2015 International Nuclear Atlantic Conference - INAC 2015
São Paulo , SP, Brazil, October 04-09, 2015
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN

USE OF MULTIVARIATE STATISTICAL TOOL FOR DATA PROCESSING IN THE ANALYSIS OF Cu, Cr, Fe, Pb, Mo AND Mg IN LUBRICATING OIL BY LIBS

[1]Luana F. N. Alves, [1]Jorge E .S. Sarkis, [1]Isabela C.A.C.Bordon

1 Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)

Av. Professor Lineu Prestes 2242

05508-000 São Paulo, SP

ludemar1@hotmail.com; jesarkis@ipen.br; isabella.bordon@gmail.com

ABSTRACT

Analysis of industrial lubricants is widely used for monitoring and predicting maintenance requirements in a broad range of mechanical systems. Laser induced breakdown spectroscopy has been used to evaluate the potentiality of the technique for the determination of metals in lubricating oils. Prior to quantitative analysis, the LIBS system was calibrated using standard samples containing the elements investigated (Cu, Cr, Fe, Pb, Mo and Mg). This study presents the usefulness of multivariate statistical techniques for evaluation and interpretation of large complex data sets in order to get more information about concentration of metals in oils lubricants is related to engine wear.

Keywords: multivariate statistical, oil sample, LIBS.

1. INTRODUCTION

Lubricant is any material which interposed between two attrition surfaces in order to reduce friction and wear. In addition, lubrication is also used to reduce oxidation and prevent rust from forming, to provide insulation in transformers; to transmit mechanical power into hydraulic machines, and sealing against dust, dirt and water [1].

Lubricant analysis is widely used for monitoring and predicting maintenance requirements in a broad range of mechanical systems. Oil monitoring is an integral part of the routine operations of industries such as marine and aviation, oil refineries, electric power generation, mining operations, public transport operators, the chemical processing industry and other industries that use heavy machinery. [2]

Therefore lubricating analysis can be used to forensic application related to rapidly provide evidence for adulteration practices against fraud for economic purposes.

Modern instrumental techniques, such as atomic absorption spectrometry [3,4,5,6,7], inductively coupled plasma-optical emission spectrometry [8], inductively coupled plasma-mass spectrometry [9,10,11,12,13], X-ray fluorescence spectrometry [14] and others have been used for the analysis.

Each technique suffers from some disadvantages: for example, AAS is slow and only allows measurements of one element at a time, AES instruments typically require liquid samples only, and XRF struggles to accurately determine the light elements. Most techniques require sample preparation and additional services, such as buffer gases and cooling water must also be available in the laboratory environment. [11]

Laser-induced breakdown spectroscopy (LIBS) is an analytical technique that has been extensively used for analysis of solid and liquid samples. The analysis of solid samples has always been the primary application; however, the analysis of liquids has also received a great deal of attention.

In this work, the concentration of Cu, Cr, Fe, Pb, Mo and Mg in 55 engine oils, which were collected at various mileage intervals, were analyzed by LIBS. Multivariate analysis techniques provide better options for interpreting of data sets. The quantification of the concentration of metals in lubricating oil can be achieved using the discriminant analysis (DA) method, which is a kind of multivariate analysis technique.

2. MATERIAL and METHODS

2.1. *Apparatus*

The experimental setup used in the current work is shown schematically in Fig. 1. The fundamental output of a High power, Q-switched, Nd:YAG laser with flat top beam profile with pulse width < 5 nsec (FWHM) and Rep Rate of 1 ~ 20 Hz; energy control with continuously variable optical attenuator, integrated laser energy monitoring; laser shutter automated for laser energy stabilization; laser pulse energy from 4.5 mJ/pulse to 100 mJ/pulse; laser spot size control from 5 to 250 microns; energy density >20 J/cm^2 at 213 nm (fluence based on laser spot sizes in the range of 30 ~ 150 micron); automated X-Y stage with 52 mm X 52 mm travel range and 0.2 micron resolution; automated Z stage with 26 mm travel range and 0.1 micron resolution; ablation spot targeting with red laser at 670 nm, automatic adjustment of sample height; LIBS detector with 6 channel CCD-based broadband spectrometers, integrated electronic pulse delay generator for gate delay adjustment from 50 nsec to 1 msec with 25 nsec step resolution, spectral range from 190 to 1040 nm.[15]

