

Supplementary Information

Nuclear Magnetic Resonance (1.40 T) and Mid Infrared (FTIR-ATR) Associated with Chemometrics as Analytical Methods for the Analysis of Methyl Ester Yield Obtained by Esterification Reaction

Sara R. M. Kollar,^a Etelvino H. Novotny,^b Claudia J. do Nascimento^c and Paulo A. Z. Suarez^a*

^aInstituto de Química, UnB, CP 4478, 70910-970 Brasília-DF, Brazil

^bEmbrapa Solos, Rua Jardim Botânico, 1024, 22460-000 Rio de Janeiro-RJ, Brazil

^cInstituto de Biociências, UNIRIO, Av. Pasteur, 458, Urca, 22290-240 Rio de Janeiro-RJ, Brazil

Table S1. Regression summary for the different models obtained using the same samples

y or sample set	NMR				PLS (x = Predicted y)		IR	OLS	
	1.40 T	7.05 T				OSC ^f	Tit.	Known	
	Tit. ^a	Known ^b	Tit.	Known	Std. ^c	Cal. ^d (2 LV) ^e			
Homogeneity of slopes model									
R ²	0.9976	0.9976	0.9956	0.9956	0.9914	0.9900	0.9979	0.9977	0.9981
B ₀	0.1633^{ns}	-0.0755^{ns}	0.1387^{ns}	-0.1015^{ns}	0.110 ^{ns}	0.2292 ^{ns}	0.2423^{ns}	-39.9582^{***}	-40.2021^{***}
B ₁	0.9853^{***}	0.9855^{***}	0.9933^{***}	0.9935^{***}	0.9978 ^{***}	0.9938 ^{***}	0.9886^{***}	65.6934^{***}	65.7234^{***}
D ₀	0.0263^{ns}	0.2126^{ns}	0.3346^{ns}	0.5748^{ns}	10.5085 ^{***}	1.5391 ^{ns}	-0.2605^{ns}	0.6991^{ns}	0.9429^{ns}
D ₁	-0.0004^{ns}	-0.0006^{ns}	-0.0141^{ns}	-0.0143^{ns}	-0.1063 ^{***}	-0.0312 ^{ns}	0.0114^{ns}	-0.7511^{ns}	-0.7811^{ns}
Lower 95% CL ^g of B ₁	0.9690	0.9694	0.9712	0.9715	0.9631	0.9683	0.9916	64.6063	64.7411
Upper 95% CL of B ₁	1.0017	1.0017	1.0156	1.0156	1.0325	1.0193	1.0052	66.7804	66.7057
Calibration models (PLS: pseudounivariate models)									
R ² of calibration	0.9994	0.9995	0.9989	0.9991	0.9972	0.9938	0.9985	0.9984	0.9994
R ² of validation	0.9951	0.9951	0.9910	0.9910	0.9728	0.9717	0.9970	0.9963	0.9963
RMSEC ^h (Bartlett $\chi^2 = 9.2400^{\text{ns}}$)	0.7680	0.6813	1.0197	0.9302	1.6104	1.8664	0.9285	1.2250	0.7761
RMSEP ⁱ (Bartlett $\chi^2 = 24.7710^{\text{***}}$)	1.2255b	1.2401b	1.6846a	1.6832a	6.7312	3.3320	1.0753b	1.1093b	1.1061b
F (RMSEP, RMSEC)	2.5462*	3.3131**	2.7292*	3.2740**	3.1872**	17.4698 ^{***}	1.3414^{ns}	1.2195^{ns}	2.0314^{ns}
Bias	0.0388^{ns}	-0.1936^{ns}	0.1315^{ns}	-0.1014^{ns}	6.0426 ^{***}	0.4233 ^{ns}	-0.1048^{ns}	0.1303^{ns}	-0.0803^{ns}
B ₀	0.1633^{ns}	-0.0755^{ns}	0.1387^{ns}	-0.1015^{ns}	23.7534 ^{***}	8.7587 ^{***}	-0.2900^{ns}	-39.9582^{***}	-40.2021^{***}
B ₁	0.9853^{***}	0.9855^{***}	0.9933^{***}	0.9935^{***}	5686.2776 ^{***}	6909.1556 ^{***}	3066.1085^{***}	65.6934^{***}	65.7234^{***}
Selectivity	nd	nd	nd	nd	0.1374	0.0775	0.9335	nd	nd
$\gamma^{-1\ddagger}$	1.38×10^{-5}	1.39×10^{-5}	1.22×10^{-5}	1.22×10^{-5}	4.78×10^{-3}	1.19×10^{-2}	2.24×10^{-3}	1.35×10^{-3}	1.35×10^{-3}
Limit of detection	4.14×10^{-5}	4.16×10^{-5}	3.66×10^{-5}	3.67×10^{-5}	1.44×10^{-2}	3.58×10^{-2}	6.72×10^{-3}	4.05×10^{-3}	4.05×10^{-3}
Limit of quantification	1.38×10^{-4}	1.39×10^{-4}	1.22×10^{-4}	1.22×10^{-4}	4.78×10^{-2}	1.19×10^{-1}	2.24×10^{-3}	1.35×10^{-2}	1.35×10^{-2}

