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DETERMINATION OF THE OCTANE NUMBER OF AUTOMOTIVE GASOLINES BY FTIR SPECTROMETRY WITH CHEMOMETRICS

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Abstract *The quality of motor fuels is more and more strictly controlled in connection with many factors - users are particularly interested in the anti-knock resistance of automotive gasolines, quantitatively expressed by the value of the research octane number (RON). The paper presents FTIR spectrometry in conjunction with chemometry as an alternative method to the standardized determination of the octane number of gasoline by a research method according to ČSN EN ISO 5164. An FTIR-PLS regression model working with spectra in the range of 650–4000 cm^{-1} was proposed for ON prediction. With this model, a very strong dependence (R=0.996) was achieved between the predicted of octane number values and the values determined by the standardized method; the calibration error was 0.414.*

Keywords *octane number, gasoline, fuels, measurement, quality, FTIR spectrometry, chemometric model*

1 INTRODUCTION

The issue of motor fuel quality is currently a carefully monitored area (Gardyński and Kałdonek, 2020; Mikulski et al., 2022; Rayapureddy et al., 2022). The increase in motorization and progress in the development of power units require high quality fuels without undesirable additives while maintaining the prescribed parameters and quality indicators (Kamiński et al., 2021). In the case of automotive gasoline, its combustion properties are particularly important for users. Anti-detonation resistance is considered the most important property, i.e. the fuel's ability to resist spontaneous acceleration of oxidation reactions in the engine cylinder. The fuel's resistance to spontaneous detonations is expressed using the octane number. Fuel octane values are obtained by measuring on a test single-cylinder engine with a variable compression ratio. International Standard ČSN EN ISO 5164 establishes the rating of liquid spark-ignition engine fuel in terms of an arbitrary scale of octane numbers using a standard single-cylinder, four-stroke cycle, variable compression ratio, carburetted, Cooperative Fuel Research (CFR) engine operated at constant speed. Research octane number (RON) provides a measure of the knock characteristics of motor fuels in automotive engines under mild conditions of operation. Determination of the octane number of fuels on a test engine is carried out due to its high purchase price, its dimensions and operating costs only during production in a refinery, during the development of new fuels and or in the case of a referee test. For this reason, alternative ways of determining ON have been sought in recent years. One possibility is Fourier transform infrared spectrometry (FTIR spectrometry) in combination with chemometric algorithms. The nature of chemometric analysis in conjunction with

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FTIR spectrometry allows specifying even those parameters that cannot primarily be characterized as chemical, i.e. they cannot be assigned a characteristic spectral band. The accuracy of calculating these parameters using FTIR chemometric models depends on the accuracy of the primary standardization method used to develop the calibration model. Examples of practical applications of FTIR spectrometry in connection with chemometric multicomponent methods in fuel analysis are published, for example, in these articles (Aleme et al., 2012; Hradecká et al., 2021).

As an alternative to standardized laboratory methods, Fodor et al. (1999) were engaged in constructing PLS regression models to attain fast and simultaneous specifications of several properties in the middle distillate fuel from the FTIR spectra. Prior to making PLS models, various preliminary steps in spectra were being tested, such as centering of primary spectra, centering 1st and 2nd derivations of the spectrum. Based on published studies, FTIR is able to estimate with certainty the following parameters: density, kinematic viscosity at 40 °C, 50% point of a distillation curve, cetane index, quantities of carbon, hydrogen, carbon-hydrogen ratio, combustion heat, mass percentage of monocyclic, dicyclic and aromatic substances, and also mass percentage of polycyclic as well as general aromatic substances.

Using FTIR spectrometry Teixeira et al. (2008) developed methodologies for the identification of adulterated gasoline with the addition of diesel, solvent, petroleum, or thinner. These materials are easily available in Brazil. The measurement was carried out with the IROX 2000 FTIR spectrometer (Grabner Instruments, Austria) and spectra were measured in the infrared part 3700–650 cm^{-1}. The PLS method was applied for developing the calibration model, the correctness of which was verified by the cross-validation method. The results showed that this method is suitable for estimating foreign materials in gasoline within the volume ratio from 0 % to 50 %, and the prediction error for all the specified diluted samples, if the PLS method was used, is lower than 2 %. As for the gasoline samples containing petroleum and turpentine, this method turned out not to be fully suitable and the sample must be subsequently tested by some other chemical analyses.

