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Determination of Saturated and Unsaturated Hydrocarbons in Petroleum Oil Pesticides using FTIR Spectroscopy

Mohamed Abdelgwad1,2, Walid Tawfik1,*, Abdallah Zedan1, Olfat Radwan2

[1] *National Institute of Laser Enhanced Sciences (NILES), Cairo University, Giza, Egypt.*

[2] *Pesticides Research analysis department, Central Agricultural Pesticides Laboratory– 7 Nadi El-Seid st, - 12618 Dokki, Giza, Egypt.*

Abstract

Petroleum oil pesticides are used as acaricides, insecticides, and herbicides. Oils can cause phytotoxicity if oils contain unsaturated hydrocarbons. Traditional chemical methods to determine unsulfonated residue (UR), such as the ASTM D483 and MT (57), depending on sulfuric acid 98% reagent. The present study introduces a new optical spectroscopic method using FTIR to determine unsaturated Petroleum oil pesticides. The integral intensities of the bands at about 1640 to 1643 cm^{-1} correspond to ν(C=C). In alkynes, (C≡C 2140-2100 cm^{-1}). Three technical petroleum oil samples are collected from three different companies in Egypt. (El-Mostakble for Chemicals Co.(S1), Kafr El-Zayate for Pesticides and Chemicals (KZ)(S2), and Misr Petroleum Refining Co(S3). FTIR results showed peaks demonstrated more absorbance while transmittance decreased in all samples at 1643 to 1640 cm^{-1} and 2121 cm^{-1} when adding 1-octene 99% and 1-Heptyne 99% to the oil of all samples. Therefore, FTIR can detect and determine unsaturated technical petroleum oils. Moreover, the method of FTIR has advantages in preventing exposure to the toxicity of acids and can differentiate between carbon double bond and triple bond.

Keywords: FTIR, Petroleum oil, unsulfonated residue, carbon-carbon double bond, carbon-carbon triple bond.

1. Introduction:

Petroleum oils that have CAS RN [64742–55–8], [64742–56–9] can be used as an acaricide, insecticide, herbicide, and adjuvant[1,2]. Paraffinic oil that is alkanes "aliphatic hydrocarbon " has the general formula C_nH_{2n+2}[3]. Environmental Protection Agency (EPA) has regulated most oil-based products sold as pesticides under the Federal Insecticide, Fungicide, and Rodenticide[4]. Petroleum oil or mineral oil is given other names (Aliphatic solvents; Dormant oils; Foliage oils, Foliar oils; Horticultural oils; Insecticidal oils; Narrow-range oils; Neutral oils; Paraffinic Oils; Petroleum-derived spray oils, and Petroleum distilled spray oils[5]. Petroleum oils contain unsaturated oils "that have one or more active double or triple bonds" cause phytotoxicity. The toxicity of unsaturated petroleum oils increases due to the oxidation of alkenes or alkynes. Therefore spray oils low in unsaturated hydrocarbons are relatively non-phytotoxic[6]. Phytotoxicity is related to the percentage of olefin or aromatic oils. Concentrated sulfuric acid can oxidize unsaturated petroleum oils, which are used to determine unsaturated hydrocarbons. Therefore it is important to calculate Unsulfonated Residue (UR) –"The UR value is an index of the amount of the product free from unsaturated hydrocarbons"[7]. According to FAO specifications for petroleum oil products, The UR value is a minimum 65% for leafless woody plants and winter use on dormant plants. In addition, a minimum of 92% shall remain unsulphonated for oil summer use or products for summer use in orchards. Also, unsulphonated residue of neutral oil shall be a minimum of 95% for oil products for summer use in glasshouses[8,9]. There are methods to determine

