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ELEMENTAL ANALYSIS OF ENGINE OILS USING ENERGY DISPERSIVE X-RAY FLUORESCENCE SPECTROSCOPY (EDXRFS) AND INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROSCOPY (ICP-AES)

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Abstract

Elemental composition of various engine oils was measured by different analytical methods: energy dispersive X-ray fluorescence spectroscopy (EDXRFS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES). Considerable differences were observed between the two methods. In case of EDXRFS strong matrix effects were detected on the calibration graphs. It was found that the preliminary sample preparation (digestion) before ICP-AES analysis resulted in the poorer accuracy of this method. Taking into consideration its matrix effect the quick, simple and cost-effective EDXRFS technique, without the necessity of sample preparation, was selected for analysis of engine oils during and after different screening tests. Complementing the screening tests of engine oils (e. g. the high temperature deposit preventing, antiwear and antifriction properties) with properly calibrated EDXFRS analysis more and important information could be obtained about the degradation and the efficiency of the additives.

Keywords: Energy dispersive X-ray fluorescence spectroscopy; Inductively coupled plasma atomic emission spectroscopy; Engine oil; Screening test

1. INTRODUCTION

Development tendencies of engine constructions, emission after-treatment systems, fuels and lubricants are determined by the ever stricter environmental regulations. In the European Union the sulphur content of fuels has been reduced to 50 mg/kg and fuels with 10 mg/kg sulphur content have to be available regionally [1-5]. The other source of emission is the engine oil because a little bit of it always burns in the combustion chamber of the engines and thus deteriorates the exhaust gas after-treatment systems of vehicles. Regarding the latest technical, economical and environmental requirements engine oils with longer drain intervals have to be used with the lowest possible content of metals, sulphur and phosphorus. Also the concentration of these elements is limited in regulations of performance levels of catalyst compatible engine oils (e. g. ACEA C levels, API CJ-4, ILSAC GF-4) [6-8].

During the use of engine oils changes in their elemental composition can be observed, which generally correlates with the decrease of the concentration of engine oil additives. References to the possible dynamics of the change in elemental composition of lubricants and its correlation with the most important properties (e.g. tribological, detergent-dispersant, etc.) were not found. However, a fast and cheap analytical method for investigating the changes in

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elemental composition of engine oils during and after screening tests would be advantageous both in developing and formulation of lubricants.

There are several methods for the quantitative and qualitative analysis of elements in new and used engine oils: inductively coupled plasma atomic/optical emission spectroscopy or mass spectroscopy (ICP-AES/OES, ICP-MS), flame or graphite furnace atomic absorption spectroscopy (FF-AAS/GF-AAS) or energy/wavelength dispersive X-ray fluorescence spectroscopy (ED/WDXRFS). For the determination of the composition of tribofilms on different test-pieces methods based on transmission or scanning electron microscopy (TEM/SEM), ultra high vacuum tribometer (UHVT), Auger electron spectroscopy or scanning Auger microscopy (AES/SAM), electron energy loss spectroscopy (EELS), X-ray or UV photoelectron spectroscopy (XPS/UPS) are used [9-15]. ICP and EDXRFS techniques are commonly used for determining elements both in liquid and solid samples. In case of these methods calibration curves are mainly linear in a concentration range of 2-3 orders of magnitude. With special ICP apparatus many elements can be detected simultaneously in a few minutes, provided that sample preparation is not required, e. g. after a simple dilution in kerosene. So it can be a fast analytical method but generally preliminary sample preparation is required. This sample preparation (e.g. digestion) is quite often complicated, time-consuming and its precision is essential to obtain accurate and reliable results. On the contrary sample preparation is not required in case of EDXRFS which is moreover a non-destructive, quick, easy and cost-effective method for elemental analysis of samples. Taking into consideration the matrix effect, having the optimized exciting and measuring parameters and the proper calibration curves many elements can be traced quickly and simultaneously by EDXRFS [15, 16].

