Quality and SAfety of Feeds and Food for Europe

THE USE OF RAMAN SPECTROSCOPY IN THE ANIMAL FEED SECTOR

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1. Introduction

As part of the EU FP7 project, Quality and Safety of Feeds and Food for Europe (QSAFFE), there are assessments being made on various "fingerprinting" methodologies with regards to determining conformity and geographical origin of imported commodities. One such technique that is being evaluated is Raman Spectroscopy. which arises from the inelastic scattering of light. It is a non-destructive technique that is becoming increasingly popular as a research tool in the food and feed sectors.

Within **Work Package 1** of QSAFFE, the possibility that oils used in the feed industry could be adulterated is being investigated. Waste oils, such as transformer oils/mineral oils, are of interest since it is possible that they could contain dioxins/polychlorinated biphenyls (PCBs). Oils used in the feed industry, such as soya oil and basic vegetable blend oil, were adulterated with up to 25% mineral oil/transformer oil, Raman spectra of the mixtures were run and chemometric analysis applied to the samples. Qualitative and quantitative chemometric models are presented.

Within **Work Package 2** of QSAFFE, the botanical and geographical origins of commodities are being investigated. Distillers dried grains with solubles (DDGS), a by-product of ethanol biofuel and beverage production where the process is focused on the ethanol yield, were highlighted as an emerging feed ingredient. In a crisis related to this commodity, it would be beneficial to prove the country of origin of the DDGS. Raman spectra of DDGS are affected to a large degree by fluorescence which masks any of the signals from Raman scattering. However, to overcome this, the oil fraction of the DDGS was extracted using accelerated solvent extraction (ASE), Raman spectra were run and chemometric analysis applied to the data and qualitative calibration models were constructed. These initial models are presented.

2. Work Package 1 Results

(i) Qualitative Analysis

A set of Basic Vegetable Blends (BVBs) and Soya oil samples adulterated with transformer oil and mineral oil were characterised using Raman spectroscopy, with the Raman instrument used to generate the spectral data shown in **Figure 1**. Typical Raman spectra of the oils used are shown in **Figure 2**. Qualitative chemometric analysis of the spectral data was carried out using SIMCA P+13 (Umetrics, Sweden). **Figure 3** shows the Cooman's Plots generated within the software showing the discrimination between pure samples and adulterated samples (0.1-25%) using the Raman spectral data.

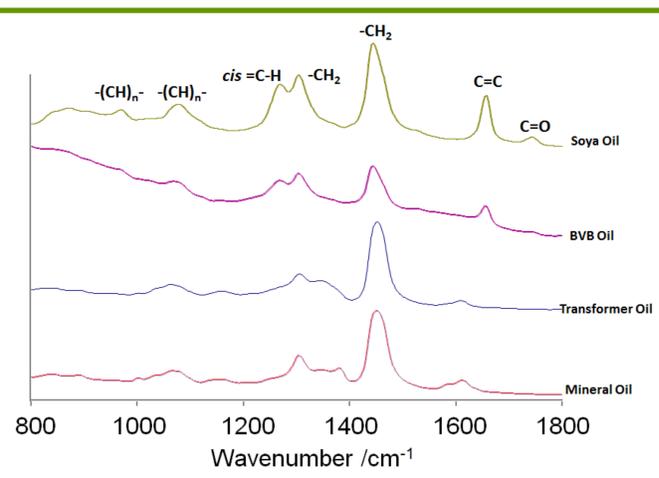*Figure 1: The Delta Nu Advantage 1064nm Raman Spectrometer*

