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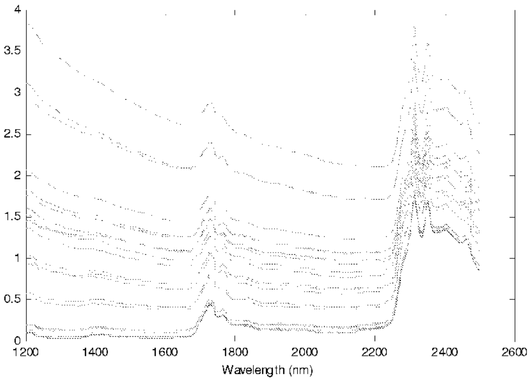
(54) Title: MONITORING OIL CONDITION AND/OR QUALITY, ON-LINE OR AT-LINE, BASED ON CHEMOMETRIC DATA ANALYSIS OF FLOURESCENCE AND/OR NEAR INFRARED SPECTRA

Fig. 1



(57) Abstract: The present invention relates to a method and a device for monitoring oil condition and/or quality based on fluorescence and/or NIR spectra as well as laboratory reference measurements on a set of oil samples. Through the use of chemometric data analysis (i.e. multivariate data analysis) the spectroscopic signals and patterns will be correlated to the laboratory reference measurements that describe the condition and/or quality of the oil. Based on this relation it is possible to predict the reference measurements and/or conditions of a new oil sample based solely on a fluorescence and/or NIR spectrum of the sample.

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Monitoring oil condition and/or quality, on-line or at-line, based on chemometric data analysis of fluorescence and/or near infrared spectra.

The present invention relates to a method and a device for monitoring oil condition and/or quality based on fluorescence and/or NIR spectra as well as laboratory reference measurements on a set of oil samples. Through the use of chemometric data analysis (i.e. multivariate data analysis) the spectroscopic signals and patterns will be correlated to the laboratory reference measurements that describe the condition and/or quality of the oil. Based on this relation it is possible to predict the reference measurements and/or conditions of a new oil sample based solely on a fluorescence and/or NIR spectrum of the sample.

This makes it possible to implement a device and a method that will work both on-line, by measuring directly in an oil stream, and at-line, where a collected sample is measured in an instrument placed close to the place of sampling.

Background

US 2007/0187617 discloses a method for monitoring the oxidation of oil samples by exposing the sample to ultraviolet irradiation and detecting in 2 narrow wavelength ranges the emitted fluorescence. The ratio between the intensity of the fluorescence emitted in the different wavelength ranges changes as a result of the oxidation of the oil, and by tracking the value of this ratio the quality of the oil can be monitored. This method only derives information from a small fraction of the wavelength range emitted from the oil sample. Furthermore, this method has limited used for analyzing unknown samples.

Other prior art techniques for detecting the content of water in oil rely on the scattering of light on water. Such techniques are sensitive to the scattering of light on for example air bubbles or other impurities, and do hence not provide a reliable measure of the water content in the sample.

Summary

It is an object of the present invention to provide a reliable method capable of predicting quality parameters of oil samples with unknown properties and/or classifying said samples in a system not requiring any drying, enrichment or concentration of the sample before determining the quality parameter and/or class, to which the sample belong.

This is possible by subjecting the sample to fluorescent and/or near infrared (NIR) spectroscopy or variants thereof, and analyzing the detected light transmitted through and/or emitted from and/or reflected from the oil sample, whereby samples may be classified. This classification and monitoring can be performed with a minimum of sample preparation if any at all.

Thus in a first aspect the present invention relates to a method of training a system for characterising an oil sample, said method comprising the steps of

a) providing a batch of oil samples having a predetermined content for training the system to recognise at least one characteristic of the sample,

b) exposing an oil sample from said batch to electromagnetic radiation within a predetermined range of wavelengths,

c) determining at least one physical spectroscopic parameter of electromagnetic radiation transmitted through and/or reflected from and/or emitted from the oil sample from said batch,

d) repeating step b) to c) until the at least one physical spectroscopic parameter of all oil samples of said batch have been determined,

e) performing data processing of the obtained physical spectroscopic parameters thereby obtaining data variables,

f) performing a multivariate data analysis of the obtained data variables obtaining model parameters describing the variation of the data variables,

g) obtaining characterisation information related to each oil sample from said batch.

In another aspect the present invention relates to a system for characterising an oil sample, said system comprising:

a) a sample domain for comprising the oil sample,

b) means for exposing the oil sample in the sample domain to electromagnetic radiation,

c) detecting means for recording at least one physical spectroscopic parameter of electromagnetic radiation transmitted and/or reflected and/or emitted from the sample,

d) computing means for performing data analysis of the at least one physical spectroscopic parameter, obtaining at least one data variable,

e) storage means for storing the at least one obtained data variable,

f) storage means for storing at least one latent variable and/or at least one multivariate model and/or at least one characterisation information of a trained prediction and/or classification system,

g) processing means for providing at least one latent variable from the at least one obtained data variable of the sample,

h) means for correlating the at least one latent data variables from the sample with latent variables of said trained system, thereby obtaining a characterisation of the oil sample, e.g. quantitative parameter predictions and/or at least one class to which the sample belongs, and

i) means for displaying the characterisation.

In a third aspect, the invention relates to a method for characterising an oil sample, comprising:

a) obtaining the oil sample,

b) exposing the oil sample to electromagnetic radiation,

c) determining at least one physical spectroscopic parameter of light transmitted and/or reflected and/or emitted from the oil sample,

d) performing data processing of the obtained at least one physical spectroscopic parameter obtaining at least one data variable,

e) storing the obtained at least one data variable,

f) providing at least one latent variable from data variables of the sample,

g) obtaining at least one latent variable from a trained prediction and/or classification system,

h) correlating latent data variables from the sample with latent variables of the trained system, to obtain quantitative predictions and/or quality predictions and/or at least one characterisation class of the sample, and

i) displaying the quantitative predictions and/or quality predictions and/or at least one characterisation class of the sample.

The method is preferably carried out in a system trained according to the present invention.

In a forth aspect, the invention relates to a system for the measurement of TBN (Total Base Number) and water in new and used lubricants, comprising

a) a sample domain for comprising an oil sample,

b) means for exposing the oil sample in the sample domain to electromagnetic radiation,

c) detecting means for recording at least one physical spectroscopic parameter of electromagnetic radiation transmitted and/or reflected and/or emitted from the sample,

d) computing means for performing data analysis of the at least one physical spectroscopic parameter, obtaining at least one data variable,

e) storage means for storing the at least one obtained data variable,

f) storage means for storing at least one latent variable and/or at least one multivariate model and/or at least one characterisation information of a trained prediction and/or classification system,

g) processing means for providing at least one latent variable from the at least one obtained data variable of the sample,

h) means for correlating the at least one latent data variables from the sample with latent variables of the trained system, thereby obtaining a characterisation of the oil sample, e.g. quantitative parameter predictions and/or at least one class to which the sample belongs, and

i) means for displaying the characterisation.

In a fifth aspect, the invention relates to a prediction and/or classification system for on-line and/or at-line monitoring of hydraulic oil and/or machine oil comprising

a) a sample domain for comprising an oil sample,

b) means for exposing the oil sample in the sample domain to electromagnetic radiation,

c) detecting means for recording at least one physical spectroscopic parameter of electromagnetic radiation transmitted and/or reflected and/or emitted from the sample,

d) computing means for performing data analysis of the at least one physical spectroscopic parameter, obtaining at least one data variable,

e) storage means for storing the at least one obtained data variable,

f) storage means for storing at least one latent variable and/or at least one multivariate model and/or at least one characterisation information of a trained prediction and/or classification system,

g) processing means for providing at least one latent variable from the at least one obtained data variable of the sample,

h) means for correlating the at least one latent data variables from the sample with latent variables of the trained system, thereby obtaining a characterisation of the oil sample, e.g. quantitative parameter predictions and/or at least one class to which the sample belongs, and

i) means for displaying the characterisation.

In a sixth aspect, the invention relates to a prediction and/or classification system for on-line and/or at-line monitoring of hydraulic oil and/or machine oil comprising

a) An optical probe for exposing oil in-situ to electromagnetic radiation,

b) detecting means for recording at least one physical spectroscopic parameter of light transmitted and/or reflected and/or emitted from the sample,

c) computing means for performing data analysis of the at least one physical spectroscopic parameter, obtaining at least one data variable,

d) storage means for storing the at least one obtained data variable,

e) storage means for storing at least one latent variable and/or at least one multivariate model and/or at least one characterisation information of a trained prediction and/or classification system,

f) processing means for providing at least one latent variable from the at least one obtained data variable of the sample,

g) means for correlating the at least one latent data variables from the sample with latent variables of the trained system, thereby obtaining a characterisation of the oil sample, e.g. quantitative parameter predictions and/or at least one class to which the sample belongs, and

h) means for displaying the characterisation.

Description of Drawings

Figure 1:	NIR spectra from oil samples
Figure 2:	Laboratory value versus the value predicted by the chemometric model and NIR spectroscop for water
Figure 3:	Laboratory value versus the value predicted by the chemometric model and NIR spectroscop for viscosity at 40 degrees
Figure 4:	Laboratory value versus the value predicted by the chemometric model and NIR spectroscop for TAN,
Figure 5:	Laboratory value versus the value predicted by the chemometric model and NIR spectroscop for TBN

Figure 6: Laboratory value versus the value predicted by the chemometric model and NIR spectroscop for Silicon

Figure 7: Emission spectra at 230 nm excitation for several oil samples.

Figure 8: Classification of new and used samples.

Figure 9: Extended Canonical Variates for new and old oil samples

Figure 10: Laboratory value versus the value predicted by the chemometric model and NIR spectroscop for viscosity. PLS model on Main engine oil in use (group 1) and Main engine new oil (group 2) for KV100. PLSC is 6. Data is preprocessed with Savitzky-Golay (w =9, O=2, d=1).

Figure 11: Laboratory value versus the value predicted by the chemometric model and NIR spectroscop for density. PLS model on Main engine oil in use and Main engine new oil (group 1 and 2) for Density. PLSC is 7. Data is preprocessed with Savitzky-Golay (w =9, O=2, d=1).

Figure 12: Laboratory value versus the value predicted by the chemometric model and NIR spectroscop for TAN. PLS model on Main engine oil in use and Main engine new oil (group 1 and 2) for TAN177. PLSC is 3. The data is preprocessed with Savitzky-Golay (w =9, O=2, d=1).

Figure 13: Laboratory value versus the value predicted by the chemometric model and NIR spectroscop for TBN. PLS model on Main engine oil in use and Main engine new oil (group 1 and 2) for TBN PLSC is 7. Data is preprocessed with Savitzky-Golay (w =9, O=2, d=1).

Figure 14: Laboratory value versus the value predicted by the chemometric model and NIR spectroscop for sulfur. PLS model on Main engine oil in use and Main engine new oil (group 1 and 2) for S. PLSC is 1. Data is preprocessed with Savitzky-Golay (w =9, O=2, d=1).

Figure 15: Laboratory value versus the value predicted by the chemometric model and NIR spectroscop for phosphor. PLS model on Main engine oil in

use and Main engine new oil (group 1 and 2) for P. PLSC is 12. Data is preprocessed with Savitzky-Golay (w =9, O=2, d=1).

Figure 16: Laboratory value versus the value predicted by the chemometric model and NIR spectroscop for vanadium. PLS model on Main engine oil in use and Main engine new oil (group 1 and 2) for V. PLSC is 7. Data is preprocessed with Savitzky-Golay (w =9, O=2, d=1).

Figure 17: Laboratory value versus the value predicted by the chemometric model and NIR spectroscop for nickel. PLS model on Main engine oil in use and Main engine new oil (group 1 and 2) for Ni. PLSC is 10. Data is preprocessed with Savitzky-Golay (w =9, O=2, d=1).

Figure 18: Laboratory value versus the value predicted by the chemometric model and NIR spectroscop for magnesium. PLS model on Main engine oil in use and Main engine new oil (group 1 and 2) for Mg. PLSC is 8. Data is preprocessed with Savitzky-Golay (w =9, O=2, d=1).

Figure 19: Laboratory value versus the value predicted by the chemometric model and NIR spectroscop for calcium. PLS model on Main engine new oil and Main engine oil in use (group 1 and 2) for Ca. PLSC is 5. Data is preprocessed with Savitzky-Golay (w =9, O=2, d=1).

Detailed description of the invention

The invention relates to quantitative prediction of physical and/or chemical values or qualitative classification of oils sample status based on spectroscopic parameters obtained from near infrared and/or luminescence spectroscopy. Fluorescence spectroscopy is used as an example of luminescence spectroscopy in the present invention. However, as described below other physical parameters may be used in the prediction and/or classification. Thus, throughout the description the term fluorescence is used as an equivalent of any luminescence type and is to be interpreted as such, unless inappropriate in specific embodiments.

Fluorescence spectroscopy is an extremely sensitive analytical tool and near infrared spectroscopy is a very precise analytical tool. The data obtained from both types of spectroscopic analyses can be considered a finger-print of the sample. Each sample gives rise to a unique spectroscopic set of physical parameters, and as is described in the present invention it is possible to form the finger-prints to predict the value of physical-chemical components of the oil, such as water, viscosity (at different temperatures), Total Base Number (TBN), Total Acid Number (TAN), carbon residue, density, flash and fire points, pour point, sulphated ash, score values in various performance tests, and the content of Particles, Silicon, Sodium, Boron, Iron, Aluminum, Chromium, Molybdenum, Copper, Lead, Tin, Nickel, Titanium, Silver, Phosphorus, Zinc, Calcium, Barium, Magnesium, and Sulfur.

The fluorescence and near infrared spectroscopic fingerprint can be used either alone or in a combination to obtain synergy in the prediction models. Furthermore, as also described by the present invention, when analysing the spectroscopic data, it has become possible to classify samples into two or more classes based on the spectra, if there is any systematic difference between the samples. The difference between the samples will mostly not relate to a single component, or a few components of the sample, but rather to a combination of a wide variety of components. This combination exhibits a pattern so complex that it is detectable by the multivariate analyses only. Examples of the classification information provided by the present invention may be any information regarding sample condition, such as information regarding presence/absence of specific components, determination if the oil is used/not used (can also be quantified), determination of which type of engine the oil is used in. The oil can be a fuel.

Thus, according to the evaluation of the spectroscopic parameters it is possible to obtain more information about an oil sample, than it is when evaluating the various chemical components in the sample individually, i.e. it is possible to obtain inter-component information. Furthermore, there is no need to know the exact composition of components in the sample, as it is either the fluorescence or the near infrared absorption spectra or the combination of these finger-prints that contain the relevant information. If so desired, in a specific application, it may be possible to give a chemical characterisation of the information used by the classification system.

For one sample normally over 100 data variables are obtained. The amount of data variables increases by the number of samples used but the number of data variables is constant for each sample. It is common practise to discard most of the spectroscopic information and use but a few selective or semi-selective spectroscopic parameters but the present invention makes use of all available information.

In a first aspect the invention relates to a method of training a prediction system for quantifying multiple chemical and/or physical parameters in an oil sample. It is the purpose of the training that a system is obtained, said system holding enough information to be used for quantitative prediction of multiple chemical and/or physical parameters in an unknown oil sample. By the term unknown is meant a sample for which no characterisation information is known and only the near infrared and/or fluorescence spectrum is known. The prediction as such is only based on a model and the measured spectroscopic fingerprint(s).

