# Turn-key on-line analysis systems based on spectroscopical methods in the Near Infrared (NIR)

User-specific system (Diode Array) in EEx p layout

Ex-protected turn-key NIR analyzer with sample conditioning system
(Analyzer shelter by BARTEC BENKE)

# NIR Analyzing Systems

**Introduction:**

We are currently witnessing a "quantum leap" in the efficiency of process analyzing technologies. Spectroscopic methods in the **NIR** (**N**ear **I**nfra**R**ed) range have become accessible for on-line applications. The new technology continues to progress: the new analyzers become more and more efficient, and the possibilities for their use in various process applications continue to grow.

The new generation of analyzers is characterized by:

- correlative optical measuring methods
- extremely short measuring cycles
- simultaneous determination of physical and / or chemical parameters.

The measuring methods give comprehensive data with high density of information about the process. These data are perfectly suitable to be used as control signals for innovative and, last but not least, profit-maximizing control concepts in process plants. Especially very complex processes can be supervised accurately and reliably with NIR-technology.

Modular design is typical of BARTEC BENKE NIR systems. Fiber optics allow coupling with a great variety of sample probes or flow-cells. This is only one of the many facts that make BARTEC BENKE NIR system configurations highly flexible.

Typically, investing in an NIR system pays off within very few months because of the following advantages:

1. Multiple parameters in a product stream can be measured with only one system. This means that one single NIR analyzer can replace several conventional measuring devices.

2. Multiplexing allows multipoint measurement with only one analyzer

3. Very short measuring cycles (typically < 1 min)

4. Very fast response - without relevant transient of the measuring system - to rapid parameter changes in the sample stream

5. Very little maintenance effort for hardware due to considerably extended endurance

6. High data density improves the identification of process conditions significantly and thus allows the application of the most modern process control concepts.

BARTEC BENKE GmbH, Germany, looks back to more than 40 years of gaining experience in planning and manufacturing process analyzing technologies. Besides other activities, our company belongs to the most important developers of NIR technology.

Our profound experience in NIR and process technologies perfectly enables us to give attention to the various specific process and environmental conditions of our customers plants. With our flexible NIR analyzing equipment we offer turn-key solutions that are perfectly matched with your particular process requirements, and thus we decisively help optimizing your process plants.

**Principle of Measurement:**

The NIR spectroscopy is based on the excitation of the sample molecules by photons in the wavelength range from 900 to 2500 nm. In this near infrared range, the overtones and combinations of the fundamental vibrations in the mid infrared can be observed. The resulting absorption bands usually are broad and strongly overlapping peaks, and they are by orders of magnitude less intensive than the fundamental bands. This apparent disadvantage proves to be one of the major advantages of NIR spectroscopy in real life, because these low absorption values allow much thicker sample layers (1 mm – 20 mm) compared to the mid infrared range. As larger sample volumes contribute to the result, the requirement for sample homogeneity is strongly reduced. Therefore compared to mid infrared measurements the need for sample preparation is minimized.

Useful absorption bands with significant intensity in the near infrared range are primarily assigned to molecules having X-H (X = C, N, O), and C=O groups, which means that almost all organic and many inorganic compounds can be analyzed by NIR spectroscopy. In contrast to the mid infrared even the water peaks have sufficiently low intensity, so that measurements in aqueous solutions become feasible.

The NIR spectrum thus contains important information about the molecular composition and structure of the sample which determine its physical and chemical properties.

Due to the spectacular evolution of special mathematical algorithms (so-called chemometrics) it has become possible to access the high content of structural information in the NIR spectra by their direct correlation with certain properties of the sample material. Chemometric calibration models help determining whole sets of qualitative and quantitative sample properties and characteristic values in real-time. The calibration models required for such computations are generated off-line based upon reference analysis results, either from the laboratory or from already existing conventional on-line process analyzers.