Figure 2: Raman Spectra of Transformer Oil, Soya Oil, Mineral Oil and Basic Vegetable Blend Oil.
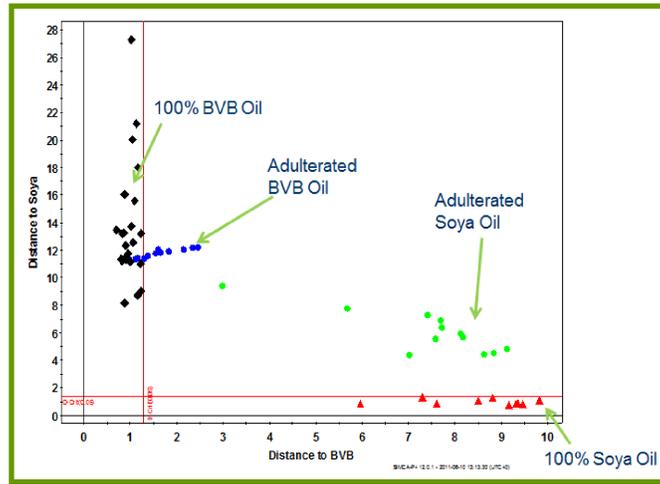

Figure 3: Cooman's Plot of models Basic Vegetable Blend (BVB) Oil (Black Squares) versus Soya Oil (Red Triangle) from the data generated using Raman data (1st Derivative, univariate scaling and Savitzky-Golay smoothing; 7 points in each sub-model and a distance of 2 between each point). BVB adulterated with Mineral Oil (Blue dots) and Soya Oil adulterated with Mineral Oil (Green dots) were used as the prediction set.

(ii) Quantitative Analysis

Quantitative analysis was carried out by applying the Partial Least Squares (PLS) chemometric algorithm to the Raman spectral data with 0.1-25% adulteration. Excellent calibration and prediction statistics were obtained for the calibration models generated. The data generated for these models are shown in **Table 1** and **Figure 4.**

| Table 1		RAMAN			
		R^2	RMSEC	RMSEP	Factors
BVB Oil /Transformer Oil	Raw Data	0.98777	1.36	1.36	10
	1st Derivative	0.98682	1.41	1.90	9
	2nd Derivative	0.97308	2.01	1.84	6
BVB Oil /Mineral Oil	Raw Data	0.98513	0.467	0.490	8
	1st Derivative	0.98835	1.24	1.51	8
	2nd Derivative	0.98906	1.20	1.70	8
Soya Oil /Transformer Oil	Raw Data	0.99855	0.467	0.490	8
	1st Derivative	0.99895	0.398	0.560	8
	2nd Derivative	0.99967	0.221	0.779	10
Soya Oil /Mineral Oil	Raw Data	0.99840	0.491	0.525	10
	1st Derivative	0.99942	0.295	0.679	10
	2nd Derivative	0.99820	0.520	0.871	8
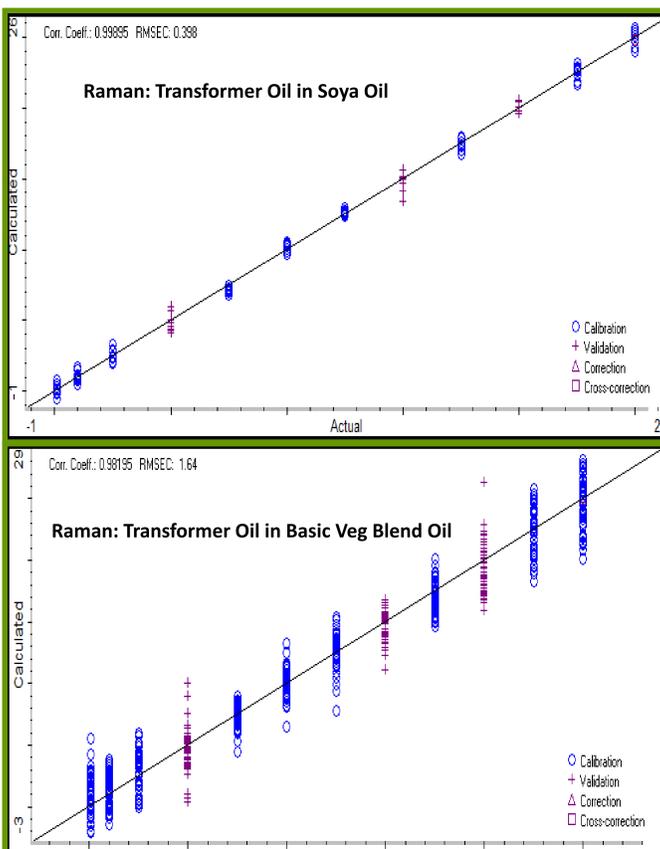
Figure 4: Examples of the PLS calibration models generated using the Raman spectral data.

