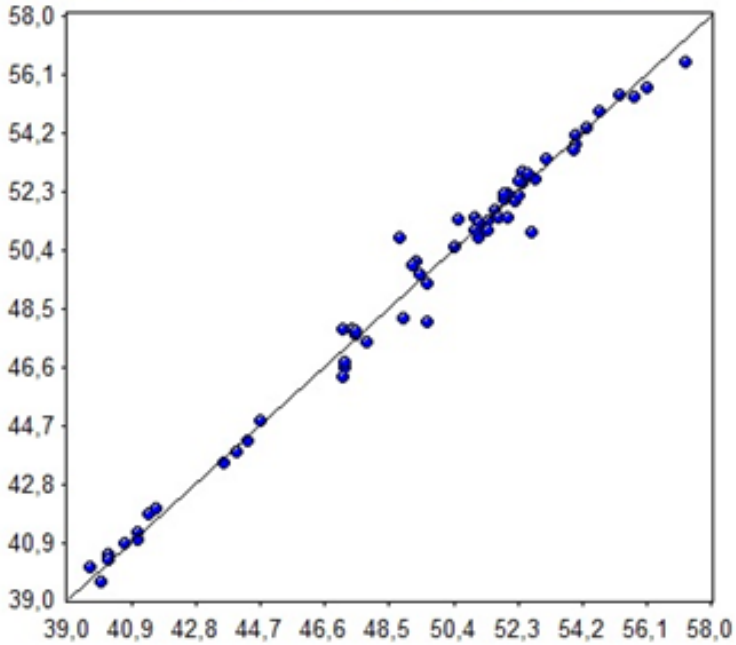
Near-Infrared Spectroscopy Application Note NIR–22

Petroleum product analysis by NIR spectroscopy (e.g., cetane index, TAN, aromatics, and sulfur)



This application note describes the determination of the cetane index, aromatics, bromine number, TAN (total acid number) and sulfur in different refinery products.

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Method description

Introduction

The process of refining, i.e., the fractional distillation of crude oil, is at the basis of many products that are closely related to daily life: refinery products are often used as a source of energy or as raw materials for everyday items. Some products that are derived from crude oil are, for example, fuels such as kerosene, fuel oil, or diesel. To ensure optimum operation of motors and improve overall product quality, different fuel parameters, like the cetane index, the aromatics and the sulfur contents, the bromine number, and the TAN (total acid number), are subject to strict control. Near infrared spectroscopy (NIRS) allows you to measure all important parameters at once, in the production process, and furnishes results in a matter of seconds.

Experimental

71 samples of petrochemical products were analyzed on a NIRS XDS RapidLiquid Analyzer using disposable glass vials with 8 mm diameter (**Table 1, Figure 1**).

Figure 1: NIRS XDS RapidLiquid Analyzer (RLA)

Table 1: Used equipment

NIRS XDS RapidLiquid Analyzer	2.9211.410
NIRS disposable glass vials, 8 mm	6.7402.000

Five different parameters were analyzed in the 71 samples (**Table 2**). The samples were taken from the production process as raw products (gasoil, EM, kerosene, diesel, coker-kerosene, coker-diesel) or as final products (JA, HEL). The samples were taken on 3–4 different days per week. Transmission measurements were performed at 35 °C in the RLA. The equilibration time was set to 30 s. The reference values were provided by the customer's reference lab.