In this work our objectives were investigating the adaptability of EDXRFS for elemental analysis of different engine oils and comparing these EDXRFS results with the data obtained by inductively coupled plasma spectroscopy. By measuring two engine oil series (engine oils for Diesel and gasoline engines) correlations were investigated between the changes of the elemental composition of engine oils during their degradation and the results of the screening tests.

2. EXPERIMENTAL

2.1. Engine oil samples

The original commercial engine oil compositions were marked with “REF” and contained commercial dispersant additives produced by MOL-LUB Ltd. (Almásfüzitő, Hungary). Diesel engine oil compositions of SAE 15W-40 viscosity grade and API CH-4/SJ performance level were marked with letter “D”, while partly synthetic gasoline engine oils of SAE 10W-40 and API SJ/CF with letter “G”. The ones indicated with 1-2-3-4 were experimental engine oils containing various experimental dispersant additives which were synthesized in our Department. Properties of experimental engine oils and the traced elements are given in Table 1. According to the data some differences were observed in the rheological properties of the experimental engine oils.

Table 1. Properties of the experimental engine oils and the traced elements

Properties	REF D	D1	D2	D3	D4	REF G	G1	G2	G3	G4
Viscosity at 40°C, mm^2/s	115.8	92.84	94.2	96.5	97.9	88.1	86.5	83.1	83.9	84.2
Viscosity at 40°C, mm^2/s	16.24	13.41	13.37	13.80	13.95	13.59	12.96	12.51	12.66	12.83
V.I.$_E$	151	145	142	145	145	157	149	147	149	152
Density at 20°C, g/cm^3	0.895	0.891	0.892	0.892	0.893	0.855	0.854	0.852	0.853	0.853
Mo-containing dispersant	-	-	-	+	-	-	-	-	+	-
Mo- and S-cont. dispersant	-	-	-	-	+	-	-	-	-	+
Ca-containing detergent	+	+	+	+	+	+	+	+	+	+
Zn-, S- and P-cont. ZnDDP	+	+	+	+	+	+	+	+	+	+

\+ *contained* - *did not contain*

2.2. Instruments

2.2.1. EDXRFS

Our analyses were carried out with a non-polarized energy dispersive X-ray fluorescence spectrometer (PHILIPS MiniPal PW 4025/02) which was controlled by PW 4051 MiniPal/MiniMate Software V 2.0A. The software also performed an integrated deconvolution function that could separate closely spaced peaks in the spectrum which otherwise could not be separated. The spectrometer was equipped with a 9 W Rh side-window tube anode, which was 90° with respect to the central ray. The fluorescence X-rays were detected with a Si-PIN detector with beryllium window and the raw signal was counted with a counter fitted with 2048 channel. The special de Kat sample holder and thin polypropylene foils were obtained from Philips Analytical B.V. In each case 5 g oil sample was dropped onto the thin polypropylene foil and the plastic sample holder was closed with the cover. Operating conditions of this experiment are summarized in Table 2. Samples did not need pre-treatment in this case.

2.2.2. ICP-AES Spectrometer

As we wanted to compare the results obtained by EDXRFS to those obtained by ICP-AES, the elemental composition of engine oils were analyzed also by GBC Integra XM type ICP-AES apparatus. The applied operating conditions are presented in Table 3.

2.2.3. High-pressure Asher

The sample preparation for the ICP analysis was made by a high-pressure asher (HPA, Austria) device. For each sample 3 repetitions were done. 0.4 g oil sample was dropped into a quartz vessel with 0.1mg accuracy. After adding 5 ml nitric acid (analytical grade, Sigma-Aldrich) the vessel was closed and put into the high-pressure asher in which the decomposition temperature program was run (T_1 = 120°C, t_1 = 60 min; T_2 = 220°C, t_2 = 90 min, while the pressure raise from the initial 80 bar to 120 bar). The content of vessel was washed into a 25 ml flask after cooling and the volume was adjusted to the mark with deionised water.

