Quality control of pyrolysis gasoline

Determination of diene value within one minute using NIRS

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 analytic solution for the determination of diene value in pyrolysis gasoline.

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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 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.

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

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

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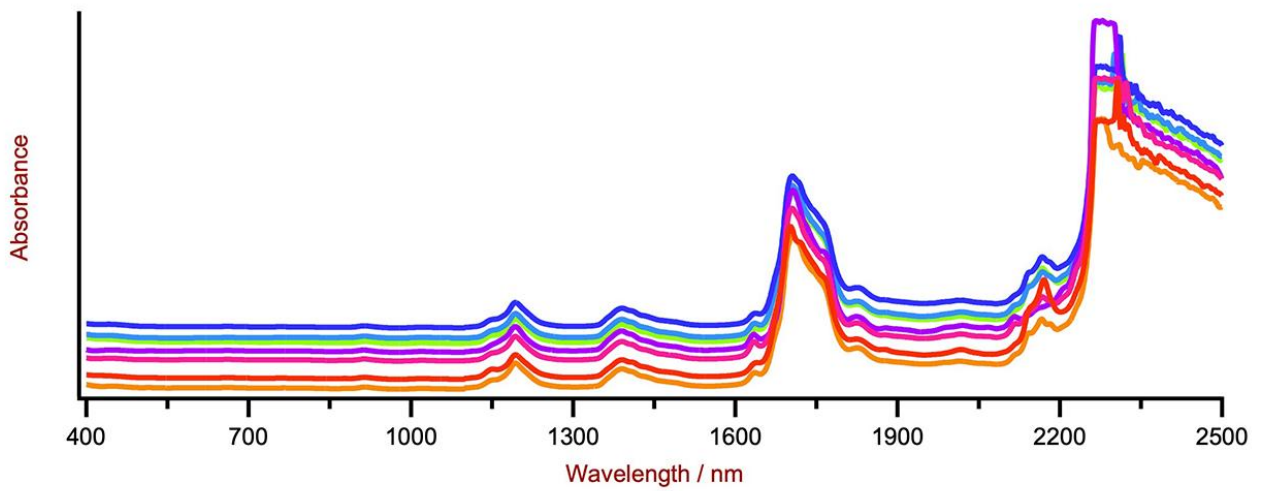
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Figure 2. Selection of pyrolysis gasoline Vis-NIR spectra obtained using a XDS RapidLiquid Analyzer and 8 mm disposable vials. For display reasons a spectra offset was applied.
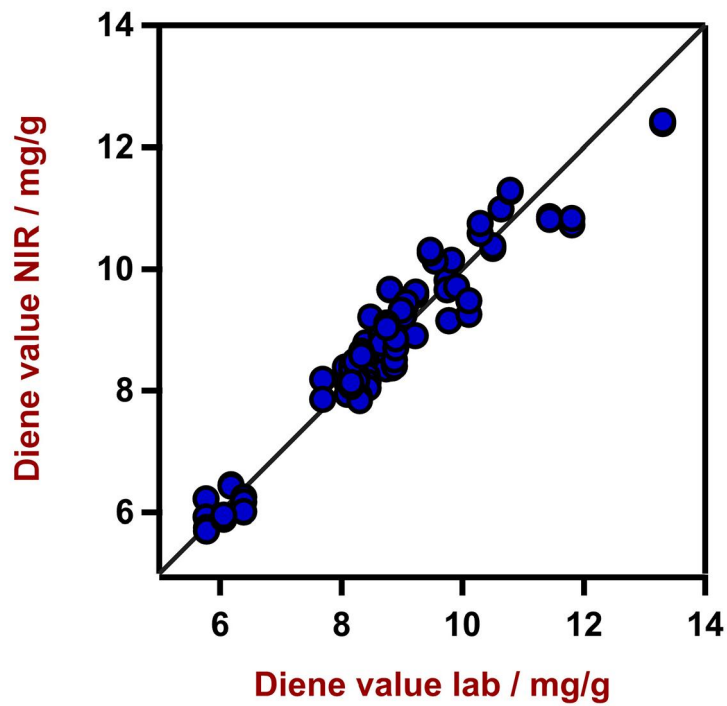

Figure 3. Correlation diagram for the prediction of the diene value using a XDS RapidLiquid Analyzer. The lab values were determined according to the UOP326-17 method.

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Table 2. Figures of merit for the prediction of the diene value using a XDS RapidLiquid Analyzer.

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

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 3**), the time to result is a major advantage of NIR spectroscopy, since a single **measurement is performed within one minute**.

Table 3. Time to result with conventional UOP-326 wet chemistry analysis

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

CONTACT

Metrohm Turkey
Ayazağa Mah. Azerbaycan
Cad. No. 3I
34396 İstanbul

info@metrohm.com.tr

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NIRS XDS RapidLiquid Analyzer
Rapid, precise analyses of liquids and suspensions of all types.

The NIRS XDS RapidLiquid Analyzer enables rapid, precise analyses of liquid formulations and substances. Precise measurement results at the push of a button make the NIRS XDS RapidLiquid Analyzer an equally reliable and simple solution for quality monitoring in laboratories and processes. The samples are transferred to quartz cuvettes designed for multiple use or disposable glass vials; a tempered sample compartment ensures reproducible analysis conditions and thus accurate measurement results.

Vision Air 2.0 Complete
Vision Air - Universal spectroscopy software.

Vision Air Complete is a modern and simple-to-operate software solution for use in a regulated environment.

Overview of the advantages of Vision Air:
- Individual software applications with adapted user interfaces ensure intuitive and simple operation
- Simple creation and maintenance of operating procedures
- SQL database for secure and simple data management

The Vision Air Complete version (66072208) includes all applications for quality assurance using Vis-NIR spectroscopy:
- Application for instrument and data management
- Application for method development
- Application for routine analysis

Additional Vision Air Complete solutions:
- 66072207 (Vision Air Network Complete)
- 66072209 (Vision Air Pharma Complete)
- 66072210 (Vision Air Pharma Network Complete)

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