Determination of the Degree of Consumption (DoC) of Lube Engine Oils Using Fluorescence Spectroscopy

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Abstract

The accreditation of a fast, inexpensive, and simple way to discriminate between different kinds of oils and their efficacy "degree of consumption (DoC)" has been developed. The fluorescence spectroscopy provides a reliable method for oil inspection without resorting to tedious separation.

Different new and used oil samples available in the local Iraqi market were investigated. While the challenge is to build a directory containing data of all the oils available in the local market. This method expected to control the falsified (forged) trademarks of motor oils and to discriminate between different oils.

The excitation-emission spectra of oil samples were determined in the range of 200 – 600 nm. The effect of the presence of trace metals on the fluorescence intensity of oils was considered by adding few milligrams of (Cu, Al, Fe) to the diluted oil solution. No major effect noticed on fluorescence intensity.

The research suggests installing a simple Spectrofluorometer into vehicles to check the DoC of the oil regularly and to notify the driver exactly when to replace the engine oil.

The obtained results indicate the applicability to execute such gadget to be installed in the vehicles for routine detection of the engine oil quality and its degree of consumption DoC. As well as demonstrate the potential of the technique in oil identification and could be further developed.

Keywords: Fluorescence, Degree of Consumption (DoC), lube oil, engine oil

Introduction

The lube oil composition is a complex mixture of hydrocarbons with different molecular masses. The lube oil producers generally use the same base-stock then add different additives up to 5% by weight [1] to improve the oil performance [2].

Lube oils are designed to lubricate the moving parts of internal combustion engines to reduce friction, provide oxidation resistance, improved deposit protection, better wear protection, better low-temperature performance over the life of the oil [2] and protect the engine from malfunctions [3]. Thus, oil testing is important to examine lubricant's quality and to discriminate between new and used oils [4]. Because of the complexity of lube oils and the many factors affecting their compositions, almost all analyses been partial and not very accurate [5].

Exhausted motor oils are hazardous wastes to the environment [6] and could reach the sources of drinking water and crops irrigation [7]. Most of the lubricants absorb UV or visible light, while few are fluorescent [8]. Organic molecules such as oils, with extended π-electron systems as for aromatic and some unsaturated aliphatic compounds, often exhibit fluorescence efficiency [9]. Compounds containing fused-rings usually exhibit high molecular fluorescence [10]. Rigid molecules or multiple ring systems tend to have large quantum yields of fluorescence while flexible molecules generally have lower quantum yields [11].

Fluorescence detectors are very selective and are about three orders of magnitude more sensitive (0.001–0.01 ng) than UV detectors as they measure the fluorescence of the analyte against an almost zero background [12].

There are many other applications for fluorescence spectroscopy, not limited to; determination of thermal stability of biocatalysts, Characterizing bio labels for live cell imaging, Hydrocarbon mixtures in petroleum oils, and Characterizing GPCR (G protein–coupled receptors) oligomerization [13]. Nevertheless, many other applications in Nanoparticle characterization, Surface chemistry research, Analytical chemistry, Pharmacology, Biotechnologies, and in crime investigation [14]. Most fluorescence measurements use to carry out in liquid media and the solutions must be very dilute in fluorimetry. Otherwise, the results may not comply with the Lambert–Beer law and linearity cannot be achieved [15]. This leads to the apparently paradoxical result that the fluorescence can diminish even though analyte concentration increases.

Molecules that naturally fluorescence inactive can convert by chemical derivation or by reacting with a fluorescent molecule to become fluorescent. The interaction of a fluorescent molecule with the solvent medium will affect both the energy and intensity of fluorescence spectra. Effects of polarization and hydrogen bonding, viscosity effects, heavy atom effect, compound formation and photo-reaction have a critical influence on the resultant fluorescence [16]. In polar media, fluoresce molecules may solvate by dipolar attraction. These effects produce differences in the equilibrium configurations of the ground and excited states [17].

The solvent can also interact with fluorophores to form excited state complexes that do not fluoresce. Selection of a solvent to minimize this effect can enhance fluorescence. In addition to the absorption and emission, Scattering may happen either due to Rayleigh scattering or by small particles in colloidal suspension (Tyndall scattering) [18]. Some of the incident energy transferred to the solvent molecules in the form of vibrational and rotational energy. Then re-emitted in longer wavelength and less energy than the excitation radiation. This is called Raman scattering, which is 100 to 1000 times weaker than Rayleigh's [19].

Unlike absorption – emission fluorimetry is synchronous fluorescence scan (SFS), in which both monochromators moves simultaneously [20]. The synchronous technique allows the stronger peaks to be increased selectively by use of a suitable stoke shift Δλ [21]. Unlike UV/visible spectroscopy, fluorescence may undergo quenching, which is a reduction in fluorescence intensity [22]. One reason for quenching is the molecular interaction when a

fluorophore is in contact with another molecule. Other reasons lead to a loss of emission from the fluorophore include energy transfer, charge transfer reactions or photochemistry [23].
The final goal of this study is to develop a sensing system uses a simple fluorometer, which can be installed in the vehicle to determine the DoC and to notify the driver when to replace the engine oil. This will ensure changing the oil only when fully depleted, which reduces costs and preserve the environment.
The reliance on the car mileage counter to replace the engine oil is not accurate enough since the consumption of oil (DoC) depends on many factors not limited to oil quality, climate, driving habit, engine efficiency, etc. Nevertheless, discrimination the quality of lube oils is of great importance as well.

Experimental Part

Instrumentation

- Cary Eclipse Fluorescence Spectrophotometer G9800A, Agilent Technologies, USA.
- Varian Cary Peltier Multicell 4 Position Cell Holder, G9808-00003, Agilent technologies, USA.
- Quartz cuvettes with four clear faces.
- Digital Analytical balance, Sartorius GD503 (0.0001g), Germany.
- Analog Water Bath, Labtech, Vietnam.

Materials and reagents

- Several motor oils from different producers available in the Iraqi market over the period Oct 2016 to May 2017, **Error! Not a valid bookmark self-reference.**1.
- Benzene (97%, BDH), Cyclohexane (99.7%, BDH), Chloroform (99.4%, Merk), Dichloromethane (98.8%, Fluka), Ethanol absolute (99.9%, BDH), n-hexane (99.9%, Scharlau), Toluene (99.5%, Himedia).
- Heavy metals (Cu, Fe, Al) as fine powders, obtained from local workshops.

Table (1): Codes and details of different motor oil samples examined in this study

Sample Code	Trademark	Origin	Volume (Lit)	SAE	API
R1	Gardul	Germany	5	5W-20	SL/CF
R2	Youkn	lraq	1	HD 50	CC/SC
R3	Hanover	Germany	5	5W-30	SN
R4	Hanover	Germany	4	20W-50	SG/CD
R5	Wagon	lraq	1	140	GL4
R6	Jumbo Royal	Iraq	1	HD 50	CC/SC
R7	Mechilon	French	5	10W-30	SN
R8*	Morris	UK	20	15W-40	HD4
R9*	Vulcan	UAE	5	50	CF
R10	Maxpro/ Mopar	USA	5	5W-20	SN
R11*	Acdelco	USA	4	10W-30	SN
R12*	Quartz	UAE	4	20W-50	SL
R13*	Petromin	USA	1	20W-50	SL/CF
R14*	Fuchs	Germany	1	20W-50	SL
R15*	Acdelco	USA	1	5W-30	SN
R16*	GAT 1	USA	5	20W-50	SL

- *SAE: The Society of Automotive Engineers*
- *API: American Petroleum Institute*
- ** Samples have a used peer. Used oil samples followed by the suffix "u".*

Optimization of Fluorescence Measurement

Different conditions been examined as a function of the fluorescence intensity as an arbitrary unit (a.u.) to optimize the test method and increasing its sensitivity. Conditions of Emission and Excitation Wavelengths pairs (EEWs), slit width of both the excitation and the emission monochromators, adjustment of the emission path length, temperature, and the contamination by the presence of wear metals in engine oil.