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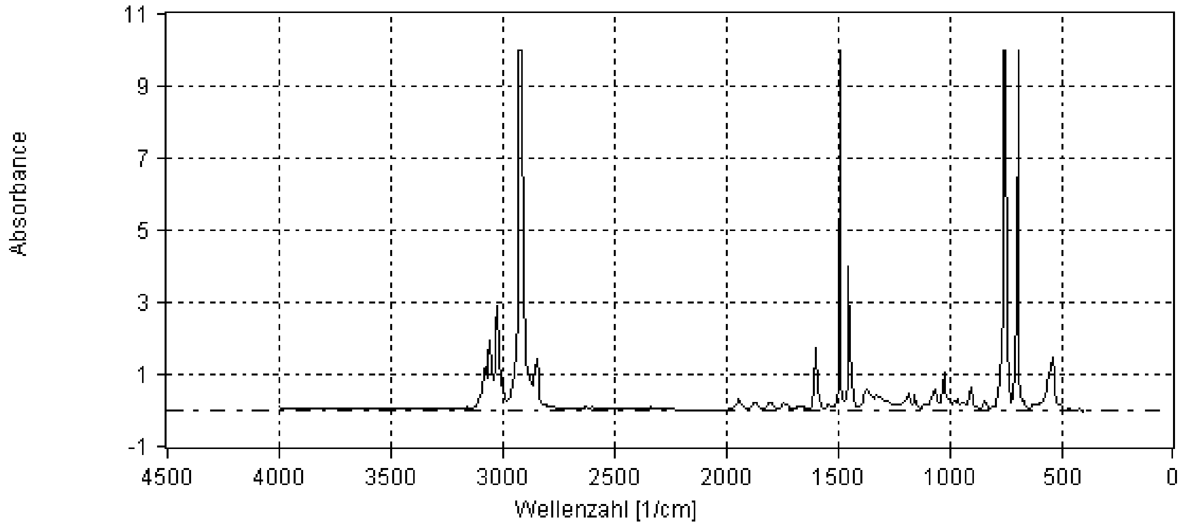
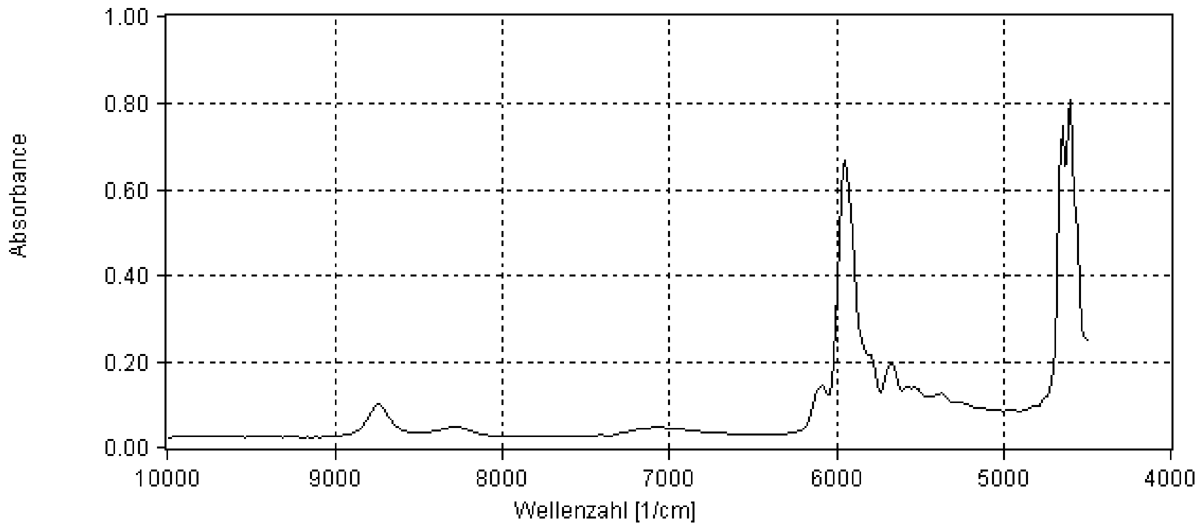
# Polystyrene – Mid Infrared Spectrum




# Polystyrene – Near Infrared Spectrum



A typical NIR spectrometer contains a halogen source for polychromatic light. The emitted light beam is dispersed by a monochrometer and then guided to a special sensor (flow-cell or immersion probe), where the non-destructive interaction of the monochromatic light and the sample takes place. During this interaction the sample molecules are changing their vibrational states according to their structure and show characteristic energy absorption. The absorption is measured by a photodetector and referenced to the discrete wavelengths. The result is a so-called spectrum that displays the light absorption over a certain spectral range. By using mathematical models the property values of interest can be derived from this spectrum. It is also possible to check whether the analyzed sample is sufficiently similar to the samples in the calibration set (outlier–detection).

