

**Summary**

An Aspectrics' MC2750 EP-NIR spectrometer covering the spectral range 1375-2750 nm was successfully employed for the quantification of corn, canola and olive oils in various mixtures containing all three oils and with accuracy consistent with the precision of the blending reference method (volumetric). Access to the spectral information in the 2000 - 2600 nm (5000 - 3850 cm<sup>-1</sup>) range was key to the identification and quantification of these vegetal oils.

**Introduction**

An Aspectrics' MC2750 EP-NIR spectrometer was coupled to an external halogen Near IR source and a 2mm. Process transmission fiber probe in order to test the device's ability to quantify the percentage volume of corn, canola and olive oils in mixtures containing all three oils.

The use of a multivariate chemometrics approach on the second order derivative Near IR spectra of all samples enabled the development of a series of three chemometrics PCR quant models, characterized by R<sup>2</sup> greater than 0.9850 both for the calibration and validation data sets, RMSECs ranging from 2.0 to 4.9%, and RMSEPs ranging from 5.0 to 5.1% (values consistent with the precision of the sample blending volumetric method), without removing any outlier from the data sets.

Access to the spectral information in the 2000 - 2600 nm (5000 - 3850 cm<sup>-1</sup>) range was key to the identification and quantification of these vegetal oils.

**Experiment****Samples:**

- Commercially available samples of canola, corn and olive oils were used for this experiment
- 17 calibration standards (mixtures and pure samples) and 15 independent validation standards (mixtures and pure samples) were prepared using volumetric method according to an orthogonal distribution model. (See Table 1)
- The precision of the reference method is 0.06 ml. for 5 ml pipettes (i.e., relative error of 1.2%). The precision of the reference method is approximately 3.6% at best.

**Apparatus:**

- Aspectrics' MC2750 EP-NIR spectrometer covering the 1375-2750 nm range
- External halogen Near IR source
- A process transmission multimode fiber probe (600 microns polyimide) with 2 mm. path length.

**Data Collection:**

- A 30-second time parameter was used for data collection. All samples were analyzed using 3 identical conditions, repeating a new background between each assay.
- Data treatment consisted of:
  - calculating absorbance spectra from a single beam intensity spectra using an open beam configuration as a background; and calculating the second order derivative for each absorbance spectrum
  - developing Principal Component Regression (PCR) based methods for the measurement of each oil in the mixture

**Results & Discussion**

Spectral ranges 1600–1950 nm and 2000–2600 nm were selected for the development of the three chemometrics methods.

Quantitative results for each assay are reported in Table 2 and are illustrated in Figures 3a, 3b, 4a, 4b, 5a and 5b.

Significant results are:

- None of the three calibration models is susceptible to false-positive results as proven by the analysis of pure oils using all three methods.
- Accuracy of the method as defined by the calculated RMSEPs is consistent with the precision of the reference sample blending volumetric method (ca. 3-4%). More precise method (gravimetric) should be used to improve reference method accuracy.
- Aspectrics' RTSS chemometrics software package was used to optimize this method. Five (5) Principal Components (PCs) were selected to develop these models. However, the number of these PCs in the series organized by decreasing contribution was 1,2,3,4 and 6. Indeed, the PC number was found to carry nothing but a systematic source of noise in the spectroscopic measurement of this particular data set and was therefore not retained in the final model in order to make the calibration more robust. This was evidenced by the fact that RMSEPs obtained when using the first five PCs were actually higher, proving that the initial model was weaker.



**Conclusion**

This experiment proves that an Aspectrics' MC2750 EP-NIR spectrometer can collect sufficient Near-IR information to allow for the difficult quantification of various oils in mixture samples containing three types of oil with no false-positive results.

Furthermore, this experiment proves the effectiveness of a transmission multimode fiber probe when coupled with the post-dispersive EP-NIR spectrometer.

Lastly, the importance of access to the extended Near IR range of 2000-2600 nm as a very significant source of spectral information enabled the application to identify and quantify the three different oils.