In another aspect the invention relates to a method of training a classification system for characterising an oil sample. It is the purpose of the training that a classification system is obtained, said system holding enough information to be used for characterising an un-classified and unknown oil sample into one of the classes of the classification system. By the term unknown is meant a sample for which no characterisation information is known.

It is also the purpose of the training of both the prediction and the classification systems that this training incorporates a validation that substantiates how well prediction and/or classification can be performed on specific samples in the future as well as improving the validation performance over time.

The electromagnetic radiation exposing the sample comprises monitoring radiation and/or excitation light.

Samples

The oil sample may be any sample suitable for spectroscopic analyses. It is an object of the present invention to acquire the necessary information from the sample using as few pre-treatments as possible, preferably without any pre-treatments as such.

Accordingly, in a most preferred embodiment the sample is transferred directly as is to be subjected to spectroscopic analysis, in order to obtain data relating to untreated samples.

The oil sample is subjected to spectroscopic analyses without drying, and preferably without any other changes in concentration. The sample may be arranged in a sample compartment being closed or open before exposing the sample to light.

Furthermore, it is possible to use a sample positioned on-line or in-line, i.e. in a process stream.

FLUORESCENCE SPECTROSCOPY

Excitation light

The physical parameters may in principle be obtained for a wide variety of excitation light wavelengths. The wavelengths are preferably selected to be within the range from 100 nm to 1000 nm, such as from 100 to 800 nm, more preferably within the range of from 200 nm to 800 nm, such as from 200 nm to 600 nm.

Normally several wavelengths are used, such as from 2 to 100 wavelengths, for instance 2-30, such as 2-10, for instance 2-6 wavelengths in order to describe an excitation-emission matrix optimally. Sets of wavelengths may be chosen so that each wavelength differs from the other by at least 0.1 nm, such as 0.5 nm, for instance at least 1 nm, such as 5 nm, for instance at least 10 nm, such as 50 nm, for instance at least 100 nm, such as 150 nm, for instance at least 250 nm, such as 500 nm, for instance at least 600 nm, such as 700 nm, and at most 750 nm.

Accordingly, more than 2 excitation light wave lengths are selected such as 4, 6, 8, 10, or more. The excitation light of each wavelength may be used simultaneously or sequentially. In a preferred embodiment 4 wavelengths are selected, such as excitation light having a wavelength of 230 nm, 240 nm, 290 nm, and 340 nm. Each sample is then subjected to excitation light of each wavelength.

The predetermined excitation light wavelength(s) is provided by use of conventional light sources combined with a dispersive element such as a monochromator and/or optical-acoustical wavelength filters and/or conventional filters as is known to a person skilled in fluorescence spectroscopy.

Measured physical emission parameters

Mostly the physical parameters to be determined in order to perform a data analysis are the intensities as a function of excitation wavelength and/or the emission wavelength. However the measurement instrument measuring the intensity may provide other information such as fluorescence lifetime, phosphorescence intensity, as well as phosphorescence lifetime, depolarisation, quantum yield, phase-resolved emission, and circular depolarization.

By the term “physical emission parameters” is meant any physical parameter capable of providing a luminescence related property of the sample.

Fluorescence intensity is easily measured at room temperature, and may therefore be chosen for many of the samples. Furthermore, a great number of organic natural products are known to be fluorescent. Phosphorescence may however also be performed at room temperature.

Luminescence lifetime in general, as well as phosphorescence lifetimes are defined as the time required for the emission intensity to drop to $1/e$ of its initial value.

When using phase resolved fluorescence spectroscopy it is possible to suppress Raman and scattered light, leading to very good results for multicomponent systems.

In luminescence polarisation measurements, spectra are obtained by scanning excitation spectra and measuring intensity with polarizers transmitting in the planes parallel and perpendicular to the polarisation plane the of exciting light. The degree of polarization or anisotropy may be calculated from the difference of the two measurements to the sum of the two measurements.

Emission

The emitted light is dispersed or filtered and detected by any suitable detector, such as a scanning camera, a photomultiplier, a diode array, a CCD or a CMOS, all in principle being viewed as two-dimensional array of several thousand or more detectors. The intensity of the light is detected on each detector. In some embodiments one-dimensional detectors may be used as well such as a photomultiplier.

The determination of the various physical parameters is done by conventional equipment known to the person skilled in the art.

In fluorescence spectroscopy emission light intensities at different wavelengths are recorded for each excitation light wavelength. Preferably the emission light is sampled with 1 nm intervals. Thereby a matrix of excitation-emission data is obtainable for each sample. Normally the spectral distribution of light emitted from the sample is ranging from 200 nm to 800 nm.

The emitted light from the samples may be focused onto the detectors by means of conventional focusing systems, as well as passing through diaphragms and mirrors.

Processing

The detectors are preferably coupled to a computer for further processing of the data. The physical parameters measured or determined by the detector are processed to a form suitable for the further mathematical calculations. This is done by allocating data variables to each physical parameter determined, thus obtaining data variables related to the physical parameters,

The physical parameters determined are often subjected to a data analysis through the data variables, such as a one-way matrix of spectral information, a two-way matrix of spectral information, a three-way matrix of spectral information, a four-way matrix of spectral information or, a five-way or higher order matrices of spectral information.

Characterizing the monitoring NIR radiation

The NIR absorption spectrum may in principle be obtained for a wide variety of radiation wavelengths. The wavelengths are preferably selected to be within the range of from 700 nm to 3000 nm, such as from 900 to 2500 nm.

Normally several wavelengths are used, such as from 2 to 5000 wavelengths. Sets of wavelength may be chosen so that each wavelength differs from the other by at least 0.1 nm, such as 0.5 nm, for instance at least 1 nm, such as 5 nm, for instance at least 10 nm, such as 50 nm, for instance at least 100 nm, such as 150 nm.

The absorption at each wavelength may be used simultaneously or sequentially. In a preferred embodiment 4 wavelengths are selected, such as monitoring light having a wavelength of 1300 nm, 1500 nm, 1700 nm, and 1900 nm. The monitoring may also use the wavelengths 2870nm and 3050nm where the absorption of electromagnetic radiation in water is strong. Each sample is then subjected to monitoring radiation of each wavelength.

The predetermined monitoring radiation wavelength(s) are provided by use of conventional light sources, dispersive elements and/or filters as is known to a person skilled in near infrared spectroscopy.

Mostly the physical NIR parameters to be determined in order to perform a data analysis are the absorbance and/or transmission values as a function of wavelength.

Near infrared signals are easily measured at room temperature, and may therefore be chosen for many of the samples. Furthermore, a great number of organic natural products are known to absorb in the near infrared region.

Near infrared light detection

The transmitted NIR radiation is detected by any suitable detector, such as a semiconductor (e.g. PbS), photo voltaic elements (e.g. InAs, InSb), or a CCD. The intensity of the light is detected on each detector. In some embodiments one-dimensional detectors may be used as well such as a photomultiplier.

In near infrared spectroscopy, absorbance and/or transmission values are recorded for each excitation light wavelength. Preferably the detection of light is sampled with 1 nm intervals.

The signals can be recorded also by fibre optic probes, transmission probes, transmission probes for process applications, or reflection/backscattering probes.

Processing fluorescence and NIR data

The near infrared and/or the fluorescence detectors are preferably coupled to a computer for further processing of the data. The physical parameters measured or determined by the detector(s) are processed to a form suitable for the further mathematical calculations. This is done by allocating data variables to each physical parameter determined, thus obtaining data variables related to the physical parameters,

The physical parameters determined are often subjected to a data analysis through the data variables, such as a one-way matrix of spectral information, a two-way matrix of spectral information, a three-way matrix of spectral information, a four-way matrix of spectral information or, a five-way or higher order matrices of spectral information or mixtures of these data structures.

Characterisation information for oil samples

To obtain a system for quantification of one or several oil quality parameters or determination of a specific condition in the oil sample it is of importance that the data relating to the spectra obtained are correlated to characterisation information regarding the same oil sample. The characterisation information relates to the values (e.g. concentrations) of physical-chemical components in the oil or the classes characterizing the samples. The characterisation information may give information of both qualitative and quantitative information.

The characterisation information must be correlated to the spectral information obtained from the sample, in order to obtain the trained system ready for testing unknown samples.

Validity

Each sample is subjected to fluorescence and/or near infrared spectroscopy before the data analysis is performed in the training of the prediction and/or classification system. The sample may be one sample from oil sample, or several samples from the same oil sample or process, each sample obtained at a different time interval or from different process streams or from different instruments.

Depending on the predictions to be performed or the classes to be identified when training the classification system it is of importance to train the system with a sufficient number of samples. The determination of the sufficient number of samples is primarily determined by the number of expected latent variables. It is preferred that the ratio of number of training samples to the expected number of latent variables is at least 5:1, preferably at least 10:1. More preferred the ratio is 50:1, and even more preferred 100:1. The more training samples, the more reliable a system. Training is a continual improvement of the system and any sample is also a training sample however to a decreasing degree over time.

The samples being classified in each class are preferably a representative group of samples to allow the most reliable classification, wherein representative is meant to mean exhibiting all variations influencing said prediction and classification. These variables can for example be oil type, process type, engine type etc.

Mathematics

A central aspect of the invention is the performance of a multivariate analysis, whereby the data variables relating to the physical spectroscopic parameters are evaluated. The latent variables being weighted averages of the data variables are obtained. The latent variables describe the variation of the data variables. Thereby, the concentration values of the oils samples can be predicted accurately and/or the samples are classified uniquely into classes. The prediction model and/or the identification of the classes is obtained when each sample is correlated to the characterisation information relating to said sample.

The multivariate statistical methods suitable for the present invention are for example represented by chemometric methods like principal component analysis (PCA), partial least squares regression (PLS), soft independent modelling of class analogy (SIMCA) and principal variables (PV).

Other multivariate statistical methods include: Principal component analysis[14], principal component regression[14], factor analysis[2], partial least squares[14], fuzzy clustering[16], artificial neural networks[6], parallel factor analysis[4], Tucker models[13], generalized rank annihilation method[9], Locally weighted regression[15], ridge regression[3], total least squares[10], principal covariates regression[7], Kohonen networks[12], linear or quadratic discriminant analysis[11], k-nearest neighbors based on rank-reduced distances[1], multilinear regression methods[5], soft independent modeling of class analogies[8], robustified versions of the above and/or obvious non-linear versions such as one obtained by allowing for interactions or crossproducts of variables, exponential transformations etc.

The term “describing the variation of the data variables” means that the latent variables retain the relevant information regarding the variation, whereas “noise” is preferably not giving any significant part in the latent variables.

Other variables

The classification system may be obtained on the spectral information only. However, in some situations it may be appropriate to incorporate other variable(s) in the multivariate analyses.

These other variables may be variables relating to the sample supplying the spectral information or they may be variables that compensate for a specific condition of the sample.

Examples hereof may be the measurement of pH and temperature in the sample before subjecting it to spectroscopy. Thereby, variations in the other variables may be compensated for in the final prediction and/or classification.

In another embodiment other variables are variables relating to the oil sample to be characterized. Examples of these variables are oil type, origin, transport history, and process conditions.

Pre-treatment

It is an advantage of the present invention that no pre-treatment of the sample is normally necessary.

However, for some of the samples it may be necessary to perform an adjustment before subjecting the sample to spectroscopy.

Examples of pre-treatment may be adjustment of pH of the sample to a predetermined value, or heating or cooling the sample to a predetermined temperature. The sample may be treated with chemicals, e.g. in order to develop fluorescent complexes involving inherently non-fluorescent molecules in the sample.

Other types of pre-treatment include addition of chemical substances, measurement under a gradient imposed by varying additions of chemical substances, and simple chromatographic pre-treatments based on either chemical or physical separation principles.

Prediction system

Another aspect of the present invention is the prediction system for quantitative assessment of oil sample quality parameters.

The system and methods according to the invention provides means for predicting one or more oil quality parameters simultaneously and/or classifying the oil samples into at least two different classes correlated to the characterisation information, obtaining a trained prediction and/or classification system.

When the prediction system has been trained as discussed above, it is ready for prediction of one or more quality parameters samples with unknown characteristics. The prediction system preferably comprises the following components:

a) a sample domain for comprising the oil sample,

b) means for exposing the oil sample in the sample domain to electromagnetic radiation,

c) detecting means for recording at least one physical spectroscopic parameter of electromagnetic radiation transmitted and/or reflected and/or emitted from the sample,

d) computing means for performing data analysis of the at least one physical spectroscopic parameter, obtaining at least one data variable,

e) storage means for storing the at least one obtained data variable,

f) storage means for storing latent variables, multivariate prediction models and characterisation information of a trained prediction system,

g) processing means for providing at least one latent variable from the at least one obtained data variable of the sample,

h) means for correlating latent data variables from the sample with latent variables of the trained system, and

i) means for displaying the prediction(s) of a sample.

Classification system

Another aspect of the present invention is the classification system for characterising an oil sample into at least one predetermined class.

When the classification system has been trained as discussed above, it is ready for classifying samples with unknown characteristics. The classification system preferably comprises the following components:

a)-e) Identical to the steps for Prediction system,

f) storage means for storing latent variables, classification models and characterisation information of a trained classification system,

g) processing means for providing latent variables from data variables of the sample,

h) means for correlating latent data variables from the sample with latent variables of the trained system, and

i) means for displaying the characterisation class(es) of a sample.

For both the prediction and the classification system the following holds:

The sample domain may be a sample chamber for accommodating a container with a liquid, a solid or a semi-solid sample. However, the sample domain may also be a domain in a process stream, vessel or engine.

The oil sample may be obtained from an oil engine, a tank, a process stream, a vessel step, or a transmission, or any other oil containing and/or using unit.

The prediction and/or classification system may be provided as a whole unit, wherein the spectroscopy of the sample is conducted by the same unit from where the data relating to the characterisation classes of the sample is displayed.

It is however contemplated within the scope of the present invention, that the system is comprised of at least two units, wherein one unit is performing the steps a) to e), and another unit is performing the steps f) to i). Other units comprising other parts of the system are also contemplated, such as one unit performing the steps a) to f) or a) to g), and the other unit performing the rest of the steps. Yet another unit may perform steps a) to c) and the remaining steps may be performed in another unit.

By the system thus divided into two units, it is possible to obtain the spectroscopic information from a wide variety of decentralized locations and perform the processing centrally. The data or the prediction and/or classification system may then be transmitted by any suitable means, such as conventional data transmission lines, telephone lines, or via internet or intranet connections.

This configuration facilitates the use of the prediction and/or classification system since any process-engineer or technician may provide the oil sample and have it subjected to spectroscopic analyses obtaining data variables without the need of being capable of conducting the processing and correlating procedures at the sampling site. The engineer or technician may then obtain the prediction and classification results of the sample data from the central unit through a secured (internet) connection.

Examples

Example 1: Prediction of oil quality parameters by NIR

Thirty-nine samples of lubricant oil, a mix of new and used, were analyzed by near infrared (NIR) spectroscopy. By chemometric data analysis the spectra were correlated to laboratory values describing the oil quality.

The 39 oil samples were analyzed in a 1 mm cuvette on a NIRSystems 6500 (Foss, Hillerød, Denmark). NIR transmission spectra were recorded in the range from 1200 nm to 2500 nm. The same 39 samples were analyzed by an international approved laboratory for the following important oil quality parameters: Water concentration, Viscosity (at 40 and 100 degrees), Total Base number (TBN), Total Acid Number (TAN), Elemental analysis (e.g. metals) and particles. The NIR spectra were correlated to the laboratory values using chemometric modeling.