## Spectroscopic Hardware

The environmental conditions in a typical process application make great demands on the installed spectrometer. For this reason, only instruments with an outstanding shock- and vibration-resistance are used in BARTEC BENKE NIR systems. In most cases, *Fourier-Transform-NIR*, *AOTF* (**A**cousto-**O**ptic **T**unable **F**ilter) or *Diode Array* systems are used. In addition to their high reliability and robustness, one of the remarkable features of these technologies is the combination of excellent photometric performance with very high scan rates.

The decision for a certain device is usually based on feasibility studies taking into consideration the requirements of the particular case.

## Sensors

The measuring cells used by BARTEC BENKE are optimal for the spectral range from 900 to 2500 nm and have an optical transmittance of at least 60%. For best possible coupling of optical fibers all cells are supplied with collimation lenses. In addition to the high optical performance, easy mounting and dismounting in case of maintenance are important criteria for our selection of cells. The choice of the particular type of measuring cell depends on the sample, the temperature requirements, sufficient resistance to pressure, and relevant regulations and standards.

If for some reason an immersion probe is needed instead of a flow-cell, alternative sensors can be easily connected to the spectrometer module because of the standardized plug-in connection. The probe may then be inserted into a pipe or a reactor via an appropriate flange connection.

## Multiplexing

There are several possibilities for multipoint measurement with only one NIR-device:

- Mechanical multiplexing or stream switching, where the different sample streams are fed sequentially into a sample conditioning system with measuring cell. This alternative only makes sense if the sample streams consist of similar products (e.g. different fractions of gasoline). For example, the total measuring period for 6 streams would take approximately 40 minutes with adequate sample conditioning.

- Optical multiplexing, where each sample stream is fed into its own sample conditioning system with its own measuring cell. An optical multiplexer switches sequentially between the individual streams with their measuring cells. The total measuring period depends primarily on the switching times of the multiplexer. For 8 sample streams, the time for a complete measuring cycle is typically about 10 minutes.

- a combination of these two methods.

The decision for one of the above mentioned methods depends on the particular case of application and the overall conditions.

## Sample Conditioning

Our experience has shown that reliable sample conditioning is an indispensable part of all NIR analyzing systems. The precision and long-term stability of spectroscopic methods under process conditions depend to a large extent on stable sample conditions. Temperature, pressure, and flow rate, are the most important parameters. Experiments show that for example the sample temperature has a significant influence on the precision of optical measurements. The variation in density that corresponds with temperature changes directly influences the measuring result. In principle, a mathematical correction of this temperature influence is possible. However, because of the large number of possible interfering factors we recommend the use of an adequate sample conditioning system that guarantees precise measuring results. With this approach, the number of degrees of freedom for the statistical modelling can be reduced to a minimum, and the calibrations become more accurate.
We have developed our own in-house standard in which the most important interfering parameters are defined. Last but not least, this is a major advantage for calibration transfer too.

A typical BARTEC BENKE sample conditioning system for NIR analysis consists of the following components:

- sample conditioning (filter, pressure reducer, water separator, heater, cooler)
- reference product feeding
- sampling (manual or automatic)
- automatic or manual sample feeding and product switching
- sensors for monitoring the product conditions
- fieldbus interfaces (optional)
- cleaning system (optional)

## ACU (Analyzer Control Unit) with the BARTEC BENKE On-line Software BOL

The ACU, together with the BOL software, represents the main control unit of the NIR analyzer. All hardware and software functions necessary for a modern system are available here. The user-specific configuration is based on an industrial PC in a 19" slide-in unit and allows maximum flexibility in adapting to existing systems.

