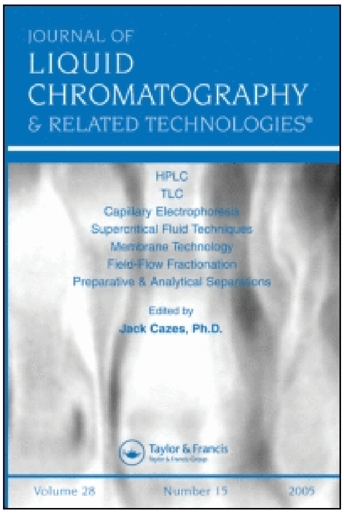

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Application of HPLC with Diode Array Detection in Tribology

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APPLICATION OF HPLC WITH DIODE ARRAY DETECTION IN TRIBOLOGY

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ABSTRACT

A strategy for the analysis of engine oils is described based on the correlation between previously developed methods and HPLC. The areas of some chromatographic peaks of oil samples were linearly correlated to: covered kilometres, the kinematic viscosity, the amount of insoluble compounds in heptane, Conradson's carbonised residue, the number of alkalinity and the carbonyl number.

INTRODUCTION

Structural study of engine oils or their residues is difficult because of the extreme complexity of these mixtures. Methods of separating these materials according to chemical classes have been reported, but even within each separate group, one finds a complex mixture of compounds (1). For many of these mixtures, spectroscopic measurements especially ^1H and ^{13}C NMR indicate the presence of alkyl plus aromatic and heterocyclic rings (2). However, obtaining more detailed structural information from NMR is difficult due to the large variety of compounds and the superposition of peaks from different chemical structures. To obtain some information about the composition of oils, any authors have exploited the HPLC method especially adsorption chromatography (3,4) and reversed phase chromatography with chemical bonded phase (5-9).

In this paper we report on a HPLC study of the degradation of oils during their use in an engine. The detection is performed by a diode array detector, simultaneously providing structural information and quantitative data. The results are compared with other analytical methods, which are used for the evaluation of the oil quality. The main aim of this work was to investigate a number of parameters to find correlation between HPLC results and another parameters that characterised the properties of oil wear.

EXPERIMENTAL

The liquid chromatograph used was a Waters equipped with a 10 ml loop, a diode array detector (Waters Model 990) and a high-pressure pump (Model 510). The oil samples (1 g) were extracted with 10 ml of methanol and the clear solution was injected into the chromatographic column (Separon C-18, 0.32 x 15 cm, 5 mm particle size, Tessek Prague). A solution of 80% methanol in water was used as the mobile phase. The mobile phase was first filtered with a 0.2 mm membrane and degassed. The flow-rate was held at 0.5 ml/min and all experiments were carried out at room temperature. All solvents were twice distilled and were of an analytical reagent grade.

The sample set selected for this study consists of two typical engine oils of different origin: MT 16p - Russia and M6W/20D - Slovakia.

RESULTS AND DISCUSSION

Care must be taken to optimise HPLC conditions for the detection and the separation process. Using a diode array detector, a suitable wave length for detection can be found.

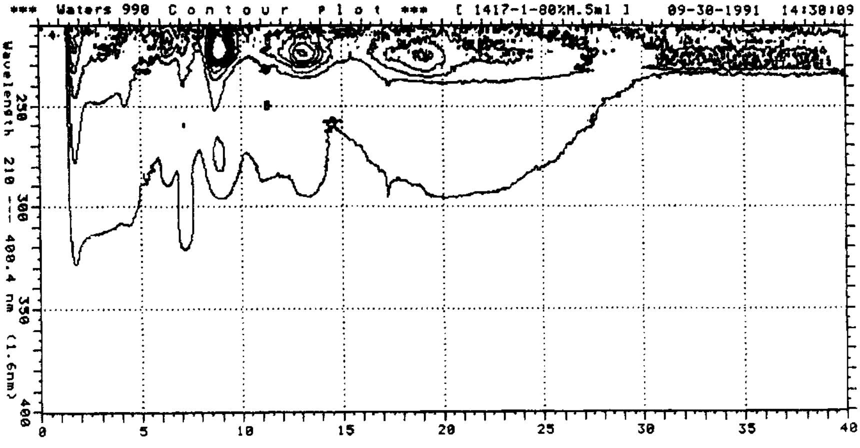

Fig.1. Contour chromatogram of oil extract MT 16p after 266 Km.