Figure 1 shows the measured NIR spectra. It is seen that there is a clear difference between the used oil samples (upper 17 curves) and fresh oil samples (lover curves).

Figures 2 to 6 display plots showing the laboratory value versus the value predicted by the chemometric model and NIR spectroscop for water (Fig 2), viscosity at 40 degrees (Fig 3), TAN (Fig 4), TBN (Fig 5) and Silicon (Fig 6). Full cross validation is used to validate the models. From the actual versus predicted plots it is clearly observed that it is possible to predict different oil quality parameters by the present invention.

Example 2: Classification of oil using fluorescence spectroscopy and chemometrics

Fifty-six lubricant oil samples, a mix of used and new oils from different engine types, were analyzed on a Fluoromax 3 Spectrograph. The samples were measured in a 2 mm quartz cuvette in front face geometry. 3D excitation/emission fluorescence landscapes were recorded on each sample with following settings: Excitation 230 nm – 400 nm, emission 250 nm – 600 nm.

FIG 7 shows emission spectra at 230 nm excitation for all samples. It is seen that there are three samples with a specific pattern having a strong signal around 180nm. This verifies that this method also can be used for revealing strongly deviating samples e.g. according to special additives, oil types etc.

Fig 8.shows the obtained classification of new and used samples where the new samples are marked with the dotted circle.

Fig 9 shows Extended Canonical Variates for the new samples (with negaive values) and old samples (with positive values)

Example 3 Prediction of oil quality parameters by NIR

149 samples of lubricant oil from main engine vessels onboard ships, a mix of used and new, were analyzed by near inferred (NIR) spectroscopy. The spectra were then correlated to different laboratory values describing the oil quality using chemometric data analysis.

The 149 samples were analyzed on a MB3600 NIR FTIR spectrometer (Q-Interline). There were used 3 mm disposable cuvets and the samples were scanned from 1100 nm to 2500 nm measuring the transmission.

The same 149 samples was send to an international approved laboratory for analysis for oil quality parameters like: Viscosity, Density, Total Base number (TBN), Total Acid Number (TAN), Elemental analysis (e.g. metals, Sulfur and Phosphor).
The NIR spectra were correlated to the laboratory values using chemometric modeling by PLS.

Figures 10 to 19 display plots showing the laboratory value versus the value predicted by the chemometric model and NIR spectroscop for viscosity at 100 degrees (Fig 10), density (Fig 11), TAN (Fig 12), TBN (Fig 13), sulfur (Fig 14), phosphor (Fig 15), vanadium (Fig 16), nickel (Fig 17), magnesium (Fig 18) and calcium (Fig 19). Full cross validation is used to validate the models. From the actual versus predicted plots it is clearly observed that it is possible to predict different oil quality parameters by the present invention.

It is clearly seen that it is possible to predict different oil quality parameters by the used method.

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Claims:

1. A method of training a system for characterising an oil sample, said method comprising the steps of

a) providing a batch of oil samples having a predetermined content for training the system to recognise at least one characteristic of the sample,

b) exposing an oil sample from said batch to electromagnetic radiation within a predetermined range of wavelengths,

c) determining at least one physical spectroscopic parameter of electromagnetic radiation transmitted through and/or reflected from and/or emitted from the oil sample from said batch,

d) repeating step b) to c) until the at least one physical spectroscopic parameter of all oil samples of said batch have been determined,

e) performing data processing of the obtained physical spectroscopic parameters thereby obtaining data variables,

f) performing a multivariate data analysis of the obtained data variables obtaining model parameters describing the variation of the data variables,

g) obtaining characterisation information related to each oil sample from said batch.

2. The method according to claim 1, furthermore comprising the step of predicting one or more oil quality parameters simultaneously and/or classifying the oil samples into at least two different classes correlated to the characterisation information, obtaining a trained prediction and/or classification system.

3. A method according to claim 1 or 2, wherein the electromagnetic radiation comprises monitoring radiation and/or excitation light.

4. The method according to any of claims 1 to 3, wherein the oil sample is obtained from an oil engine, a tank, a process stream, a vessel step, or a transmission, or any other oil containing and/or using unit.

5. The method according to any of the previous claims, wherein the step of determining at least one physical spectroscopic parameter comprises determining the absorption of electromagnetic radiation transmitted through the sample.

6. The method according to any of the previous claims, wherein step g) further comprises selection of latent variables being weighted averages of data variables.

7. The method according to any of the previous claims, wherein the wavelength of the excitation light is in the range of from 100 nm to 1000 nm, such as from 100 to 800 nm, such as from 200 nm to 800 nm, such as from 200 nm to 600 nm.

8. The method according to any of the previous claims, wherein the physical spectroscopic parameter determined is selected from the group of fluorescence intensity, fluorescence lifetime, phosphorescence intensity, phosphorescence lifetime, depolarisation, quantum yield, phase-resolved emission, and circular depolarization.

9. The method according to any of the previous claims, wherein the spectral distribution of electromagnetic radiation emitted from the oil sample is in the range from 200 nm to 800 nm.

10. The method according to any of the previous claims, wherein the spectral distribution of electromagnetic radiation transmitted through and/or reflected from the oil sample is in the range from 750 nm to 3000 nm, such as from 1100 to 2500, such as 1300 to 1900nm.

11. The method according to claim 10, wherein several wavelengths are used, such as from 2 to 5000 wavelengths.

12. The method according to claim 11, wherein said several wavelengths are chosen so that each wavelength differs from the other by at least 0.1 nm, such as 0.5 nm, for instance at least 1 nm, such as 5 nm, for instance at least 10 nm, such as 50 nm, for instance at least 100 nm, such as 150 nm.

13. The method according to claim 11 or 12, wherein absorption of electromagnetic radiation at each of said several wavelengths may be measured simultaneously or sequentially.

14. The method according to any of claims 11 to 13, wherein 4 wavelengths are selected, such as monitoring radiation having a wavelength of 1300 nm, 1500 nm, 1700 nm, and 1900 nm.

15. The method according to any of claims 10 to 14, wherein the monitoring radiation is having wavelengths in ranges where the absorption of electromagnetic radiation in water is strong such as at 1300-1400nm, 1900-2000nm, 2150-2200nm, 2870nm and 3050nm.

16. The method according to any of claims 10 to 15, wherein the physical NIR parameters to be determined in order to perform a data analysis are the absorbance and/or transmission and/or reflectance values as a function of wavelength.

17. The method according to any of claims 10 to 16, wherein the NIR radiation is detected by any suitable detector, such as a semiconductor (e.g. PbS), photo voltaic elements (e.g. InAs, InSb), or a CCD.

18. The method according to any of claims 10 to 17, wherein absorbance and/or transmission and/or reflectance values are recorded with a 1 nm sampling interval.

19. The method according to any of the previous claims, wherein the signals are be recorded by fibre optic probes, transmission probes, transmission probes for process applications, or reflection/backscattering probes.

20. The method according to any of the previous claims, wherein the ratio of number of training samples to the expected number of latent variables is at least 5:1, preferably at least 10:1, more preferably 50:1, and even more preferred 100:1

21. The method according to claim any of the previous claims, wherein the multivariate data analysis is selected from the group of: Principal component analysis, principal component regression, factor analysis, partial least squares, fuzzy clustering, artificial neural networks, parallel factor analysis, Tucker models, generalised rank annihilation method, Locally weighted regression, ridge regression, total least squares, principal covariates regression, Kohonen networks, linear or quadratic discriminant analysis, k-nearest neighbours based on rank-reduced distances, multilinear regression methods, soft independent modelling of class analogies, robustified versions of the above and/or obvious non-linear versions such as one obtained by allowing for interactions or cross products of variables, and exponential transformations.

22. The method according to any of the previous claims, wherein the data analysis of step f) is selected from a one-way matrix of spectral information, a two-way matrix of spectral information, a three-way matrix of spectral information, a four-way matrix of spectral information and, a five-way or higher order matrix of spectral information or mixtures hereof.

23. The method according to claim 22, wherein at least one other variable related to the oil sample is included in the multivariate analyses of step f)

24. The method according to claim 23, wherein the at least one other variable is are selected from a pH value of the sample, concentration of any other relevant compound in the sample, temperature or any other physical property of the sample or property of the oil sample or the place from which the sample was taken.

25. The method according to any of the previous claims, wherein the sample is pre-treated before subjecting the sample to step c).

26. The method according to claim 25, wherein the pre-treatment comprises adjustment of pH of the sample to a predetermined value.

27. The method according to any of the previous claims, wherein the oil quality parameter relates to at least one of the group of the Water Concentration, Total Base Number (TBN), Total Acid Number (TAN), Viscosity (at different temperatures) and the content of Particles, Silicon, Sodium, Boron, Iron, Aluminum, Chromium, Molybdenum, Copper, Lead, Tin, Nickel, Titanium, Silver, Phosphorus, Zinc, Calcium, Barium, Magnesium, or Sulfur.

28. The method according to any of the previous claims, wherein the characterising of an oil sample takes place at-line or on-line.

29. A system for characterizing an oil sample, comprising

a) a sample domain for comprising the oil sample,

b) means for exposing the oil sample in the sample domain to electromagnetic radiation,

c) detecting means for recording at least one physical spectroscopic parameter of electromagnetic radiation transmitted and/or reflected and/or emitted from the sample,

d) computing means for performing data analysis of the at least one physical spectroscopic parameter, obtaining at least one data variable,

e) storage means for storing the at least one obtained data variable,

f) storage means for storing at least one latent variable and/or at least one multivariate model and/or at least one characterisation information of a trained prediction and/or classification system,

g) processing means for providing at least one latent variable from the at least one obtained data variable of the sample,

h) means for correlating the at least one latent data variables from the sample with latent variables of said trained system, thereby obtaining a characterisation of the oil sample, e.g. quantitative parameter predictions and/or at least one class to which the sample belongs, and

i) means for displaying the characterisation.

30. The system according to claim 29, wherein the electromagnetic radiation comprises radiation monitoring radiation and/or excitation light.

31. The system according to claim 29 or 30, wherein the detection means for recording at least one physical spectroscopic parameter comprises means for determining the absorption of electromagnetic radiation transmitted through the sample.

32. The system according to any of claims 29 to 31, wherein the detection system is arranged to detect emitted light from the oil sample having a wavelength in the range of from 100 nm to 1000 nm, such as from 100 to 800 nm, such as from 200 nm to 800 nm, such as from 200 nm to 600 nm.

33. The system according to any of claims 29 to 32, wherein the physical parameter determined is selected from the group of fluorescence intensity, fluorescence lifetime, phosphorescence intensity, phosphorescence lifetimes, depolarisation, quantum yield, phase-resolved emission, and circular depolarization.

34. The system according to any of claims 29 to 33, wherein the detecting means is selected from a one-dimensional detector, a scanning camera, a CCD, a CMOS, a diode array, or a photomultiplier.

35. The system according to any of claims 29 to 34, wherein the detection system is arranged to detect electromagnetic radiation transmitted through and/or

reflected from the oil sample having a wavelength in the range of from 750 nm to 3000 nm, such as from 1100 to 2500, such as 1300 to 1900nm.

36. The system according to claim 35, wherein several wavelengths are used, such as from 2 to 5000 wavelengths.

37. The system according to any of claims 35 to 36, wherein said several wavelengths are chosen so that each wavelength differs from the other by at least 0.1 nm, such as 0.5 nm, for instance at least 1 nm, such as 5 nm, for instance at least 10 nm, such as 50 nm, for instance at least 100 nm, such as 150 nm.

38. The system according to any of claims 35 to 37, wherein absorption of electromagnetic radiation at each of said several wavelengths may be measured simultaneously or sequentially.

39. The system according to any of claims 35 to 38, , wherein the detection means comprises means for detecting electromagnetic radiation at 4 wavelengths, such as means for monitoring radiation having a wavelength of 1300 nm, 1500 nm, 1700 nm, and 1900 nm.

40. The system according to any of claims 35 to 39, wherein the detection means comprises means for detecting electromagnetic radiation in the wavelength ranges, where the absorption of electromagnetic radiation in water is strong such as at 1300-1400nm, 1900-2000nm, 2150-2200nm, 2870nm and 3050nm.

41. The system according to any of claims 35 to 40, wherein the physical NIR parameters to be determined in order to perform a data analysis are the absorbance and/or transmission and/or reflectance values as a function of wavelength.

42. The system according to any of claims 35 to 41, wherein the detection means comprises means for detecting NIR radiation, such as a semiconductor (e.g. PbS), photo voltaic elements (e.g. InAs, InSb), or a CCD.

43. The system according to any of claims 35 to 42, comprising means for recording absorbance and/or transmission and/or reflectance values with a 1 nm sampling interval.

44. The system according to any of claims 29 to 43, being divided into at least a first unit and a second unit, wherein said first unit comprises the parts a) to at least e) of the system, and the second unit comprises the remaining parts of claim 29.

45. The system according to any of claims 29 to 44, further comprising means for measuring at least one other variable of the sample.

46. The system according to claim 45, wherein the at least one other variable is selected from a pH value of the sample, concentration of any other relevant compound in the sample, temperature or any other physical property of the sample or property of the sample or the place from which the sample was taken.

47. The system according to any of claims 29 to 46, further including means for entering at least one other variable.

48. The system according to any of claims 29 to 47, further comprising means for pre-treating the sample prior to an exposure to electromagnetic radiation.

49. The system according to claim 48, wherein the means for pre-treatment comprises means for adjusting the pH of the sample to a predetermined value.

50. The system according to any of claims 29 to 49, wherein the characterization of the oil sample relates to at least one of the group of the Water Concentration, Total Base Number (TBN), Total Acid Number (TAN), Viscosity (at different temperatures) and the content of Particles, Silicon, Sodium, Boron, Iron, Aluminum, Chromium, Molybdenum, Copper, Lead, Tin, Nickel, Titanium, Silver, Phosphorus, Zinc, Calcium, Barium, Magnesium, and Sulfur.

51. The system according to any of claims 29 to 50, comprising means for the predicting a quality and/or quantity parameter of an oil sample and/or classifying an oil sample takes place at-line or on-line.

52. A method for characterising an oil sample, comprising

a) obtaining the oil sample,

b) exposing the oil sample to electromagnetic radiation,

c) determining at least one physical spectroscopic parameter of light transmitted and/or reflected and/or emitted from the oil sample,

d) performing data processing of the obtained at least one physical spectroscopic parameter obtaining at least one data variable,

e) storing the obtained at least one data variable,

f) providing at least one latent variable from data variables of the sample,

g) obtaining at least one latent variable from a trained prediction and/or classification system,

h) correlating latent data variables from the sample with latent variables of the trained system, to obtain quantitative predictions and/or quality predictions and/or at least one characterisation class of the sample, and

i) displaying the quantitative predictions and/or quality predictions and/or at least one characterisation class of the sample.

53. A method according to claim 52, wherein the electromagnetic radiation comprises monitoring radiation and/or excitation light.

54. The method according to claim 52 or 53, wherein the oil sample is obtained from an oil engine, a tank, a process stream, a vessel step, or a transmission.