Degree of Consumption (DoC) for lube oil

DoC has been determined for some lube oils by measuring the fluorescence intensity at a certain EEWs for each pair of the fresh/consumed oil at different proportions.

Results and Discussion

Sampling

Eight out of 16 oil samples collected in pairs (new/used). Solvents like strong acids, strong bases or even acetone were avoided while cleaning the quartz cuvettes as they might attach to their walls [20].

Factors affecting Fluorescence Measurements

A number of parameters have been studied intensely to determine the optimized conditions.

Setting up EEWs pairs

Finding the right EEWs pairs is of great importance to maintain sensitivity. EEWs found automatically using the function "Prescan" available in the spectrofluorometer software. While manual recognition of the EEWs was accomplished by setting the excitation monochromator to the of the maximum wavelength (λ_{max}) UV/Vis absorption spectrum. Then the emission monochromator is set to the highest emission intensity obtained, and scan the excitation radiation again to specify the best corresponding excitation wavelength. Both approaches gave almost the same EEWs results.

Emission intensities have been compared for different couples of new/used oil samples under identical measurement conditions, as appears in Figure (1-5).

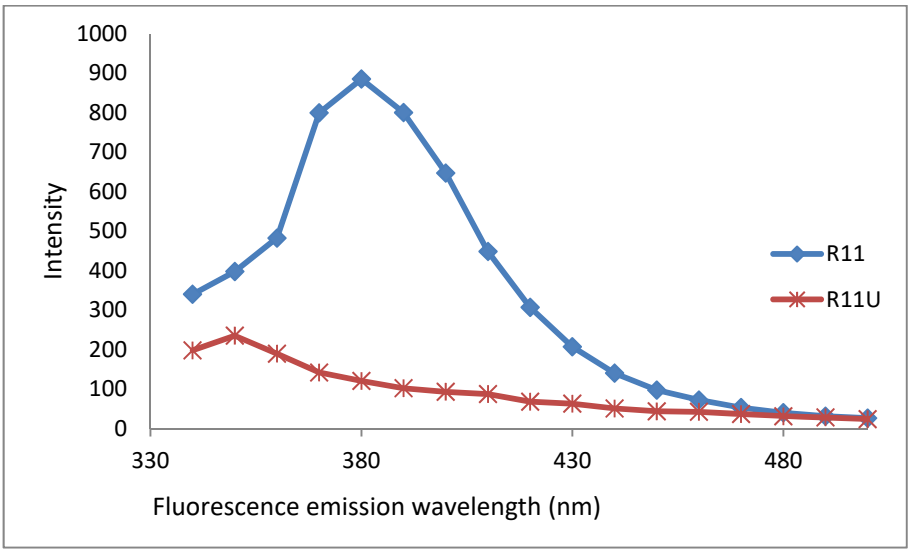

Figure (1): Comparing the fluorescence spectra for 5.18 mg/l of R11 vs. R11u oil samples in benzene

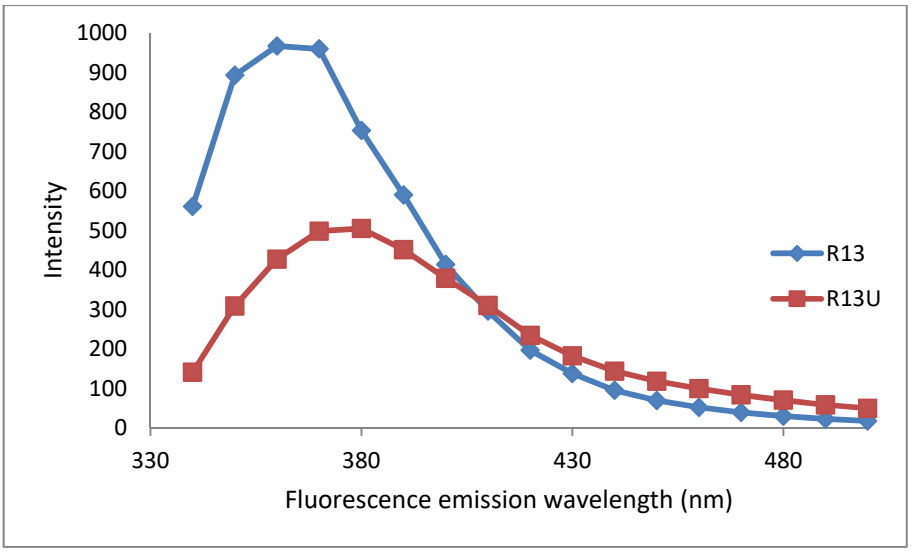

Figure (2): Comparing the fluorescence spectra for 2.59 mg/l of R13 vs. R13u oil samples in toluene

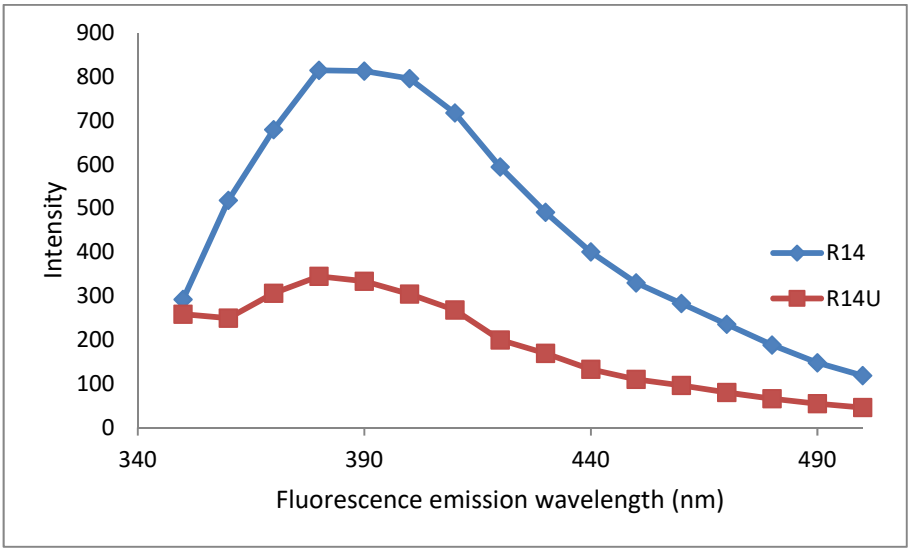

Figure (3): Comparing the fluorescence spectra for 1.295 mg/l of R14 vs. R14u oil samples in hexane

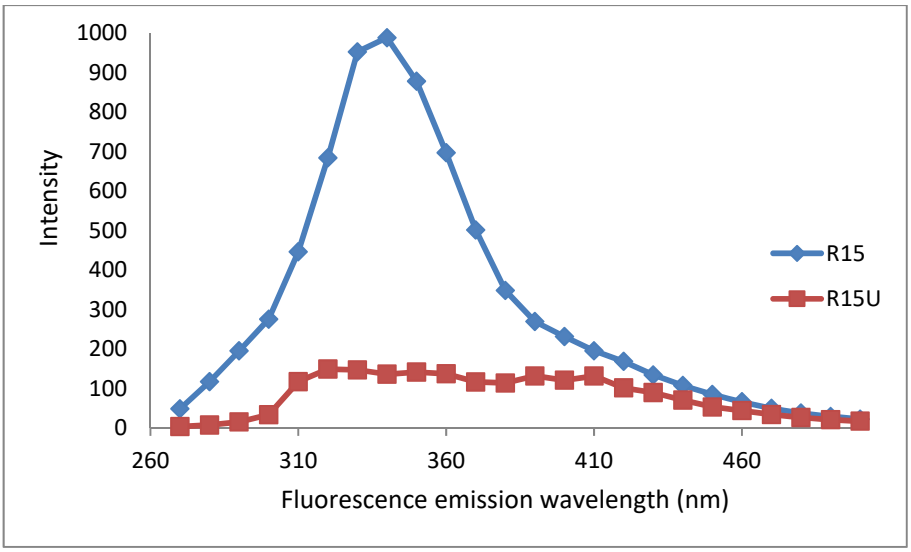

Figure (4): Comparing the fluorescence spectra for 1.295 mg/l of R15 vs. R15u oil samples in hexane