Table 2. EDXRFS operating conditions

Properties	S	P	Ca	Zn	Mo
Target	S K_a line	P K_a line	Ca K_a line	Zn K_a line	Mo L_a line
Detector	Si-PIN	Si-PIN	Si-PIN	Si-PIN	Si-PIN
Voltage, kV	5	5	8	15	30
Current, μA	500	800	30	300	1
Filter	None	Kapton	None	None	None
Medium	Helium	Helium	Helium	Helium	Helium
Measuring time, s	180	180	180	180	180

Table 3. Properties of the GBC Integra XM sequential type ICP-AES apparatus

Nebulizer	Concentric Meinhard type with a cyclonic spray chamber
RF-generator	40.68 MHz crystal-controlled
Power	1200 W (optimal)
Reflected power	20 W
Torch	Dismountable, quartz
Use of Argon gas	external (cooler) gas: 10 l/min, plasma gas: 0.5 l/min, sprayer gas: 0.5 l/min
Height of observation	6 mm above the induction coil
Optical system	Czerny-Turner vacuum-monochromator
Grating	Holographic, 1800 grooves/mm
Focal length	0.75 m
Resolution	0.018 nm 1st order, 0.009 nm 2nd order
Optical range	160-800 nm
Detector	Photoelectron multiplier
Elements (I: atom-, II: ion lines)	Wavelength of emission lines used for analysis, nm
Mo II	202.031
S I	182.563
Zn I	213.857
P I	213.617
Ca II	317.933
Ca I	422.673

Table 4. Properties of calibration curves

Method	Element	Equation	Conf. interval	Lin. regr. coeff.
EDXRFS	Mo	y = 0.095x + 1.79	± 5.47	0.997
	Zn	y = 0.241x + 3.02	± 6.95	0.998
	P	y = 0.102x + 2.22	± 7.75	0.995
	Ca	y = 0.090x + 2.28	± 6.74	0.995
	S	y = 0.516x + 5.13	± 19.10	0.995
ICP-AES	Mo	y = 0.199x + 1.93	± 24.38	0.990
	Zn	y = 0.193x + 2.15	± 18.56	0.995
	P	y = 0.185x + 5.30	± 25.11	0.998
	Ca	y = 0.184x + 5.77	± 25.64	0.991
	S	y = 0.189x + 4.61	± 19.10	0.995

Table 5. Concentrations of the elements in the standard solution measured by different methods (mg/kg)

Method	Mo	Zn	P	Ca	S
Theoretical	489	1520	1503	1517	1511
EDXRS*	487 ± 0.7	1519 ± 1.6	1499 ± 1.3	1516 ± 1.1	1507 ± 0.9
ICP-AES*	480 ± 19.9	1515 ± 25.4	1494 ± 23.0	1527 ± 25.9	1495 ± 30.1

** 3 independent measurements*

2.3. Screening methods of engine oils

The high temperature deposit preventing effect of experimental engine oils was determined by a panel coker. According to the test method the engine oil was periodically splashed by a stirrer to an aluminium plate, which was heated to 300°C. During the 9 hours the apparatus was dismounted in every 3 hours, the deposit formed on the plates was measured with 0.1 mg accuracy and in a special lighted box a photo was taken by a digital camera [17].

The antiwear and antifriction effects of the engine oils were tested by a modified Stanhope Seta four-ball tester according to the ASTM D2783-88 standard test method. Starting and stopping of the apparatus and the measurement of oil temperature in the sample holder in every second were done by a computer. Antifriction efficiency was characterized by the average final temperature at the end of the test (T_{max}). Antiwear efficiency was evaluated by the average wear scar diameter measured on the stationary balls [18].

