

Near-Infrared Spectroscopy for Petrofuel Analysis

A guide to boost efficiency of your product screening and QC testing

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1 Near Infrared Spectroscopy for the Petro Industry

Undoubtedly, there is a trend nowadays towards stricter quality assurance and quality control in the producing industries, such as the petro industry. At the same time, this trend is accompanied by a stronger focus on cost-saving and time-efficient methods so that more testing will not automatically result in higher costs.

The drivers for companies to voluntarily implement more testing and quality practices are:

- Cost pressure: Testing can reveal costly out-of-spec products. Those can be stopped in time.
- Increased competition: Quality practices provide a competitive edge and can be used as a marketing tool; customers are aware of such practices, which, in turn, raises brand value.
- Scarcity of resources: Qualified staff is difficult to find; therefore, the aim is to implement checks that can be carried out by non-specialists.

Near infrared spectroscopy (NIRS) is a method that addresses these drivers mentioned above and is particularly suited for making quality control and product screening more efficient at lower cost.

This application booklet provides you with an overview of the application possibilities and benefits of near infrared spectroscopy in the petro industry. It covers several topics, starting with the basic principle how NIRS works, information on relevant ASTM norms in the petro industry, selected applicative examples, and concluding with detailed information on cost savings.

1.1 UNDERSTANDING NIRS AND ITS POTENTIAL

For more than 30 years now, NIRS has been an established method for fast and reliable quality control within different industries. Being, however a second-

ary method, companies still do not consistently consider the implementation of NIRS as a tool for product screening and quality control. Limited experience regarding application possibilities or a general hesitation of implementing new methods could be the reason. In the chapter, «NIRS: how does it work and how to implement» a brief introduction is given to this fascinating technology followed by an implementation guideline according to ASTM D6122-20 and ASTM D8340-20.

1.2 MULTIPLE PARAMETERS IN JUST ONE MEASUREMENT

How many analytical methods do you typically need to qualify your samples? One, two, or even more? What do you consider to be an acceptable waiting time per analysis? One major advantage of NIRS is the determination of multiple parameters in just 30 seconds with no sample preparation! The non-invasive light-matter interaction used by NIRS, influenced by physical as well as chemical sample properties, makes NIRS a suitable method for the determination of both property types. Application notes included in this document will provide you with real application examples, e.g. for the analysis of gasoline, PyGas and lubricants.

1.3 REDUCE YOUR RUNNING COSTS BY UP TO 90%

Costs of chemicals and toxic reagents are a major pain point when using wet chemical analysis. By this means, not only the purchasing costs of the chemicals are a significant expenditure, but also the process of chemical disposal. Both factors have an impact on total quality assurance and quality control costs, which do obviously affect overall product margins. NIRS being a non-destructive, chemical free technology has the potential to significantly

reduce costs. In our white paper «Boost efficiency in the QC laboratory: How NIRS helps reduce costs up to 90%» the economic advantage of NIRS compared to conventional methods is discussed.

1.4 NIRS AND POLYMERS – WHAT IS THE BENEFIT?

The advantage of NIRS for the analysis of petro products is that it is a fast technique, it does not need any sample preparation, does not require any chemicals, and can determine chemical as well as physical parameters. These characteristics mean that it can be used successfully at several different steps along the production chain of petro products. Examples include checks following the production and distribution of gasoline and for oil condition monitoring of lube oils.

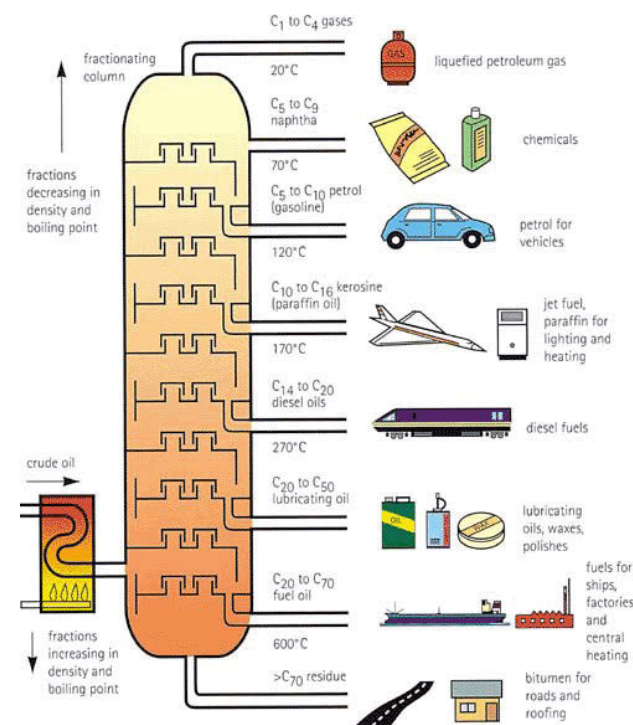


Figure 1: Petro products obtained from fractional distillation of crude

Nowadays, oil and gas are produced in almost every part of the world, from the small 100 barrels-a-day private wells to the large bore 4.000 barrels-a-day wells. Despite this great variation in size, many parts of the process are quite similar. Oil refining aims to provide a defined range of products according to agreed specifications. Simple refineries use a distillation column to separate crude into fractions, and the relative quantities are directly dependent on the crude used. Therefore, it is necessary to obtain a range of crudes that can be blended to a suitable feedstock to produce the required quantity and quality of end products. The basic products from fractional distillation are shown in Figure 1.

Near-infrared (NIR) spectroscopy is a method that is particularly suited for making quality control of the end products shown in Figure 1 more efficient and cost-effective as. Furthermore, NIRS is accepted by the ASTM as an alternative method. Dedicated ASTM methods for method development, method validation and results validation are presented later in this booklet.

Where in the refining process can NIR Spectroscopy be used?

The refining process can be split up in three different parts:

- Up-stream
- Mid-stream
- Down-stream

Up-stream describes the process of crude oil converted into intermediate products. Refineries are in general huge complexes with a lot of explosion dangerous areas. Therefore, these refineries are reluctant to transport samples from the different processes to the laboratory. For obvious reasons in most cases in line measurements are preferred. These types of measurements are typically done by process NIR analyzers.

Mid-stream has many more opportunities for the DS2500 Petro Analyzer, see Figure 2

Fuel is constantly checked for quality as it is received and supplied, and many terminals test fuel quality prior to off-loading the truck. The total time for receiving and off-loading fuel into a storage tank is approximately 30 minutes, so a fast analysis like NIR is very advantageous.

Down-stream at the gas stations and fuel depots the regulatory agencies require many of the same parameters measured by NIR as in the production of gasoline and diesel. There is a huge advantage if the analysis can be done on-site using fresh samples, without having to transport them to testing laboratories.

Some of the parameters that can be measured are shown in Table 1.

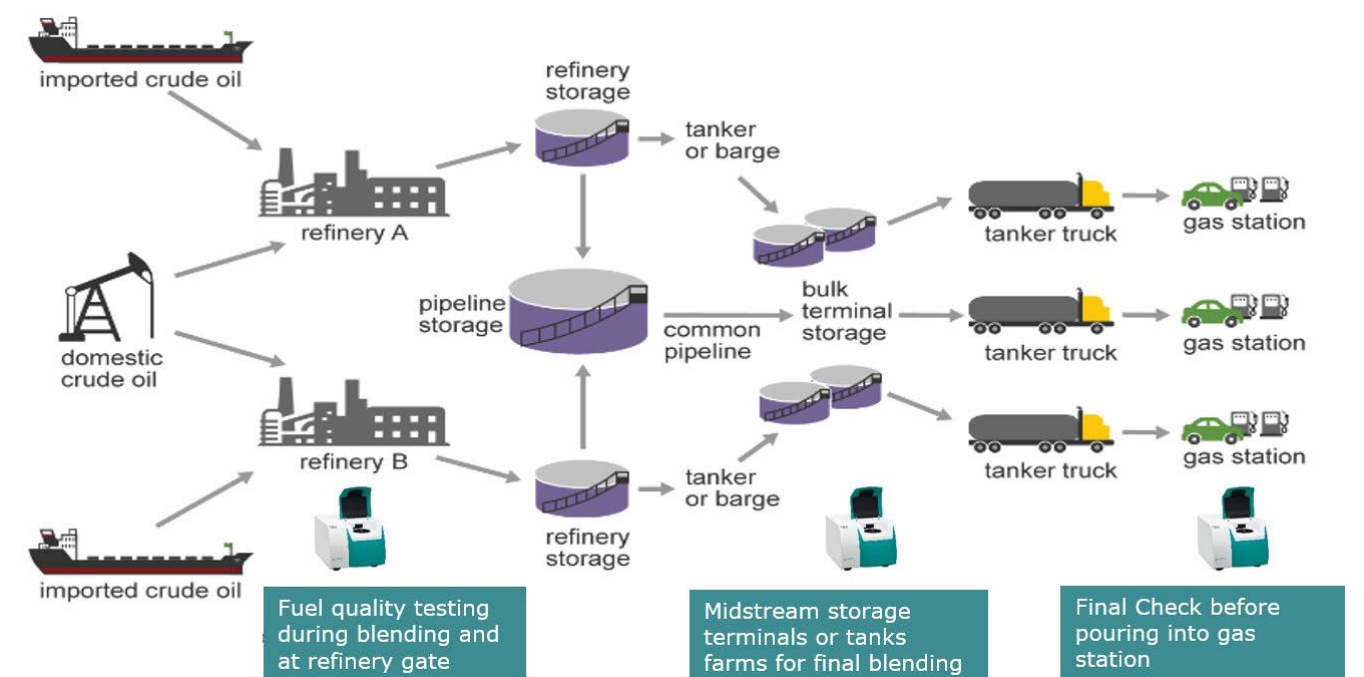


Figure 2: Flow of crude oil and gasoline to your local gas station

2 NIR spectroscopy: how does it work and how to implement it

Petro product	Parameter	Conventional method	Advantage NIR
Gasoline	RON/MON	CFR Engine	<ul style="list-style-type: none"> Results within 30 seconds Low running costs
	Ethanol content	GC	<ul style="list-style-type: none"> Results within 30 seconds Low maintenance
Diesel	Cetane Number	CFR engine	<ul style="list-style-type: none"> Results within 30 seconds Low running costs
	CFPP	Standardized filter device	<ul style="list-style-type: none"> Time saving No cleaning of equipment
	Flash point	Flash point tester	<ul style="list-style-type: none"> Results within 30 seconds No cleaning of equipment
	FAME	GC	<ul style="list-style-type: none"> Results within 30 seconds Low maintenance
Pygas	Diene Value	Titration	<ul style="list-style-type: none"> Time & cost saving No chemicals needed No chemically educated operator needed
	Bromine Index	Titration	<ul style="list-style-type: none"> Time & cost saving No chemicals needed No chemically educated operator needed
Lubricants	Kinematic Viscosity	Viscometer	<ul style="list-style-type: none"> Time savings No cleaning of equipment
	TBN	Titration	<ul style="list-style-type: none"> Time & cost saving No chemicals needed No chemically educated operator needed
	TAN	Titration	<ul style="list-style-type: none"> Time & cost saving No chemicals needed No chemically educated operator needed

Table 1 Examples for use of NIRS for selected petro products

2.1 WHEN LIGHT HITS MATTER

Light and matter interact – an effect undetectable most of the time, but something we probably all have experienced when we forgot to apply a sun protector on a sunny day. This unwanted process of a sunburn is caused by light high in energy, which indicates that the interaction of light and matter is very much depended on the applied light energy. Therefore, it is common to categorize light into energy levels or respective wavelength ranges with the following relationship between these quantities:

$$E = \frac{hc}{\lambda}$$

with E = light energy, h = Planck constant; c = light constant, and λ = wavelength of the light.

The range for near-infrared light is for example defined to be λ =800-2500 nanometers. At this energy level, molecule vibrations are induced, which are very specific to the sample and its properties. With the use of specific NIR analyzers such as the [DS2500 Petro Analyzer](#) the interaction can be visualized as absorption spectra. Figure 3 displays such spectra together with the effect that signals for some wavelength regions are more intensive.

The reason is that NIR light mainly interacts with groups like CH, NH, OH, and SH, which makes NIRS an ideal method to quantify chemical parameters like ethanol content, diene value, fatty acid methyl ester (FAME) or water content to name just a few. Furthermore, the interaction is also dependent upon the matrix of the sample itself, which also allows the detection of physical parameters such as RON/MON, Cetane Index, Specific Gravity, Flash Point, or Viscosity.

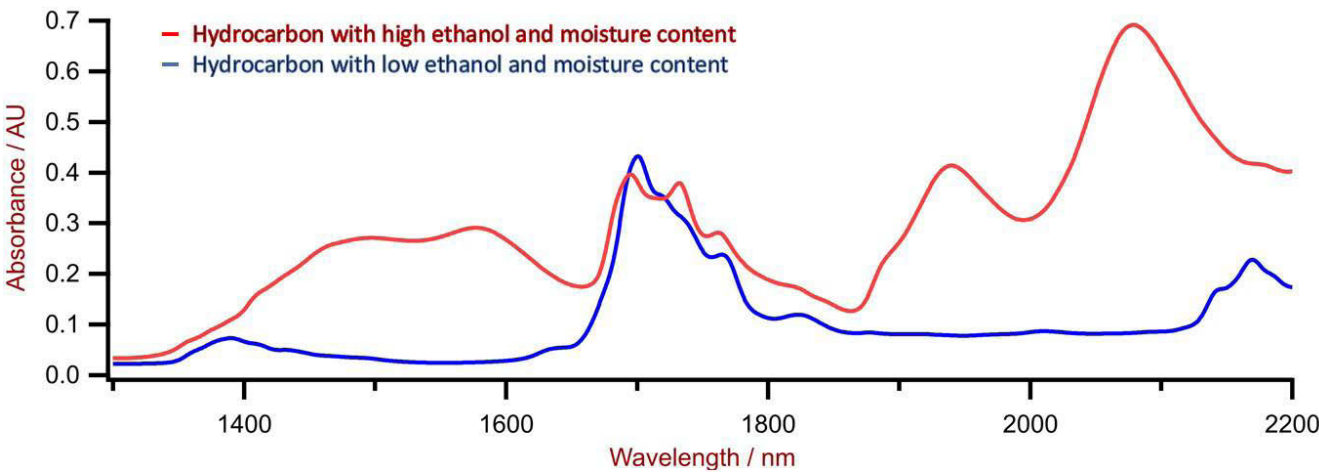


Figure 3 Hydrocarboin and ethanol and moisture absorption spectra resulting from the interaction of NIR light with the respective samples.

Since the shape of the spectra is directly related to all parameters of interest, multiple parameters can be determined during routine analysis with just one spectrum, making NIRS one of the fastest techniques for quality control and product screening. The workflow of spectra collection and a more detailed description of the advantages of this technology is given in the next chapter.

2.2 NIRS: SAMPLE HANDLING AND MEASUREMENTS

NIRS can be used to analyze different types of samples, such as liquids, suspensions, solids and creams. Since in the petro industry mainly liquid samples are analyzed we will focus on this sample type. The most important step to obtain representative spectra and therefore results lie in the selection of the correct sample vessel.

2.2.1 Liquid sample measurement

The sample vessels for liquid sample analysis can be categorized by the sample color, its viscosity and how challenging the application is:

- Almost all samples are typically analyzed with a system that can accommodate disposable glass vials of different diameters. This is for example the case with the with the [DS2500 Petro Analyzer](#) and vial holder for 10mm, 8mm, 4mm or 2mm vials (Figure 4).
- The most common disposable vial size is 8mm, This one is used for uncolored or lightly colored samples of low to medium viscosity.
- In case of more viscous samples, the 10mm vial can be used, which allows for easier sample filling.
- In case the sample is more strongly colored, vials of lower diameter are recommended to avoid saturation of specific parts of the spectrum.
- For challenging applications in which the detection limit is low, quartz cuvettes are recommended. The drawback of those vessels is that they need to be cleaned after each measurement. (Figure 4c).



Figure 4. DS2500 Petro Analyzer (4a), Sample holder (4b), glass vials (4c) and quartz cuvettes (4d)

The measuring mode typically used for these kinds of liquid samples is referred to as **transmission**. For transmission (Figure 5b), the NIR light, will travel through the sample while being absorbed. Unabsorbed NIR light reflects to the detector. In less than 30 seconds, the measurement is completed, and the results are displayed.

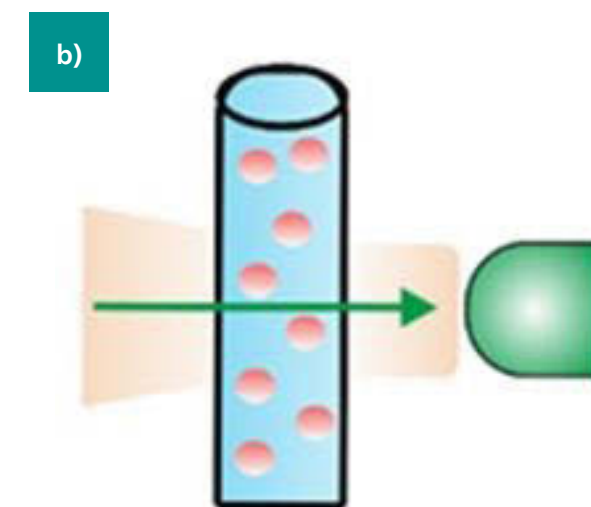


Figure 5 Schematic display of the light path interacting with a sample during transmission.