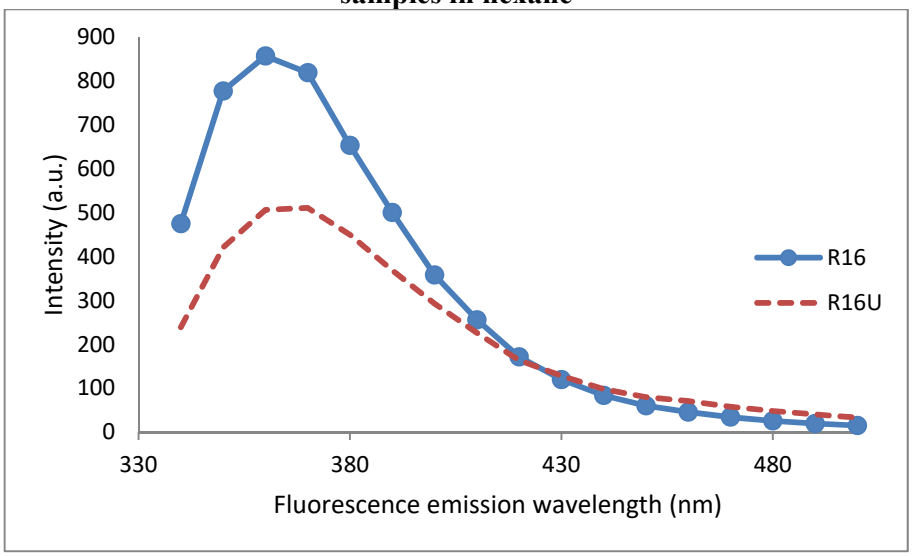

Figure (5): Comparing the fluorescence spectra for 2.59 mg/l of R16 vs. R16u oil samples in hexane

Setting up the radiation slits widths

The best slit width of both the excitation and the emission monochromators were tested by changing the slit width of both monochromators individually. Better sensitivity obtained with wider slit widths.

However, if the priority is to selectively discriminate a specific analyte in a mixture then, the usage of narrower slits will be necessary [17] [24].

As it is clear from the figure (6); that the optimized value for the excitation-slit width was 10 nm while the best emission-slit width was 5 nm. However, the emission intensity was out of scale when both excitation and emission slits widths were set to 10 nm.

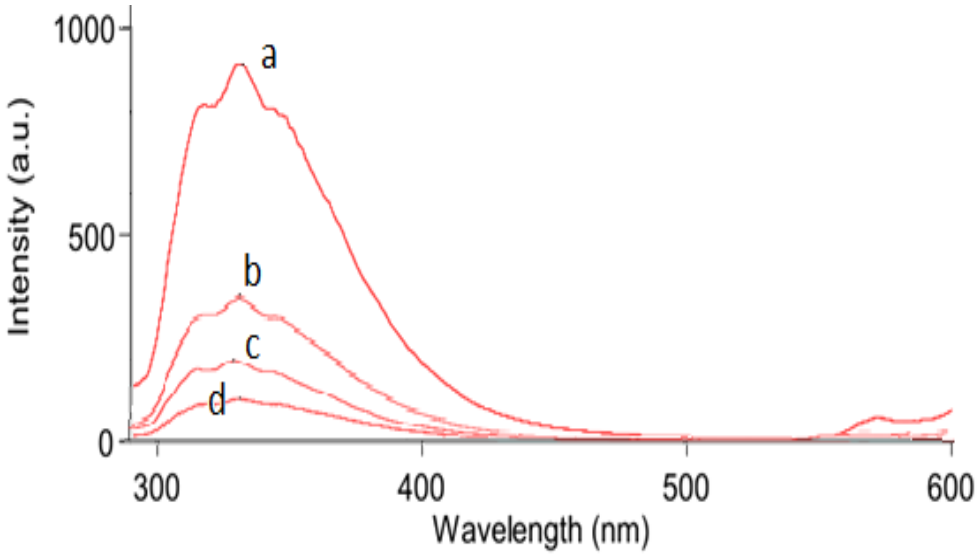

Figure (6): Overlay fluorescence spectra for the following slits widths a: (ex10, em5), b: (ex5, em5), c: (ex10, em2.5), d: (ex2.5, em5) in nm. Oils were dissolved in ethanol.

The influence of emission path length

The emission path length is the perpendicular distance between the excitation beam passing through the sample and the cuvette facet facing the detector.

Longer paths may lead to self-quenching caused by the unexcited molecules between the fluorescent analytic and the emission detector those may absorb the emitted light [23].

When an engine oil consumed, it become darker, then a shorter path length will be a good solution to reduce the optical density.

A Varian Peltier Multicell 4 Position Cell Holder, figure (7), used to control the emission path length so that the incident beam passes closer to the cuvette face in front of the detector. This will shorten the thickness facing the detector, figure (8).

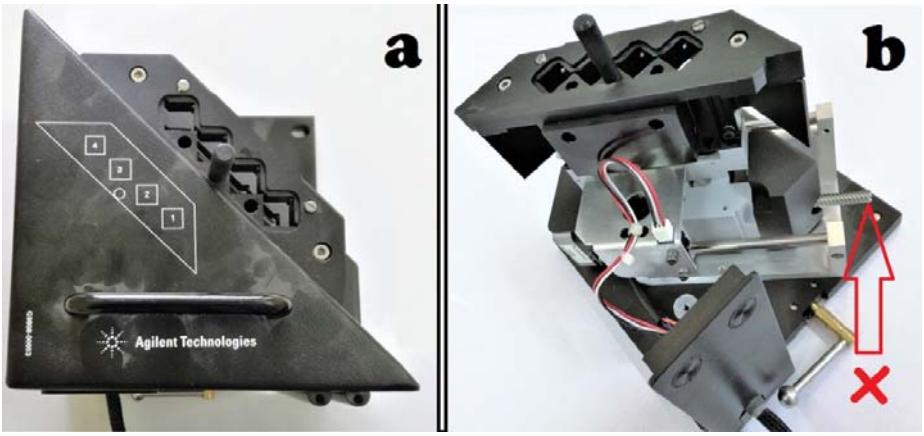

Figure (7): Varian Peltier Multicell 4 Position Cell Holder from Agilent Technology; a) a top view, b) partially dissembled, x) manual fine adjustment knob

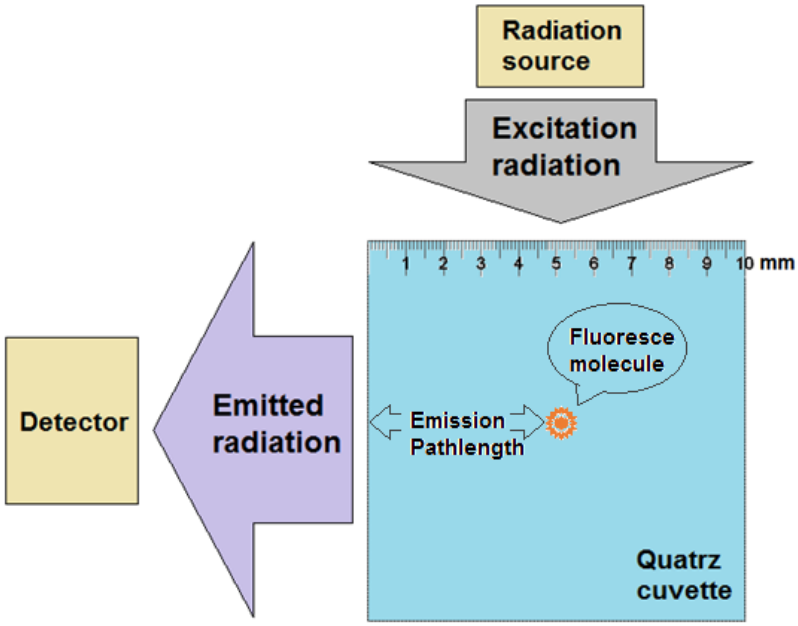

Figure (8): Controlling the emission path length by shifting the cuvette

The multicell holder has been dissembled partially to enable controlling the cell position manually; this made the adjustment very easy and accurate by turning a fine adjustment knob. The effect of the cuvette position has examined as a function of the fluorescence intensities obtained, table (2).