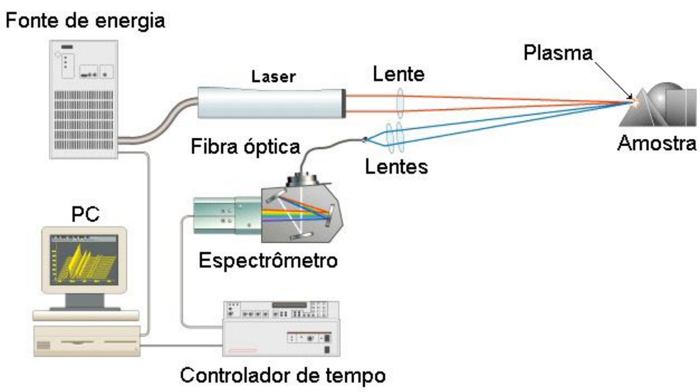

Fig.1. Experimental setups used for liquid LIBS. [16]

2.2.Sample preparation

Commercially available ConostanR S-21 blended oil standards [17], have been used for all calibrations reported in this work. Our S-21 oil set spanned the concentration range of 12,5–500 ppm for each analyzed element. The certified reference material (CRM) of wear metals in lubricating oils (1084th SRM) [18] obtained from the National Institute of Standards and Technology (NIST, Gaithersburg, MD) was used for validation of the methodology.

For LIBS analysis about 50 ml of each oil sample was collected in a dark bottle. Each oil sample were added dropwise in a filter paper (34 mm in diameter and 1.5 mm wide) commercially available. The filter papers were cut and arranged in all supports test Styrofoam so that the oil was not deposited on any surface below the paper, as showed in Fig.2. Approximately 0.02 g of oil were spreaded evenly over the surface. The samples were placed to dry in an oven at a temperature of 30 degrees for 15 minutes.

Fig. 2. Deposition of samples paper substrate using polystyrene as a support.

2.3.Statistical analysis

The number of classes was determined using the Sturges equation (Equation 01), based on Km values, where K is the number of classes and n the amount of data [19].

$$K = 1 + 3{,}322 \cdot \log(n) \qquad \text{eq. 01}$$

Statistical tests were performed using the software STATISTICA10 (Statsoft). The Kruskal- Wallis test was applied in order to identify statistical differences between the classes due to metal concentrations. Data were log-transformed and the discriminant canonical analysis was performed to determine which metal coefficients distinguished the classes and to identify any statistical similarity among data due to overlapping of statistical ellipses.

3. RESULTS AND DISCUSSION

3.1. Stuarges equation

A total of 55 samples were analyzed. The highest and the lowest Km values were 219,349 km and 5,540 km, respectively; therefore the observed range was 213,803 was observed. According to the Sturges equation, data were separated in 7classes based on the Km values. However, because the last two had a very small n, they were joined into 6 classes.

Table 1: Classes according to Sturges equation.

1	2	Lowest Km	Highest Km	n	**class**
>=	<	5540	36084	14	**A**
		36084	66628	9	**B**
		66628	97172	7	**C**
		97172	127716	7	**D**
		127716	158260	9	**E**
		158260	999999	9	**F**

3.2. KRUSKAL-WALLIS nonparametric test

Kruskal- Wallis test was applied and detected statistical differences ($p<0.05$). Significant differences between classes were detected by testing a *post hoc* multiple mean comparisons tests ($p <0.05$). These tests and boxplot graphs are presented, as followed (tables 2 -7; figures 3-8)

Table 2: Multiple Comparisons between the classes for Cu.