3. RESULTS AND DISCUSSION

3.1. Calibration curves

For the calibration of both apparatus standard solutions of sulphur (LOT No. 1002112), calcium (LOT No. 507921), zinc (LOT No. 507417), phosphorus (LOT No. 503515) and molybdenum (LOT No. 506620) (supplier: Conostan Ltd.) were used in oil matrix (contained only hydrocarbon molecules). The series of standard samples containing five different elements in oil matrix (with regard to the engine oil samples which contained mainly base oils) were used to determine the five point calibration graphs in the concentration range of 0-3000 mg/kg. It was necessary to select a suitable analytical line by the measurement of elemental concentration of samples with X-ray method. In case of this experiment the K_a line of sulphur, phosphorus, calcium, zinc and the L_a line of molybdenum were used. In case of EDXRFS the concentration of samples was calculated from measured raw intensities and the intensities of relevant analytical lines were corrected for the background intensity employing the MiniPal/MiniMate Software V 2.0A, which applied an α-correction method. In case of ICP-AES matrix matches method was used during calibration and raw signals were not corrected. The main properties of calibration graphs obtained by both methods are given in Table 4.

According to data in Table 4 significant differences were observed between calibration graphs measured with different instruments and analytical methods because no matrix effect was observed in case of ICP-AES technique while considerable effect of the other elements on the properties of calibration graphs was found when EDXRFS method was used. This is the consequence of the well known phenomena that the chemical environment is an important parameter in case of X-ray spectrometry. The linearity of calibration graphs was proved by the analysis of linear regression coefficients. They are also shown in Table 4. According to the results very good regression coefficients (>0.99) and no bias were observed in case of both methods.

Table 4 shows also the mathematical equation of the calibration curves and their confidence intervals.

For checking the application possibility of calibration graphs the standard solutions were diluted in oil matrix and their solution with known concentration was produced (Table 5). Then the elemental concentrations of this sample were measured by both analytical techniques. According to data the accuracy of analysis of each element was much better in case of EDXRFS (RSD=0.15-0.47%), than in case of ICP-AES method (RSD=5.60-7.25%). Probably the differences in the sample preparation of the methods caused the better correlation of EDXRFS. EDXRFS technique is a non-destructive analytical method, which did not require sample preparation before measuring, whereas samples had to be digested in case of ICP-AES analysis and thence less precision could be reached.

3.2.Elemental analysis of engine oils before screening tests

For the selection of the method for further analysis the original engine oils were analyzed with EDXRFS and ICP-AES apparatus, too. The results and the differences in percentage are shown in Table 6.

Comparing the results it was pointed out that the differences in the range of 270-4400 mg/kg were inside the margin of error. Considering all detected elements the average of differences was only 1% and 3.9% in absolute value. EDXRFS results for phosphorus and sulphur were always lower than results obtained by ICP-AES. The differences between the two methods for phosphorus and sulphur were 2.1-7.3% and 0.5-6.4%, respectively. Greater molybdenum concentrations were always measured with the EDXRFS and the differences were in the range of 1.4-7.7%, while in case of zinc the elemental content measured with ICP-AES technique was only one time greater (this was only 16 mg/kg) and the differences were between 1.3 and 7.0%. When concentration of calcium was measured usually (seven out of ten times) greater values of the elemental content were observed in case of ICP-AES technique, furthermore the interval of the deviation was 0.8-6.8%. In case of the three exceptions, observed at the calcium determination, the concentrations measured with ICP-AES method were only 31 mg/kg less than those measured with the EDXRFS technique. It was found that the differences between the results could be derived from the uncertainty of the two methods (digestion, greater deviation of ICP-AES results) and these differences (average 41 mg/kg, maximum 198 mg/kg) were acceptable. Taking our experimental results into consideration it was found that the EDXRFS method can be capable for quick, simple and cost-effective elemental analysis of engine oils.

3.3. Elemental analysis of engine oils after screening tests

3.3.1. Analysis during and after Panel Coking Test

The change of chemical composition of experimental engine oils was traced during the high temperature deposit preventing effect tests [17]. After 3, 6 and 9 hours samples were taken from the investigated engine oils and their elemental contents were analyzed by EDXRFS. Results are shown in Table 6. The deposits formed on the plates were basically derived from the oxidation of the hydrocarbon molecules of the base oils and a smaller part from the decomposition of the additives. As it is known, engine oils consist of mainly base oils (about 85%) and different types of additives in smaller concentration (less than about 15%). From the point of view of the application of engine oils it is important, among other things, that these additives could prevent or reduce the deposit formation and the oxidation of base oils. Using the EDXFRS method important information about the efficiency of the additives could be obtained.

