Separation & Identification of Organic Compounds in Lubricating Oil Additives Using TLC & GC-MS

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Abstract

Thin layer chromatography (TLC) and Gas Chromatography-Mass Spectrometry (GC-MS) techniques are proposed for qualitative analysis of lubricating oil additives (Hitec 2915). The additives were dissolved in heptanes, extracted with mixed solvents heptane: acetonitrile (3:2) and spotted on TLC paper. The best combination solvents as developer for TLC analysis were carbon tetrachloride: heptanes (9:1) mixture. Each separated streak was scraped, redissolved in acetonitrile and evaporated to 0.5 ml volume then analyzed by GC-MS for identification. Fourteen compounds[*2-Ethyl-1-hexanol; 2-(t-butyl)-phenol; 2,4-bis-(t-butyl)-1-methoxy benzene; 2,6-bis-(t-Butyl)-2,5-cyclohexadiene-1,4-dione; 2,4-bis-(t-Butyl)-phenol; 3,5 - bis- (t-Butyl)-phenol; Decanoic acid methyl ester; Tridecanol; 1,1-Diphenyl hydrazine; 1,2-Benzene dicarboxylic acid dibutyle ester; S-Triazol 1, 5-A-pyridine 8-amino 2-phenyl; Phenol-2, 6-bis-(t-butyl); Phenol-2,5-bis-(t-butyl); Phenol - 2,4,6-Tris-(t-butyl*)**]**were identified in this study. The mass spectral data obtained for each separated compound were compared with the standard spectral data (library search similarity) of each compound.

Keywords: Separation, Lubricating Oil Additives, GC-Mass, TLC.

Introduction

Satisfactory lubricant performance is, in many instant, a direct result of the additives package blended with the base oil (either natural or synthetic) lubricant. The chemistry of lubricant additives involves complex technology using a wide range of chemical functionality; additives are a mixture of components derived from both organic and inorganic chemicals. Additives selectivity is dependent upon the specific properties that are desired from the lubricant, for example the neutralization of combustion acid residues from fuels employs additives that are naturally alkaline, such as certain phenols, aromatic amines, and thiophosphates are excellent antiwar additives. Braun and Omeis [(1)] have comprehensively reviewed the general class of chemicals that typically compose an additives package. Among these components are corrosion and oxidation inhibitors. Numerous phenols and aromatic amines are used as antioxidants, mainly sterrically hindered phenols secondary aromatic amines[(2-7)] .Benzotriazol derivative are the typically chemical used as anticorrosion (metal deactivator) additives in lubricating oils[(8-10)]. So, because of these variety and undisclosed chemical composition of additives, analysis of lubricating oil additives is important for quality control of oils and for developing substitute or new products. Various techniques [(11-22)] have been tried in analysis of additives in a variety of matrices, and the majority of these techniques were not applicable to the requirements of our particular project either because of a different matrix or for single known additives [(23-26)].

This paper reports a qualitative analysis of the components in an additives blended with base oil (the refining of petroleum crude oil), by using solvent extraction, thin-layer chromatography (TLC), and gas chromatography/mass spectroscopy techniques.

Materials and Methods

Instrumentation

Analyses were carried out using a Shimadzu gas chromatography 15A-Mass spectrometer QP 1000A (GCMS QP1000A), provided with data processor and library search system LSS-20 for spectral data. The GC column was 3% OV-17 (3m x2.1mm ID).

Chemicals

The additives package for oil (Hitec 2915) used in this study were obtained from Al-Dora refinery. All the solvents (Heptanes, Acetonitrile, and Carbon tetrachloride) used in this work were purchased from either Fluaka AG or BDH ltd (analytical grade). Silica gel 60 F-254 powder was obtained from E, Merck.

