



NIR APPLICATION NOTE NIR-024

Quality control of pyrolysis gasoline

Determination of diene value within one minute

Pyrolysis gasoline (Pygas) is a by-product 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.

EXPERIMENTAL EQUIPMENT

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.

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. The respective figures of merit (FOM) display the expected precision of a prediction during routine analysis.

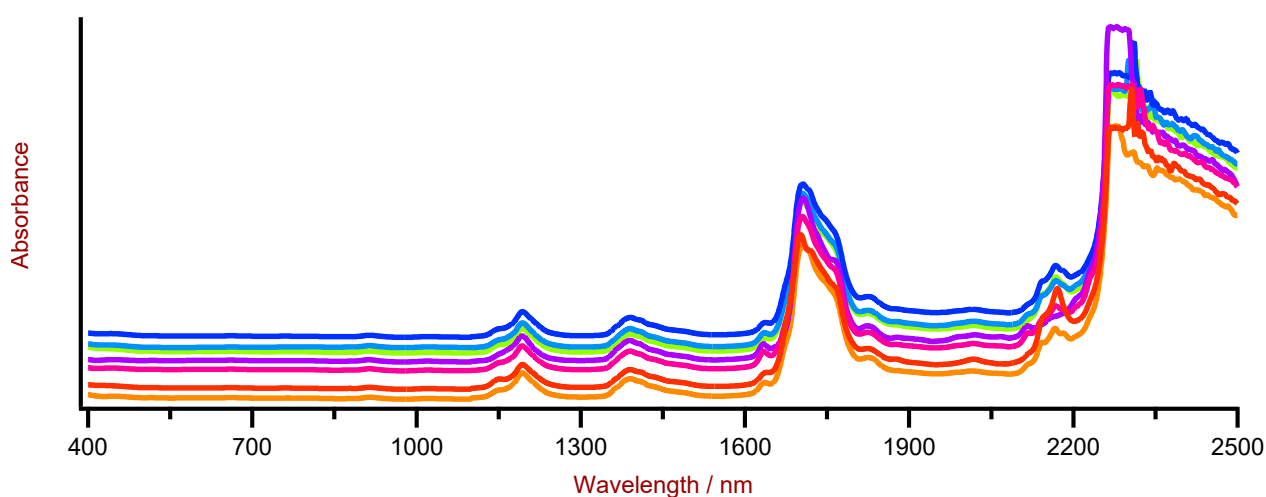
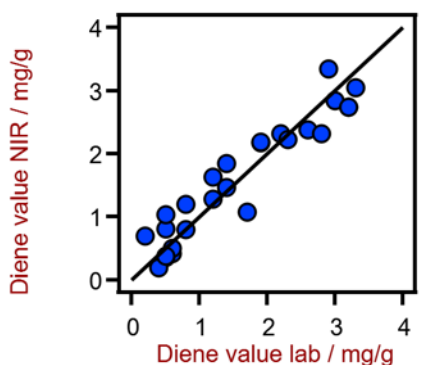


Figure 2. Selection of pyrolysis gasoline Vis-NIR spectra obtained using a XDS RapidLiquid Analyzer and 8 mm disposable vials. For display reasons a spectra offset was applied.

RESULT DIENE VALUE



Figures of Merit	Value
R ²	0.912
Standard Error of Calibration	0.36 mg/g
Standard Error of Cross-Validation	0.45 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 hr; reflux, hydrolysis, titration

Analytes: Diene value
Matrix: Pyrolysis gasoline
Industry: Petrochemical Industry
Standards: ASTM E1655