FTIR TECHNOLOGY AND MULTIVARIATE ANALYSIS FOR ENGINE OIL QUALITY PREDICTION

E.Aranzabe, E. Gorritxategi, A. Arnaiz, I. Garmendia (TEKNIKER)

N. Etxebarria, G. Arana (EHU-UPV)

PRESENTATION STRUCTURE

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

OBJECTIVE

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
▪Low BN/High AN	▪Contamination with acids	▪Corrosive components ▪Oxitation/nitration product
▪Oxiditation,nitration	▪High Temperature ▪Improper combustion ▪Over-extended interval	▪Excesive peak power ▪Inadequade cooling ▪High blow-by ▪Incorrect spark timing ▪Very lean mixture,oxidation ▪Slighly lean-nitration
▪Viscosity increase	▪Oxidation,nitration ▪Contamination ▪Over extended drain interval	▪High temperature,improper combustion ▪Water, blow-by
▪High insolubles	▪Contamination	▪Oxidation, nitration, wear elements ▪Dirt, dust, filtration problems
▪Water present	▪Condesation, leakage	▪Low temperature operation, blow-by ▪Exhausted restriction, faulty seals,heat gasket. Craked liner,crackeed head ▪Oil cooler leak
▪High trace elements	▪Wear,contamination	▪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:

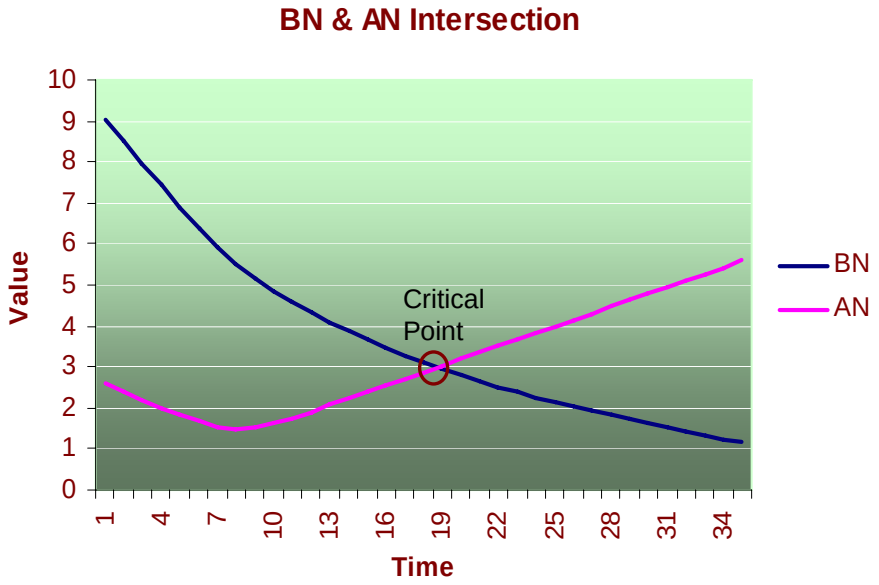
Additive type	% Additive	Engine
Ashless	< 0.1%	(BN 1-3) 2S natural gas
Low ash content	0,1-0,5%	(BN 3-6) SI natural gas
Medium ash content	0,5-1%	(BN 5-10) SI DF natural gas
High ash content	>1%	(BN 10+) SI-DF landfill gas

Higher ash content → higher BN

WHAT IS BASE NUMBER?

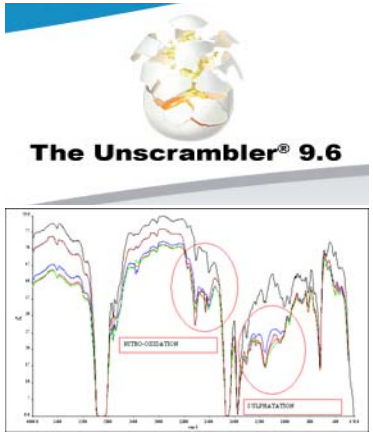
- Oil degradation indicator.
- It represents the oil alkalinity value.
- During the aging process, BN tends to diminish.
- Degraded oil: 50% original BN value.