Cetane number (CN) is an important property that indicates the ignition quality of fuels and especially diesel fuel. Barra et al. (2020) successfully used partial least squares regression (PLSR) to predict diesel cetane number based on FTIR. The proposed model was characterized by a high correlation coefficient between actual and predicted CN values (R=0.99), with small calibration and prediction error values (RMSEC=0.28 and RMSEP=0.42) compared to previously published models developed using spectroscopic techniques, namely NIR and Raman spectroscopy.

Kardamakis et al. (2010) dealt with the modelling of octane number prediction using a research method on 384 gasoline samples. Infrared spectrometry, combined with other chemometric methods, presents accurate and versatile technique for specifying an octane number by a research method. In this case, the functional model for specifying the RON was constructed on the basis of combining the linear prediction of the IR spectra and multiple linear regression. When calculating the RON of real samples, the error did not exceed 0.3 units.

FTIR spectrometry in combination with multidimensional statistical (chemometric) methods is increasingly used in the quality control of petrochemical products. The contribution presents the results of the design of the FTIR chemometric model for determining the research octane number of automotive gasolines.

2 CHEMOMETRIC METHODS IN FTIR SPECTROMETRY

The simplest spectral quantitative analysis is based on the premise that Lambert-Beer law is valid, i.e. a linear dependence is displayed between absorbance (or transmittance) and concentration of measured analytes (otherwise under constant experimental conditions). If the aforementioned premises are not met, quantitative chemical as well as physicochemical parameters can be determined by means of chemometric methods that measure the entire spectral areas, and are based on the principle

of multidimensional mathematical & statistical methods (e.g. Principal Components Analysis (PCA), Partial Least-Squares (PLS) regression, Principal Components Regression (PCR), Classical Least-Squares (CLS) regression, etc.). Then the result of calibration is influenced not only by the height or area of bands, but also angle and curvature of the infrared spectrum (Sejkorová et al., 2021).

For each monitored fuel parameter, a calibration FTIR regression model must be constructed using an appropriate set of fuel samples. For a set of calibration samples, the monitored quality parameter must be determined by the standardized ASTM method. In practical applications of FTIR spectrometry in conjunction with multivariate statistical methods, PLS and PCR regression methods have found the widest application in fuel analysis. During the FTIR - PLS calibration, a mathematical relationship is created between the matrix of absorbance data and the matrix of parameter values determined by the standardized method. This is realized by determining the number of principal (abstract) components and simultaneous regression and rotation of the transformed matrices. The criterion for choosing a suitable FTIR-PLS calibration model is the Root Mean Square Error of Calibration (RMSEC) (Sejkorová et al., 2020) and the correlation coefficient (R) in Equation (1).

$$R = \frac{\sum_{i=1}^{m}(c_{ir} - \bar{c}_r)(c_{ie} - \bar{c}_e)}{\sqrt{\sum_{i=1}^{m}(c_{ir} - \bar{c}_r)^2 \sum_{i=1}^{m}(c_{ie} - \bar{c}_e)^2}} \quad (1)$$

where: c_{ie} is a predicted value of an i-th calibration sample, $\bar{c}_e$ is an average predicted value, c_{ir} stands for a value of a parameter of the i-th calibration sample defined based on a standardized method, $\bar{c}_r$ is an average value of the parameter determined using a standardized method and m is a total number of calibration samples.

The reliability of the proposed FTIR-PLS regression model is verified for an independent set of samples by comparing the predicted values of the FTIR calibration model with the values obtained by the standardized method. The reliability of the model is expressed by the coefficient of the Root Mean Square Error of Prediction (RMSEP). In the absence of a set of external samples, a cross-validation method, the coefficient of the Root Mean Square Error of Cross-validation (RMSECV), is used to verify the predictive ability of the model.

3 MATERIALS AND METHODS

3.1 Samples and determination of octane number

A total of 33 gasoline samples and their components, provided by the company Česká rafinérská, a.s., Litvínov, were used to create and verify calibration models for determining the octane number using FTIR spectrometry in conjunction with chemometry. The set of these samples was divided into 26 calibration samples and 7 validation samples. The predictive ability of the proposed model was verified by validation samples. The parameters of the research octane number of all samples were measured on the WAUKESHA test engine (USA) according to the ČSN EN ISO 5164 methodology.

