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# Application of chemometrically processed derivative thermogravimetric data for quality control of M-20 Bp, MS-20 p, Marinol CB SAE-30 and DS-11 oils

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#### Abstract

The application of used engine lubricating oils for further service was evaluated on the basis of chemical and thermal analyses. The most substantial chemical variables, namely kinematic viscosity at 323 and 373 K, flash point and content of foreign solids and oxide ash were determined. The two groups of thermal variables were determined based on the TG and DTG curves. The temperatures for onset, end and successive mass losses were read from the TG curves, whereas the temperature range of DTG peak, peak temperature, peak height and peak width at a half of peak height were read from the DTG curves. To find the relation between the chemical and thermal variables, regression and principal component (PCA) analyses were applied. Good linear relations were found between majority of chemical and thermal variables. The results of PCA indicate that the TG and DTG techniques are very useful in defining the degree of wear of used lubricating oils. © 1998 Elsevier Science B.V. All rights reserved.

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#### 1. Introduction

It is well recognized that the thermoanalytical techniques play an important role in the solution of a variety of problems in the field of petroleum products. The utility of DSC, DTA and TG has been documented in a number of studies which concern fuel and lubricating oils, greases, paraffin waxes, petrolatums and asphalts [1]. They are useful for investigation of phase transitions, problems concerning the evaporation of volatile components from heavy fractions, determination of the thermal stability, study of the pyrolysis and kinetics. For example, Al-Sammerrai and Barbooti [2] proposed TG as a quick method of analysis which was proved to be useful in distinguishing between lubricating greases and also provided significant information on the relative composition of these products. Recent advances in DSC technology has been utilized by Stank and Mullay [3] to quantify ingredient levels in mixtures containing mineral oils and microcrystalline and paraffin waxes. The method utilizes both enthalpy of crystallization data as well as a comparison of peak shapes with reference scan.

It is well known from common practice that identification of studied products and estimation of their physicochemical parameters requires a comparison of thermoanalytical curves [4]. In the former case, the differences between the shape of experimental curves are evaluated; in the latter, the theoretical curve most

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similar to the measured one is searched. The curves may be compared by fitting or by means of quantities describing the shape of the curve. In the case of DTA curve, the evaluation consists of peak-related data (width, height area and shape index) and temperature (onset, extrapolated onset, peak and final temperature) characteristics [5]. On the other way, TG curve is characterized by plateau, initial and final temperature as well as reaction interval.

A little information is only available in the case of interpretation of DTG curves. Dávid and Zelenyánszki [6] described the transformation of DTG curves obtained with TG one. By this method a relative rate constant is obtained, eliminating the great deviation of the DTG curve from the real kinetic shape. It may be used in the comparative evaluation of the thermal stabilities of materials. Siracusa and Cucinotta [7] reported data concerning the correlation between the area of DTG and DTA peaks and the amount of sample analyzed. The linearity between the peak areas and the sample amounts is verified in the entire investigated range for the DTG peak, whereas for DTA one a discontinuity was observed. These results make the use of DTG curves for kinetic measurements preferable.

The present study designs to assess the quality of lubricating oils by comparing the peak-related and temperature characteristics of the DTG curves. Taking into account that full evaluation of the lubricating oils on the basis of chemical, TG and DTG analyses produces a multivariate problem, this work is an attempt to resolve these problems by using chemometric analysis [8–10]. The primary scope of these methods is to get an overview of the dominant patterns or major trends in a large data matrix contains the results of many relevant measurements. This analysis is widely used in resolving many problems in the field of chromatography [11–13].

### 2. Experimental

#### 2.1. Materials

In this study M-20 Bp, MS-20 p, Marinol CB SAE-30 and DS-11 motor lubricating oils, both new and used, were employed. The samples were

taken, in accordance with Polish Standard [14], directly from the oil system of marine engines after these had run for periods from a few to a few thousand hours. They were thoroughly mixed before each analysis.