The procedure to obtain NIR spectra already highlights two major advantages of NIRS: **simplicity** regarding sample measurement and **speed**:

- **Fast** technique with results in **less than 1 minute**.
- **No sample preparation** required – liquids and solids can be measured in original forms.

Other advantages of NIRS are listed below and will be discussed later:

- **Low cost** per sample – no chemicals or solvents needed.
- **Environmentally friendly** technique – no waste generated.
- **Non-destructive** – precious samples can be reused after analysis.
- **Easy** to operate – inexperienced users are immediately successful.

The next section explains in more detail how a NIRS prediction model is developed and implemented in the laboratory workflow.

2.3 HOW TO IMPLEMENT NIRS IN YOUR LABORATORY WORKFLOW

NIRS as a secondary technique requires prior to be used for routine analysis the development of so-called prediction models. This is similar to other analytical methods, for example HPLC, where a series of standard solutions of the analyte must be prepared and measured to create a calibration curve.

In NIRS spectra with known parameter values (gathered with a primary method such as titration) are collected and stored in a so called calibration set. This set is used to develop the prediction model which refers to a correlation between the primary values and the NIR spectra. In the Metrohm spectroscopy software Vision Air the created prediction

models and the measurement specific settings (e.g. sample vessel type, number of spectra etc.) are embedded in an operating procedure (OP). This guarantees the correct workflow of the analysis during routine analysis.

The following section describes a workflow for the implementation of NIRS in a QC laboratory environment in accordance with the ASTM D6122 and ASTM D8340 guidelines. More details about these guidelines are provided in chapter 2.5. For illustrative purposes, the workflow is described using a real example.

A laboratory at a company which produces petro products has purchased a NIR analyzer with the intention to use it for rapid moisture (as an alternative to Karl Fischer titration), and for the determination of the Octane Number (as an alternative to the CRR engine). According to chapter 2.2.1, a calibrated Metrohm DS2500 Petro Analyzer measuring in transmission is the suitable analyzer configuration. The workflow is summarized in Figure 6.

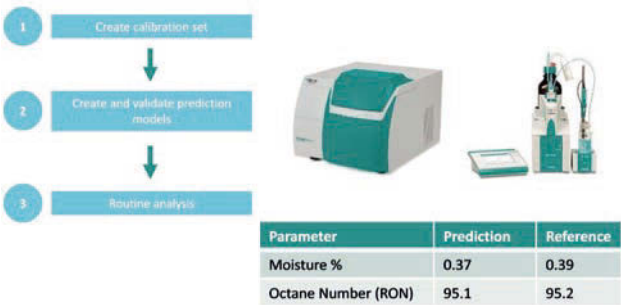


Figure 6 Workflow for NIRS method implementation.

2.3.1 Step 1 – Create calibration set

A calibration set is required to create prediction models, as mentioned earlier. This set is used to «train» the system to correctly interpret spectra (e.g. moisture content and Octane number) measured during routine analysis. These calibration set samples must cover the complete expected concentration range of the parameters tested for the method to be robust. This reflects other techniques (e.g. HPLC) where the calibration standard curve needs to span the complete expected concentration range. Therefore, if you expect the moisture content of a substance to be between 0.1% and 0.4%, then the training/ calibration set must cover this range as well.

In this example, 10 Gasoline samples with moisture levels between 0.18 – 0.73% and RON values between 94.5. – 98.7 are measured using both the DS2500 petro Analyzer and the respective primary methods (KF titration and CFR engine). The obtained spectra are then linked with the moisture and octane number values using the Vision Air Software (Figure). Subsequently, this data set (known as a calibration set) is used for prediction model development.

Time	Sample number	Octane Number	Octane Number Ref.	Moisture Content (%)	Moisture Content Ref.
3/2/2020 1:10:28 PM	Sample 10	—	95.8	—	0.11
3/2/2020 1:10:17 PM	Sample 9	—	95.2	—	0.17
3/2/2020 1:10:06 PM	Sample 8	—	96.0	—	0.31
3/2/2020 1:09:56 PM	Sample 7	—	94.8	—	0.43
3/2/2020 1:09:46 PM	Sample 6	—	98.1	—	0.51
3/2/2020 1:09:34 PM	Sample 5	—	97.7	—	0.09
3/2/2020 1:09:24 PM	Sample 4	—	96.3	—	0.12
3/2/2020 1:09:13 PM	Sample 3	—	96.1	—	0.28
3/2/2020 1:09:06 PM	Sample 2	—	95.6	—	0.29
3/2/2020 1:08:55 PM	Sample 1	—	95.1	—	0.33

Figure 7 Display of 10 NIR measurements linked with RON and moisture reference values obtained with Karl Fischer titration and CFR engine.

2.3.2 Step 2 – Create and validate prediction models

The next step is to identify spectral regions that correlate with the moisture and Octane Number value, respectively. To enhance the visibility of these differences, mathematical calculations such as the first or second derivative are applied (8).

Once visually identified, the software will attempt to correlate the selected spectral regions with the values sourced from the primary method(s). The result is a correlation diagram for water detection along with the respective figures of merit, including the Standard Error of Calibration (precision) and the correlation coefficient (R2) shown in figure 9. The same procedure is carried out for the second parameter discussed here, octane number.

Again, this process is similar to the general working procedures with techniques like HPLC. When creating a calibration curve with HPLC, typically the peak height or peak intensity (surface) is linked with a known internal standard concentration. Here, only one variable is used (peak height or surface) therefore this procedure is known as univariate data analysis. To create the correlation for NIRS, a spectral range (approximately 1900–2000 nm for the water peak) and therefore multiple absorbance values are used. Therefore, NIRS is known as a multivariate data analysis technology.

The ideal number of spectra in a calibration set depends on the variation in the sample (temperature, viscosity, chemical distribution, etc.). In this example, we used 10 Gasoline samples, which is a good starting point to check the application feasibility. However, to build a robust model which covers all sample variations, more sample spectra are required. As a rule, approximately 40–50 sample spectra will provide a suitable prediction model in most cases.

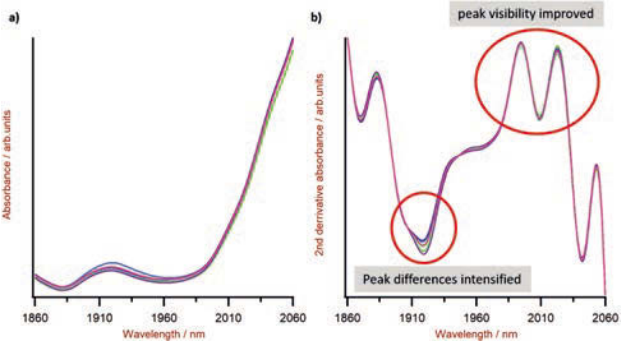


Figure 8 Example of the intensifying effect on spectra information by using mathematical calculation: a) without any mathematical optimization and b) with applied second derivative highlighting the spectra difference at 1920 nm and intensifying the peaks near 2010 nm.

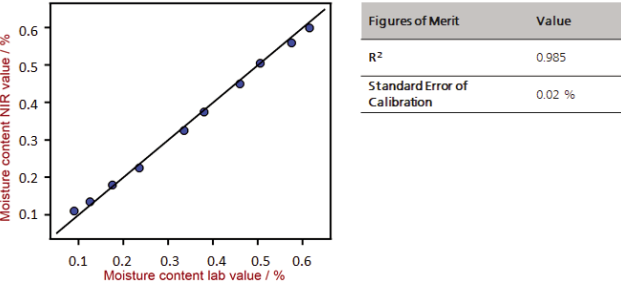


Figure 9 Correlation plot and Figures of Merit (FOM) for the prediction of water content in gasoline samples using NIRS.

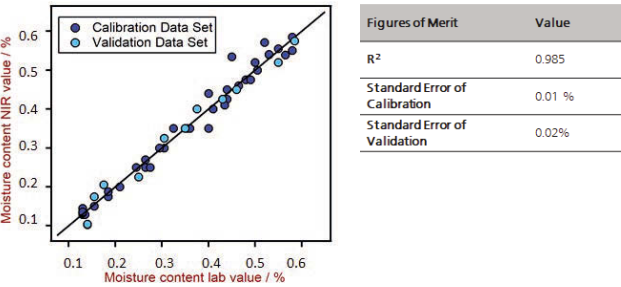


Figure 10 Correlation plot and Figures of Merit (FOM) for the prediction of water in Gasoline samples using NIRS. The split set function in Vision Air Complete allows generation of a validation data set, which is used to validate the prediction model.

This data set comprised of 40–50 spectra is also used to validate the prediction model. This can be done using the Vision Air Complete software, which splits the data set into two groups of samples:

- 1) Calibration set 75%
- 2) Validation set 25%

As before, a prediction model is created using the calibration set, but the predictions will now be validated using the validation set. Results for the gasoline samples are shown in Figure 10 and display a correlation plot with the respective figures of merit, which include the Standard Error of Calibration (precision of the calibration set prediction), Standard Error of Validation (precision of the validation set prediction), and R^2 .

Users that are inexperienced with NIR model creation and do not yet feel confident with it can rely on Metrohm support, which is known for its high-quality service. They will assist you with the prediction model creation and validation.

Samples











































						Operating procedure	Time	Sample number	Octane Number	Moisture Content [%]
						Petro Analysis	3/2/2020 4:03 PM	Sample 19	96.7	0.22
						Petro Analysis	3/2/2020 4:02 PM	Sample 18	98.1	0.17
						Petro Analysis	3/2/2020 4:01 PM	Sample 17	95.2	0.59
Sample event										
! Moisture Content: 0.06% is above operating procedure action limit 0.55%										
						Petro Analysis	3/2/2020 4:01 PM	Sample 16	97.3	0.32
						Petro Analysis	3/2/2020 4:01 PM	Sample 15	95.0	0.37
						Petro Analysis	3/2/2020 4:00 PM	Sample 14	96.4	0.19

Figure 11 Overview of a selection of NIR predicted results, with clear pass (no box) and fail (red box) indications.

2.3.3 Step 3 – Routine analysis
The beauty of the NIRS technique comes into focus now that the prediction model has been created and validated.

Gasoline samples with unknown moisture content and unknown Octane Number can now be analyzed at the push of a button. The NIRS DS2500 Petro Analyzer will display results for those parameters in less than a minute. Typically, the spectrum itself is not shown during this step—just the result—sometimes highlighted by a yellow or red box to indicate results with a warning or error as shown in Figure 11.

Another display possibility is the trend chart, which allows for the proactive adjustment of production processes. Warning and action limits are highlighted here as well (figure 12).

In summary, the maximum effort needed to implement NIRS in the laboratory is in the beginning of the workflow, during collection and measurement of representative samples that span the complete concentration range. The prediction model creation and validation, as well as implementation in routine

analysis, is performed with the help of the Metrohm Vision Air Complete software and can be completed within a short period. Additionally, our Metrohm NIRS specialists will happily support you with the prediction model creation if you require assistance.

At this point, take note that there are cases where NIRS can be implemented directly without any prediction model development, using Metrohm pre-calibrations. These are robust, ready-to-use operating procedures for certain samples, such as gasoline, diesel and jet-fuel based on real product spectra. Visit the Metrohm pre-calibration website or contact your local Metrohm sales representative for more information.

In the next section, we will go into more detail on the ASTM norms for NIR spectroscopy in the petro industry.

2.4 NIR AS AN ASTM COMPLIANT TOOL IN THE PETRO INDUSTRY

For more than 30 years now, NIRS has been an established method for fast and reliable quality control within the Petrochemical industry. Many companies, however, still do not consistently consider the implementation of NIRS in their QA/QC labs. Limited experience regarding application possibilities or a general hesitation of implementing NIR as an alternative technology could be the reason. Many companies are not aware that nowadays there are many ASTM references on how to implement NIR Spectroscopy as an alternative technology.

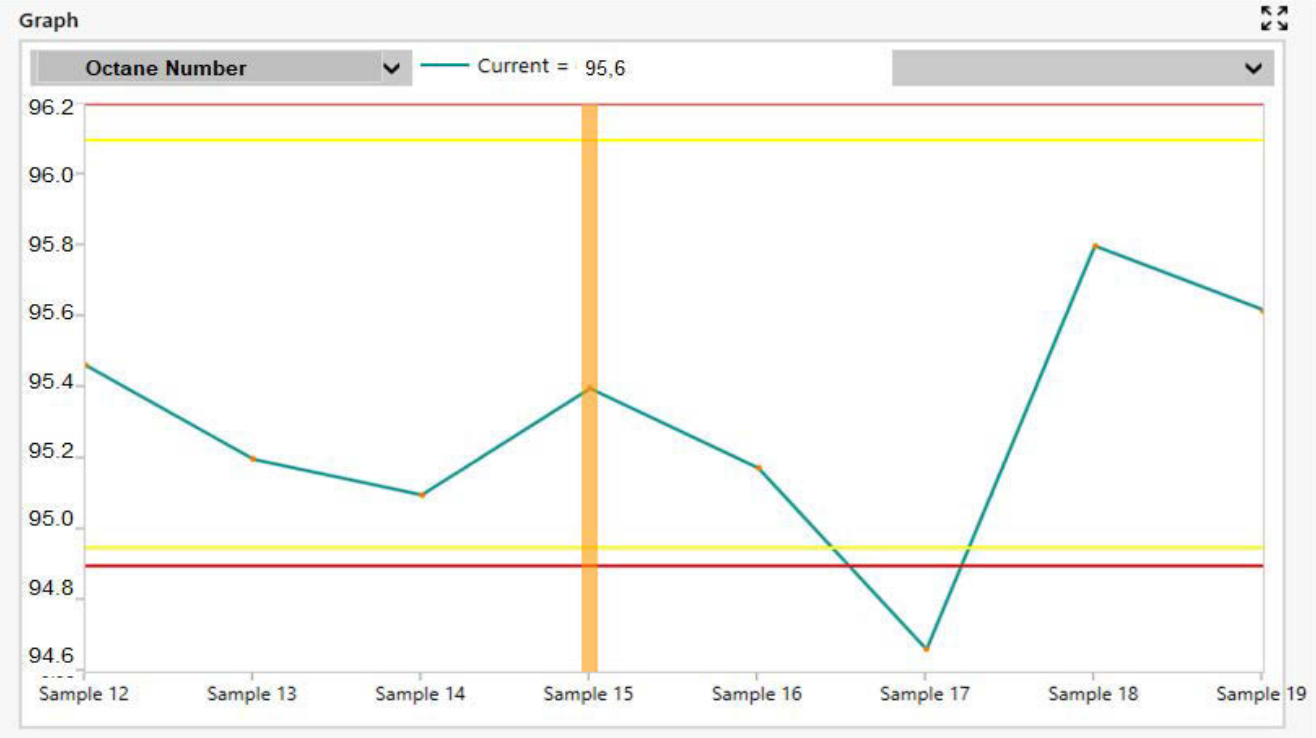


Figure 12 Trend chart of NIR Octane Number analysis results. The parallel lines indicate defined warning (yellow) and action (red) limits.

NIR related ASTM guidelines are shown in Figure 13 below.

ASTM E 1655 (Method development quantitative NIR analysis) and ASTM E 1790 (Method development qualitative NIR analysis) are applicable for all industries like Polymer, Chemical, etc.

ASTM D 6122 (Method validation of performance NIR analysis), ASTM D8321 (Development and validation of multivariate analysis) and ASTM D8340 (Performance qualification) are dedicated for petrochemical Industry. These three standards were just released recently in 2020.

METHOD DEVELOPMENT:

ASTM E1655-17: Standard Practices for Infrared Multivariate Quantitative Analysis

These practices cover a guide for the multivariate calibration of near infrared spectrometers used in determining the physical or chemical characteristics of materials. These practices are applicable to analyses conducted in the near-infrared (NIR) spectral region (roughly 780 to 2500 nm).

ASTM E1790-04(2016): Standard Practice for Near Infrared Qualitative Analysis

This practice covers the use of near-infrared (NIR) spectroscopy for the qualitative analysis of liquids and solids. The practice is written under the assumption that most NIR qualitative analyses will be performed with instruments designed specifically

for this purpose and equipped with computerized data handling algorithms.

METHOD VALIDATION:

ASTM D6122-20: Standard Practice for Validation of the Performance of Multivariate Online, At-Line, Field and Laboratory Infrared Spectrophotometer, and Raman Spectrometer Based Analyzer Systems

This practice covers requirements for the validation of measurements made by laboratory, field, or process (online or at-line) near infrared analysers, used in the calculation of physical, chemical, or quality parameters of liquid petroleum products and fuels. These requirements include following topics:

- Analyzer calibration
- Correlation of NIRS Vs Lab method (Treated & Untreated samples)
- Probationary validation
- General & Continual validation

RESULTS VALIDATION:

ASTM D8321-20: Standard Practice for Development and Validation of Multivariate Analyses for Use in Predicting Properties of Petroleum Products, Liquid Fuels, and Lubricants based on Spectroscopic Measurements.

This practice covers a guide for the multivariate calibration of near-infrared (NIR) spectrophotometers used in determining the physical, chemical, and performance properties of petroleum products, liquid fuels including biofuels, and lubricants.

This practice is applicable to analyses conducted in the near infrared (NIR) spectral region (roughly 780 nm to 2500 nm). Main purpose for this standard is to establish the validity of test results during calibration.

ASTM D8340-20: Standard Practice for Performance-Based Qualification of Spectroscopic Analyzer Systems

This practice covers requirements for establishing performance-based qualification of a NIR method versus the Primary Test Method (PTM). Furthermore, it includes the prescriptive requirements and instrument considerations. Prescriptive requirements regarding multivariate models, including Multi Linear Regression (MLR), Partial Least Square (PLS), Principle Component Regression (PCR), Cross validation, and Outlier statistics.

