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THERMOGRAVIMETRIC AND PRINCIPAL COMPONENT ANALYSES IN QUALITY ASSESSMENT OF LUBRICATING OILS

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Abstract

The suitability of the derivative thermogravimetric and principal component analyses for the assessment of service performance of lubricating oils has been studied. A total sum of 179 samples has been examined, including M-20 Bp, MS-20 p, Marinol CB SAE-30 and DS-11 oils. The results indicate that principal component analysis greatly assisted in the analysis of the quality of lubricating oils by derivative thermogravimetric technique. Considering that, this multivariate statistical method can be applied to the differentiation of oil samples taking into account degree of their degradation in the oil system of an engine.

Keywords: lubricating oils, principal component analysis, TG

Introduction

It is well known from common practice that the quality assessment of lubricating oils on the basis of their physicochemical properties requires considerable labour [1]. In this respect an investigation was undertaken to utilize the changes taking place in the course of the degradation of oils, which should be reflected by the thermal decomposition curves, for the quality assessment of lubricating oils [2–4].

Nevertheless, full evaluation of the lubricating oils on the basis of chemical methods, as well as using thermogravimetric (TG) and derivative TG (DTG) analyses produce a multivariate problem. For these reasons this work is an attempt to resolve these problems by using principal component analysis (PCA) [5–7]. This procedure provides an approximation of a data matrix (X) in terms of the product of two small matrices T and P. These matrices contain the essential data patterns of X. Plotting the columns of T gives a figure of the dominant object patterns of X. Similarly, plotting the rows of P shows the complementary variable patterns.

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Experimental

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 oils were taken directly from the oil system of marine engines after these had run for periods from a few to a few thousand hours. The samples were taken in accordance with Polish Standard [8]. They were thoroughly mixed before each analysis.

TG and DTG measurements

The DTA, TG and DTG curves of the thermal decomposition of lubricating oils were recorded using a OD-103 derivatograph (MOM, Hungary). All measurements were made under identical conditions. A weighed amount (200 mg) of oil in a platinum crucible (9.5 mm diameter) was heated under the furnace atmosphere at a heating rate of 5 deg·min^{-1} up to a final temperature of 973 K. α-Al_2O_3 was used as reference material. Each curve was registered at least three times.

The temperatures for the onset (T_0) and the end (T_{100}) of the thermal decomposition were read from the TG and DTG curves, whereas 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}) were read solely from the TG curves.

The temperature range of the DTG peak (ΔT) 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 denotes width of the peak at a half of its height.

Calculations

A data matrix X, consisting of $K = 1,2...k$ variables and $N = 1,2...n$ objects, was the starting point for further calculations. As variables were used the temperatures which represents successive mass losses (T_0, T_1, T_5, T_{15}, T_{30}, T_{50}, T_{75} and T_{100}) and parameters form the DTG peak (ΔT, T_p, h and w). From the data matrix X its standarized version Z and correlation matrix R were calculated. The correlation matrix R was used as a starting matrix in principal component analysis. Principal component (PC) were determined by considering eigenvalues and associated eigenvectors. For plotting purpose only two first principal component score vectors (t_1 and t_2) and corresponding loading vectors

(p_1 and p_2) were used. These account over 83% of variability in each case. In this way, several variables were reduced to two principal component scores.

Results and discussion

PC analysis of M-20 Bp lubricating oils

The data matrix for M-20 Bp samples was taken from [2, 9]. For the evaluation of oil samples on the basis of DTG methods, it consists of 35 objects (oil samples) and 4 variables (parameters read from the DTG curve). Two data classes are presented – high and low quality oils. The classification problem to turn into distinguish between these two categories on the basis of the DTG data.