From the Figure (9-10), the fluorescence intensity of the oil samples is inversely proportional to the emission path length facing the detector.
This been expected, as the number of the unexcited molecules existing in the emission path those causing quenching by absorbing the fluorescent light is reduced.

Table (2): The emission intensity of R11 oil sample vs. path length

Emission Path length (mm)	Emission wavelength (nm)	Intensity (A.U.)
1	535.07	498.195
2	531.04	551.822
4	531.94	530.776
5	531.94	510.339
6	528.05	442.854
7	521.94	281.476
9	525.97	252.306

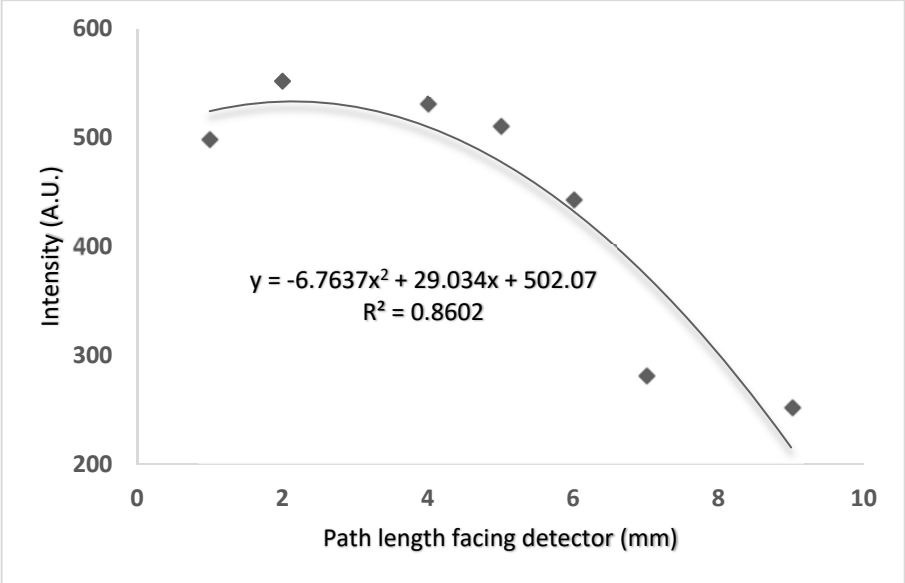

Figure (9): Fluorescence intensity of the oil samples is inversely proportional to the emission path length facing the detector

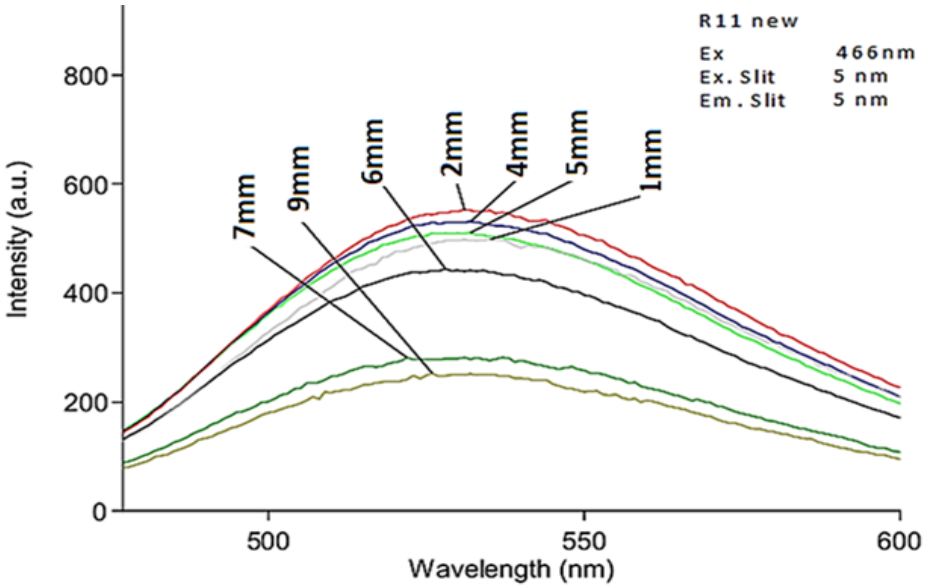

Figure (10): Fluorescence intensity versus emission path length

Temperature effect

Oil samples were tested over a range of temperature (10 to 50) C° as a function of their emission intensity, **Error! Reference source not found.**11-14. Nevertheless, some oil samples did not exhibit fluorescence activity when tested at ranges of (35-50) C°, which may relate to the loss of rigidity. As the molecules, those excited to a higher electronic excited state may lose their electronic energy by converting it to vibrational without emitting radiation [15].

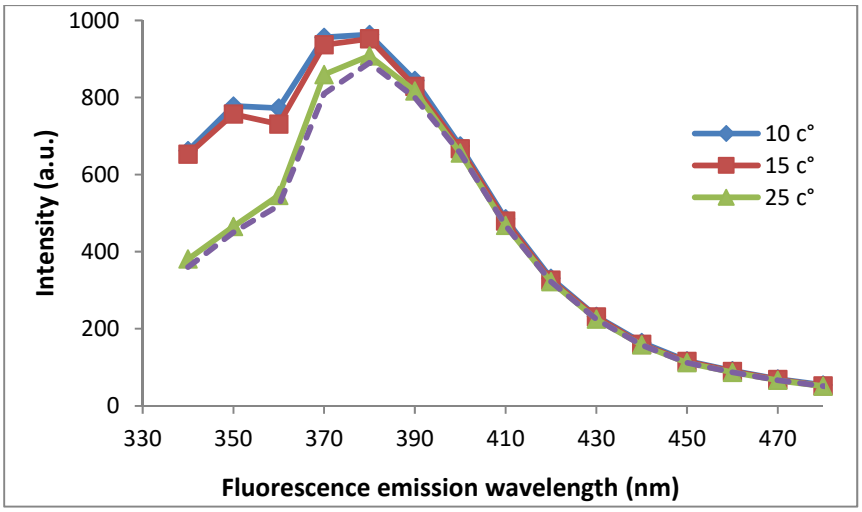

Figure (11): Fluorescence spectra for 5.18 mg/l of R11 in benzene at different temperatures, best intensity obtained at 10 ºC

