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APPLICATION OF PRINCIPAL COMPONENT ANALYSIS AND THERMOANALYTICAL METHODS IN EVALUATION OF LUBE OILS

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ABSTRACT

Multivariate classification and comparison using principal component analysis have been carried out on the data obtained from thermal and classical analysis of lubricating (lube) oil samples. The results indicate that this statistical method greatly assists the analyst in assessment of the quality of lube oils, particularly in connection with thermal analysis. Some preliminary suggestions concerning selection of the thermoanalytical data are described.

INTRODUCTION

Thermoanalytical methods, such as differential thermal analysis (DTA), thermogravimetry (TG) and derivative TG (DTG), are being used more and more frequently for the examination of fuel and lubricating oils.

DTA study of mineral oils showed that the existence of very long hydrocarbon chains shifts the ranges of melting and crystallization to lower temperatures [1]. The enthalpy values of these two transitions showed a similar trend. DTA has been found to be a rapid and precise method for determination of the thermal stability of lubricating oils, both petroleum-based and synthetic, under oxidative conditions [2]. The usefulness of TG as a method for the control of the chemical composition of motor oils has been reported. A study showed that each oil is characterized by definite distributions of the weight losses at temperatures above which no further changes occur in the sample [3]. The measurements also showed the usefulness of TG and DTG as rapid means of technological evaluation of the properties of fuel and lubricating oils [4].

The complex chemical composition and heat transformations occurring in an atmosphere of air made classical interpretation of the results of thermal decomposition of lubricating oils difficult. Based on analysis of the shape of the TG and DTG curves the characteristic parameters for oils can be indicated, such as the temperatures of the initial, final and sequential mass losses [4–6]. The above-mentioned parameters are linearly related to viscos-

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ity and flash point and can be used as a measure of the range of applicability of lubricating oils.

Nevertheless, full evaluation of the lubricating oils on the basis of classical methods, as well as using thermoanalysis, presents multiple problems. This work is an attempt to resolve these problems using principal component analysis (PCA) [7,8]. PCA provides an approximation of a data matrix **X** in terms of the product of two small matrices, **T** and **P**. These matrices capture the essential data patterns of **X**. Plotting the columns of **T** gives a picture of the dominant object patterns of **X**.

EXPERIMENTAL

Samples for testing

In this study, M-20 Bp, MS-20 p and Marinol CB SAE-30 lubricating oils, both new and used, were investigated. The oils were taken directly from the oil systems 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 PN-66/C-4000 [9]. They were thoroughly mixed before each analysis. A shaking period of 5 min is necessary for any sludge to be homogeneously suspended in the oil.

Testing procedure

The DTA, TG and DTG curves for the thermal decomposition of lubricating oils were recorded using the OD-103 derivatograph (MOM, Budapest, Hungary). All measurements were carried out under the same conditions. A weighed sample of 200 mg of oil in a platinum crucible was heated under the furnace atmosphere at a temperature increase rate of 5 K min^{-1} up to a final temperature of 973 K. α-Al_2O_3 was used as reference material. Each curve was recorded at least three times.

The initial (T_0) and final (T_{100}) temperatures of thermal decomposition were read from the TG and DTG curves, whereas the temperatures of 1%, 5%, 15%, 30%, 50% and 75% losses in mass (T_1, T_5, T_{15}, T_{30}, T_{50} and T_{75}) were read exclusively from the TG curves.

For determination of the kinetic viscosity of used oils at 323 K and 373 ± 0.02 K, a Pinkevitch viscosimeter was used in accordance with Polish Standard PN-73/C-04011 [10]. The flash point was measured by the Pensky–Martens method according to Polish Standard PN-75/C-04009 [11]. For the determination of foreign solids in the lubricating oils, Polish Standard PN-58/C-04089 [12] was employed. The procedure for determination of the content of oxide ash, as well as the analytical results of the above determinations, have been published elsewhere [4,5].