Regarding the required accuracy of the NIR method the expected agreement & user requirements is that the Standard Error of Prediction for the NIR value should be equal or smaller than the laboratory method reproducibility.

DS2500 Petro analyzer and Vision Air in compliance with ASTM D8340-20

Temperature stability, section 5.4:

There are prescriptive requirements included for this significance and use of the NIR Analyzer. Section 5.4 requires sample temperature to be carefully controlled in analyzer system hardware or that effects of temperature change be compensated in modeling

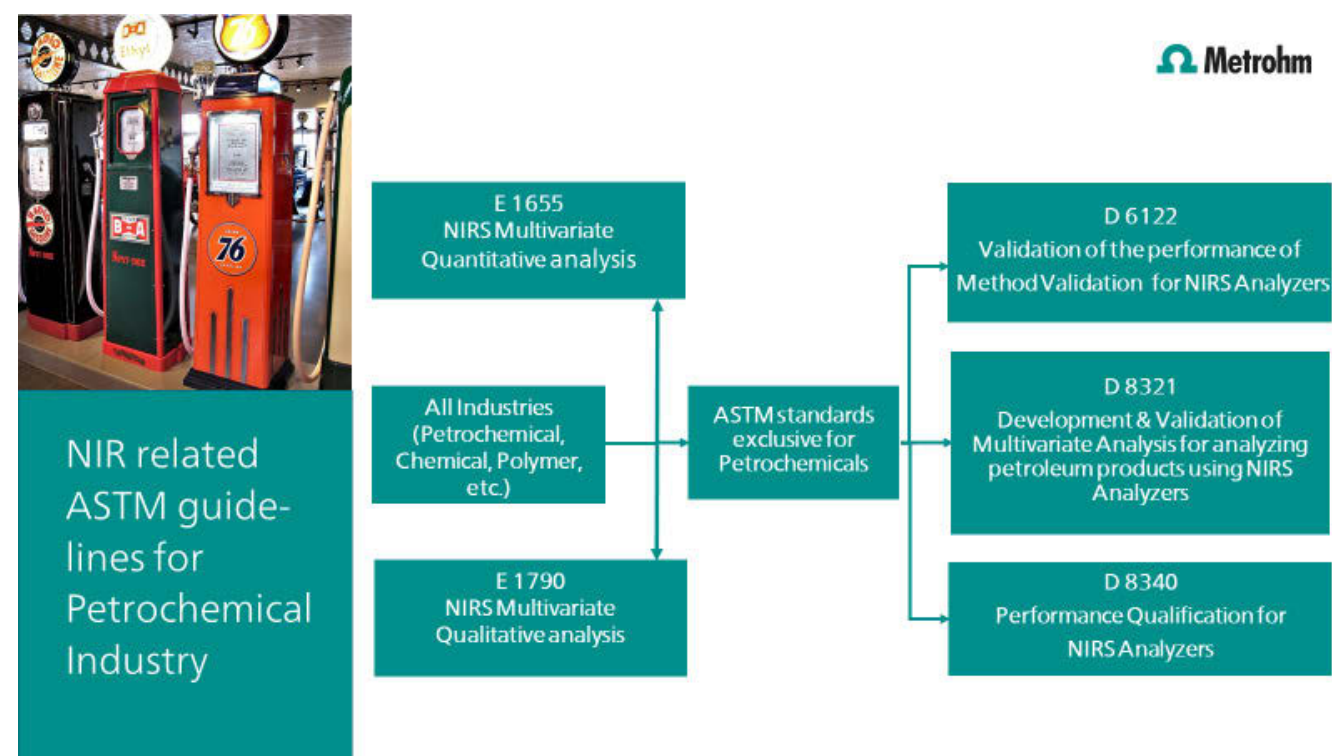


Figure 13. NIR related ASTM guidelines, overview

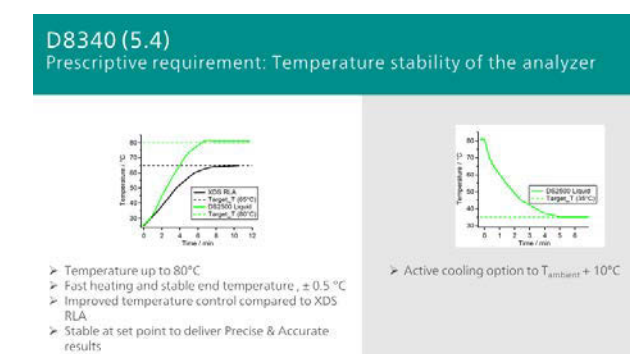


Figure 14. Temperature stability DS2500 Petro Analyzer

or software. Metrohm solution for the DS2500 Petro analyzer is shown in Figure 14.

Analyzer wavelength accuracy & precision, section 6.3:

Section 6.3 requires that the analyzer shall include a means of demonstrating that it is operating within the vendor's specification. Therefore, the analyzer shall incorporate instrument performance tests to demonstrate that it is operating within historically expected limits. Furthermore, the analyzer shall have a means of validating wavelength/frequency precision and accuracy. Also, the wavelength precision must be sufficient to allow spectra to be collected and used in creating a multivariate model that meets or exceeds user's specifications. The wavelength precision of the analyzer used for calibration and the

analyzer to analyzer wavelength accuracy and reproducibility must be sufficient to allow analyzers to be validated by Practice D6122. Solution in Metrohm's Vision Air software is shown in Figure 15.

Vendor created global multivariate model, section 8.2.2:

The multivariate model can be that of a standardized test method, a user/vendor-created global multivariate model, or a user-created site-specific multivariate model. A global multivariate model is one developed by use of samples and data that may represent materials produced at multiple facilities or locations. Some locations may start with a global model and add site-specific sample to it. Available pre-calibrations for the DS2500 Petro analyzer are listed in Figure 16.

Outlier statistics 9.3, 9.4. and, 9.5

In these sections the requirements of outlier handling are described. Identification and handling of outliers is important to the success of meeting this performance-based practice. It is permissible for the identification and handling of outliers to be performed by the same or separate software used for generating predictions from spectra. For analysis of a sample for the purposes of determining property values, the software shall indicate whether the spectrum is identified as an outlier, based on the criteria set by the user. The sample analysis may indicate that expected performance is not reached for a sample identified as an outlier. Vision Air is Metrohm's universal software for Vis-NIR spectroscopy. Vision Air accounts for the unique needs of each type of instrument user. It offers specific interfaces optimized

for the most common tasks, simplifying routine measurement, method development, outlier handling and both data and instrument management. Vision Air is also compatible with third party software like Unscrambler. See Figure 17.

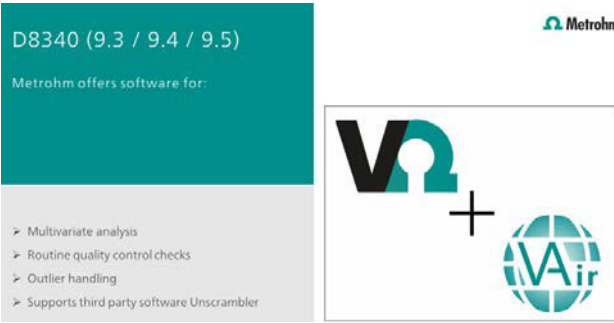


Figure 17. Vision Air, Metrohm's universal software for lab Vis-NIR Spectroscopy

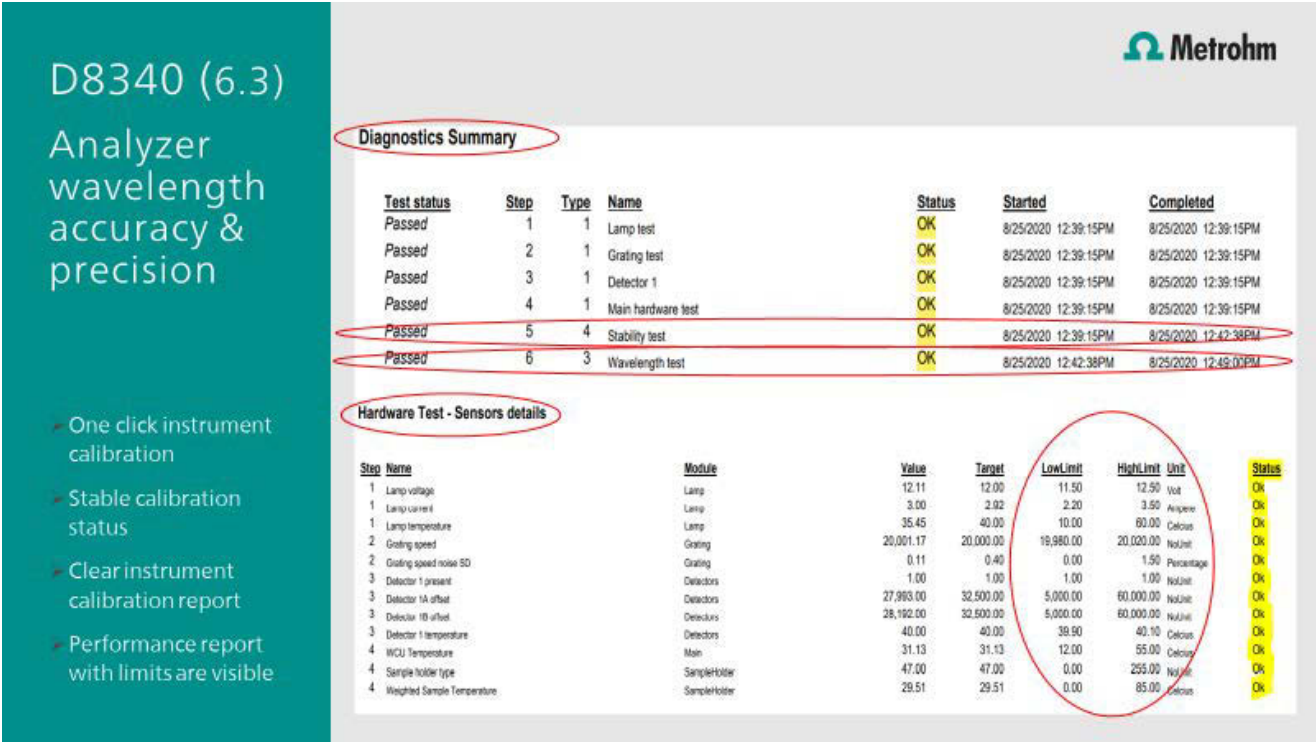


Figure 15. Wavelength accuracy & precision

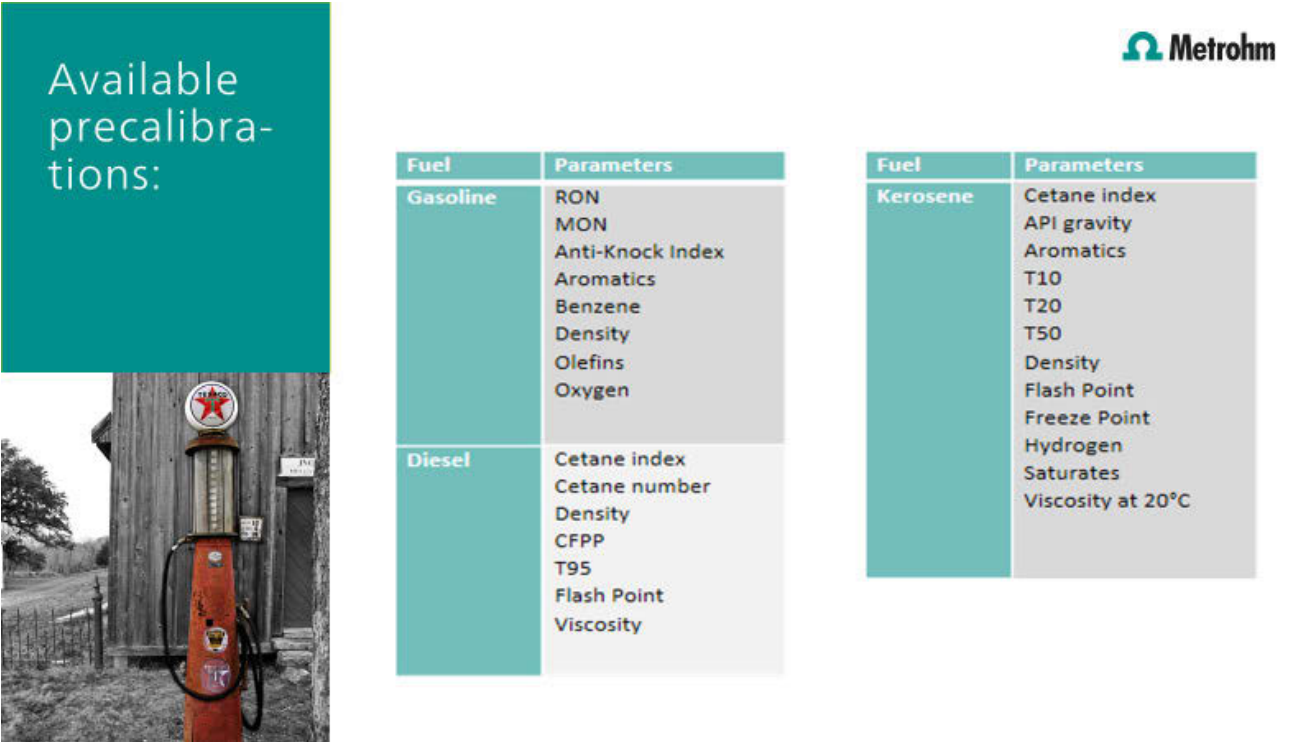


Figure 16. Available pre-calibration by Metrohm for the petrochemical industry

2.5 CONCLUDING REMARKS ON NIR SPECTROSCOPY IN THE PETRO INDUSTRY

Typical requirements from management are usually that quality control should be quick, operating costs should be low, feedback should be fast, and operation should be easy and safe. Typical requirements from the user are usually that analysis should be accurate and precise, it should be easy to use and, fast and safe. NIR Spectroscopy is compliant with all these requirements and as shown herein the technology is supported by several ASTM guidelines for method development, method validation and results validation. This means that with NIR Spectroscopy in the Petrochemical industry you are not only improving the efficiency of your screening and quality control of petrochemical products, but you are also fully adhering to internationally accepted standards.

In the next chapter, a selection of handpicked applications is presented to provide an overview of the many possibilities with NIRS.

3 Overview of the many possibilities with NIRS



NIR APPLICATION NOTE NIR-022

Quality control of gasoline

Rapid determination of RON, MON, AKI, aromatic content, and density

In recent years, there has been a significant push to reduce the environmental impacts of fuels through improvements to fuel quality. This requires engines to be more efficient, along with increasing the octane content of fuel so higher compression engines can be utilized. The determination of key quality parameters of gasoline, namely research octane number (RON, ASTM D2699-19), motor octane number (MON, ASTM D2700-19), anti knock index (AKI), aromatic content (ASTM D5769-15), and density, conventionally requires several different analytical methods, which are laborious and need trained personnel. This application note demonstrates that the XDS RapidLiquid Analyzer, operating in the visible and near-infrared spectral region (Vis-NIR), provides a cost-efficient and fast solution for the multiparameter analysis of gasoline.

EXPERIMENTAL EQUIPMENT

Gasoline samples were measured with the XDS RapidLiquid Analyzer (RLA) in transmission mode over the full wavelength range (400–2500 nm). Reproducible spectrum acquisition was achieved using the built-in temperature controlled sample holder. For convenience, disposable vials with a path length of 8 mm were used, which made a cleaning procedure unnecessary. The Metrohm software package Vision Air Complete was used for data acquisition and prediction model development.

Table 1. Hardware and software equipment overview

Equipment	Metrohm number
XDS RapidLiquid Analyzer	2.921.1410
Disposable vials, 8 mm diameter, transmission	6.7402.000
Vision Air 2.0 Complete	6.6072.208



Figure 1. XDS RapidLiquid Analyzer and 8 mm disposable vial filled with a gasoline sample.

RESULT

The obtained Vis-NIR spectra (Figure 2) were used to create prediction models for the determination of several key fuel parameters. The quality of the prediction models was evaluated using correlation diagrams, which display a correlation between the Vis-NIR prediction and primary method values. The respective figures of merit (FOM) display the expected precision of a prediction during routine analysis.