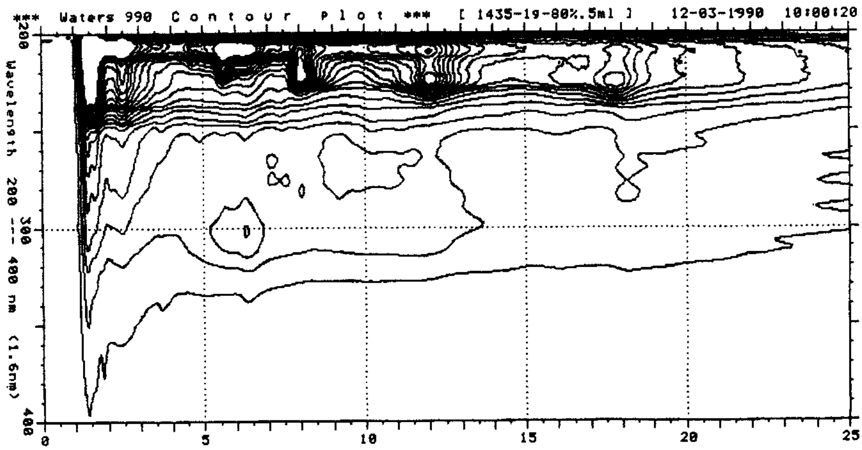

Fig.2. Contour chromatogram of oil extract M6W/20D after 1963 Km.

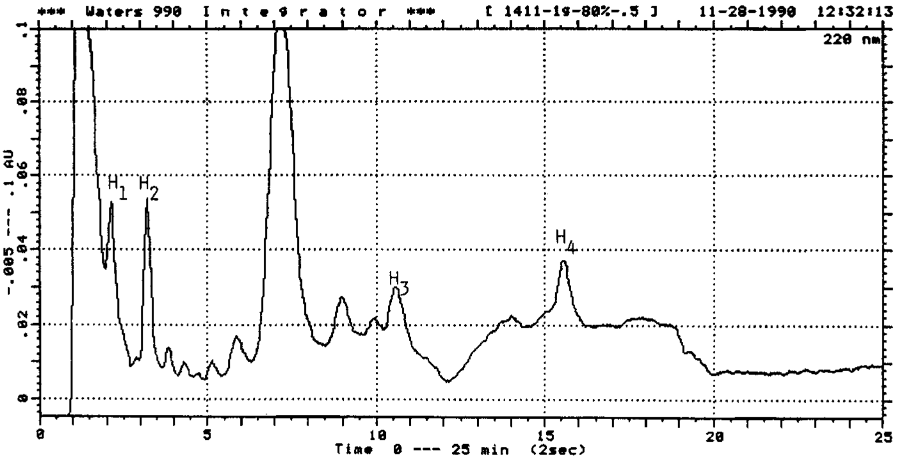

Fig. 3. Chromatogram of oil extract MT 16p, detection at 220 nm.

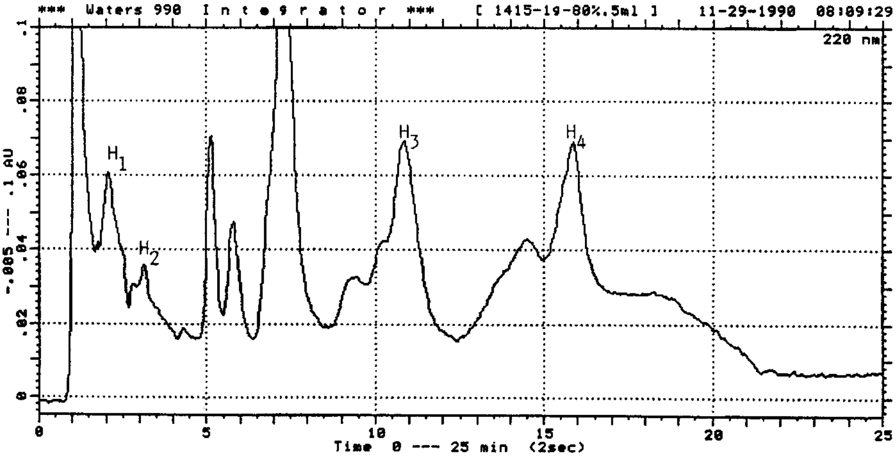

Fig. 4. Chromatogram of oil extract MT 16p after 1392 Km. Detection at 220 nm.

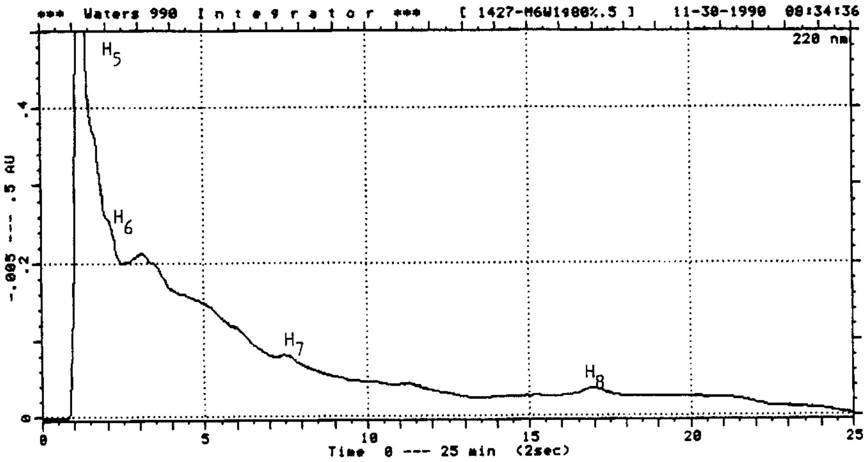

Fig. 5. Chromatogram of oil extract M6W/20D. Detection at 220 nm.

