



Lubricant quality control: A chemometric approach to assess wear engine in heavy machines

Rodolfo Francisco Lara^a, Silvana Mariela Azcarate^{b,c}, Miguel Ángel Cantarelli^{b,c}, Ivana Marcela Orozco^a, María Eugenia Caroprese^a, Marianela Savio^{b,c,*}, José Manuel Camiña^{b,c,*}

^a Facultad de Ingeniería, Universidad Nacional de San Juan, Av. Del Libertador Gral. San Martín, 1109 5400 San Juan, Argentina

^b Facultad de Ciencias Exactas y Naturales, Universidad Nacional de La Pampa, Av. Uruguay, 151 6300 Santa Rosa, La Pampa, Argentina

^c Instituto de Ciencias de la Tierra y Ambientales de La Pampa, Mendoza, 109 6300 Santa Rosa, La Pampa, Argentina

ARTICLE INFO

Article history:

Received 31 October 2014

Received in revised form

3 December 2014

Accepted 15 January 2015

Available online 22 January 2015

Keywords:

Wear metals

Lubricant oils

Machine monitoring

Chemometrics techniques

ABSTRACT

Used lubricants assessment could be suitable to reveal wear mechanisms undergoing in a machine. In the proposed work an effective, reliable and cost-efficient technique combining inductively coupled plasma optical emission spectrometry (ICP-OES) and chemometrics was developed to perform wear analysis for industrial application. Thus, multielemental determination of a large amount of used lubricants from diesel heavy machines (truck, bulldozer, loaders and backhoe) was carried out by ICP-OES. Multivariate analysis was done by the non supervised method principal component analysis (PCA) and supervised method sequential discriminant analysis (SDA). The recognition ability for the groups was highly satisfactory. For PCA, the main three principal components explained 99.98% of total variance for samples lubricants. SDA allowed, in training and prediction sets, a correct classification of 97.12% and 95.75% respectively for the lubricant analyzed samples, obtaining three groups classified according to the use. The outcomes demonstrate that lubricant wear effect could be assessed quickly and accurately, having great potential to become a very useful tool in the machine monitoring industry.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Under normal operation conditions engine and turbine components present continuous wear; the use of lubricant oils could minimize this fact [1]. Accurate data on the wear characteristics are relevant to assess the status of the machinery and reliability in mechanical systems. The quantitative determination of metals in used lubricant oils is performed to monitor and diagnoses engine wear, in order to attain preventive maintenance procedures, increasing equipment reliability before the collapse [1,2]. Metals in lubricating oil could emerge from various sources, such as wear from friction or corrosion of the engine components, contamination and additives [3–5].

Wear analysis has gained commercial interest and several analytical methodologies based on atomic spectrometric techniques have been developed to determine elemental composition of lubricants [1,3,6–11]. Thus, chemical data from lubricant analysis

reveals the presence and amount of metallic wear particles in the lubricating. Inductively coupled plasma atomic emission spectroscopy (ICP-OES) is an efficient technique to simultaneously measure almost all metals, including refractory metals, and some non-metals. It has been considered by several workers to determine trace elements related to the wear in lubricating oils, due to its excellent conditions for elemental excitation and continuous sampling capability, which results in a higher productivity in the analysis of a large amount of samples, making easy the automation of methods for routine multi-element determinations [1,2,8,9].

Pretreatment in complex organic samples for trace elements analysis has always been a challenge in analytical chemistry. In fact, it is one of the most relevant and decisive stages in the whole analytical procedure for trace elements determination [12,13]. In the analytical determination of elements in crude oils and their sub-products by spectroscopic instrumental techniques, it is necessary to submit samples to a variety of treatment in order to make them compatible to sample introduction systems and atomizers. Various methods have been reported for the preparation of samples prior to instrumental analysis [1,14–16]. Direct introduction of organic sample solution has been proposed, but could involve transport interference problems due to physical

* Corresponding authors at: Facultad de Ciencias Exactas y Naturales, Universidad Nacional de La Pampa, Av. Uruguay, 151 6300 Santa Rosa, La Pampa, Argentina. Tel.: +54 2954 245220/30; fax: +54 2954 432535.