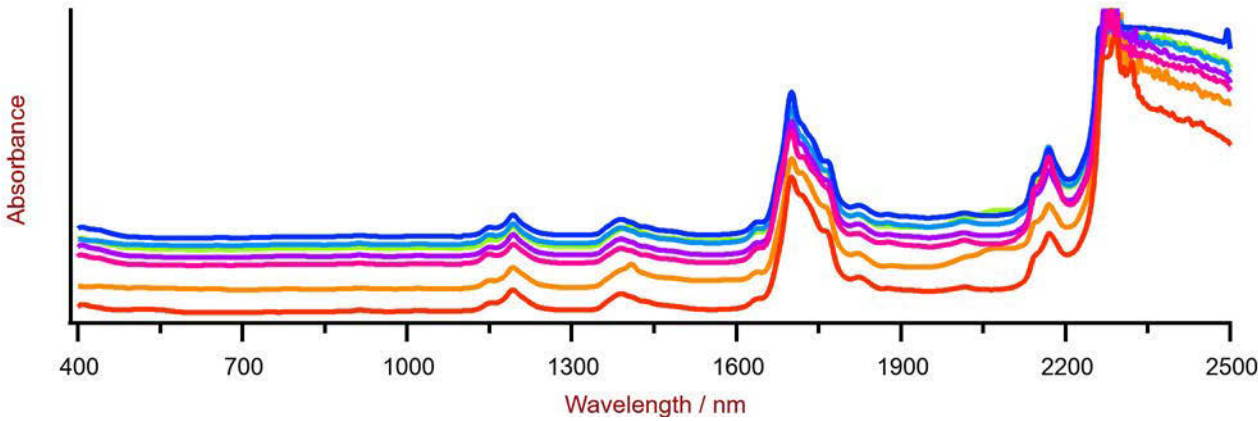
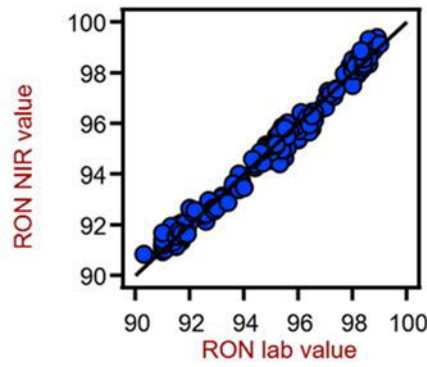


Figure 2. This selection of gasoline Vis-NIR spectra was obtained using a XDS RapidLiquid Analyzer and 8 mm disposable vials. For display reasons a spectra offset was applied.

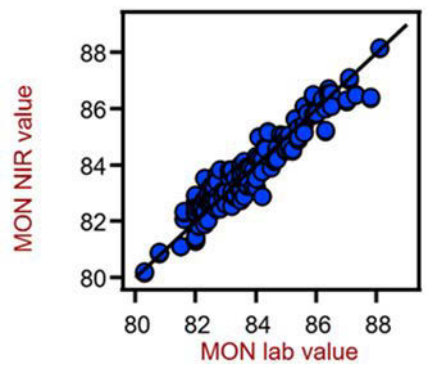
RESULT RON VALUE



Figures of Merit	Value
R ²	0.989
Standard Error of Calibration	0.26
Standard Error of Cross-Validation	0.29

Figure 3. Correlation diagram and the respective figures of merit for the prediction of the RON value in gasoline using a XDS RapidLiquid Analyzer. The reference lab values were determined according to CFR engine tests under controlled conditions.

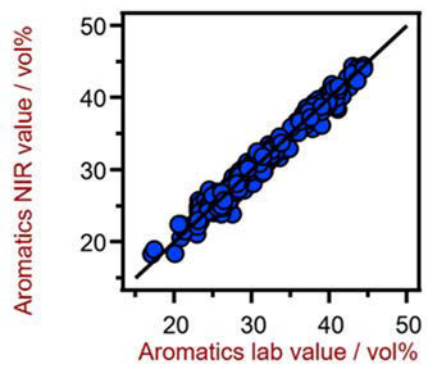
RESULT MON VALUE



Figures of Merit	Value
R ²	0.889
Standard Error of Calibration	0.50
Standard Error of Cross-Validation	0.53

Figure 4. Correlation diagram and the respective figures of merit for the prediction of the MON value in gasoline using a XDS RapidLiquid Analyzer. The reference lab values were determined according to CFR engine tests under controlled conditions.

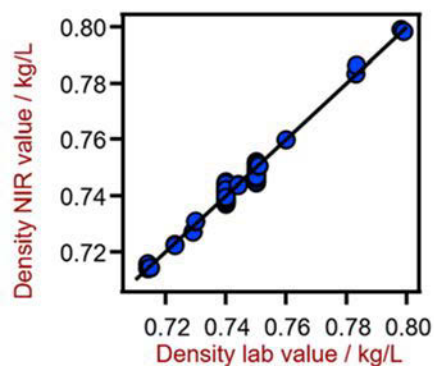
RESULT AROMATICS CONTENT



Figures of Merit	Value
R ²	0.974
Standard Error of Calibration	0.97 vol%
Standard Error of Cross-Validation	1.07 vol%

Figure 5. Correlation diagram and the respective figures of merit for the prediction of the aromatics content in gasoline using a XDS RapidLiquid Analyzer. The lab values were determined with gas chromatography/mass spectrometry techniques.

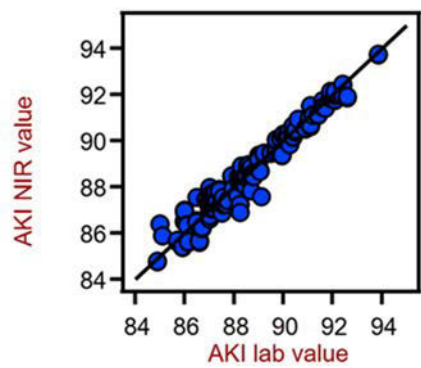
RESULT DENSITY



Figures of Merit	Value
R ²	0.973
Standard Error of Calibration	0.0021 kg/L
Standard Error of Cross-Validation	0.0023 kg/L

Figure 6. Correlation diagram and the respective figures of merit for the prediction of gasoline density using a XDS RapidLiquid Analyzer. The lab values were determined using a density meter.

RESULT AKI VALUE



Figures of Merit	Value
R ²	0.945
Standard Error of Calibration	0.45
Standard Error of Cross-Validation	0.46

Figure 7. Correlation diagram and the respective figures of merit for the prediction of AKI value in gasoline using a XDS RapidLiquid Analyzer. The reference lab values were determined according to CFR engine tests under controlled conditions.

CONCLUSION

This application note shows the feasibility of NIR spectroscopy for the analysis of RON, MON, AKI, aromatic content, and density. In comparison to wet

chemical methods (Table 2), the time to result is a major advantage of NIR spectroscopy, since a single measurement is performed within one minute.

Table 2. Time to result with conventional testing methods

Parameter	Method	Time to result
RON	CFR engine test	~30 minutes per sample
MON	CFR engine test	~30 minutes per sample
AKI	CFR engine test	~30 minutes per sample
Aromatic content	Gas Chromatography	~45 minutes per sample

To view the information for all key parameters and to get the latest information, please check out our pre-calibrations:

www.metrohm.com/pre-calibrations

Analytes:

RON, MON, AKI,
Aromatics content, Density

Matrix:

Gasoline

Industry:

Petrochemical Industry

Standards:

ASTM D2699
ASTM D2700-19



Quality Control of Diesel

Fast and straightforward determination of cetane index, flash point, CFPP, D95, and viscosity

The cetane index (ASTM D613), flash point (ASTM D56), cold filter plug point (CFPP) (ASTM D6371), D95 (ISO 3405), and viscosity at 40°C (ISO 3104) are key parameters to determine for diesel quality. The primary test methods are labor intensive and challenging due to the need to use different analytical methods.

This application note demonstrates that the XDS RapidLiquid Analyzer, operating in the visible and near-infrared spectral region (Vis-NIR) provides a **cost-efficient and fast** solution for the **simultaneous determination** of these key parameters in diesel. Vis-NIR spectroscopy allows for the analysis of diesel in **less than one minute without sample preparation or using any chemical reagents**.

EXPERIMENTAL EQUIPMENT

Diesel samples were measured in transmission mode with a XDS RapidLiquid Analyzer (RLA) over the full wavelength range (400–2500 nm). The built-in temperature controlled sample chamber was set to 30°C to provide a stable sample environment. For convenience reasons, disposable vials with a path length of 8 mm were used, which made a cleaning procedure obsolete. The Metrohm software package Vision Air Complete was used for data acquisition and prediction model development.

Table 1. Hardware and software equipment overview

Equipment	Metrohm number
XDS RapidLiquid Analyzer	2.921.1410
Disposable vials, 8 mm diameter, transmission	6.7402.000
Vision Air 2.0 Complete	6.6072.208



Figure 1. XDS RapidLiquid Analyzer with 8 mm disposable vial filled with a diesel sample.

RESULT

The obtained Vis-NIR spectra (Figure 2) were used to create prediction models for the determination of key diesel parameters. The quality of the prediction models was evaluated using correlation diagrams, which display the correlation between Vis-NIR prediction and primary method values. The respective figures of merit (FOM) display the expected precision of a prediction during routine analysis.

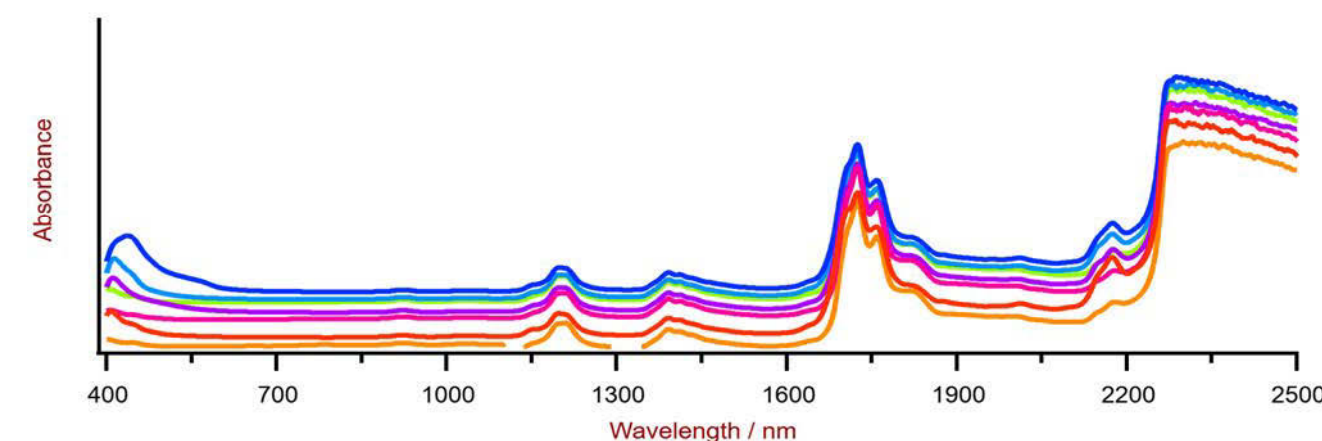


Figure 2. Selection of diesel Vis-NIR spectra obtained using a XDS RapidLiquid Analyzer and 8 mm disposable vials. For display reasons a spectra offset was applied.

RESULT CETANE INDEX

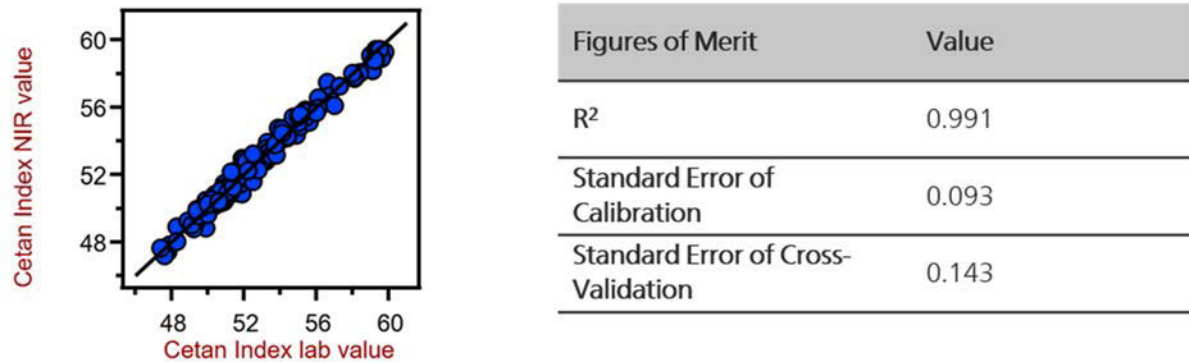


Figure 3. Correlation diagram and the respective figures of merit for the prediction of the cetane Index using a XDS RapidLiquid Analyzer. The cetane index lab value was calculated based on the density and distillation range.

RESULT FLASH POINT

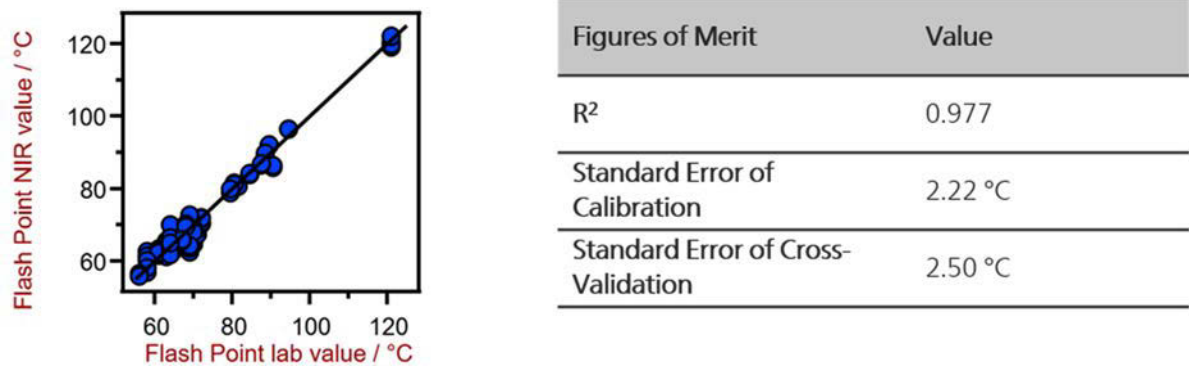


Figure 4. Correlation diagram and the respective figures of merit for the prediction of Flash Point using a XDS RapidLiquid Analyzer. The flash point lab value was evaluated using a dedicated flash point analyzer.

RESULT CFPP

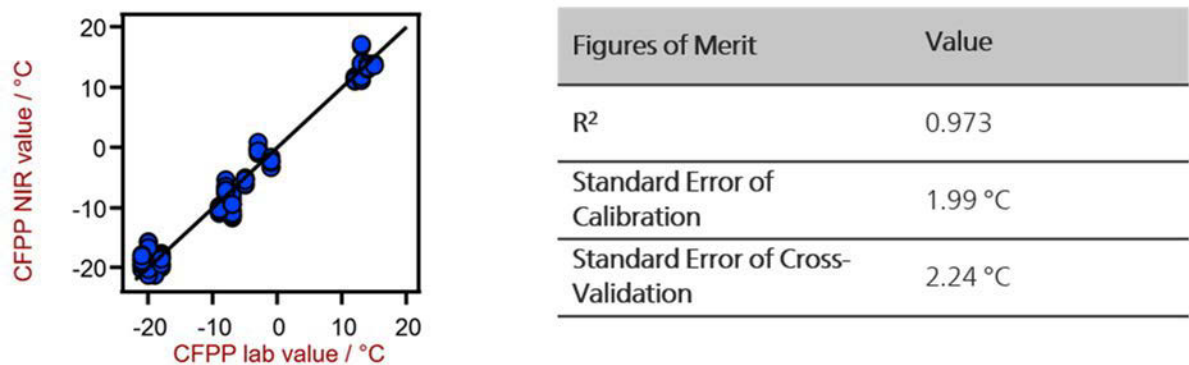


Figure 5. Correlation diagram and the respective figures of merit for the prediction of CFPP using a XDS RapidLiquid Analyzer. The lab value was evaluated using flow meters.

RESULT D95

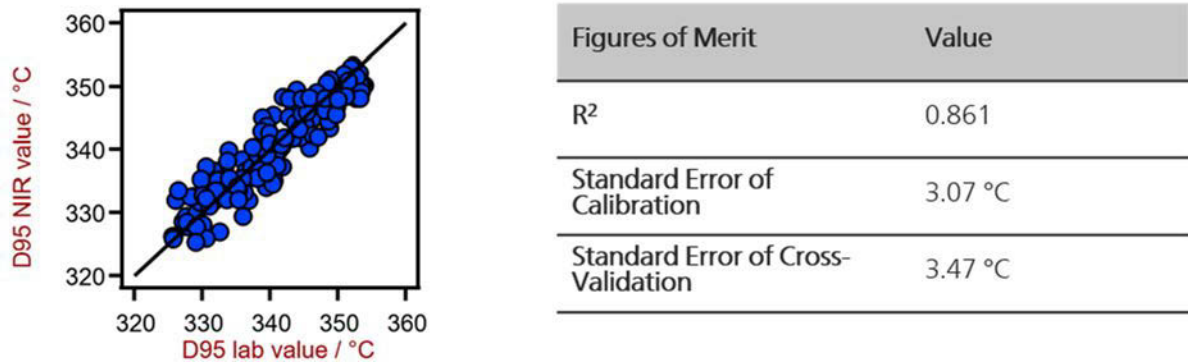


Figure 6. Correlation diagram and the respective figures of merit for the prediction of D95 value using a XDS RapidLiquid Analyzer. The D95 lab value was evaluated using distillation.

RESULT VISCOSITY

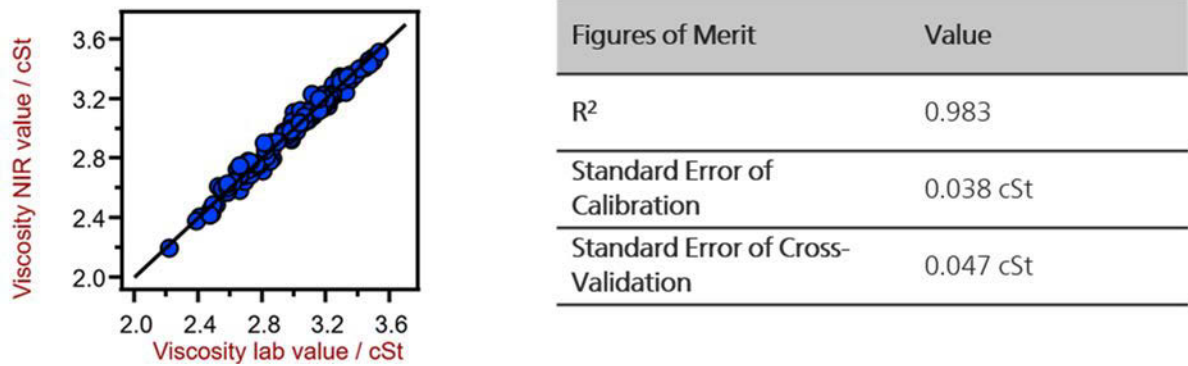


Figure 7. Correlation diagram and the respective figures of merit for the prediction of Viscosity at 40°C using a XDS RapidLiquid Analyzer. The viscosity lab value was evaluated using viscometry.