Calibration Set (all data in % v/v)			
Sample #	Corn Oil	Canola Oil	Olive Oil
1	0	100	0
2	0	100	0
3	100	0	0
4	100	0	0
5	0	0	100
6	0	0	100
7	10	20	70
8	10	70	20
9	10	70	20
10	20	10	70
11	20	10	70
12	20	70	10
13	33	33	33
14	33	33	33
15	70	10	20
16	70	20	10
17	70	20	10

Validation Set (all data in % v/v)			
Sample #	Corn Oil	Canola Oil	Olive Oil
1	0	100	0
2	0	100	0
3	100	0	0
4	100	0	0
5	0	0	100
6	0	0	100
7	10	20	70
8	10	70	20
9	20	10	70
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11	20	70	10
12	33	33	33
13	70	10	20
14	70	10	20
15	70	20	10

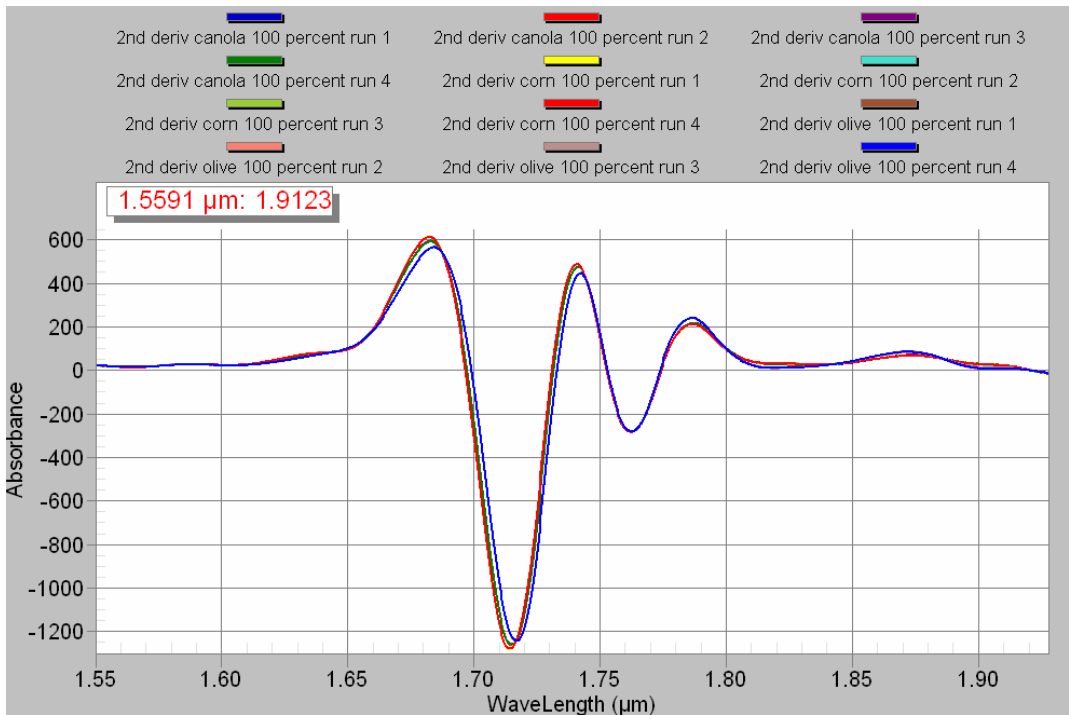
**Table 1:** Calibration and validation standards sets



	Corn Oil Calibration Stats			Canola Oil Calibration Stats			Olive Oil Calibration Stats		
R2	0.9950			0.9896			0.9983		
RMSEC	3.4 % v.v			4.9 % v.v			2.0 % v.v		
N	17			17			17		
Sample #	Ref (%)	Calc(%)	Diff(%)	Ref (%)	Calc(%)	Diff(%)	Ref (%)	Calc(%)	Diff(%)
1	0	5	5	100	92	-8	0	3	3
2	0	-1	-1	100	102	2	0	2	2
3	100	99	-1	0	2	2	0	-1	-1
4	100	104	4	0	-6	-6	0	1	1
5	0	-4	-4	0	6	6	100	96	-4
6	0	-2	-2	0	2	2	100	100	0
7	10	19	9	20	15	-5	70	72	2
8	10	8	-2	70	69	-1	20	15	-5
9	10	11	1	70	64	-6	20	20	0
10	20	21	1	10	10	0	70	72	2
11	20	22	2	10	3	-7	70	71	1
12	20	17	-3	70	81	11	10	10	0
13	33	34	1	33	32	-1	33	34	1
14	33	31	-2	33	36	3	33	33	0
15	70	65	-5	10	13	3	20	20	0
16	70	71	1	20	23	3	10	9	-1
17	70	67	-3	20	22	2	10	8	-2

