Introduction

Eralytics produces the Eraspec spectrometer that operates in the MID-IR region approximately in the 630 to 4000 cm-1 frequency domain. The vast majority of organic chemical compounds absorb in this region, demonstrating the analytical interest of these type of instruments.

The FT-IR instruments are fast and reliable analyzers that perform with equal ease simultaneous determinations of chemical composition and physical properties that can be correlated to quality specification of products and performance parameters.

Light Absorption   Basic Vibration modes

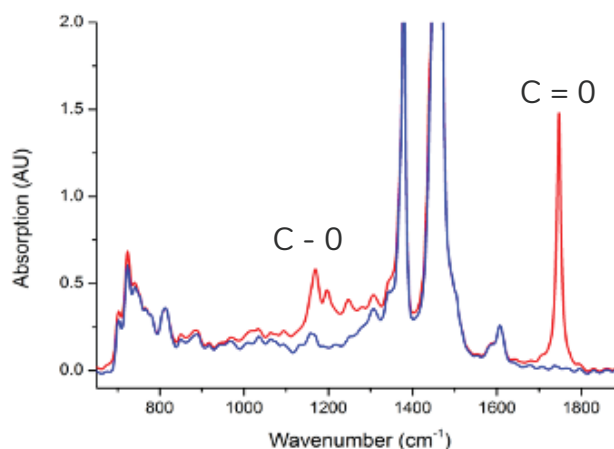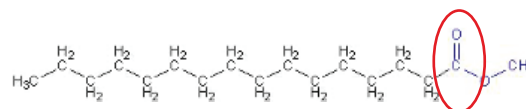$$A(v) = -log\left(\frac{I(v)}{I_0(v)}\right) = \alpha(v) \cdot C \cdot l$$
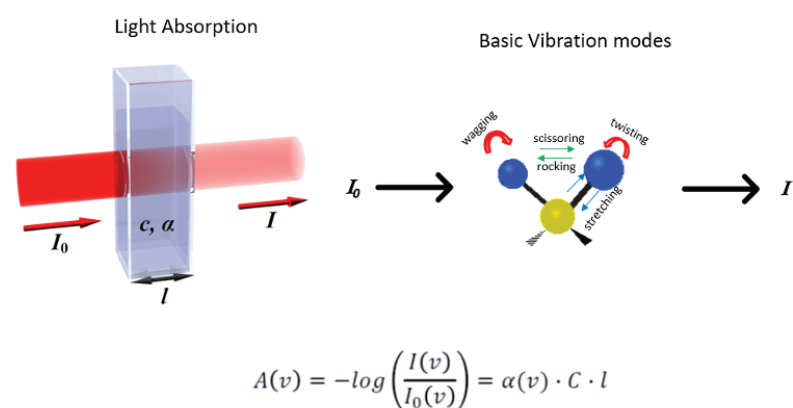
Common characteristics of these instruments are their intrinsic capabilities of removing matrix effects and account for contaminants that might degrade the final quality of the fuels. These instruments do not require any type of sample preparation or sample manipulation, perform automatic measurements of light absorbance according to Beer - Lambert's law. It's operation require little technical skills of the users.

The absorption of light is mainly due to the different vibration modes of the bonds of organic chemicals present in the analyte as illustrated above.

From this equation we measured the absorption of determined peaks or regions and calculate the concentration which is the only unknown for a particular instrument type.

After the sample is introduced into the cell the scan begins to acquire the data according to the method's settings. The instrument determines the overall absorption spectrum of the sample in the Middle Infrared region, approximately from 450 up to 6500 cm $^{-1}$.

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The original signal o interferogram is Fourier transformed to a frequency domain absorption spectrum illustrated in the spectrum below.

Composition and Properties Analysis

Once the frequency domain characteristic spectrum is obtained it can be compared with the data base or library built in the instrument. A cluster analysis that groups sets of objects (data) in such a way that objects of the same group (clusters) are similar in properties to each other and to other objects like for example an unknown sample.