E-mail addresses: marianelasavio@gmail.com (M. Savio), jcaminia@gmail.com, jcaminia@exactas.unlpam.edu.ar (J.M. Camiña).

properties, matrix effect, etc. Thus, total destruction of organic matter is still the most reliable procedure for metal determinations in petroleum and their sub-products [17]. In order to avoid element losses, as well as to prepare greater number of samples simultaneously, the use of sulphanic acid as ashing agent had been reported as a simple, rapid and precise procedure, because improves the release of wear metals in used lubricating oils and the accuracy of the analytical results [14].

The current efforts in tribology research groups focuses on the development of methods for the classification of wear particles, with the aim of revise manufacturing processes, machine condition monitoring and failure analysis in engineering components. However, the most common techniques are based in surface topography characterization, which is usually time consuming and expensive [18–22]. This fact suggests the need to find different procedures for a rapid and easy evaluation of the oil formulations, in particular when a large number of oil samples are considered. Through the years, chemometrics has provided a substantial support in different fields of chemistry. It could be regarded as a powerful tool for be implemented as useful in wear metal classification analysis. Principal component analysis (PCA) have been recently proposed as a chemometric tool to differentiate the performance of engine oils evaluating natural and artificial degradation of lubricating oils [23]. In this sense, chemometrics along with the determination of several elements by ICP-OES could be used to attempt understanding the phenomenon that occurs during lubricant wear.

Accordingly, in this work the possibility of using chemometric techniques to provide early information on wear modes occurring and the condition of a machine was investigated. The elemental determination was routinely carried out by ICP-OES in a large amount of used lubricants in diesel engines of trucks, bulldozer, loaders and backhoe. Chemometric data analysis was performed by principal component analysis (PCA) and sequential discriminant analysis (SDA) to assess the effect of use time related to the wear, as an equipment maintenance program for diesel heavy machines engines.

2. Material and methods

2.1. Instrumentation

An inductively coupled plasma atomic emission spectrometer, Perkin Elmer ICP-OES 7300 DV (Waltham, MA) was used. Instrument conditions were: peak hopping measurement mode, read delay time of 45 s, 2 s lecture time, 40 s flush time, 1 reading per replicate and 3 replicates. The argon gas with a minimum purity of 99.996% was supplied by Praxair (Córdoba, Argentina).

2.2. Reagents and samples

Ultrapure water (18.2 MΩ cm) used to prepare all standards and samples solutions, was obtained by a Millipore Synergy Ultrapure Water System (Darmstadt, Germany). Concentrated nitric acid (65%v/v) was purchased from Sigma-Aldrich (Germany), Hydrochloric acid (37%v/v) and sulphanic acid (> 99%) from Merck (Darmstadt, Germany) and hydrogen peroxide acquired from Sigma (St. Louis, MO). All glasses and other lab materials were cleaned by soaking in 10% HNO₃, and rinsing with ultrapure water. Synthetic standard stock solutions (1000 mg l⁻¹) of Ag, Al, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sn, V, Zn were obtained from Fluka (Switzerland). Calibration standard solutions were prepared by step-wise dilutions of the stock solution in ultrapure water and acidified with nitric acid. The selected parameters on ICP-OES for the determination of the evaluated metals

were conformed to those recommended by Perkin-Elmer. The solutions were introduced into the plasma at 1.5 mL min⁻¹ applying 1300 W RF power and 0.8 L min⁻¹ nebulizer gas flow rate.

The analyzed lubricant engines oil samples were a total of 1018 samples corresponding to: trucks (532 samples), bulldozers (120 samples), loaders (255 samples) and backhoes (111 samples). Oil samples were collected bimonthly after use (in the lubricant change) from every machine during two years (among June 2012 to June 2014) in plastic flask, labeled and saved until analysis. All the analyzed lubricants were normal type and 15W40.