#### 2.2. TG and DTG measurements

The DTA, TG and DTG curves of thermal decomposition of oils were recorded using the OD-103 derivatograph (MOM, Budapest, Hungary). All measurements were carried out under the same conditions. A 200 mg sample of oil in a platinum crucible was heated under the furnace atmosphere at a heating rate of 5 K min<sup>-1</sup> up to a final temperature of 973 K.  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was used as reference material.

The temperature range of the DTG peak ( $\Delta T$ ) was read as the temperature interval between the points of departure from and return to the base line. The peak temperature ( $T_p$ ) represents the temperature of maximum height of the DTG peak, whereas the peak height (*h*) was read as the distance between the base line of the DTG curve and the peak tip. The peak width at a half of the peak height ( $w_{1/2}$ ) denotes width of the peak at a half of its height.

## 2.3. Calculations

A data matrix **X**, consisting of K=1,2,...,k variables and N=1,2,...,n objects, was the starting point for further chemometric investigations. Three sets of variables were used. Those for chemical methods were the kinematic viscosities at 323 and 373 K, the flash point, foreign solids and oxide ash contents; those for TG analysis were the temperatures of onset  $(T_0)$  and end  $(T_{100})$  of thermal decomposition and the temperatures for 1, 5, 15, 30, 50 and 75% mass losses  $(T_1, T_5, T_{15}, T_{30}, T_{50}$  and  $T_{75}$ ), and those for DTG analysis were the temperature range of DTG peak  $(\Delta T)$ , peak temperature  $(T_p)$ , peak height (h) and peak width at a half of peak height  $(w_{1/2})$ .

From the data matrix **X** its standardized version and correlation matrix were calculated. The correlation matrix was used as a starting matrix in principal component analysis (PCA). Principal components were determined by considering eigenvalues and associated eigenvectors. Interpretation of obtained patterns was performed graphically.



Fig. 1. TG and DTG curves of the thermal decomposition of M-20 Bp oils, which are arranged according to decreasing values of the kinematic viscosity and flash point: (A) low, (B) middle and (C) high degree of wear of the oil. The DTG variables for these oils are compiled in Table 2.

#### 3. Results and discussion

# 3.1. Quality assessment of lubricating oils by the DTG technique

The chemical composition of lubricating oils alters with the service time of these products. In Fig. 1 the TG and DTG curves of random samples of M-20 Bp oils are presented, which are worn to various degree. The lowering of the values of kinematic viscosity and flash point is well reflected by the shape of TG and DTG curves. The exact analysis of their shape has shown that along with increasing extent of oils weariness the temperature range of the DTG peak and the peak width at a half of the peak height become broaden whereas the peak temperature and the peak height become lower.

The graphical way of the DTG curve interpretation is illustrated in Fig. 1, whereas a statistical evaluation of these data is compiled in Table 1. It shows that the DTG technique has been acknowledged as a precise one, the particular results differing only slightly from one another [15]. The least scatter of results is observed in the case of determining  $\Delta T$  and  $T_{\rm p}$ . The values of the coefficients of variation qualify them into the class of less accuracy scientific measurements. Determination of  $w_{1/2}$  is only classified as technical measurement.

The values of  $\Delta T$ ,  $T_{\rm p}$ , *h* and  $w_{1/2}$  for studied oils are listed in Tables 2 and 3. A comparison of these data

Table 1

Statistical evaluation of the determination of peak-related and temperature characteristics of the DTG curve as an example of a random sample of the used M-20 Bp lubricating oil. The calculations were based on 21 determinations

Thermal variable	Arithmetic mean	Standard dev	iation	Confidence	Coefficient of	
		S		inter var 10.95	variation, /c	
$\Delta T/K$	309.8	5.59	1.22	309.8±2.54	1.80	
$T_{\rm p}/{\rm K}$	708.0	8.94	1.95	$708.0{\pm}4.07$	1.26	
h/mm	93.1	2.92	0.64	93.1±1.33	3.14	
w <sub>1/2</sub> /mm	16.1	1.28	0.28	$16.1 {\pm} 0.58$	8.00	