CONCLUSION

This study demonstrates the feasibility of NIR spectroscopy for the analysis of the key parameters of diesel samples. In comparison to the standard methods, **no sample preparation is needed**. Samples are analyzed as they are, which allows for simple operation when using NIR spectroscopy.

To view the information for all key parameters and to get the latest information, please check out our pre-calibrations:

www.metrohm.com/pre-calibrations



NIR APPLICATION NOTE NIR-086

Quality Control of Diesel Exhaust Fluid

Fast determination of urea content with high accuracy

The quality control of diesel exhaust fluids (DEF) is key to ensure the optimal catalytic performance and prevent damage to the exhaust system in diesel vehicles. The standard method to determine urea content is measuring the refractive index (ISO 22241-2:2019). The issue is that although this method is fast, it is not as accurate as other methods (e.g., HPLC). This application note demonstrates that the DS2500 Liquid Analyzer provides a **fast solution with high accuracy** for the determination of urea in DEF. With **no sample preparation or chemicals needed**, visible near infrared (Vis-NIR) spectroscopy allows for the analysis of diesel exhaust fluids in **less than a minute**.

Analytes:	Cetane Index, Flash Point, Viscosity, CFPP, D 95
Matrix:	Diesel
Industry:	Petrochemical Industry
Standards:	ASTM E1655

NIR Application Note AN-NIR-080
Version 1 – 2020-03
AW NIR CN-0006

EXPERIMENTAL EQUIPMENT

Aqueous urea samples with different urea content from 0.5% to 40% (v/v) were measured in transmission mode with a DS2500 Liquid Analyzer over the full wavelength range (400–2500 nm). Reproducible spectrum acquisition was achieved using the built-in temperature control at 40 °C. For convenience, disposable vials with a path length of 2 mm were used, which made cleaning of the sample vessels unnecessary. The Metrohm software package Vision Air Complete was used for all data acquisition and prediction model development.

Table 1. Hardware and software equipment overview

Equipment	Metrohm number
DS2500 Liquid Analyzer	2.921.1410
Disposable vials, 2 mm diameter, transmission	6.749.2020
Vision Air 2.0 Complete	6.6072.208



Figure 1. DS2500 Liquid Analyzer and a diesel exhaust fluid sample filled in a disposable vial.

RESULT

All 16 measured Vis-NIR spectra (Figure 2) were used to create a prediction model for quantification of the urea content. The quality of the prediction models was evaluated using correlation diagrams, which display a very high correlation between Vis-NIR prediction and primary method values. The respective figures of merit (FOM) display the expected precision of a prediction during routine analysis.

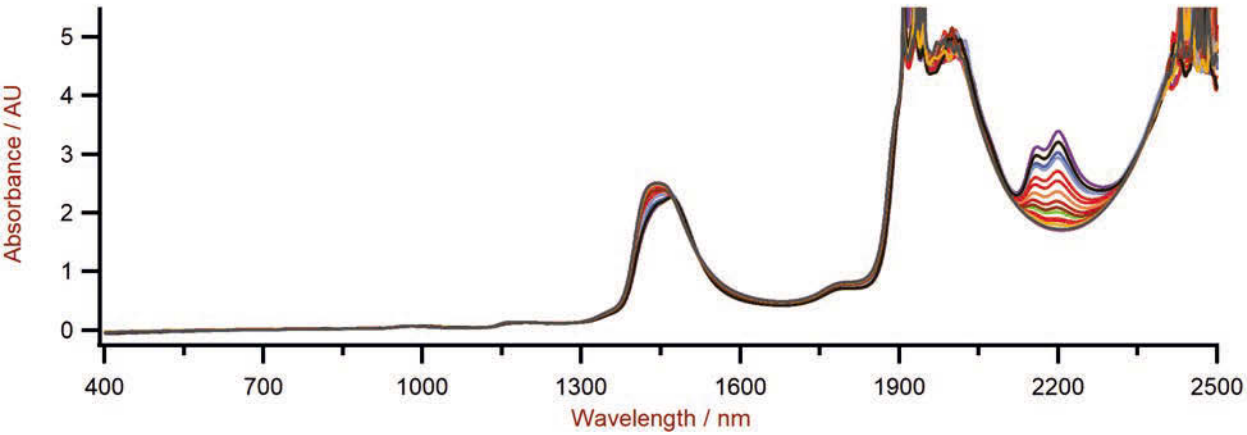
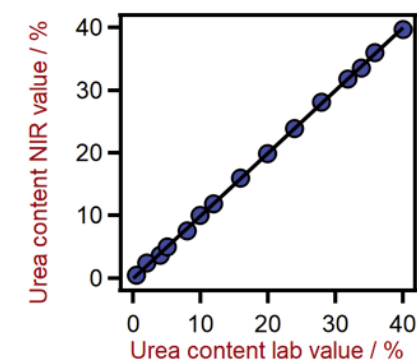


Figure 2. Vis-NIR spectra of diesel exhaust fluids with varying urea content measured on a DS2500 Liquid Analyzer.

RESULT UREA CONTENT



Figures of Merit	Value
R ²	0.999
Standard Error of Calibration	0.23 %
Standard Error of Cross-Validation	0.25 %

Figure 3. Correlation diagram and the respective figures of merit for the prediction of urea content in diesel exhaust fluids using a DS2500 Liquid Analyzer.

CONCLUSION

This application note demonstrates the feasibility of the DS2500 Liquid Analyzer for the determination of urea content in diesel exhaust fluids. Vis-NIR spectroscopy enables a fast determination with high accuracy, and therefore represents a suitable

alternative to the standard method. Additionally, it should be pointed out, that for further parameters such as density, similar NIR methods can be developed.

Table 2. Time to result for the urea content determination in aqueous urea solutions using HPLC

Parameter	Method	Time to result and workflow
Urea content	HPLC	~5 min (preparation) + ~10 min (HPLC)

Analytes: Nitrogen – amines, amides

Matrix: Amide; Fuels – fossil

Industry: Petrochemical Industry

Standards: ASTM E1655



NIR APPLICATION NOTE NIR-024

Quality control of pyrolysis gasoline

Determination of diene value within one minute

Pyrolysis gasoline (pygas) is a byproduct of ethylene production, which contains unwanted conjugated diolefins making it unsuitable as a motor fuel. To overcome this limitation, the olefin content needs to be reduced below 2 mg/g pygas in a selective hydrogenation unit (SHU). The diene value, or maleic anhydride value (MAV), is usually determined by the Diels-Alder wet chemical method (UOP326-17).

This wet chemical method requires several hours to perform by highly trained analysts. In contrast to the primary method, near-infrared spectroscopy (NIRS) is a cost-efficient and fast analytical solution for the determination of diene value in pyrolysis gasoline.

EXPERIMENTAL EQUIPMENT

99 pygas samples were analyzed on a NIRS XDS RapidLiquid Analyzer equipped with 8 mm disposable glass vials. All measurements were performed in transmission mode from 400 nm to 2500 nm. The temperature control was set to 40 °C to provide a stable sample environment. For convenience reasons disposable vials with a pathlength of 8 mm were used, which made a cleaning procedure obsolete. The Metrohm software package Vision Air Complete was used for data acquisition and prediction model development.

Table 1. Hardware and software equipment overview

Equipment	Metrohm number
XDS RapidLiquid Analyzer	2.921.1410
Disposable vials, 8 mm diameter, transmission	6.7402.000
Vision Air 2.0 Complete	6.6072.208



Figure 1. Samples filled in disposable vials with 8 mm path length.

RESULT

The obtained Vis-NIR spectra (Figure 2) were used to create a prediction model for the diene value determination. To verify the quality of the prediction model, correlation diagrams were created which display the correlation between Vis-NIR prediction and primary method values (Figure 3). The respective figures of merit (FOM) display the expected precision of a prediction during routine analysis.

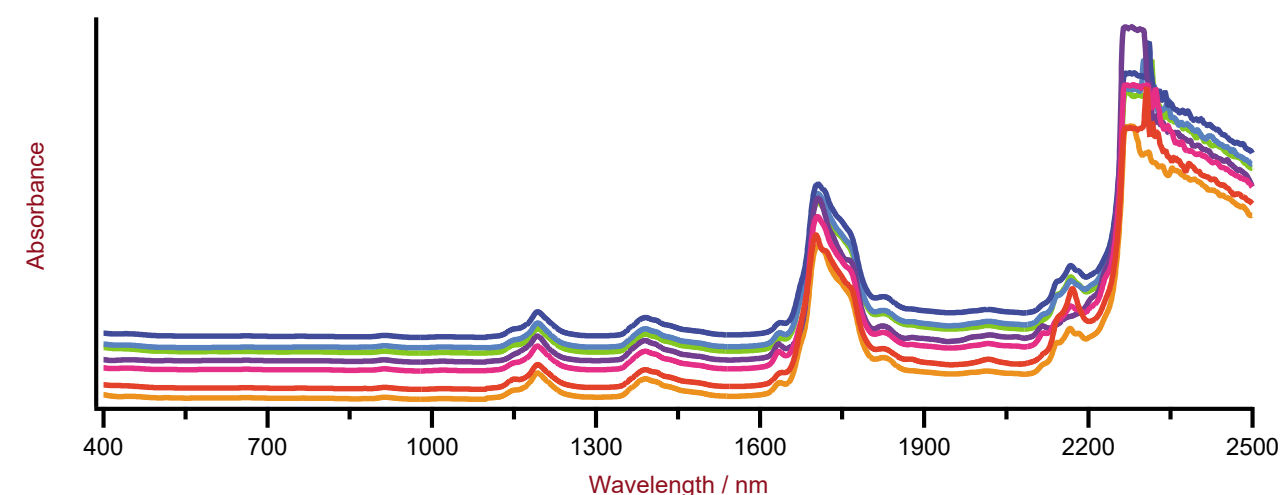
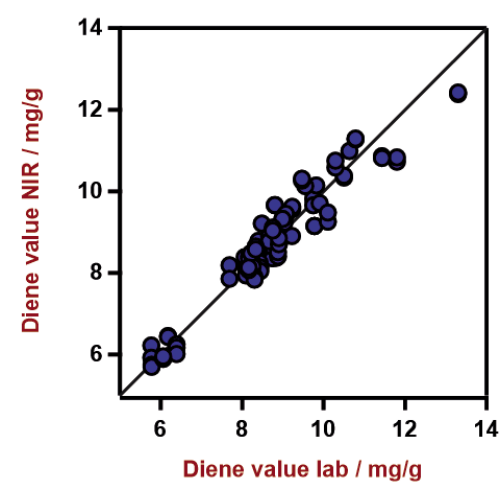


Figure 2. Selection of pyrolysis gasoline Vis-NIR spectra obtained using a XDS RapidLiquid Analyzer and 8 mm disposable vials. For display reasons a spectra offset was applied.

RESULT DIENE VALUE



Figures of Merit	Value
R ²	0.9253
Standard Error of Calibration	0.42 mg/g
Standard Error of Cross-Validation	0.46 mg/g

Figure 3. Correlation diagram and the respective figures of merit for the prediction of the diene value using a XDS RapidLiquid Analyzer. The lab values were determined according to the UOP326-17 method.

CONCLUSION

This application note shows the feasibility of NIR spectroscopy for the analysis of diene value in

pyrolysis gasoline. In comparison to the wet chemical method UOP326-17 (Table 2), the time to result is a major advantage of NIR spectroscopy, since a single measurement is performed within one minute.

Table 2. Time to result with conventional UOP-326 wet chemistry analysis

Parameter	Method	Time to result and workflow
Diene value	Diels-Alder (UOP326-17)	~6 hrs: reflux, hydrolysis, titration

Analytes:	Other
Matrix:	Fuels – fossil
Industry:	Petrochemical Industry
Standards:	ASTM D6122; ASTM E1655

NIR Application Note AN-NIR-024
Version 3 – 2021-11



NIR APPLICATION NOTE NIR-094

Bromine number in pyrolysis gasoline

Fast determination of bromine number without chemicals

Pyrolysis gasoline (pygas) and its distillate fractions often contain high levels of reactive unsaturated compounds, making it unusable as a motor fuel. In addition to the amount of diolefins (determined by the Diels-Alder method), the total amount of aliphatic olefinic components also need to be monitored. The standard method to quantify the degree of unsaturation (bromine number) in unsaturated hydrocarbons is titration.

This wet chemical method requires cooling of the sample below 5 °C to minimize side reactions like oxidation or substitution. In contrast to the primary method, near-infrared spectroscopy (NIRS) needs no sample preparation and is able to determine the bromine number within one minute. NIRS technology fulfills ASTM norms D8321 and D6122.

EXPERIMENTAL EQUIPMENT

180 pygas samples were analyzed on a Metrohm DS2500 Liquid Analyzer equipped with disposable glass vials. All measurements were performed in transmission mode from 400 nm to 2500 nm. The temperature control was set to 40 °C to provide a stable sample environment. For convenience reasons, disposable glass vials with a pathlength of 8 mm were used, which made a cleaning procedure unnecessary. Data acquisition and prediction model development were performed with the software package Vision Air complete.

Table 1. Hardware and software equipment overview

Equipment	Metrohm number
DS2500 Liquid Analyzer	2.921.1410
Disposable vials, 8 mm diameter, transmission	6.7402.000
Vision Air 2.0 Complete	6.6072.208

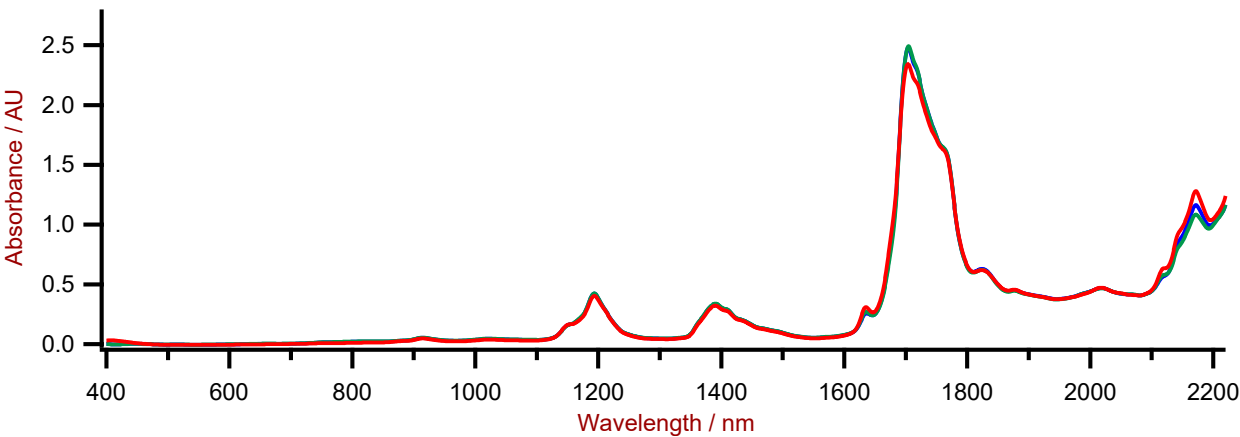


Figure 2. Selection of different pyrolysis gasoline Vis-NIR spectra obtained using a DS2500 Liquid Analyzer and 8 mm disposable vials.

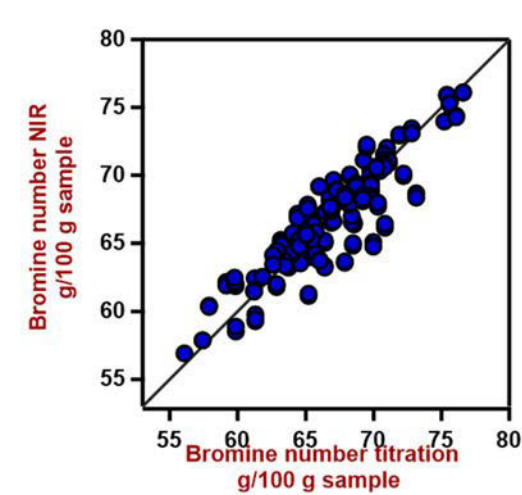


Figure 1. DS2500 Liquid Analyzer.

RESULT

The obtained Vis-NIR spectra (Figure 2) were used to create a prediction model for bromine number determination in pygas. To verify the quality of the prediction model, correlation diagrams were created which display the correlation between Vis-NIR prediction and primary method values. The respective figures of merit (FOM) are displayed in Figure 3.

