Oleochem*ir* Analyzer for Oil and Fat Analysis Pre-calibrated for Iodine Value (IV) and %Trans AOCS Standard Procedure for Iodine Value

Introduction

The most popular processing technique for oils and fats is hydrogenation and this has been largely responsible for the growth of the margarine and shortening industries. Hydrogenation lessens the amount of unsaturation and also hardens the oils. By controlling how far hydrogenation proceeds, oils can be produced with different properties that are adapted to everyday use. The degree of hydrogenation (or saturation) is determined through a chemical test called Iodine Value (IV) and the type of unsaturation (cis or trans).

IV is also used to track or verify oil saturation in a variety of refining and production environments. These include fractionation, interesterification, acidolysis, saponification, and epoxification. Furthermore, IV is also used to verify oil authenticity and quality at shipping docks and distribution stations.

The double bonds responsible for unsaturation can occur in the cis and trans configuration (see Figure 1). It is now widely accepted that consuming the trans configuration is detrimental to health. Mandates for trans labeling not only affect commercial baking, frying and food processing, but also establish trans requirements from oil suppliers, namely, the refining and hydrogenation industries that process crude oils. Hydrogenation is seen as the main culprit of trans production. However, there are many other steps in oil processing that can influence the trans content, such as deodorization and oil extraction. An efficient means to track trans levels during processing will allow oil producers to minimize the amount of trans present in their final products.

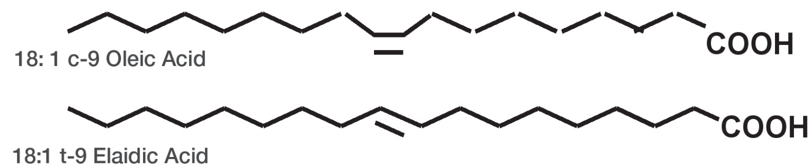


Figure 1

ABB's Oleochem*ir* Analyzer is based on the laboratory FT-NIR model FTLA2000-CH10 that offers a reliable solution for the rapid and easy determination of IV and %Trans. The FTLA2000-CH10 is pre-calibrated for the parameters of Iodine Value (IV) and %Trans. This means that the IV determination is based on a global calibration in accordance with the AOCS approved standard procedure Cd 1e_01. In the same way the %Trans determination is based on a global calibration applicable to the same wide range of oils as for IV. The effect of this is that the Analyzer is pre-calibrated for the two key oil properties for quality control (IV and %Trans) and requires no model development using site calibration samples, but simply a validation at startup. Analysis of additional properties can be provided on request.

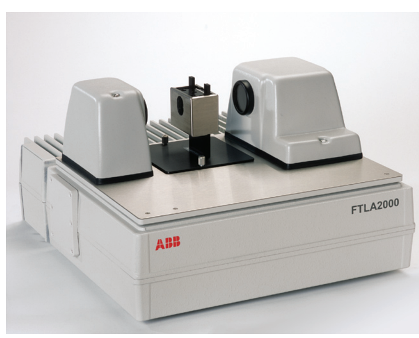


Figure 2

Description

The analyzer is very robust and can be placed in a central location near the production process for rapid (less than two minutes) and successive measurements. Samples from several reactors or other refining control points can be brought to this location for analysis. This gives the plant the ability to track reaction trends. The system is designed for use by plant personnel without any training in chemical analysis.

The following examples were done using an FTLA2000-CH10 Oleochem*ir* Analyzer (Figure 2). In this configuration, the Oleochem*ir* Analyzer scans the sample through 8 mm HPLC autosampler vials (approximate pathlength of 6.6 mm) that cost less than 18¢ per vial. Solid fats were preheated in a water bath to the liquid state and transferred to the vials with a disposable pipette. The sample vials were preheated in a temperature-controlled block (75°C) for two minutes before being analyzed. This ensures that the samples were completely in the liquid phase. For each spectrum, 128 co-added scans of the sample were referenced to 128 co-added scans of an open path reference at a resolution of 16 cm^{-1}.

