed with an increase in wavelength when the contaminat increases to 80%.

The wavelength and the corresponding absorbance for the intergrade contamination of PMS by DPK also shows increments in the absorbance values as the contaminant increases from 20% to 80%. The wavelength decreased at 20% contamination and increased at 40%. At 60% increase in contamination, it decreased and subsequently increased at 80% contamination.

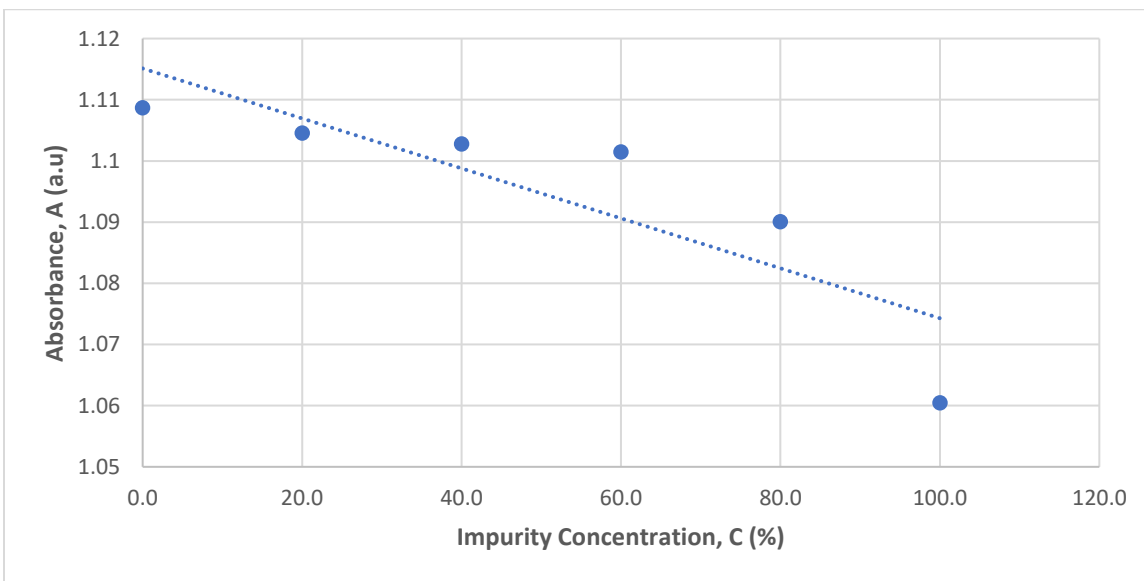
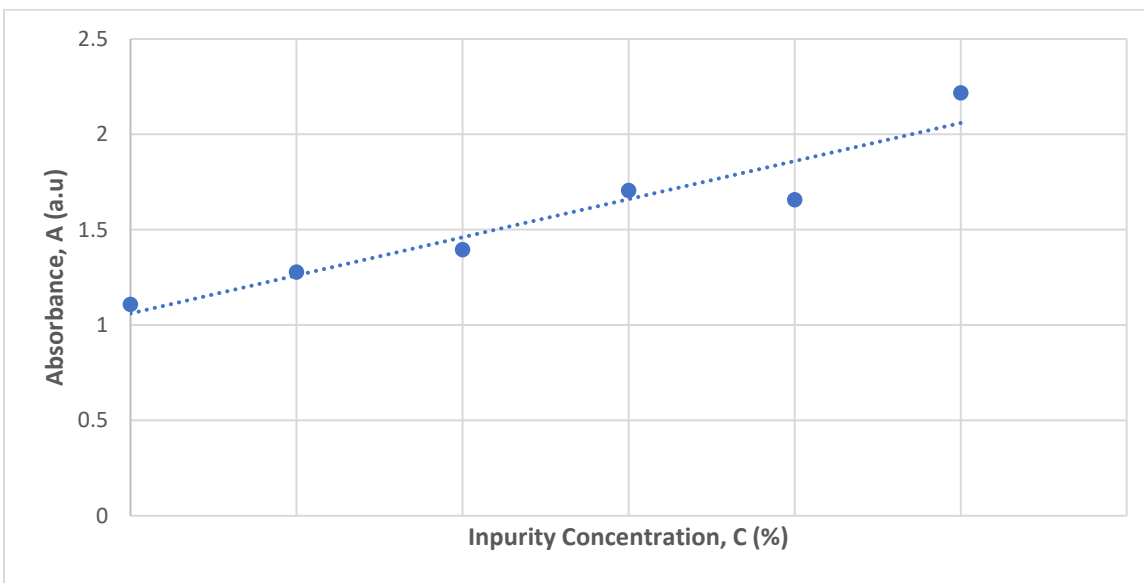
For the DPK/AGO mixes, the wavelength increases from 20% contamination until 60% contamination. At 80% contamination, the wavelength decreased slightly while the absorbance increased from 20% to 80% contamination.