3.2 Scanning of FTIR spectra

Infrared spectra were taken with a Nicolet iS10 spectrometer (Thermo Scientific) with an ATR attachment (total attenuated reflectance technique). The OMNIC control software enables the spectrometer parameters to be set, controls the measurements itself and performs the required subsequent operations with the spectra. Spectra of gasoline samples and their components were measured in the spectral range of 4000–650 cm^{-1}. Measurement parameters: resolution 4 cm^{-1}, number of spectrum accumulations 64.

The measured data were processed by the computer program TQ analytik version 8 (Thermo Fisher Scientific, Inc., USA).

4 RESULTS AND DISCUSSION

At the beginning of the experiment, RON was measured for all 33 gasoline samples and their components, and their spectra were taken for all these samples. The FTIR-PLS calibration models were created and validated for the determination of RON in the range of 88 to 102 ON units, i.e. the values that were determined by the standardized method. Fig. 1 shows a detail of the spectra of selected calibration samples.

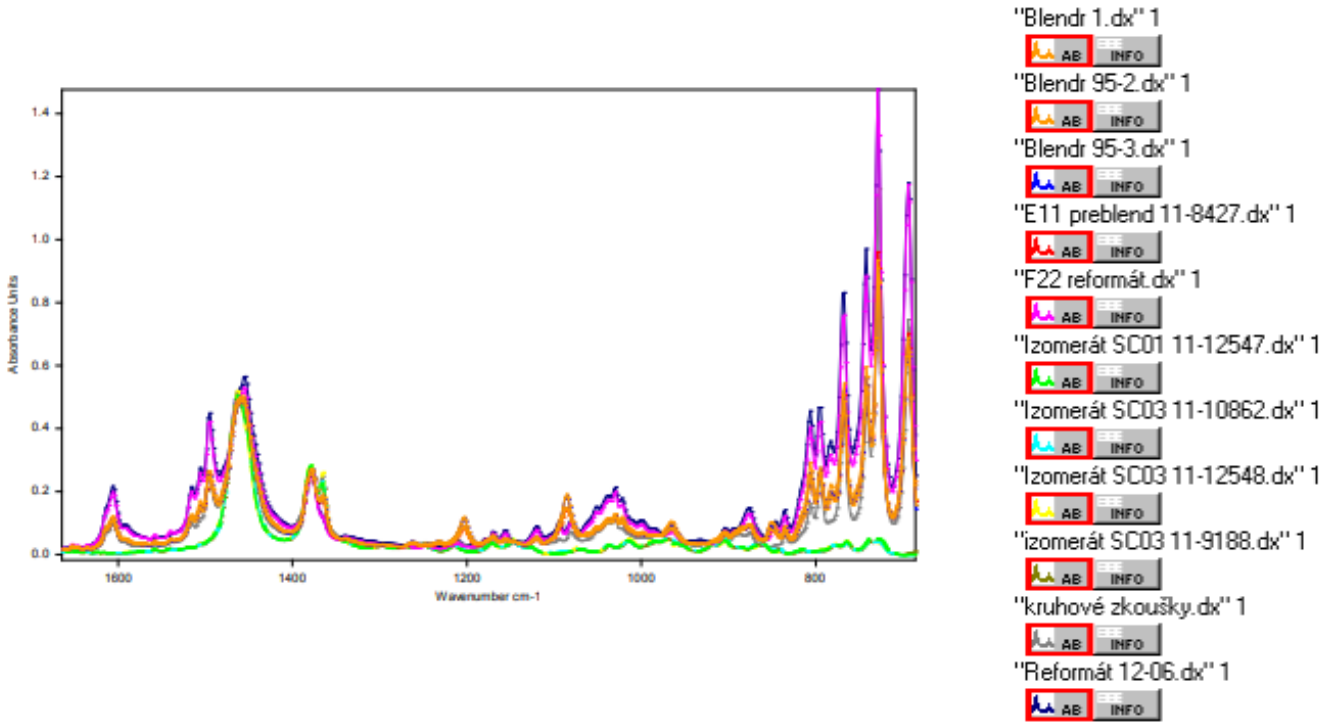

Fig. 1: Detail of spectra of selected gasoline calibration samples (1,700–650 cm^{-1})

FTIR-chemometry for the determination of RON was applied to the spectrum area where the change in the spectral signal (absorbance) is most correlated with the change of RON measured according to the methodology of ČSN EN ISO 5164. The entire sensed spectral range of 650–4,000 cm^{-1} was tested, as well as its part in region 650–1050 cm^{-1}. The calibration output for the PCR and PLS methods is a linear regression between the input quantitative values, in this case RON, and the values predicted by the calibration model. The result is the root mean square error of calibration (RMSEC) and the correlation coefficient (R), which characterizes the linear relationship between the dependent variable and the linear combination of the set of independent variables of the calibration series.