RESULT BROMINE NUMBER



Figures of Merit	Value
R ²	0.836
Standard Error of Calibration	1.84
Standard Error of Cross-Validation	1.89

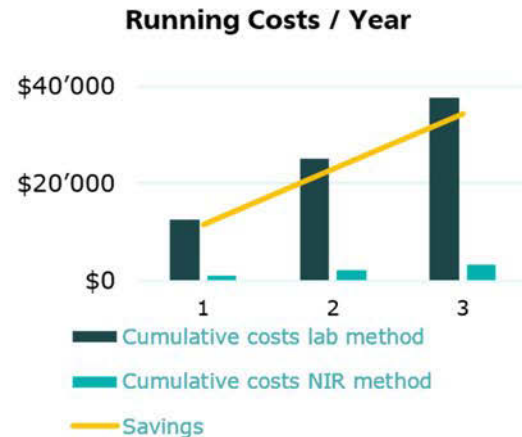
Figure 3. Correlation diagram and the respective figures of merit for the prediction of the bromine number using a DS2500 Liquid Analyzer.

CONCLUSION

This application note shows the feasibility of NIR spectroscopy for the analysis of bromine number in pyrolysis gasoline. In contrast to the wet chemical method used in ASTM D1159 (Figure 4), no sample

preparation or chemicals are required with NIR spectroscopy.

Aside from the bromine number, additional quality parameters like diene value can be determined in the same sample with NIR spectroscopy.



	Lab method	NIR method
Number of analyses (per day)	10	10
Costs of consumables and chemicals/measurement	\$6	\$0.50
Time spent per measurement	30 min	1 min
Total running costs / year	\$12,533	\$1,125

Figure 4. Comparison of costs and time to result (one-fold determination) with the conventional wet chemistry lab method and NIRs.

Analytes:	Bromine number
Matrix:	Fuels – fossil
Industry:	Petrochemicals & biofuels
Standards:	ASTM D1159; ASTM D8321; ASTM D6122



Quality Control of fermentation processes

Multiparameter determination within one minute

The production of biofuels from renewable feedstock has grown immensely in the past several years. Bioethanol is one of the most interesting alternatives for fossil fuels, since it can be produced from raw materials rich in sugars and starch. Ethanol fermentation is one of the oldest and most important fermentation processes used in the biotechnology industry. Although the process is well-known, there is a great potential for its improvement and a proportional reduction in production costs. Due to the seasonal variation of feedstock quality, ethanol producers need to monitor the fermentation process to ensure the same quality product is achieved.

Near-infrared spectroscopy (NIRS) offers **rapid and reliable prediction** of ethanol content, sugars, Brix, lactic acid, pH, and total solids at any stage of the fermentation process.

EXPERIMENTAL EQUIPMENT

Production of ethanol from corn goes through three typical steps: milling / liquefaction of corn into starch mash, fermentation of starch mash with yeast, and finally purification of the resulting ethanol by distillation. A total of 206 samples (117 for Brix index) of fermentation mash were analyzed on the DS2500 Solid Analyzer. Due to the large amount of solids present in the samples, all measurements were performed in reflection mode using the DS2500 Large sample cup (Figure 1). The samples were measured in rotation to collect spectral data from several areas. Spectral averaging of signals from several spots helped to reduce sample inhomogeneity. The Metrohm software package Vision Air Complete was used for all data acquisition and prediction model development.

Table 1. Hardware and software equipment overview

Equipment	Metrohm number
DS2500 Analyzer	2.922.0010
DS2500 Large Sample Cup	6.7402.050
Vision Air 2.0 Complete	6.6072.208



Figure 1. Fermentation mash sample placed on the DS2500 Solid Analyzer.

RESULT

All 206 measured Vis-NIR spectra (Figure 2) were used to create a prediction model for quantification of the key fermentation parameters. The quality of the prediction model was evaluated using correlation diagrams, which display a very high correlation between the Vis-NIR prediction and the reference values. The respective figures of merit (FOM) display the expected precision of a prediction during routine analysis.

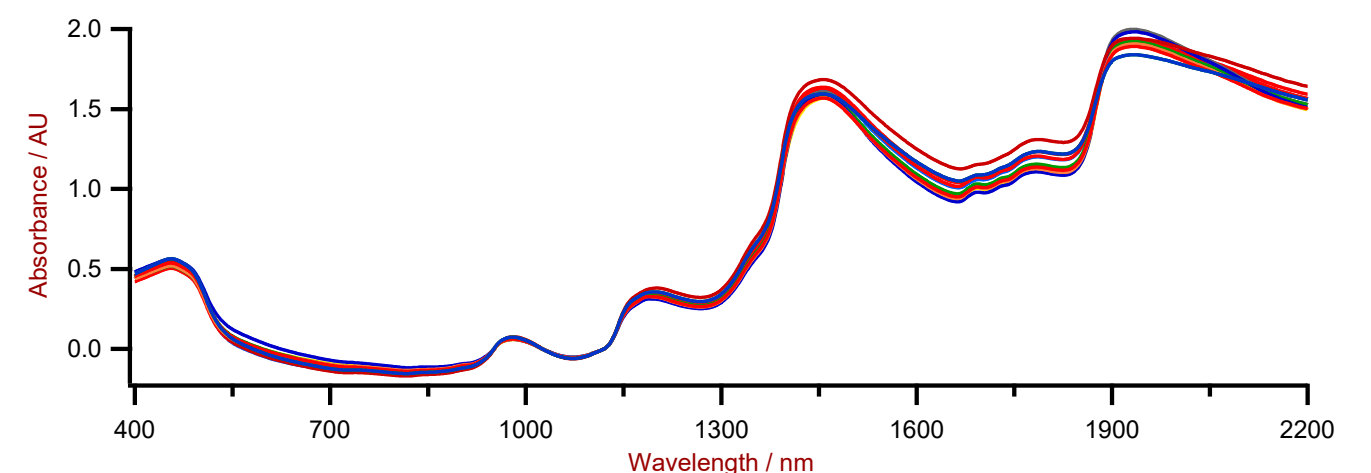


Figure 2. Vis-NIR spectra of fermentation mash samples analyzed on a DS2500 Solid Analyzer.

RESULT ETHANOL CONTENT

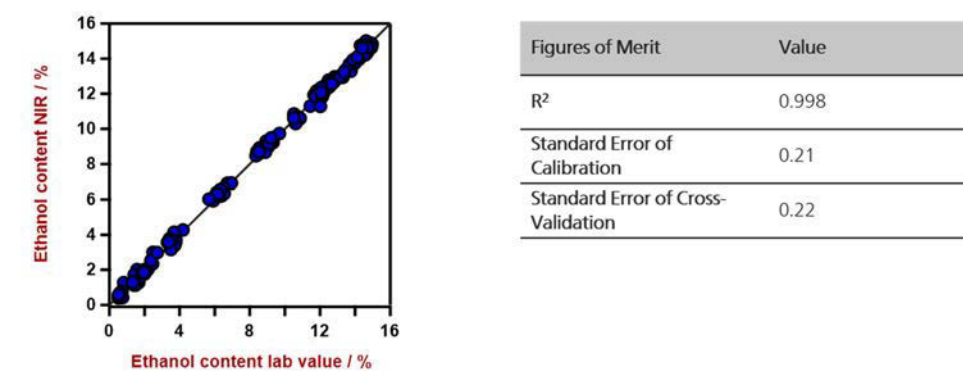


Figure 3. Correlation diagram and the respective figures of merit for the prediction of ethanol content using a DS2500 Solid Analyzer. The relative viscosity lab value was evaluated using HPLC.

RESULT TOTAL SUGAR CONTENT

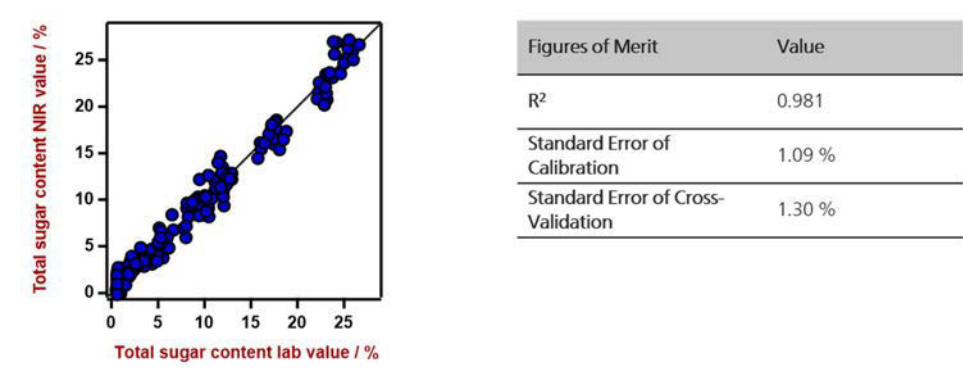


Figure 6. Correlation diagram and the respective figures of merit for the prediction of the total sugar content. The sugar content lab value was measured using HPLC.

RESULT SOLID CONTENT

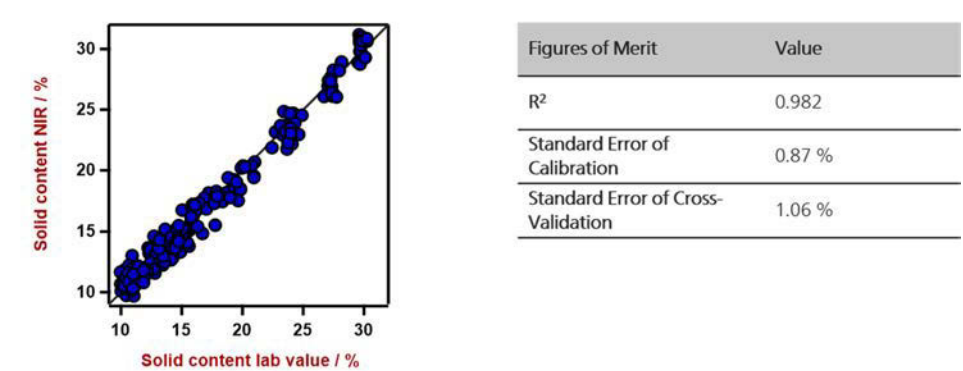


Figure 4. Correlation diagram and the respective figures of merit for the prediction solid content using a DS2500 Solid Analyzer. The lab value was evaluated by LOD balance.

RESULT GLUCOSE CONTENT

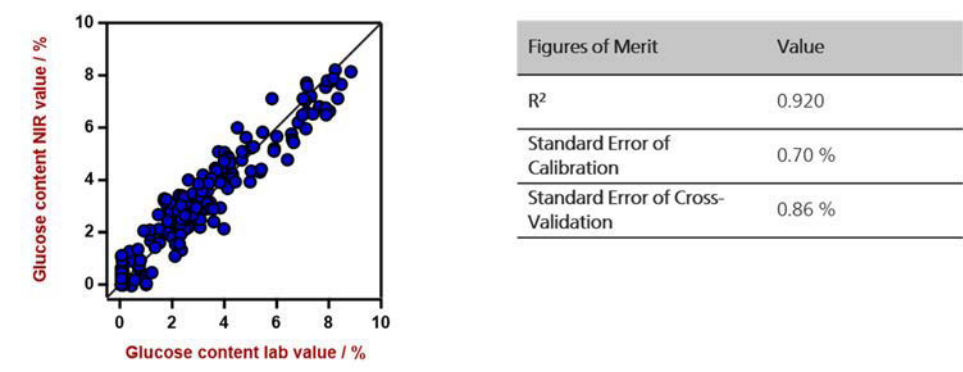


Figure 7. Correlation diagram and the respective figures of merit for the prediction of glucose content. The glucose content lab value was measured using HPLC.

RESULT BRIX INDEX

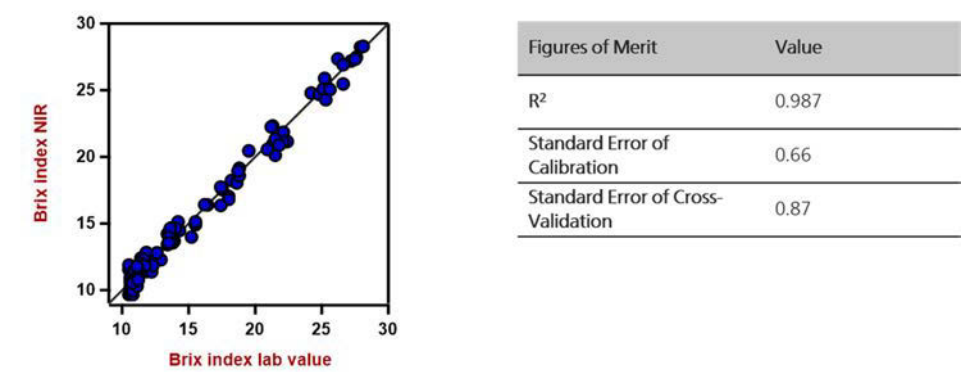


Figure 5. Correlation diagram and the respective figures of merit for the prediction of Brix index values. The lab value was measured using a refractometer.

RESULT LACTIC ACID CONTENT

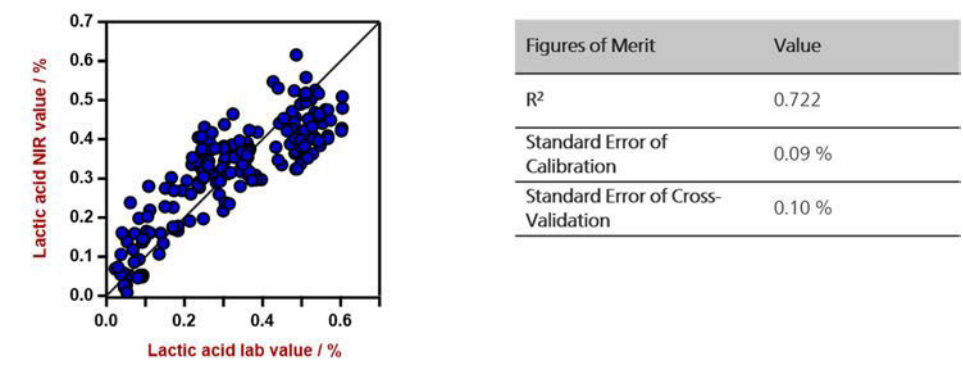


Figure 8. Correlation diagram and the respective figures of merit for the prediction of lactic acid content. The lactic acid lab value was evaluated using HPLC.

RESULT PH VALUE

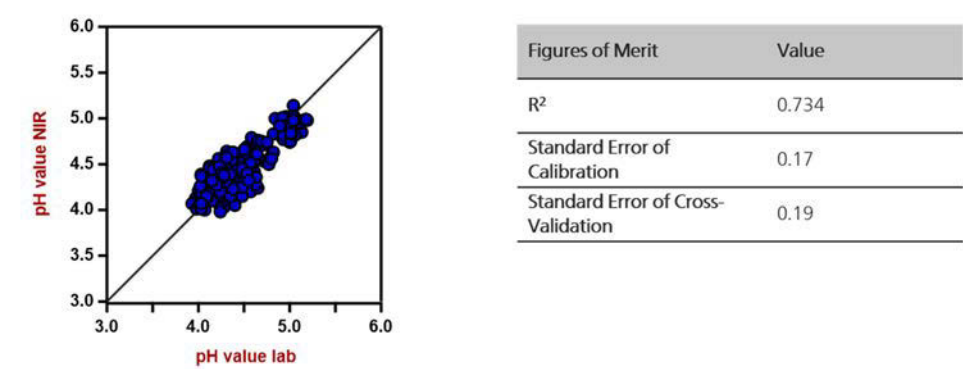


Figure 9. Correlation diagram and the respective figures of merit for the prediction of pH value. The pH lab value was measured using a pH meter.

RESULT MALTOTRIOSE CONTENT

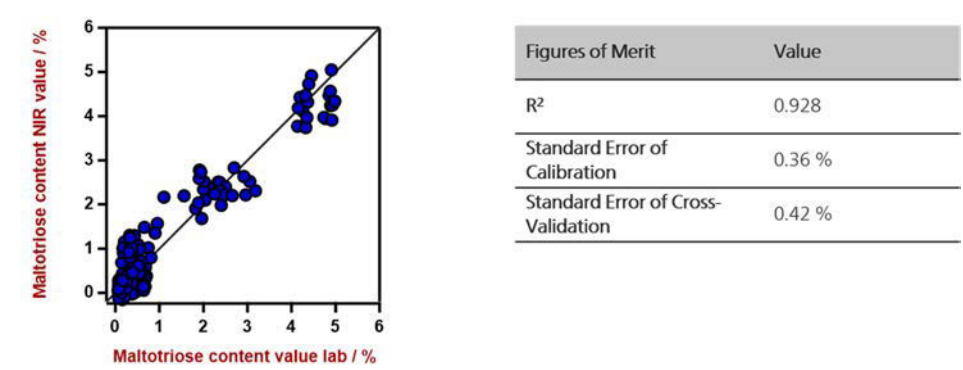


Figure 10. Correlation diagram and the respective figures of merit for the prediction of maltotriose content. The maltotriose lab value was measured using HPLC.

RESULT DEXTRIN CONTENT

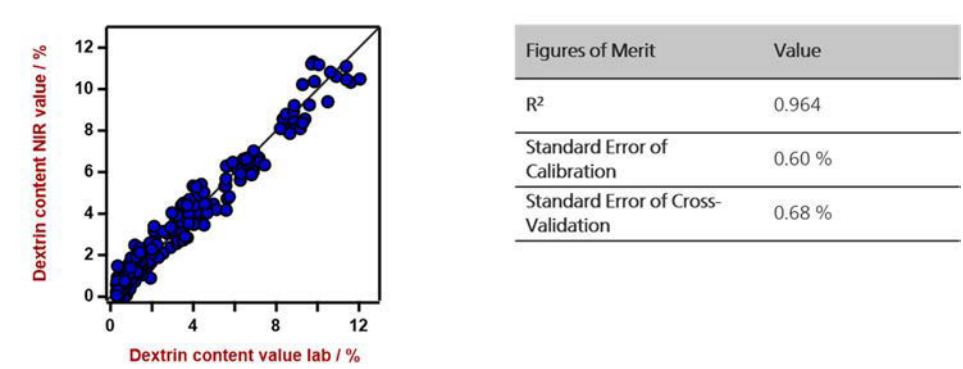


Figure 11. Correlation diagram and the respective figures of merit for the prediction of dextrin content. The dextrin lab value was measured using HPLC.