55. The method according to any of claims 52 to 54, wherein the wavelength of the excitation light is in the range of from 100 nm to 1000 nm, such as from 100 to 800 nm, such as from 200 nm to 800 nm, such as from 200 nm to 600 nm

56. The method according to any of claims 52 to 55, wherein the spectral distribution of light emitted from the oil sample is ranging from 200 nm to 800 nm.

57. The method according to any of claims 52 to 56, wherein the physical spectroscopic parameter determined is selected from the group of fluorescence intensity, fluorescence lifetime, phosphorescence intensity, phosphorescence lifetime, depolarisation, quantum yield, phase-resolved emission, and circular depolarization.

58. The method according to any of claims 52 to 57, wherein the detection system is arranged to detect electromagnetic radiation transmitted through and/or reflected from the oil sample having a wavelength in the range of from 750 nm to 3000 nm, such as from 1100 to 2500, such as 1300 to 1900nm.

59. The method according to claim 58, wherein several wavelengths are used, such as from 2 to 5000 wavelengths.

60. The method according to claim 59, wherein said several wavelengths are chosen so that each wavelength differs from the other by at least 0.1 nm, such as 0.5 nm, for instance at least 1 nm, such as 5 nm, for instance at least 10 nm, such as 50 nm, for instance at least 100 nm, such as 150 nm.

61. The method according to claim 59 or 60, wherein absorption of electromagnetic radiation at each of said several wavelengths may be measured simultaneously or sequentially.

62. The method according to any of claims 59 to 61, wherein 4 wavelengths are selected, such as monitoring radiation having a wavelength of 1300 nm, 1500 nm, 1700 nm, and 1900 nm.

63. The method according to any of claims 59 to 62, wherein the monitoring radiation is having wavelengths in ranges, where the absorption of electromagnetic radiation in water is strong such as at 1300-1400nm, 1900-2000nm, 2150-2200nm, 2870nm and 3050nm.

64. The method according to any of claims 59 to 63, wherein the physical NIR parameters to be determined in order to perform a data analysis are the absorbance and/or transmission and/or reflectance values as a function of wavelength.

65. The method according to any of claims 59 to 64, wherein the NIR radiation is detected by any suitable detector, such as a semiconductor (e.g. PbS), photo voltaic elements (e.g. InAs, InSb), or a CCD.

66. The method according to any of claims 59 to 65, wherein absorbance and/or transmission and/or reflectance values are recorded with a 1 nm sampling interval.

67. The method according to any of claims 52 to 66, wherein the signals are be recorded by fibre optic probes, transmission probes, transmission probes for process applications, or reflection/backscattering probes.

68. The method according to any of claims 52 to 67, wherein the data analysis of step d) is selected from a one-way matrix of spectral information, a two-way matrix of spectral information, a three-way matrix of spectral information, a four-way matrix of spectral information and, a five-way or higher order matrix of spectral information or mixtures hereof.

69. The method according to any of claims 52 to 68, wherein at least one other variable related to the oil sample is included as data variable.

70. The method according to claim 69, wherein the at least one other variable is selected from a pH value of the sample, concentration of any other relevant

compound in the sample, temperature, viscosity, flash point, or any other physical property of the sample or the place from which the sample was taken.

71. The method according to any of claims 52 to 70, wherein the sample is pre-treated before subjecting the sample to step b).

72. The method according to claim 71, wherein the pre-treatment comprises adjustment of pH of the sample to a predetermined value.

73. The method according to any of claims 52 to 72, wherein the classification of an oil sample takes place at-line or on-line.

74. A system for the measurement of TBN (Total Base Number) and water in new and used lubricants, comprising

a) a sample domain for comprising an oil sample,

b) means for exposing the oil sample in the sample domain to electromagnetic radiation,

c) detecting means for recording at least one physical spectroscopic parameter of electromagnetic radiation transmitted and/or reflected and/or emitted from the sample,

d) computing means for performing data analysis of the at least one physical spectroscopic parameter, obtaining at least one data variable,

e) storage means for storing the at least one obtained data variable,

f) storage means for storing at least one latent variable and/or at least one multivariate model and/or at least one characterisation information of a trained prediction and/or classification system,

g) processing means for providing at least one latent variable from the at least one obtained data variable of the sample,

h) means for correlating the at least one latent data variables from the sample with latent variables of the trained system, thereby obtaining a characterisation of the oil sample, e.g. quantitative parameter predictions and/or at least one class to which the sample belongs, and

i) means for displaying the characterisation.

75. A system according to claim 74, furthermore comprising means for predicting fuel quality and fuel contaminants such as polymers, lubricant soot levels/insoluble levels, lubricant viscosity, fuel contamination of lubricants and TAN (Total Acid Number).

76. A prediction and/or classification system for on-line and/or at-line monitoring of hydraulic oil and/or machine oil comprising

a) a sample domain for comprising an oil sample,

b) means for exposing the oil sample in the sample domain to electromagnetic radiation,

c) detecting means for recording at least one physical spectroscopic parameter of electromagnetic radiation transmitted and/or reflected and/or emitted from the sample,

d) computing means for performing data analysis of the at least one physical spectroscopic parameter, obtaining at least one data variable,

e) storage means for storing the at least one obtained data variable,

f) storage means for storing at least one latent variable and/or at least one multivariate model and/or at least one characterisation information of a trained prediction and/or classification system,

g) processing means for providing at least one latent variable from the at least one obtained data variable of the sample,

h) means for correlating the at least one latent data variables from the sample with latent variables of the trained system, thereby obtaining a characterisation of the oil sample, e.g. quantitative parameter predictions and/or at least one class to which the sample belongs, and

i) means for displaying the characterisation.

77. A prediction and/or classification system for on-line and/or at-line monitoring of hydraulic oil and/or machine oil comprising

a) An optical probe for exposing oil in-situ to electromagnetic radiation,

b) detecting means for recording at least one physical spectroscopic parameter of light transmitted and/or reflected and/or emitted from the sample,

c) computing means for performing data analysis of the at least one physical spectroscopic parameter, obtaining at least one data variable,

d) storage means for storing the at least one obtained data variable,

e) storage means for storing at least one latent variable and/or at least one multivariate model and/or at least one characterisation information of a trained prediction and/or classification system,

f) processing means for providing at least one latent variable from the at least one obtained data variable of the sample,

g) means for correlating the at least one latent data variables from the sample with latent variables of the trained system, thereby obtaining a characterisation of the oil sample, e.g. quantitative parameter predictions and/or at least one class to which the sample belongs, and

h) means for displaying the characterisation.

FIGS.

Fig. 1

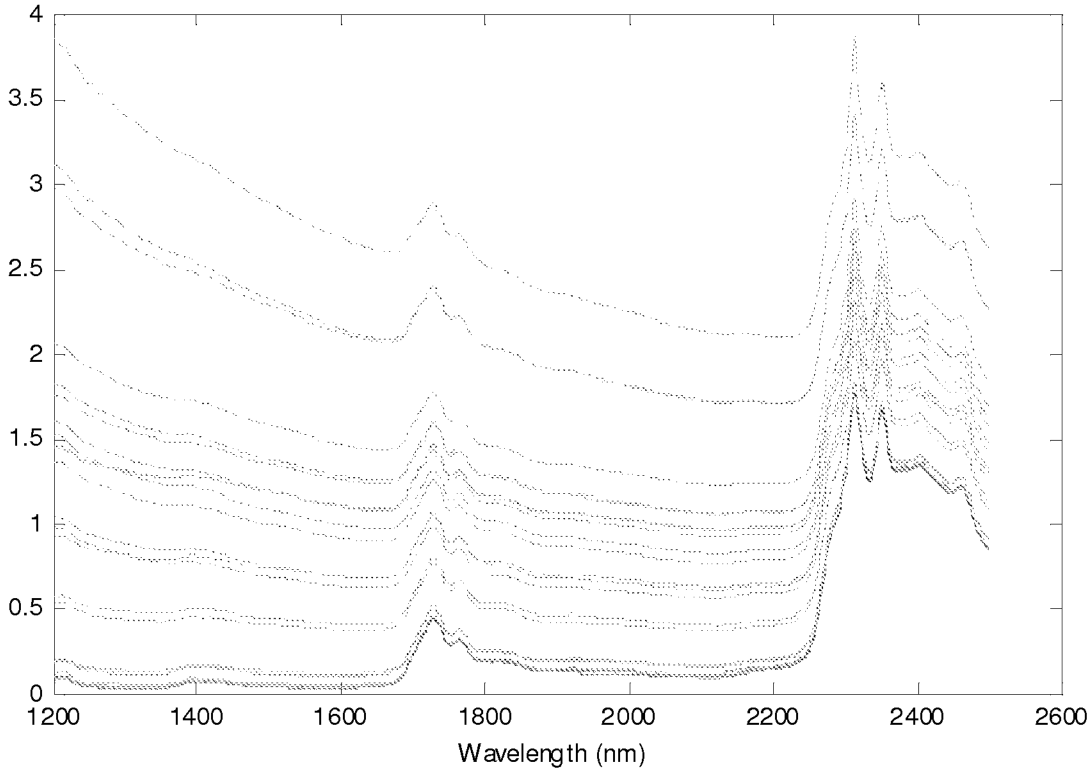

4
3.5
3
2.5
2
1.5
1
0.5
0
1200
1400
1600
1800
2000
2200
2400
2600
Wavelength (nm)

Fig 2

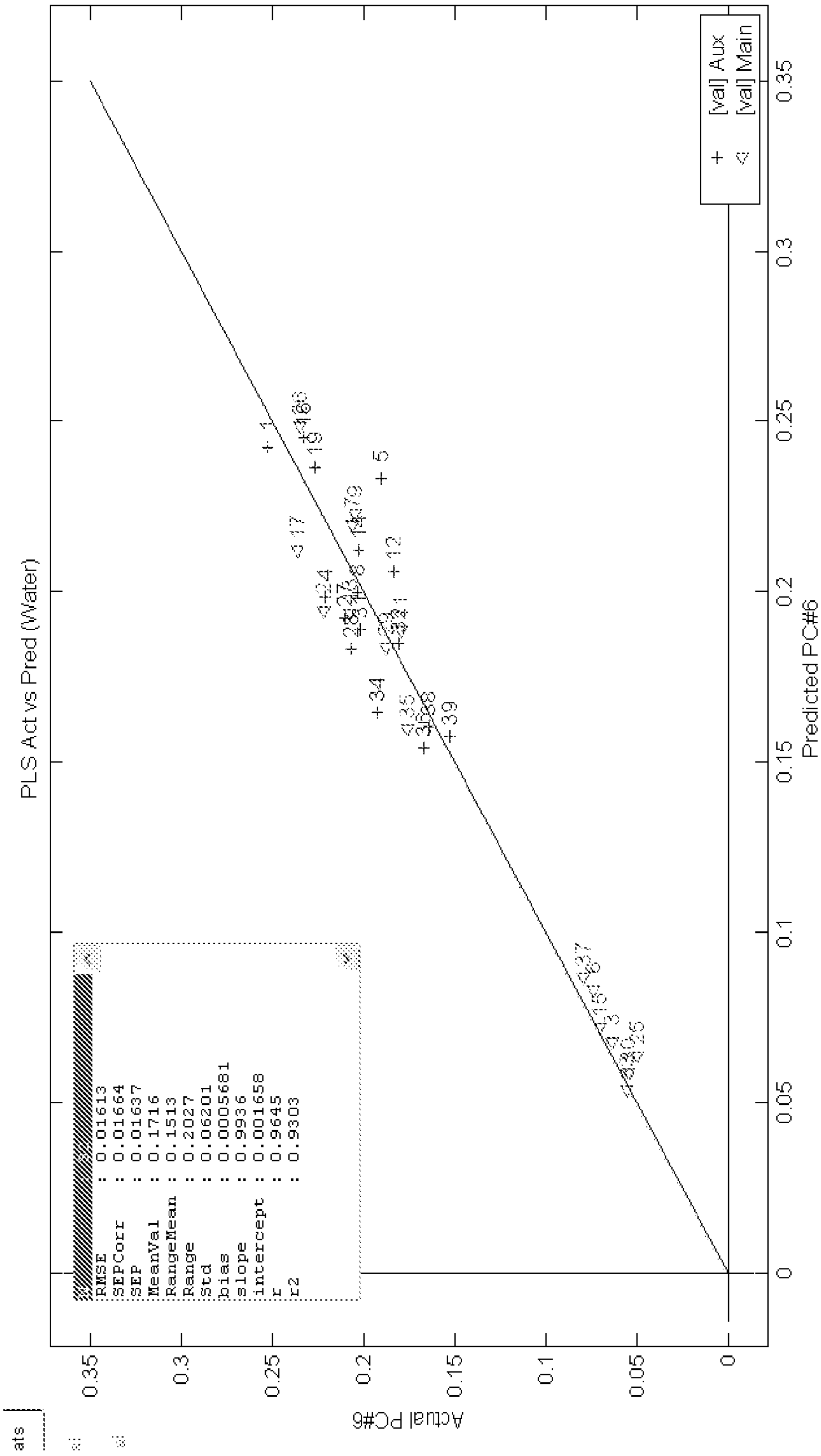
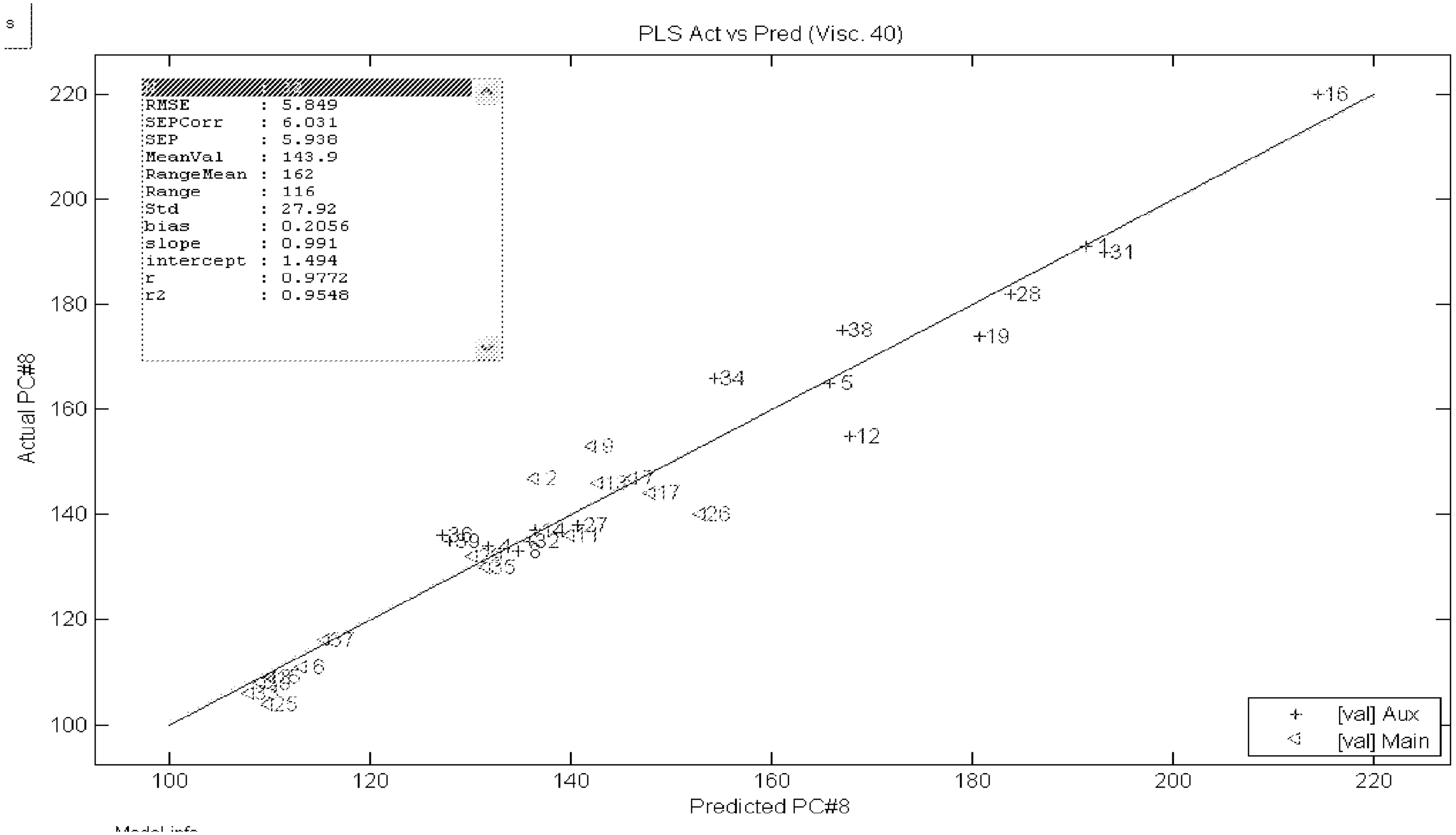