2.3. Analytical procedure

A mixture of 10.0 g used lubricating oil and 1.0 g sulphanic acid was heated in a beaker. The coke formed was muffled at 550 °C until the ash was free of carbon particles (approx. 45 min). The ash was cooled, dissolved with 20 mL HCl (dilution 1:1) and digested in a boiling water bath.

Fifty random samples of lubricating oil were spiked with the elements standard solutions to final concentrations of 50 µg L⁻¹ of each one, to evaluate the recovery due the sample treatment. A blank solution was always measured and taken into consideration.

The concentrations of the 19 elements (Ag, Al, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sn, V, Zn) were determined by direct nebulization into ICP-OES. Calibration models for each element were performed against aqueous standards and were obtained using five different concentration levels in triplicate. The regression coefficient (*r*²) values of such straight ranged from 0.987 to 0.999.

2.4. Data analysis

A matrix with rows representing lubricant samples and columns corresponding to metal concentrations was created for the chemometric calculations. PCA was used as exploratory technique. SDA was applied to obtain classification rules. A data pretreatment was made in order to avoid the differences in measurement units. Autoscaling is the most widely used scaling technique [24]. All data were autoscaled for every variable. The Unscrambler version X v.10.3 software package (Thronheim, Norway) was used for the statistical analysis.

3. Results and discussion

3.1. Instrument and sample optimization

Sample preparation is a decisive step for the establishment and application of a spectroanalytical technique. For lubricant oils analysis, their chemical composition and size of particles in wear remains could determine the method of choice. Organic solvents have been used by several authors to dissolve oil samples, as the same time as ICP-OES has been chosen for trace elements determination [10,17,25,26]. The main drawback of this sample preparation is that many times, large solid particles present in used lubricants are complicated to dissolve, resulting in sensitivity loss in the nebulization, atomization and detection of wear metals by ICP-OES. For this reason, direct dissolution of oils with organic solvents for element determination, it is not proper to be used if samples contain large amounts particles bigger than 10 µm. The proposed size limit depends on the instrument used as well as its properties [25,26]; for that, these issues were tackled in our work following sample preparation proposed by Ekanem, Udoh, and coworkers [14,16]. Using sulphanic acid as an auxiliary reagent, organic material is burned remaining only in inorganic ashes. Sulphanic acid strengthens metals release in the digestion stage

Table 1

Figures of merit of elemental determination in lubricant oil samples treated with sulphanic acid (proposed method), $n=10$.

Analyte	Wavelength used [nm]	LOD ^a [$\mu\text{g L}^{-1}$]	LOD ^b [mg Kg^{-1}]	LOQ ^b [mg Kg^{-1}]
Ag	328.068	4.7	0.024	0.078
Al	396.153	19.0	0.095	0.314
Ba	233.527	2.7	0.014	0.045
Ca	317.933	6.7	0.034	0.111
Cr	267.716	4.7	0.024	0.078
Cu	327.393	6.5	0.033	0.107
Fe	238.204	3.1	0.016	0.051
K	766.490	0.6	0.003	0.010
Mg	285.213	1.1	0.006	0.018
Mn	257.610	0.9	0.005	0.015
Mo	202.031	5.3	0.027	0.087
Na	589.592	46.0	0.230	0.759
Ni	231.604	10.0	0.050	0.165
P	213.617	51.0	0.255	0.842
Pb	220.353	28.0	0.140	0.462
Sn	189.927	17.0	0.085	0.281
Si	251.611	0.3	0.002	0.005
V	290.880	5.9	0.030	0.097
Zn	206.200	3.9	0.020	0.064

^a Instrumental limit of detection.

^b Procedure limit of detection.

and increases metals recovery. The optimal wavelengths for the determination of metal by ICP-OES are described in Table 1.