Table 2	
Results of the DTG analysis of the M-20	Bp, MS-20 p and DS-11 lubricating oils

No.	M-20 Bp lubricating oil			No.	MS-20p lubricating oil			No.	DS-11 lubricating oil					
	$\Delta T/K$	$T_{\rm p}/{\rm K}$	<i>h</i> /mm	w <sub>1/2</sub> /mm		$\Delta T/K$	$T_{\rm p}/{\rm K}$	<i>h</i> /mm	w <sub>1/2</sub> /mm		$\Delta T/K$	$T_{\rm p}/{ m K}$	<i>h</i> /mm	w <sub>1/2</sub> /mm
1	290	708	98.0	14.0	1	285	698	87.0	20.5	1	300	688	72.0	26.0
2	295	708	92.5	16.0	2	290	708	86.0	20.5	2	295	688	71.0	26.5
3	290	713	95.5	14.5	3	310	708	83.0	21.0	3	285	683	68.5	28.0
4	290	708	95.5	15.5	4	350	688	67.0	20.5	4	300	693	73.5	26.5
5	295	708	92.0	16.5	5	340	698	76.0	21.0	5	295	698	69.5	27.5
6	375	698	71.0	20.5	6	265	713	87.5	20.0	6	295	688	69.5	27.5
7	310	708	93.0	16.0	7	275	703	87.0	20.0	7	290	693	71.5	27.0
8	320	703	90.0	17.5	8	305	708	85.5	21.0	8	305	708	74.0	26.0
9	300	708	94.0	16.0	9	295	698	87.0	20.0	9	300	698	72.5	26.5
10	295	718	95.0	14.0	10	275	708	85.0	23.0	10	295	698	69.5	28.0
11	300	718	98.5	15.0	11	280	703	85.0	21.5	11	300	688	70.0	28.0
12	300	718	96.0	14.5	12	330	703	75.0	18.5					
13	305	713	97.0	15.0	13	315	708	78.0	20.0					
14	320	708	88.0	15.0	14	340	703	71.0	21.0					
15	315	708	94.5	13.0	15	285	703	81.5	21.5					
16	300	708	94.0	17.0	16	310	698	80.0	20.5					
17	295	708	93.5	15.5	17	290	708	82.5	23.5					
18	315	713	96.0	15.0	18	280	698	89.5	23.5					
19	300	708	93.0	15.5	19	290	703	86.0	21.5					
20	295	703	92.0	16.5	20	310	708	85.5	21.5					
21	310	713	89.5	16.5	21	305	703	83.5	21.0					
22	315	718	90.5	16.5	22	350	683	70.0	19.5					
23	305	708	89.0	17.0	23	325	703	78.0	20.0					
24	300	708	92.5	16.5	24	265	713	85.0	21.0					
25	295	718	96.0	13.0	25	275	698	83.5	21.5					
26	305	713	93.5	15.5	26	280	698	84.0	22.0					
27	295	713	94.5	16.5	27	280	703	86.0	20.0					
28	305	703	95.0	15.0										
29	320	718	96.5	13.5										
30	305	713	96.5	17.5										
31	305	713	91.5	16.0										
32	310	713	94.5	14.0										
33	295	708	96.0	13.5										
34	335	708	89.0	16.5										
35	285	713	97.0	13.0										

with the results of chemical analyses, as presented in Refs. [16–18], shows that the change of chemical composition of the product due to process of its weariness is well reflected by the parameters read from DTG curves.