	Corn Oil Validation Stats			Canola Oil Validation Stats			Olive Oil Validation Stats		
R2	0.9906			0.9904			0.9894		
RMSEP	5.0 % v/v			5.0 % v/v			5.1 % v/v		
n	15			15			15		
Sample #	Ref (%)	Calc(%)	Diff(%)	Ref (%)	Calc(%)	Diff(%)	Ref (%)	Calc(%)	Diff(%)
1	0	-1	-1	100	101	1	0	-4	-4
2	0	1	1	100	100	0	0	1	1
3	100	104	4	0	-7	-7	0	3	3
4	100	96	-4	0	4	4	0	1	1
5	0	-7	-7	0	10	10	100	96	-4
6	0	-3	-3	0	4	4	100	99	-2
7	10	15	5	20	10	-10	70	71	1
8	10	17	7	70	73	3	20	21	1
9	20	15	-5	10	10	0	70	69	-1
10	20	9	-11	70	72	2	10	15	5
11	20	10	-10	70	66	-4	10	17	7
12	33	33	0	33	34	1	33	33	0
13	70	67	-3	10	15	5	20	15	-6
14	70	69	-1	10	5	-5	20	36	16
15	70	68	-2	20	20	0	10	8	-2

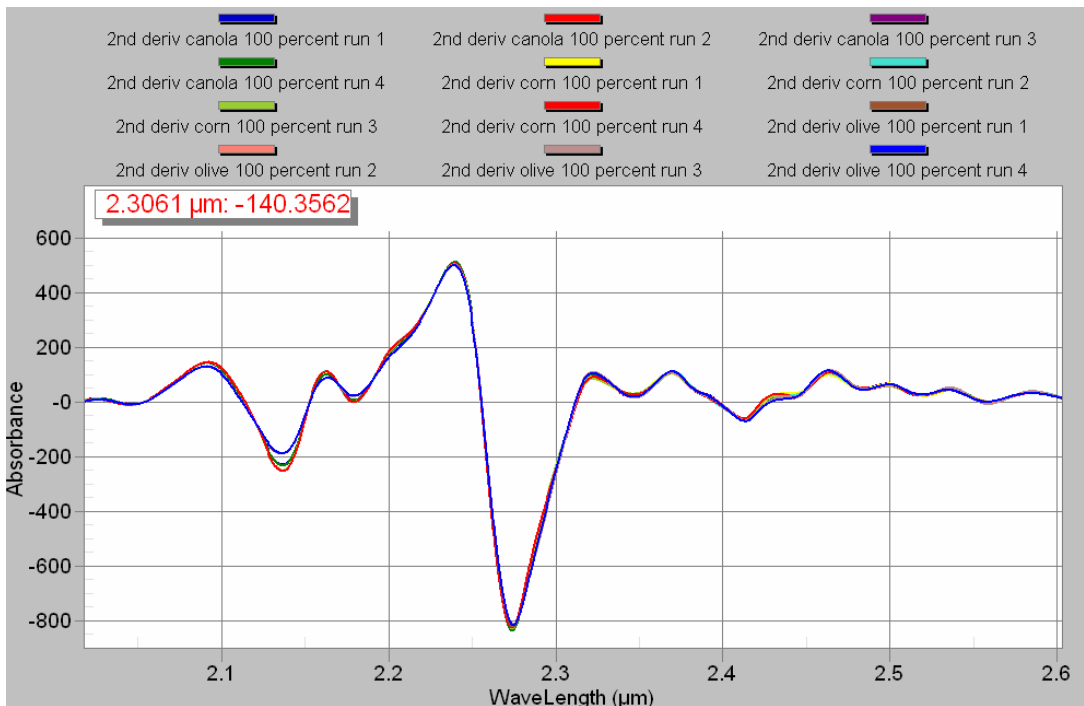
**Table 2:** Individual assay calibration and validation results