One of the AOCS approved methods for the determination of %Trans is by means of mid IR spectroscopy using a heated horizontal ATR or transmission. Here, we determine %Trans at the same time as IV using disposable vials in the near IR. This is done because the sampling is easier than for mid IR spectroscopy where sample cleanup is required before analyzing the next sample. With disposable vials, no cleanup is required after analysis and the total analysis time is under 2 minutes per sample.

The Global IV and %Trans Calibrations

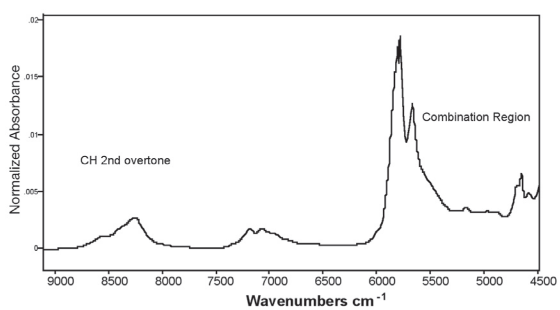
The global IV calibration contains over 1200 samples of oils and fats obtained from a variety of refining and production facilities, more specifically from 20 plants located all around the world (Table 1). The degree of saturation varies from 0 to 190 IV units. The global calibration for %Trans is based on the same wide range of oils as for IV.

Canola	Coconut	Cottonseed	Soybean	Walnut
Cocoa Butter	Crude Tallow	Sunflower	Castor	Almond
Palm Kernel	Palm Olein	Palm Stearin	Linseed	Safflower
Corn	Olive	Rapeseed	Crude Palm	
Milk Fat	Beef Tallow	Fish	Margarine Blend	

Table 1

Figure 3 shows the FT-NIR spectrum for a typical crude vegetable oil. The NIR region of the electromagnetic spectrum contains combination and overtone information. The calibrations for IV and %Trans occur in the region where the C-H second overtone band occurs namely, the band observed between 9100 cm^{-1} and 7560 cm^{-1} (Figure 4). This region contains most information on conjugation.

Figure 3



In order to compensate for scattering effects from the sample and pathlength differences derived from the disposable glass vials, all of the spectra were pre-processed using normalization, baseline correction and mean centering. Normalization renders the spectra pathlength independent and eliminates errors due to small variations in vial size.

Figure 4

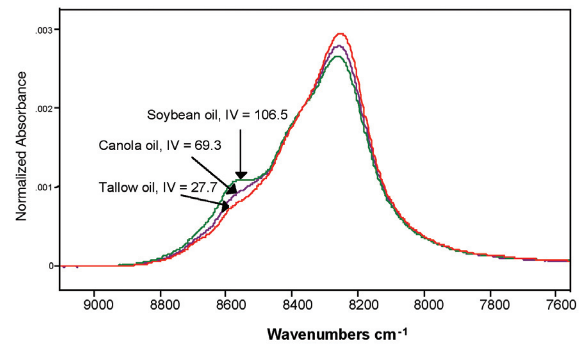
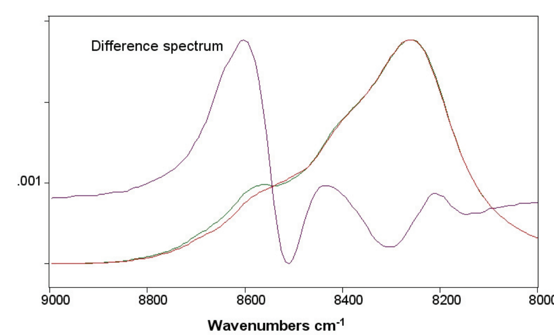


Figure 4 shows the normalized spectra in the region sensitive to IV and %Trans. The shoulder at 8580 cm^{-1} is consistent with the number of double bonds in each sample given by the high correlation between IV and spectral response.