Calculations

A data matrix **X**, consisting of $K = 1, 2, \ldots, k$ variables and $N = 1, 2, \ldots, n$ objects, was the starting point for further chemometric investigations. Two sets of variables were used. Those for classical methods were the kinematic viscosities at 323 K and 373 K (exception for M-20 Bp oils, where only the viscosity at 373 K was used), flash point, foreign solids content and oxide ash content; those for thermoanalytical methods were the temperatures T_0, T_1, T_5, T_{15}, T_{30}, T_{50}, T_{75} and T_{100}, which represent successive mass losses. From the data matrix **X** its standardized version **Z** and correlation matrix **R** were calculated. The correlation matrix **R** was used as a starting matrix in principal component analysis. Principal components (PC) were determined by considering eigenvalues and the associated eigenvectors. For plotting purposes, only the first two principal component score vectors (t_1 and t_2) were used. These explain over 80% of the variability in each case. In this way, five variables (classical method) and eight variables (thermoanalytical method) were reduced to two principal component scores, t_1 and t_2.

For evaluation of the data, software developed in our laboratory for IBM-PC compatible microcomputers was used.

RESULTS AND DISCUSSION

Differentiation of M-20 Bp lubricating oils

The data matrices for M-20 Bp oil samples were taken from ref. 4. For the evaluation of oil samples on the basis of classical methods, the matrix consists of 35 objects (oil samples) and four variables. The following sequence of eigenvalues was found: 2.56, 1.00, 0.38, 0.06. The number of PC scores was estimated from the sequence of the eigenvalues. Only eigenvalues greater than 1 were considered; in this case over 89% of the total variance is explained by this rule. Figure 1 shows the PC score plot for all 35 samples. Sample 6 is an outlier, and Sample 34 is also divergent by virtue of the diagonal line of the plot. These two oils had undergone the longest running time and did not fulfil the standards criteria [10–12]. It can therefore be concluded that the classification problem can be resolved using classical methods.

For the evaluation of oil samples on the basis of thermoanalytical methods, the data matrix **X** with 35×8 dimensions was applied. The following sequence of eigenvalues was found: 5.89, 1.45, 0.39, 0.12, 0.06, 0.04, 0.02, 0.01. A two PC scores model was therefore chosen, which explains 93% of the total variability. Figure 2 shows the t_1 vs. t_2 plot. Comparing Figs. 1 and 2, it can be concluded that discrimination between the oils is at

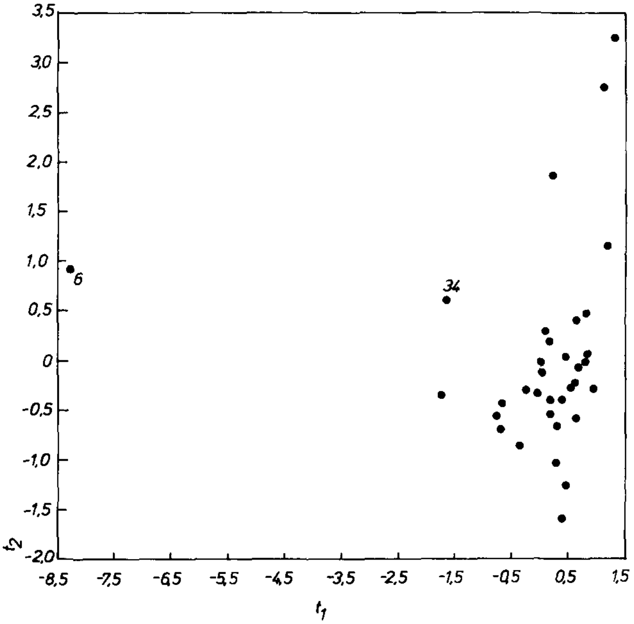

Fig. 1. Principal component scores plot derived from M-20 Bp lubricating oils. Classical methods of analysis were used. The outliers are numbered.