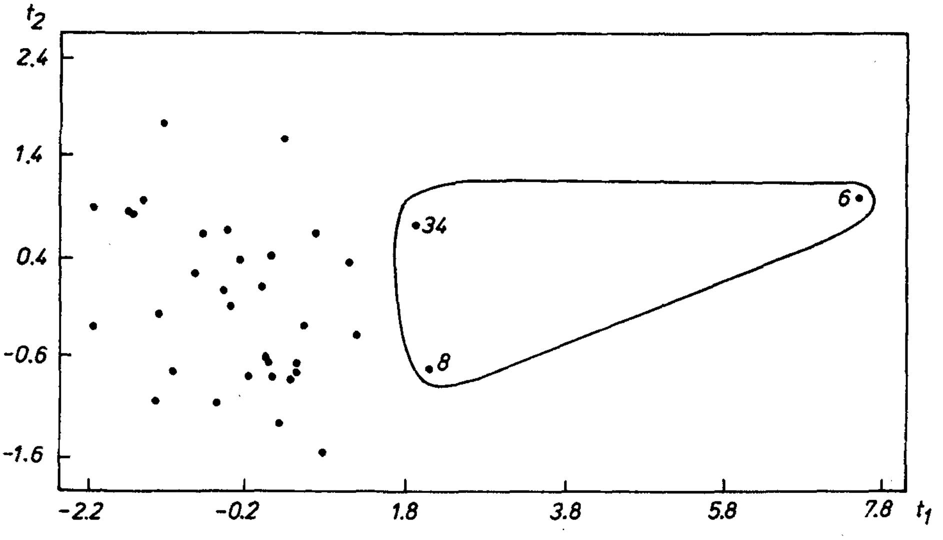

Fig. 1 Principal component scores plot derived from DTG analysis of M-20 Bp lubricating oils. Unserviceable oils are numbered and circled

As the result of calculations 4 eigenvalues was found which explain as follows: 69.44, 17.14, 10.15 and 3.27% of the total variability. Only two first eigenvalues were considered, in this case over 86% of the total variance is explained. Figure 1 shows the PC score plot for all 35 samples. Three samples are clearly distinguished from the others. These correspond to the most highly used oils and confirm earlier finding that the discrimination between the oils using DTG method is as good as or even better than that achieved by classical and TG methods [10].

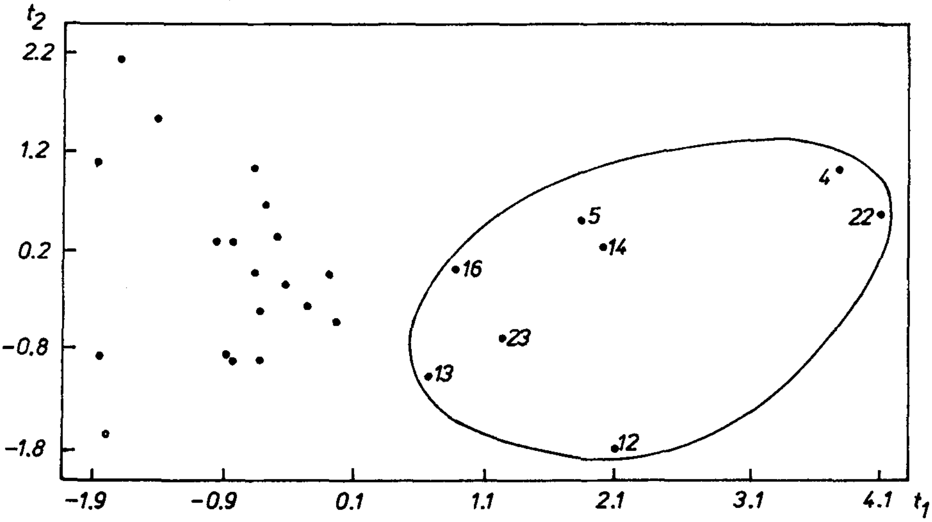

Fig. 2 Principal component scores plot derived from DTG analysis of M-20 p lubricating oils. Unserviceable oils are numbered and circled

PC analysis of MS-20 p lubricating oils

The data matrix for MS-20 p oil samples was taken from [2, 9]. Figure 2 shows the t_1 *vs.* t_2 plot achieved on the DTA results. This plot was obtained using a starting data matrix of 27*4 dimensions. The calculated eigenvalues were explained as follows: 62.47, 21.15, 13.31 and 3.07% of the total variability. The first two PC score model explains over 83% of the total variance. Comparison between the results obtained by classical, TG and DTG techniques leads to the conclusion that the discrimination ability by these methods is similar [10]. Samples 4, 5, 12, 13, 14, 16, 22 and 23, which represent the most highly used oils, are clearly separated from the others.