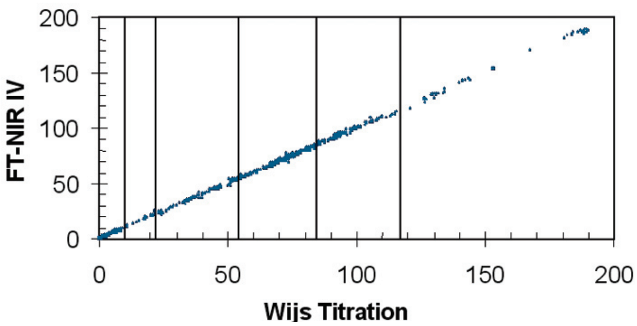
The degree of saturation is expressed as the Iodine Value (IV). This parameter is easily measured with the Oleochem*ir* analyzer. In order to verify that this region can be used to measure trans without intercorrelation effects with IV, spectra are plotted with the same IV and a different trans value (Figure 5). Notice from the difference spectrum (i.e. the green spectrum – the red spectrum) that most of the trans information occurs near 8610 cm^{-1}.

Figure 5



A multivariate model was designed with partial least squares (PLS). Figure 6 shows the correlation plot of FT-NIR predicted values vs. the average known IV from the Wijs AOCS certified method across the entire IV range. Rather than use one model for the entire range, several calibration models are used at various intervals. This permits smaller errors of analysis at low IV compared with high IV.

Figure 6



All of the calibrations are downloaded into a method. The method uses three discrimination mechanisms for model selection. They are spectral residuals, concentration range and factors. For routine analysis, model selection occurs automatically in the software and is hidden from the user. Table 2 below shows the standard error of prediction (SEP) and repeatability from several unknown samples. The repeatability of the measurement was measured by scanning 10 vials filled with the same oil or fat.

Table 2

Iodine Value range	0 - 10	10 - 30	30 - 60	60 - 90	90 - 120	120 - 190
SEP Uncertainty (1 sigma)	0.25	0.44	0.30	0.40	0.76	0.82
Repeatability (1 sigma)	0.08	0.10	0.08	0.10	0.12	0.15

Both IV and %Trans can be determined using a global calibration for all types of oils and fats. A global calibration can be used directly without need for any calibration work. These calibrations were developed with strict control on the primary method. The data collected must be from an accepted and highly reproducible source method. A global calibration for trans is shown below based on capillary GC method. The samples from two separate processors were used and each processor provided trans data derived from the capillary GC reference method. Figure 7 shows the correlation plot for FT-NIR predicted %Trans values vs. capillary GC method (correlation plot) giving a SEP of 0.7 %Trans and a repeatability of 0.1 (Table 3).

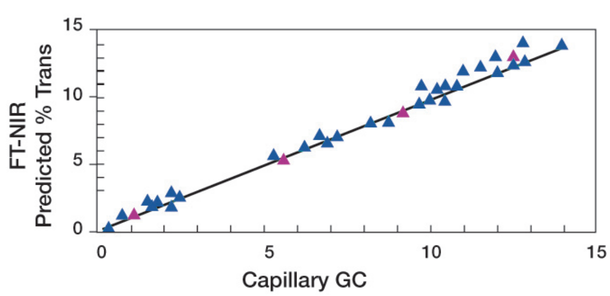


Figure 7

Figure 8 shows the correlation plot at higher trans levels. This data was derived from a single processor that used the GC method giving a SEP of 1.6 %Trans and a repeatability of 0.6 (Table 3).

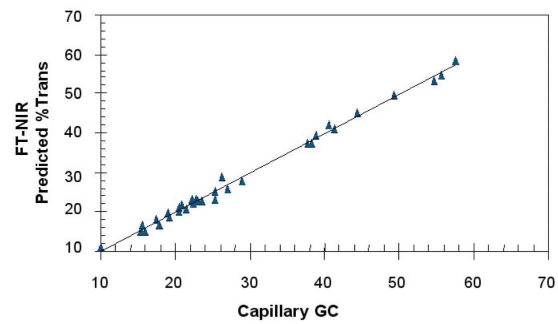


Figure 8

Although the error (± 1 %Trans) for the GC derived data is much higher than the reference data derived from the MIR, it is not method dependent. Data range, data distribution, sample type and reproducibility of each unique lab will contribute to the uncertainty and repeatability of the measurement. Based on our experience, we have observed errors from 0.4 to 1.0 %Trans (1 sigma) with no dependency on the primary method used. Table 3 below shows the results for the Global %Trans calibrations.