BN - AN Interception Critical Point



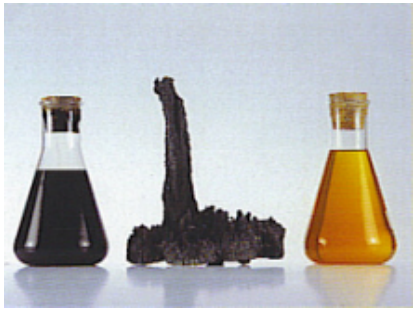
BN MEASUREMENT

- 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

BN MEASUREMENT

IR SPECTRA DATA

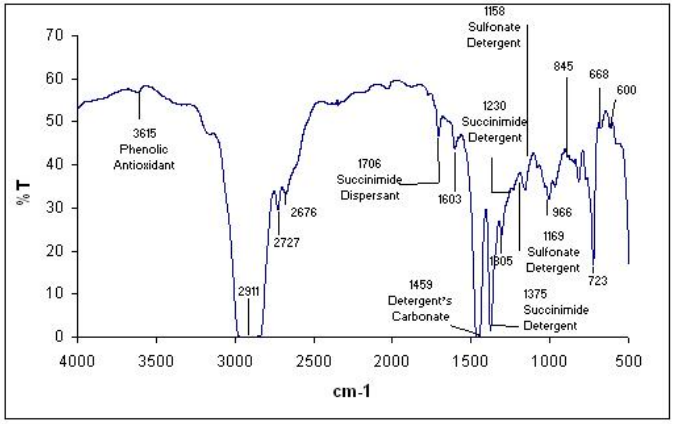
- Spectrometer: FTIR Perkin Elmer Spectrum ONE
- 4000-600 cm-1 range, by using SeZn cells

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: ±0.04 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

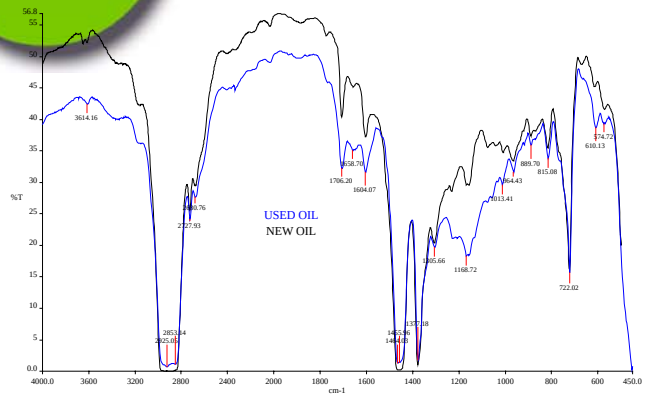
- BP ENERGOL IC DG 40
- BP ENERGOL IC DG 40S
- MOBIL PEGASUS 705
- ENERGAS NG5

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

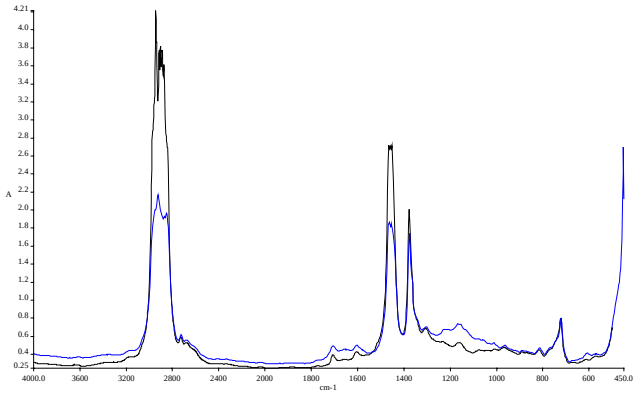
1. Conversion to absorbance
2. Substract the spectra of fresh oil

