ООО «Эндресс+Хаузер»
117105, г. Москва, Варшавское шоссе, д. 35, стр. 1, ком.42
Тел.: +7 (495) 783-28-50; Факс: +7 (495) 783-28-55;
e-mail: info@ru.endress.com;
http://www.ru.endress.com

Endress+Hauser

Gazpromneft-ONPZ
644040 Omsk,
Gubkin ave., 1
Chief metrologist
Dmitry An

Contact person
Dmitry Konstantinov
Phone: +7 495 740 5400 EXT. 122
dmitry.konstantinov@endress.com

Moscow. July 21, 2022

Test Report and Results for Laboratory Raman Spectrometers from Endress+Hauser Optical Analysis, Inc.

From March 22 to April 8, 2022, the quality control laboratory (QCL) of Gazpromneft-ONPZ tested Raman Rxn2 spectrometers manufactured by Endress+Hauser Optical Analysis, Inc. The objectives of the tests were to determine the possibility of using Raman spectrometers to measure the fractional composition, cetane number, cold filter plugging point, and density of commercial diesel products, as well as the accuracy of the Raman spectrometer compared to the reference methods used by QCL.

Test progress

From March 22 to March 25, the spectra of working and control samples were taken by two analyzers with lasers of different wavelengths (785 and 993 nm) to determine the effect of fluorescence and the type of laser best suited for building a model. As a result of the analysis of the collected spectra, the manufacturer recommended the spectrometer with a laser wavelength of 993 nm. Settings for the analysis time and the number of collected spectra of one sample were recommended that simulate closely the actual operating conditions of spectrometers in technological processes.

From April 4 to 8, analyzer with a wavelength of 993 nm was used for the second stage of spectra collection with the settings recommended by the manufacturer. As a result, 99 spectra were obtained (79 working samples and 20 control samples). Spectra and laboratory data on working samples was transferred to a specialized organization for processing the results and building chemometric models.

Test results

After processing the spectra, control samples data (measurement values determined by the model) was obtained for all parameters. The data is presented in the table:

Sample number	cetane number	Density at 15 °C, kg/m3	Cold Filter Plugging Point	D10 – temperature (^{0}C) at which 10% of the	E250 – % of distillate	D90 – temperature (^{0}C) at which 90%	D95 – temperature (^{0}C) at which 95%

ООО «Эндресс+Хаузер»
117105, г. Москва, Варшавское шоссе, д. 35, стр. 1, ком.42
Тел.: +7 (495) 783-28-50; Факс: +7 (495) 783-28-55;
e-mail: info@ru.endress.com;
http://www.ru.endress.com

				volume is distilled	volume up to 250 ^{0}C	of the volume is distilled	of the volume is distilled
79	49,7851	841,6069	-11,0200	207,3017	39,1291	338,2451	353,5529
80	54,1164	836,6732	-9,9731	225,4020	25,0514	337,4126	350,1917
81	48,4953	830,5036	-39,4325	188,4868	46,9161	321,5093	335,6534
82	57,6986	829,1295	-19,6714	252,1458	14,1418	334,9538	342,5605
83	51,1379	850,3545	-7,7238	227,8799	22,5587	342,3252	357,3050
84	51,6424	849,2955	-3,1154	230,5907	21,7514	347,0043	359,8522
85	51,6794	853,1775	-1,1140	236,9127	15,1185	343,4223	356,2612
86	49,9991	842,1646	-6,8878	203,1992	35,1144	339,2855	354,5928
87	55,5724	836,4842	-9,1848	230,3672	22,1330	339,3215	351,8050
88	50,9952	830,4861	-36,2420	198,9657	42,1495	324,2721	337,7972
89	52,3263	820,3328	-45,3933	214,5408	46,8718	280,7012	292,3983
90	52,4331	848,4438	-5,1571	238,5995	21,4608	334,6944	353,5954
91	52,4884	852,1068	-1,3737	235,2729	18,4353	347,3273	361,9575
92	52,2797	851,6299	-1,0169	219,4573	14,5853	348,4065	362,9823
93	51,4187	852,4485	1,4040	241,0713	11,8421	349,2681	360,8535
94	51,1932	842,4369	-7,6863	213,6830	30,0655	341,6367	356,6580
95	51,5651	833,9535	-36,3098	207,4002	39,0120	326,1322	339,2892
97	51,2450	844,5458	-5,6920	216,7552	29,3248	341,7606	356,8873
98	51,8871	831,4878	-38,4195	202,2772	38,7085	325,3905	338,7482
99	52,8490	851,0853	-1,9614	237,6995	16,0073	347,9387	362,5752

The obtained results were processed in accordance with the results verification procedure for in-line analyzers of Gazpromneft-ONPZ (ASTM D6122-19). Verification data yields positive results, the necessary correlation with the laboratory has been achieved.

Notes and restrictions

With a good correlation of data with the results of laboratory measurements, there are deviations at some points. Therefore, during the

ООО «Эндресс+Хаузер»
117105, г. Москва, Варшавское шоссе, д. 35, стр. 1, ком.42
Тел.: +7 (495) 783-28-50; Факс: +7 (495) 783-28-55;
e-mail: info@ru.endress.com;
http://www.ru.endress.com

verification process, the procedure for eliminating questionable results (in accordance with ASTM D6122-19) was applied.

In the process of data analysis and model building, it was determined that the model has a wide range, but the filling of the entire range is uneven (primarily for the minimum and maximum values). As the model continues to operate, range adjustments may be required, as more data is acquired and compared with laboratory measurements.

However, the results analysis Committee noted that none of the previous analysis methods used at the plant had given such accurate and reliable results on such a small number of samples.

Conclusions

The tests indicate that Raman spectroscopy is suited for use in the process of continuous (in-line) analysis for measuring the fractional composition, cetane number, Cold Filter Plugging Point, and density of commercial diesel products.

The results obtained make it possible to apply this chemometric model for in-line measurements with the required accuracy.

During the tests, the time of one measurement was determined to be 2 minutes 30 seconds. The objectives of controlling and managing the process of mixing diesel products is achieved when the rate at which values are obtained for each stream is ones every 15 minutes. Thus, a four-channel analyzer can be used for the process application.

Dmitry Konstantinov
Group Manager
Solutions Business Development
Endress+Hauser LLC