3.2. Analytical performance

A total of nineteen elements (Ag, Al, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sn, V, and Zn) were determined by ICP-OES following selected sample preparation. Table 1 displays the figures of merit for the trace elements determination in lubricant oil samples. Considering the complexity of the sample, the analytical performance was satisfactory. The recommended procedure involved low limits of detection (LOD) for most analytes (between 0.002 mg Kg^{-1} for Si, and 0.255 mg Kg^{-1} for P). LOD and limits of quantification (LOQ) were calculated as blank signal added of 3.3 and 10 times, respectively, the standard deviation of a blank for ten replicate measurements ($n=10$). The relative standard deviation (RSD, $n=5$), used to estimate the precision, was smaller than 5% for all elements. The precision of the proposed method was usually equal or better than that obtained for the analysis of conventional digested samples. In all cases, the determinations were carried out following the recommended method by comparison against simple aqueous standards.

3.3. Analytical validation and application to real samples

Recovery studies were carried out with fifty random samples by standard addition. The samples were spiked with $50 \mu\text{g L}^{-1}$ of every element and prepared as indicated in 2.3. In this study, was evaluated the accuracy of the results by comparison (t -test, 95% confidence interval) with an independent sample treatment. In all cases, quantitative recoveries (above $95 \pm 7\%$) were obtained.

The proposed method for sample preparation using sulphanic acid was applied for the determination of wear metals in lubricating oils. Table 2 shows the average concentration and standard deviation of the 19 elements determined by ICP-OES, in the 1018 samples of heavy equipment (trucks, bulldozers, loaders and backhoes). The concentrations of the elements in every machine were quite different, which could be associated to the power of engine, use condition, etc. Although of differences that were found, the multivariate models showed that they were not affected by the type of machine.

In all cases Ag, Ba, Sn, and V concentrations were lower than LOD. The presence of Al, Ca, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Si and Zn was evidenced in one or more lubricant samples collected from the heavy equipment.

3.4. Principal component analysis

Principal component analysis (PCA) is a non supervised method, which was performed as a descriptive tool to visualize the data in two dimensions. This method provides new variables as linear combinations of the original variables, which are called principal components (PCs), allowing the visualization of samples in a new dimensional space and the assessment of those variables that most contribute to the classification of samples [27,28].

In the present work, PCA was applied to select the most important variables for the model in a matrix formed by 10 columns (elemental concentrations) and 1080 rows corresponding to the lubricant samples. PCA model was built using as initial variables, the elemental concentrations determined for Al, Ca, Cu, Fe, K, Mg, Na, P, Si and Zn. PCA model obtained using only three principal components, explains more than 99.98% of the total variance of the system. Fig. 1 shows the classification attained by PCA through the scores plot of samples in the bi-dimensional space of the first two PCs. From this exploratory analysis, three groups clearly separated could be observed. Each group formed corresponds to different ranges of use degree which could be related with wear over time of the lubricants used on heavy machines, namely: used more than 280 h (Group A), used from 210–280 h (Group B), and used from 50 to 210 h (Group C).

Loading vectors could be considered as the connection between the initial variables and the PCs [29]. In this case, loadings are the coefficients of the linear combination for all the elemental concentrations (initial variables) and represent the influence of these variables in the explanation of the data variance. Thus, it is necessary to determine elements in which the greatest differences are found. In order to establish these differences, loadings were analyzed. Fig. 2 exposes the loading of every variable on each PC. Accordingly, the most important elements (variables) used in the PCA model include P, Ca, Mg and Zn. It can observe that PC-1 is influenced positively by calcium and zinc, while PC-2 is mainly associated positively to phosphorus. Mg had a minor influence, but it was retained to use three principal components in the model, which allowed to obtain a 99.98% of explained variance (Fig. 3), indicating that all the information was correctly modeled by PCA.

The use degree of lubricant could be determined by changes on the elemental composition and classification was reached mainly because the variation of P. According to this, P concentration was higher in the less used lubricants, but it decrease while the hours of use of lubricant increase. Thus, the less used lubricants (group C) had more P content, while the lesser concentration of P (group A) represents the more used lubricant situation. The correlation between the variations of initial phosphorous concentrations with the increase in the use hours of the lubricants could be explained because most widely used additives in engine oil contain phosphorous that might partially volatilize during engine operation [17]. On the other hand, it was found a little increasing in the concentration of Zn in the more used lubricants, which can be attributed to a possible wear engine.