Depend.: Cu	Multiple Comparisons p values (2-tailed); Cu (Luana2_ POR CLASSE.sta) Independent (grouping) variable: CLASSE Kruskal-Wallis test: H (5, N= 55) =40.68344 p =.0000					
	A R:8.6071	B R:19.889	C R:32.000	D R:38.714	E R:36.556	F R:46.278
A		1.000000	0.024133	0.000737	0.000666	0.000001
B	1.000000		1.000000	0.295760	0.409882	0.007133
C	0.024133	1.000000		1.000000	1.000000	1.000000
D	0.000737	0.295760	1.000000		1.000000	1.000000
E	0.000666	0.409882	1.000000	1.000000		1.000000
F	0.000001	0.007133	1.000000	1.000000	1.000000	

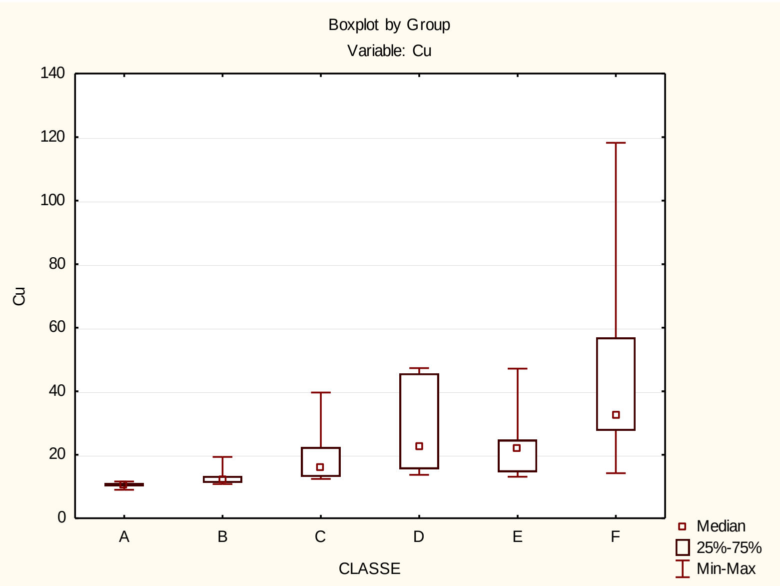

Figure 3: Boxplot for Cu ($\mu g.g^{-1}$) based on table 2.

Table 3: Multiple Comparisons between the classes for Cr.

Depend.: Cr	Multiple Comparisons p values (2-tailed); Cr (Luana2_ POR CLASSE.sta) Independent (grouping) variable: CLASSE Kruskal-Wallis test: H (5, N= 55) =30.63199 p =.0000					
	A R:12.500	B R:20.556	C R:30.286	D R:35.071	E R:36.000	F R:44.278
A		1.000000	0.247121	0.035073	0.008946	0.000052
B	1.000000		1.000000	1.000000	0.612819	0.025250
C	0.247121	1.000000		1.000000	1.000000	1.000000
D	0.035073	1.000000	1.000000		1.000000	1.000000
E	0.008946	0.612819	1.000000	1.000000		1.000000
F	0.000052	0.025250	1.000000	1.000000	1.000000	