It was found that the concentration of the investigated elements, due to the decomposition of the additives, always decreased during the panel coking test (Figure 1) and molybdenum-, calcium-, zinc-, phosphorus- and sulphur containing compounds formed deposits on the surface of panels. These elements could only be derived from the additives and their presence in the solid deposits was proved by scanning electron microscopy (SEM).

Table 6. Elemental composition of engine oils before and after screening tests

Engine oil	Element	Fresh engine oils, mg/kg			Engine oils after screening tests (EDXRFS), mg/kg			
					Panel coking test duration			After four-ball test
		ICP-AES	EDXRFS	Diff.*, %	3 h	6 h	9 h	
REFD	Zn	1174	1196	1.87	1068	1037	1028	1118
	P	1463	1432	2.12	1338	1301	1282	1353
	Ca	4267	4225	0.98	4098	4073	4057	4152
	S	3027	2958	2.28	2903	2883	2867	2891
D1	Zn	1232	1216	1.30	1084	1049	1038	1167
	P	1537	1453	5.47	1295	1267	1255	1429
	Ca	4204	4235	0.74	4127	4076	4059	4230
	S	2973	2912	2.05	2864	2855	2846	2901
D2	Zn	1166	1206	3.43	1124	1111	1108	1140
	P	1366	1285	5.93	1179	1159	1145	1273
	Ca	4101	4132	0.76	4041	4033	4024	4117
	S	3048	3034	0.46	2964	2917	2899	2939
D3	Mo	404	421	4.13	381	359	345	399
	Zn	1246	1327	6.50	1195	1170	1163	1300
	P	1513	1416	6.41	1321	1284	1261	1408
	Ca	4235	4129	2.50	3999	3975	3958	3892
	S	3061	2895	5.42	2842	2818	2801	2856
D4	Mo	429	462	7.69	422	409	405	447
	Zn	1201	1285	6.99	1174	1158	1154	1202
	P	1450	1367	5.72	1245	1230	1221	1304
	Ca	4379	4305	1.69	4195	4176	4179	4245
	S	3015	2870	4.81	2793	2775	2770	2804
REFG	Zn	1156	1191	3.03	1095	1063	1052	1172
	P	1421	1389	2.25	1307	1267	1254	1341
	Ca	2502	2476	1.04	2401	2381	2374	2465
	S	2996	2892	3.47	2850	2841	2838	2772
G1	Zn	1138	1187	4.31	1089	1079	1072	1182
	P	1495	1453	2.81	1343	1308	1296	1241
	Ca	2465	2410	2.23	2294	2259	2251	2268
	S	3037	2918	3.92	2859	2830	2813	2849
G2	Zn	1131	1191	5.31	1087	1052	1041	1155
	P	1420	1338	5.77	1254	1205	1193	1309
	Ca	2509	2430	3.15	2334	2317	2310	2418
	S	3052	2905	4.82	2854	2848	2843	2867
G3	Mo	283	287	1.41	241	228	217	251
	Zn	1142	1220	6.83	1128	1112	1110	1206
	P	1432	1328	7.26	1217	1185	1171	1284
	Ca	2414	2251	6.75	2124	2100	2088	2248
	S	3082	2884	6.42	2821	2799	2784	2762
G4	Mo	274	285	4.01	242	229	225	256
	Zn	1136	1216	7.04	1084	1056	1045	1194
	P	1347	1275	5.35	1141	1108	1101	1139
	Ca	2240	2254	0.63	2155	2112	2110	2136
	S	2912	2730	6.25	2654	2612	2607	2663

