Application Note AN-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.

Figure 1. DS2500 Liquid Analyzer.

Table 1. Hardware and software equipment overview.

Equipment	Metrohm number
DS2500 Liquid Analyzer	2.929.0010
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 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.

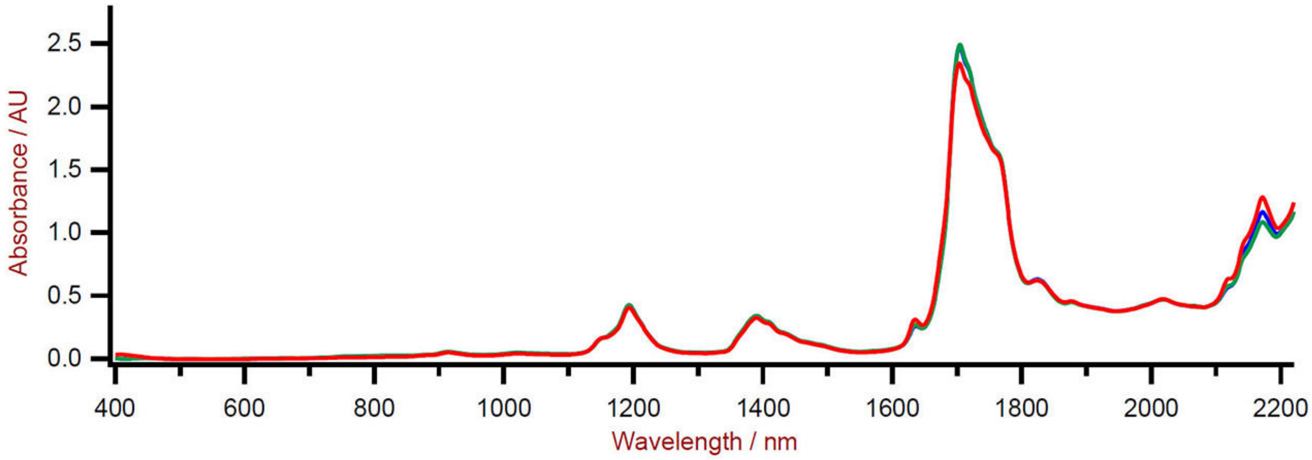

Figure 2. Selection of different pyrolysis gasoline Vis-NIR spectra obtained using a DS2500 Liquid Analyzer and 8 mm disposable vials.

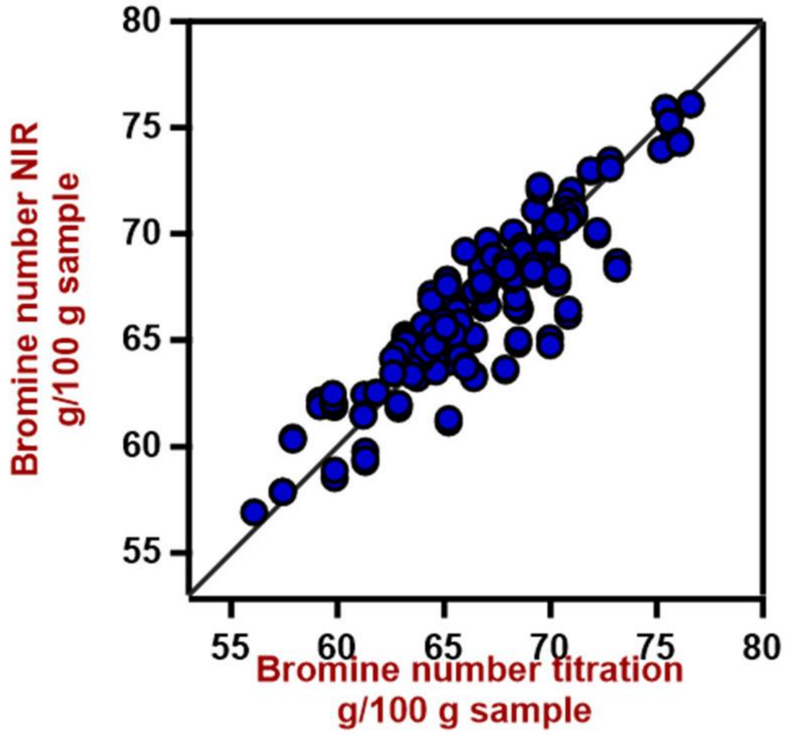

Figure 3. Correlation diagramm for the prediction of the bromine number using a DS2500 Liquid Analyzer.

Table 2. Figures of merit for the prediction of the bromine number using a DS2500 Liquid Analyzer.

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

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 and Table 3), 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.

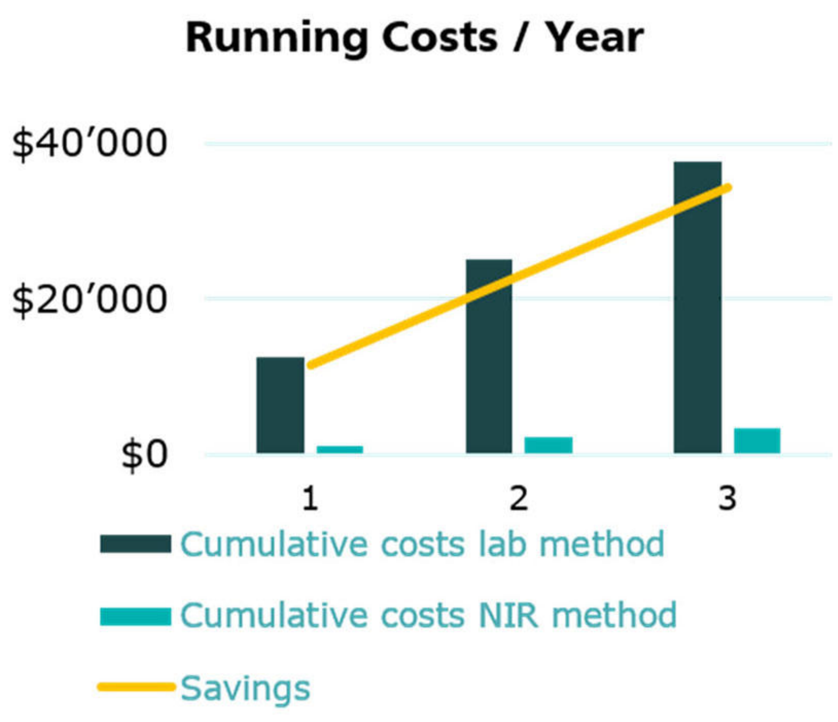

Figure 4. Comparison of running costs per year with the conventional wet chemistry lab method and NIRS.

Table 3. Comparison of costs and time to result (one-fold determination) with the conventional wet chemistry lab method and NIRS.

	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

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