3. Work Package 2 Results

The oils obtained from DDGS were run on the Raman spectrometer and the spectral data (**Figure 5**) was subjected to qualitative chemometric analysis. **Figure 6** shows the Principal Component analysis (PCA), Partial Least Squares Discriminant Analysis (PLS-DA) and Orthogonal Partial Least Squares Discriminant Analysis (OPLS-DA) models obtained. Results appear to indicate that the oils can be discriminated based on the country of origin of the DDGS. Although at this stage it is not known why the differences between the groups is observed, it is speculated that it may be due in part to differences in the carotenoid content of the oils.
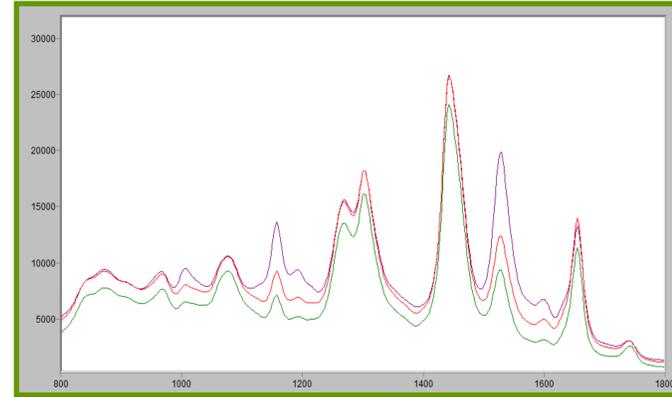
DDGS → Accelerated Solvent Extraction → Oil

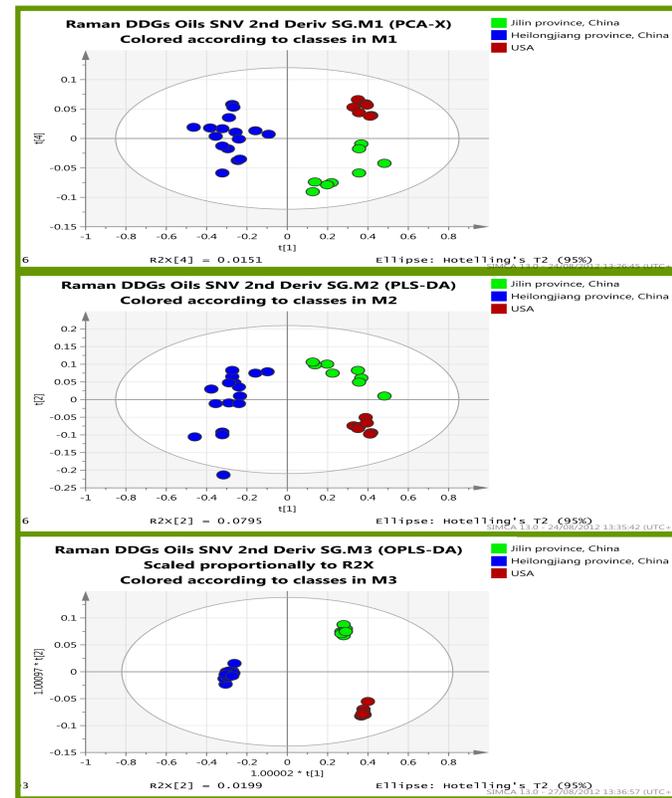*Figure 5: Typical Raman spectra of the DDGS oils*

Figure 6: Chemometric analysis showing PCA model (upper), PLS-DA (middle) and OPLS-DA model (lower) showing discrimination between the oils from DDGS based on their origin.

4. Summary

❖ Raman spectral data collected for animal feed oils adulterated with mineral oil and transformer oil

❖ Qualitative and Quantitative analysis of the data using chemometric algorithms produced excellent calibration models

❖ Oils obtained from DDGS subjected to Raman spectral analysis followed by chemometric processing

❖ Initial results appear to indicate that country of origin of DDGS may be discerned using Raman spectroscopy and chemometrics