Red: Measured IR spectrum
Blue: Fit to spectrum
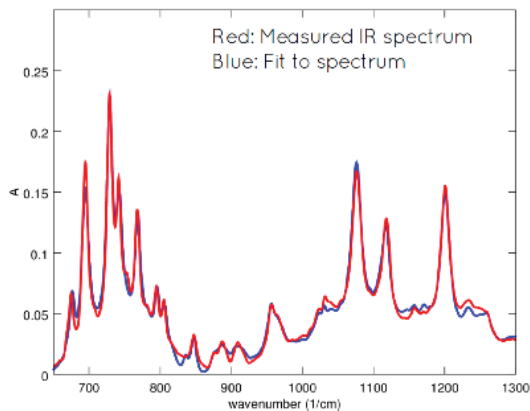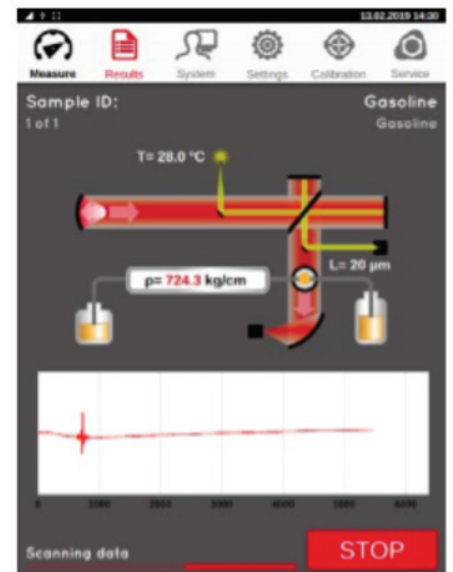
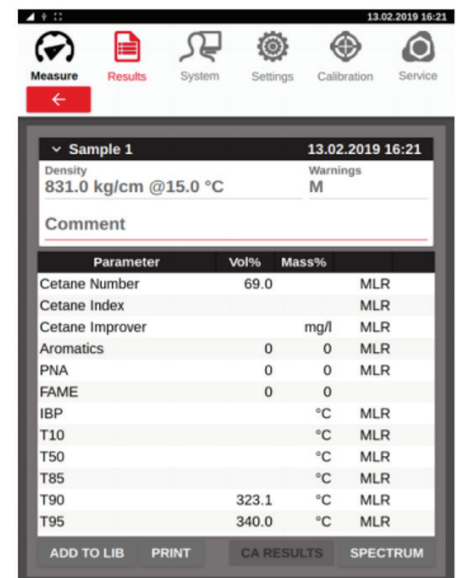$$A (Sample) - A (Data Base) \leq n * Limit$$
$$\text{for all } A_i (Components)$$

When this equation is satisfied in the first 3 iterations the reference sample parameters in the data base are transferred to the unknown and the results is denoted as Cluster Analysis "n".

In conclusion Cluster analysis looks at the spectroscopic fingerprint of the unknown sample. If this fingerprint is the same as one or several reference samples already in a database the instrument will give very precise results, because the properties of this sample are already known. When there is no agreement the analysis is stopped and a Multi Linear Regression analysis (MLR) takes place.

Multivariate Calibration for Concentrations of individual compounds

The Eraspec calculates a fit with known reference spectra of pure substances oxygenates, alkyl aromatics etc. to determine the concentration of each substance. If an unknown substance is detected in the sample the instrument will give a warning. Qualification normally proceed in accordance with standards like D5845 for oxygenates and D6277 for benzene content in gasoline.

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Eraspec utilizes a multivariate k-matrix calibration model to determine individual concentrations of aromatics, olefins and oxygenates as described in E1655[1].

A set of 140 samples gravimetrically prepared in a blank sample of petroleum ether for the aromatics and in an oxygen free gasoline for the oxygenates described in D5845[2] where recorded in the region of 630 cm^{-1} to 4000 cm^{-1}. When an unknown sample is recorded and Fourier transformed, the spectrum is compared to this library set of 140 samples to get the concentration of individual components. The spectrum of pure substances is calculated by subtraction of the spectrum of the standard and the spectrum of the matrix.

To validate the calibration model the Standard Error of Cross Validation is calculated as well as the 95% Confidence Interval and any possible concentration outside the confidence interval. When there are no parameters falling outside the Confidence Interval the model is considered validated.

By removing 26 samples corresponding to medium concentration samples values a new calibration with 114 subset samples is performed and the 26 samples are compared to the original values for Total Oxygenates and Total Oxygen. The new SEV, Confidence Interval and zero samples falling outside the interval proves that the model is validated. This k-matrix model is then integrated to the Eraspec software for the analysis of unknowns. This calibration is transferable to all Eraspec instruments. All instruments have been standardized by the Eralytics Quality Control Dept.

Any baseline correction needed when there are variations is performed with a low absorbance of a blank petroleum ether measured at low resolution. This spectrum is subtracted then from all spectra measured at full resolution and typically Cyclohexane is the substance used for standardization. Cyclohexane is very suitable due to its abundance of absorption peaks of different intensities and locations in the frequency domain. To improve the results of concentration a corrected result is generated by adjusting the gain and offset by the equation:

Corrected result = square * result + gain * result + offset

Multi Linear Regression Analysis

It has been established that the instrument is using databases (libraries) with samples with known properties to compare the unknown samples to the spectra in the library utilizing chemometric models like cluster analysis or MLR to predict these values.

The basic concepts are based in the generation of a linear model of the type:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \cdots + \beta_k x_k + \varepsilon$$

Where "y" is the dependent variable; $xi......xk$ are the independent variables and ε is the error normally distributed with an average value of zero.

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MLR uses the entire data base to obtain the coefficients of the spectral areas selected for the calculation of the properties. For MLR to work properly it is required a data base of at least 40 samples with known reference values for the properties needed.

MLR introduces a statistic useful concept that indicates how well an unknown sample is represented in the data base of the instrument. It is known as the Mahalonobis Distance where by the smaller the Maha. Distance is the better the unknown sample is represented in the data base.