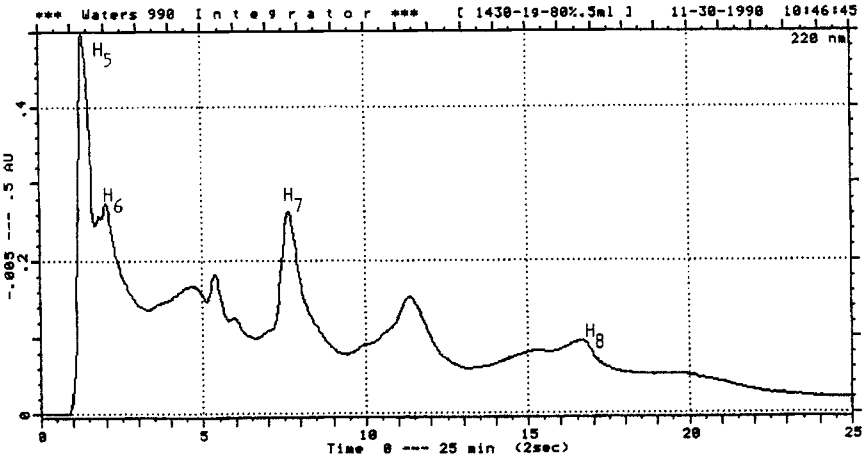

Fig. 6. Chromatogram of oil extract M6W/20D after 898 Km. Detection at 220nm.

Table 1. The results of oil analyses.

Oil MT-16p.

	KM	VIS	AIS	CCR	ALK	CN	H_1	H_2	H_3	H_4
1	0	15.2	0.38	0.1	2.05	0.01	1.6	5.0	2.4	4.6
2	499	14.7	0.57	1.10	1.47	0.06	2.5	1.7	1.4	8.0
3	1072	14.8	0.81	1.29	2.09	0.16	3.4	1.5	0.5	9.1
4	1392	14.9	0.92	1,28	1.99	0.20	3.8	0.8	1.1	9.6
5	2200	15.7	1.89	1.56	1.90	0.23	3.8	1.4	0.6	10.9
6	2660	15.6.	1.24	1.49	1.98	0.29	4.9	0.8	0.3	10.4
7	3240	17.3	1.52	1.63	1.90	0.24	5.3	0.6	0.5	12.2
8	3723	17.2	1.72	1.50	2.24	0.28	5.7	2.0	1.1	10.4
9	4172	17.9	1.74	1.63	2.28	0.31	4.6	0.2	0.8	11.7
10	4724	18.2	1.78	1.69	2.05	0.31	5.9	0.9	0.2	13.0
11	4953	16.7	1.74	1.55	2.06	0.23	4.7	1.9	0.7	9.0

Oil M6W/20D.

	KM	VIS	AIS	CCR	ALK	CN	H_5	H_6	H_7	H_8
1	0	20.4	0.40	2.93	14.21	0.01	96.1	0.2	0.1	1.0
2	500	16.2	0.87	2.90	12.37	0.24	70.6	3.2	11.4	2.2
3	898	16.1	0.85	3.25	11.19	0.13	61.3	1.5	16.7	2.2
4	1231	15.8	0.95	3.68	13.53	0.08	35.5	0.4	19.0	2.2
5	1480	16.2	1.01	3.56	13.85	0.12	36.5	0.3	15.8	4.3
6	1713	15.8	1.08	3.77	13.88	0.05	44.6	0.2	15.1	3.4
7	1963	16.2	1.12	3.75	14.24	0.01	54.6	0.0	15.6	4.1
8	2212	16.6	1.18	3.88	14.62	0.01	59.0	0.0	12.9	4.5
9	2462	16.2	1.08	3.91	14.68	0.02	52.2	0.0	12.8	4.4

KM - covered kilometres

VIS - kinematic viscosity in $mm^2\ s^{-1}$

CN - carbonyl number

ALK - number of alkalinity in mass %

Table 1 (continued).

CCR - Conradson's carbonised residue IR, 1720 cm^{-1}

AIS - amount of insoluble compound in heptane, 0.45 micrometer Mill.