* absolute value

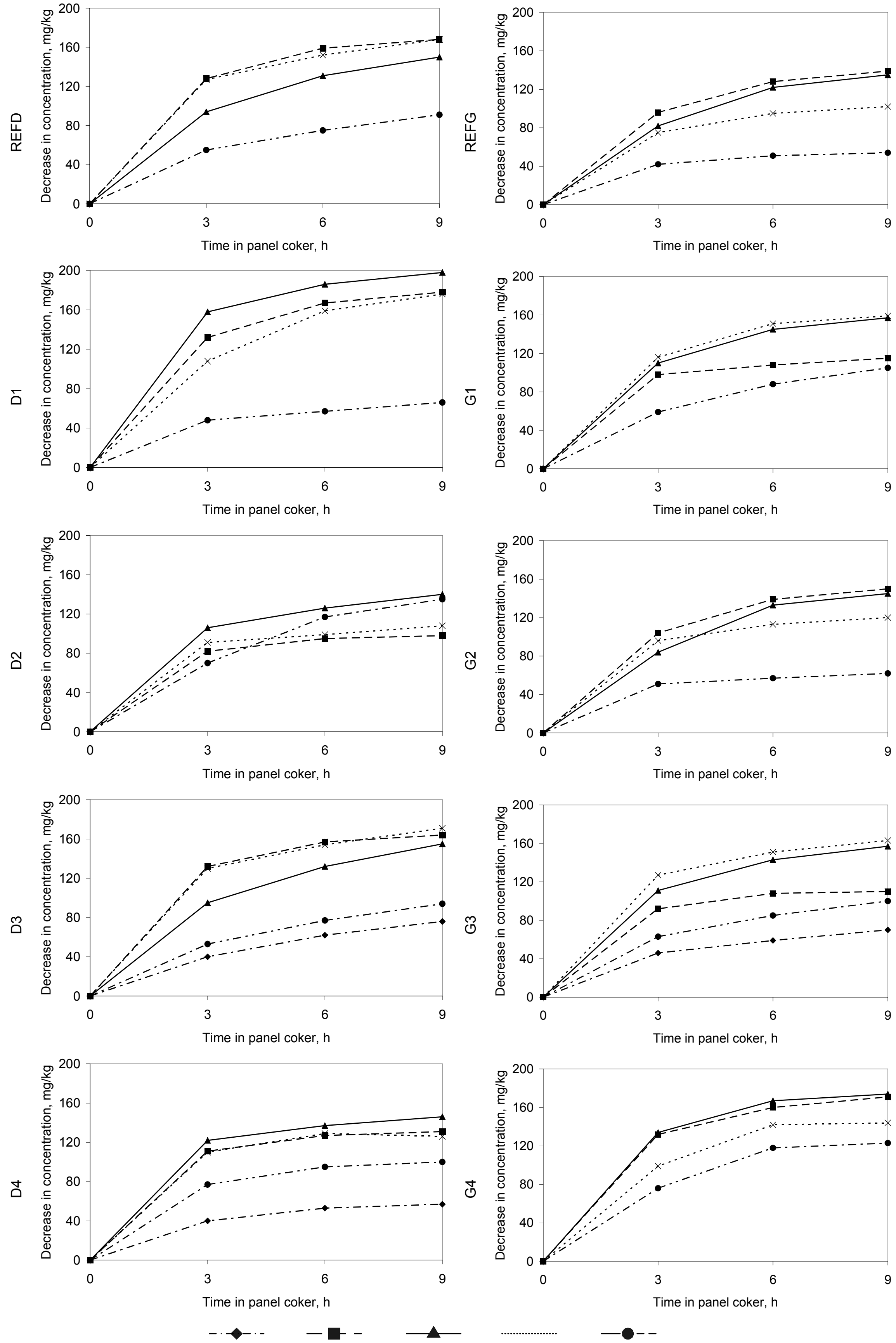

Figure 1. Decreases in concentrations during panel coking test

According to our results the concentration of molybdenum decreased by the highest percentage. After the 9 hour test the original concentration of the molybdenum (420-460 mg/kg in Diesel engine oils, 285 mg/kg in gasoline engine oils) decreased by 12-24%, which demonstrated that the molybdenum containing experimental additive was prone to decomposition. The decrease of the concentration of zinc and phosphorus was usually smaller (9-14%) furthermore the differences between the changes of these two elements were only 2-3%. This could be caused by the ZnDDP additive, which concentration was about 1% in each engine oil, and its zinc and phosphorus content was nearly equal. Therefore it is not surprising that during the degradation of ZnDDP nearly equivalent quantity of zinc and phosphorus were accumulated in the deposits because no other additives contained these two elements. During our tests the calcium and sulphur content of the engine oils decreased only by 2-7%, due to the high oxidation stability of the calcium-salicylate type detergent, which was present in the compositions. The decomposition of the sulphur containing additives (ZnDDP and experimental dispersant) and also the sulphur compounds of base oils resulted in significant decrease of sulphur contents.

Decreases of concentrations were the greatest in the first 3 hours while in the second and third periods the concentration changes lessened (Figure 1).

Table 7. Deposits on panels in panel coking test

Engine oil	Deposits, mg		
	3 h	6 h	9 h
REFD	12.6	20.3	29.0
D1	22.5	24.9	34.0
D2	8.9	10.1	22.8
D3	20.2	25.8	28.3
D4	23.6	30.2	41.2
REFG	5.9	7.4	9.8
G1	12.3	14.3	16.0
G2	6.5	14.2	14.3
G3	11.9	14.0	18.3
G4	14.4	19.2	21.1

According to our previous experiments, it was found that the first 3 hour period was the most critical from the point of view of the quantities of deposits (Table 7). In the first 3 hour period the quantities of deposits were in good correlation with the decreases of concentrations measured with EDXRFS (Figure 1 and Table 7). In the second and third time periods it could not be observed. Its reason could be that the other non-detected elements (from hydrocarbons of base oil) formed deposits. Based on our results in the first 3 hours the decomposition of additives was dominant because decreases of concentrations were the greatest while in the other two periods mainly the oxidation of hydrocarbons of base oil took place.