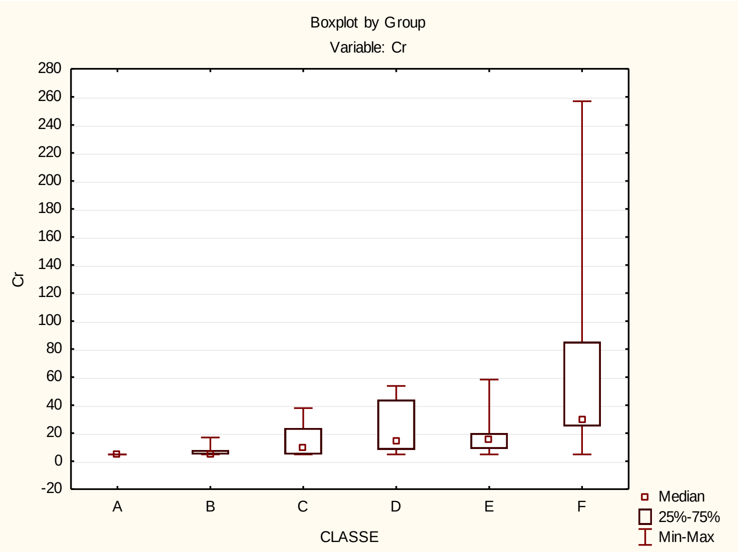

Figure 4: Boxplot for Cr (μg.g-[1]) based on table 3.

Table 4: Multiple Comparisons between the classes for Pb.

Depend.: Pb	Multiple Comparisons p values (2-tailed); Pb (Luana2_ POR CLASSE.sta) Independent (grouping) variable: CLASSE Kruskal-Wallis test: H (5, N= 55) =42.96921 p =.0000					
	A R:8.5714	B R:19.111	C R:32.286	D R:35.500	E R:37.833	F R:48.111
A		1.000000	0.020784	0.004234	0.000287	0.000000
B	1.000000		1.000000	0.635498	0.197619	0.001846
C	0.020784	1.000000		1.000000	1.000000	0.749746
D	0.004234	0.635498	1.000000		1.000000	1.000000
E	0.000287	0.197619	1.000000	1.000000		1.000000
F	0.000000	0.001846	0.749746	1.000000	1.000000	

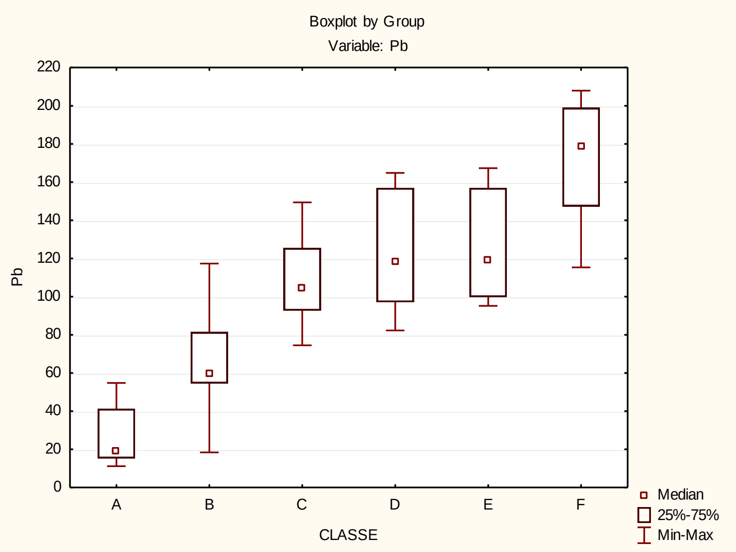

Figure 5: Boxplot for Pb (µg.g-[1]) based on table 4.

Table 5: Multiple Comparisons between the classes for Fe.

Multiple Comparisons p values (2-tailed); Fe (Luana2_ POR CLASSE.sta)
Independent (grouping) variable: CLASSE
Kruskal-Wallis test: H (5, N= 55) =41.05151 p =.0000

Depend.: Fe	A R:8.7857	B R:19.944	C R:30.143	D R:36.000	E R:39.389	F R:46.667
A		1.000000	0.059690	0.003644	0.000117	0.000000
B	1.000000		1.000000	0.701154	0.150515	0.006041
C	0.059690	1.000000		1.000000	1.000000	0.610441
D	0.003644	0.701154	1.000000		1.000000	1.000000
E	0.000117	0.150515	1.000000	1.000000		1.000000
F	0.000000	0.006041	0.610441	1.000000	1.000000	