Sample Preparation and Separation

Sample (20 gram) of the lubricating oil additive (Hitec 2915, package) was dissolved in 120 ml of heptane and transferred into separating funnel. Then 80 ml of acetonitrile was added, shacked well for 10 minutes and left to separate. The extraction was repeated four times with acetonitrile. The separating layers of acetonitrile were collected and passed through a funnel contained a piece of clear and dry cotton. The acetonitrile was concentrated to 1 ml approximately, and 5µL spotted five times with capillary tube on 20x20 cm of TLC plate(plate was precoated with silica gel 60 F-254 layer of 0.25mm thickness). Carbon tetrachloride: Heptane (9:1) mixture was used to develop the sample contents .After 15 cm for developing, the plate was lifted up and dried in room temperature .The separated spots were identified by iodine vapor and UV light 254 nm.

The same developing was repeated for the residual quantity of the concentrated extract on 20x20 cm TLC plate (plate was precoated with silica gel 60 F-254 layer of 1mm thickness, prepared and activated freshly). Dropping pipette fitted with piece of cotton in the end side was used to transfer the quantity of concentrated extract on TLC plate as streak .After the separation to streak bands, each separated streak band was scraped, dissolved in 5ml acetonitrile and then filtered to remove the silica gel .The acetonitrile was concentrated to 0.5 ml.

One µL of acetonitrile for each streak was injected on GC-Mass (3% OV-17 column).

Operating Conditions

Gas chromatography: GC was operated with the injection port at 220^{o}C. The column temperature was programmed from 80^{o}C to 250^{o}C at a rate of 5^{o}C/min, the flow rate of helium carrier gas was 50ml/min and the size of injection sample was 1 µL.

Mass spectrometer: MS spectrometer was operated using electron impact energy of 70 ev. Integrated ion chromatograms were obtained through running the mass spectrometer in the repeated scan mode. The result mass spectral data of each separated compound was identified by similarity search technique, which based on base peak ion intensity and other fragmentation ions.

Results and Discussion

The additive blended with a large quantity of abase oil is often difficult to analyze, because they consist of various types of components in small quantities, they need to be extracted from the base oil before analysis It was found that the mixed solvents heptane: acetonitrile (3:2) is the most suitable extraction solvent to separate the additives from the base due to the immiscibility between the two solvents and the maximum extractable amount of the base oil by the heptane layers. On the other hand, different developing solvents were tried on the TLC plates, but it has been found that carbon tetrachloride: heptane (90:10) is the best combination solvent as shown in Fig.(1).

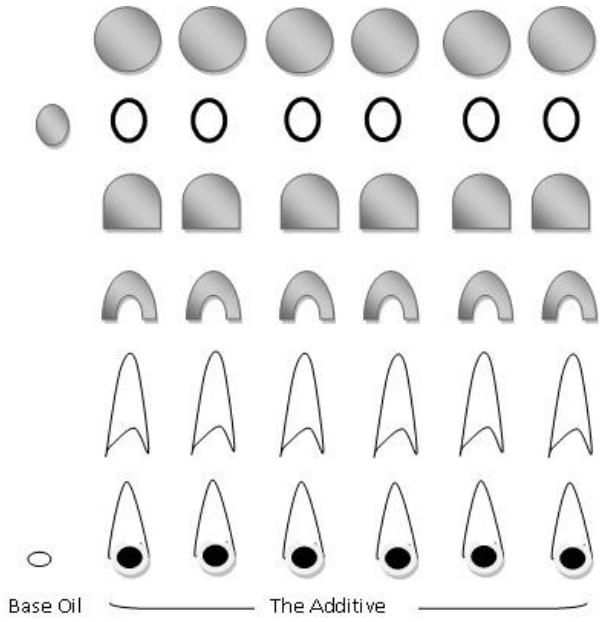

Fig.(1) Thin-layer chromatogram of the base oil and the extract of additive (Hitec 2915).

Six separated spots have been obtained from each spot of the extracted additive. The fifth light spot is corresponding to a trace residual amount of base oil in the acetonitrile

layer. This is confirmed by the comparison with the stock base oil spot on the TLC plate.