The ACU organizes the complete measuring process, which comprises:

- selection of sample streams
- administration of the calibration models for the different parameters
- measurement itself
- pretreatment of the measuring signal (transformations)
- calculation of the measurement values
- supporting the measuring certainty (outlier-detection)
- communication with the process control system (e.g. Modbus)
- realization of the 4-20 mA current-loop outputs
- control and monitoring functions of sample conditioning
- realization of necessary delay times
- triggering of optical or mechanical multiplexers (if applicable)
- system monitoring (generation of service and error alarms)
- storage and visualization of spectral, reference and system data
- realization of additional digital / analog inputs
- allocation of reference values
- remote maintenance of the system via modem interface (telephone line)

**Calibration Development**

For the parameters that are to be measured with the NIR analyzer, calibration models have to be developed by means of suitable statistical methods. The most common of these so-called chemometric methods are:

- Multiple Linear Regression (MLR)
- Partial Least Squares Regression (PLSR)
- Principal Components Regression (PCR)

Calibration development is an iterative process which comprises:

- collecting and inspecting data (spectra, reference values)
- developing models with chemometric methods
- selecting the best model by statistical criteria
- validating the model by prediction of independent samples
- using the model for routine analysis

For calibration development the spectral data of a sufficiently large product sample set and the reference analysis data of the corresponding samples are required. The reference values for each parameter (octane number, vapor pressure etc.) can either be determined in the laboratory or by means of on-line reference analyzers. The intermediate coupling to existing on-line analyzers during calibration development allows to get representative sample material in a very efficient way.
The collection of these data is planned together with the user whose support is required. The sample material used for calibration has to represent the product variations that are typical for the measuring site. Variations that have to be taken into consideration are for example:

- seasonal variations (summer and winter products)
- process-related parameter variations within the products (e.g. changes in catalyst activity)
- usage of varying raw materials and components

With the calibration data set representing the situation on site an experienced chemometrician at BARTEC BENKE performs the chemometric modeling. However, the user can carry out the calibration development in his own organization as well if he has adequately skilled personnel at his disposal.
In routine operation of the NIR analyzing system the maintenance of the mathematical models is reduced to a minimum thanks to our innovative multi–modelling–technology. It can even be taken over by the plant staff without specific knowledge in this field.
The efficient support of our users concerning the model maintenance is additionally ensured by our remote maintenance of the complete analyzing system via modem.

The time schedule for the calibration primarily depends on the product variations that have to be taken into consideration. In case of considerable seasonal variations the total calibration process can take a year. For this reason we offer a calibration support for 12 months.

Generally the calibration of an NIR analyzing system can be divided into three phases:

| | |
|---|---|
| Phase 1<br>5 – 10 days | - installation and on-site test of the system<br>- training of your staff with the installed equipment<br>- aligning the procedures for data collection<br>- loading of start calibrations (derived from spectra of our in-house database or from laboratory samples of the user)<br>- connection of the NIR analyzing system to on-line reference systems (if available)<br>- system start-up |
| Phase 2<br>Approx. 3 months | - on-line data collection and sampling (optimal adaptation of the calibration database to the plant production)<br>- calibration development by BARTEC BENKE and transfer of updated models via modem<br>- validation of developed calibrations by means of independent samples from the production line<br>- release of the system for routine operation |
| Phase 3<br>Approx. 9 months | - acquisition of data representing further seasonal or other basic product variations<br>- calibration updates are planned in accordance with the user or initiated by outlier-detection. |

After phase 3 has been completed, the system works in stand–alone mode. In case calibration updates should become necessary because of basic product changes, BARTEC BENKE will take over these tasks with pleasure.

## Applications

Monitoring of process and quality parameters

The application potential for NIR spectroscopy is extremely large and developing spectacularly. Only a few representative examples are given, including the indirect determination of physical and chemical parameters as described in international standards (ASTM, DIN, IP, etc.), for example:

- Composition of the material (identity and concentration of the individual components)
- Quality parameters (e.g. octane number of gasoline)
- Characteristic physical properties (e.g. boiling point)
- Parameters for technical applications (e.g. low-temperature behavior)

Applications in different branches of industry:

- Petrochemical industry

  motor- and aviation fuels
  combustibles and heating oils
  lubricating oils
  paraffins

- Chemical industry

  esterification processes
  polymerization reactions
  detergents
  pesticides
  paints and varnishes

- Cosmetic industry

  shampoo
  disinfectants

- Food and beverage industry

  alcoholic beverages
  vegetable oils
  fermentation processes

Here are some actual examples for properties determined by NIR spectroscopy:

Petrochemical industry

- knock resistance
  MON, RON, cetane number
- volatility
  boiling point, vapor pressure
- low-temperature behavior
  viscosity, cloud-point, CFPP, freezing point, pour-point
- organic components
  aromatics, paraffins, olefins,
  alcohols
- penetration, oil content in paraffins