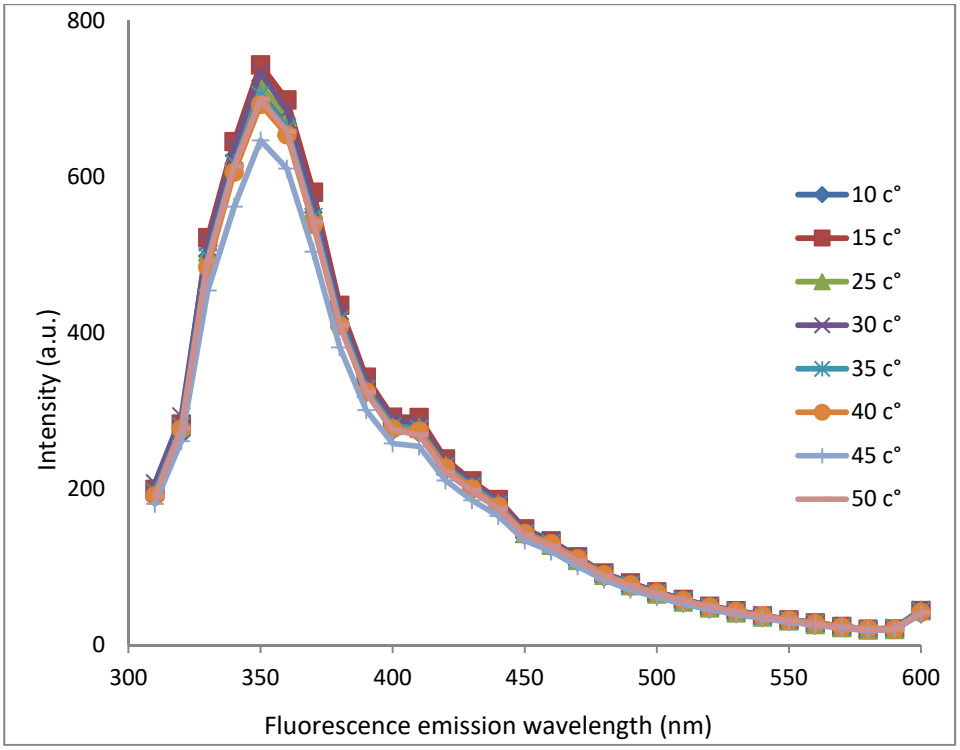

Figure (12): Fluorescence spectra for 1.295 mg/l of R11u in toluene at different temperatures, best intensity obtained at 15Cº

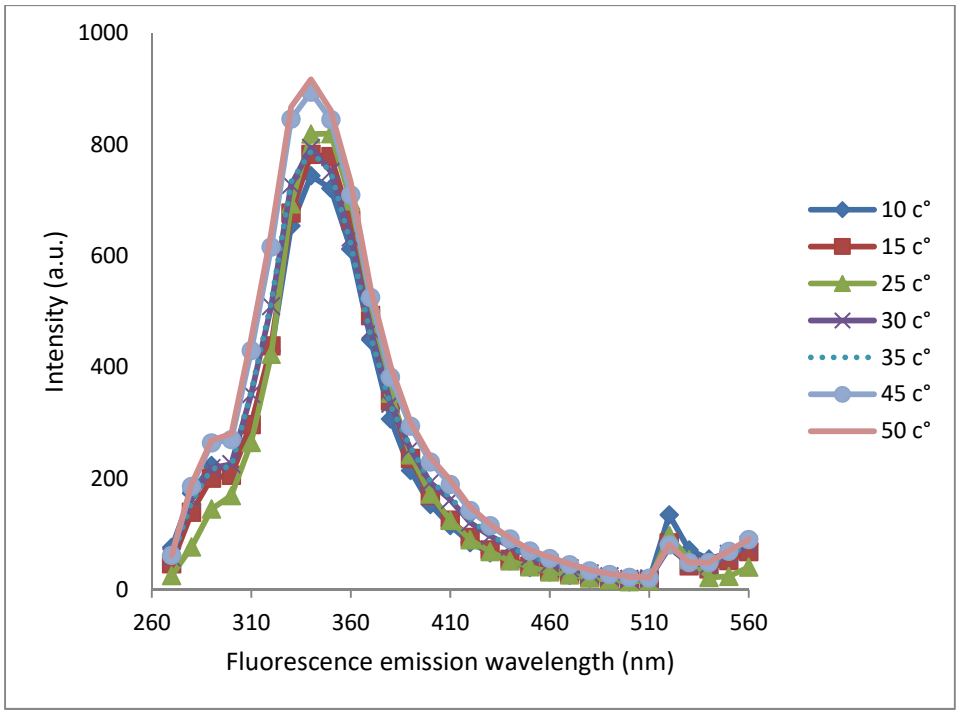

Figure (13): Fluorescence spectra for 1.295 mg/l of R15 in hexane at different temperatures. The best intensity obtained at 50C°

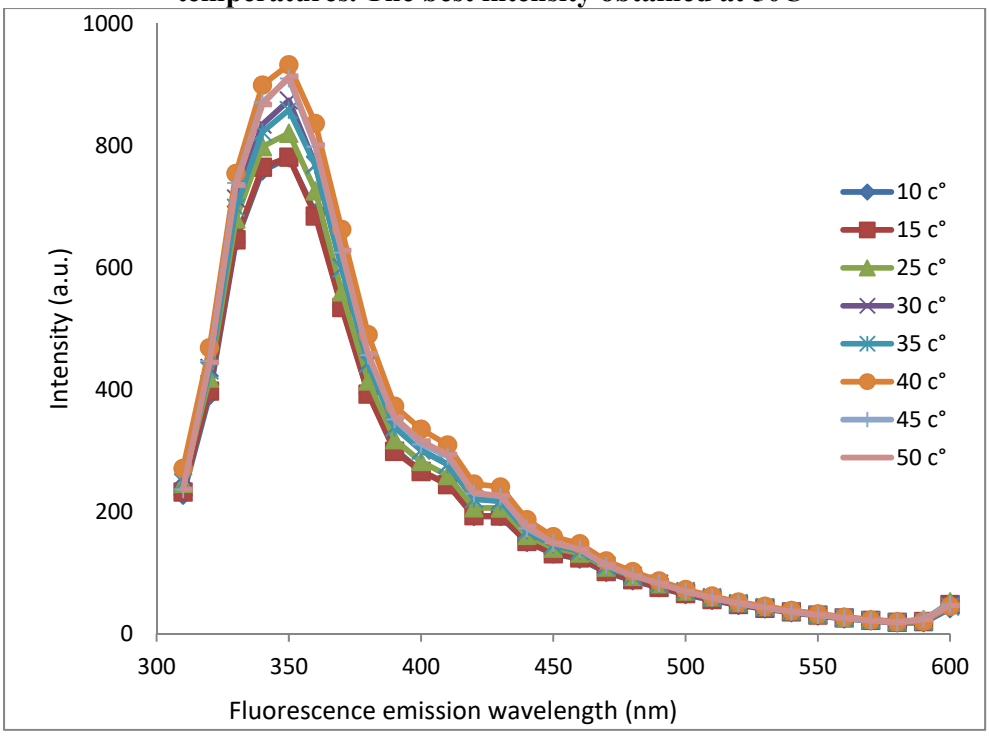

Figure (14): Fluorescence spectra for 2.59 mg/l of R15u in hexane at different temperatures. The best intensity obtained at 40C°

Metal Contamination

Engine oil contaminates with some metals produced as a result of the friction of the rubbing of the moving mechanical metallic parts of the engine. This may affect the fluorescence activity of the lube oil due to increased rigidity when some organic chelating agents complexes with a metal ion.

Accordingly, small amounts of the metals those expected to compose the engine alloy (aluminum, iron, and copper) added to the lube oil samples to examine their effect as a function of fluorescence activity, figure (15-20). The examined effects were not significant.