To express the strength of relation between the DTG variables and those of the chemical ones, linear correlation coefficients were calculated. As it is shown in Table 4 and Fig. 2, except for the peak temperature and in some cases the peak height at a half of peak height, the correlation coefficients assume positive values. Except for the peak width at a half of peak height in the case of MS-20 p, Marinol CB SAE-30 and DS-11 oils, the correlation coefficients in the case of other DTG variables and the kinematic viscosity as well as the flash point (except of DS-11 oils) are characterized by higher values than the critical ones at the probability of 0.05 [19]. No correlation either exists in the case of the peak temperature and the flash point for M-20 Bp and Marinol CB SAE-30 oils and the kinematic viscosity for DS-11 oils. The same can be said about the correlations between the foreign solids content and the DTG variables. As with

Table 3 Results of the DTG analysis of the Marinol CB SAE-30 lubricating oils

No.	Marinol				No.	CB SAE-30			No.	lubricating oil				
	$\Delta T/K$	$T_{\rm p}/{ m K}$	<i>h</i> /mm	w <sub>1/2</sub> /mm		$\Delta T/K$	$T_{\rm p}/{ m K}$	<i>h</i> /mm	w <sub>1/2</sub> /mm		$\Delta T/K$	$T_{\rm p}/{ m K}$	<i>h</i> /mm	w <sub>1/2</sub> /mm
1	335	683	83.0	17.0	37	330	683	76.0	24.0	73	250	693	85.0	24.0
2	320	683	80.0	25.0	38	320	693	82.0	21.0	74	285	683	79.0	23.0
3	290	693	88.0	18.0	39	310	693	72.0	25.0	75	295	683	75.0	24.0
4	300	683	88.0	19.0	40	290	683	78.5	23.5	76	350	663	76.0	20.0
5	320	663	75.0	21.0	41	300	678	73.0	25.0	77	260	683	82.0	22.0
6	310	663	79.0	23.0	42	305	698	82.0	21.0	78	315	678	83.0	19.5
7	290	723	87.0	19.0	43	295	683	79.0	24.0	79	295	683	82.0	21.5
8	260	678	84.0	23.0	44	285	693	85.0	23.0	80	300	683	75.0	26.0
9	285	678	83.0	20.0	45	310	668	73.0	21.5	81	325	673	76.5	22.0
10	275	683	78.0	24.0	46	305	668	81.0	22.0	82	320	688	82.0	20.0
11	280	678	83.0	22.0	47	290	673	78.0	23.5	83	270	683	85.0	24.5
12	285	683	82.0	22.0	48	360	668	67.0	22.0	84	350	673	77.0	20.0
13	290	683	79.0	24.0	49	380	663	76.0	21.0	85	325	683	80.0	21.5
14	270	673	79.0	24.0	50	255	698	85.0	18.5	86	320	683	81.0	21.0
15	300	673	80.0	21.0	51	320	688	84.0	20.0	87	305	663	72.0	25.0
16	290	678	76.0	24.0	52	270	698	92.0	18.0	88	270	683	88.0	20.5
17	380	663	67.0	22.5	53	285	678	76.0	21.0	89	295	683	80.0	22.0
18	370	668	78.0	21.0	54	270	678	78.0	24.0	90	250	703	90.0	24.5
19	295	683	80.0	19.0	55	300	683	83.0	19.0	91	240	718	88.0	23.5
20	305	693	83.5	21.0	56	355	668	73.0	20.0	92	280	693	85.0	23.5
21	270	673	78.0	24.0	57	245	698	84.0	26.0	93	275	683	86.0	20.0
22	305	703	88.0	21.0	58	355	663	70.0	18.0	94	240	718	90.0	22.0
23	280	683	83.0	21.0	59	370	663	75.0	19.0	95	255	688	82.0	22.5
24	295	683	84.0	22.0	60	310	693	80.0	22.0	96	260	678	78.5	24.0
25	290	683	85.0	22.5	61	285	683	80.5	24.0	97	285	683	83.0	23.0
26	300	683	85.0	18.5	62	315	683	81.5	20.5	98	295	693	83.0	23.0
27	270	678	79.0	21.0	63	330	673	81.5	20.5	99	280	683	82.0	24.5
28	290	703	82.0	22.0	64	280	693	82.5	22.0	100	265	678	88.0	19.0
29	285	678	74.0	26.0	65	340	683	79.5	21.5	101	255	683	84.0	20.0
30	325	683	76.5	24.0	66	310	663	79.0	23.0	102	265	683	78.0	24.0
31	295	708	82.5	21.5	67	300	683	76.0	26.0	103	285	673	86.0	22.0
32	280	683	81.0	23.0	68	305	688	80.0	21.0	104	290	663	78.0	24.0
33	285	673	86.0	21.0	69	275	693	78.0	23.0	105	290	683	82.0	23.0
34	290	693	88.5	23.5	70	330	678	77.0	24.0	106	295	688	84.0	24.0
35	275	683	85.0	20.0	71	305	683	77.0	24.0					
36	320	683	71.0	20.5	72	275	683	84.0	20.0					

the oxide ash, however, correlations exists only in a few cases.