Chemical industry

- OH-number, iodine number, acid number
- chain-length, molecular weight
- tensides
- washing active substances
- degree of esterification
- water content in polymer dispersions
- content of amino and acid groups

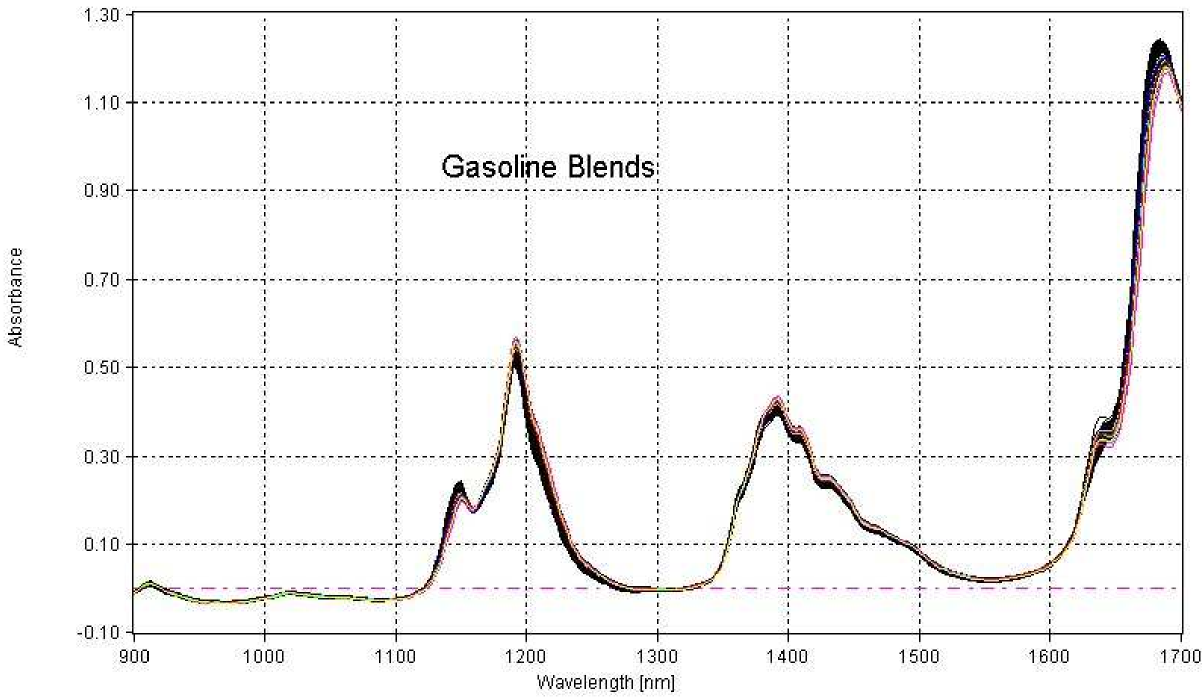
Cosmetic industry

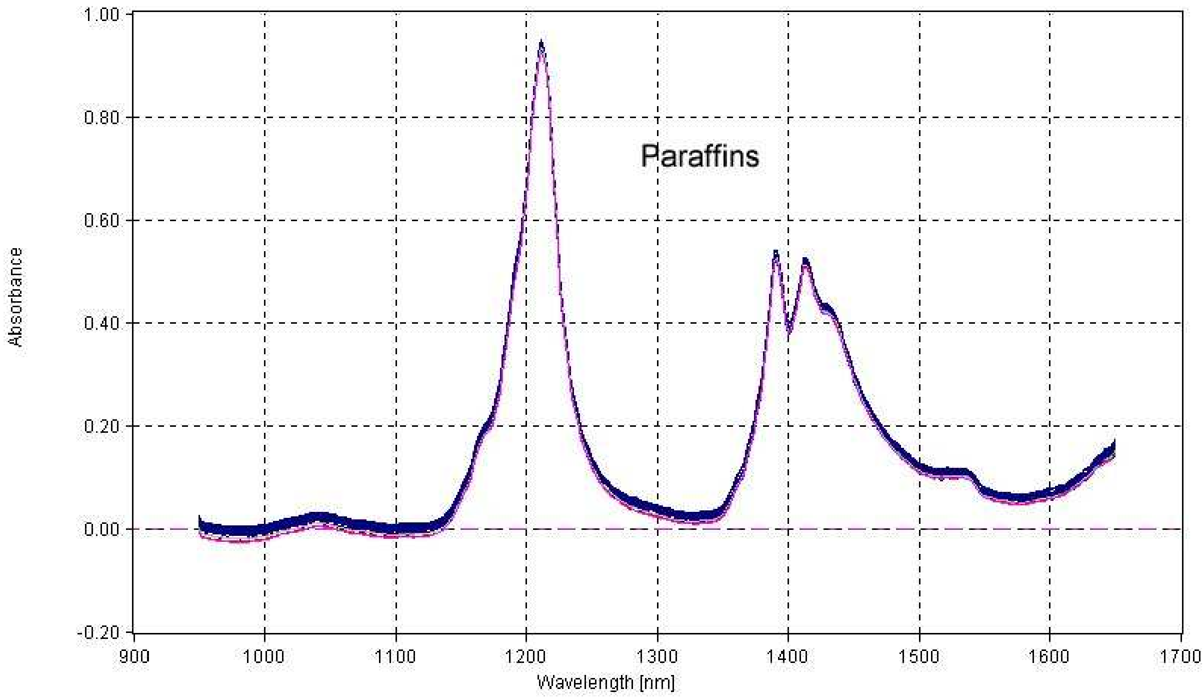
- active ingredients
- tensides
- moisture content
- glycerin content
- content of free fatty acids