H_1- area of peak at 2.1 min,	H_2 - area of peak at 3.2 min.
H_3- area of peak at 10.7 min	H_4 - area of peak at 15.8 min.
H_5- area of peak at 1.2 min. ,	H_6 - area of peak at 2.1 min.
H_7- area of peak at 7.5 min.	H_8 - area of peak at 16.9 min.

To obtain a robust method, single wavelength detection should be performed at an optimised bandwidth to monitor simultaneously a large group of compounds with high sensitivities. Most of the analytes has their maximum absorbance in the range of 200 - 220 nm (Figs. 1 and 2) and as it can be seen from the contour chromatographic records, the detection at 220 nm is the best. The conditions of the separation were chosen so that in the chromatogram the most numbers of peaks were observed.

To examine the correlation between HPLC results and other parameters, some peaks from chromatograms were selected. The areas of the chromatographic peaks of oil samples were correlated to: covered kilometres (KM), the kinematic viscosity (VIS), the amount of insoluble compounds in heptane (AIS), Conradson's carbonised residue (CCR), the number of alkalinity (ALK), and the carbonyl number (CN). In Figs. 3-6 representative chromatograms of methanol extract analysed by HPLC are shown. Covered kilometres, peak areas and other results of analyses of oils are summarised in Table 1. If the value of a correlation coefficient is more than 0.8, it indicates a good agreement between considered parameters. The correlation coefficients are presented in Table 2.

In the case of MT 16p, oil a good correlation between the peak areas H_4 (elution time 15.8 min.) and two parameters was found. It can be seen that the compounds, which are eluated at 15.5 min., have carbonyl group (the value of correlation coefficient is 0.82) and high Conradson's carbonised residue. The similar conclusion can be made for the peak H_1

Table 2. Correlation coefficients.

Oil MT 16p.

	H_1	H_2	H_3	H_4
	0.79	-0.13	-0.31	0.70
VIS	0.84	-0.32	-0.56	0.69
AIS	0.91	-0.59	-0.79	0.92
CCR	-0.11	-0.53	-0.15	-0.14
ALK	0.82	-0.71	-0.82	0.82
CN	0.88	-0.31	0.54	0.73
KM	0.88	-0.31	0.54	0.73

Oil M6 W/20D.

	H_5	H_6	H_7	H_8
VIS	0.83	-0.16	-0.94	-0.55
AIS	-0.75	-0.23	0.75	0.88
CCR	-0.71	-0.70	0.57	0.82
ALK	-0.09	-0.76	-0.26	0.50
CN	-0.72	0.91	0.25	-0.29
KM	-0.63	-0.55	0.53	0.92

KM - covered kilometres VIS - kinematic viscosity in $mm^2\ s^{-1}$

CN - carbonyl number ALK - number of alkalinity in mass %

CCR - Conradson´s carbonised residue IR, 1720 cm^{-1}

AIS - amount of insoluble compound in heptane, 0.45 micrometer Mill.

H_1- area of peak at 2.1 min, H_2 - area of peak at 3.2 min.

H_3- area of peak at 10.7 min H_4 - area of peak at 15.8 min.

H_5- area of peak at 1.2 min. H_6 - area of peak at 2.1 min.

H_7- area of peak at 7.5 min. H_8 - area of peak at 16.9 min.

but these compounds have more polar properties (according to the correlation coefficient H_1-AIS) and their concentration increase according to covered kilometres (H_1-KM). These substances must be formed during the degradation of oil. The expected agreement was found between H_1 and AIS. From the chromatographic point of view the more polar compounds are less soluble in heptane. On the other hand, the correlation was not found between the number of alkalinity and HPLC results. It can be assumed that the eluated compounds have neutral properties and they have no influence on the alkalinity. The area of H_3 correlated only with carbonyl number and it indicates that the compounds eluated at10.7 min. contain carbonyl group and their concentration decreased with covered kilometres (negative value of correlation coefficient). The area of H_2 peak has no significant influence on the followed parameters and it can by assumed that these compounds are not changed during the experiment.

A similar conclusion can be made in the case of M6W/20D oil. Good correlation between H_8 and number of covered kilometres was found. It indicates that these compounds are decomposed during the experiments. The correlation between H_8 and the content of insoluble compounds in heptane was not expected. This phenomena can be explained on the base of decomposition of substances and the formation of new less polar compounds. According to the values of correlation coefficients H_7-VIS and H_5-VIS, it can be assumed that the compounds are formed from the substances that have a viscostatic function in oil and they are eluated at 1.2 min.

To summarise, the HPLC method represents a useful analytical approach for the characterisation of the oil degradation during their use in engines. Naturally, every kind of oil must be evaluated separately. The main advantage of the method is the speed of analysis and the possibility to substitute some another methods.

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