PLS Act vs Pred (Water)
Predicted PC#6
Actual PC#6
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
+ [val] Aux
◁ [val] Main
RMSE : 0.01613
SEPCorr : 0.01664
SEP : 0.01637
MeanVal : 0.1716
RangeMean : 0.1513
Range : 0.2027
Std : 0.06201
bias : 0.0005681
slope : 0.9936
intercept : 0.001658
r : 0.9645
r2 : 0.9303
ats

Fig 3



```
RMSE       : 5.849
SEPCorr    : 6.031
SEP        : 5.938
MeanVal    : 143.9
RangeMean  : 162
Range      : 116
Std        : 27.92
bias       : 0.2056
slope      : 0.991
intercept  : 1.494
r          : 0.9772
r2         : 0.9548
```

Fig 4

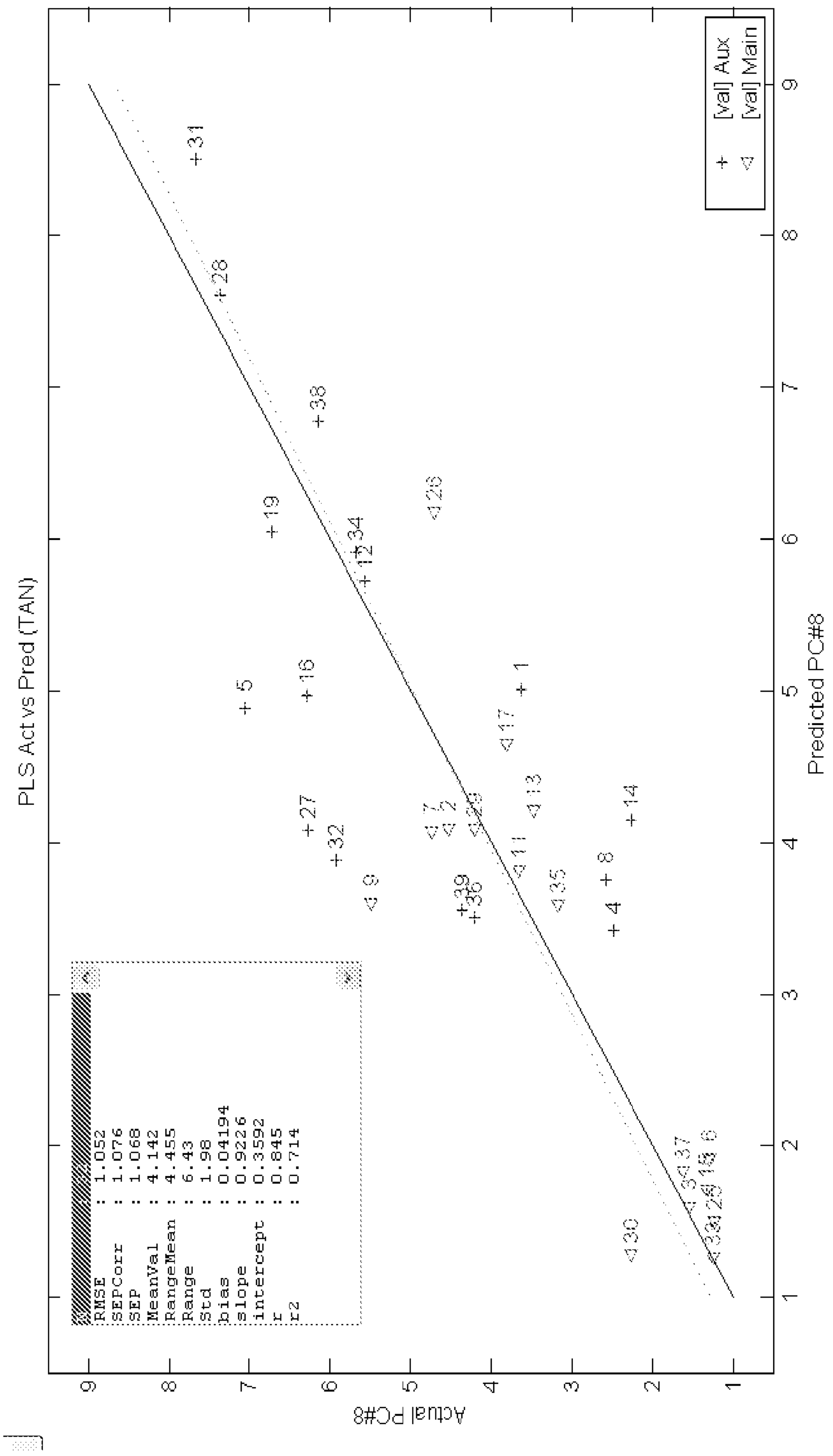

PLS Act vs Pred (TAN)
Actual PC#8
Predicted PC#8
1
2
3
4
5
6
7
8
9
+ [val] Aux
◁ [val] Main
RMSE : 1.052
SEPCorr : 1.076
SEP : 1.068
MeanVal : 4.142
RangeMean : 4.455
Range : 6.43
Std : 1.98
bias : 0.04194
slope : 0.9226
intercept : 0.3592
r : 0.845
r2 : 0.714
+31
+28
+38
◁26
+19
+34
+12
+5
+16
+1
◁17
◁13
+14
+27
◁7
◁2
◁29
+32
◁11
+8
◁9
+39
+36
◁35
+4
◁30
◁37
◁6

Fig 5

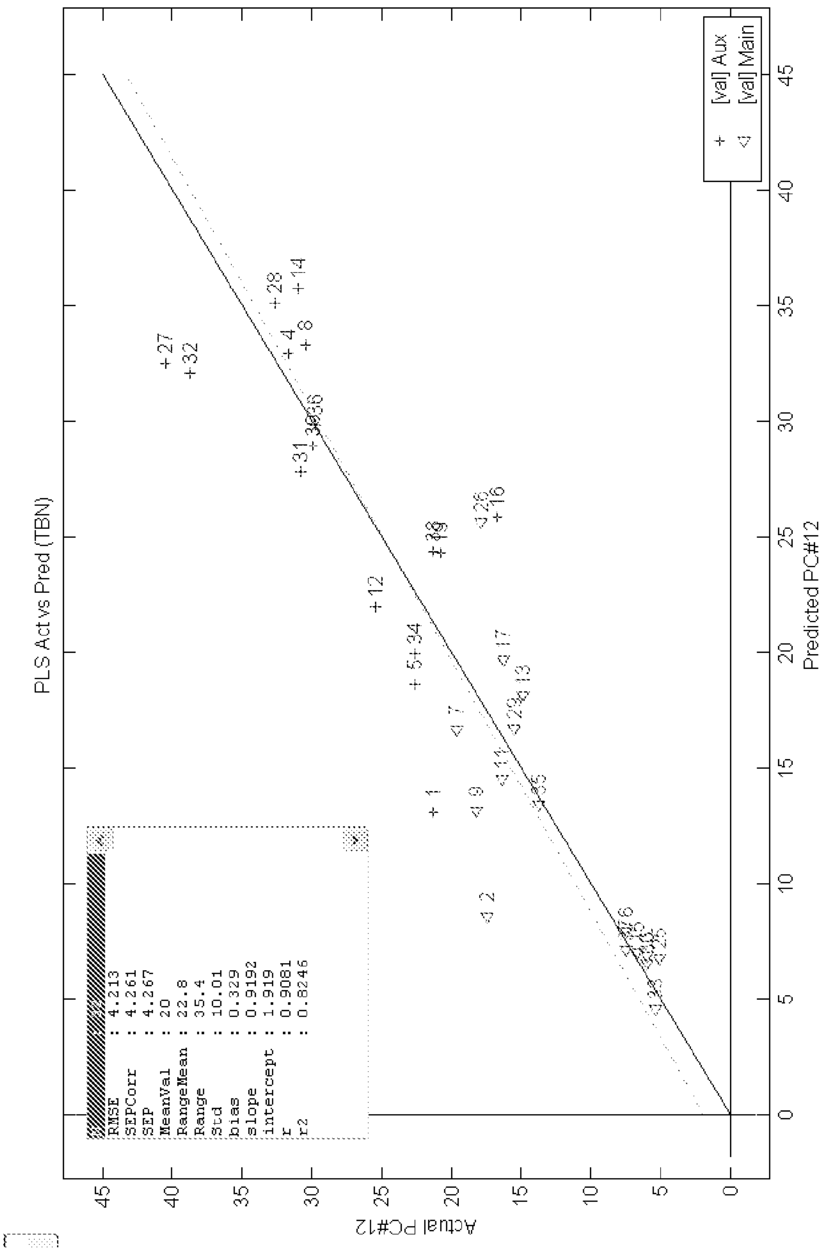

PLS Act vs Pred (TBN)
Predicted PC#12
Actual PC#12
0
5
10
15
20
25
30
35
40
45
+ [val] Aux
◁ [val] Main
RMSE : 4.213
SEPCorr : 4.261
SEP : 4.267
MeanVal : 20
RangeMean : 22.8
Range : 35.4
Std : 10.01
bias : 0.329
slope : 0.9192
intercept : 1.919
r : 0.9081
r2 : 0.8246
+27
+32
+28
+14
+4
+8
+31
+36
+16
◁26
+19
+12
+5
+34
◁17
◁13
◁7
◁29
◁11
+1
◁9
◁35
◁2
◁6
◁25
◁33

Fig 6

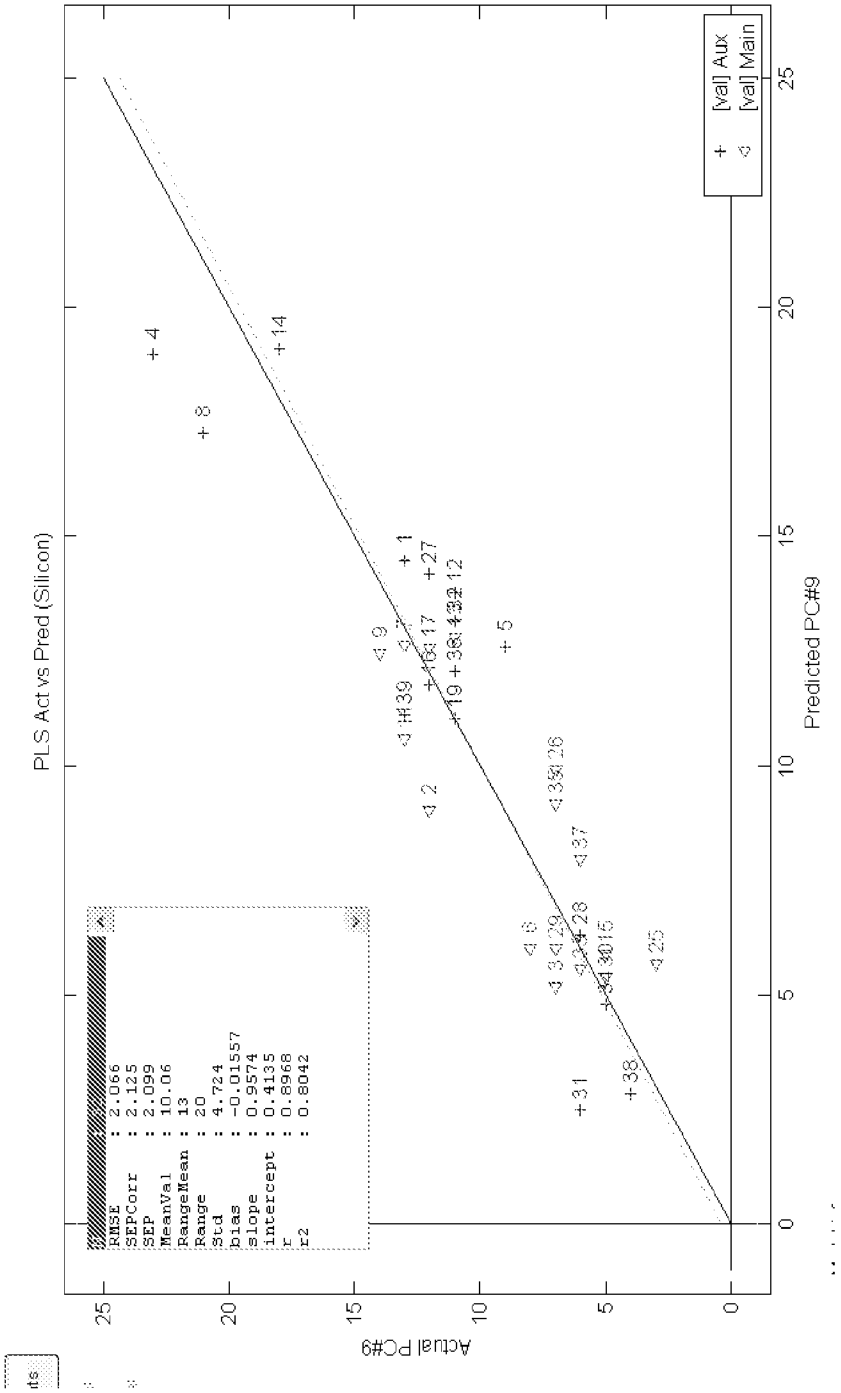

PLS Act vs Pred (Silicon)
Actual PC#9
Predicted PC#9
0
5
10
15
20
25
+ [val] Aux
◁ [val] Main
RMSE : 2.066
SEPCorr : 2.125
SEP : 2.099
MeanVal : 10.06
RangeMean : 13
Range : 20
Std : 4.724
bias : -0.01557
slope : 0.9574
intercept : 0.4135
r : 0.8968
r2 : 0.8042
+ 4
+ 14
+ 8
+ 1
+ 27
12
+ 5
◁ 9
17
+ 19
◁ 39
◁ 2
26
◁ 37
◁ 6
29
+ 28
15
◁ 25
+ 31
+ 38

FIG 7.