The separation chromatogram of each scraped streak, which collected from TLC plate using GC-MS, are shown in Figs.(2-6). The most fragment ions and their relative intensities for the identification compounds by GC-MS are shown in Table (1). From the investigation of spectra, it appears that the (Hitec 2915) additive contain a major quantities of numerous sterricaly hindered phenols (antioxidants). Streak No.1 contained only 2-Ethyl-1-hexanol as shown in Fig.(2) and Table (1), while Streak No.2 gave minor quantities of 2-(t-butyl)-phenol and 2,4-bis (t-butyl)-methoxy benzene as illustrated in Fig.(3) and table1. Streak No.3 consist of bis-Phenols, long chain alcohol, decanoic acid ester and dione (see Fig.(4) and Table (1)). 1, 1-Diphenyl hydrazine and large quantity of s-Triazolo 1, 5-A pyridine, 8-amino-2phenyl were identified in streak No.4; these two compounds are well known as anticorrosion compounds. In addition, streak No.4 contain small quantity of diester. Streak No.6 gave a major peak of di and tri-tert-butyl phenol. A number of isomers of di-tert-butyl phenol are identified in this streak, which theoretically, can be formed during the alkylation of phenol. In addition to molecular peak, the fragment ion M-15(base peak) is significant for identification of di and tri-tert-butylated phenols by means of mass spectroscopy. These types of hindered phenols and alcohols can be used as antioxidant in plastic, rubber, fuel and lubricating oils [(5)].

Moreover, decanoic acid methyl ester and 1, 2-benzenedicarboxylic acid dibutylester are found in streak No.3 and No.4 respectively. These esters can be used as viscosity improver.

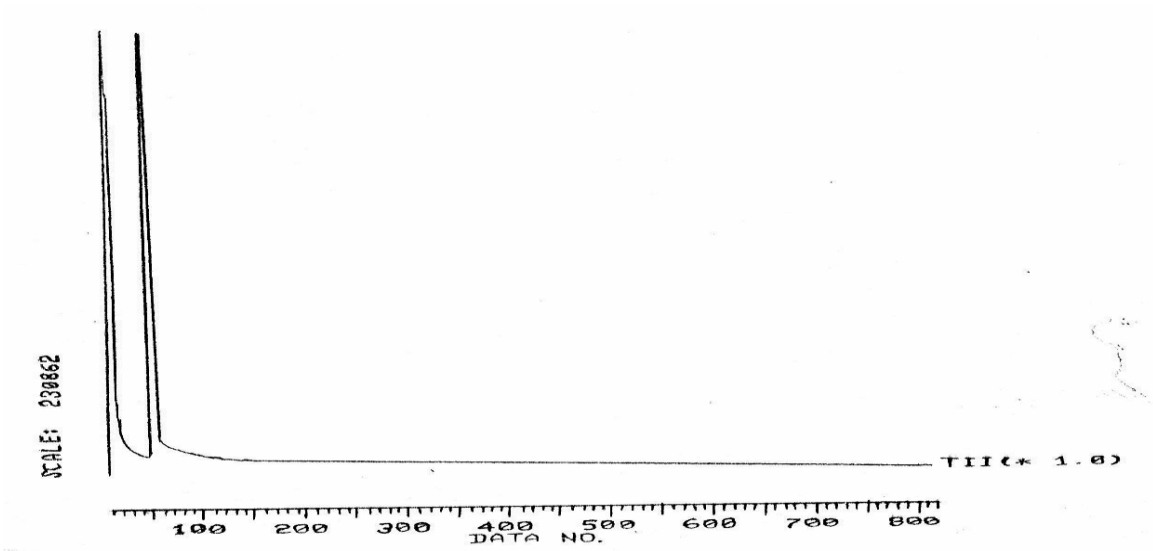

Fig.(2) Total ion chromatogram for streak No.1.