Table 2: Overview of analyzed sample parameters

Sample name	Cetane index [-]	Bromine number [g/100g]	TAN [mg/g]	Aromatics content [wt%]	Sulfur content [wt%]
EM 2	49.6	9.16	0.46	26.6	0.26
gasoil 2	56.1	1.52	0.48	-	0,37
EM 2	48.9	7.56	0.45	28.1	0.20
diesel 5009	51.7	-	-	-	-
EM 4	48.8	6.91	0.85	26.4	0.25
EM 2	40.7	8.08	-	19.8	0.13
EM 4	49.2	7.49	0.76	28.0	0.24
EM 4	49.3	10.5	0.74	27.0	0.29
diesel 2	53.1	-	2.79	-	0.42
kerosene 2	41.1	0.42	0.01	-	0.04
kerosene 1	40.2	1.29	0.46	19.2	0.12
kerosene 1	40.0	1.42	0.40	-	0.12
kerosene 2	41.1	0.29	0.03	-	0.04
kerosene 2	41.1	0.42	0.01	22.4	0.15
gasoil 1	47.5	1.02	0.19	-	0.14
diesel 5012	51.0	-	-	-	0.33
gasoil 2	57.2	-	0.40	-	-
gasoil 1	47.5	-	0.18	-	0.11
EM 3	41.4	12.5	0.22	19.9	0.11
EM 3	41.6	12.3	0.28	18.7	0.13
gasoil 2	55.7	2.84	0.52	31.2	0.40
kerosene 1	39.7	1.38	0.28	-	0.09
kerosene 1	40.2	-	0.34	-	0.10
kerosene 2	40.0	-	0.03	-	0.02
coker diesel	54.7	27.6	0.24	25.7	0.71
coker kerosene	44.0	45.4	0.41	20.4	0.48
coker diesel	54.0	27.3	0.19	27.0	0.72
coker diesel	53.9	19.6	0.10	26.8	-
coker kerosene	44.3	44.1	0.53	19.5	0.48
coker kerosene	44.7	47.2	-	18.6	0.47
coker kerosene	43.6	35.0	0.46	19.3	-
coker diesel	55.3	30.7	-	25.8	0.69
Finished product 1	-	-	-	17.2	-
finished product 2	-	-	-	17.7	-
finished product 2	-	-	-	19.0	-
finished product 2	-	-	-	15.9	-
finished product 3	-	-	-	19.0	-
finished product 1	-	-	-	16.8	-
finished product 2	-	-	-	17.7	-
finished product 2	-	-	-	17.1	-
finished product 2	-	-	-	16.0	-
finished product 8	52.0	-	-	-	0.00301
finished product 8	52.7	-	-	-	0.00210
finished product 11	52.0	-	-	-	0.00444
finished product 8	52.3	-	-	-	0.00354
finished product 3	51.9	-	-	-	0.00405
finished product 10	52.0	-	-	-	0.00429
finished product 8	51.0	-	-	23.6	0.02700
finished product 7	50.5	-	-	-	0.00420
finished product 7	52.6	-	-	26.2	0.00368
finished product 3	51.9	-	-	-	0.00240
finished product 7	51.1	-	-	22.6	0.00420

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finished product 10	52.0	-	-	-	0.00420
diesel 1	47.2	1,44	1.30	-	0.26
diesel 1	47.1	1.30	1.30	25.9	0.27
diesel 2	54.0	2.81	2.48	-	0.45
diesel 1	47.8	1.93	1.17	-	0.24
diesel 2	52.4	2.46	2.55	31.3	0.46
diesel 1	47.2	-	1.08	-	0.22
diesel 2	52.4	2.35	2.50	-	0.46
diesel 5048	50.4	-			
diesel 5008	49.6	-	-	-	-
diesel 5006	51.6	-	-	-	-
diesel 5013	49.4	-	-	-	-
diesel 5012	52.2	-	-	19.0	-
diesel 5012	52.0	-	-	-	-
diesel 5008	51.4	-	-	-	-
diesel 5006	54.3	-	-	-	-
diesel 5006	52.3	-	-	-	-
diesel 5012	51.1	-	-	-	-
diesel 5013	52.8	-	-	-	-

Method development and results

For each of the five parameters, a quantitative model was developed.

Cetane index:

Reference values for the cetane index were provided for 65 of the 71 samples. The values were in the range of 39.7–57.2 and they were spread regularly across the range. **Table 3** shows the parameters used for the method development.

Table 3: Parameters of the calibration of the cetane index

Calibration range	39.7 – 57.2 cetane index
Wavelength region	1150–2200 nm
Math pretreatment	2nd derivative
Method	PLS
Factors	7
R^2	0.9883
SEC	0.56
SECV	0.65

The full NIR region was used to build the calibration. The VIS range was excluded. A PLS model with 7 factors was built on the 2nd derivative data of the 65 samples. **Figure 2** shows the NIR data versus the reference data.

PLS method development for the cetane index revealed a correlation between the NIR and the reference values, which was characterized by R^2 = 0.9883 and a SEC = 0.56. The calibration was cross-validated with a SECV = 0.65.