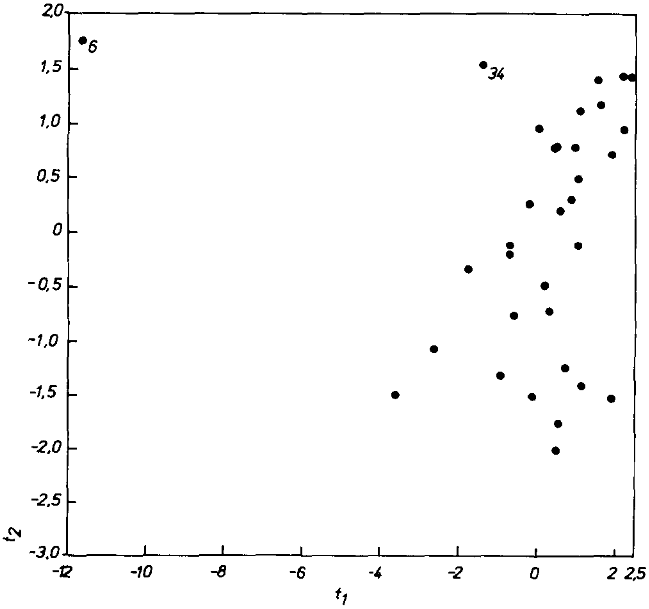

Fig. 2. Principal component scores plot derived from M-20 Bp lubricating oils. Thermoanalytical methods were used. The outliers are numbered.

least as good using thermoanalytical methods, or even better, than that by classical methods.

Differentiation of MS-20 p lubricating oils

The data matrices for MS-20 p samples were taken from ref. 4. The data matrix **X** used for the evaluation of oil samples on the basis of classical methods had 27 × 5 dimensions. The following sequence of eigenvalues was found: 3.60, 1.00, 0.30, 0.09, 0.003. The two PC scores model explains 93% of the total variability. Figure 3 shows the t_1 vs. t_2 plot. Seven samples are clearly distinguished from the others; these correspond to the most highly used oils. The results confirm our earlier finding that classical methods are suitable for assessment of the service performance of oils.

Figure 4 shows the t_1 vs. t_2 plot for MS-20 p samples obtained on the basis of thermoanalytical methods. This plot was obtained using a starting data matrix (X) of 27 × 8 dimensions. The calculated eigenvalues were as follow: 6.11, 1.21, 0.41, 0.20, 0.04, 0.01, and two values below 0.01. The first two PC scores model explains 91% of the total variability. Comparison between Figs. 3 and 4 leads to the conclusion that the discrimination ability of classical and thermoanalytical methods is similar. Samples 4, 14, 22, 12, 23, 5 and 13, which represent the most highly used oils, are clearly separated from the others. On the opposite side of the plot, samples 19, 24, 7, 11 and 10 form a cluster which represents oils in good lubricating condition.

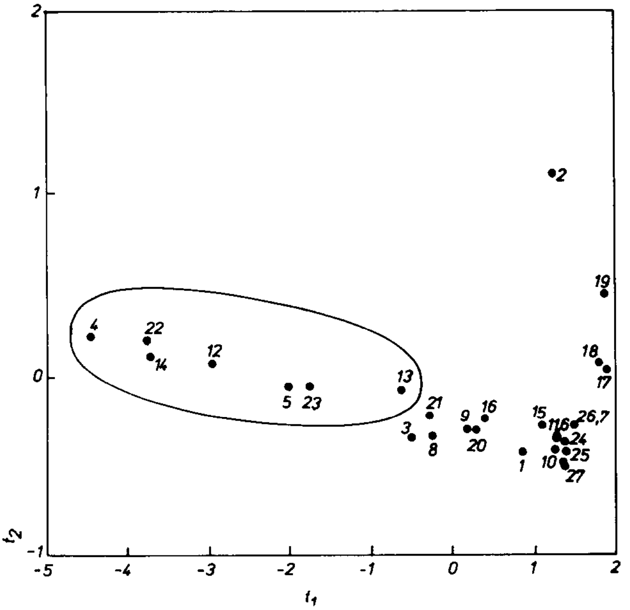

Fig. 3. Principal component scores plot derived from MS-20 p lubricating oils. Classical methods of analysis were used. The outliers are circled.