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

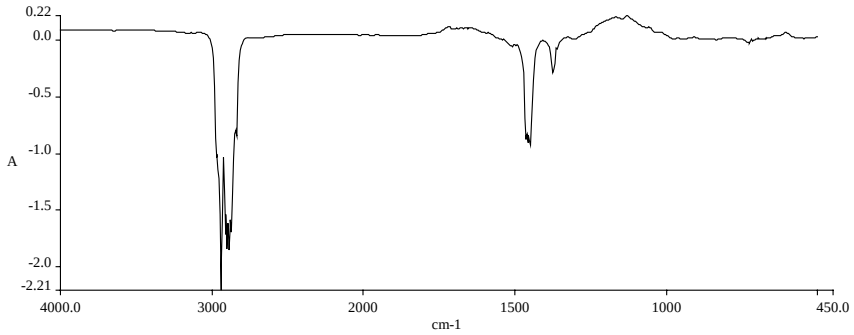
DATA PRETREATMENT



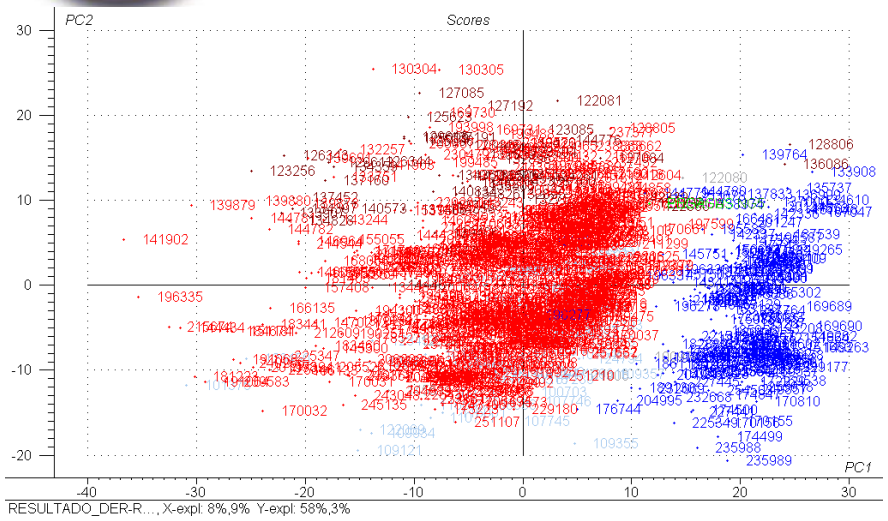
Absorbance



Reference substraction

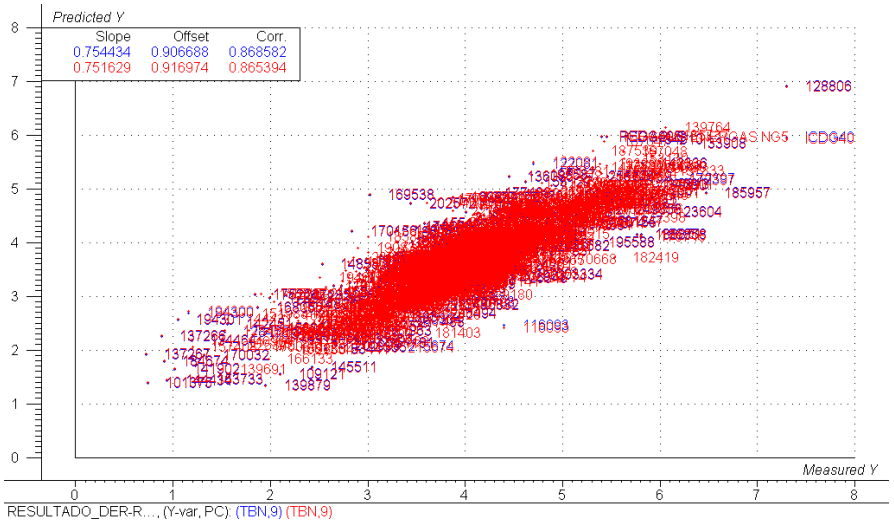


PLS1 ALGORITHM



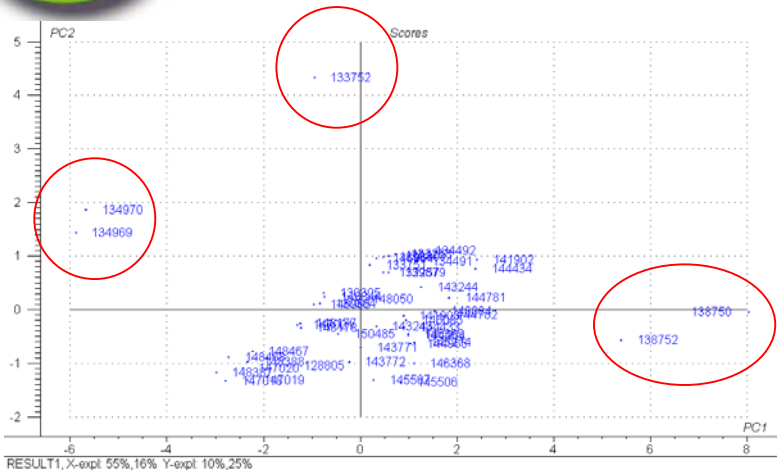
SCORES DIAGRAM SHOWS THAT THERE ARE TWO DIFFERENT GROUPS OF OILS AND THEIR BEHAVIOUR IS DIFFERENT