From the practical point of view the relations between kinematic viscosity at 323 and 373 K as well as flash point, and temperature range of the DTG peak and peak height are of most significance. From the linear equation y=a+bx, where y is the chemical variable and x the DTG one, the chemical data can be found after the temperature range and the peak height had been read from the DTG curve. The exemplary equations are listed in Table 5.

# 3.2. Comparison of the results by chemometric analysis

In order to extract systematic information, the experimental data were subjected to multivariate analysis. The data matrix for PCA was taken from Tables 2 and 3 and Refs. [16–18]. For the calculations 12 matrices were constructed, three for each type of oil (chemical, TG and DTG measurements).

As a result of calculations, any number of the chemical, TG and DTG variables were reduced to

Table 4					
Correlation coeff	ficients betweer	n the thermoa	nalytical and	d chemical	values

Chemical variable	DTG variable							
	$\Delta T/K$	T <sub>p</sub> /K	<i>h</i> /mm	w <sub>1/2</sub> /mm				
M-20 Bp ( <i>n</i> =35)								
Kinematic viscosity at 373 K	-0.88	0.54	0.90	-0.59				
Flash point	-0.92	0.39	0.81	-0.55				
Foreign solids content	-0.12	0.08	-0.02	-0.01				
Oxide ash	-0.56	0.59	0.67	-0.37				
MS-20 p ( <i>n</i> =27)								
Kinematic viscosity at 323 K	-0.91	0.52	0.92	0.46				
Kinematic viscosity at 373 K	-0.90	0.55	0.93	0.45				
Flash point	-0.98	0.55	0.89	0.45				
Foreign solids content	-0.16	0.02	0.22	0.43				
Oxide ash	-0.75	0.24	0.69	0.58				
Marinol CB SAE-30 (n=106)								
Kinematic viscosity at 323 K	-0.94	0.57	0.67	0.27				
Kinematic viscosity at 373 K	-0.92	0.60	0.68	0.24				
Flash point	-0.79	0.37	0.56	0.14				
Foreign solids content	-0.29	0.22	0.09	0.13				
Oxide ash	-0.51	0.21	0.34	0.06				
DS-11 ( <i>n</i> =11)								
Kinematic viscosity at 323 K	0.73	0.47	0.79	-0.74				
Kinematic viscosity at 373 K	0.66	0.05	0.51	-0.42				
Flash point	-0.19	-0.67	-0.24	0				
Foreign solids content	0.48	0.55	0.52	-0.43				
Oxide ash	0.53	0.13	0.56	-0.42				

the lesser extent of the descriptive dimensions than essential number of variables. Two significant principal components are extracted in each case that together explained at least 83% of the total variance. The first principal component (PC1) dominates and describes the linear structure with the main variance in the data. In the case of the TG analysis of MS-20 p oils it explains over 76% of variance, and on the other



Kinematic viscosity at 323 K in m<sup>2</sup>/s

Fig. 2. Relationship between the temperature range of the DTG peak and the kinematic viscosity at 323 K for Marinol CB SAE-30 oils.