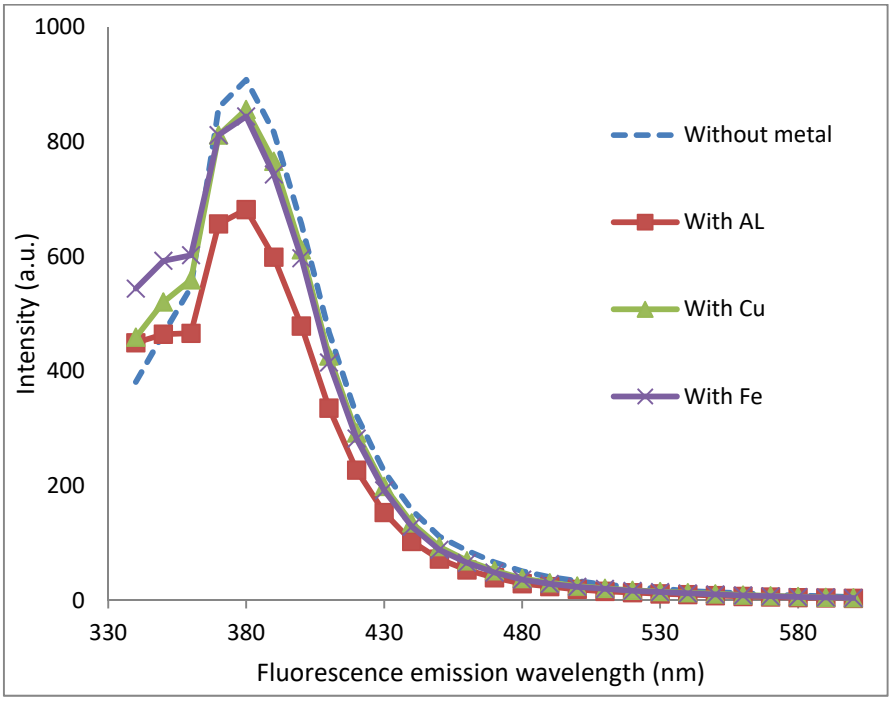

Figure (15): Fluorescence spectra for 5.18 mg/l of R11 in benzene with traces of different metals

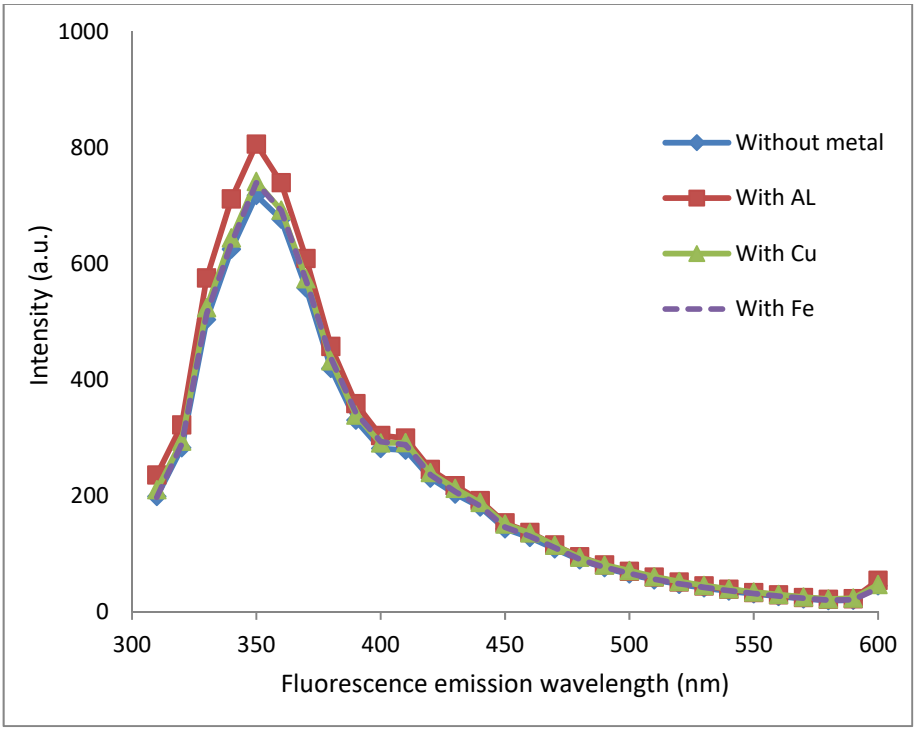

Figure (16): Fluorescence spectra for 1.295 mg/l of R11u in toluene with traces of different metals

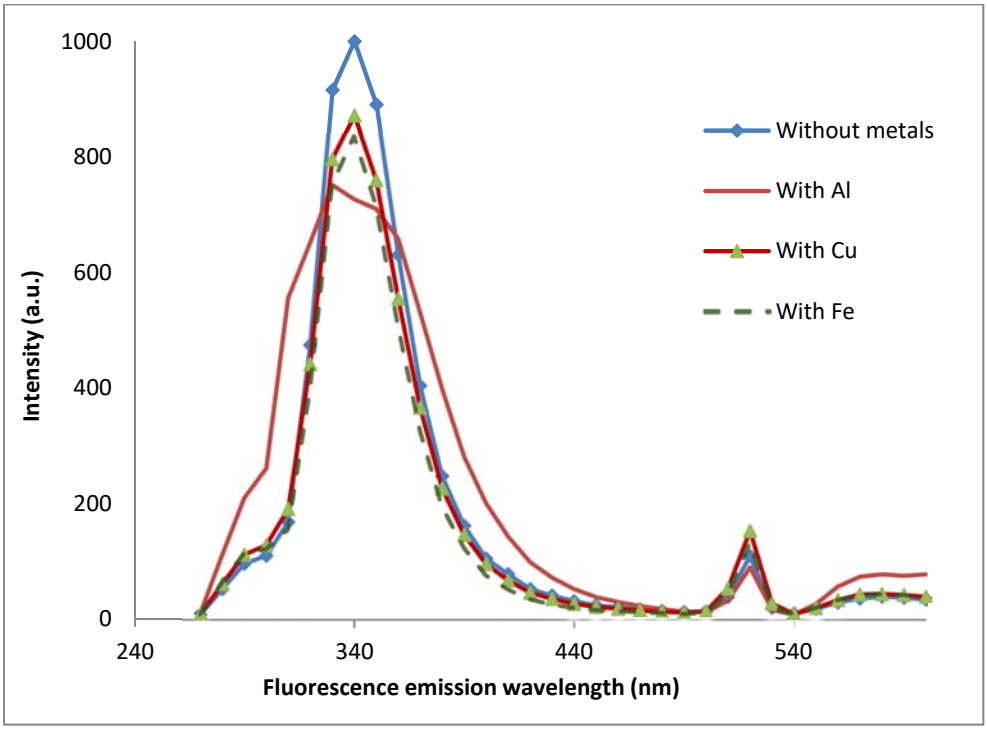

Figure (17): Fluorescence spectra for 1.295 mg/l of R15 in hexane with traces of different metals

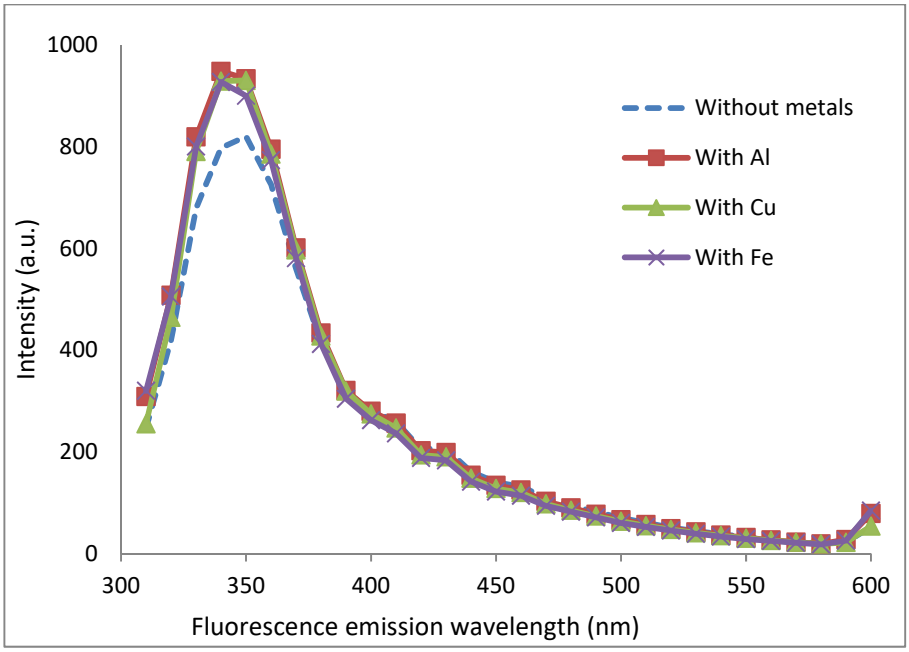

Figure (18): Fluorescence spectrum for 2.59 mg/l of R15u in hexane with traces of different metals