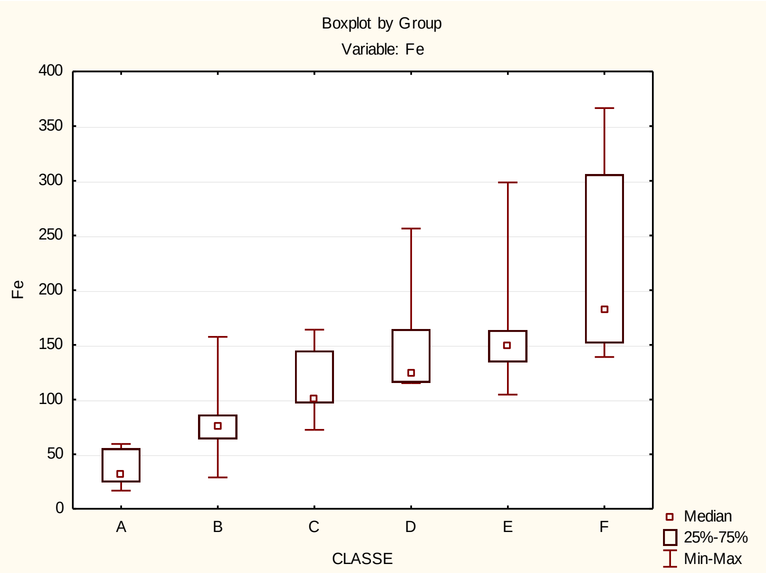

Figure 6: Boxplot for Fe (µg.g-[1]) based on table 5.

Table 6: Multiple Comparisons between the classes for Mo.

Depend.: Mo	Multiple Comparisons p values (2-tailed); Mo (Luana2_ POR CLASSE.sta) Independent (grouping) variable: CLASSE Kruskal-Wallis test: H (5, N= 55) =43.17299 p =.0000					
	A R:47.071	B R:36.500	C R:22.786	D R:25.357	E R:17.056	F R:6.8889
A		1.000000	0.015867	0.05118C	0.000174	0.000000
B	1.00000C		1.000000	1.00000C	0.15051E	0.001324
C	0.015867	1.000000		1.00000C	1.00000C	0.734373
D	0.05118C	1.000000	1.000000		1.00000C	0.332545
E	0.000174	0.150515	1.000000	1.00000C		1.000000
F	0.00000C	0.001324	0.734373	0.33254E	1.00000C	

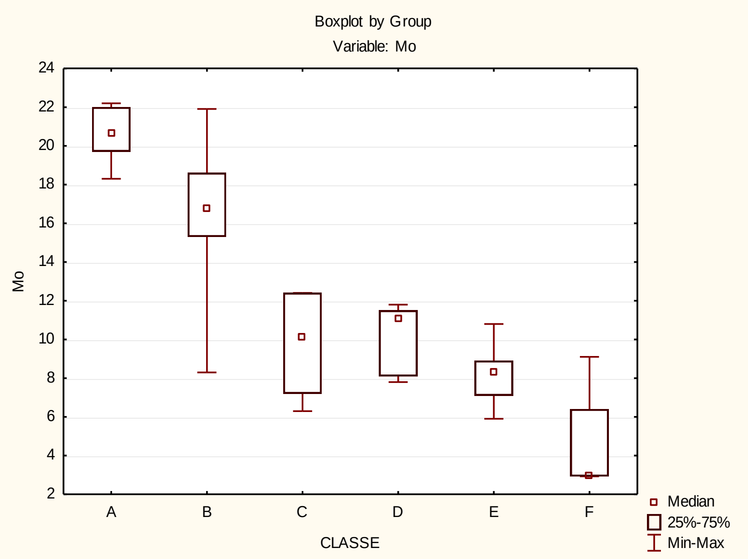

Figure 7: Boxplot for Mo (μg.g-[1]) based on table 6.

Table 7: Multiple Comparisons between the classes for Mg.