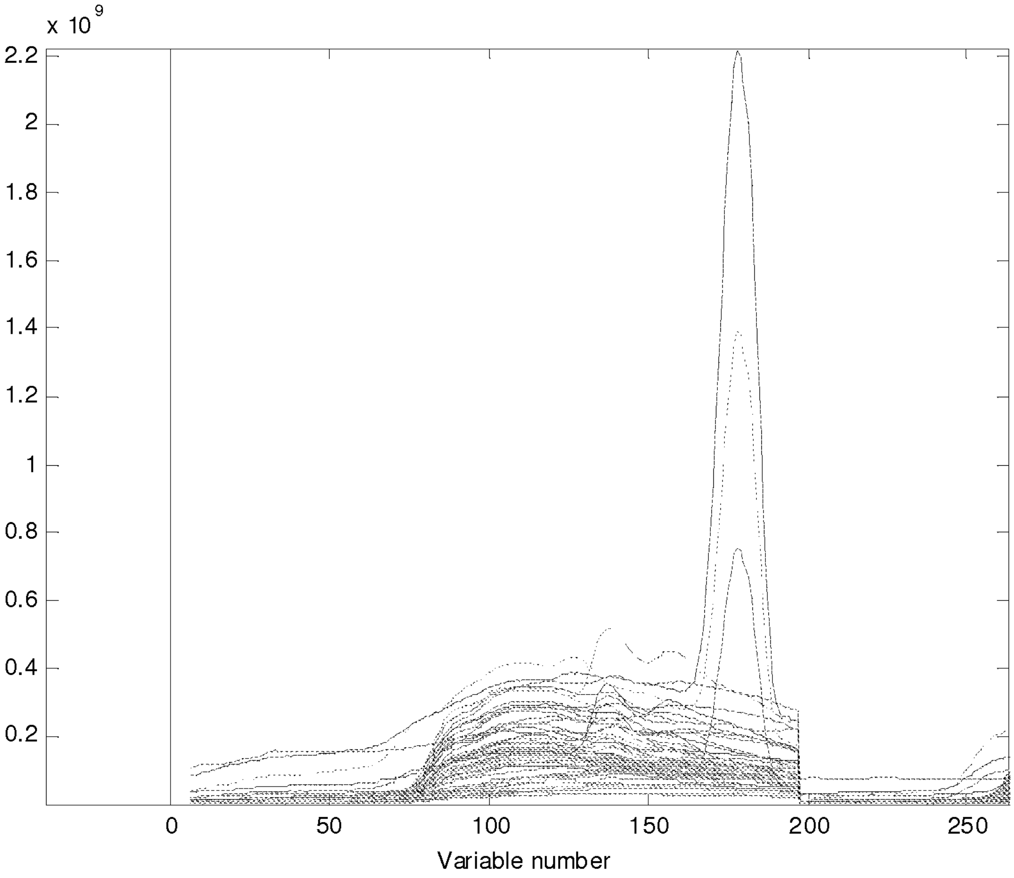

x 10^9
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
50
100
150
200
250
Variable number

Fig 8

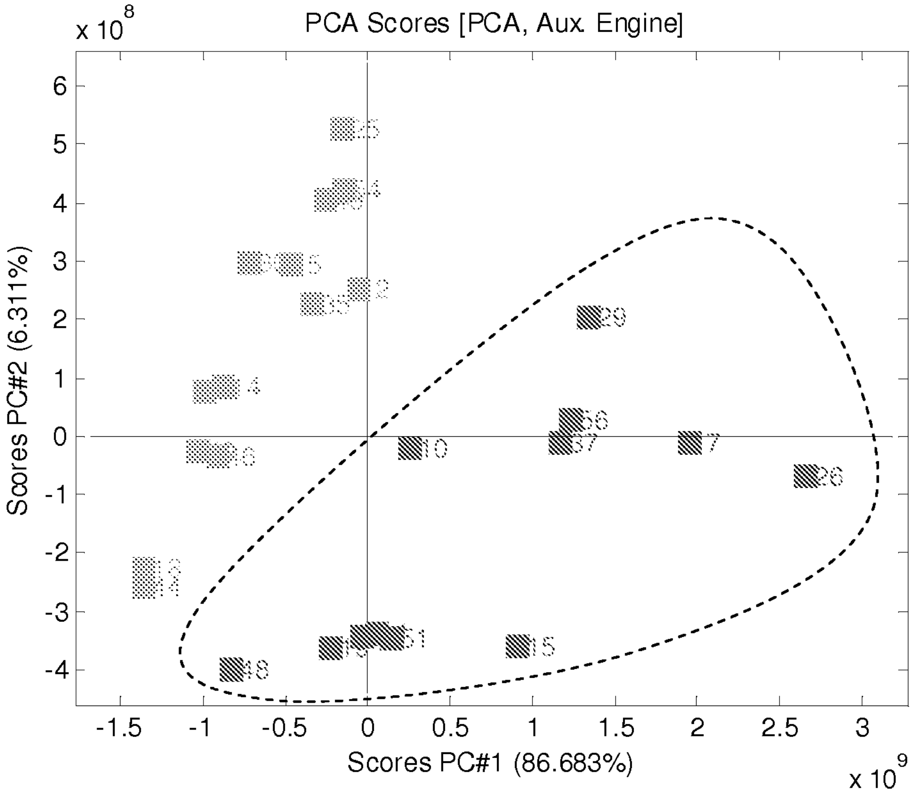

PCA Scores [PCA, Aux. Engine]
x 10^8
6
5
4
3
2
1
0
-1
-2
-3
-4
Scores PC#2 (6.311%)
-1.5
-1
-0.5
0
0.5
1
1.5
2
2.5
3
Scores PC#1 (86.683%)
x 10^9
25
54
5
2
29
4
56
37
7
10
26
51
15
48

FIG 9

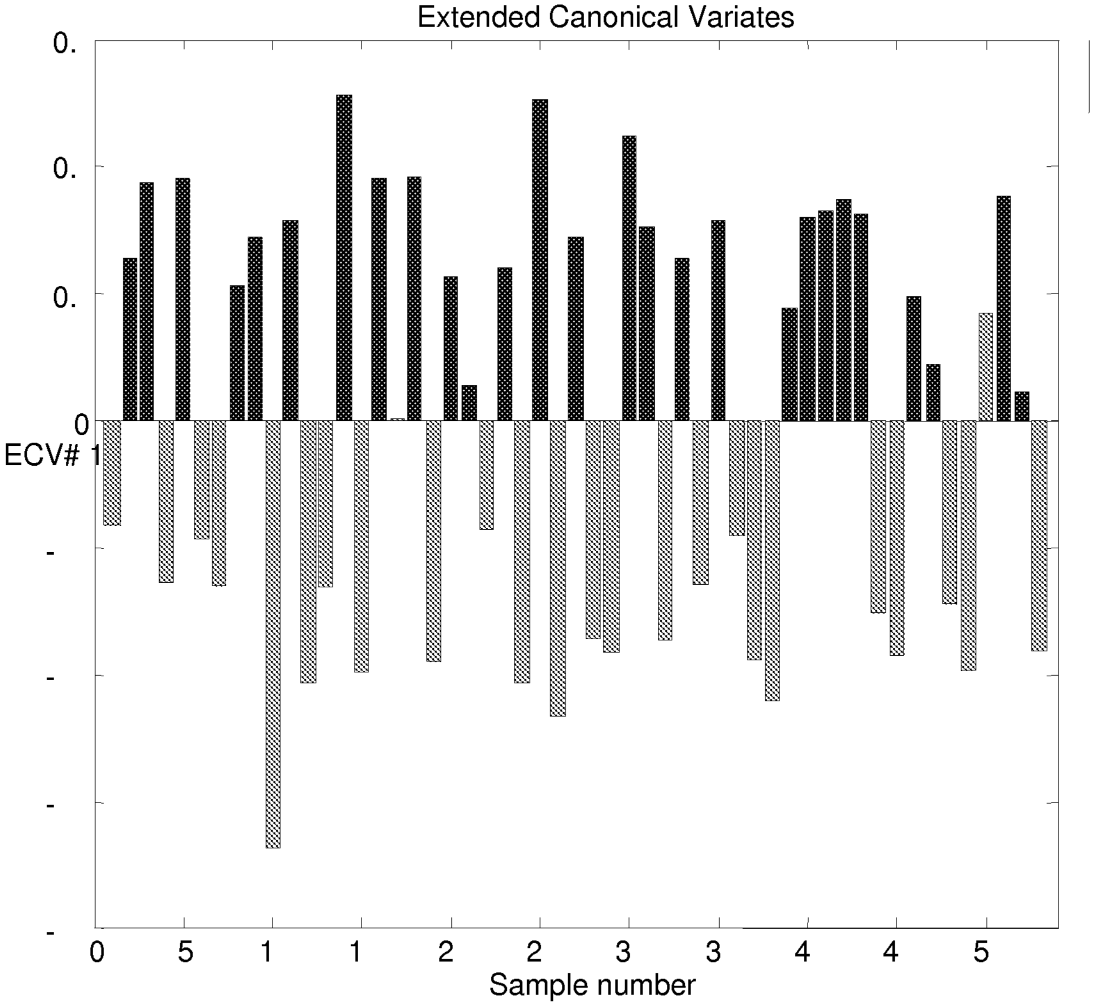

Extended Canonical Variates
0.
0.
0.
0
ECV# 1
-
-
-
-
0
5
1
1
2
2
3
3
4
4
5
Sample number

Fig 10

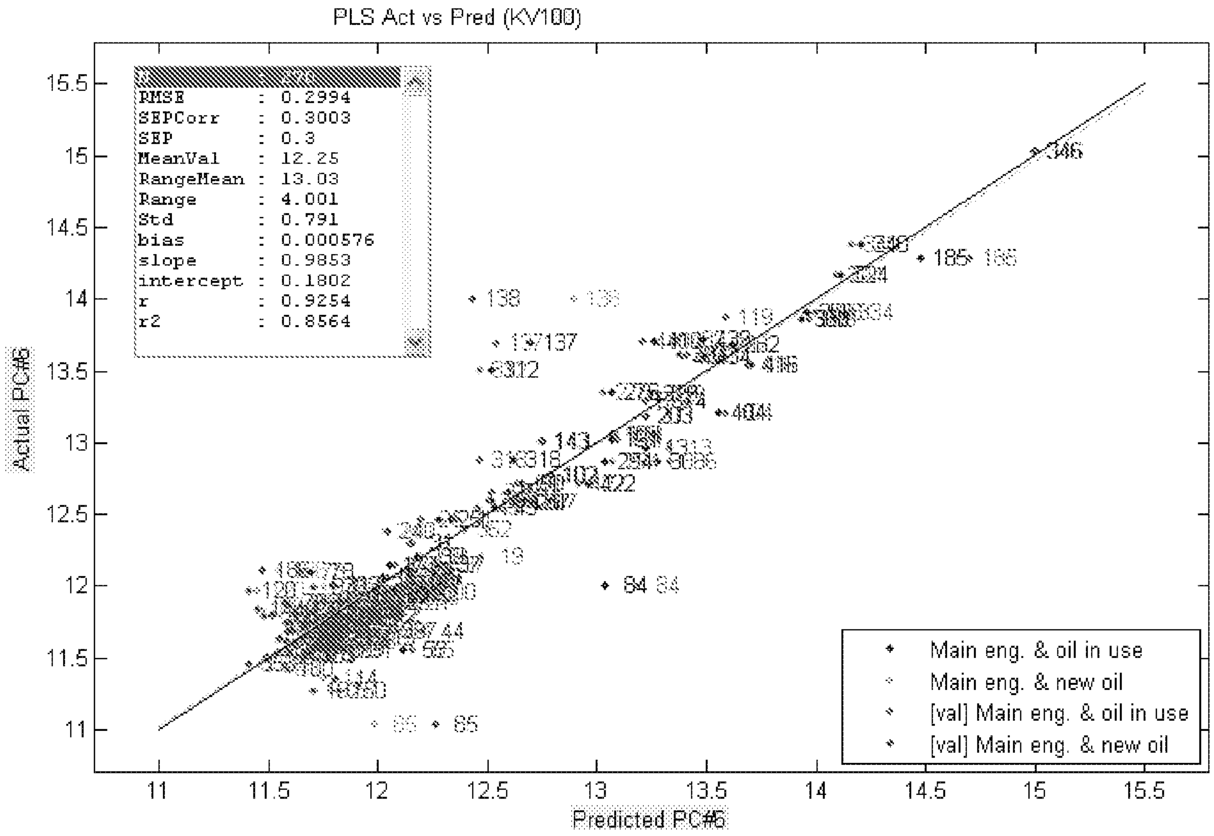

PLS Act vs Pred (KV100)
RMSE : 0.2994
SEPCorr : 0.3003
SEP : 0.3
MeanVal : 12.25
RangeMean : 13.03
Range : 4.001
Std : 0.791
bias : 0.000576
slope : 0.9853
intercept : 0.1802
r : 0.9254
r2 : 0.8564
Actual PC#6
Predicted PC#6
15.5
15
14.5
14
13.5
13
12.5
12
11.5
11
11
11.5
12
12.5
13
13.5
14
14.5
15
15.5
346
185
138
137
119
143
19
84
85
Main eng. & oil in use
Main eng. & new oil
[val] Main eng. & oil in use
[val] Main eng. & new oil

Fig 11

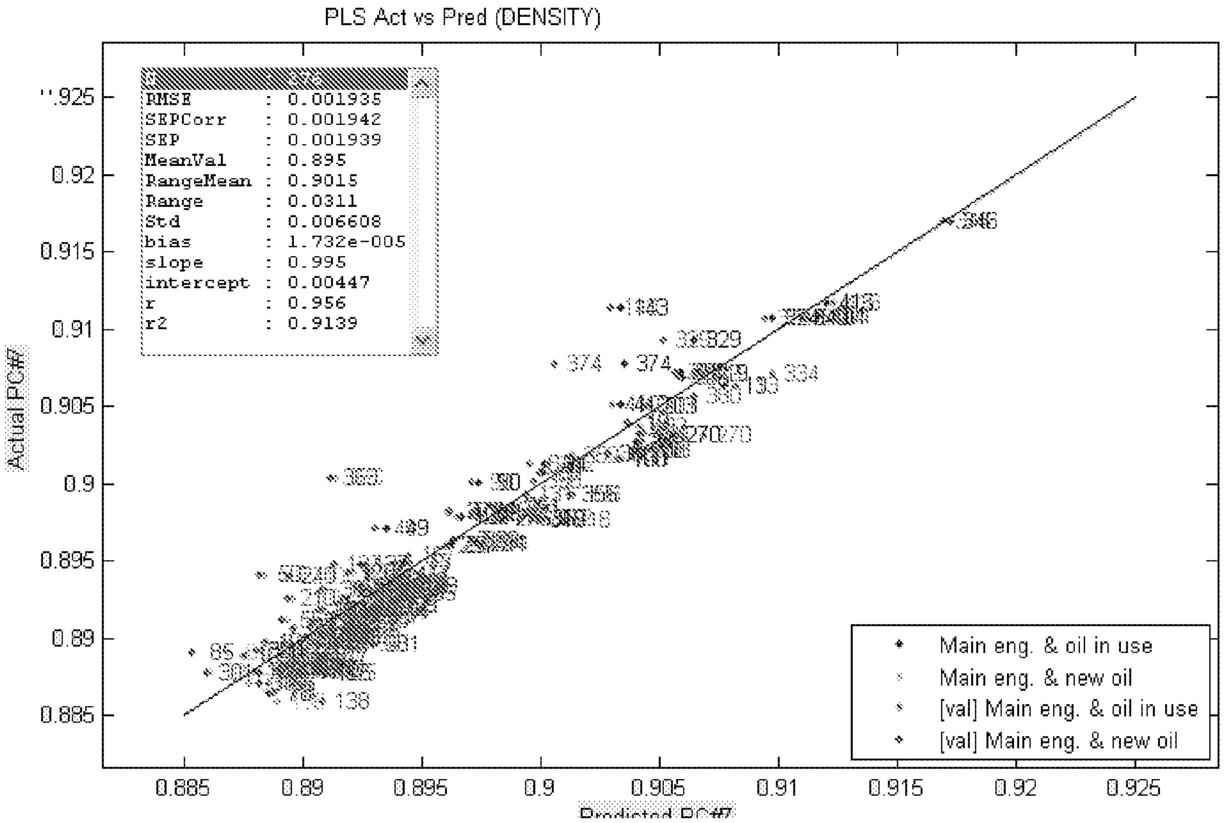

PLS Act vs Pred (DENSITY)
RMSE : 0.001935
SEPCorr : 0.001942
SEP : 0.001939
MeanVal : 0.895
RangeMean : 0.9015
Range : 0.0311
Std : 0.006608
bias : 1.732e-005
slope : 0.995
intercept : 0.00447
r : 0.956
r2 : 0.9139
Actual PC#7
Predicted PC#7
0.925
0.92
0.915
0.91
0.905
0.9
0.895
0.89
0.885
Main eng. & oil in use
Main eng. & new oil
[val] Main eng. & oil in use
[val] Main eng. & new oil
346
413
143
329
374
374
334
133
330
270
270
353
350
356
449
85
301
138