CONCLUSION

This application note demonstrates the feasibility to determine multiple key parameters of the fermentation process with NIR spectroscopy. Corn fermentation is a well-established process which typically runs for 55–60 hours. Samples are extracted from fermenters every few hours and sent to the

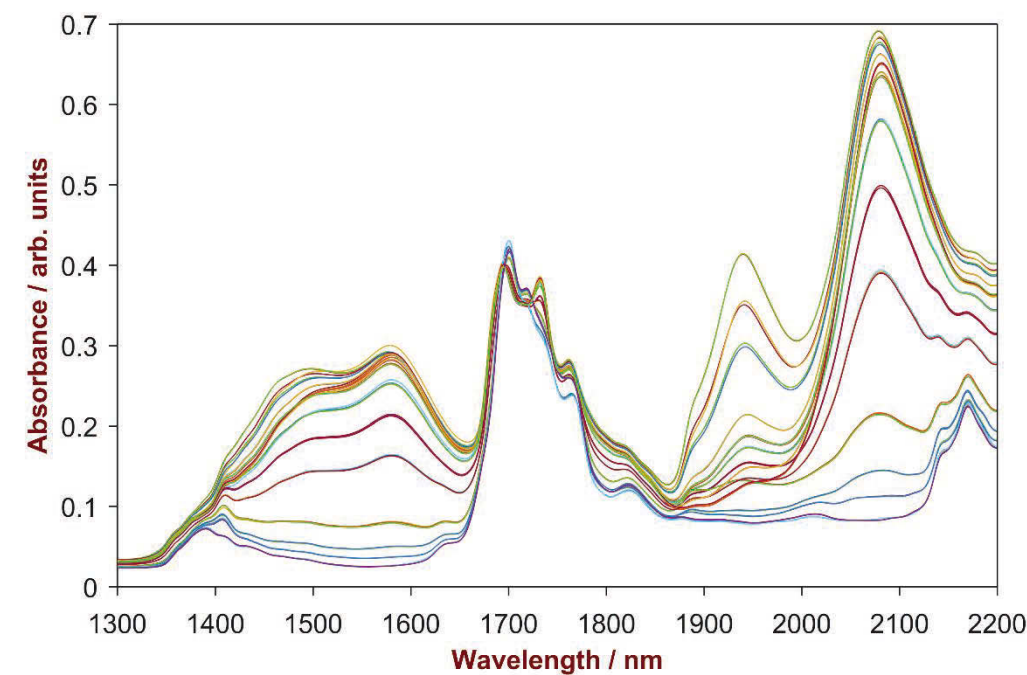
laboratory for analytical measurement. Several analytical methods need to be used to monitor key quality parameters for the fermentation process. Vis-NIR spectroscopy enables a fast alternative with high accuracy, and therefore represents a suitable single method to monitor the fermentation process.

Table 2. Time to result overview for the different parameters

Parameter	Method	Time to result
Ethanol, Sugars	HPLC	~30–45 min
Brix index	Refractometer	~3–5 min
pH	pH meter	~3–5 min
Solids	LOD Balance	~10–15 min

Analytes:	Alcohols; Carbohydrates; pH value; Physical parameters; Reaction monitoring
Matrix:	Fuels – biogenic; Plant biomass
Industry:	Petrochemicals & biofuels
Standards:	ASTM E1655

Moisture analysis of ethanol-hydrocarbon blends by Vis-NIR spectroscopy



This Application Note shows that visible near-infrared spectroscopy (Vis-NIRS) can determine water content in ethanol-hydrocarbon blends. Vis-NIRS is a fast alternative to conventional lab methods: it accelerates raw material inspection, process monitoring, and final product control.

Method description

Introduction

Water damages both fuel tanks and engine parts. Rust and corrosion in the tank create hard particulates that are passed along by the fuel, causing engine wear. Component life is also shortened by water etching, erosion, cavitation, and spalling. It can also cause indirect damage through microbial growth and fuel oxidation. Water has always caused rust and corrosion, but modern fuel systems are much less tolerant than older, lower pressure systems. Manufacturers now specify zero free water must reach the engine. [1]

To ensure zero free water fallout, water must be kept below its saturation point so that it stays dissolved. Saturation points vary from roughly 0.005% to 0.18% based on temperature and on the petro diesel / biodiesel ratio.

Removing excess water from fuel can be a challenge. The most effective approach is to take every reasonable measure to prevent water from entering tank, and to monitor it regularly. [2]

ASTM Standard D6304 (Standard Test Method for Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fischer Titration) calls for the use of coulometric KF titration in the manufacturing, purchase, sale, or transfer of petroleum products to predict the moisture content of petroleum products. [3] However, KF titration involves toxic solvents and requires a well-trained operator for highly reproducible results, resulting in relatively high costs for routine analysis. In this application note, it is demonstrate that Vis-NIRS is a good alternative to routine KF titration for saving both time and money.

Experimental

51 ethanol-hydrocarbon blend samples with moisture values from coulometric KF-titration were provided to evaluate the correlation between changes in spectral data and moisture values. The constituent value ranges from 0.0026–1.2016% moisture. 47 samples were used to develop a prediction model; four samples were used for external validation.

The spectra were collected in transmission mode on a NIRS XDS RapidLiquid Analyzer over the full wavelength range (400–2500 nm). The samples were placed in quartz glass cuvettes with 2 mm path length and analyzed at room temperature. The software package Vision Air 2.0 Complete was used for data acquisition, data management and development of the quantification method, see Table 1 / Figure 1.

Table 1: Used equipment and software.

Equipment	Metrohm code
NIRS XDS RapidLiquid Analyzer	2.921.1410
NIRS quartz glass cuvettes, 2 mm path length	6.7401.210
Vision Air 2.0 Complete	6.6072.208



Figure 1: The NIRS XDS RapidLiquid Analyzer was used for spectral data acquisition over the wavelength range from 400 nm to 2500 nm.

Results

Figure 2 shows the dominant water bands with a correlation between increasing moisture content and increasing absorbance. These water absorption bands at 1380–1670 nm and 1875–1990 nm were used to build a quantitative prediction model.

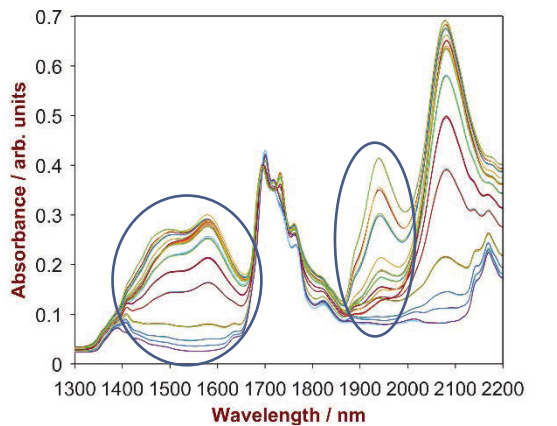


Figure 2: Non pre-treated spectra of 47 ethanol / hydrocarbon blends samples in the region of 1300–2200 nm. The typical water bands around 1400 nm and 1900 nm are highlighted.

Method description

A Partial Least Squares (PLS) model using 6 factors shows a high correlation between the provided reference values and the calculated values ($R = 0.999$) and low Standard Errors (SEC = 0.0097%, SECV = 0.0116% and SEP = 0.0120%), see **Figure 3**. Parameters used for method development and the figures of merit are listed in **Table 2**.

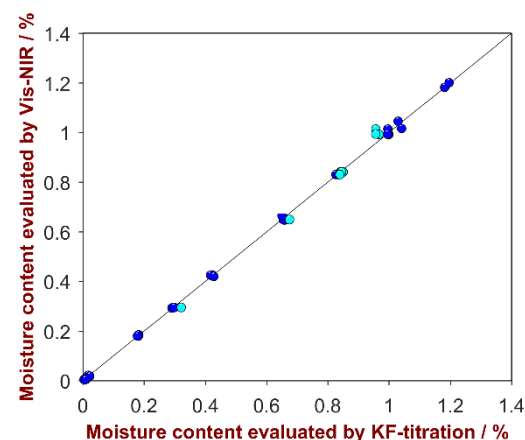


Figure 3: Correlation plot of the predicted moisture content Vis-NIRS versus the KF titration values. Displayed are the calibration (blue) and the validation data (turquoise).

Table 2: Results of the quantitative method development for moisture content.

Regression model	PLS with 6 factors
Pre-treatment	none
Wavelength range	1380–1670 nm, 1875–1990 nm
R^2	0.999
SEC	0.0097%
SECV	0.0116%
SEP	0.0120%
Range	0–1.2% moisture

Internal cross-validation was applied to verify the performance of the quantitative models during development. The model was then externally validated using new samples, each one measured in triplicate, the results of which are summarized in **Table 3**.

Table 3: Comparison of moisture content of external validation samples determined by KF titration with Vis-NIR prediction.

	NIR [%]	KF TIT [%]
Sample 1	0.426 ± 0.005	0.420
Sample 2	0.665 ± 0.002	0.665
Sample 3	0.827 ± 0.007	0.831
Sample 4	0.056 ± 0.010	0.058

Summary

This application work demonstrates how Vis-NIRS provides a rapid and accurate method for the determination of moisture content in ethanol-hydrocarbon blends. The spectral changes observed in an NIR spectrum correlate to the amount of moisture in a given sample. The results of the calibration and validated for moisture determination by Vis-NIR spectroscopy showed that it can predict moisture within $\pm 0.0120\%$.

References

- [1] <http://www.mycleandiesel.com/pages/ProblemWater.aspx>
- [2] <http://www.mycleandiesel.com/pages/SolutionWater.aspx>
- [3] <https://www.astm.org/Standards/D6304.htm>

NIR APPLICATION NOTE NIR-096

Quality Control of Diesel

Moisture determination within one minute using NIRS

Fuels can incorporate traces of water during the production process, in transport, and while in storage. Excessive water in fuels poses several problems. For example, elevated water content in diesel fuel promotes biological growth in storage tanks, which could lead to metal corrosion and formation of sludge and biofilms. This in turn can cause blockage of fuel filters and therefore damage vehicle fuel injection systems.

The standard specification for diesel fuel quality includes multiple parameters, but water contamination is the biggest risk factor. According to the European Committee for Standardization, the maximal acceptable amount of water in diesel for commercialization is 200 mg/L (ppm) (EN 590). Usually, this is determined by Karl Fischer (KF) titration, yet this method requires chemicals and takes about five minutes to perform. This Application Note describes how near-infrared spectroscopy (NIRS) is a faster and more cost-efficient alternative to KF titration for the **prediction of water content** in diesel fuel.

EXPERIMENTAL EQUIPMENT

Samples of diesel with varying water contents (from 103 to 379 mg/L) were measured with a DS2500 Liquid Analyzer in transmission mode (400–2500 nm). Reproducible spectrum acquisition was achieved using the built-in temperature control at 40 °C: For convenience, disposable vials with a pathlength of 8 mm were used, which made cleaning of the sample vessels unnecessary. The Metrohm software package Vision Air Complete was used for all data acquisition and prediction model development.

Table 1. Hardware and software equipment overview

Equipment	Metrohm number
DS2500 Liquid Analyzer	2.921.1410
DS2500 Holder 8 mm vials	6.749.2020
Disposable vials, 8 mm	6.7402.000
Vision Air 2.0 Complete	6.6072.208



Figure 1. DS2500 Liquid Analyzer and a sample filled in a disposable vial.

RESULT

The obtained Vis-NIR spectra (Figure 2) were used to create a prediction model for quantification of the moisture content in diesel samples. The quality of the prediction model was evaluated using the correlation diagram, which displays a very high correlation between the Vis-NIR prediction and the reference values. The respective figures of merit (FOM) display the expected precision of a prediction during routine analysis.

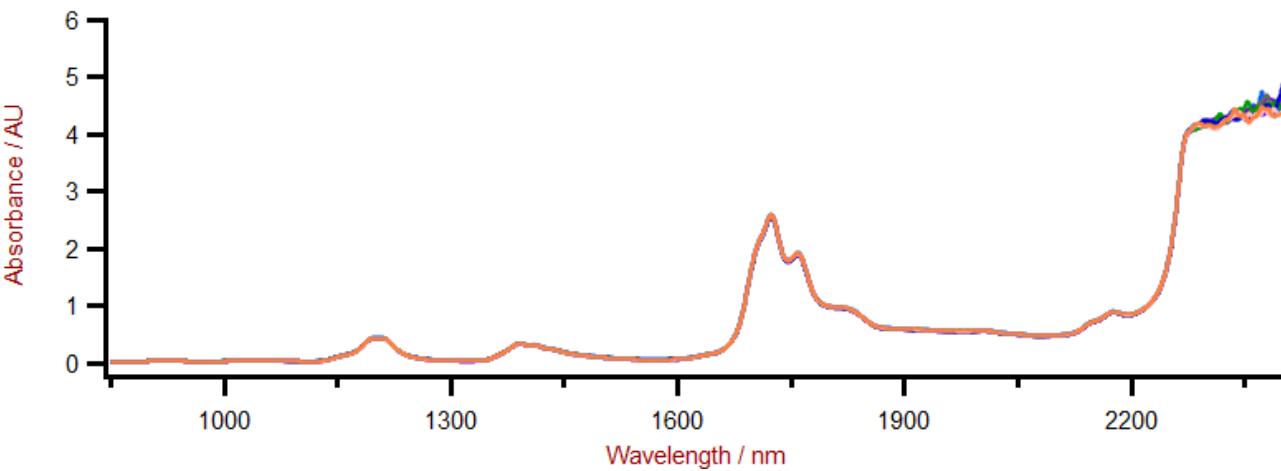
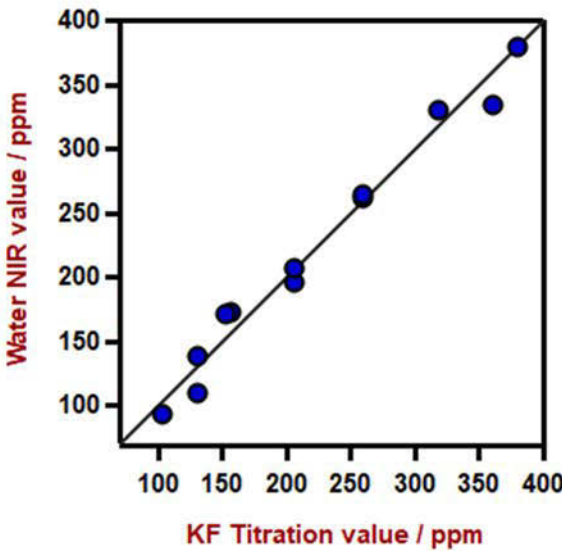


Figure 2. Vis-NIR spectra of diesel samples analyzed on a DS2500 Liquid Analyzer.

RESULT WATER CONTENT IN DIESEL



Figures of Merit	Value
R ²	0.9776
Standard Error of Calibration	16 ppm
Standard Error of Cross-Validation	21 ppm

Figure 3. Correlation diagram and the respective figures of merit for the prediction of water content in diesel using a DS2500 Liquid Analyzer. The lab value was evaluated using KF titration.

CONCLUSION

This application note demonstrates the feasibility to determine a key parameter of the quality control of diesel fuel (water content) with NIR spectroscopy. The main advantages of Vis-NIR spectroscopy over

wet chemical methods are that running costs are significantly lower and time-to-result is significantly reduced. Additionally, no chemicals are required and the technique is non-destructive to samples.

Table 2. Time to result overview for KF titration

Parameter	Method	Time to result
Water	Karl Fischer titration	~ 5 minutes



TBN determination in lubricants

Quality control of total base number without toxic chemicals

Alkaline additives in engine lubricants are used to prevent the build-up of acids and as a result, they inhibit corrosion. The total base number (TBN) indicates the amount of basic additives present in samples and thus can be used as a measure for the degradation of the lubricant. Depending on the application, the TBN value varies from 7 mg KOH/g in lubricants for combustion engines up to 80 mg KOH/g for marine grade lubricants.

The standard test method for TBN in lubricants is potentiometric titration according to ASTM D2896. This method requires the use of toxic reagents (e.g., tetraethylammonium bromide) and the cleaning procedure is labor-intensive. In contrast to the primary method, near-infrared spectroscopy (NIRS) is a fast analytical technique which does not produce any chemical waste and completes the TBN analysis in less than one minute.

EXPERIMENTAL EQUIPMENT

23 marine cylinder lubricants and 37 engine lubricants were analyzed on a Metrohm DS2500 Liquid Analyzer equipped with 2.5 mm flow cell. All measurements were performed in transmission mode from 400 nm to 2500 nm. In this feasibility study, a flow cell was used to automate the sample handling and measurement. Data acquisition and prediction model development was performed with the software package Vision Air complete.

Table 1. Hardware and software equipment overview

Equipment	Metrohm number
DS2500 Liquid Analyzer	2.929.0010
DS2500 Holder for flow cells	6.7493.000
Vision Air 2.0 Complete	6.6072.208



Figure 1. DS2500 Liquid Analyzer.