**Figure 1:**

Example of second order derivative of EP-NIR spectra of canola, corn and olive oil zoomed in on the 1600-1950 nm region.

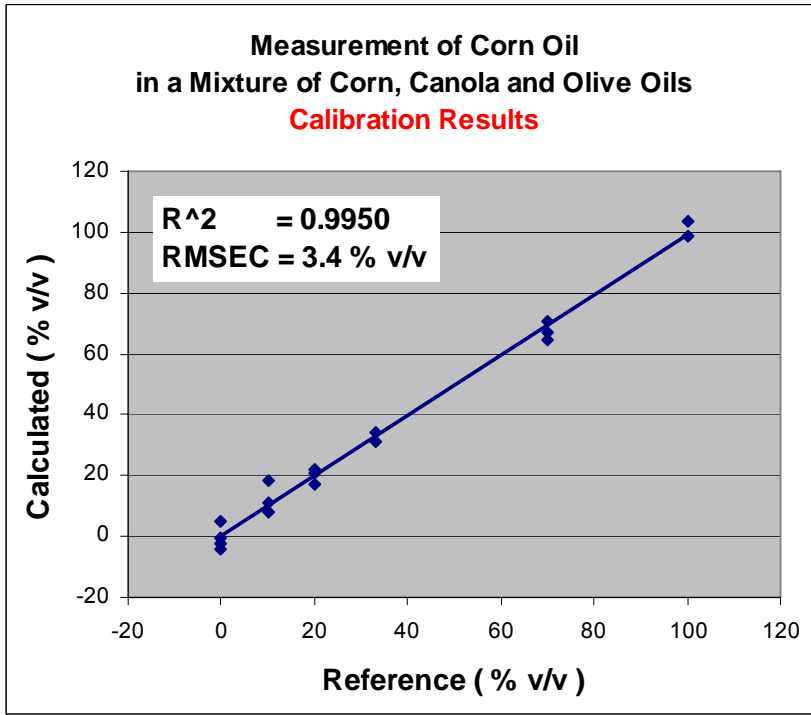
Data collected in 30 seconds using a process transmission multimode fiber probe (600 microns polyimide) with 2 mm. path length.



**Figure 2:**

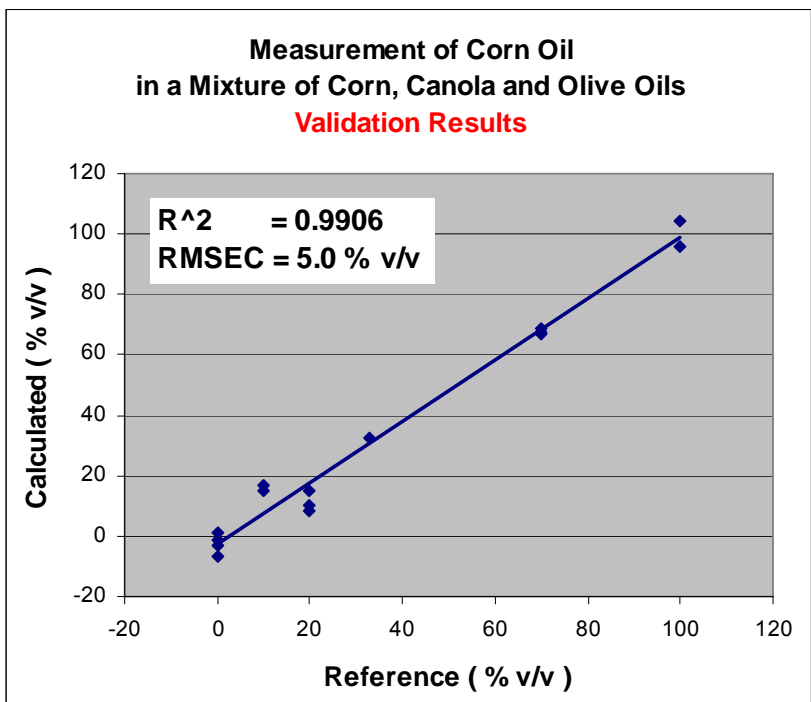
Example of second order derivative of EP-NIR spectra of canola, corn and olive oil zoomed in on the 2000-2600 nm region.

