SECOND ORDER MULTIVARIATE CALIBRATION METHODS IN BIODIESEL/DIESEL BLENDS ANALYSIS

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Biodiesel have gained large environmental interest due to its renewability and low emissions after engine combustion [1]. When blended with petrodiesel this mixture, as any kind of other combustibles, have many important parameters to be analyzed, as biodiesel content, viscosity, density, cetane number, etc. Classical methods in combustible analysis are almost all univariated, time consuming and need some sample preparation. Multivariate spectroscopic methods has been proposed in the literature for analysis of biofuels or their blends using first order calibration as using near infrared spectroscopy [2]. Few applications could be found with second order spectroscopic data for determination of parameters in (bio)combustibles [3,4]. This work proposed second and first order multivariate calibration methods to determine biodiesel content and density in soybean biodiesel/diesel blends using excitation emission matrix fluorescence (EEMF). Different methods are used to developed multivariate calibration, using scores from PARAFAC (parallel factor analysis), performing N-PLS (N-Way partial least squares) and unfolded-PLS. A recently algorithm proposed by Bro and Vidal [5], EEMizer ver. 1.2, also was used to perform automatic PARAFAC models eliminating, if necessary, lowest excitations wavelengths variable and sample outliers, a correction for Rayleigh (and Raman) scattering could be perform, not in this case. This algorithm's response is the EEMqual parameter that is give for each number of factors used to decompose the three-way matrix indicating the quality for PARAFAC models using different numbers of factors.

Methods	Parameter	#LV/Fac	RMSEC	RMSECV	RMSEP	R^2
PARAFAC MLR	Biod. Cont.	2	2.28	2.48	1.80	0.845
	Density	2	0.685	0.755	0.715	0.896
N-PLS	Biod. Cont.	2	2.22	2.52	2.44	0.831
	Density	3	0.647	0.802	0.750	0.899
U-PLS	Biod. Cont.	3	1.89826	2.34	2.52	0.862
	Density	3	0.633	0.804	0.902	0.892

The above table shows the principal parameters obtained for calibration and validation of multivariate models in EEMF data. The promising results obtained show that the use of EEMF and multivariate methods got good models for predicting these parameters on the samples.

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