3.5. Sequential discriminant analysis.

Sequential discriminant analysis (SDA) is a supervised method that was performed to evaluate if the lubricant samples could be mathematically distinguished according to their use degree. The variables most significant obtained in PCA were used again to obtain the SDA model.

Table 2

Proposed analytes determination in used lubricant oils collected in two years campaign in a private company of Argentina, average and standard deviation of the 1018 oil engines samples.

Analyte [mg Kg ⁻¹]	Trucks	Bulldozers	Loaders	Backhoes
Ag	< LOQ	< LOQ	< LOQ	< LOQ
Al	4.86 ± 0.75	5.50 ± 0.67	6.07 ± 0.81	5.41 ± 0.66
Ba	< LOQ	< LOQ	< LOQ	< LOQ
Ca	2844.35 ± 233.42	1786.25 ± 191.82	3063.22 ± 485.23	2966.32 ± 356.13
Cr	< LOQ	< LOQ	< LOQ	1.82 ± 0.33
Cu	4.01 ± 0.53	2.69 ± 0.87	1.51 ± 0.19	7.06 ± 0.89
Fe	20.56 ± 2.37	14.68 ± 1.56	12.53 ± 0.23	36.31 ± 0.45
K	10.52 ± 1.41	6.05 ± 0.56	5.12 ± 0.69	12.07 ± 1.56
Mg	23.03 ± 2.51	12.24 ± 1.36	31.15 ± 0.47	23.32 ± 1.58
Mn	2.80 ± 0.75	< LOQ	< LOQ	< LOQ
Mo	3.48 ± 0.77	< LOQ	< LOQ	60.61 ± 0.78
Na	2.95 ± 0.63	5.05 ± 0.66	3.89 ± 0.51	3.54 ± 0.71
Ni	< LOQ	< LOQ	< LOQ	< LOQ
P	839.35 ± 97.63	1403.51 ± 185.63	1192.54 ± 87.42	962.63 ± 114.51
Pb	1.73 ± 0.59	< LOQ	< LOQ	3.73 ± 0.47
Si	7.54 ± 0.83	8.87 ± 0.95	7.23 ± 0.91	9.71 ± 1.25
Sn	< LOQ	< LOQ	< LOQ	< LOQ
V	< LOQ	< LOQ	< LOQ	< LOQ
Zn	1378.23 ± 143.62	817.05 ± 104.33	1338.53 ± 157.22	1427.11 ± 137.63

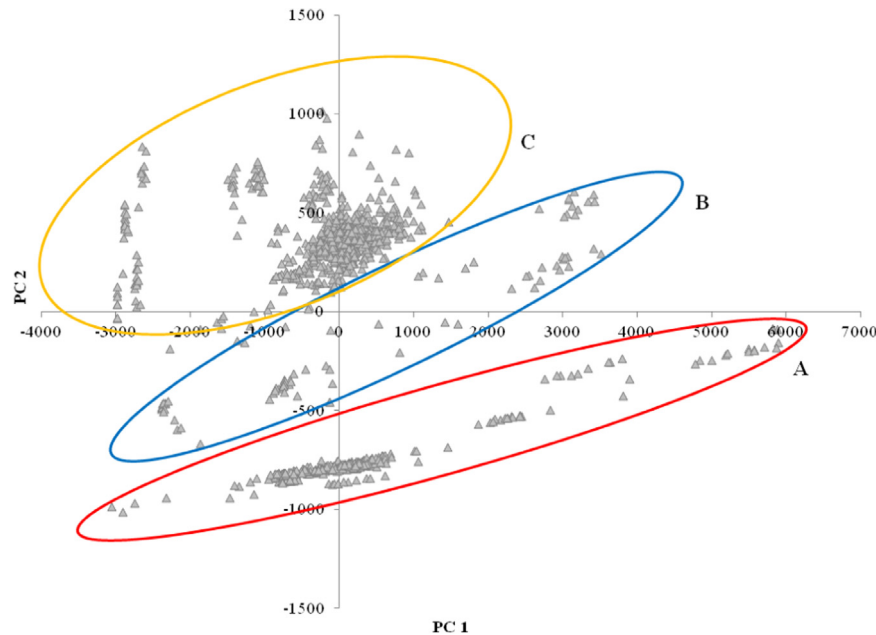


Fig. 1. Scores plot for PCA model, showing three discriminated groups according to use degree of lubricants.