*Corresponding author e-mail: walid_tawfik@niles.edu.eg.; Walid Tawfik).
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unsulfonated residue (UR), such as ASTM D483 "Test Method for Unsulfonated Residue of Petroleum Plant Spray Oils" and MT (57) "unsulfonated residue (UR) of natural oil"[10]. Both techniques depend on sulfuric acid 98% reagent. Sulfuric acid is considered a carcinogen, handled with extreme caution, and corrosive; contact severely irritates, burns the skin and eye, and may lead to blindness. Sulfuric acid can irritate the nose and can irritate the lungs. Higher exposures may cause lung fluid build-up (pulmonary edema)[11,12]. Due to the toxicity of sulfuric acid[13], optical spectroscopic methods can be used to determine unsaturated and saturated petroleum oils used as pesticides, especially FTIR, used for rapid analysis of crude oil[14]. FTIR technique and Michelson interferometer are presented. Considering radiation from the electromagnetic spectrum, the mid-IR range in the wavenumbers interval from 400 cm^{-1} to 4000 cm^{-1}[15]. FTIR can investigate C=C stretch from 1680-1640 cm^{-1}, =C–H stretch from 3100-3000 $cm^{-1,}$ and =C–H bend from 1000-650 cm^{-1}. In alkynes, each band in the spectrum can be assigned at –C≡C– stretch from 2260-2100 cm^{-1},–C≡C–H: C–H stretch from 3330-3270 $cm^{-1,}$ and –C≡C–H: C–H bend from 700-610 cm^{-1}[16–18]. Aliphatic compounds consist of the symmetrical and asymmetrical stretching (ν) and bending (δ) vibrations of the methyl (CH3) and methylene (CH2) at 2962 cm^{-1} -CH_3 stretching, 2874 cm^{-1} -CH_2 stretching and 1457 cm^{-1} and 1372 cm^{-1} -CH_2 bending [19,20].

The present study introduces a new optical spectroscopic method for determining carbon-carbon triple bond and a double bond in petroleum oil pesticides.

2. Materials and Methods:

Three technical petroleum oils were collected from three Egyptian companies. (El-Mostakble for Chemicals Co.(S1), Kafr El-Zayate for Pesticides and Chemicals (KZ)(S2), and Misr Petroleum Refining Co(S3). MT (57) unsulfonated residue of neutral Oil method is followed to study unsaturated mineral oils where sulfuric acid 98% reagent (Molecular weight 98.07 g/mol, Molecular formula H_2SO_4, CAS No. 7664-93-9 and Grad: Extra Pure) is used.

FTIR device is introduced to study unsaturated technical petroleum oils samples where 1-octene 99% (Molecular weight 112.21, CAS No. 111-66-0, Linear formula $CH_3(CH_2)_5CH=CH_2$, Catalog Number 30125 and Lot Number A0436924) and 1-Heptyne 99% (Molecular weight 96.17, CAS No. 628-71-7, Linear formula $CH_3(CH_2)_4C\equiv CH$, Catalog Number 22346 and Lot Number A0416074) were added to detect C=C and C≡C wave numbers. Samples S1, S2 and S3 were taken in three glass bottles 25ml separately. Added 2.3706 g of 1-octene 99% and 1.9262 g of 1-Heptyne 99% in a glass bottle and completed by adding S1 where total weight became 14.6122g. For sample S2, we weighed 1.725 g of 1-octene 99% and 1.437 g of 1-Heptyne 99% in another glass bottle, then added S2, where the total weight was 15 g. The case of S3, weights 1.27994g of 1-octene 99% and 1.7649 g of 1-Heptyne 99% in a new glass bottle. We have completed the total weight to 12.4556g by adding S3. FTIR was used to get the spectrum for six samples.

3. Creation Equation for Calculations

$$A = -\log\frac{T\%}{To\%}$$

Where A is absorbance T_o%, intensity in the background spectrum; and T% is intensity in the sample spectrum[17,21].

If A1 is C=C absorbance at wavenumber 1642 cm^{-1} for the unknown sample, and A2 is C=C absorbance at the exact wavenumber for both unknown sample "petroleum oil "plus Knwon concentration of "1-octene where added to the oil". Therefore the following formula can be used.

$$\text{Conc. un}\% = (Conc.un\% + Conc.kn\%)\frac{A1\%}{A2\%}$$

Where $Conc_{Un}$ %: is the concentration of C=C in Unknown oil, $Conc._{Kn}$ %: is the concentration of 1-octene added to the oil, A1 is the absorbance of unknown oil at wave number 1642 $cm^{-1,}$ and A2 is the absorbance of unknown oil plus concentration of 1-octene at wavenumber 1642 cm^{-1}.