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Table 5

Linear regression equations for the relation between the chemical variable and the temperature range of the DTG peak for lubricating oils. The standard error of the estimation of intercept ( $S_a$ ) and slope ( $S_b$ ) of the linear equation y=a+bx, and the *R*-squared ( $R^2$ ) are indicated in the parentheses

Chemical variable	Linear regression equation				
M-20 Bp					
Kinematic viscosity at 373 K	42.01 (2.22) $-7.64 \times 10^{-2}$ (7.25 $\times 10^{-3}$ ) $\Delta T$ (77.06)				
Flash point	786.79 (22.90)–1.04 (7.49×10 <sup>-2</sup> ) $\Delta T$ (85.40)				
MS-20 p					
Kinematic viscosity at 323 K	563.83 (39.04) $-1.47$ (1.30 $\times 10^{-1}$ ) $\Delta T$ (83.62)				
Kinematic viscosity at 373 K	$61.65 (4.28) - 1.48 \times 10^{-1} (1.42 \times 10^{-2}) \Delta T (81.23)$				
Flash point	794.54 (15.33)–1.11 (5.09×10 <sup>-2</sup> ) $\Delta T$ (94.97)				
Marinol CB SAE-30					
Kinematic viscosity at 323 K	$165.08(3.79) - 3.50 \times 10^{-1}(1.27 \times 10^{-2}) \Delta T(87.99)$				
Kinematic viscosity at 373 K	24.61 $(5.70 \times 10^{-1}) - 4.55 \times 10^{-2} (1.91 \times 10^{-3}) \Delta T$ (84.54)				
Flash point	626.81 (12.27)-5.38×10 <sup>-1</sup> (4.11×10 <sup>-2</sup> ) $\Delta T$ (62.30)				
DS-11					
Kinematic viscosity at 323 K	$-1.91(22.82)+2.48\times10^{-1}(7.70\times10^{-2}) \Delta T(53.47)$				
Kinematic viscosity at 373 K	$2.47 (3.59) + 3.21 \times 10^{-2} (1.21 \times 10^{-2}) \Delta T (43.78)$				

hand, 53% for the DTG analysis of Marinol CB SAE-30 oils. The second one, PC2, explains the next variance in the data, from 15% for the TG analysis of MS-20 p oils to 33% in the case of the chemical analysis of DS-11 oils. The remaining principal components, PC3 and the following, describes only a few or even hundredth part of percent of the total variance in the data. Considering the foregoing, it stands to reason that for the purpose of plotting only the first two principal component score vectors (PC1 and PC2) may be used.

A comparison of the results achieved by the chemical, TG and DTG measurements have been presented as an example of MS-20 p lubricating oils. In this case, the matrices have the following dimensions:  $27 \times 5$  for the chemical,  $27 \times 8$  for the TG and  $27 \times 4$  for the DTG data. The principal component object (sample) score was calculated for each oil sample. The positions of the MS-20 p oil samples on the plane determined by the PC1 and PC2 axes are displayed in Fig. 3. The pattern score describes the location of the oil samples in two-dimensional plane and reveals information about relationship between object.

As already shown, there are two clear clusters on each pattern and some oil samples show distinctive behaviour. Comparison of the results achieved from

the chemical, TG and DTG measurements leads to the conclusion that the discrimination ability by these methods is similar. Samples 4, 5, 12, 13, 14, 22 and 23, which represent the most highly used oils, are clearly separated from the others. The second cluster mark by the dashed line includes the highest quality oils - samples 6, 7, 10, 11, 17, 18, 19, 24 and 25. In the case of analysis by the chemical methods, samples 26 and 27 are included to the highest quality oils. It is undoubtedly in accord with their values of the kinematic viscosity at 323 and 373 K, but the flash point for these oils is lower than the requirements of Polish Standard [16]. Compounds do not belonging to either cluster have intermediate values of the kinematic viscosity and flash point and do not meet the standard. Therefore, it can be concluded that the classification problem can be resolved using DTG technique when compared with the chemical and TG measurements.