The SDA was applied to the initial matrix; 644 and 374 random samples were used for the training set and the validation set respectively. The model consists of linear equations involving all or some of the selected variables [30,31]. SDA generates all the combinations of variables and selects the combination that reproduces a discriminant function showing the least number of classification errors.

In this study, discriminant functions (D) were obtained to classify data samples into three groups and two discriminant functions were needed to fully partition the data

$$D_1 = -5.76 - 3.310^{-4}\text{Ca} - 5.110^{-4}\text{Mg} + 3.010^{-4}\text{Zn} - 0.01\text{P}$$

$$D_2 = -1.88 - 988 - 9.110^{-4}\text{Ca} - 0.01\text{Mg} + 6.110^{-4}\text{Zn} + 5.810^{-5}\text{P}$$

Table 3 shows SDA results. The recognition ability for the groups was highly satisfactory, analyzed samples were 97.12% and 95.75% correctly classified in the training and prediction sets, respectively. Three groups were obtained, classified according to the wear over

time or use degree: group A (lubricants used more than 280 h), group B (lubricant used between 210–280 h), and group C (lubricants used from 50 to 210 h). The occurrence of different wear metals in lubricating oils naturally depends on the machine studied and the materials of its components. Nevertheless, multivariate models were not affected by the type of machine. Table 3 demonstrates low errors for training and validation step (from 0 to 3.22%) in the three groups, indicating that the model fit adequately and also, corroborating the previous classification obtained by PCA. These low errors allow using these models to assess the degree of use or wear over time of the lubricants as quality control tools.

4. Conclusion

The present work evidences an advance in the comprehension of wear over time of use in lubricants based on their elemental composition. PCA, non supervised chemometric tool, allowed the

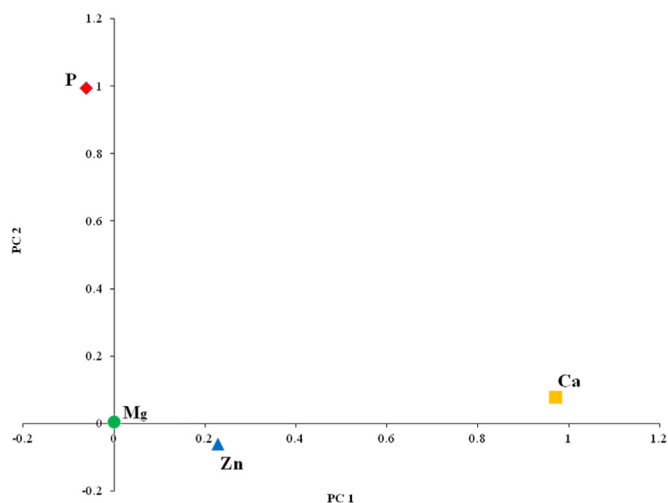


Fig. 2. Loadings plot, showing the most important variables and their influences on the PCA model.

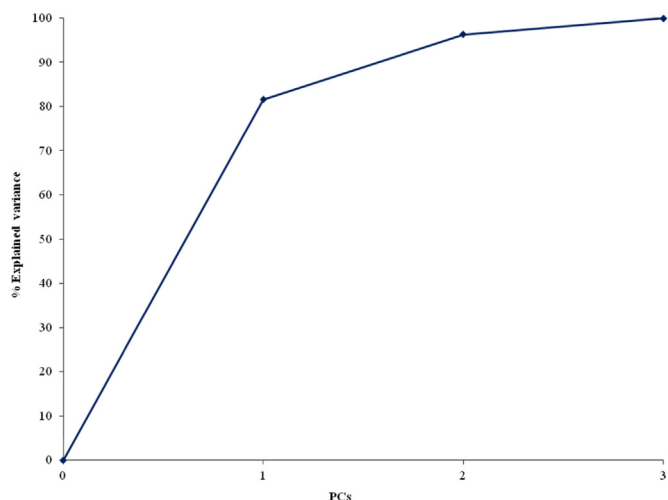


Fig. 3. Percentage of explained variance (cumulative), indicating the percentage of the original information on each principal component.