PC analysis of Marinol CB SAE-30 lubricating oils

The data matrix for Marinol CB SAE-30 samples was taken from [3, 9]. In the case of evaluation of oil samples on the basis of DTG results, the data matrix has 106*4 dimensions. As the result of calculations 4 eigenvalues was found which explain as follows: 53.14, 29.72, 11.71 and 5.43% of the total variability. Only two first eigenvalues were considered, in this case over 82% of the total variance is explained. Figure 3 shows the PC score plot for all 106 samples. Twenty seven samples are clearly distinguished on the right-hand side of the plot. These correspond to the low quality oils. Therefore it can be concluded that the classification problem can be resolved using DTG technique as compared with classical and TG methods [10].

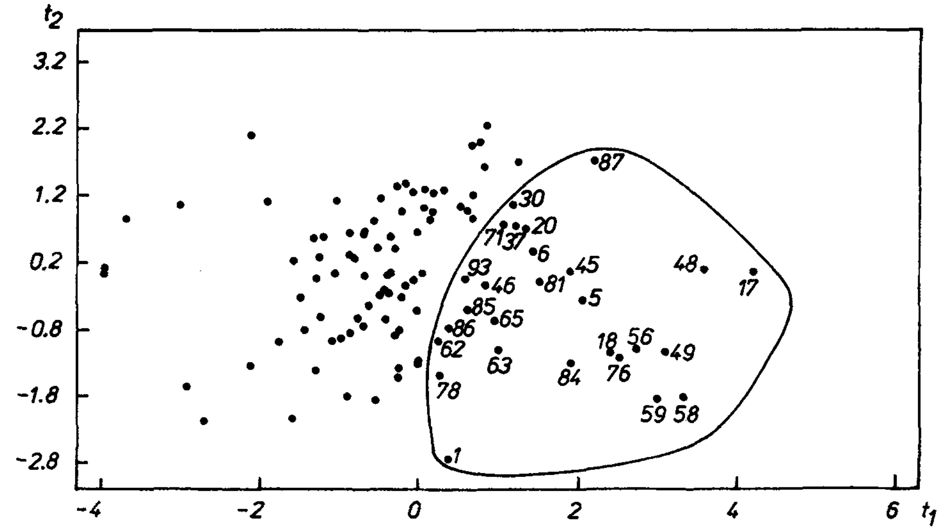

Fig. 3 Principal component scores plot derived from DTG analysis of Marinol CB SAE-30 lubricating oils. Unserviceable oils are numbered and circled

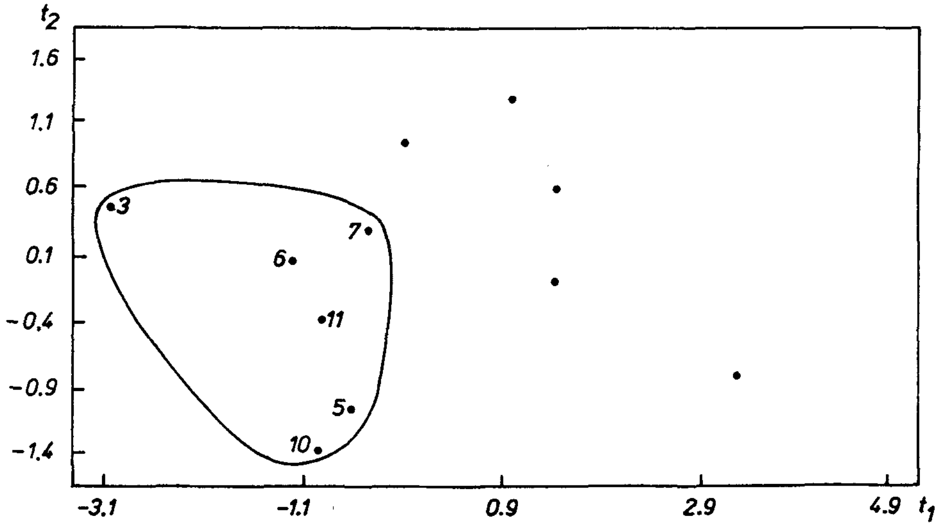

Fig. 4 Principal component scores plot derived from DTG analysis of DS-11 lubricating oils. Unserviceable oils are numbered and circled