The regression model created by the PLS algorithm using the entire spectral region 650–4000 cm^{-1} appeared to be the most accurate of the proposed models, where the correlation coefficient reached a value of 0.996 and an RMSEC=0.414 (see Fig. 2).

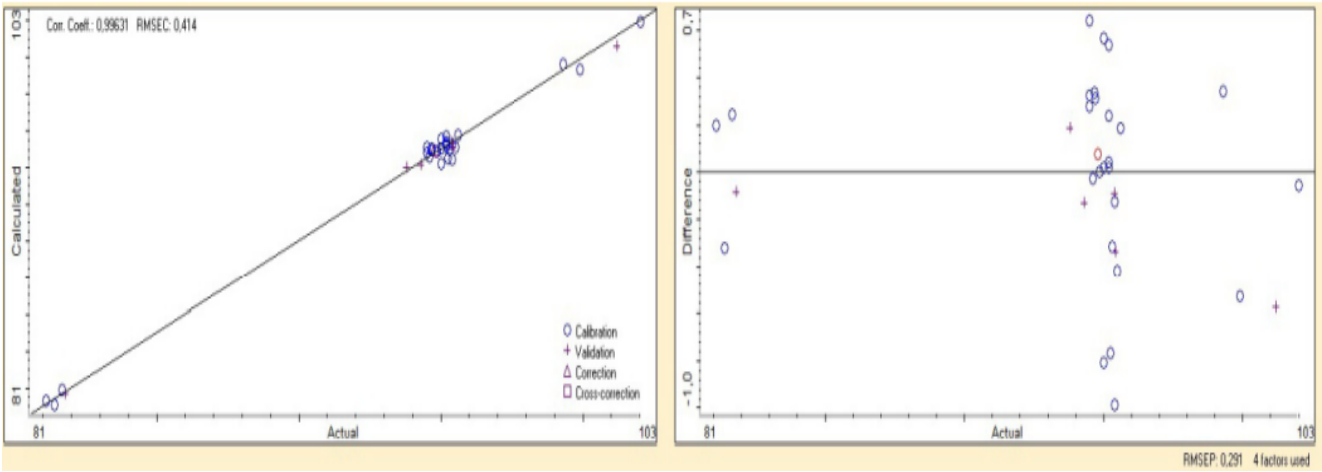

Fig. 2: Calibration model of RON determination by the FTIR-PLS regression method

The parameter of the quality of the predictive ability of the created calibration model is the root mean square error of prediction (RMSEP), which should be minimal because it is the deviation expected in future predictions. RMSEP reached a value of 0.291. The error of cross-validation of the given model reached a good value of RMSECV=0.569. PRESS diagnostics indicated how the value of the predicted residual error of the sum of squares changes with the number of factors used to calibrate the octane number of active PLS method. Four PLS factors were selected as optimal by diagnostics.

The results of the external validation of the calibration model are shown in Tab. 1. The table shows that the error of determining the octane number by the PLS chemometric algorithm is higher than the error of determining the octane number by the reference method on the engine, which is ± 0.4 units.

Tab. 2 Results of external validation of the best FTIR-PLS model

validation sample	Measured RON	Predicted RON
Blendr 95-1	95.25	94.46
Preblend 11-9468	94.70	94.44
BA95 11-9922	95.40	94.18
F22 Reformát	102.02	101.84
Izomerát SC03 11-12548	81.66	81.49
Reformát CCR 11-10912	99.90	98.87
THD BA95 11-10618	95.30	94.83

The proposed FTIR-PLS calibration model was also tested on real gasoline samples taken at gas stations. Most of the results of determining the octane number of gasolines by the FTIR method did not correspond to the expected values. This can be explained by the fact that for the constructs of the calibration models were used as calibration samples gasoline components and not real gasoline samples of the same type as the as the evaluated samples.

5 CONCLUSIONS

FTIR spectrometry has been widely used in the petrochemical industry in recent years. The article presents the output of the FTIR-PLS model design for the prediction of research octane number. Because the spectra and RON of mainly gasoline components were used for the design of the FTIR-PLS model, satisfactory results were not obtained when measuring real gasoline samples.

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