Table 3

Classification ability of sequential discriminant analysis (SDA) model for prediction and validation sets in different lubricants according to use degree.

Training	A	B	C	Total	Error (%)
A	200	1	0	201	0.50
B	0	42	1	43	2.38
C	0	0	400	400	0
Validation	A	B	C	Total	Error (%)
A	97	1	0	98	1.03
B	0	31	1	32	3.22
C	0	0	244	244	0
Total	297	75	646	1018	1.18

visualization of three different groups according to the use degree. The most important variables for the model were defined, including P, Ca, Mg and Zn. By means of SDA supervised method, it was possible to confirm the previous classification by PCA, obtaining a low error of prediction for the three obtained groups. The decrease in phosphorous concentrations observed in this analysis could be indicator of changes in lubricants, preventing a possible engine breakdown in the machine. For all the exposed, the described chemometric method demonstrated to be a powerful tool suitable in wear metal analysis in lubricants, allowing an early machine

condition monitoring. In addition, it is a trustworthy and cost-efficient technique to be applied for quality control in heavy vehicles and lubricant factories. However, further studies must be performed for other type of lubricants or machines. On the basis of the obtained results, it could be recommended to perform the change of lubricants in heavy machines before 280 h of use.

Acknowledgment

The authors would like to thank Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT) and Universidad Nacional de La Pampa (UNLPam) for supporting this research.