Data collected in 30 seconds using a process transmission multimode fiber probe (600 microns polyimide) with 2 mm. path length.



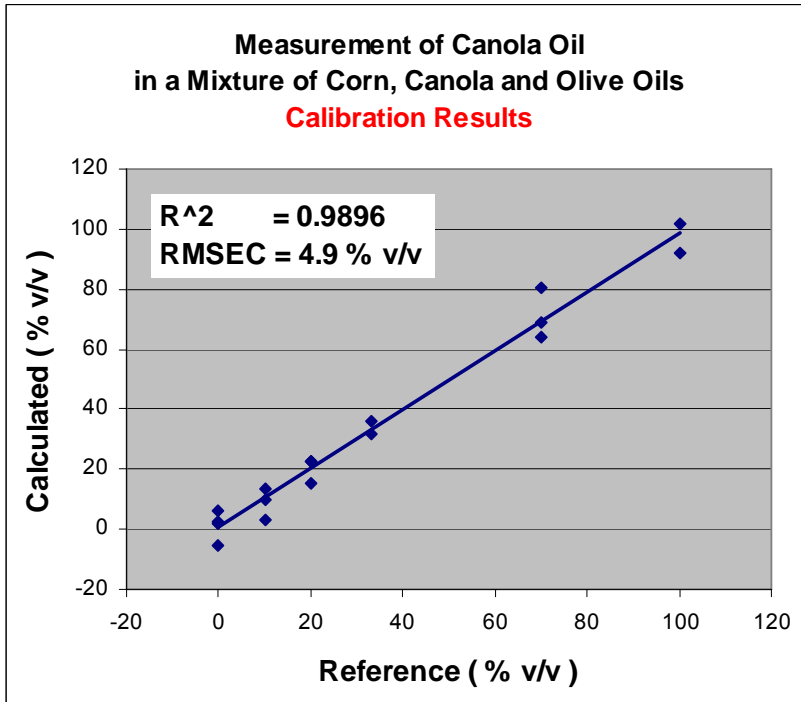
**Figure 3a:**

Calibration results when measuring percentage of corn oil in a mixture of corn, canola and olive oil.