Depend.: Mg	Multiple Comparisons p values (2-tailed); Mg (Luana2_ POR CLASSE.sta) Independent (grouping) variable: CLASSE Kruskal-Wallis test: H (5, N= 55) =40.28670 p =.0000					
	A R:46.857	B R:36.667	C R:25.357	D R:21.643	E R:13.611	F R:11.389
A		1.000000	0.056143	0.010112	0.000018	0.000003
B	1.000000		1.000000	0.941533	0.034009	0.012252
C	0.056143	1.000000		1.000000	1.000000	1.000000
D	0.010112	0.941533	1.000000		1.000000	1.000000
E	0.000018	0.034009	1.000000	1.000000		1.000000
F	0.000003	0.012252	1.000000	1.000000	1.000000	

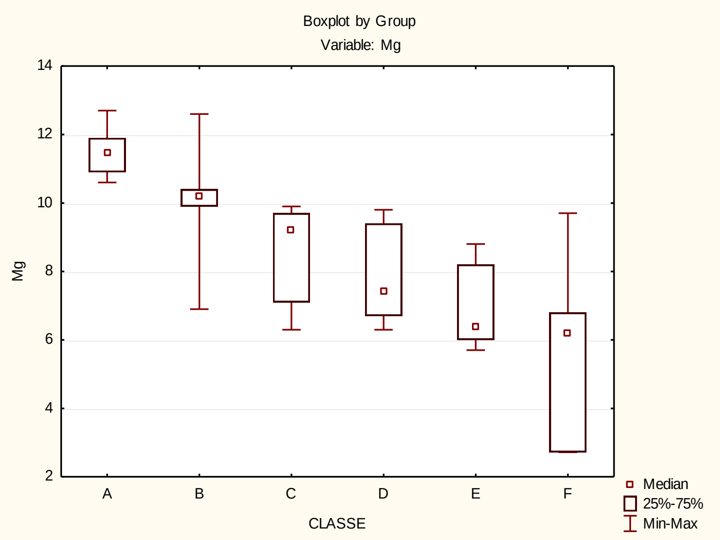

Figure 8: Boxplot for Mg (μg.g-1) based on table 7.

In Figures 3-8 we can see that there is an increased concentration of Cu, Cr, Pb, Fe, are directly related to the quality and wear of the parts constituting the engines, such as cylinders, pistons, gears, rings, shafts , oil pump, crankshaft, supports, etc. Thus, such concentrations tend to increase with the use of oil (20). And the decline in the concentration of Mo and Mg metals, come from the fact that these elements are added to lubricating oils as additives. The additives are degraded (that is the process that reduces the oil capacity to meet their functions) due to the different conditions that are submitted within the motor, as high temperatures, high speeds, corrosion, contamination, aging etc. (21).

3.3. Canonical discriminant analysis

For the discriminant analysis, it considered only the functions that met the following assumptions: 1) those that have p <0.05; and 2) those which have eigenvalue greater than or equal to 1 and / or 3) the individual variance is> or equal to 10%.The discriminant analysis using concentration data of the collected samples detected two significant functions (p<0.05) (Table 8). Scatter plot of functions is presented in Fig.9. The elements Pb and Mo presented the highest coefficients and contributed most to the discriminatory power of functions 1 and 2.

Table 8: Parameters of discriminant analysis.

Wilks' λ:: 0.15811		p<0,0000
Funções discriminantes	I	II
Autovalor	5.11325	0.5796
Variância acumulada	0.89	1.00
X^2	113.38*	22.85*
Graus de liberdade	10	4
Variáveis	Coeficientes padronizados da função discriminante	
Pb	-0.4271	-0.926
Mo	0.7102	-1.16
	Médias das variáveis canônicas	
A	2.8551	0.6309
B	1.2758	-0.4555
C	-0.7369	-0.5121
D	-0.6317	-1.0440
E	-1.3326	-0.3798
F	-3.3199	1.0643

They were considered most influential coefficients of the same order of magnitude and above 0.6 (60%). The function 1, who influenced the data were. All classes and the concentration of Pb 2 In the function, all classes and the concentration of Pb and Mo.

In the figure 9 below is the result of discrimination where we can see that there is a difference in the concentration of metals Km.

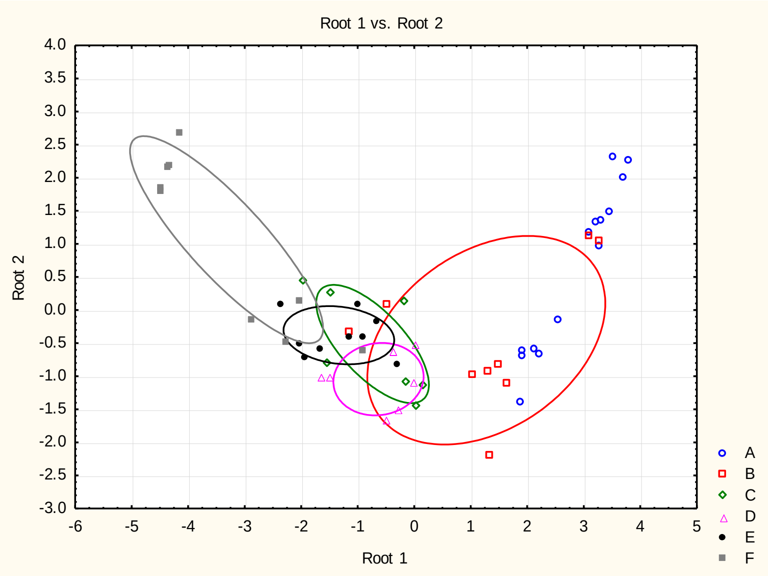

Figure 9: Discriminant function discriminant function I versus II.

In the figure 9 we can observe that is possible to perform the differentiation of cars groups although there was a correspondence between classes A-E and ellipses were overlapped. Only class F was distinguished.

4. CONCLUSIONS

The concentrations and distribution patterns of the wear metals considerably varied among the vehicles, which might be attributed to differences in the types of engine oil and the condition of the vehicle.

The use of sequential tools Statistics Stuarges equation, Kruskal-Wallis and Canonical discriminant analysis to analyze a large number of samples with multiple variables demonstrated to be effective for evaluation and interpretation of large complex data, helping in the interpretation of how the concentration of metals in oils lubricants is related to engine wear.

This work can be used in the future for expertise and evaluation of engine wear.

5. ACKNOWLEDGMENTS

The authors wish to acknowledge Chemical Institute of the University of Sao Paulo for the collaboration in this work.

6. REFERENCES

1 . PETROBRAS. Site < www.petrobras.com.br>. Accessed in Jun of 2013.

2. Pavel Yaroshchyk, Richard J.S. Morrison, Doug Body, Bruce L. Chadwick. **Quantitative determination of wear metals in engine oils using LIBS: The use of paper substrates and a comparison between single- and double-pulse LIBS.** Spectrochimica Acta Part B: Atomic Spectroscopy, Volume 60, Issues 7–8, 3. August 2005, Pages 1482 – 1485 .

3. Zmozinski Ariane V.; de Jesus Alexandre; Vale Maria G. R.; et al. **Determination of calcium, magnesium and zinc in lubricating oils by flame atomic absorption spectrometry using a three-component solution.** TALANTA. Volume: **83**. Issue: **2**. Pages: **637-643**. Published: **DEC 15 2010**.

4. Absorption spectrometry using least-square background correction and internal standardization. Analytical letters. Volume: **44**. Issue: **12**. Pages: **2150-2161**. Published: **2011**.