References

- [1] Aucélio RQ, de Souza RM, de Campos RC, Mielekey N, da Silveira CLP. The determination of trace metals in lubricating oils by atomic spectrometry. *Spectrochim Acta B* 2007;62:952–61.
- [2] Souza RM, Da Silveira CLP, Aucélio RQ. Determination of refractory elements in used lubricating oil by ICPOES employing emulsified sample introduction and calibration with inorganic standards. *Anal Sci* 2004;20:351–5.
- [3] Dahmani R, Gupta N. Spectroscopic analysis of automotive engine oil. *Proc SPIE Int Soc Opt Eng* 2001;179–83.
- [4] Juránek R, Machalík S, Zemčík P. Analysis of wear debris through classification. In: *Lecture Notes in Computer Science* (including subseries Lecture notes in artificial intelligence and lecture notes in bioinformatics); 2011. p. 273–83.
- [5] Pignalosa G, Knochen M. Determination of wear metals in lubricating oils using flow injection AAS. *At Spectrosc* 2001;22:250–7.
- [6] Gonçalves IM, Murillo M, González AM. Determination of metals in used lubricating oils by AAS using emulsified samples. *Talanta* 1998;47:1033–42.
- [7] Hardaway C, Sneddon J, Beck JN. Determination of metals in crude oil by atomic spectroscopy. *Anal Lett* 2004;37:2881–99.
- [8] Kuokkanen T, Perämäki P, Välimäki I, Rönkkömäki H. Determination of heavy metals in waste lubricating oils by inductively coupled plasma–optical emission spectrometry. *Int J Environ An Chem* 2001;81:89–100.
- [9] Vähäoja P, Välimäki I, Heino K, Perämäki P, Kuokkanen T. Determination of wear metals in lubrication oils: A comparison study of ICP-OES and FAAS. *Anal Sci* 2005;21:1365–9.
- [10] Vähäoja P, Välimäki I, Roppola K, Kuokkanen T, Lahdelma S. Wear metal analysis of oils. *Crit Rev Anal Chem* 2008;38:67–83.
- [11] Stachowiak GW, Batchelor AW, Stachowiak GB. Wear particle analysis. *Tribol Ser* 2004;44:253–94.
- [12] Savio M, Ortiz MS, Almeida CA, Olsina RA, Martinez LD, Gil RA. Multielemental analysis in vegetable edible oils by inductively coupled plasma mass spectrometry after solubilisation with tetramethylammonium hydroxide. *Food Chem* 2014;159:433–8.
- [13] Mester Z, Sturgeon RE. Sample preparation for trace element analysis. Amsterdam: Elsevier Science; 2003.
- [14] Ekanem EJ, Lori JA, Thomas SA. The determination of wear metals in used lubricating oils by flame atomic absorption spectrometry using sulphuric acid as ashing agent. *Talanta* 1997;44:2103–8.
- [15] Duyck C, Mielekey N, Porto da Silveira CL, Aucélio RQ, Campos RC, Grinberg P, et al. The determination of trace elements in crude oil and its heavy fractions by atomic spectrometry. *Spectrom Acta B* 2007;62:939–51.
- [16] Udoh AP, Thomas SA, Ekanem EJ. Application of p-xylenesulphonic acid as ashing reagent in the determination of trace metals in crude oil. *Talanta* 1992;39:1591–5.
- [17] Nadkarni RA. Elemental analysis of fuels and lubricants: recent advances and future prospects. ASTM International; 2005.
- [18] Stachowiak GP, Stachowiak GW, Podsiadlo P. Automated classification of wear particles based on their surface texture and shape features. *Tribol Int* 2008;41:34–43.
- [19] Stachowiak GW, Podsiadlo P. Characterization and classification of wear particles and surfaces. *Wear* 2001;249:194–200.
- [20] Stachowiak GW, Podsiadlo P. Classification of tribological surfaces. *Tribol Int* 2004;37:211–7.
- [21] Stachowiak GW, Podsiadlo P. Towards the development of an automated wear particle classification system. *Tribol Int* 2006;39:1615–23.
- [22] Stachowiak GW, Batchelor AW, Stachowiak GB. Characterization of test specimens. *Tribol Ser* 2004;44:115–50.
- [23] Besser C, Dörr N, Novotny-Farkas F, Varmuza K, Allmaier G. Comparison of engine oil degradation observed in laboratory alteration and in the engine by chemometric data evaluation. *Tribol Int* 2013;65:37–47.
- [24] Esbensen K. Multivariate data analysis. In practice. 5th Edition. Oslo: CAMO Process AS; 2002.
- [25] Jantzen E, Buck V, Kaegler SH. Influence of particle size on wear assessment by spectrometric oil analysis I: atomic absorption spectrometry. *Wear* 1983;87:331–8.

- [26] Guinat E. Spectrometric oil analysis: atomic emission spectrometric analysis of wear metals in lube oils by RDE method. *Tribol Int* 1985;18:246.
- [27] Terrab A, Hernanz D, Heredia FJ. Inductively coupled plasma optical emission spectrometric determination of minerals in thyme honeys and their contribution to geographical discrimination. *J Agric Food Chem* 2004;52:3441–5.
- [28] Tormen L, Chaves ES, Saint'Pierre TD, Frescura VLA, Curtius AJ. Determination of trace elements in fuel ethanol by ICP-MS using direct sample introduction by a microconcentric nebulizer. *J Anal At Spectrom* 2008;23:1300–4.
- [29] Urbano M, Luque de Castro MD, Pérez PM, García-Olmo J, Gómez-Nieto MA. Ultraviolet–visible spectroscopy and pattern recognition methods for differentiation and classification of wines. *Food Chem* 2006;97:166–75.
- [30] Chen D, Chen Y, Hu S. Correlative components analysis for pattern classification. *Chemom Intell Lab Syst* 1996;35:221–9.
- [31] Besalú E, Castellanos M, Sanchez JM. Sequential discriminant classification of environments with different levels of exposure to tobacco smoke. *Sci Total Environ* 2014;490:899–904.