The same equation can be used to calculate the concentration of C≡C. Where $Conc._{Un}$ %: is the concentration of C≡C in Unknown oil, $Conc._{kn}$ %:is the concentration of 1-heptyne added to the oil, A1 is the absorbance of unknown oil at wavenumber 2121cm^{-1} and A2 is the absorbance of unknown oil plus concentration of 1-heptyne at wavenumber 2121 cm^{-1}.

4. Results and Discussions:

Results of unsulfonated residue (UR) using MT 57 are shown in Table (1). The present data refers to 97.6% for S1, 100% for S2, and 99.9% for S3. According to FAO specifications for petroleum oil pesticides, S1, S2, and S3 have been able to apply in woody plants, foliar applications, and greenhouses or glass houses. There are many notes in MT 57 to get high accuracy, such as the 98.6% sulphuric acid must be carefully standardized, as slight variations in concentration can substantially affect the result. In addition, an oil bath or steam oven maintained at 98 + 2°C may be used in place of the water bath, and If the unsulfonated oil layer is so dark that the interface between oil and acid is not visible, a few drops of water should be added carefully to form an intermediate layer. Therefore, the S1, S2, and S3 results can be considered very closed or the same result.

Table (1) shows unsulfonated residues results by using the MT 57 method for S1, S2, and S3

Samples name	Density	Unsulfonated Residue(UR)
S1	0.844 g/cm^3	97.60 %
S2	0.845 g/cm^3	100%
S3	0.849 g/cm^3	99.9%

FTIR method for detecting unsaturated petroleum oil pesticides is free from strong acids.