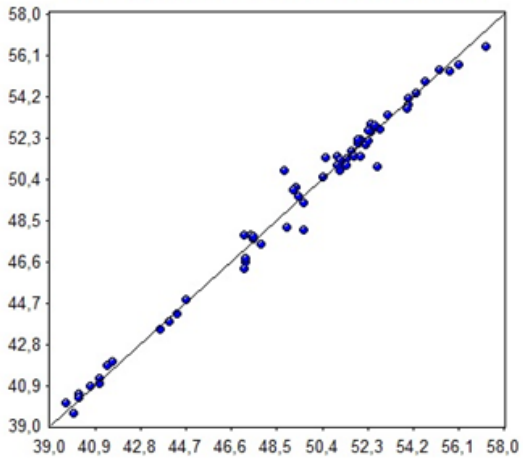

Figure 2: Calibration set for the cetane Index – NIR data vs. reference data

Bromine number:

Reference values for the bromine number were provided for 31 of the 71 samples. The values were in the range of 0.29–47.2 g/100 g. **Table 4** shows the parameters for the method development.

Table 4: Parameters of the calibration of the bromine number

Calibration range	0.29 – 47.2 g/100g
Wavelength region	1150 – 2200 nm
Math pre-treatment	2nd derivative
method	PLS
factors	5
R^2	0.9831
SEC	2.1
SECV	2.7

The full NIR region was used to build the calibration for the bromine number. The VIS range was excluded. A PLS model with 5 factors was built on the 2nd derivative spectral data of the 31 samples. **Figure 3** shows NIR data versus reference data.

The PLS method development for the bromine number revealed a correlation between the NIR and the reference values, which was characterized by R^2 = 0.9831 and a SEC = 2.1. The calibration was cross-validated with a SECV = 2.7. The bromine number of the various samples was split into four groups according to the product type. Especially the coker samples exhibit very high bromine numbers compared to the kerosene, diesel, and gasoil samples.

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Method description

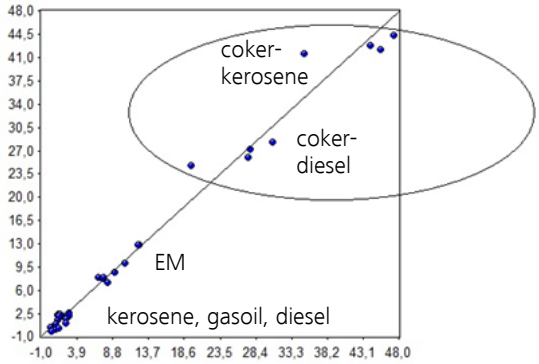

Figure 3: Calibration set for bromine number – NIR data vs. reference data

TAN (Total Acid Number):

TAN reference values were provided for 40 of the 71 samples. The values were in the range of 0.01–2.79 mg KOH/g. **Table 5** shows the parameters for the method development.

Table 5: Parameters of the calibration of the TAN

Calibration range	0.01 – 2.79 mg KOH/g
Wavelength region	1150 – 2200 nm
Math pre-treatment	2nd derivative
method	PLS
factors	6
R^2	0.9004
SEC	0.248
SECV	0.308

The full NIR region was used to build the calibration for the determination of the TAN. The VIS range was excluded. A PLS model with 6 factors was built on the 2nd derivative data of the 40 samples. **Figure 4** shows NIR versus the reference data.

The PLS method development for the TAN revealed a correlation between the NIR and the reference values, which was characterized by R^2 = 0.9004 and a SEC = 0.248. The calibration was cross-validated with a SECV = 0.308. The TAN values of the various samples were split into two groups. To improve the calibration and to get a more robust method more samples of a TAN value over 1.5 mg KOH/g need to be included into the development.