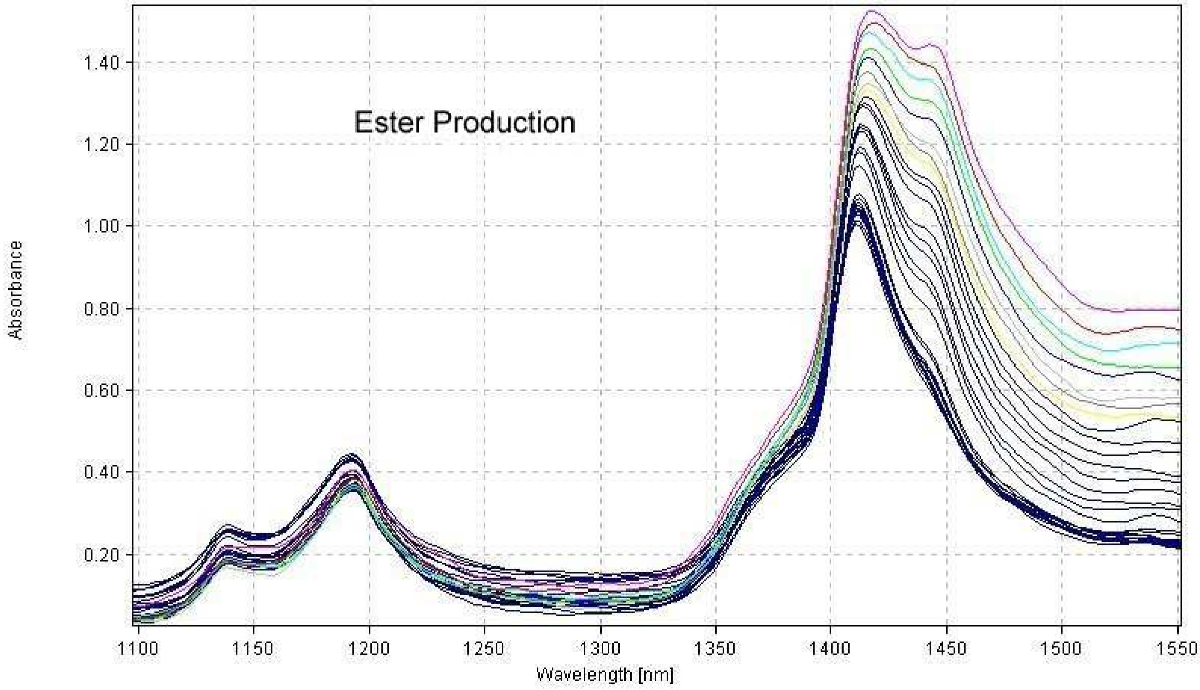
Food and beverage industry

- original gravity
- alcohol content
- oil content
- moisture content

# NIR spectra of some products




Ester Production
Absorbance
1.40
1.20
1.00
0.80
0.60
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0.20
1100
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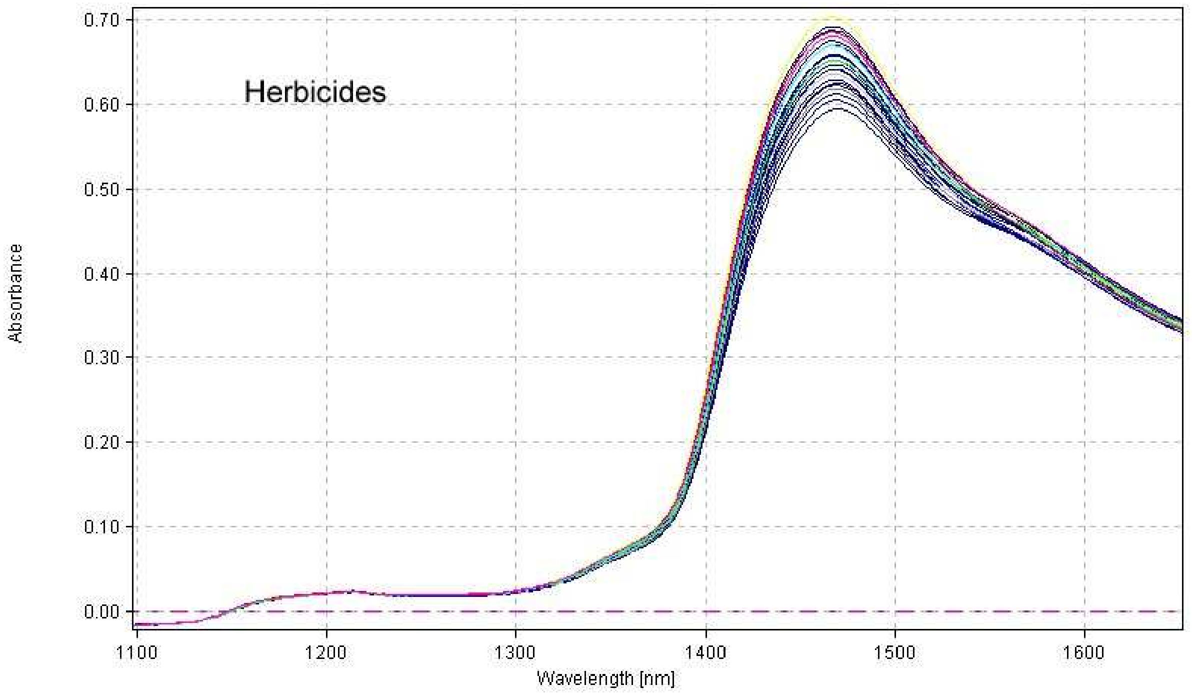
1550
Wavelength [nm]