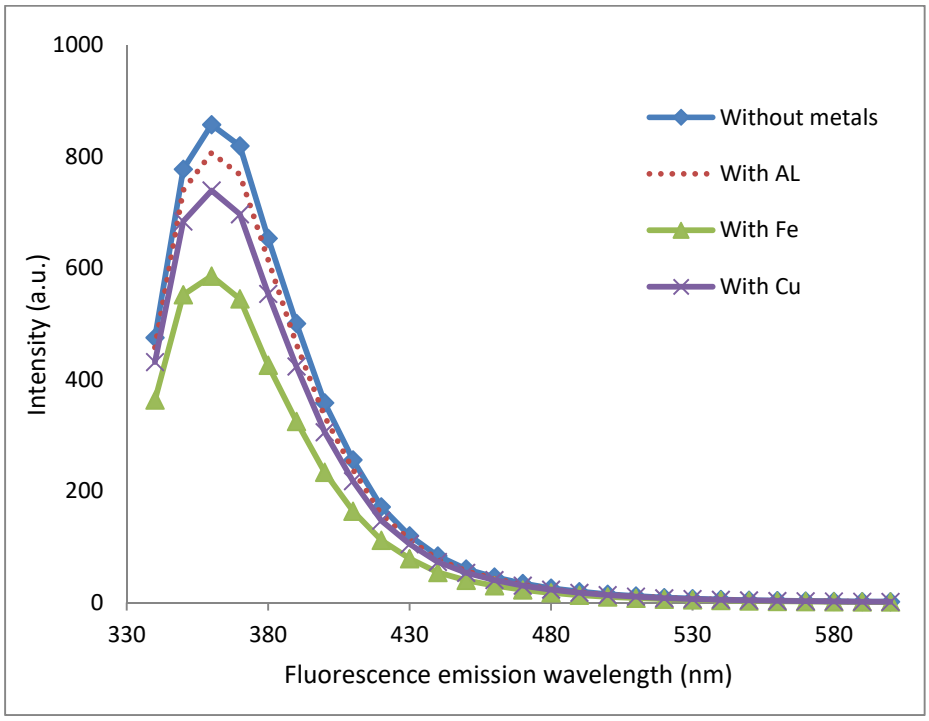

Figure (19): Fluorescence spectra for 2.59 mg/l of R16 in hexane with traces of different metals

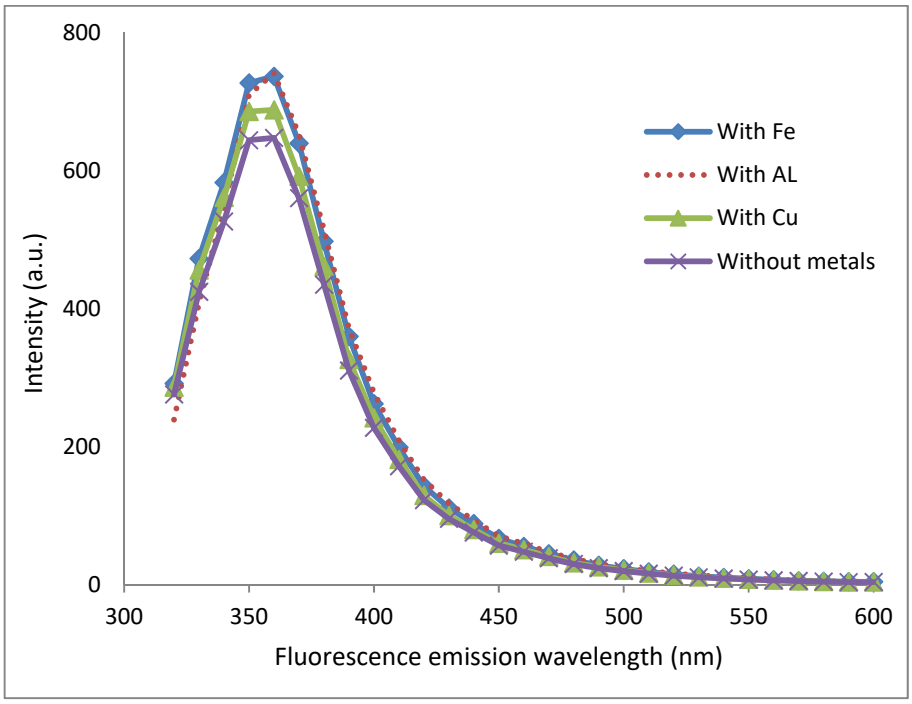

Figure (20): Fluorescence spectra for 1.295 mg/l of R16u in hexane with traces of different metals

Direct measurement of fluorescence

The fluorescence of all oil samples was measured directly without dilution. The selected EEWs were obtained by the function "Prescan" for each oil separately, Figure (21). The excitation and emission slits widths were 5 nm for both monochromators. The temperature was controlled to 24±1C° during measurements.

The resultant intensity for each oil sample considered as the 100% intensity of the fresh new oil which can be used for later comparison, table (3).

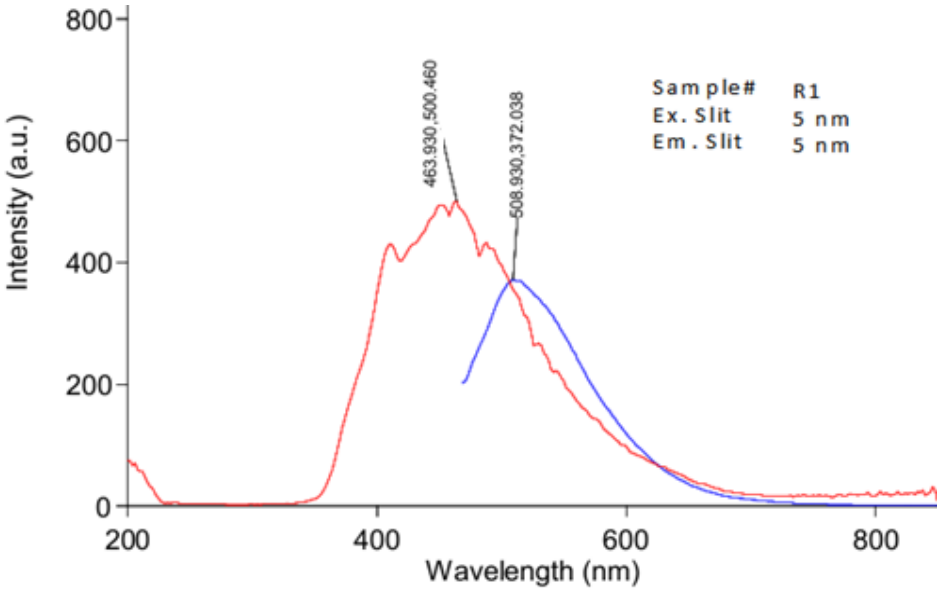

Figure (21): Pre-scan fluorescence spectrum of R1 oil sample

Table (3): Fluorescence spectra for new motor oils

Oil Sample	Excitation (nm)	Emission (nm)	Intensity (a.u.)
R1	464	510	319
R2	532	583	344
R3	386	481	750
R4	408	442	387
R5	408	442	387
R6	532	583	283
R7	474	514	554
R8	464	473	73
R9	494	535	339
R10	462	532	206
R11	464	528	501
R12	462	503	562
R13	464	509	184
R14	350	578	465
R15	462	527	474
R16	462	499	830

Degree of Consumption (DoC) of lube oil

Direct measurement of lube oil without the need for any sample preparation with no residues generated and a very short analysis time is of great significance.