**Calibration Curves for the Different Intergrades and the Absorbance/ Concentration Response Function**

Absorbance data from Table 3 have been used to provide Calibration Curves for the different binary intergrades

Figure 2(a)-(c). From the calibration curve, the Absorbance/Concentration Response Function can be determined for each of the binary intergrade.

From the concentration value and the extrapolated values of the absorbance, the calibration curves for the different intergrade contamination in 20% variations were plotted. The calibration equations obtained from the plotted curves are used in determination of intergrade contamination accordingly.



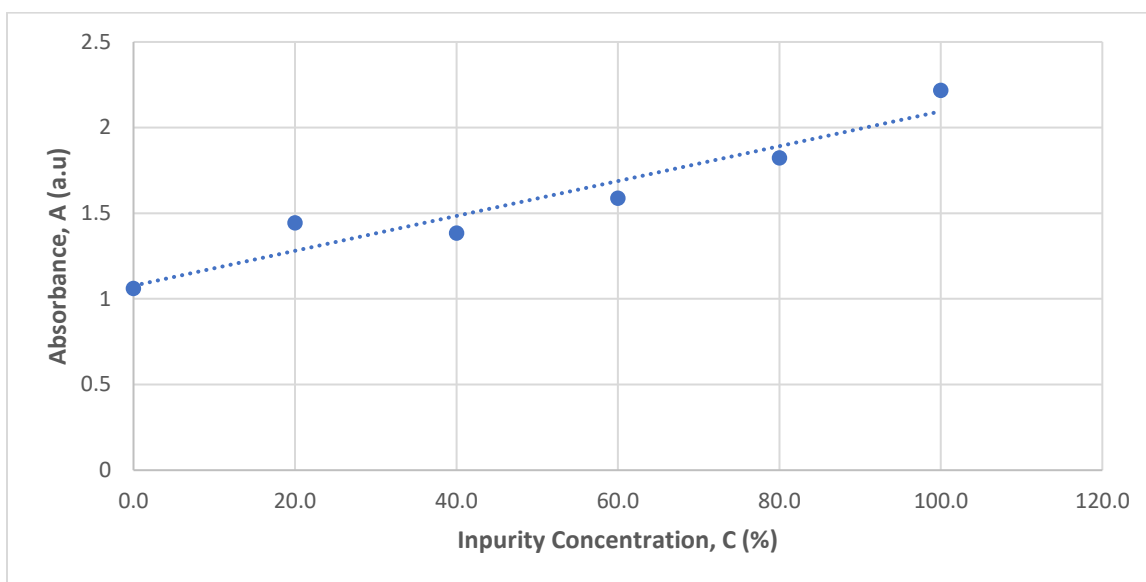


Figure 3: Intergrade Calibration Curves for (a) PMS/AGO (b) PMS/DPK (c) DPK/AGO

From figure 3(a), (b) and (c), the calibration curve for the PMS/AGO, PMS/DPK and DPK/AGO, the Absorbance/Concentration Response Function of the binary intergrades are provided as Equation 2(a), 2(b) and 2(c) respectively.