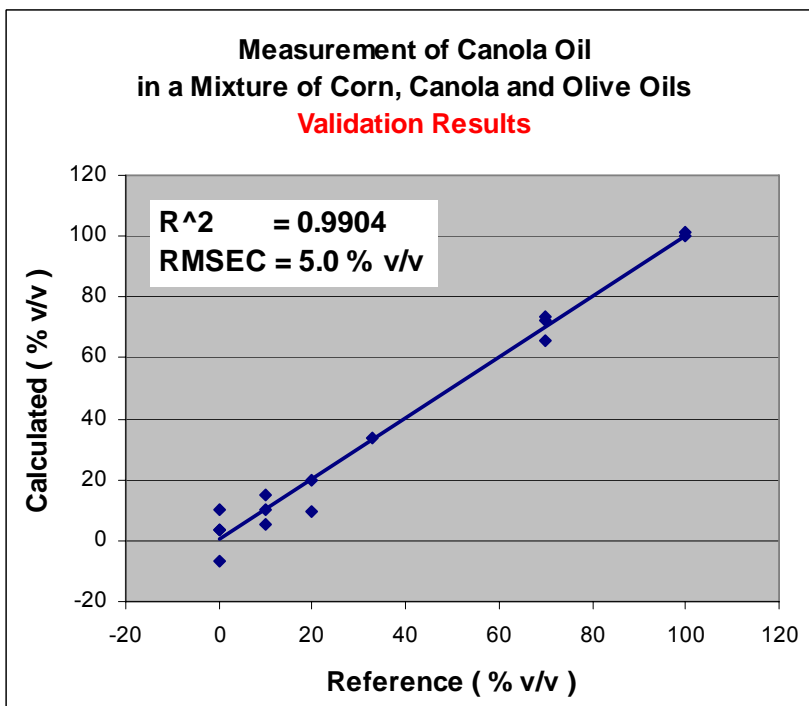
**Figure 3b:**

Validation results when measuring percentage of corn oil in a mixture of corn, canola and olive oils.



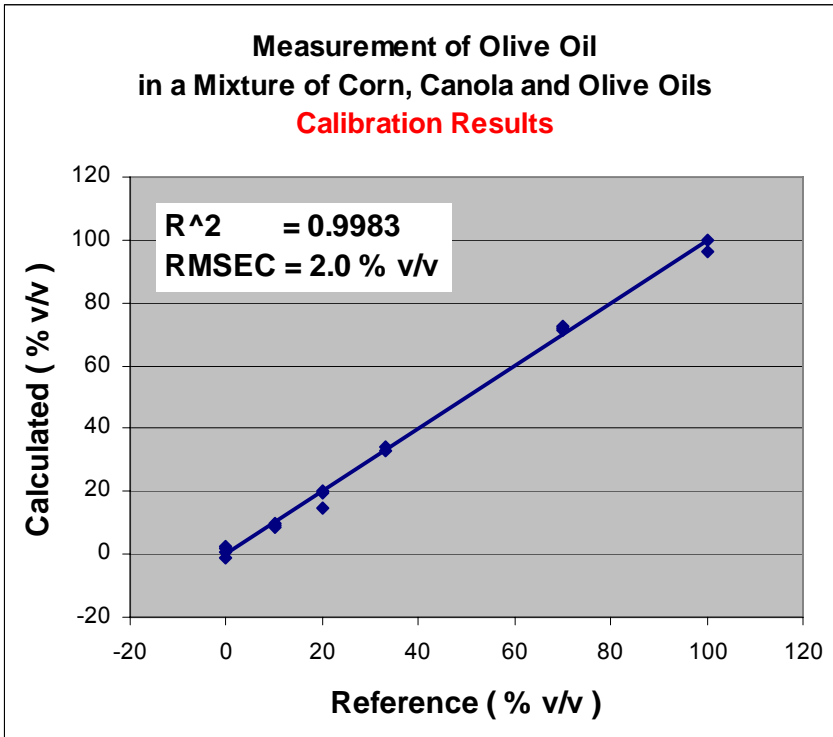
**Figure 4a:**

Calibration results when measuring the percentage of canola oil in corn, canola and olive oil mixture