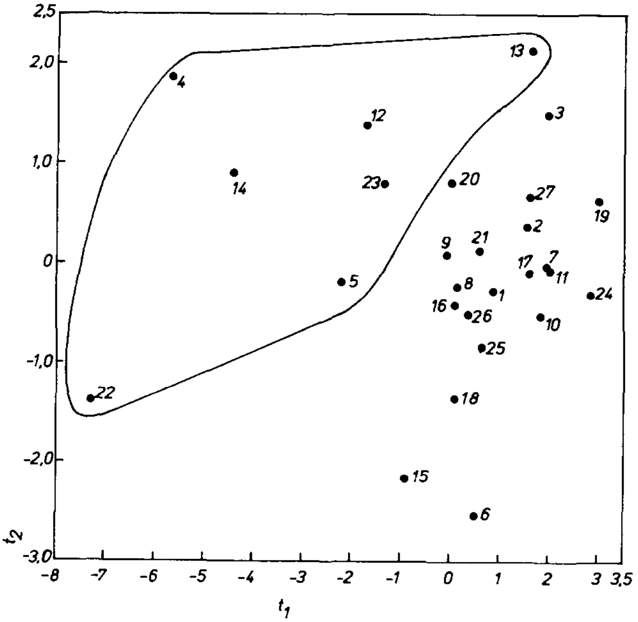

Fig. 4. Principal component scores plot derived from MS-20 p lubricating oils. Thermoanalytical methods were used. The outliers are circled.

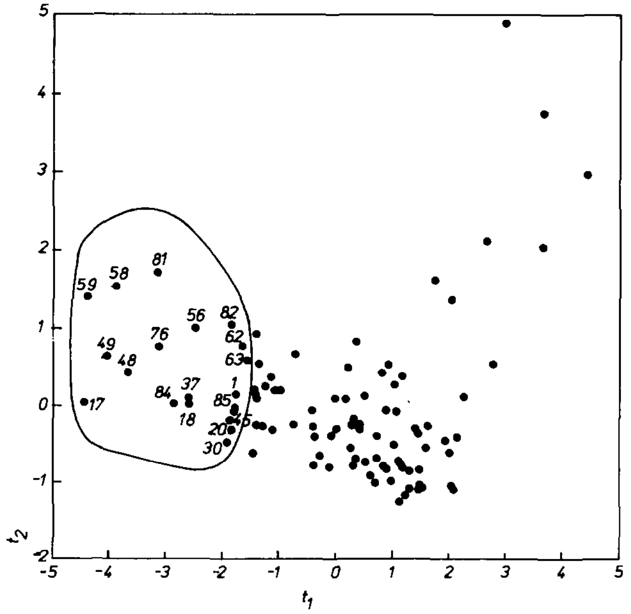

Fig. 5. Principal component scores plot derived from CB SAE-30 lubricating oils. Classical methods of analysis were used. Oils with long service performance are numbered and circled. A full list of PC scores is given in Table 1.

TABLE 1

First two principal component scores (t_1 and t_z) for Marinol CB SAE-30 lube oil samples