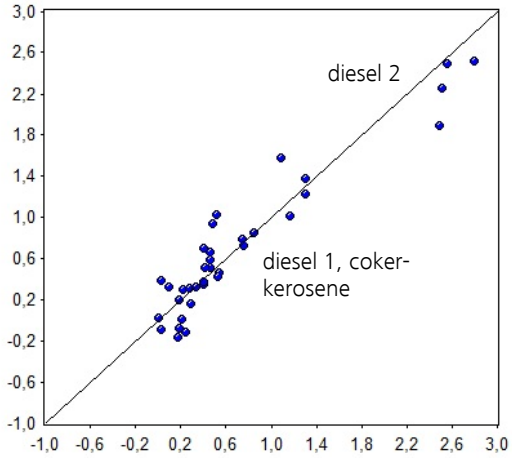

Figure 4: Calibration set for the TAN – NIR data vs. reference data

Aromatics content:

Reference values of the aromatics content were provided for 26 of the 71 samples. They were in the range of 15.9–31.3 wt%. **Table 6** shows the parameters for the method development.

Table 6: Parameters of the calibration of the aromatics content

Calibration range	15.9–31.2 wt%
Wavelength region	1150–2200 nm
Math pre-treatment	2nd derivative
method	PLS
factors	4
R^2	0.9633
SEC	0.849
SECV	0.990

The full NIR region was used to build the calibration for the determination of the aromatics content. The VIS range was excluded. A PLS model with 4 factors was built on the 2nd derivative data of the 26 samples. **Figure 5** shows NIR versus the reference data.

The PLS method development for the aromatics content revealed a correlation between the NIR and the reference values, which was characterized by R^2 = 0.9633 and a SEC = 0.849. The calibration was cross-validated with a SECV = 0.990.

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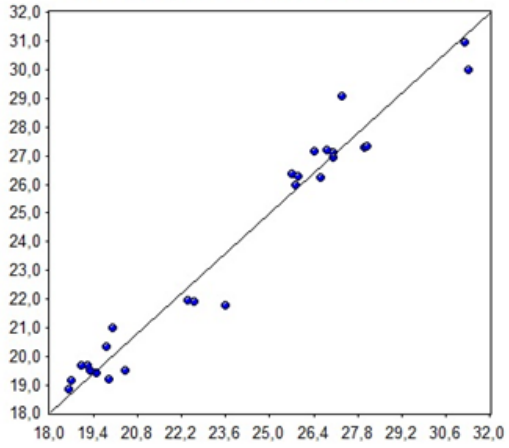

Figure 5: Calibration set for aromatics content – NIR vs. reference data

Sulfur content:

Reference values of the sulfur content were provided for 47 of the 71 samples. Only 35 of them were used for the method development because the finished products have a sulfur content > 0.05 wt%, which is below the detection limit of NIRS. **Table 7** shows the parameters of the method development.

Table 7: Parameter of method development for the calibration for the sulfur content

Calibration range	2.5–1760 mg/kg
Wavelength region	1150–2200 nm
Math pre-treatment	2nd derivative
method	PLS
factors	5
R^2	0.9719
SEC	0.035
SECV	0.040

The full NIR region was used to build the calibration of the sulfur content. The VIS range was excluded. A PLS model with 5 factors was built on the 2nd derivative data of the 35 samples. **Figure 7** shows NIR versus the reference data.

The PLS method development for the sulfur content revealed a correlation between the NIR and the reference values, which was characterized by R^2 = 0.9719 and a SEC = 0.035. The calibration was cross-validated with a SECV = 0.040.

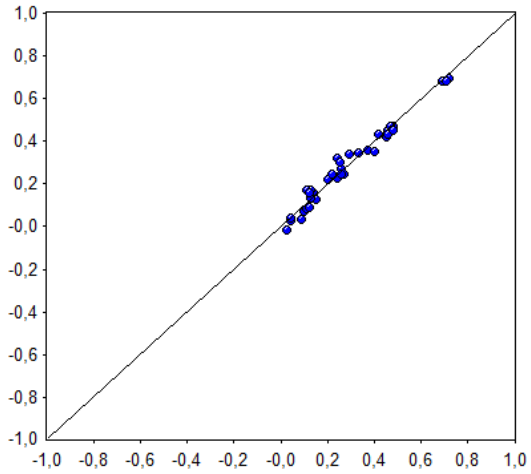

Figure 6: Calibration set for sulfur content – NIR vs. reference data

Conclusions

NIR XDS RLA Analyzer can be used to make a quantitative analysis on different important parameters of refinery products.

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