The Mahalannobis Distance concept in general and the Normalized Mahalannobis Distance in particular leads to the term "Outlier" meaning that when the unknown sample is not well represented in the data base and their properties cannot be interpolated from the library universe, this means that it lies outside the factory data base. In which case we can either expand our data base or populate around this measurement result by creating a customer library to increase the measurement accuracy.
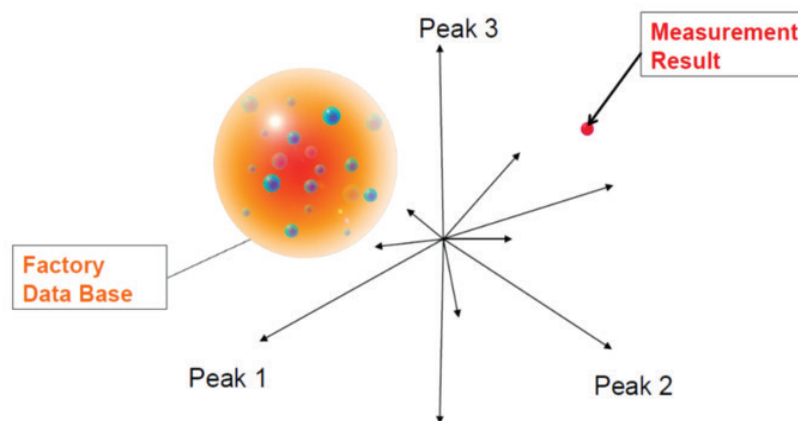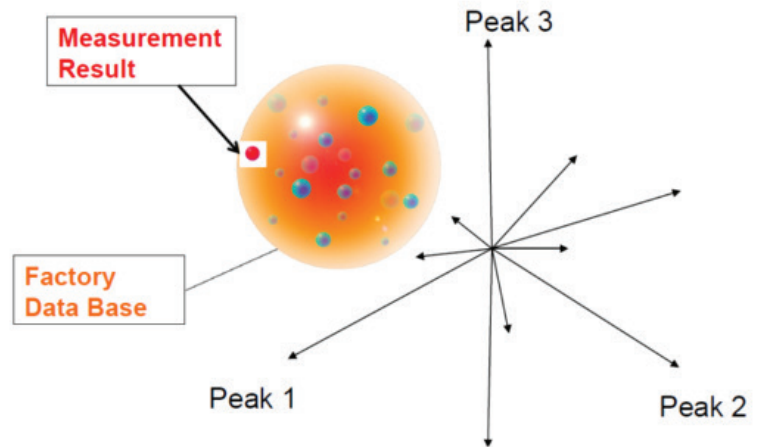
The presence of an Outlier demonstrate that the statistical model is not applicable to the sample being analyzed. In other words, the properties of the unknown cannot be found by interpolation of the data on which the multivariate model is based.

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There is a possibility of utilizing multiple databases at the same time in which case the Eraspec will consider it as a large universe of data. Eralytics however, strongly recommends to build a customer data base by adding typical samples from the customer. Eralytics offer a seamless easy few step to create a library and to add new reference values. All libraries active at the moment of the calculations will be treated as a single data base making the outlier case a simple one for normal interpolation of analytical properties.
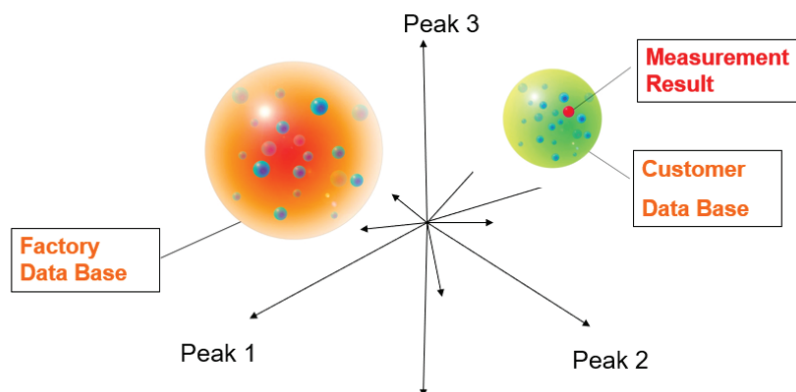
Eralytics combines Density with the Eraspec spectral analysis by building in a U-tube modules that determines density complying with D7777 and D4052.

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..\ERALYTICS\ERASPEC\New Brochure ERASPEC 2017.pdf

Density Module built in the Eraspec analyzer

References

1. **ASTM E1665** Standard Practice for Infrared Quantitative Analysis. *Annual Book of Standards Vol.* 03.06
2. **ASTM D5845** Standard Test Method for Determination of MTBE, ETBE, TAME, DIPE, Methanol, Ethanol and tert-Butanol in Gasoline by Infrared Spectroscopy. Annual Book of Standards Vol. 05.02
3. **ASTM D4052** Standard Practice for Infrared Multivariate Quantitative Analysis
4. **ASTM D7777** Standard Test Method for Density, Relative Density and API Gravity of Liquid Petroleum by Portable Digital Density Analyzer. *Annual Book of Standards Vol.* 05.05.