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



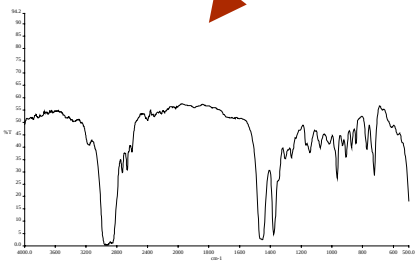
DETECTION OF OUTLIERS

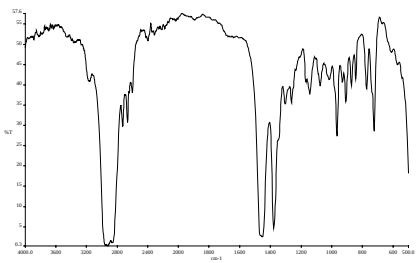
ONLY ONE TYPE OF OIL SELECTED

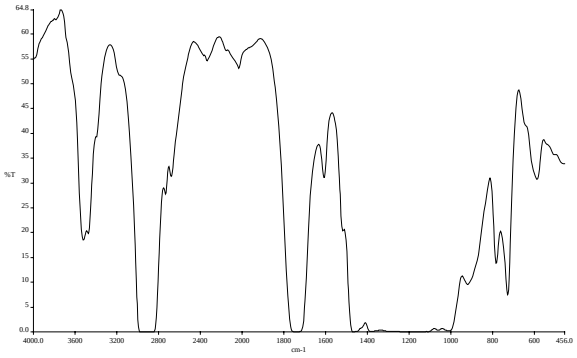


OUTLIERS CAUSED BY

- INSTRUMENT ERROR



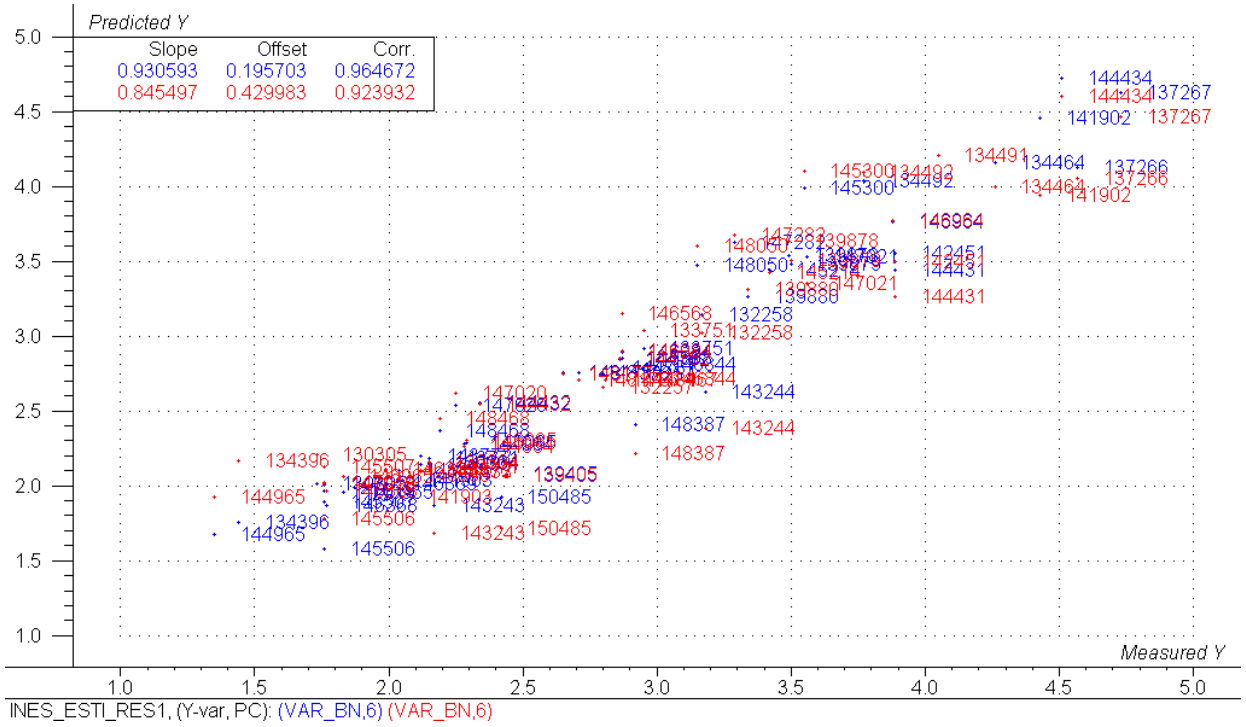




- THE OIL WAS NOT THE ASSUMED ONE

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

FUTURE WORKS

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

Estíbaliz Aranzabe
earanzabe@tekniker.es