^aTit. y is the titrated FAME concentration; ^bknown y is the known concentration; ^cthe calibration samples set is only the standard samples (n = 21); ^dCal. 39 real samples were added to the calibration samples set; ^e2 LV: the only model with two latent variables, the others used only one LV; ^fOSC: orthogonal signal correction using the Cal. samples set; ^gCL: confidence limit; ^hRMSEC: root mean square error of calibration; ⁱRMSEP: root mean square error of prediction, the Bartlett χ^2 test was performed comparing the RMSEC and RMSEP of the final models (bold columns), RMSEP values followed with the same letters are not significantly different at $p < 5\%$. nd: not determined; $\gamma^{-1\ddagger}$: inverse of analytical sensitivity. Statistical significance level: ns: not significant; * $p < 5\%$; ** $p < 0.5\%$; *** $p < 0.05\%$.

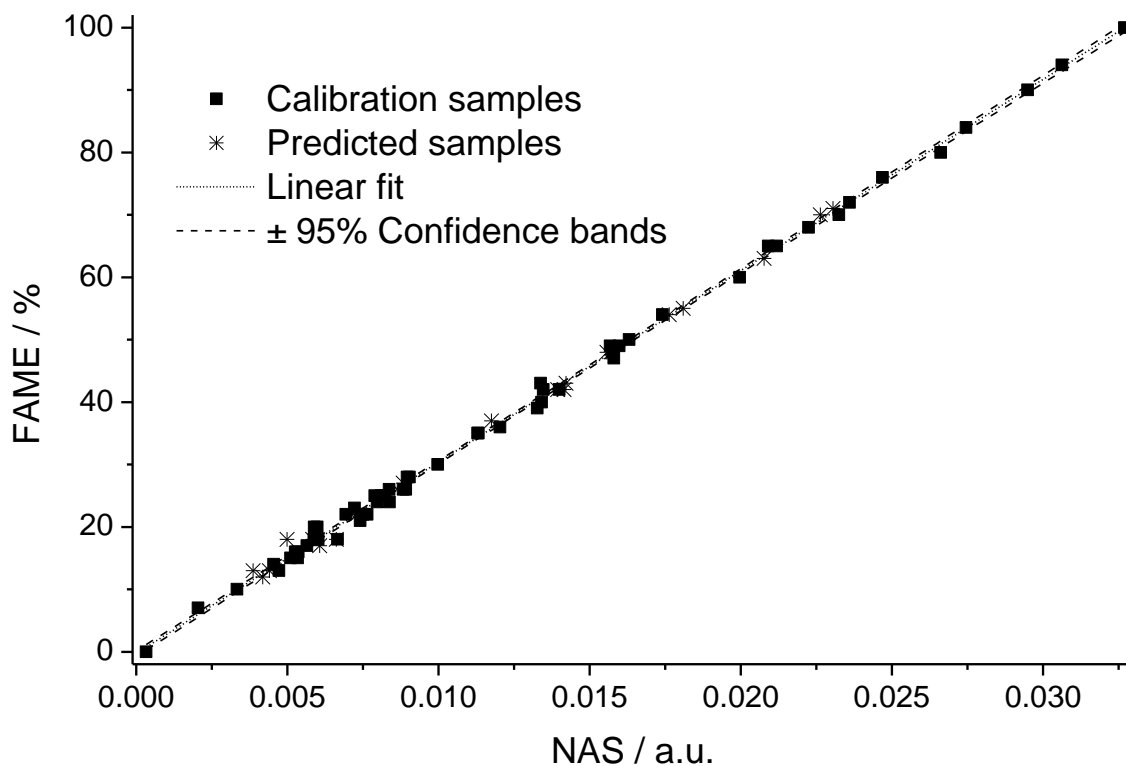


Figure S1. Pseudounivariate calibration curve ($R^2 = 0.9985$ and $RMSEP = 1.0753$), obtained with standard and real samples and FAME titrated concentrations, and predicted FAME concentration of real samples. The used \mathbf{X} matrix is the full FTIR-ATR spectra after orthogonal signal correction. The net analyte signal (NAS) is calculated according to Bro and Andersen.¹

Reference

1. Bro, R.; Andersen, C. M.; *J. Chemom.* **2003**, *17*, 646.