RESULT

The obtained Vis-NIR spectra (Figure 2) were used to create a prediction model for the total base number determination. To verify the quality of the prediction model, correlation diagrams were created which display the correlation between Vis-NIR prediction and primary method values. The respective figures of merit (FOM) display the expected precision of a prediction during routine analysis (Figure 3).

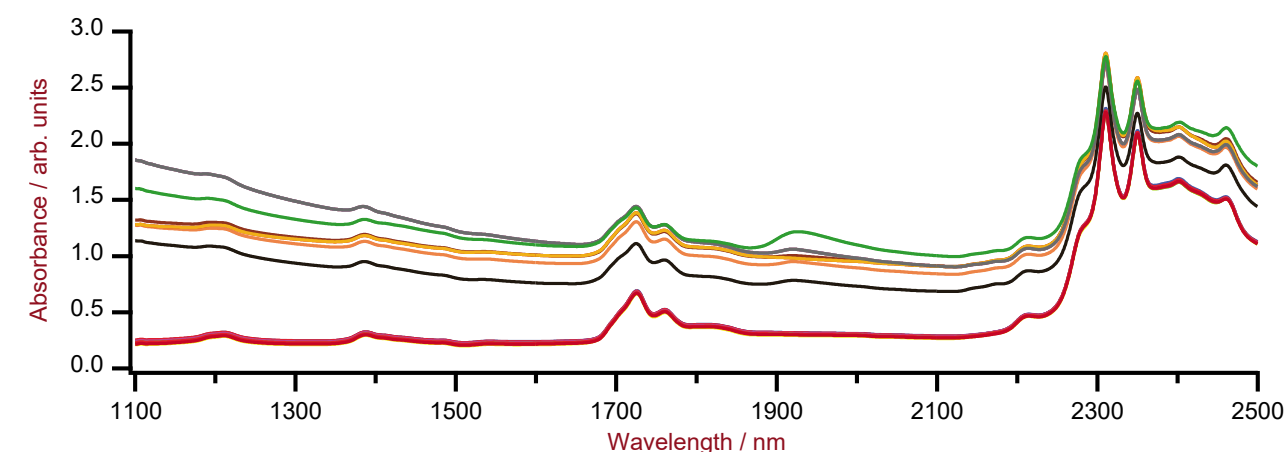
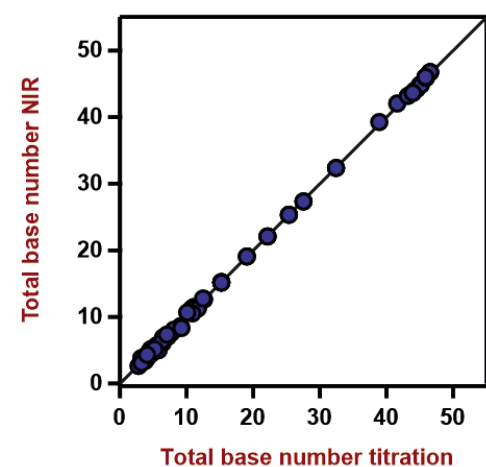


Figure 2. Selection of Vis-NIR spectra of marine cylinder lubricants and engine lubricants obtained using a DS2500 Liquid Analyzer with a 2.5 mm flow cell.

RESULT TBN IN COMBINED LUBRICANTS



Figures of Merit	Value
R ²	0.998
Standard Error of Calibration	1.1
Standard Error of Cross-Validation	1.2

Figure 3. Correlation diagram and the respective figures of merit for the prediction of TBN in lubricants using a DS2500 Liquid Analyzer. The lab values were determined using titration.

CONCLUSION

This application note shows the feasibility of NIR spectroscopy for the analysis of total base number in

marine cylinder and engine lubricants. In comparison to the wet chemical method (Table 2), no sample preparation or chemicals are needed with NIR spectroscopy.

Table 2. Time to result with conventional titration method ASTM D2896

Parameter	Method	Time to result
Total base number	Titration	~5–10 minutes

Analytes:	Base number, TBN
Matrix:	Lubricants
Industry:	Petrochemicals & biofuels
Standards:	ASTM D2896; ASTM E1655
Method:	Spectroscopy (NIRS/Raman)

NIR Application Note AN-NIR-097
Version 1 – 2021-12



NIR APPLICATION NOTE NIR-041

Quality Control of Lubricants

Fast and chemical-free determination of the Acid Number, viscosity, moisture content, and color number of lubricants

For lubricant analysis, determination of the Acid Number (ASTM D664), viscosity (ASTM D445), moisture content (ASTM D6304), and color number (ASTM D1500) require the use of multiple analytical technologies and, in part, large volumes of chemicals. Time to result can therefore be quite a long and costly process.

This application note demonstrates that the XDS RapidLiquid Analyzer operating in the visible and near-infrared spectral region (Vis-NIR) provides a fast and cost-efficient alternative for the determination of the AN, viscosity, moisture content, and color number of lubricants. With **no sample preparation or chemicals needed**, Vis-NIR spectroscopy allows for multi parameter analysis of lubricants in **less than one minute**.

EXPERIMENTAL EQUIPMENT

Lubricant samples were measured with a XDS RapidLiquid Analyzer in transmission mode over the full wavelength range (400–2500 nm) (Figure 1). Reproducible spectrum acquisition was achieved using the instrument’s built-in temperature control (at 40 °C). For convenience, disposable vials with a pathlength of 8 mm were used, which made cleaning of the sample vessels unnecessary. The Metrohm software package Vision Air Complete was used for all data acquisition and prediction model development.

Table 1. Hardware and software equipment overview

Equipment	Metrohm number
XDS RapidLiquid Analyzer	2.921.1410
Disposable vials, 8 mm diameter, transmission	6.7402.000
Vision Air Complete	6.6072.208

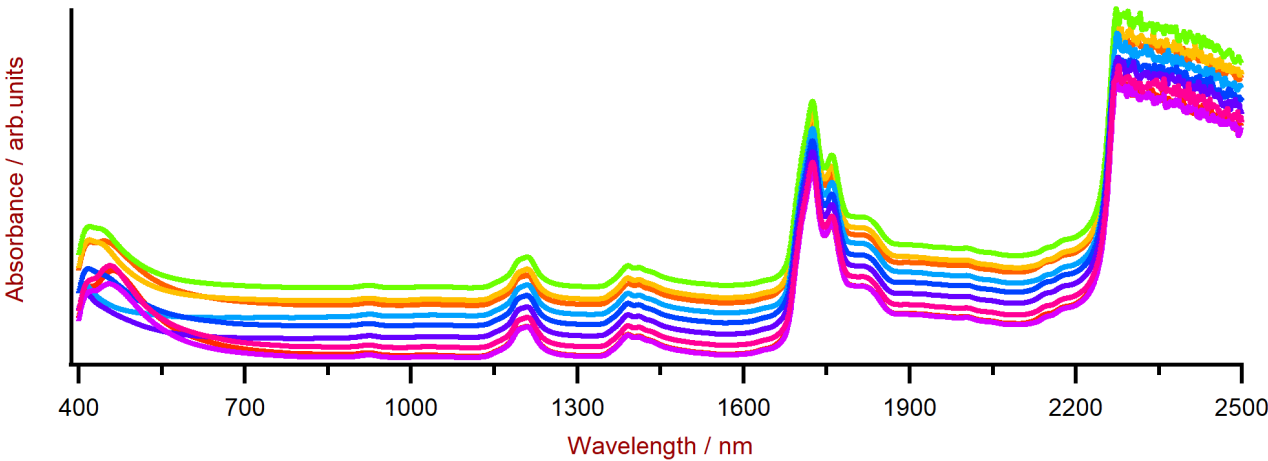


Figure 2. Selection of lubricant oil Vis-NIR spectra obtained using a XDS RapidLiquid Analyzer and 8 mm disposable vials. For display reasons a spectra offset was applied.

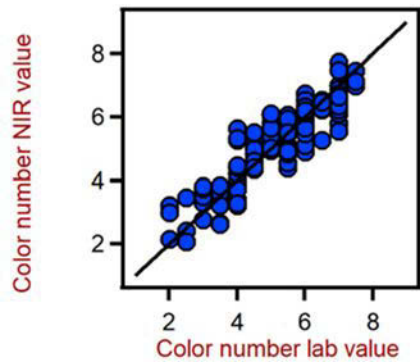


Figure 1. XDS RapidLiquid Analyzer and lubricant samples.

RESULT

The obtained Vis-NIR spectra (Figure 2) were used to create prediction models for quantification of the Acid Number, viscosity, moisture content, and color number in lubricants. Correlation diagrams, which display the relationship between Vis-NIR prediction and primary method values, are used to determine the quality of the prediction models. The respective figures of merit (FOM) display the expected precision of a prediction during routine analysis.

RESULT COLOR NUMBER



Figures of Merit	Value
R ²	0.700
Standard Error of Calibration	0.841
Standard Error of Cross-Validation	0.916

Figure 6. Correlation diagram and the respective figures of merit for the prediction of the color number in lubricants using a XDS RapidLiquid Analyzer. The lab value was evaluated using photometry.

CONCLUSION

The following application note demonstrates the feasibility of NIR spectroscopy for the analysis of key quality parameters in lubricants. In comparison to

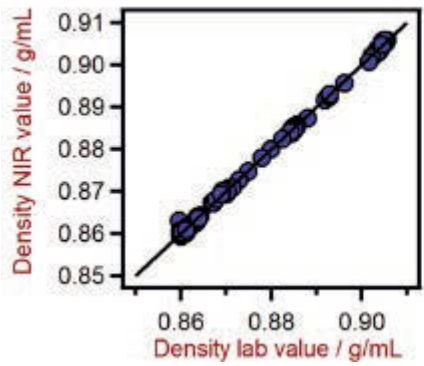
wet chemical methods (Table 2), the time to result is a major advantage of NIR spectroscopy, since all parameters are determined in a single measurement in less than a minute.

Table 2. Time to result overview for the different quality control parameters.

Parameter	Method	Time to result
Acid Number	Titration	~5 min
Viscosity	Viscometry	~4 min
Moisture content	KF Titration	~5 min
Color number	UV-Vis Photometer	~1 min

Analytes:	Acid number; Physical parameters – viscosity, density, etc.; Moisture/water
Matrix:	Lubricants
Industry:	Petrochemical
Standards:	ASTM E1655

RESULT DENSITY CONTENT



Figures of Merit	Value
R ²	0.991
Standard Error of Calibration	0.0005 g/mL
Standard Error of Cross-Validation	0.0005 g/mL

Figure 3. Correlation diagram and the respective figures of merit for the prediction of the density content of PE using a DS2500 Solid Analyzer. The density lab value was evaluated using densimetry.

CONCLUSION

This application note demonstrates that the density of PE can be determined easily with NIR

spectroscopy. Since **no sample preparation is needed**, samples are analyzed as they are, which allows for simple operation leading to highly precise results (0.0005 g/mL, see **Figure 3**).

Analytes:	Density
Matrix:	PE
Industry:	Polymer Industry
Standards:	ASTM E1655

NIR Application Note AN-NIR-081
Version 1 – 2020-03



NIR APPLICATION NOTE NIR-071

Quality Control of Lubricants

Unassisted, rapid determination of the Acid Number by automated NIR spectroscopy according to ASTM E1655

Acid Number (AN) analysis of lubricants (ASTM D664) can be a lengthy and costly process due to usage of large amounts of chemicals and required cleaning steps of the analytical equipment between each measurement.

This application note demonstrates that the XDS RapidLiquid Analyzer operating in the visible and near-infrared spectral region (Vis-NIR) provides a cost-efficient, fast alternative for the determination of the acid number of lubricants. With **no sample preparation or chemicals needed**, Vis-NIR spectroscopy allows for the analysis of AN in **less than a minute**.

EXPERIMENTAL EQUIPMENT

Lubricant samples were measured in transmission mode over the full wavelength range (400 nm to 2500 nm) using a XDS RapidLiquid Analyzer in combination with an 815 Robotic USB Sample Processor, which can carry a total of 141 samples. Reproducible spectrum acquisition was achieved using the built-in temperature control (at 30°C) of the XDS RapidLiquid Analyzer. The Metrohm software packages Tiamo and Vision Air Complete were used for all data acquisition and prediction model development.

Table 1. Hardware and software equipment overview

Equipment	Metrohm number
XDS RapidLiquid Analyzer	2.921.1410
815 Robotic USB Sample Processor XL (Sample Rack 141 x 11 ml)	2.815.0010
800 Dosino	2.800.0020
5.0 mm flow cell	Hellma
Vision Air complete	6.6072.208
Tiamo	6.6056.021

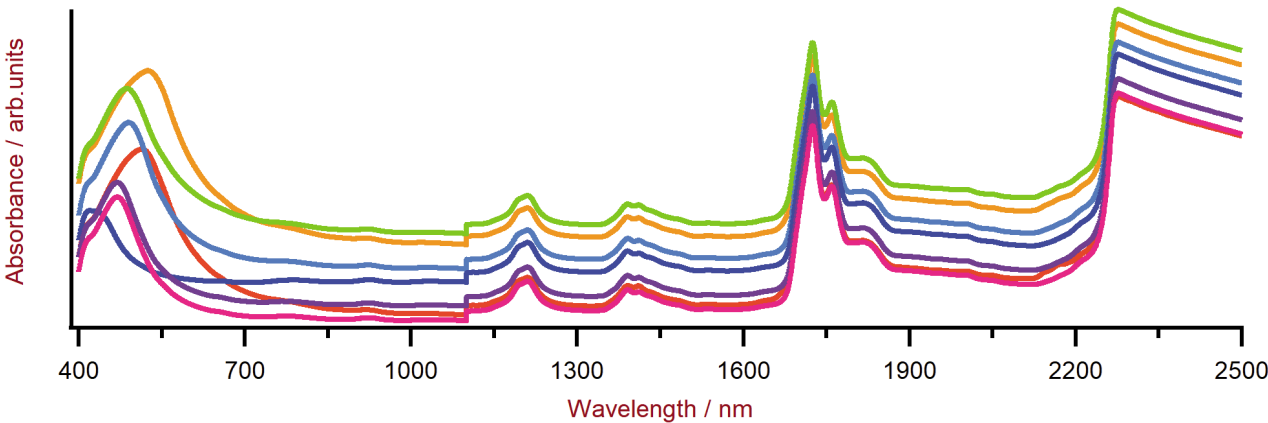


Figure 2. Selection of lubricant Vis-NIR spectra obtained using a XDS RapidLiquid Analyzer and 5.0 mm flow cell. For display reasons a spectra offset was applied.

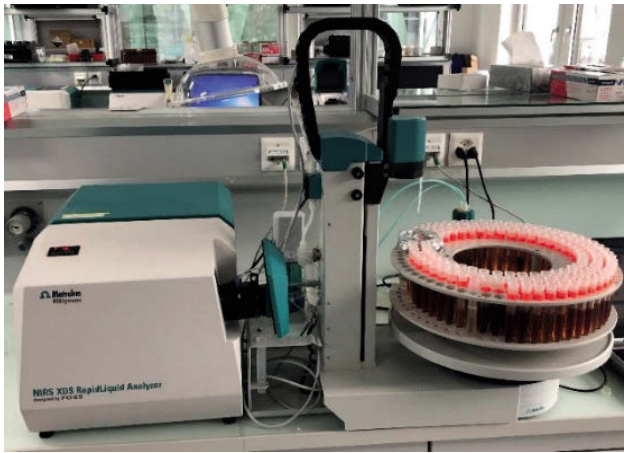
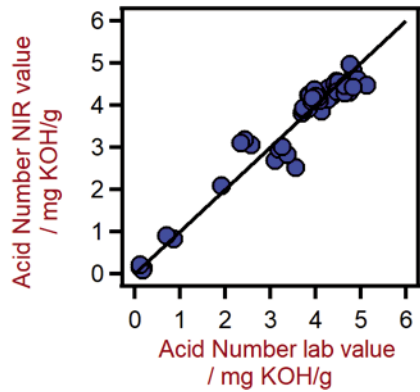


Figure 1. XDS RapidLiquid Analyzer with 5.0 mm flow cell and the 815 Sample Processor.

RESULT

The obtained Vis-NIR spectra (Figure 2) were used to create prediction models for quantification of the Acid Number in lubricants. The quality of the prediction models was evaluated using correlation diagrams, which display the relationship between Vis-NIR prediction and primary method values. The respective figures of merit (FOM) display the expected precision of a prediction during routine analysis.

RESULT ACID NUMBER



Figures of Merit	Value
R ²	0.950
Standard Error of Calibration	0.344 mg KOH/g
Standard Error of Cross-Validation	0.395 mg KOH/g

Figure 3. Correlation diagram and the respective figures of merit for the prediction of the Acid Number in lubricants using a XDS RapidLiquid Analyzer. The Acid Number content lab value was evaluated using titration.

CONCLUSION

This study demonstrates the feasibility of NIR spectroscopy for the analysis of the Acid Number in lubricants. In comparison to wet chemical methods

running costs are significantly reduced when using NIR spectroscopy (Figure 4).



	Lab method	NIR method
Number of analysis (per day)	10	10
Cost of operator (per hour)	\$25	\$25
Costs of consumables and chemicals: Acid Number	\$10	\$1.50
Time spent per analysis	10 min	4 min
Total running costs / year	\$31,875	\$7,125

Figure 4. Comparison of running costs for the determination of the Acid Number with titration (ASTM D664) and NIR spectroscopy.

Analytes: Acid Number
Matrix: Lubricants
Industry: Petrochemical
Standards: ASTM E1655