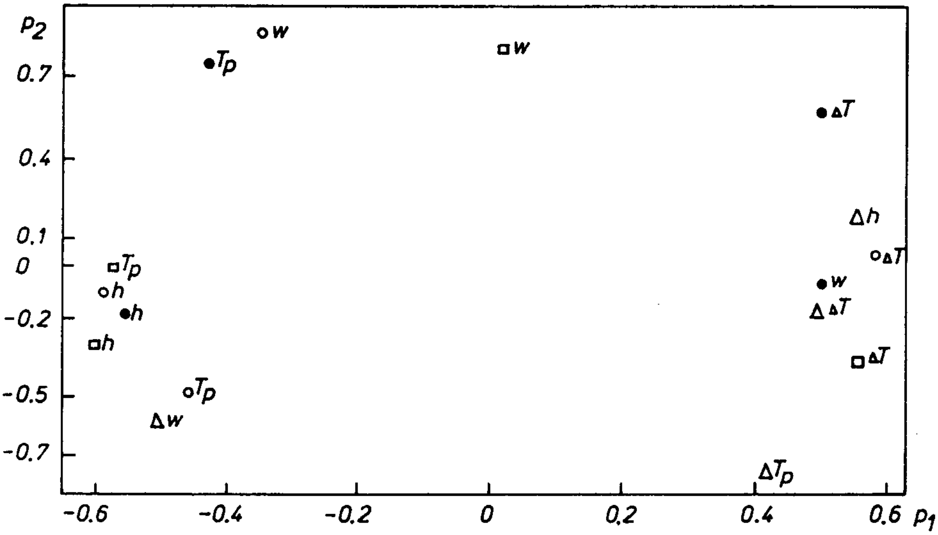

Fig. 5 Loading scores plot derived from DTG analysis of (•) M-20 Bp, (o) MS-20 p, (□) Marinol CB SAE-30 and (Δ) DS-11 lubricating oils

PC analysis of DS-11 lubricating oils

The data matrix for DS-11 oil samples was taken from [4, 9]. Figure 4 shows the t_1 *vs.* t_2 plot using a starting data matrix of 11*4 dimensions. The 4 eigenvalues was calculated which explain as follows: 71.44, 17.56, 8.72 and 2.28% of the total variability. The first two PC score model explains over 89% of the total variance. Samples 3, 5, 6, 7, 10 and 11 represent the most highly used oils and are clearly separated from the other.

To illustrate which variables are responsible for the observed behaviour, the loading vectors p_1 *vs.* p_2 were plotted. It is shown on Fig. 5. From this figure it can be seen that all examined variables are largely responsible for the separation of lubricating oils into two groups – high and low quality oils.

Conclusions

The principal component method of data handling is a fruitful approach in the assessment of the quality of lubricating oil samples differs in the service performance.

These studies confirm that the discrimination between the oils using DTG technique is as good as or even better than that achieved by classical and TG methods.

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Zusammenfassung — Es wurde die Eignung von DTG und Hauptkomponentenanalyse zur Abschätzung der Tauglichkeit von Schmierölen untersucht. Dabei wurden insgesamt 179 Proben, einschließlich M-20 Bp, MS-20p, Marinol CB SAE-30 und DS-11 Ölen untersucht. Die Ergebnisse zeigen, daß die Hauptkomponentenanalyse die Analyse der Schmierölgüte durch DTG weitestgehend unterstützt. Diese mehrdimensionale statistische Methode kann zur Unterscheidung von Ölproben unter Berücksichtigung ihres Zersetzungsgrades im Ölsystem einer Maschine angewendet werden.