$$\lambda_{PMS/AGO} = 0.0100C_{PMS/AGO} + 1.0609 \quad (2a)$$

$$\lambda_{PMS/DPK} = -0.0004C_{PMS/DPK} + 1.1151 \quad (2b)$$

$$\lambda_{DPK/AGO} = 0.0102C_{DPK/AGO} + 1.0771 \quad (2c)$$

For 1(a), (b) and (c), the Coefficient of Determination,  $R^2$  is 0.9028, 0.7308 and 0.9155 implying a 90.28%, 73.08% and 91.55% dependence of the Absorbance, A on the Concentration, C of the impurity in the mixture. The  $R^2$  value is a measure of how well a linear regression model fits a dataset and it is a proportion of the variance in the Absorbance (A), which is the response variable, that can be explained by the Concentration (C) which is the predictor variable. It can range from 0 to 1 in which a value of 0 indicates that the response variable cannot be explained by the predictor variable at all; or a value of 1 indicating that the response variable can be perfectly explained without error by the predictor variable. Thus, the higher the value of  $R^2$ , the better it can be indicated that the response variable can be perfectly explained without error by the predictor variable more.

It can thus be stated in this study that the Absorbance can be indicated or explained by the Impurity Concentration by a factor  $\geq 0.7308$  or 73.08%. To this extent, Equation 1(a)-(c) can also reliably provide the Impurity Concentration in an intergrade mixture when the measured absorbance is known. The high correlation coefficient values ( $R^2 \geq 0.73$ ) across all binary mixtures evidenced a strong linear relationship between absorbance and percent impurity concentration, supporting the suitability and accuracy of UV-Vis spectrophotometer technology in

quantitative measurements of intergrade contamination of refined petroleum product.

## CONCLUSION

This study demonstrates that UV-Vis spectroscopy is a reliable, sensitive, and quantitative analytical method for detecting and measuring adulteration rates in binary mixtures of AGO, DPK, and PMS. The method is based on changes in absorbance, an indicator of chromophore concentration, in which the absorbance change linearly follows the Beer-Lambert law, regardless of changes in adulteration rate. Spectral analysis of the pure, uncontaminated fuels revealed characteristic absorption ranges in the UV region, primarily due to aromatic components. Comparative analysis showed significant overlap between 232.77 nm and 360.19 nm in the absorption regions of AGO, DPK, and PMS. AGO exhibited the highest absorbance, an important characteristic for contamination detection. Spectral analysis of binary contaminated samples confirmed concentration-dependent changes. For PMS contaminated with DPK, as the DPK concentration increases from 20% to 80%, the absorbance systematically increased from 1.1846 a.u. to 1.3681 a.u. in the 243–319 nm range. For PMS contaminated with AGO, because AGO inherently exhibits high absorbance, contamination resulted in a significant increase in both absorbance and characteristic wavelengths up to a maximum of 1.7057 a.u. at 349.10 nm for 60% AGO. This indicates a spectral shift from pure PMS. Also, for AGO contaminated with DPK, the absorbance systematically increased from 1.4442 a.u. at 20% DPK to 1.8232 a.u. at 80% DPK in the range of 244–361 nm. This confirms a reliable relationship between the blend ratio and the spectral response. Furthermore, the derived calibration curves provide a robust and practical tool for

calculating the concentrations of DPK in PMS, AGO in PMS, and DPK in AGO up to 73.08% accurately. With advantages such as rapid analysis time, minimal sample preparation, and instrument accessibility, this validated method will be an important and concrete resource for fuel quality control laboratories and regulatory agencies. The establishment of this method will contribute to strengthening quality assurance protocols, ensuring compliance with fuel standards, protecting engine performance, and protecting consumers' interests from the harmful effects of fuel adulteration.

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