The fluorescence intensity was examined for 1.5 mL of new oil samples after spiked by different aliquots of consumed oil of the exact same brand and type. These tests were carried out in optimized conditions to test the DoC. table (4), figures (22-31).

Table (4): Fluorescence intensity versus the spiked volume for some New/Used oil couples. As the table is very long some records those not affecting the overview have omitted

Oil Sample	Volume of consumed oil (ml)	Excitation (nm)	Emission (nm)	Stokes shift	Intensity (a.u)	DoC %
R11	0	464	540	76	501	0%
R11	0.05	464	540	76	332	34%
R11	0.1	464	540	76	298	41%
R11	0.75	464	540	76	4	99%
R12	0	462	511	49	562	0%
R12	0.05	462	511	49	317	44%
R12	0.1	462	511	49	205	64%
R12	0.9	462	511	49	3	99%
R14	0	530	581	51	465	0%
R14	0.05	530	581	51	403	13%
R14	0.1	530	581	51	385	17%
R14	2.35	530	581	51	7	98%
R15	0	462	514	52	474	0%
R15	0.05	462	514	52	387	18%
R15	0.1	462	514	52	331	30%
R15	0.65	462	514	52	7	99%
R16	0	462	506	44	830	0%
R16	0.05	462	506	44	543	35%
R16	0.1	462	506	44	325	61%
R16	2.1	462	506	44	4	100%

For each oil sample, the fluorescence intensity has been drawn against the added volume portions of the peer used oil. The slope and the linearity obtained from the sketch of the second order polynomial function for the curve represents DoC and the oil quality, i.e. higher slope and R2 values means better oil quality, figure (22).

However, the suggested relation between DoC and the sample composition became clearer by plotting the value of logarithm to the base ten of the DoC against the added volume of consumed oil, then getting the exponential trend line of the curve, figure (23).

The resultant slope and linearity values represent the oil quality since high values mean the oil preserve lubricating properties and can endure larger volumes of the consumed residues without changing its properties. Therefore, the next graphs conclude that the oil coded R14 has the best quality than the other samples since it has the highest values for slope, table (5).

Table (5): A comparison for the quality of some oil samples as a function of the corresponding slope and linearity extracted from the graphs of the fluorescence intensity of fresh oils (1.5 ml each) versus the added volume of its peer consumed oil

Oil Sample	Emission (nm)	Before Log(10)		After Log(10)	
		Slope	Linearity R^2	Slope	Linearity R^2
R11	540	-217.3700	0.7001	0.6285	0.989
R12	511	-121.9400	0.535	0.9729	0.976
R14	581	105.2100	0.612	55.2345	0.968
R15	514	-320.0300	0.720	0.3950	0.961
R16	506	98.7300	0.483	32.3665	0.963

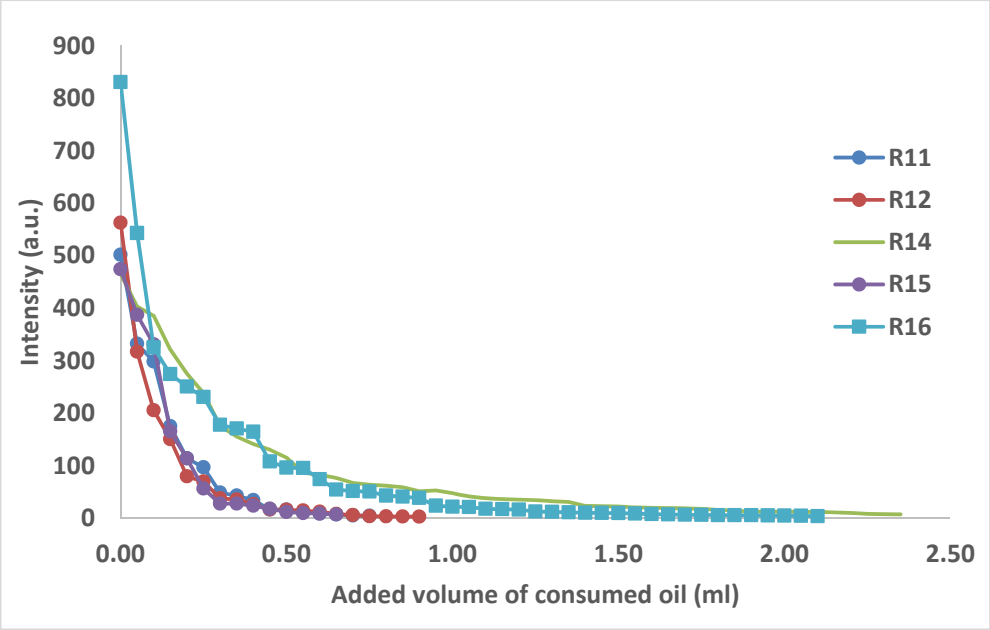

Figure (22): A comparison for the fluorescence intensity of some fresh oils (1.5 ml each) versus an added volume of its peer consumed oil

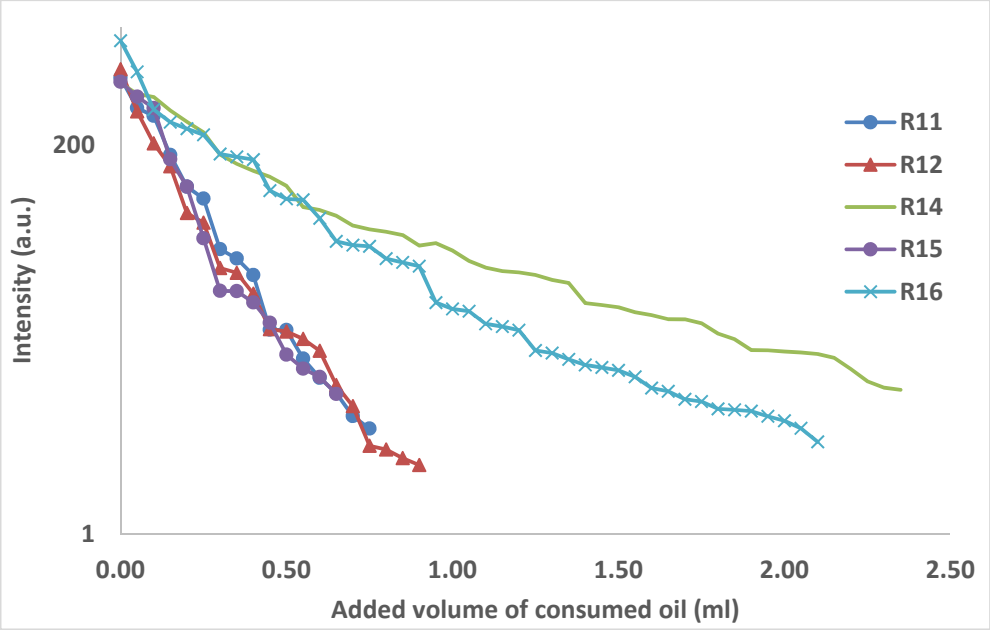

Figure (23): A comparison for the logarithmic scale to the base 10 of fluorescence intensity of some fresh oils (1.5 ml each) versus an added volume of its peer consumed oil

Conclusion

The experimental findings have indicated that fluorescence spectroscopy is easy, affordable, sensitive, fast, and an efficient way to identify and discriminate between different lube oils. As the measured fluorescence intensity of the of the new and used oil samples is proportional to the degree of consumption DoC of the oil. In addition, DoC is applicable and can be of great economic and environmental benefit.

The major obstacle in this study is the lack of an updated indexed library implying data of all oils available in the local market. Such data is vital for oil comparison and verification.

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