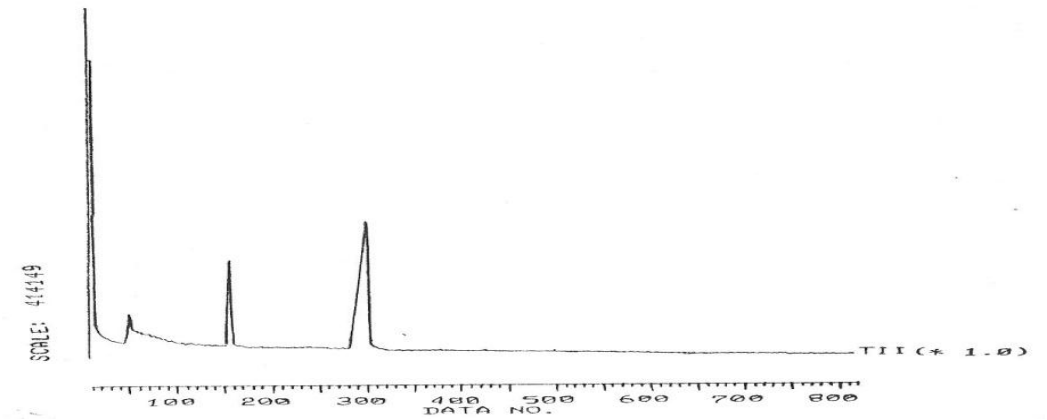

Fig.(3) Total ion chromatogram for streak No.2.

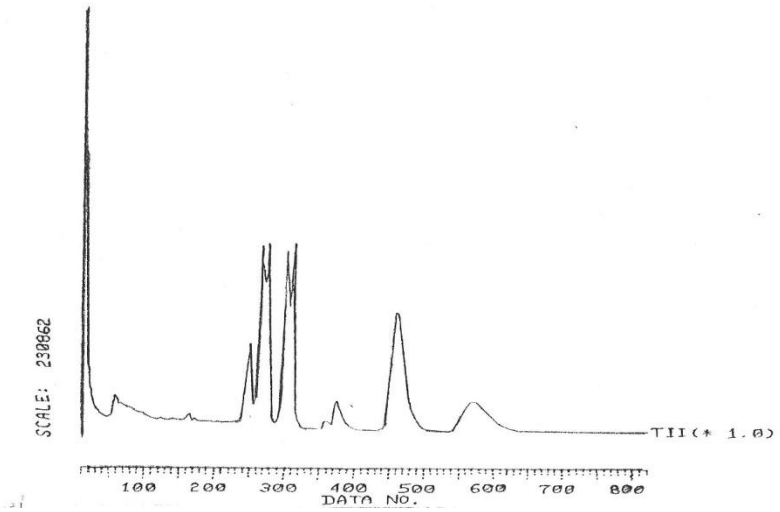

Fig.(4) Total ion chromatogram for streak No.3.

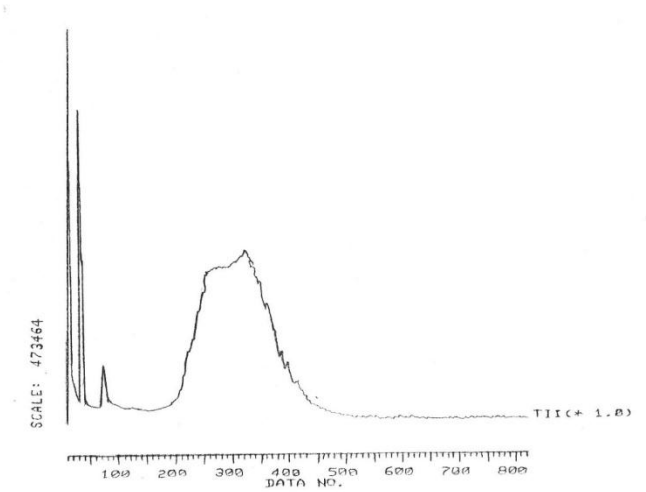

Fig.(5) Total ion chromatogram for streak No.4.