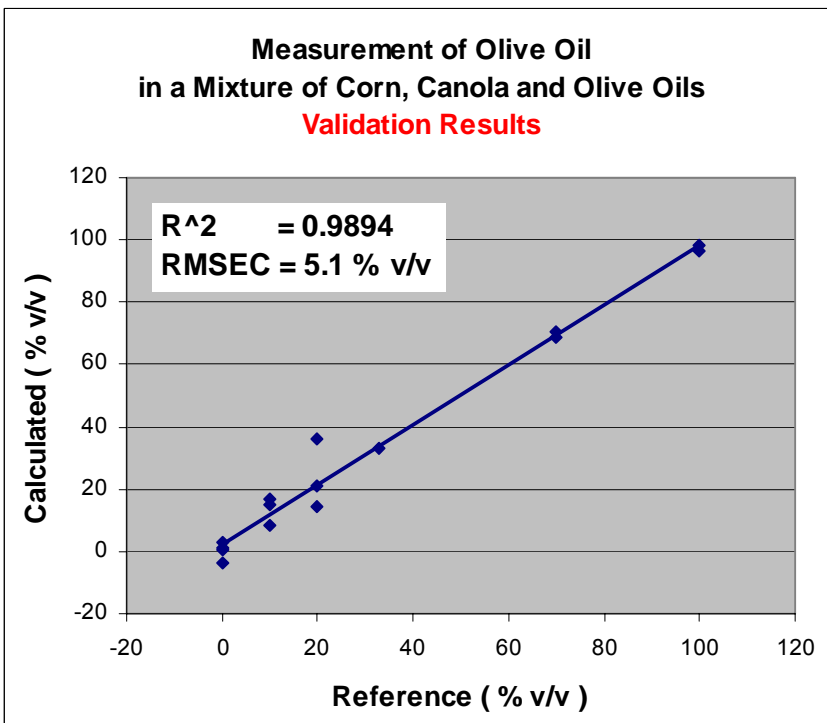
**Figure 4b:**

Validation results when measuring the percentage of canola oil in corn, canola and olive oil mixture



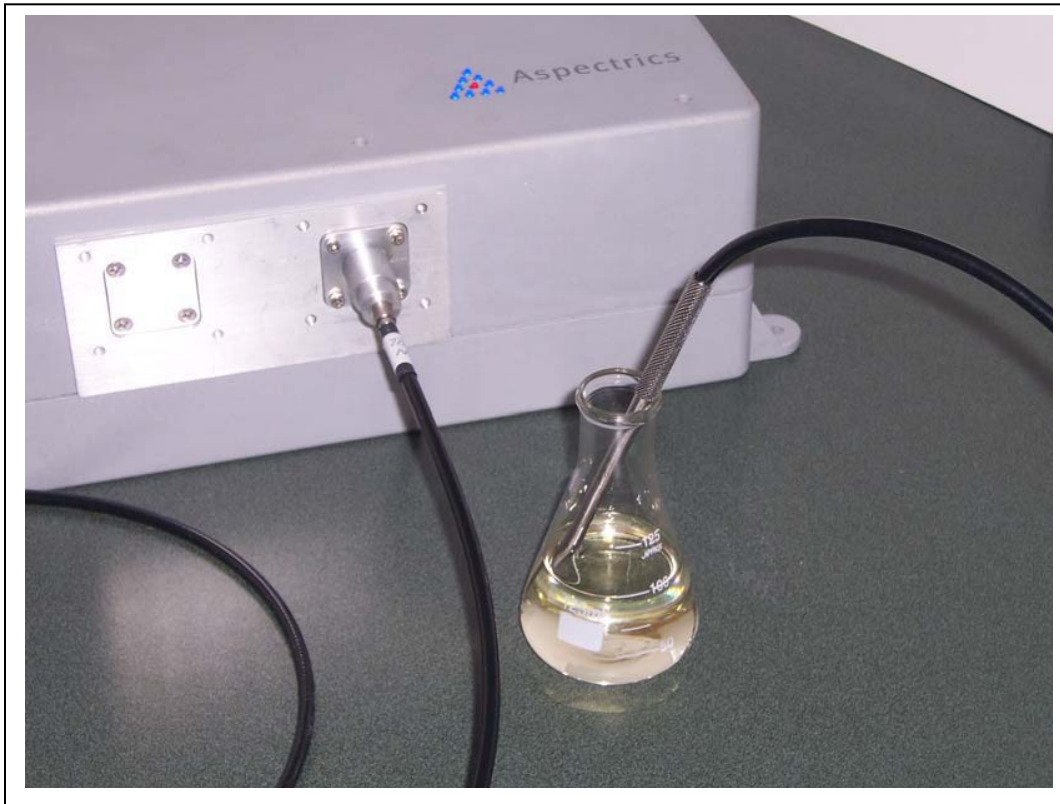
**Figure 5a:**

Calibration results when measuring the percentage of olive oil in corn, canola, and olive oil mixture



**Figure 5b:**

Validation results when measuring the percentage of olive oil in corn, canola, and olive oil mixture



**Figure 6:**

Aspectrics' MC2750 EP-NIR spectrometer with process transmission multimode fiber probe (600 microns polyimide), 2 mm. path length