Fig 12

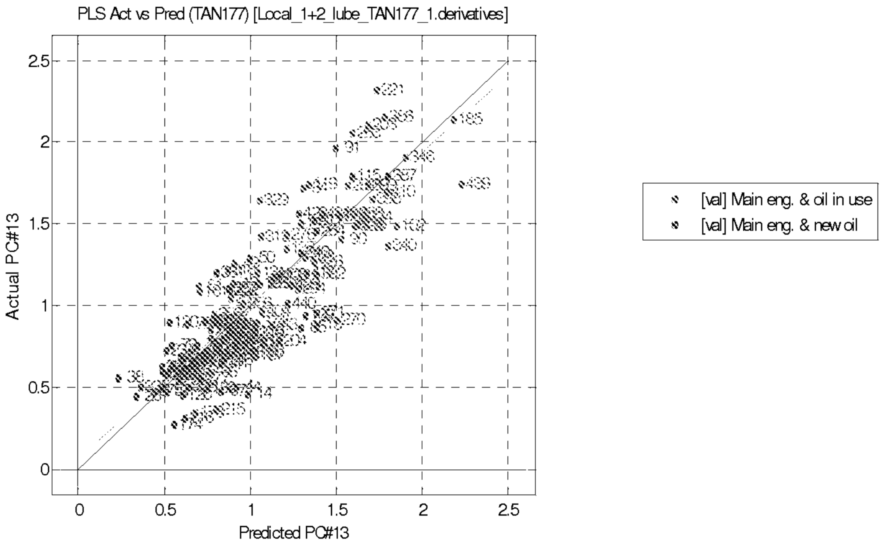

PLS Act vs Pred (TAN177) [Local_1+2_lube_TAN177_1.derivatives]
Actual PC#13
Predicted PC#13
0
0.5
1
1.5
2
2.5
[val] Main eng. & oil in use
[val] Main eng. & new oil

Fig 13

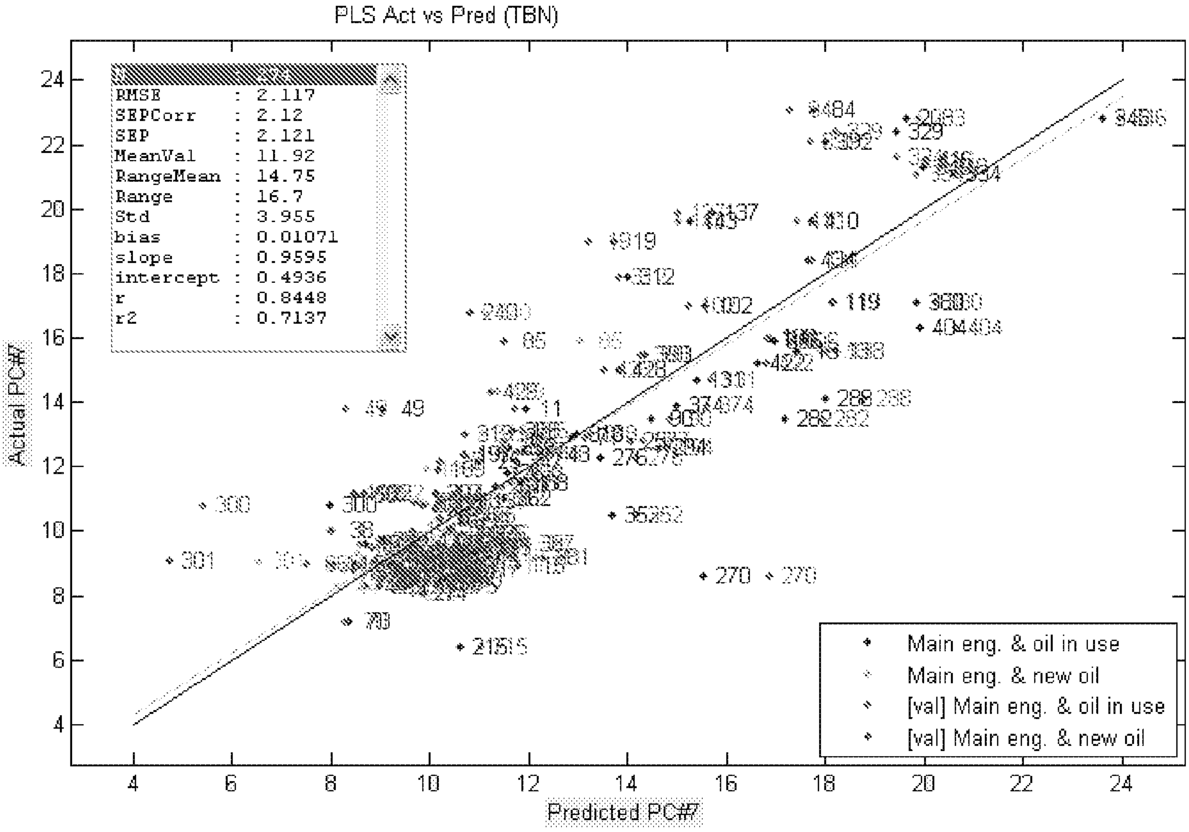

PLS Act vs Pred (TBN)
RMSE : 2.117
SEPCorr : 2.12
SEP : 2.121
MeanVal : 11.92
RangeMean : 14.75
Range : 16.7
Std : 3.955
bias : 0.01071
slope : 0.9595
intercept : 0.4936
r : 0.8448
r2 : 0.7137
Actual PC#7
Predicted PC#7
24
22
20
18
16
14
12
10
8
6
4
4
6
8
10
12
14
16
18
20
22
24
Main eng. & oil in use
Main eng. & new oil
[val] Main eng. & oil in use
[val] Main eng. & new oil
300
301
49
85
119
270
329
404
288
282
276
11
1919
312

Fig 14

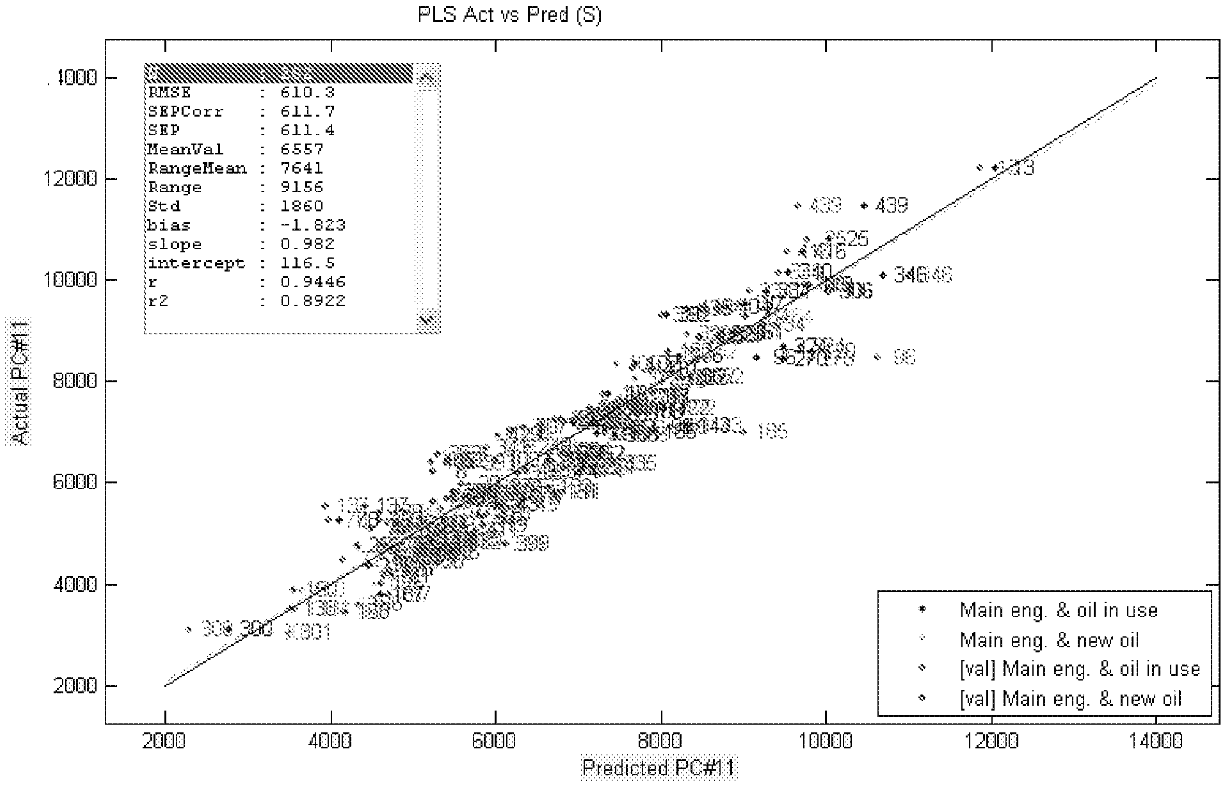
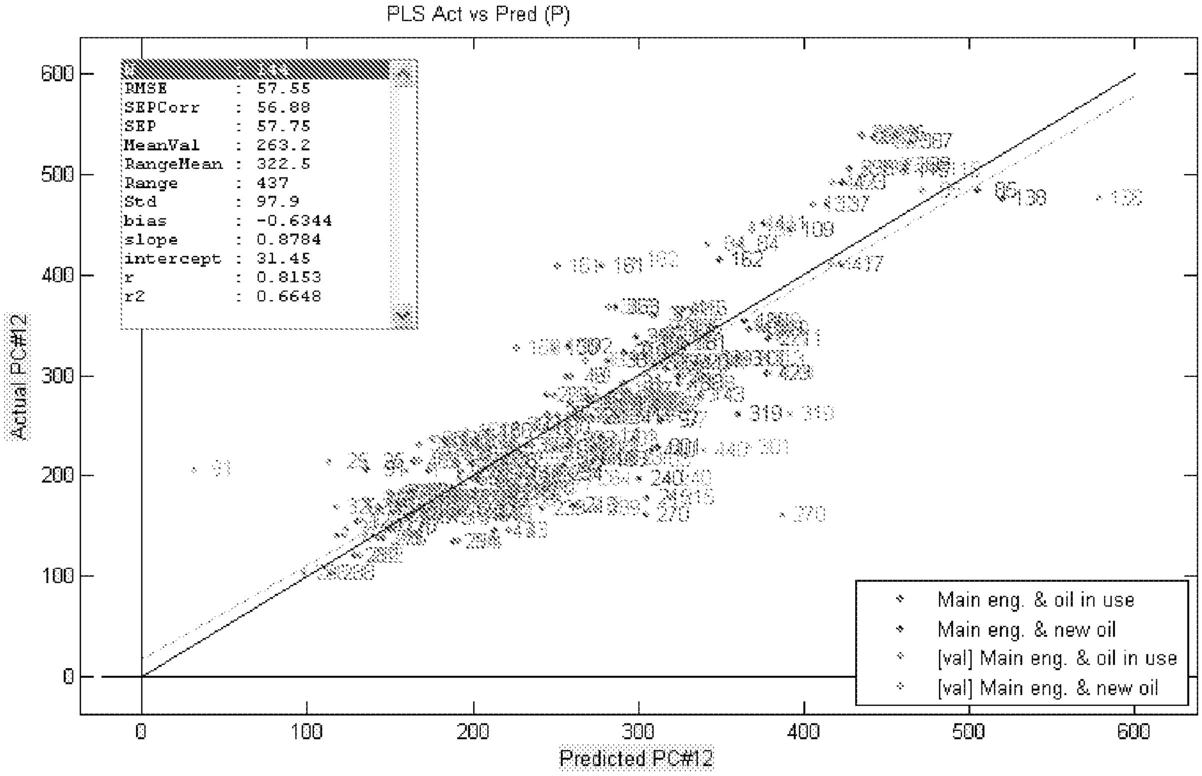

PLS Act vs Pred (S)
RMSE : 610.3
SEPCorr : 611.7
SEP : 611.4
MeanVal : 6557
RangeMean : 7641
Range : 9156
Std : 1860
bias : -1.823
slope : 0.982
intercept : 116.5
r : 0.9446
r2 : 0.8922
Actual PC#11
Predicted PC#11
1000
12000
10000
8000
6000
4000
2000
2000
4000
6000
8000
10000
12000
14000
Main eng. & oil in use
Main eng. & new oil
[val] Main eng. & oil in use
[val] Main eng. & new oil
439
439
346
96
185
133
300
300
301

Fig 15



```
RMSE        : 57.55
SEPCorr     : 56.88
SEP         : 57.75
MeanVal     : 263.2
RangeMean   : 322.5
Range       : 437
Std         : 97.9
bias        : -0.6344
slope       : 0.8784
intercept   : 31.45
r           : 0.8153
r2          : 0.6648
```