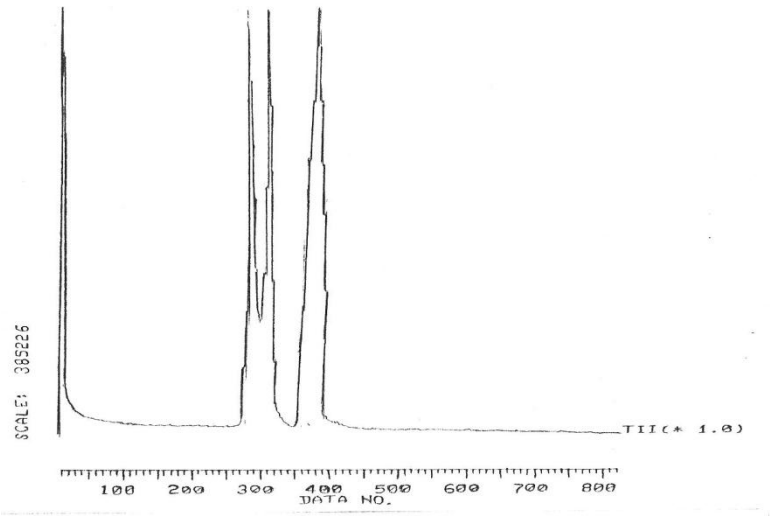

Fig.(6) Total ion chromatogram for streak No.6.

Table (1)
Mass spectral data of the identified compounds.

Streak No.	DT*	Identified Compound	Mass Spectral Data (m / z)** (Intensities)
	47	2-Ethyl-1-hexanol	130(M) 57 43 41 55 56 70 - 100 36 34 23 21 20
1	155	2-(t-butyl)-Phenol	150(M) 135 107 91 115 136 41 44 100 77 16 14 10 8
2	280	2,4-bis-(t-butyl)-methoxy Benzene	220(M) 191 57 41 206 207 192 2 100 36 20 18 15 15
	257	2,6-bis-(t-butyl)-2,5-cyclohexadiene -1,4-one	220(M) 41 177 57 43 66 135 38 100 53 52 42 37 18
3	272	2,4-bis(butyl)-Phenol	206(M) 191 57 41 192 73 91 14 100 66 28 11 10 4
	315	3,5-bis(t-butyl)-Phenol	206(M) 191 57 41 192 43 163 16 100 61 30 16 11 5
	490	Decanoic acid methyl ester	186(M) 74 43 87 41 55 57 - 100 50 47 33 25 20
	622	Tridecanol	200(M) 43 41 55 57 69 83 - 100 94 90 60 40 22
	32	1,1-Diphenyl hydrazine	184(M) 169 168 167 83 51 170 - 100 60 30 22 21 11
4	75	1,2-Benzene dicarboxylic acid dibutyl ester	278(M) 149 29 41 150 57 223 - 100 11 10 9 7 6
	205	s-Triazolo-1,5-A-pyridine 8-amino 2-phenyl	210(M) 211 209 55 80 105 65 100 12 10 5 3 3 3
	282	2,6-bis- (t-butyl)Phenol	206(M) 191 57 41 131 163 192 22 100 33 16 11 11 10
6	319	2,5- bis- (t-butyl)Phenol	206(M) 191 57 163 192 41 91 15 100 19 17 15 12 9
	358	2,4,6-tris-(t-butyl)Phenol	262(M) 247 57 248 41 29 80 11 100 44 20 18 7 6

Data number of scanning, # Molecular ion, $Mass to charge ratio.

Conclusion

This work demonstrates the feasibility of TLC and GC-MS techniques to identify the antioxidants (hindered phenols, alcohols and triazols) in the additives package blended with the base oil. Moreover, other compounds, like anticorrosion and other modifiers can also be identified.

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الخلاصة

تم في هذه الدراسة استخدام تقنية كرواتوغرافيا الطبقة الرقيقة و كروماتوغرافيا الغاز – مطيافية الكتلة للتحليل النوعي لمضافات دهون التزييت وتطبيقه على نموذج (Hitec 2915). اذيب نموذج الزيت المختار في مذيب الهيبتان و استخلص باستخدام مزيج من مذيبات الهيبتان والاسيتونتريل بنسبة (٣:٢) وعينات من المستخلص تم فصلها باستخدام كروماتوغرافيا الطبقة الرقيقة باستخدام مزيج من مذيبي رابع كلوريد الكاربون والهبتان بنسبة (٩:١). تم قشط المناطق المفصولة واذابتها في مذيب الاسيتونتريل و بخر الى حجم ٠.٥ مللتر و شخصت النواتج باستخدام تقنية (GC-MS). حيث بينت النتائج وجود (١٤) مركب عضوي: