



FTIR TECHNOLOGY AND MULTIVARIATE ANALYSIS FOR ENGINE OIL QUALITY PREDICTION

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- Objective
- Importance of gas engine control
- What is Base Number?
- Base Number measurement
- Data pretreatment
- PLS1 Algorithm
- Conclusions
- Future works



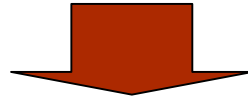
Base Number (BN) is one of the basic parameters to control an engine lubricating oil. The method usually applied to analyse lubricating oil BN is **highly toxic** for humans and environment, **expensive** and **time consuming**. **Multivariate analysis** on **Fourier Transform InfraRed (FT-IR)** spectroscopy results has led to a new method to **quantify BN in engine oils**.



IMPORTANCE OF GAS ENGINES CONTROL



- *Gas Engines* are very used in Cogeneration plants (CHP)
- *Work conditions*: high loads & temperature, long period of time. Lubricated components (bearing, gears, seals) in **DANGER**



There's no pre-established period of oil change.
A correct maintenance must be applied



IMPORTANCE OF GAS ENGINES CONTROL



Oil condition	Primary cause	Due to
<ul style="list-style-type: none"> Low BN/High AN 	<ul style="list-style-type: none"> Contamination with acids 	<ul style="list-style-type: none"> Corrosive components Oxidation/nitration product
<ul style="list-style-type: none"> Oxidation, nitration 	<ul style="list-style-type: none"> High Temperature Improper combustion Over-extended interval 	<ul style="list-style-type: none"> Excessive peak power Inadequate cooling High blow-by Incorrect spark timing Very lean mixture, oxidation Slightly lean-nitration
<ul style="list-style-type: none"> Viscosity increase 	<ul style="list-style-type: none"> Oxidation, nitration Contamination Over extended drain interval 	<ul style="list-style-type: none"> High temperature, improper combustion Water, blow-by
<ul style="list-style-type: none"> High insolubles 	<ul style="list-style-type: none"> Contamination 	<ul style="list-style-type: none"> Oxidation, nitration, wear elements Dirt, dust, filtration problems
<ul style="list-style-type: none"> Water present 	<ul style="list-style-type: none"> Condensation, leakage 	<ul style="list-style-type: none"> Low temperature operation, blow-by Exhausted restriction, faulty seals, heat gasket. Cracked liner, cracked head Oil cooler leak
<ul style="list-style-type: none"> High trace elements 	<ul style="list-style-type: none"> Wear, contamination 	<ul style="list-style-type: none"> High load, fuel impurities Corrosion, coolants Air/oil filters

IMPORTANCE OF GAS ENGINES CONTROL



- In relation to their ash content, according to ASTM D-874, the oils are classified:

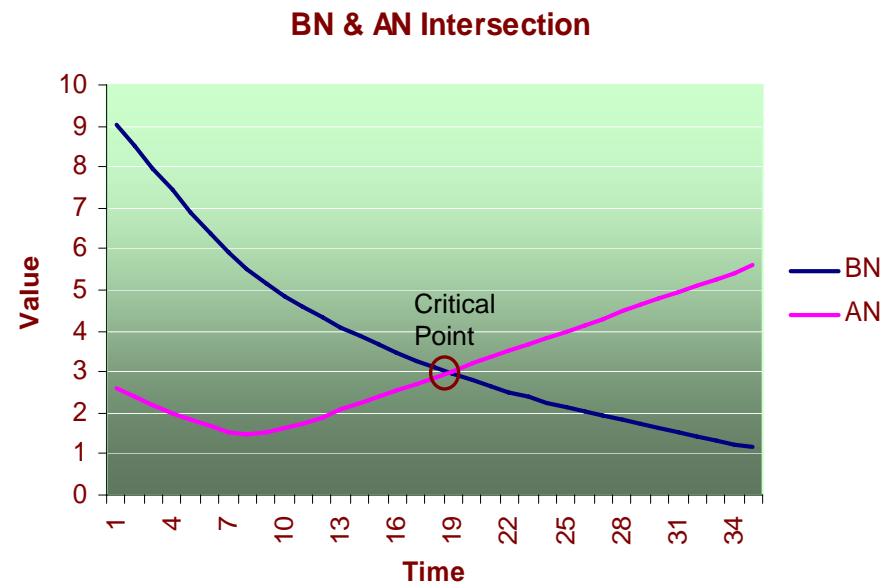
Additive type	% Additive	Engine
Ashless	< 0.1%	(BN 1-3) 2S natural gas
Low ash content	0,1-0,5%	(BN 3-6) SI natural gas
Medium ash content	0,5-1%	(BN 5-10) SI DF natural gas
High ash content	>1%	(BN 10+) SI-DF landfill gas

Higher ash content  higher BN

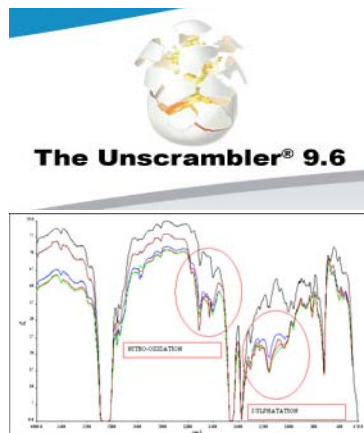
WHAT IS BASE NUMBER?

- Oil degradation indicator.
- It represents the oil alkalinity value.
- During the aging process, BN tends to diminish.
- Degraded oil: 50% original BN value.

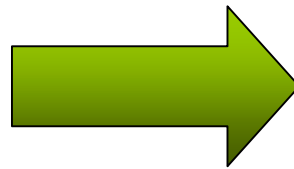
BN - AN
Interception
Critical Point



- Basic Number (BN) is an oil aging indicator.
- Until now, BN has been gotten from lab analytical methods (quite expensive).
- We have developed a new method using:
 - **Spectroscopy (MIR).**
 - **Chemometrics**
- This new method has been developed for gas engine oils.



Unscrambler



Spectroscopy



BN = OIL STATUS

IR SPECTRA DATA

- Spectrometer: FTIR Perkin Elmer Spectrum ONE
- 4000-600 cm^{-1} range, by using SeZn cells



BN DATA:



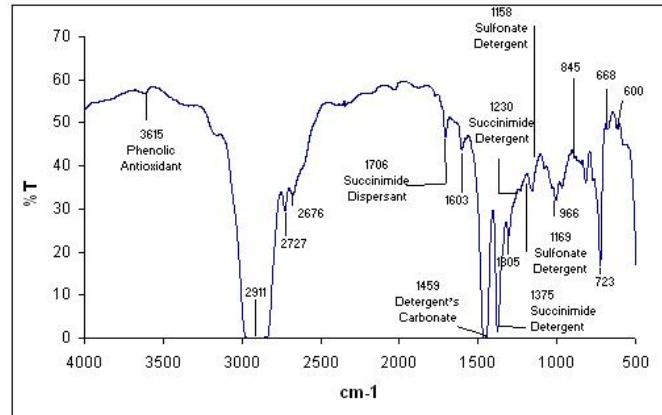
- BN titroprocessor Mettler-Toledo DL50 + Quanto
- D2896-03 Standard Test Method for Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration
- Method uncertainty: $\pm 0.04 \text{ mgKOH/g}$.



BN MEASUREMENT



WHY FTIR?- Bands related with to oil alkalinity



Acid Number (AN)	Base Number (BN)
Water content (3520 -3220 cm^{-1})	Phenolic antioxidant (3670 -3627 cm^{-1})
C=O Aldehydes carboxylic acids (1850 -1612 cm^{-1})	Detergent's carbonate (1520 -1500 cm^{-1})
C=O Conjugated ketones (1750 -1700 cm^{-1})	Succinimide detergent (1240 -1215 cm^{-1})
C=O Aldehydes, carboxylic acids (1690 -1640 cm^{-1})	Sulfonate detergent (1180 -1145 cm^{-1})
C-O Esters (1175 -1135 cm^{-1})	Zinc dialkyl dithiophosphate- ZDDP (1050 -970 cm^{-1})
	Zinc dialkyl dithiophosphate- ZDDP (690 -620 cm^{-1})



BN MEASUREMENT



FTIR SPECTROSCOPY

No sample preparation required

Time of analysis: 2 minutes

No hazardous reactives (only heptane for cleaning)

Small quantity of waste



BASE NUMBER (TITRATION)

Sample preparation required

Clorobenzene

Acetic acid

Hazardous waste





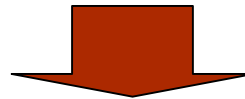
DATA PRETREATMENT



1057 samples of different type of gas engine oils

- BP ENERGOL IC DG 40
- BP ENERGOL IC DG 40S
- MOBIL PEGASUS 705
- ENERGAS NG5

The parameter to be predicted is the oil BN variation with regard to the fresh oil

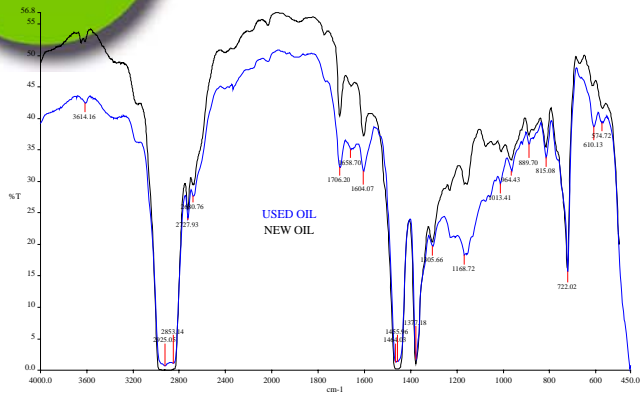


1. Conversion to absorbance
2. Subtract the spectra of fresh oil

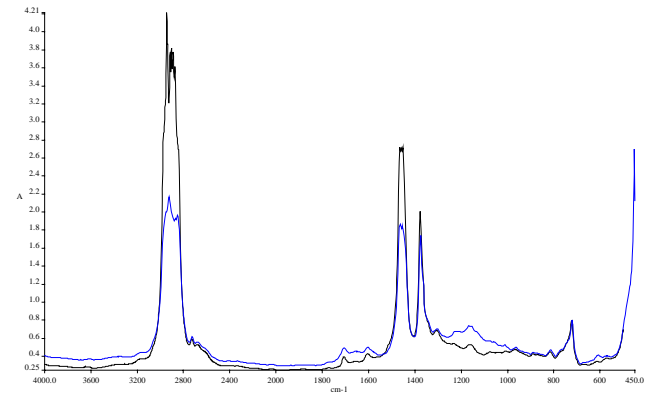
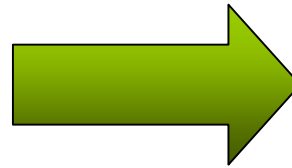
The aim is to obtain a correlation between the spectra variation and the BN variation



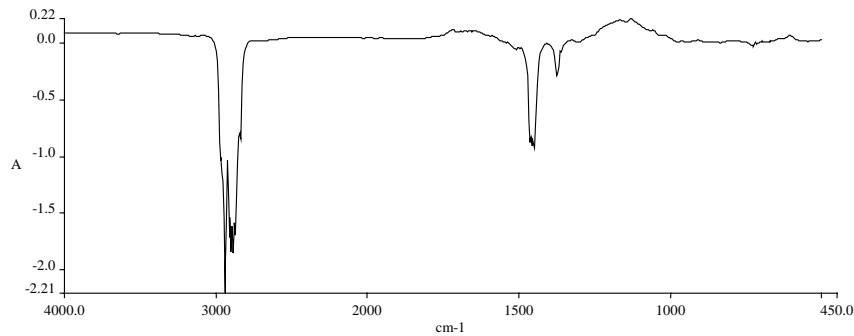
DATA PRETREATMENT



Absorbance

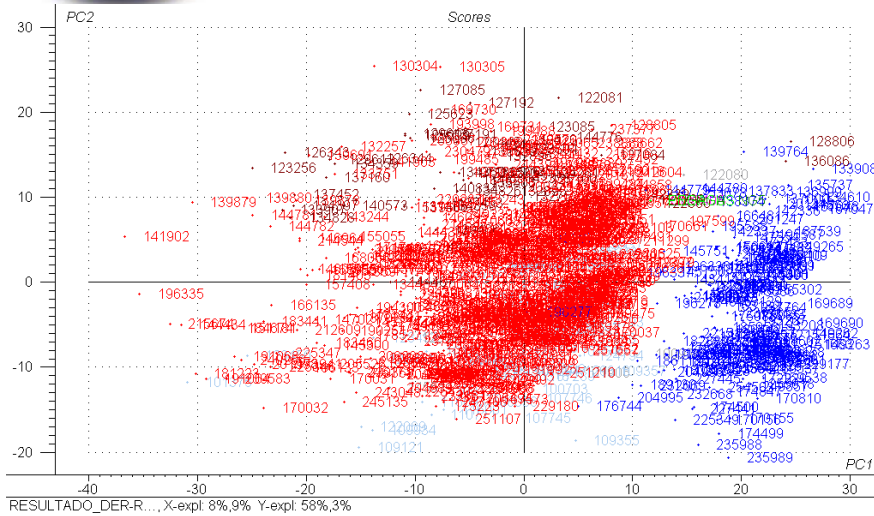


Reference subtraction



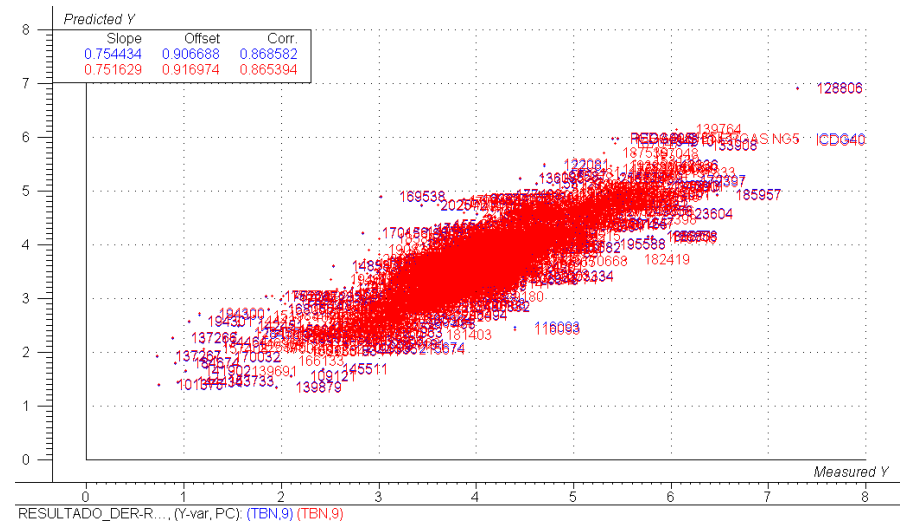


PLS1 ALGORITHM



SCORES DIAGRAM SHOWS THAT THERE ARE TWO DIFFERENT GROUPS OF OILS AND THEIR BEHAVIOUR IS DIFFERENT

PLS REGRESSION RESULTS
Without outliers detection
Slope: 0.75 Offset: 0.90 R=0.86

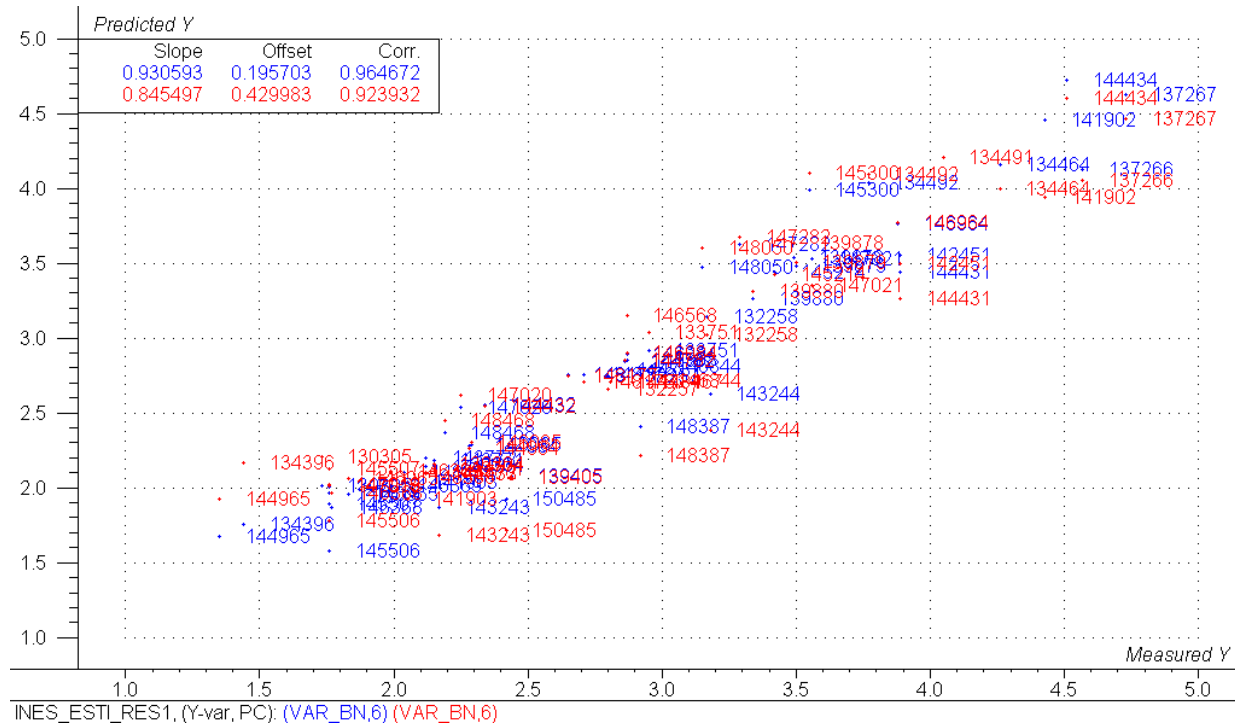




PLS1 ALGORITHM



FINAL RESULTS



After Removing outliers
 Slope: 0.93 Offset: 0.19 R=0.96



PLS1 ALGORITHM



VALIDATION

BN Method uncertainty:
 ± 0.04 mgKOH/g.

NEW Method uncertainty:

SAMPLE	PREDICTED	OBSERVED	RESIDUAL
146369	2.012	1.99	0.021
141903	2.036	2.05	-0.014
144964	2.279	2.280	-0.001
146085	2.286	2.289	-0.003
148178	2.753	2.710	0.043
144782	2.844	2.86	-0.016
133751	2.917	2.95	-0.033
132258	3.138	3.17	-0.032
139880	3.26	3.34	-0.08
134464	4.161	4.26	-0.0099



CONCLUSIONS



- Good results for BN prediction with one type of oil.
- An improvement is needed for the BN prediction of all types of engine oils.
- Advantages of the new method.

Cost estimation

	Time	Materials	Labour	Wastes	Cost
Lab method	10 min	solvents	Sample and solvent preparation	Acids, chlorinated wastes	60€
New method	<2 min	null	null	<10gr oil	2€



FUTURE WORKS



FUTURE WORK

- On-line controlling of the lubricant by means of FTIR
- Improvement of BN prediction

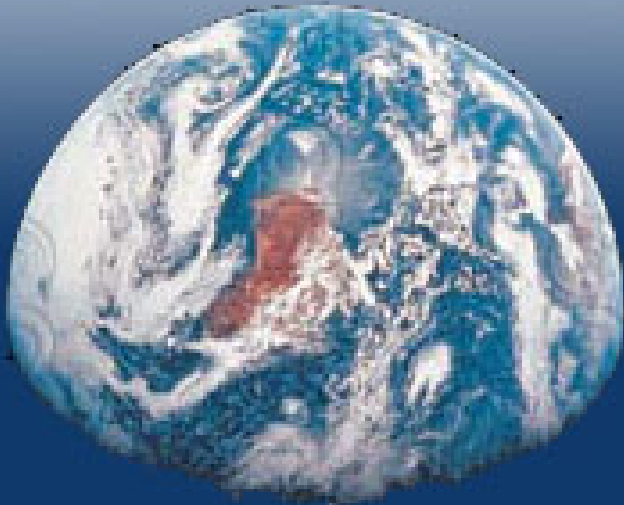


AFTER DE SPECTROSCOPIC DATA PRETREATMENT COURSE.....

how to improve our method?

- Applying 2nd derivative to spectral data
- Selecting the best bands to BN prediction

Thanks for your attention



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