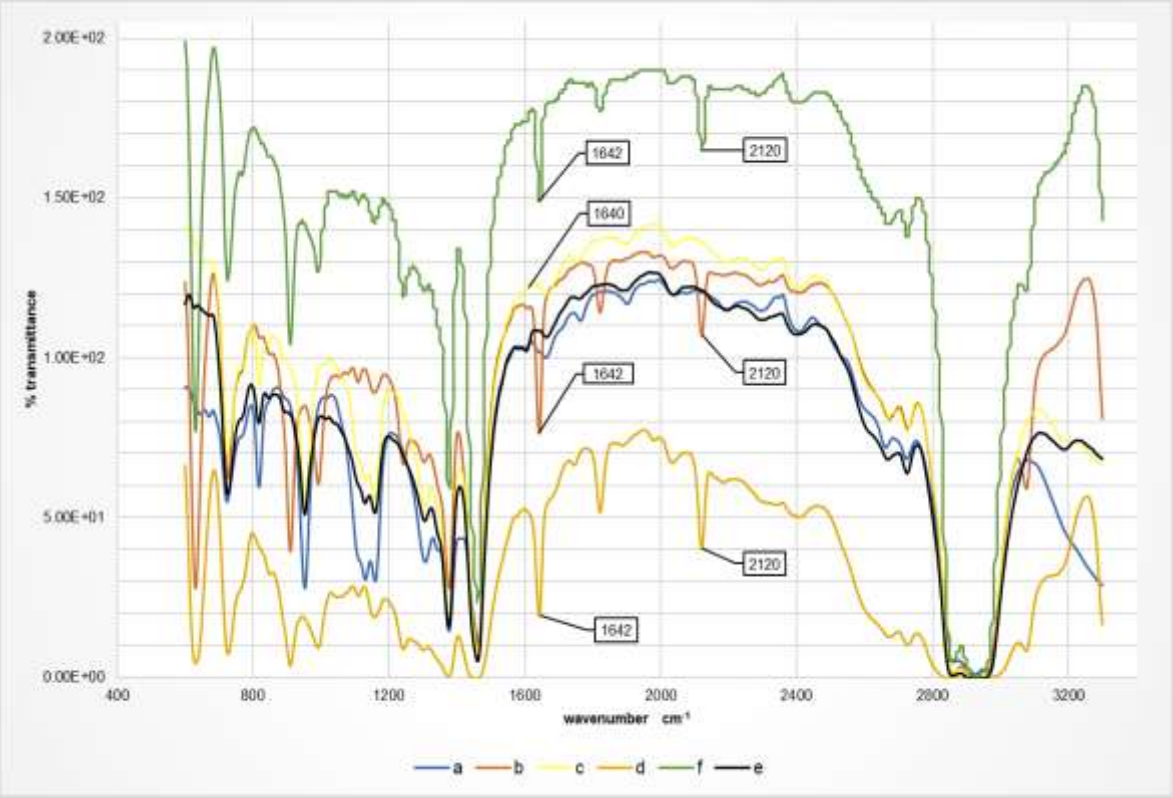

Figure (1) show spectrums of a (S1), b (S1 + 16.22% (w/w) of 1-octene and 13.18 %(w/w) of 1-heptyne), c (S2), d (S2 + 11.5% (w/w) of 1-octene and 9.58 %(w/w) of 1-heptyne), e (S3) and f (S3 + 10% (w/w) of 1-octene and 13.69% (w/w) of 1-heptyne)

FTIR technique has data that can be used to compare oils. Figure (1) show spectrums of S1, S2, S3, S1 plus 16.22% (w/w) of 1-octene and 13.18 %(w/w) of 1-heptyne, S2 plus 11.5% (w/w) of 1-octene and 9.58 %(w/w) of 1-heptyne and S3 plus 10% (w/w) of 1-octene and 13.69% (w/w) of 1-heptyne. Data present in figure (1) for spectrum (S1) show absorbance at wavenumbers 1376 cm^{-1}, 1462 cm$^{-1,}$ and 2860 to 2965 cm$^{-1,}$ which refers to C-H Methyl rock, C-H Scissoring and C-H Stretching,

respectively. The absorption of wavenumbers due to saturated hydrocarbon chain in petroleum oil. Spectrum a presents the absence of wavenumbers 1640 to 1643 cm^{-1} and 2120 to 2122 cm^{-1}. Therefore, no absorbance for C=C and C≡C. Therefore, FTIR can be used for qualitative analysis of saturated technical petroleum oil.

It is evident in spectrum b that the addition of 16.22% (w/w) of 1-octene and 13.18% (w/w) of 1-heptyne to S1 appear signals at wavenumber 1642 cm^{-1} and 2120 $cm^{-1,}$ respectively. The reduction in %transmittance refers to the absorption from C=C and C≡C In spectrum a, S2, spectrum c shows a signal at 1640 cm^{-1}. It refers to C=C. The absorbance is 0.0067 at wavenumber 1640 cm^{-1}. The addition steps of 11.5% (w/w) of 1-octene and 9.58%(w/w) of 1-heptyne to S2 are applied to get signals at wave numbers 1642 cm^{-1} and 2120 cm^{-1}. Therefore, %transmittance reduces due to the absorption from C=C and C≡C; as shown in the "d" spectrum.

Spectrum "e" for S3 doesn't show signals at wavenumber 1640 to 1643 cm^{-1} and 2120 to 2122 cm^{-1}. Absence signals refer to absorbance equal to zero for C=C and C≡C.

The additional step of 10% (w/w) of 1-octene and 13.69% (w/w) of 1-heptyne to S3 is showed in spectrum f. Addition steps help in the detection and calculation of concentration in all samples

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Table (2) results summary for concentration present of C=C and C ≡ C

Samples	**Absorbance of A1 at wave number 1640 to 1642 cm^{-1}**	**Absorbance of A2 at wave number 1640 to 1642 cm^{-1}**	**$Conc._{Un}$ % for C=C**
S1	0	0.22	0
S2	0.0067	0.4385	0.18
S3	0	0.0426	0
Samples	**Absorbance of A1 at wave number 2120 to 2123 cm^{-1}**	**Absorbance of A2 at wave number 2120 to 2123 cm^{-1}**	**Conc.Un % for C ≡ C**
S1	0	0.07	0
S2	0	0.1198	0
S3	0	0.0869	0

Table (2) shows that S1 sample has 100% of saturated technical petroleum oil, S2 sample has 99.82% of saturated technical petroleum oil, and S3 sample has 100% of saturated technical petroleum oil.

5. Conclusion

The present study proves that FTIR is a powerful tool for determining C=C and C≡C in petroleum oil pesticides. It can be used as a modern and new technique. FTIR technique has advantages better than the traditional ASTM D483 and MT (57) methods, where FTIR can be used to determine saturated and unsaturated petroleum oils and differentiate between C=C and C≡C. Also, FTIR devices can save data and use software for results analysis—furthermore, Rapid technique, nondestructive sample, and high accuracy.

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