3.3.2. Analysis after Four-ball Wear Test

Changes in the elemental contents of investigated engine oils were detected after the antifriction and antiwear tests carried out with the Stanhope Seta four-ball instrument [18]. These results can also be seen in Table 6. The data showed that – as it was observed also in panel coking tests – the concentration of all elements decreased during the four-ball wear test. The decrease of calcium and sulphur sometimes exceeded 100 mg/kg (2.5-3.5 %). Probably, as result of tribochemical reactions, FeS_2 and MoS_2 were formed on the sliding surfaces which caused the decrease of the concentration of sulphur, furthermore the degradation of the calcium containing detergent could occur, too. The change of molybdenum concentration in Diesel engine oils (marked with D) was only a few percent while in case of gasoline engine oils (marked with G) it was around 10 %.

The percentage of the decrease of zinc and phosphorus contents changed in a wider range. The maximum value of the decrease was 6% and 15 % in case of zinc and phosphorus, respectively (G1 oil). In contrast to the results obtained during panel coking in some cases 10% differences were found between the concentration changes of these two elements. After four-ball wear test these phenomena could also be well detected by the EDXRFS technique. Based on the results obtained by various tests we supposed that under the different experimental conditions the degradation of ZnDDP occurred in different ways. In the panel coking test the temperature of the panel and the oil, which was splashed onto it, were 300°C, while the temperature of rest of the oil in the apparatus was around 150°C. In the sample holder of the four-ball apparatus the temperature of the oil was about 70-80°C during the tests, while close to the sliding surfaces higher temperature (some hundred °C heat flashes) and higher pressure occurred which led to the selective degradation of the additives and to the formation of a tribolayer.

In case of engine oils with poorer antiwear (higher wear scar diameter) or antifriction efficiencies (higher T_{max}) the overall changes in the concentrations of effective tribolayer forming elements were the smallest (Figure 2 and Table 8). Engine oils with good antiwear or antifriction properties showed the greatest overall decreases in concentrations. Thus it was found that in case of engine oils with poor or good antifriction and antiwear properties extreme concentration changes could be measured with the EDXRFS method.