Sample	Thermoanalytical method		Classical methods	
	t_1	t_2	t_1	t_2
C-1	−1.728	0.248	−1.834	−0.094
C-2	0.794	0.760	−1.426	0.082
C-3	2.305	−0.509	0.735	−0.401
C-4	1.103	−1.028	0.937	−0.848
C-5	−4.318	−0.619	−1.501	−0.206
C-6	−3.645	−0.621	−0.734	−0.246
C-7	5.630	3.129	0.278	−0.569
C-8	0.579	−1.493	0.869	−0.762
C-9	−0.091	−1.154	0.318	−0.784
C-10	1.302	−0.806	1.591	−0.549
C-11	1.325	−0.031	0.851	−0.815
C-12	0.408	−0.794	0.335	−0.187
C-13	1.350	−1.010	1.214	−0.832
C-14	0.023	−1.542	0.546	−0.747
C-15	−1.474	−1.063	0.539	−0.700
C-16	−0.086	−0.551	0.439	−0.269
C-17	−5.561	1.448	−4.481	0.038
C-18	−3.763	1.155	−2.618	0.009
C-19	−0.483	−0.772	−0.117	−0.796
C-20	−1.051	0.342	−1.845	−0.302
C-21	−1.170	−1.308	−0.286	−0.664
C-22	3.327	0.808	0.442	−0.340
C-23	0.874	−1.012	1.305	−0.866
C-24	−0.533	−0.463	0.494	0.113
C-25	0.217	−1.376	0.710	−1.015
C-26	0.812	−0.035	1.051	−0.086
C-27	0.769	−0.776	2.971	4.914
C-28	2.514	0.652	−1.468	−0.623
C-29	−1.203	−0.920	−0.403	−0.780
C-30	−1.070	1.258	−1.835	−0.285
C-31	3.211	0.679	0.362	−0.713
C-32	0.897	−0.651	0.289	0.249
C-33	−1.178	−0.766	−0.084	0.394
C-34	2.764	0.102	0.639	−0.904
C-35	1.482	−0.377	0.721	−0.674
C-36	−0.461	0.714	−1.250	0.254
C-37	−1.104	1.129	−2.606	0.100
C-38	0.379	0.778	−1.392	−0.253
C-39	1.298	0.067	−1.274	−0.277
C-40	−0.327	−0.504	−0.358	−0.418
C-41	−1.376	−0.577	−0.397	−0.268
C-42	1.937	0.759	−0.029	0.101
C-43	0.651	−0.535	0.170	0.081
C-44	2.215	−0.957	0.555	−0.751
C-45	−2.952	−1.030	0.978	0.188
C-46	−3.311	−0.048	−0.715	0.657

TABLE 1 (continued)

Sample	Thermoanalytical method		Classical methods	
	t_1	t_2	t_1	t_2
C-47	−1.356	−0.724	0.822	0.417
C-48	−5.774	1.467	−3.694	0.433
C-49	−6.001	1.951	−4.074	0.628
C-50	4.131	0.297	1.233	−1.196
C-51	−2.333	1.154	0.005	−0.320
C-52	3.310	−0.360	2.108	−1.119
C-53	−0.574	−0.277	0.362	0.811
C-54	0.746	−0.289	2.627	2.127
C-55	−0.185	−0.492	−1.112	−0.307
C-56	−3.204	0.078	−2.500	1.004
C-57	1.535	1.808	2.034	1.352
C-58	−3.118	2.797	−3.898	1.514
C-59	−2.922	3.661	−4.428	1.370
C-60	0.768	1.020	−1.086	0.181
C-61	1.482	−0.170	1.174	−0.765
C-62	−1.323	0.785	−1.447	0.917
C-63	−2.148	1.414	−1.385	0.538
C-64	2.178	−0.168	1.931	−0.458
C-65	−1.351	1.144	−1.793	−0.037
C-66	−2.705	−0.946	−1.563	0.584
C-67	−0.034	−0.791	1.168	0.367
C-68	0.106	0.639	−0.433	−0.062
C-69	2.518	1.735	1.727	1.611
C-70	−1.982	1.025	−1.646	0.782
C-71	−0.819	0.096	−1.142	0.357
C-72	1.943	−0.455	1.405	−0.319
C-73	3.026	0.678	2.775	0.530
C-74	0.707	−0.128	1.018	0.258
C-75	−1.221	−0.267	−1.449	0.164
C-76	−3.359	1.648	−3.131	0.761
C-77	1.168	−0.791	2.142	−0.424
C-78	−1.062	−0.003	−1.053	0.201
C-79	−0.842	0.064	0.923	0.516
C-80	−0.331	0.082	0.304	−0.185
C-81	−3.487	−0.028	−3.191	1.681
C-82	−0.636	1.168	−1.864	1.044
C-83	1.218	−1.174	2.241	0.097
C-84	−4.274	0.112	−2.883	0.018
C-85	−1.081	1.031	−1.733	0.147
C-86	−0.682	1.062	−1.900	−0.197
C-87	−4.442	−0.756	−1.926	−0.468
C-88	0.218	−1.510	1.049	−0.516
C-89	−0.122	0.675	0.211	0.492
C-90	7.013	2.163	3.669	3.751
C-91	5.139	2.602	4.415	2.975
C-92	3.151	−0.152	1.458	−1.110
C-93	2.216	−0.152	1.539	−1.103