% Trans range	0 - 15	15 - 60
SEP Uncertainty (1 sigma)	0.7	1.6
Repeatability (1 sigma)	0.1	0.6

Table 3

Validation examples

An example of the site validation of the Global IV model is shown in Figure 9. The performance of the FTLA2000-CH10 was tested on 30 European soy samples. The graph at the Figure 9 shows the results using the global IV calibration to predict IV of oils collected from various sources. The standard error of prediction reported is 0.17 IV.

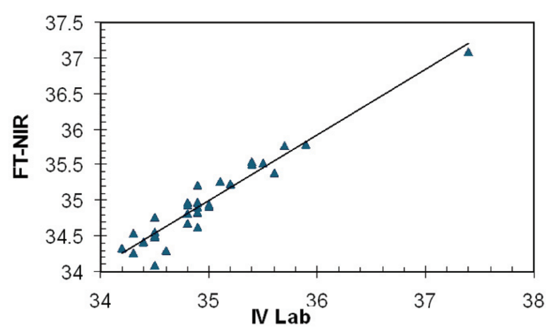


Figure 9

The Figure 10 presents the correlation plot for validation. Statistics show the mean IV predicted on each sample vs. the average known IV from the Wijs AOCS certified method for the entire IV range using smalley standards as well as several pure standards. It is common that local labs may have a bias in their titration compared with an average of 20 plants that have provided the smalley samples. Therefore validation may be required to establish the agreement with a local customer's lab.

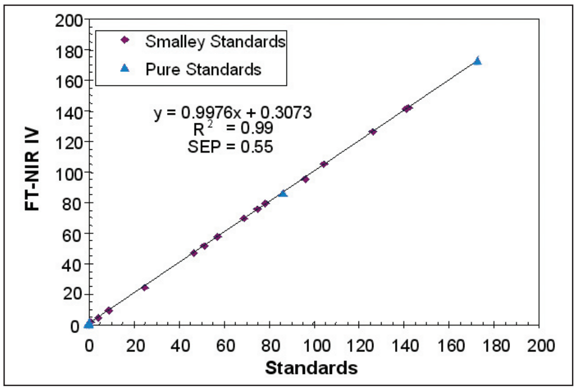


Figure 10

Maintenance

The FTLA2000-CH10 requires minimal maintenance. ABB recommends preventive source replacement every 10 months and laser replacement every 3 years. This insures a low probability of unscheduled failure of the analyses.

Conclusions

ABB has been manufacturing Oleochem*ir* analyzers for many years. The FTLA2000-CH10 is a very useful and robust instrument offering a Global calibration for the 2 majors characterization parameters in oils and fats (IV and %Trans). The Global calibrations are designed for a wide selection of oils and fats, which were derived from over 20 production facilities worldwide. The wide variation in samples used to develop the Global calibrations provides robustness of analysis. This reliability ensures fast return on investment.

In summary, there are three major advantages of using the FTLA2000-CH10 Analyzer for these measurements over traditional methods. First, this method provides the user with a faster method of analysis than the traditional IV and %Trans methods. Secondly, no sample preparation is needed, thus eliminating the usage of solvents and reagents in the plant. Thirdly, the inherent stability and reproducibility of FT-NIR provide precisely the same analysis results from unit to unit as well as the same results over time without drift. This last advantage can initialize a standardization scheme throughout an organization. Although these analyses were specific to laboratory analysis, an online process control strategy can be implemented using similar calibration protocols. On-line measurements will be implemented to further enhance control of oil production. The Oleochem*ir* analyzer brings oil and fat production to a high standard of uniformity with minimal variation over time.

The FTLA2000-CH10 has been fully tested worldwide with over 70 units validated in many facilities. By intensive research and development activities, and through a close partnership with more than 70 Oleochem*ir* clients, ABB has developed a unique expertise in oil and fat analysis by FT-NIR.

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