Herbicides
Absorbance
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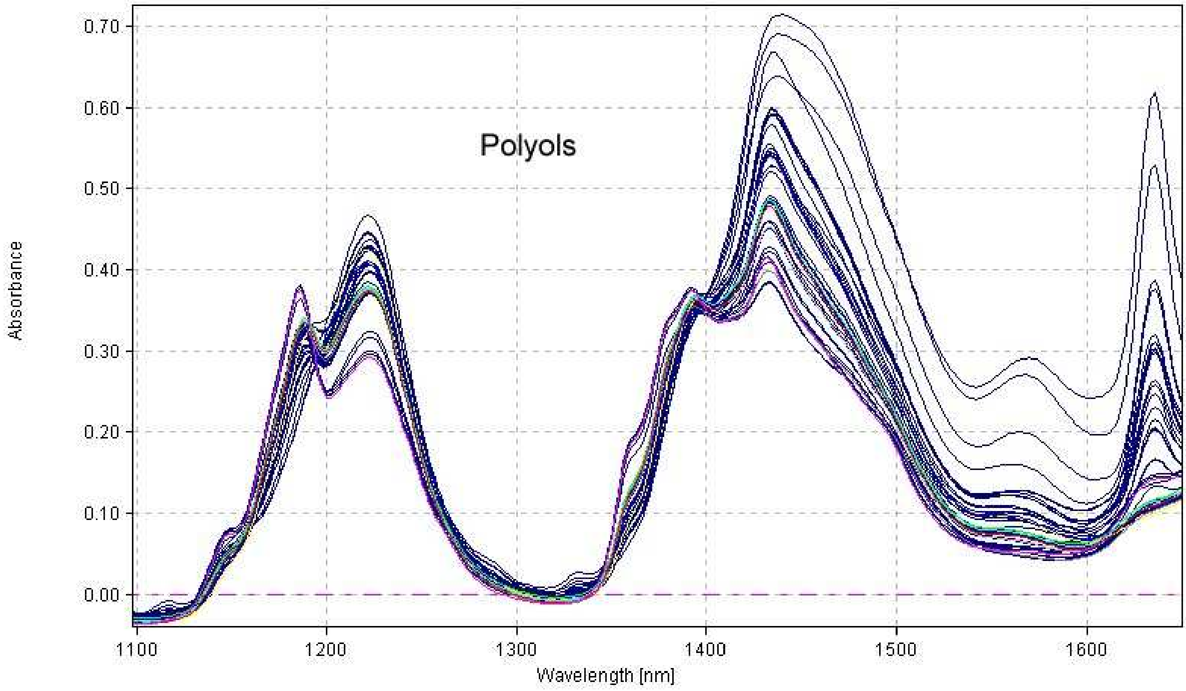
Wavelength [nm]


Polyols
Absorbance
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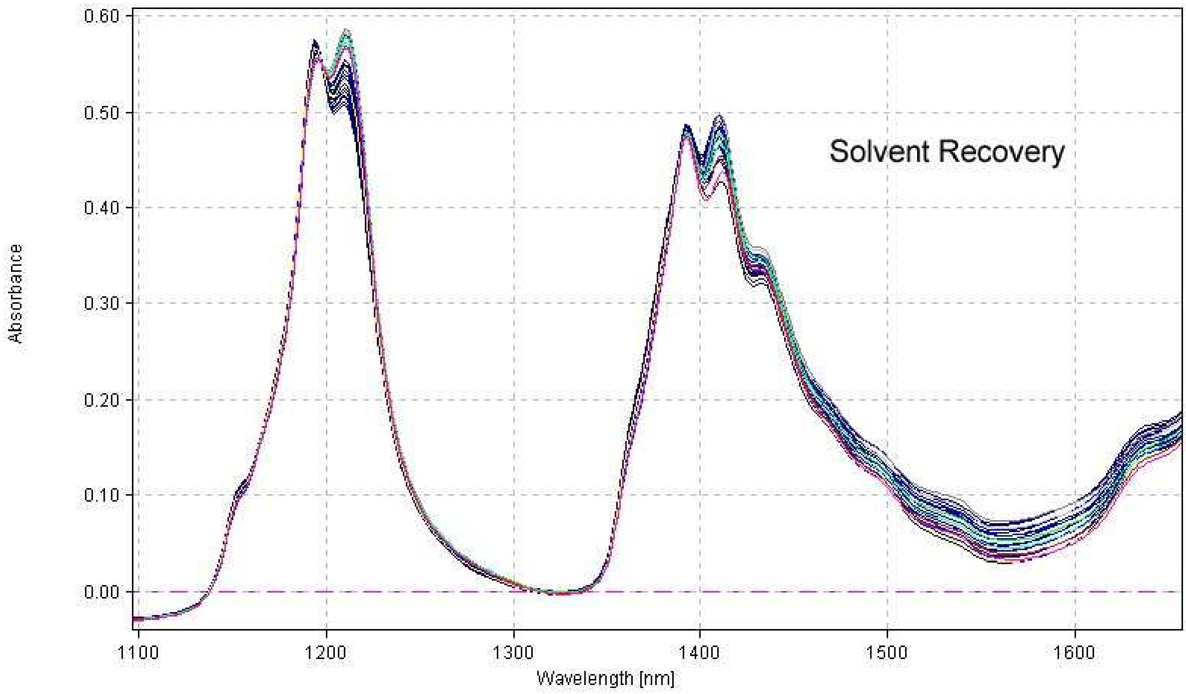
Solvent Recovery
Absorbance
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