Taking into account the loadings (weights) of the principal components, it can be established that the kinematic viscosity, flash point and oxide ash contents have a high loading in the PC1 for chemical analysis of MS-20 p oils. The PC2 contains information mainly from the foreign solids content. It suggests that the effect of foreign solids content on the quality of oils may be different and not strongly correlated with



Fig. 3. Scatterplots of the first two principal component vectors (PC1 and PC2) for MS-20 p oils. Classification of samples based on the: (A) chemical, (B) TG and (C) DTG analyses. Low and high quality oil samples are numbered.

variables loading PC1. Exact analysis of DTG data indicates that the PC1 is loaded mostly by the temperature range of DTG peak and peak height, whereas the PC2 describes mainly the peak width at a half of its height. The latter and the peak temperature are also partly indicated in the first factor.

By plotting the first two component loading factors (W1 and W2), the graph shows the complementary variable patterns that reveals information about relationships between variables. As shown in Fig. 4, the chemical, TG and DTG variables, most useful in the quality assessment of oil samples studied, can be extracted. In the case of the chemical analysis there are the kinematic viscosity at 323 and 373 K and flash point; the  $T_0$ ,  $T_1$ ,  $T_5$ ,  $T_{15}$  and  $T_{30}$  for the TG measurements, and for the DTG analysis there are the  $\Delta T$  and *h*. The usefulness of the  $T_p$  and  $w_{1/2}$  has a less value. These results have been confirmed by calculations performed on a newly formed matrix comprising 27 samples of MS-20 p oil and the above chosen 10 variables. The following sequence of 10 positive eigenvalues were found: 9.18, 0.49 and eight values below 0.2. In Fig. 5(A), the two-dimensional PC1 and PC2 score pattern has been constructed which explains 96.7% of the total variance. Samples 1 and 15 are additionally included to the group of the highest quality oils, these oils differs only slightly from the standard [16]. It can also be concluded that the kinematic viscosity at 323 and 373 K, flash point,  $T_0$ ,  $T_1$ ,  $T_5, T_{15}, T_{30}, \Delta T$  and h are equivalent in quality control of lubricating oils. All these variables have a high loading in the PC1, only  $\Delta T$  has a negative sign. This conclusion is confirmed by the first two component loading factors pattern, as is presented in Fig. 5(B). Exactly the same findings have been obtained in the case of M-20 Bp, Marinol CB SAE-30 and DS-11 lubricating oils.

### 4. Conclusions

These studies confirm that the discrimination between the oils using the DTG technique is as good as or even better than that achieved by the chemical and TG analysis. The regression analysis indicates that by making use of appropriate linear regression equations, the kinematic viscosity values and flash point for the examined oils can be found based on the temperature range of DTG peak and peak height.

Principal component analysis makes possible the reduction of the dimensionality of data space and provide concentration of systematic information pre-



Fig. 4. Scatterplots of the first two principal component loadings factors (W1 and W2) for MS-20 p oils. (A) Chemical variables: (1) kinematic viscosity at 323 K, (2) kinematic viscosity at 373 K, (3) flash point, (4) foreign solids content and (5) oxide ash content; (B) TG variables: (1)  $T_0$ , (2)  $T_1$ , (3)  $T_5$ , (4)  $T_{15}$ , (5)  $T_{30}$ , (6)  $T_{50}$ , (7)  $T_{75}$  and (8)  $T_{100}$ ; and (C) DTG variables: (1)  $\Delta T$ , (2)  $T_p$ , (3) h and (4)  $w_{1/2}$ .

viously dispersed over many variables in a few common abstract factors. This method is the fruitful approach in the assessment of the quality of lubricat-



Fig. 5. (A) Scatterplots of the first two principal component vectors (PC1 and PC2) for MS-20 p oils. Calculations include ten chemical, TG and DTG variables; (B) Scatterplots of the first two principal component loadings factors (W1 and W2) for MS-20 p oils. Variables are numbered: (1) kinematic viscosity at 323 K, (2) kinematic viscosity at 373 K, (3) flash point, (4)  $T_0$ , (5)  $T_1$ , (6)  $T_5$ , (7)  $T_{15}$ , (8)  $T_{30}$ , (9)  $\Delta T$  and (10) h.

ing oil samples which differ in the service performance. The relationship between the degree of wear of used lubricating oils reflect well as measured by different way.

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