5. Christiane Duyck, Norbert Miekeley, Carmem L. Porto da Silveira, Ricardo Q. Aucélio, Reinaldo C. Campos, Patrícia Grinberg, Geisamanda P. Brandão. **The determination of trace elements in crude oil and its heavy fractions by atomic spectrometry**. Review Article *Spectrochimica Acta Part B: Atomic Spectroscopy, Volume 62, Issue 9, September 2007, Pages 939-95.*

6. Guidroz JM; Sneddon J. **Fate of vanadium determined by nitrous oxide-acetylene flame atomic absorption spectrometry in unburned and burned Venezuelan crude**

oil . MICROCHEMICAL JOURNAL. Volume: **73**. Issue: **3**. Pages: **363-366.** Published: **DEC 2002.**

7. Smith JH; Sneddon J. **Determination of zinc by flame atomic absorption spectrometry in unburned and burned venezuelan crude oil**. ANALYTICAL LETTERS. Volume: **34**. Issue: **11**. Pages: **1949-1954**. Published: **2001.**

8. Roseli M. de Souza, André L.S. Meliande, Carmem L.P. da Silveira, Ricardo Q. Aucélio. **Determination of Mo, Zn, Cd, Ti, Ni, V, Fe, Mn, Cr and Co in crude oil using inductively coupled plasma optical emission spectrometry and sample introduction as detergentless microemulsions**. Chemistry Department, Pontifícia Universidade Católica do Rio de Janeiro (PUC-RJ), Rio de Janeiro 22453-900, Brazil. Available online 17 February 2006.

9. De Souza Jefferson R.; Dos Santos Eider Fernando; Duyck Christiane B.; et al. **Comparison of parallel flow and concentric micronebulizers for elemental determination in lubricant oil, residual fuel oil and biodiesel by Inductively Coupled Plasma Optical Emission Spectrometry**. SPECTROCHIMICA ACTA PART B-ATOMIC SPECTROSCOP. Volume: **66** Issue: **5** Pages: **356-361**. Published: **MAY 2011**.

10. Estelle Ricard & Christophe Pécheyran & Georgia Sanabria Ortega & Alain Prinzhofer & Olivier F. X. Donard. **Direct analysis of trace elements in crude oils by high-repetition-rate femtosecond laser ablation coupled to ICPMS detection**. Analytical and Bioanalytical Chemistry. Published on the web on February 2011.

12. A. V. Soin*a,b*, T. A. Maryutina*a,b*, T. V. Arbuzova*b*, and B. Ya. Spivakov*a.* Sample Preparation in the **Determination of Metals in Oil and Petroleum Products by ICP MS.** Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences,ul. Kosygina 19, Moscow, 119991 Russia**,** United Research and Development Centre, Leninsky pr. 55/1 build. 2, Moscow, 119333, Russia. Received July 20, 2009; in final form, October 21, 2009.

13. Jens Heilmann, Sergei F. Boulyga and Klaus G. Heumann. **Development of an isotope dilution laser ablation ICP-MS method for multi-element determination in crude and fuel oil samples.** Published on the web 6th February 2009.

14. Zararsiz A; Kirmaz R; Arikan P. **Determination of wear metals in used lubricating oils by X-ray fluorescence**. Nuclear instruments & methods in physics research section b-beam interactions with materials and atoms. Volume: 108 Issue: 4 Pages: 385-388 Published: MAR 1996**.**

15. Training Handout. Applied Spectra. Fremont. 2010.

16. Figure adapted from < http://www.appliedphotonics.co.uk.>. Accessed in 03/01/14.

17. Site < http://www.conostan.com/products/metals.asp>. Accessed in Oct.2014

18. Site < http://www.nist.gov/srm/>. Accessed in Feb.2014

19. VIEIRA, S. **Introdução à Bioestatística**. 2.ed. Rio de Janeiro: Campus, 1991.

20. Silveira, E. L. C.; Caland, L. B.; Moura, C. V. R.; Moura, E. M. Determinação de contaminantes em óleos lubrificantes usados e em esgotos contaminados por esses lubrificantes. **Quim. Nova,** v. *29*, p. 1193, 2006.

21. Ekanem, E. J.; Lori, J. A.; Thomas, S. A.; The determination of wear metals in used lubricating oils by flame atomic absorption spectrometry using sulphanilic acid as ashing agent. **Talanta**, v. *44*, p. 2103, 1997.