TABLE 1 (continued)

Sample	Thermoanalytical method		Classical methods	
	t_1	t_2	t_1	t_2
C-94	5.586	1.632	3.633	2.035
C-95	1.802	−1.602	1.011	−0.994
C-96	0.891	−1.612	1.302	−1.121
C-97	0.962	−0.801	1.484	−1.047
C-98	0.535	−0.675	1.121	−0.733
C-99	−0.996	−2.775	1.484	−0.837
C-100	0.607	−1.501	2.053	−1.046
C-101	2.136	−1.279	2.014	−0.614
C-102	2.175	−1.082	1.629	−0.278
C-103	−1.555	−2.070	1.117	−1.272
C-104	−1.694	−0.414	0.891	−0.060
C-105	−0.125	−0.644	1.464	−0.365
C-106	2.517	0.134	1.106	−0.991

Differentiation of Marinol CB SAE-30 lubricating oil samples

The data matrix for the CB SAE-30 oil samples was taken from ref. 5. For the evaluation of oil samples on the basis of classical methods the matrix

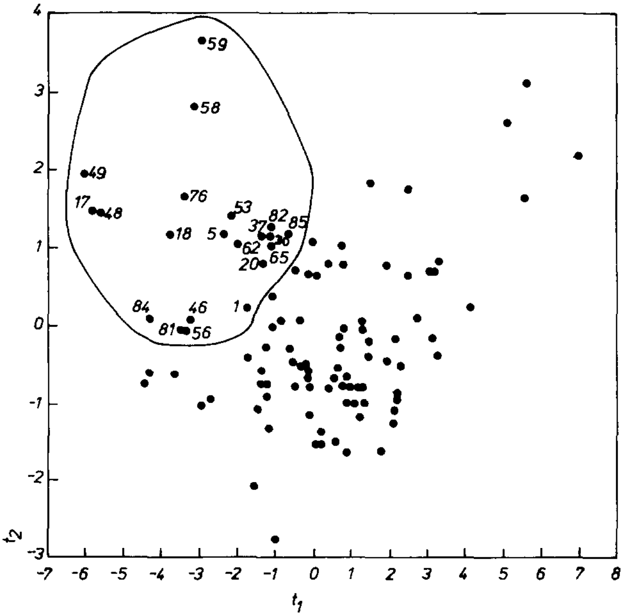

Fig. 6. Principal component scores plot derived from Marinol CB SAE-30 lubricating oils. Thermoanalytical methods were used. Oils with long service performance are numbered and circled. A full list of PC scores is given in Table 1.

consists of 106 objects (oil samples) and five variables. The following sequence of eigenvalues was estimated: 3.22, 1.00, 0.58, 0.20, 0.01. The two PC scores model adopted here describes over 83% of the total variance. Figure 5 shows the PC score plot for all 106 samples. The oils that have been in service the longest, which do not fulfil the standard, are numbered (a full list of the PC scores is given in Table 1); these are clustered on the left-hand side of the plot.

For the evaluation of oil samples on the basis of thermoanalytical methods, the data matrix **X**, with dimensions 106×8, was applied. The following sequence of eigenvalues was found: 5.81, 1.31, 0.50, 0.14, 0.11, 0.07, 0.03, 0.02. Thus a two PC scores model was chosen which explains 88% of the total variability. Figure 6 shows the t_1 vs. t_2 plot. The oils having long service performance, which do not fulfil the standard, are numbered, and are grouped on the upper left side of the plot. Comparing Figs. 5, and 6, it can be concluded that the discrimination between the oils using thermoanalytical methods is as good as or even better than that achieved by classical methods.

CONCLUSIONS

Our results indicate that principal component analysis greatly assists the analyst in assessment of the quality of lube oils. Using this method, the multivariate problem can be effectively reduced to two variables. Our results show the comparable classification ability of classical and thermoanalytical methods. Moreover, the classification procedure can be based only on thermoanalysis and computerized data transformation. In this work the classical methods were used only for comparison. Our results suggest the possibility of constructing equipment for automated oil evaluation based on a derivatograph coupled with a microcomputer.

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