Table 8. Results of four-ball tests

Engine oil	Wear scar diameter, mm	T_{max}, °C
REFD	0.69	72
D1	0.94	77
D2	0.71	73
D3	0.70	74
D4	0.76	72
REFG	0.82	75
G1	0.65	72
G2	0.77	75
G3	0.78	75
G4	0.67	72

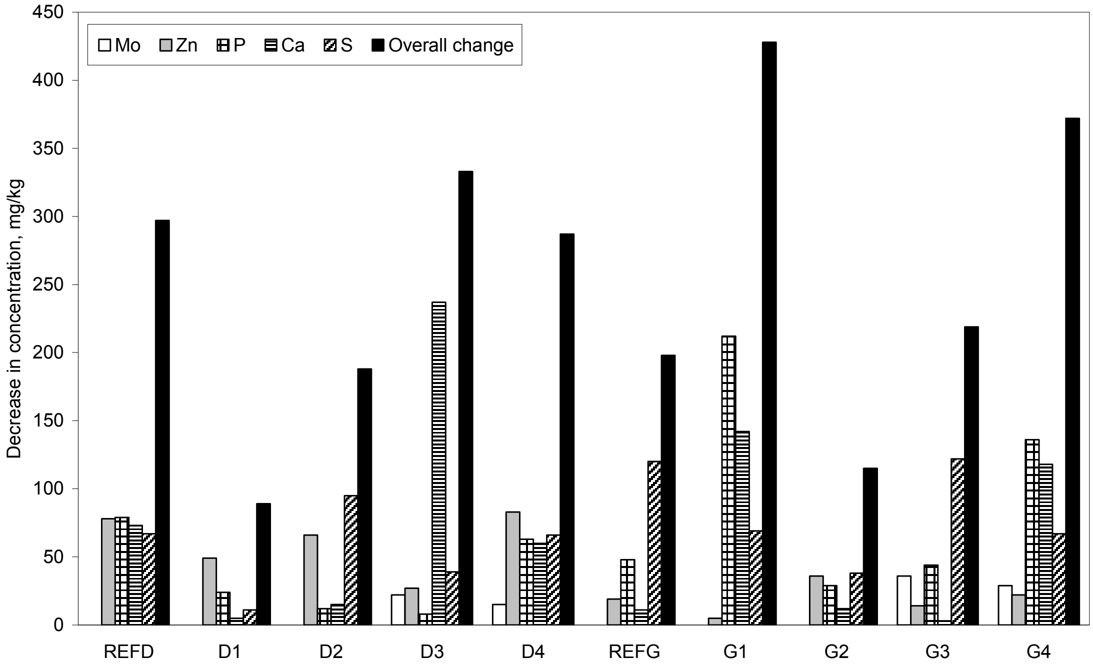

Figure 2. Decreases in concentrations after four-ball test

4. CONCLUSION

Due to the ever stricter environmental regulations of engine oils there is an increasing demand on the determination of their elemental content. For analysis X-ray fluorescence, atomic emission and absorption spectroscopy techniques are most commonly used. In our experimental work the elemental composition (sulphur, calcium, zinc, phosphorus and molybdenum) of various engine oils (engine oils for Diesel and gasoline engines) was measured by different analytical methods: energy dispersive X-ray fluorescence spectroscopy (EDXRFS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES). Comparing the data considerable differences were observed between the two methods. In case of EDXRFS strong matrix effects on the calibration graphs could be detected. Additionally it was found that the preliminary sample preparation (digestion) before ICP-AES analysis resulted in the poorer accuracy of this method. Taking into consideration its matrix effect the quick, simple and cost-effective EDXRFS technique without the necessity of sample preparation was selected for further analysis of engine oils during and after different screening tests. Complementing the determination of the high temperature deposit preventing, antiwear and antifriction effects of engine oils with the EDXFRS analysis more and important information could be obtained about the deterioration and the efficiency of the additives. It was also found that after proper calibration the EDXRFS method can be advantageously used in the analysis of engine oils before and after screening tests.

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