Fig 16

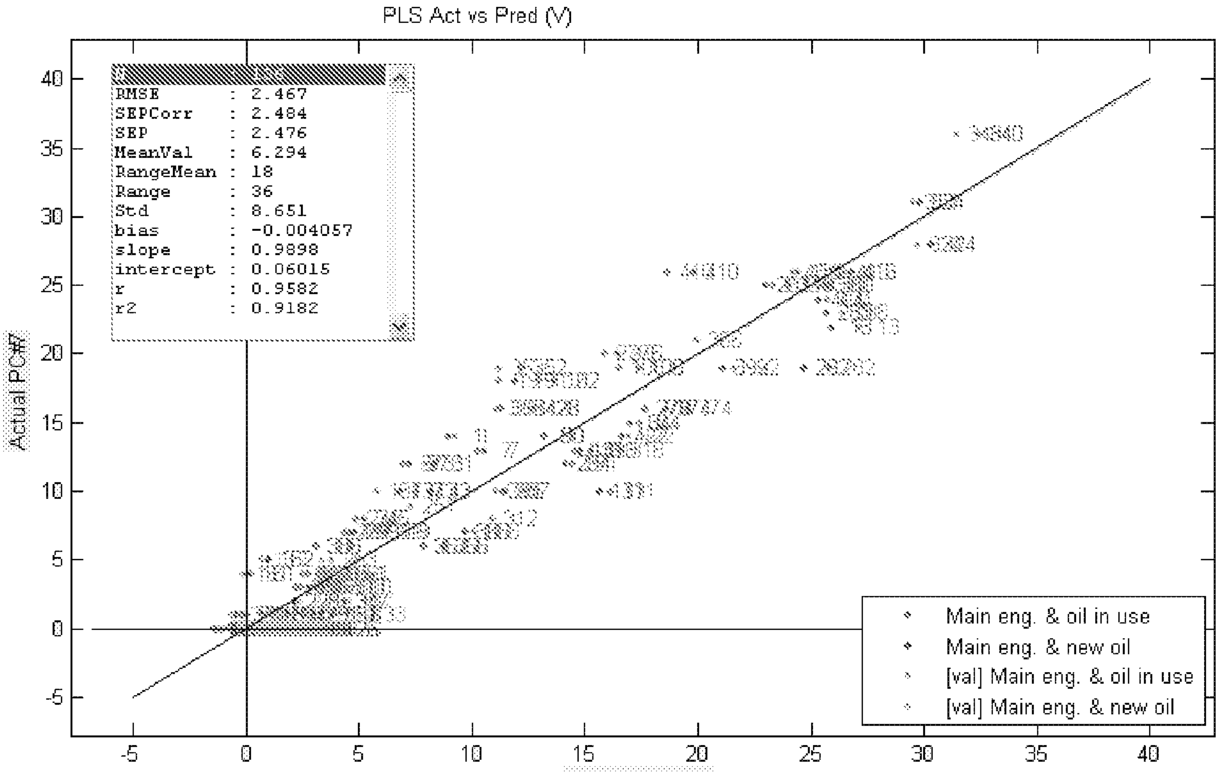

PLS Act vs Pred (V)
RMSE : 2.467
SEPCorr : 2.484
SEP : 2.476
MeanVal : 6.294
RangeMean : 18
Range : 36
Std : 8.651
bias : -0.004057
slope : 0.9898
intercept : 0.06015
r : 0.9582
r2 : 0.9182
Actual PC#7
40
35
30
25
20
15
10
5
0
-5
-5
0
5
10
15
20
25
30
35
40
Main eng. & oil in use
Main eng. & new oil
[val] Main eng. & oil in use
[val] Main eng. & new oil

Fig 17

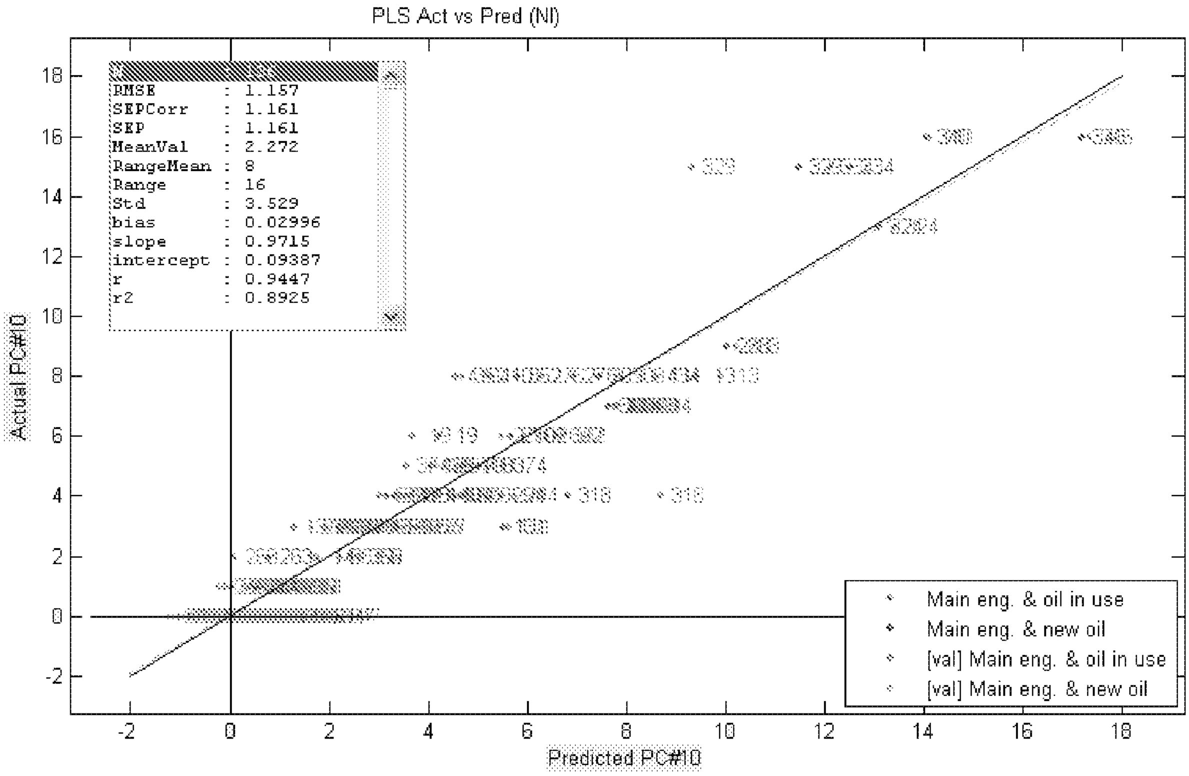

PLS Act vs Pred (NI)
RMSE : 1.157
SEPCorr : 1.161
SEP : 1.161
MeanVal : 2.272
RangeMean : 8
Range : 16
Std : 3.529
bias : 0.02996
slope : 0.9715
intercept : 0.09387
r : 0.9447
r2 : 0.8925
Actual PC#10
Predicted PC#10
-2
0
2
4
6
8
10
12
14
16
18
Main eng. & oil in use
Main eng. & new oil
[val] Main eng. & oil in use
[val] Main eng. & new oil

Fig 18

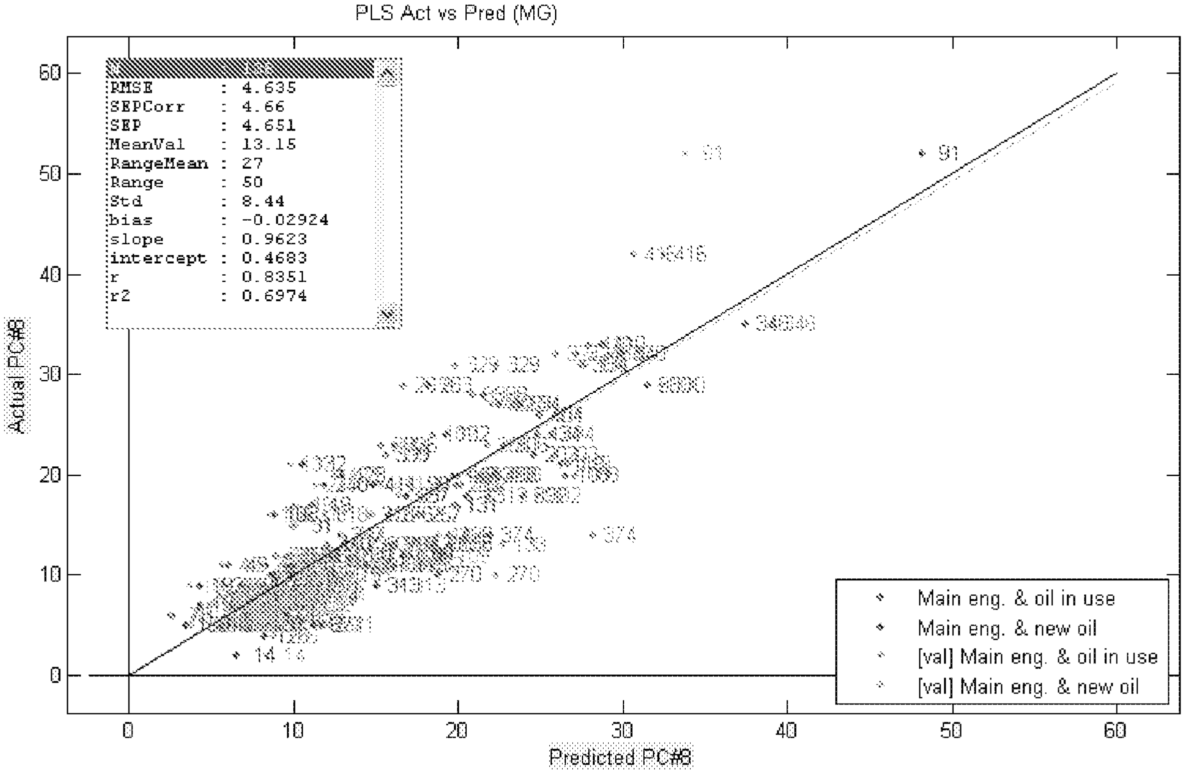
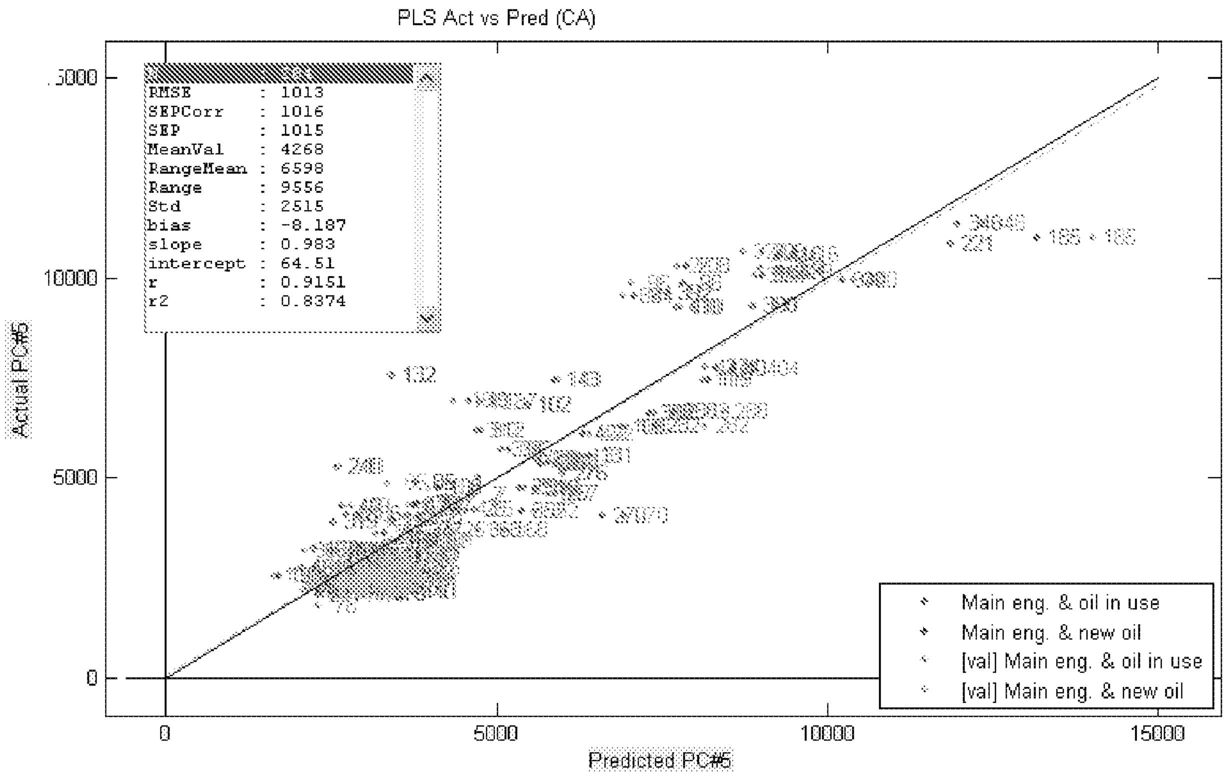

PLS Act vs Pred (MG)
RMSE : 4.635
SEPCorr : 4.66
SEP : 4.651
MeanVal : 13.15
RangeMean : 27
Range : 50
Std : 8.44
bias : -0.02924
slope : 0.9623
intercept : 0.4683
r : 0.8351
r2 : 0.6974
Actual PC#8
Predicted PC#8
0
10
20
30
40
50
60
Main eng. & oil in use
Main eng. & new oil
[val] Main eng. & oil in use
[val] Main eng. & new oil
91
329
374
270
14

Fig 19


PLS Act vs Pred (CA)
RMSE : 1013
SEPCorr : 1016
SEP : 1015
MeanVal : 4268
RangeMean : 6598
Range : 9556
Std : 2515
bias : -8.187
slope : 0.983
intercept : 64.51
r : 0.9151
r2 : 0.8374
Main eng. & oil in use
Main eng. & new oil
[val] Main eng. & oil in use
[val] Main eng. & new oil
Actual PC#5
Predicted PC#5
0
5000
10000
15000
0
5000
10000
15000

INTERNATIONAL SEARCH REPORT

International application No
PCT/DK2008/050329

A. CLASSIFICATION OF SUBJECT MATTER
INV. G01N21/35 G01N21/64 G01J3/44 G01N33/22 G01N33/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
G01N G01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2004/084623 A1 (LONG YICHENG [CA] ET AL) 6 May 2004 (2004-05-06) paragraphs [0002], [0003], [0005], [0009], [0011] - [0015], [0029] - [0035]; claim 3; figure 1 -----	1-7, 10-32, 34-55, 58-77

-/--

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Date of the actual completion of the international search 19 March 2009	Date of mailing of the international search report 26/03/2009
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Duijs, Eric

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ABBAS O ET AL: "Application of chemometric methods to synchronous UV fluorescence spectra of petroleum oils" FUEL, IPC SCIENCE AND TECHNOLOGY PRESS, GUILDFORD, GB, vol. 85, no. 17-18, 1 December 2006 (2006-12-01), pages 2653-2661, XP025235882 ISSN: 0016-2361 [retrieved on 2006-12-01] abstract paragraphs [0001], [0002], [0004] -----	1-9, 20-34, 44-57, 67-77
X	US 6 455 850 B1 (COATES JOHN [US] ET AL) 24 September 2002 (2002-09-24) column 1, lines 15-55; figure 7 column 4, line 54 - column 5, line 62 column 7, line 49 column 15, lines 46-67 column 33, lines 13-35 -----	1-77
X	CANECA A R ET AL: "Assessment of infrared spectroscopy and multivariate techniques for monitoring the service condition of diesel-engine lubricating oils" TALANTA, ELSEVIER, AMSTERDAM, NL, vol. 70, no. 2, 15 September 2006 (2006-09-15), pages 344-352, XP025000781 ISSN: 0039-9140 [retrieved on 2006-09-15] abstract paragraphs [0001] - [0003], [0005] -----	1-7, 10-32, 34-55, 58-77
X	US 2004/106204 A1 (CHIMENTI ROBERT J L [US] ET AL CHIMENTI ROBERT J L [US] ET AL) 3 June 2004 (2004-06-03) paragraphs [0001] - [0008], [0024] - [0048], [0073] - [0087] -----	1-7, 10-32, 34-55, 58-77

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/DK2008/050329

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2004084623 A1	06-05-2004	NONE	
US 6455850 B1	24-09-2002	NONE	
US 2004106204 A1	03-06-2004	NONE	